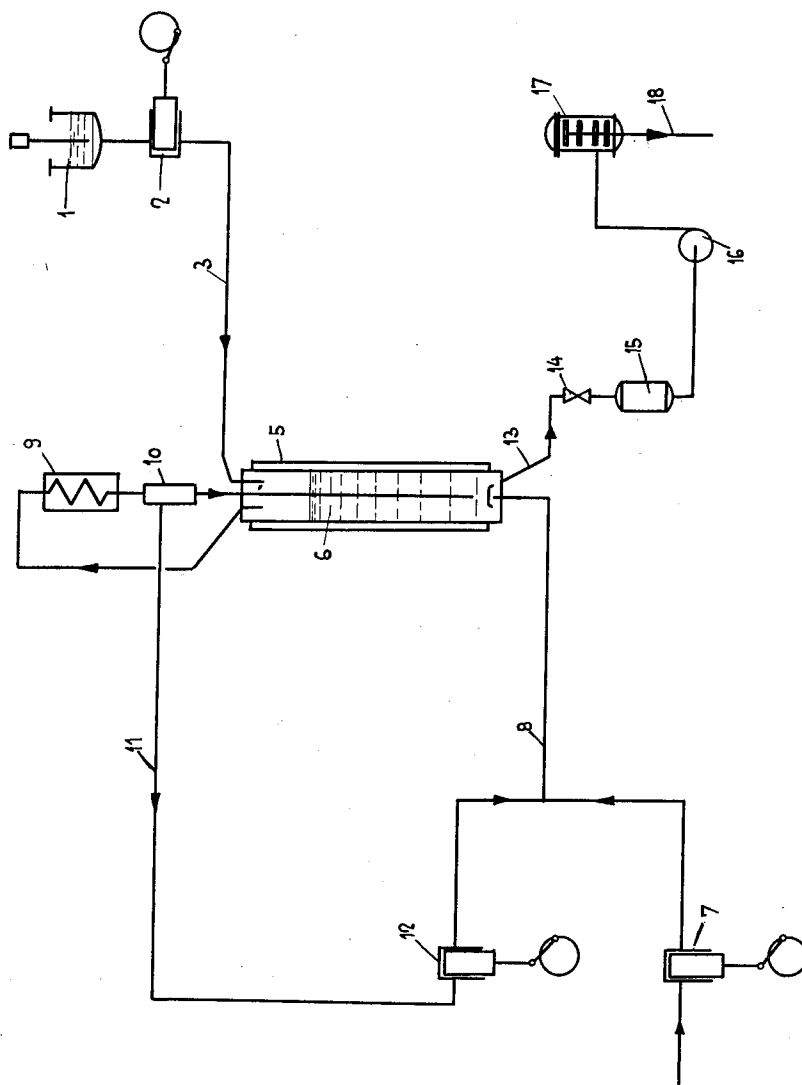


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SACCHAROSE TO GLYCEROL AND GLYCOLS
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PROCESS FOR THE DIRECT HYDROGENATION SPLITTING OF SACCHAROSE TO GLYCEROL AND GLYCOLS

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The invention hereinafter described relates to a process for the hydrogenation splitting of saccharose (cane sugar) directly to glycerol and glycols. Numerous processes have been described for converting cane sugar and other carbohydrates into hexitols and polyalcohols with a lower number of carbon atoms by hydrogenation, or hydrogenation splitting. The process employed usually comprises inverting the cane sugar with acid and then removing the acid after converting it into a difficultly soluble salt. The invert sugar obtained is then hydrogenated under certain given conditions to a mixture of sorbitol and mannitol. If it is desired to obtain glycerol and glycols, the said mixture of sorbitol and mannitol must be subjected to hydrogenation splitting under vigorous conditions. In order to obtain glycerol and glycols, therefore, three steps are usually necessary:

- (1) Inversion of cane sugar.
- (2) Hydrogenation of the invert sugar to a mixture of sorbitol and mannitol.
- (3) Hydrogenation splitting of the sorbitol-mannitol mixture to glycerol and glycols.

Processes have been described by which polysaccharides are hydrogenated directly to glycerols and glycols. Thus the oldest German patent specification related to this subject, namely patent specification No. 541,362, gives examples showing how saccharose, starch or cellulose, for instance, can be hydrogenated directly to glycerol and glycols. But here again the method basically consists in first carrying out inversion or hydrolysis by means of the acid formed in the treatment of the di- or polysaccharide, this hydrolysis being followed by hydrogenation of the resulting monosaccharides to hexitol and hydrogenation splitting of the hexitol to glycerol and glycols.

Furthermore, it is known that these direct hydrogenations of di- or polysaccharides only take place with strong decomposition and poor yields since the catalysts used are very sensitive to acid.

It has already been proposed to work with special catalysts which split off acid substances or substances which are acid in reaction, as for example in Dutch specification No. 60,860. Here also the di- or polysaccharide is first inverted or hydrolyzed and then hydrogenated. But, as mentioned above, hydrogenation in acid medium gives poor yields and is accompanied by the formation of decomposition products. It has also been known for a long time that hydrogenation of monosaccharides to hexitols and hydrogenation splitting of the hexitols to glycerol and glycols proceed better in a slightly alkaline medium than in a neutral or, worse still, an acid medium. Thus, in U.S. Patent 2,004,135, for example, a process is described by which the hydrogenation is carried out in the presence of a hydrogenation catalyst which contains a weakly basic compound. For the known glycerogen process (FIAT 872) which has been carried out on a technical scale for many years, the instructions also are to work at a pH of about 8, i.e., under slightly alkaline conditions, but this is for the classical method of (a) inversion, (b) hydrogenation to sorbitol and mannitol, (c) hydrogenation splitting to glycerol and glycol.

It also has previously been recommended, when using

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special catalysts, to use sodium carbonate as promoter for the direct hydrogenation of carbohydrates as, for example, in the U.S. patent specification No. 2,201,235. In this process, an alkaline carbonate in a quantity of 0.1–10% calculated on the catalysts or 0.01–1% calculated on the saccharose is preferably used as promoter. Furthermore, hydrogenation is carried out in the presence of methanol. In U.S. Patent 2,325,206, the process is also carried out in the presence of alkali, at an initial pH of 10.8. The particulars given only apply, however, when special copper catalysts are used. According to U.S. Patent 2,325,207, it also is necessary to work with very special copper catalysts, and for that reason, in a solution of aqueous methanol, which does not render the process more economical.

All the previously known processes for obtaining glycerol and glycols from saccharose have either the disadvantage that the process must be carried out in three steps, namely (a) inversion, (b) hydrogenation to sorbitol, (c) hydrogenation splitting to glycerol and glycol, or the disadvantage that it is necessary to work in the presence of special catalysts (in some cases in methanolic solution).

It has now been found that the hydrogenation splitting of saccharose to glycerol and glycols can be carried out in the presence of practically any technically feasible catalyst, provided that alkali is added to ensure a pH of 11–12.5, preferably 12, at least at the start of the hydrogenation. For technical purposes, it is preferable to use catalysts which are simple and inexpensive to prepare, relatively insensitive to poisons, and which can be used repeatedly and are easily regenerated, particularly nickel catalysts which are precipitated on carriers, such as kieselguhr or aluminum oxide. The process according to the invention, however, is, by no means, limited to the use of these catalysts. The hydrogenation splitting of the saccharose may also be carried out in the presence of Raney nickel or nickel-magnesium oxalate (according to Langenbeck) if the initial pH is adjusted to 12 by addition of alkali. Quite recently, it has been proposed to convert the monosaccharides directly to glycerol and glycols in the presence of very special nickel copper catalysts, the hexitol stage being by-passed. In this process, however, it still is necessary to carry out the complicated step of inversion, when using saccharose, and to neutralize the acid used and then separate it. As is known, sugars in general, including saccharose, are very sensitive to alkalis. Particularly at high temperatures, e.g., above 100° C., complete decomposition of the sugar may occur. It, therefore, was very surprising to find that the hydrogenation splitting of saccharose, which takes place only with strong decomposition or with poor yields when carried out under weakly acid, neutral or weakly alkaline conditions up to pH 10, proceeds smoothly and without any decomposition if the saccharose solution which is being hydrogenated is adjusted to a pH of 12. The other reaction conditions may be varied within wide limits.

The temperature at which this process is carried out is preferably 180–250° C. The pressure may be varied within the widest limits. Excellent results are obtained at 60 atmospheres above atmospheric pressure. The proportion of the most valuable of the splitting products, namely glycerol, may be further increased by raising the pressure to 1,000 atmospheres above atmospheric pressure, whereby the yield in glycerol, calculated on the conversion, may rise to more than 40%.

As the process of the invention was further developed, it was discovered that the yield in glycerol and glycols could be still further improved to a considerable extent if the hydrogenation splitting of the saccharose solution was carried out in thin layers, the hydrogen being passed in countercurrent to the saccharose solution.

By this thin layer treatment of the saccharose solution,

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in which the saccharose solution preferably trickles downwards in a tube packed with filling bodies such as Raschig rings or saddle bodies while the hydrogen is passed upward inside the tube, the reaction mixture always remains exposed for a uniform length of time to the reaction conditions so that reductions in yield cannot be caused either by too long or by too short durations of dwell.

In this method, the hydrogen is saturated with steam, to an extent depending on the reaction conditions. When the hydrogen has left the column, the steam condenses and separates. The reaction product can be concentrated to a greater or lesser extent during hydrogenation, according to the amount of hydrogen circulated.

This manner of raising the concentration was not possible in the previous processes, because it would have led to a simultaneous increase in the concentration of the saccharose, with consequent decomposition of the saccharose. In the process according to the invention, the reaction product trickles in the form of a thin film, e.g., over the filling bodies, while no intermixing takes place between the saccharose solution entering the tube and the converted reaction product. Consequently, the yields rise to about 95–100%. The concentration attained during this process cannot bring about any decomposition of the saccharose because the saccharose enters the reaction chamber in the form of a dilute solution and, under the reaction conditions selected in accordance with the invention, the saccharose is converted before the concentration can rise to a level at which decomposition of the saccharose might occur.

The reaction times, which were about 2–3 hours in the older processes, are reduced to less than 10 minutes, preferably between 2 and 5 minutes in the new process.

The process according to the invention has one further advantage. More volatile constituents which always are formed in small amounts in hydrogenation splitting, namely lower alcohols, acids, etc., are removed with the condensate. The product leaving the reaction tube, therefore, has a greater degree of purity than the products obtained by the previous processes.

The invention now will be further illustrated by the following examples. However, it should be understood that these are given merely by way of explanation, not of limitation, and that numerous changes in the details may be made without departing from the spirit and the scope of the present invention as hereinafter claimed.

In all the results given in the examples, the following should be noted: In no case is there any unconverted saccharose left; the conversions stated relate to sorbitol and mannitol which have been formed and not converted. The figures given for the yields refer to the conversion of sorbitol and mannitol to glycols. The catalyst, which generally contains the metal components in a quantity of 15–25 percent by weight calculated on the saccharose initially charged, is generally used in a quantity of 10–15% by weight.

Example 1

A 10% aqueous saccharose solution is subjected to hydrogenation splitting at 180° C. and at 60 atmospheres excess pressure for 3 hours in the presence of nickel on kieselguhr, with thorough mixing. The pH is adjusted to 12 with $\text{Ca}(\text{OH})_2$, for which 10% $\text{Ca}(\text{OH})_2$ calculated on the sugar is required. The hydrogenation product obtained is clear, colorless and odorless. The conversion is 42.5%. The following are obtained, the percentage being calculated on the conversion: 12.2% pentitol, 18.2% erythritol, 34.2% glycerol, 10.6% ethylene glycol and 6.1% propylene glycol.

Strong decomposition occurs if the calcium hydroxide is omitted. The hydrogenation product then is yellow to brown in color, has a strong, pungent odor and reduces Fehling's solution in the cold, owing to the presence of acetal.

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Example 2

Pressure, 130 atmospheres excess pressure; temperature 200° C.; pH 12; time 3 hours.

10% aqueous saccharose solution, catalyst nickel on kieselguhr. With an 84% conversion, one obtains, calculated on the conversion, 10% pentitol, 4% lactate, 14.2% erythritol, 23% glycerol, 11% ethylene glycols, 7.7% propylene glycol, 3.2% butanediol. If the adjustment of the pH to 12 is omitted, a conversion of only about 30% is obtained.

Example 3

Comparison of hydrogenation splitting of saccharose with that of sorbitol/mannitol. If saccharose and sorbitol/mannitol, respectively, are subjected to hydrogenation splitting under the same conditions, namely 230° C., 130 atmospheres excess pressure, 1½ hours, pH 12, 10% solution, nickel on kieselguhr, the following results are obtained:

	cane sugar	sorbitol-mannitol
conversion.....	98.4	98.6
pentitol.....	2.3	2.3
erythritol.....	10.0	8.4
glycerol.....	32.0	25.5
ethylene glycol.....	15.2	19.0
propylene glycol.....	21.2	14.5
butanediol.....	6.7	4.1

The efficiency and conversion rate thus are just as good in the direct hydrogenation splitting of cane sugar as in the hydrogenation splitting of a mixture of sorbitol and mannitol, but in the former there is the added advantage that inversion and hydrogenation to sorbitol are bypassed, which makes the process very much simpler.

Example 4

200° C., 130 atmospheres excess pressure, 3 hours, pH 12, 10% solution, nickel on aluminum oxide. Conversion 50.0%, pentitol 4.7%, erythritol 12.7%, glycerol 36.6%, ethylene glycol 21.2%, propylene glycol 25.8%.

The following examples, 5–8, are continuous operations and are given with reference to the accompanying drawing which is a flowsheet for such processes.

Example 5

The advantage of the process become particularly marked when the operation is carried out continuously. 5 liters per hour of a 10% aqueous saccharose solution mixed with 12% hydrogenation catalyst (nickel on kieselguhr) are conveyed from a mixing vessel 1 with stirrer by means of pump 2 through pipe 3 to an autoclave 6 which has a capacity of 16 liters and which is provided with a heating jacket 5. At the same time, fresh hydrogen is supplied to the autoclave from compressor 7 through pipe 8. The hydrogen not consumed in the reaction vessel is decompressed and, after passing through condenser 9 and separator 10, is conveyed through pipe 11 and compressor 12 to be mixed with the fresh hydrogen coming from compressor 7. 5 liters per hour of the reaction product are removed from the reaction vessel 6 through pipe 13 to pass through valve 14 into an expansion vessel where it is decompressed. From there, the decompressed reaction product is pumped by a pump 16 to filter 17, where it is freed from catalyst. Most of the catalyst is returned to the mixing vessel 1 to be used again. The reaction product which is freed from catalyst is removed through pipe 18. The amount of reaction liquid in the reaction vessel 6 is 12 liters, so that with an hourly input of 5 liters fresh solution and simultaneous removal of 5 liters reaction product, the duration of dwell is approximately 2½ hours. The amount of hydrogen through the cycle is 350 liters per hour, measured under the pressure of the reaction, and the amount of fresh hy-

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drogen supplied is 200 liters per hour, measured at atmospheric pressure.

The pressure is 60 atmospheres excess pressure, the temperature 210° C. A conversion of 82.9% is obtained. This comprises 11.4% erythritol, 42.8% glycerol, 17.8% ethylene glycol, and 24.6% propylene glycol. From this, it may be seen that the continuous method gives good results even when there is only a slight excess pressure.

Example 6

In the same apparatus and under otherwise similar conditions as in Example 5 a pressure of 300 atmospheres is employed instead of 60 atmospheres. The following results are obtained.

Conversion 56.5%, erythritol 11.8%, glycerol 48.5%, ethylene glycol 4.2%, propylene glycol 16.9%. Corresponding to the higher pressure, the conversion at 300 atmospheres is less than at 60 atmospheres, but the formation of undesirable byproducts also is reduced.

Example 7

In an apparatus similar to the one described in Example 5, but in which the autoclave 6 is filled with Raschig rings, a starting solution of 10% saccharose in water is treated with hydrogen, the temperature of the reaction being 200° C. and the pressure 300 atmospheres. Nickel on kieselguhr is used as catalyst. The duration of dwell is 3 minutes, the amount of hydrogen circulated is 200 l./h., the throughput of saccharose solution is 6 l./h. The rate of production is approximately 2 l./h., the rate of condensation is 4 l./h. The concentration of the reaction solution after leaving the autoclave is 30%.

Example 8

The conditions are the same as in Example 7. Raney nickel is used as catalyst. The circulated quantity of hydrogen is 300 l./h. The concentration of the reaction solution is approximately 40%. The conversion is 97%.

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Example 9

Same conditions as in Example 1. By the old method, the reaction product contains approximately 3% lower alcohols (methyl alcohol, ethyl alcohol, propyl alcohol) calculated on the cane sugar initially charged. By the new method, the reaction product is free from lower alcohols.

We claim as our invention:

1. A process for the direct production of glycerol and glycols from aqueous saccharose solutions in a single stage by catalytic hydrogenation splitting, which comprises starting said hydrogenation at a pH of substantially 12, and carrying out said hydrogenation within 2-10 minutes at temperatures of 180-250° C., at pressures of 50-250 atmospheres and with hydrogenation catalysts selected from the group consisting of nickel on kieselguhr, nickel on aluminum oxide and Raney nickel.
2. A process for the direct continuous production of glycerol and glycols from aqueous saccharose solutions in a single stage by hydrogenation splitting in a reactor, which comprises continuously passing said solutions downward in said reactor in thin layers, and contacting the same countercurrently with hydrogen, while carrying out said hydrogenation at a constant pH of substantially 12, at temperatures of 180-250° C., at pressures of 50-250 atmospheres for 2-10 minutes, using catalysts selected from the group consisting of nickel on kieselguhr, nickel on aluminum oxide and Raney nickel.

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