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ACCELERATOR FOR CATALYTIC HYDRO-
GENATION OF SUGARS

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The present invention relates to improvements in the production of polyhydric alcohols by the catalytic hydrogenation of saccharides.

More particularly the invention relates to a means for improving the rate of reduction of saccharides by hydrogenation under acid conditions in the presence of a catalyst.

The invention has particular reference to an improvement in the catalytic hydrogenation process for making polyhydric alcohols from sugars under acid conditions comprising the use of a reduction accelerating substance during the hydrogenation.

The following is a general description of the process for hydrogenating sugars in acid solution as described more in detail and claimed in the copending application of James T. Power, Ser. No. 225,349. The accelerators according to the present invention are designed for use in this process as an improvement thereon.

The process in its broadest aspect involves the catalytic hydrogenation of saccharides under acid conditions until the reduction of the saccharide to the polyhydric alcohol or alcohols has been carried out to the desired extent. More specifically the process involves the use of heat and pressure and of a hydrogenating metal catalyst such as reduced nickel. In the case of monosaccharides the process generally produces substantial quantities of polyhydric alcohols containing the same number of carbon atoms as the starting saccharide. In the case where the disaccharide sucrose is taken as the starting sugar, it is probably not reduced directly but is probably first hydrolyzed to 6-carbon atom monosaccharides which are then reduced to the corresponding polyhydric alcohols. The disaccharide lactose, depending upon conditions, may be reduced in whole or in part to lactositol, or may be inverted in whole or in part to glucose and galactose which are then reduced. Where invert sugar (which is a mixture of equal quantities of glucose and fructose) is taken as the starting sugar, the reduction produces a polyhydric alcohol mixture containing 25% of mannitol, the balance being a sorbitol-containing product of either low or high sorbitol content, and of excellent color. In many cases polyhydric alcohols having fewer carbon atoms than the original sugar, may be produced. In general the type of product yielded by the process described herein will be determined in large measure by the type of starting sugar selected, although the type of product obtained may be varied to a considerable extent by the conditions of the re-

duction, and especially by the pH of the initial mixture.

Various mono- and di-saccharides, such as glucose, invert sugar (such as that prepared by the inversion of sucrose with sulfuric acid by known processes), sucrose, dextrine, black strap molasses, "Hydrol" which is the molasses from manufacture of glucose from corn syrups and which contains glucose, oligosaccharides (di-, tri-, and tetra-saccharides) and dextrine, lactose, invert lactose, and rare sugars such as d-galactose, l-fructose, l-rhamnose, d-xylose, etc., or mixtures of the foregoing, may be successfully reduced to the corresponding polyhydric alcohol or alcohols. A valuable feature of the process is that in the case of polysaccharides such as dextrine, and oligosaccharides such as sucrose, and lactose, conditions may be selected such that hydrolysis to monosaccharides and reduction of the monosaccharides produced take place substantially simultaneously. However, in the case of a reducing disaccharide such as lactose, conditions may be such that reduction to lactositol takes place either to the substantial exclusion of inversion or in addition to inversion.

In place of using pure neutral monosaccharides, the acid mixtures of hydrolyzed products obtained by hydrolyzing polysaccharides or oligosaccharides with acid may be used directly in the process. In this manner the addition of acid in the preparation of the initial mixture is dispensed with. This facilitates carrying out the process by the elimination of the steps of removal of the hydrolyzing acid, and renders the process less expensive.

The saccharide selected is mixed with a suitable medium, preferably water, to form a mixture of suitable concentration for reduction. The amount of water in the initial mixture should be sufficient to enable the reduction to proceed, under the conditions of temperature and pressure employed, without burning, charring, or caramelization of the organic components during the reaction. In practice, it is preferred to use a 30-50% concentration, although concentrations outside of this range, such as concentrations above 50% or below 30%, may be employed if desired.

Acid is added to the aqueous saccharide mixture thus prepared, in such amount as to yield a mixture of the sugar, acid and water having a pH of below 7.0. In general in the reduction of monosaccharides capable of yielding sorbitol, the lower the pH of the initial sugar solution, that is, the greater the amount of acid present, the lower

the sorbitol content of the polyhydric alcohol product.

In the case where a polysaccharide or an oligosaccharide has previously been subjected to hydrolysis with an acid, the mixture of monosaccharide and acid obtained may be diluted with water to the desired concentration of sugar and acid, adjusted, if desired, to the desired pH by the addition of acid or of alkali, and subjected to catalytic hydrogenation under the conditions outlined below. Thus sucrose may be inverted with sulfuric acid, and the inverted mixture containing the inverting acid, diluted with water to the correct concentrations of sugar and acid, and the resulting solution subjected to reduction. Lactose may be similarly inverted to galactose and glucose prior to the reduction, if desired.

Examples of acids which may be used are: inorganic acids such as sulfuric acid, boric, and phosphoric acid, and organic acids such as acetic acid. Other acids may be used provided they are of a type which do not attack the catalyst and the reactants to an objectionable extent. In place of using a single acid, a plurality of acids may be employed, if desired.

The amount of acid present in the initial mixture is variable within the range necessary to produce an initial pH below 7.0 and as low as 1.0. Greater amounts of acid than that necessary to yield a pH lower than 1.0 are generally not desirable because of tendency to charring and discoloration upon reduction.

As the catalyst for carrying out the reduction, any base metal or other suitable reducing catalyst may be used, but it is preferred to use a base metal reducing catalyst such as nickel. Three types of nickel catalyst which have been found very suitable for use in the practice of the invention are: reduced nickel supported on diatomaceous earth (kieselguhr), Raney nickel catalyst and reduced nickel chromate supported on diatomaceous earth.

Frequently the catalyst is somewhat alkaline, and its addition causes a slight rise in the pH of the mixture of water, saccharide and acid. Usually this rise will not be sufficient to bring the pH up to, or over, 7.0. If this rise is sufficient to bring the pH up to, or over, 7.0, this effect should be compensated for by adding to the aqueous saccharide mixture a slight excess of acid, sufficient to cause the pH of the mixture containing the catalyst to be at the proper figure. This addition of acid may be either before or after the addition of the catalyst.

The amount of catalyst employed is preferably from 5 to 15% on the weight of sugar taken for reduction. The use of amounts of catalyst above 15% is permissible but does not produce sufficient shortening of the time of reduction to be warranted while the use of amounts of catalyst below 5% frequently increases the length of time of reduction to such an extent as to render the process uneconomical. Within the range set forth above, it is preferred to use 10% of catalyst, since this amount produces substantially maximum acceleration of the reaction. Under certain circumstances as where some other factor in the reaction is not at a desirable value, as for example, where the hydrogen pressure available is slightly lower than desired, it may be desirable to increase the amount of catalyst up to 15%, or even higher, in order to compensate for the retarding effect of lowered pressure.

Reduction may be carried out in any suitable

type of apparatus wherein the reaction chamber is closed and is capable of withstanding the pressures and temperature employed. The process may be carried out either as a batch process in an autoclave, or it may be carried out continuously in apparatus designed for continuously subjecting the reaction mixture simultaneously to the action of the catalyst, to the higher pressure of hydrogen required and to the proper temperature, for a sufficient length of time to complete the reduction. The apparatus should be such that the reacting mixture is subjected to agitation, in order that the reaction may proceed uniformly in all parts of the reacting mixture. In the case of continuous apparatus, the continuous movement of the liquid reacting mass is sufficient to accomplish this result. In the case of batch operation in an autoclave, externally driven stirrers or shaking devices may be used, or other methods of securing the desired agitation may be employed.

In preparing to carry out the reduction using an autoclave, the saccharide, water and acid are first charged into the autoclave in any order or manner. If desired, the previously prepared mixture of saccharide, water and acid may be charged into the autoclave or the separate ingredients may be added and the mixture stirred for complete and homogeneous intermingling. The catalyst is next added, preferably without contact with air in order to avoid oxidation of the catalyst. The autoclave is now closed and connected to a high pressure hydrogen supply. The pressure of hydrogen gas within the autoclave is allowed to build up to the desired extent, whereupon the autoclave is sealed off and disconnected from the hydrogen line and the reduction is begun by heating, accompanied by continuous agitation of the contents of the autoclave.

The reduction is carried out at a pressure considerably above atmospheric, usually around 1500 lbs. per sq. inch in order to cause the reaction to proceed at a rate which is commercially feasible. Greater initial pressure does not produce sufficiently greater speed of reaction to warrant the expense involved. However, lower initial pressures, say as low as 500 lbs. per sq. inch may be used. During the course of the reaction the pressure may rise as much as 500 lbs. per sq. inch due to the elevation of the temperature so that the maximum pressure during the reaction may be as high as 2000 lbs. per sq. in. but this may be compensated for to some extent by absorption of hydrogen as the reduction proceeds. Therefore, the range of pressure employed in the reduction is generally from 500-2000 lbs. per sq. inch.

The temperature at which the reduction is carried out is preferably in the neighborhood of from 140° C. to 160° C. A temperature of 150° C. is especially desirable in that the reaction proceeds at maximum speed at this temperature with very little danger of charring or discoloration. Temperatures above 160° C. cause an undue tendency towards charring. However, temperatures below 140° C., down to room temperature (say 20° C.), may be used if desired.

The reduction is generally allowed to proceed until substantially all of the sugar has been reduced. In the case where an autoclave is used, it will usually take from 50 to 75 minutes to bring the temperature of the reaction mass up to the preferred figure of 150° C. The time during which the preferred temperature will be main-

tained will vary considerably, but in general, heating is continued until the reduction has been carried to the desired degree of completion. In most instances this time will approximate 90 minutes, although it may be greater than this for greater completeness of the reduction. In general, this time at the preferred temperature will fall within the range of one to three hours.

Upon completion of the reaction the heating and agitation of the reaction mass are discontinued, and the pressure of hydrogen is reduced to atmospheric in the case of a batch process employing an autoclave, or the reacted mass is removed from the reaction zone in the case of a continuous process. The liquid mass of reduced sugar, acid, and catalyst is removed from the vessel and filtered. The filtrate is then treated to recover the polyhydric alcohol contained therein by known processes.

By hydrogenation under acid conditions control over the purity and type of products is extended to a point heretofore unattainable. For example, the reduction of glucose in accordance with the acid process accomplishes the direct production of sorbitol syrups which are substantially or completely mannitol-free, which have either low or high sorbitol content, as determined by pyridine number, as desired, and which are of good color, whereas reduction under alkaline conditions yields a product containing considerable quantities of mannitol, organic acids and other decomposition products. Monosaccharides and lactose can be reduced in acid solution mainly to the corresponding polyhydric alcohol or alcohols, and polysaccharides and other oligosaccharides to the polyhydric alcohols corresponding to the monosaccharide derivable therefrom by hydrolysis, since little or no isomerization to other sugars takes place and therefore little or no reduction product of such isomeric sugars is produced. This enables the ready production of sorbitol and sorbitol syrup of high purity (high pyridine number) from the corresponding saccharides. In the reduction of saccharides in acid solution, the preponderant polyhydric alcohol or alcohols in the product may be those corresponding to the saccharide employed, there being little or no polyhydric alcohol formed by reduction of saccharide isomers. On the other hand, the product may contain in addition to substantial quantities of the corresponding polyhydric alcohol or alcohols, substantial or preponderant amounts of other polyhydric bodies which are not formed by reduction of saccharide isomers, for example, polyhydric alcohols such as the desoxy polyhydric alcohols as for example desoxy hexitols and desoxy pentitols or polyhydric bodies which are not true polyhydric alcohols as for example anhydro derivatives of polyhydric alcohols. In this manner there may be produced from glucose, without the production of mannitol, products of low sorbitol content (low pyridine number) and containing, in addition to sorbitol, a relatively large amount of other polyhydric alcohols, such as desoxy polyhydric alcohols, for example desoxy hexitols such as saccharitols, desoxy pentitols, etc., and a substantial amount of still other polyhydric bodies such as anhydro hexitols. By "desoxy polyhydric alcohol" is meant an aliphatic polyhydric alcohol in which a hydroxyl group has been replaced by hydrogen. By "saccharitol" is meant hexitol in which one hydroxyl group is replaced by hydrogen.

Thus it will be seen that the reduction of glucose under acid conditions is capable of yielding directly a low pyridine number sorbitol syrup (pyridine number not over approximately 50) and no or substantially no mannitol. Such a syrup is very advantageous since it shows no crystallizing or gelling tendencies even in concentrations as high as 80% solids due to its complexity and is therefore very well suited for conditioning applications. This syrup is obtained immediately from glucose and in the highest possible yield since substantially no mannitol is formed. In general, such a product is produced by reducing in a solution of low pH.

Attempts to reduce glucose to sorbitol without simultaneous production of large amounts of mannitol under alkaline conditions above pH 7.0, using pressure catalytic hydrogenation are not successful because the isomerization of glucose to fructose and mannose takes place and the isomeric hexahydric alcohols are produced upon reduction of these sugars. On the other hand, when reduction takes place under acid conditions, enolization of glucose is reduced to a minimum or is completely eliminated and the product consists essentially of sorbitol and non-hexitol components.

According to the present invention it has been found possible to increase the rate at which reduction occurs in a process such as above described by having present in the reaction mixture a small amount of an accelerator in the form of an ion of an alkali (including ammonium) or alkaline earth metal. The accelerator is usually in the form of the cation of a salt. The anion of the salt in general makes no difference in the accelerating effect. Certain acids and acid radicals are recognized as poisons to the catalysts used in hydrogenation and it will be obvious to those familiar with catalytic hydrogenation that such anions should be avoided in selecting the accelerator salt to be used. For instance, chlorides, sulfides, arsenates and selenates are specific poisons to nickel catalysts as are substances which would give free sulphur.

Some of the specific salts that can be used as accelerators are the acetates, gluconates, sulfates, phosphates, and borates of ammonium, sodium, potassium, barium, calcium, strontium and magnesium. Other salts of these metals with organic or inorganic acids can be used provided the anion does not affect the catalyst adversely. Even insoluble salts such as the sulfate and borate of calcium have been found to exert the accelerating effect.

It will usually be convenient to add the accelerator in the form of a salt but if the sugar to be reduced contains a large amount of acid the metallic ion can be introduced as a hydroxide for instance or in other suitable form. Where a molasses or "hydrol" with high organic acid content is employed this latter procedure can be resorted to, although it will be apparent that the salts of the metals and the acids present will be formed.

The accelerator is added to the sugar solution before the start of the reduction. The amount of accelerator required varies somewhat with the nature of the particular salt used and with the concentration of sugar, but in general it has been found preferable to use from about one to five mol percent. of the cation in the accelerator based on the amount of sugar in the

solution. Substantially smaller amounts than this produce negligible acceleration and substantially greater amounts retard the rate of reduction below that value obtained when the preferred quantity of accelerator is employed. It is to be understood, however, that larger amounts of accelerator than five mol percent. can be employed advantageously in many cases but it will usually be preferred to use the smallest amount of accelerator capable of increasing the rate of reduction by a substantial amount.

It has previously been proposed to reduce sugars in the presence of weakly alkaline buffer salts such as calcium carbonate. According to this prior art practice, a feebly alkaline condition was produced and the reduction was carried out in this condition. The advantage of the buffer was attributed in part to the effect of preventing an acid condition which would attack and partially destroy the catalyst. As pointed out above, the reduction of sugars in alkaline media results in the formation of mixtures of polyhydric alcohols as a result of the isomerization of the sugars occasioned by the alkali. Particularly in the case of glucose, reduction in alkaline medium results in the production of mannitol in addition to sorbitol which is the direct reduction product of glucose.

Applicant has now discovered that he can obtain the advantages of reduction in acid media and at the same time obtain an increased rate of reduction by adding to the sugar before reduction small quantities of alkali or alkaline earth metals or ammonium, usually in the form of salts thereof. These salts are not added for their alkalinizing effect, since according to the invention the solution must be initially acid, but because they appear to be accelerators of the reduction. The action of these metals in the reduction is not understood but it may reside in imparting additional activity to the catalyst. Even after the addition of these materials the applicant's process is carried out at a pH below 7.0. If the effect of adding the catalyst and the salt to the sugar solution is to give the solution a pH of 7.0 or greater, a suitable quantity of acid is added to adjust the pH to a value below 7.0.

The following examples describe the reduction of glucose but it is to be understood that the invention is not restricted to this sugar but is applicable to the catalytic hydrogenation of any of the reducible sugars or sugars capable of hydrolysis in the process to produce reducible sugars.

For accurate comparison, all of the examples reported below were conducted under conditions which were identical except for the accelerator. A solution of 40% cerelose (anhydrous glucose) in water was reduced in each instance at a hydrogen pressure which was initially 1500 lbs. per sq. inch and at an activating temperature of 150° C. The total reduction time was 240 minutes at the end of which time the pressure

was released, the reaction bomb opened and the product removed and analyzed. The time required to heat up the bomb and its contents to the operating temperature varied from 55-70 minutes, averaging about 60 minutes. In the examples given below, the mixture of glucose, water, catalyst and accelerator gave a pH below 7.0 in each case. Where more alkaline substances are present in the mixture, however, it will frequently be found necessary to add acid to adjust the pH to a value below 7.0. The catalyst used was reduced supported nickel and was used in the quantity of 10% (weighed before being reduced), by weight of the sugar.

The catalyst was prepared as follows:

290 grams nickel nitrate hexahydrate dissolved in 400 ml. distilled water was ground in a large porcelain ball mill with porcelain balls for 16 hours with 250 grams acid washed diatomaceous earth. This mixture was slowly poured with stirring into a solution of 170 grams ammonium carbonate in 1 liter of distilled water. The precipitate was filtered with suction and washed with 4 portions of 125 ml. distilled water, then dried in an oven at 110° C. for 16 hours. The cake was pulverized, then re-dried for 4 hours. The weight of the catalyst preparation was 358.8 grams. The acid washed diatomaceous earth was prepared as follows:

250 grams diatomaceous earth in the form known as Super Cel was digested on a steam bath with 1 liter of C. P. nitric acid (sp. gr. 1.42) for 21 hours in a porcelain dish. The mass was taken up in 1 liter of distilled water and filtered on a 19 cm. Buchner funnel, then washed with distilled water until the washings were just faintly acid to methyl red. The mass was then dried in an oven at 110° C. and stored in stoppered bottles.

Reduction of catalyst

7.5 grams of the above catalyst preparation were placed in a glass combustion tube (Corning #172) 15 mm. x 600 mm. and held in place with a small plug of glass wool. The catalyst was evenly distributed over seven inches of the tube allowing a free gas space past the material.

The tube was placed in an electric combustion furnace and after being swept out with a rapid stream of hydrogen was heated to 450° C. for one hour with a continual flow of hydrogen of 50-60 cc./min. as measured at the exit end of the tube with a pneumatic trough. The tube was then removed from the furnace and allowed to cool while a slow stream of hydrogen was passed over the catalyst. The reduced catalyst was kept in an atmosphere of hydrogen. When charging the catalyst into the bomb, a rapid stream of hydrogen was passed through the tube. The catalyst was used within 3 hours after its preparation was complete.

Examples 1 and 2 report reductions according to the invention in which alkali metal salt accelerators were used.

Ex.	Accelerator	Mol. per cent	pH of solution		Per cent sugar reduced			Yield	P. N.
			Start	Finish	After 120 min.	After 180 min.	After 240 min.		
1	NH ₄ Ac	1	5.7	4.4	94.9	98.8	99.86	94.6	80.0
2	KAc	1	6.7	4.2	95.0	99.5	99.95	99.0	87.8

In Examples 3 to 6 the reductions were made in accordance with the invention using alkaline earth metal salt accelerators.

The effect of the chloride ion, one of the catalyst poisons previously described, is shown in the following examples of reductions using cal-

Ex.	Accelerator	Mol. per cent	pH of solution		Per cent sugar reduced			Yield	P. N.
			Start	Finish	After 120 min.	After 180 min.	After 240 min.		
3	BaAc ₂	1	6.5	4.3	98.6	99.9	99.9	95.5	80.5
4	CaSO ₄	1	6.5	4.4	87.1	94.2	99.7	95.0	85.3
5	SrAc ₂	1	6.6	4.4	94.6	99.3	99.95	96.8	81.5
6	MgAc ₂	1	6.7	4.4	96.4	99.0	99.97	95.7	77.5

Example 4 shows a reduction in accordance with the invention in which a substantially in-

cium chloride which is not an accelerator because of the retarding effect of the anion.

Ex.	Added material	Mol. per cent	pH of solution		Per cent sugar reduced			Yield	P. N.
			Start	Finish	After 120 min.	After 180 min.	After 240 min.		
13	CaCl ₂	1	6.8	3.2	55.4	78.6	84.1	75.2	-----
14	CaCl ₂	2	6.5	3.2	53.2	71.1	78.5	76.5	64.0

soluble salt (CaSO₄) was used as an accelerator.

For comparison with the above examples of reductions made in accordance with the invention, the following examples report reductions performed under the same conditions but omitting the accelerators.

Examples 13 and 14 show that the chloride ion not only has no accelerating effect but has a pronounced retarding action on the reduction.

By "pyridine number," abbreviated P. N., as used herein is meant an index of sorbitol content of sorbitol-containing material. This index is

Ex.	Added material	Mol. per cent	pH of solution		Per cent sugar reduced			Yield	P. N.
			Start	Finish	After 120 min.	After 180 min.	After 240 min.		
7	None	-----	7.2	4.8	72.4	89.4	97.2	93.4	76.3
8	H ₃ BO ₃	.058	4.8	4.5	78.7	94.2	99.2	90.5	77.5
9	HAc	1	3.4	4.6	62.9	70.2	73.2	91.8	72.6

The rates of reduction in Examples 7 to 9, particularly the amount of sugar reduced at 120 minutes, show by contrast the advantages of the accelerators. Examples 8 and 9 show the effect of reducing with boric acid and acetic acid which give the same anions in solution as their alkali and alkaline earth metal salts. However, these acids are not accelerators for the reduction whereas their salts are.

The effect of varying the amount of accelerator is shown in Examples 10, 11 and 12.

determined by crystallizing sorbitol from sorbitol-containing products in the form of a sorbitol-pyridine complex, filtering the crystalline complex, adding water to it to decompose the complex into pyridine and sorbitol, driving off the pyridine by vacuum distillation with water, dehydrating the sorbitol residue and weighing it as sorbitol. The procedure is specific for sorbitol since no other polyhydric material, such as sugar, mannitol, etc., exhibits the same behavior with pyridine. The pyridine number is the

Ex.	Accelerator	Mol. per cent	pH of solution		Per cent sugar reduced			Yield	P. N.
			Start	Finish	After 120 min.	After 180 min.	After 240 min.		
10	CaAc ₂	2	6.6	4.6	94.7	98.9	99.95	83.8	67.8
11	CaAc ₂	5	6.6	4.2	87.4	-----	94.5	87.2	70.5
12	CaAc ₂	10	6.5	4.1	86.9	89.3	91.5	74.3	53.8

The greatest amount of acceleration in the foregoing table is exhibited in Example 10 at 2 mol % concentration of calcium acetate. All values above 2% show a lower rate of reduction although it is to be noted that even in the case of 10% concentration the rate is substantially higher to 120 minutes than the reduction during the same period in Examples 7, 8 or 9 which omit the accelerator.

weight of sorbitol crystallized from anhydrous pyridine as above multiplied by 100, and divided by the weight of the sample (ash, moisture and sugar free). The pyridine number for pure sorbitol is about 95. The preparation of the sorbitol pyridine complex and its treatment to free sorbitol therefrom is described by Strain in J. Am. Chem. Soc., vol. 56, page 1757 (1934). The pyridine number of a sorbitol-containing prod-

uct is an index of its crystallizing tendency from relatively highly concentrated aqueous solutions. The higher the pyridine number the greater the crystallizing tendency.

The foregoing examples of reductions using accelerators according to the invention show improved rates of reduction and also, in general, at the moderate acidities of the examples, improved P. N.'s of the product. In the case of glucose reduction, sorbitol is the direct reduction product and the P. N. therefore indicates the extent of transformation of the glucose since a high P. N. implies high sorbitol content and low content of by-products, hence high P. N. means little transformation whereas low P. N. means more transformation. Thus, while the acid reduction process gives, in general, a lower yield of by-products at moderate acidities, the accelerators disclosed herein exhibit the effect of even further reducing the by-product yield of such acid reductions.

The invention contemplates an accelerator comprising an alkali (including ammonium) or alkaline earth metal. As before stated, the metal will be in the form of a salt and the anion can be any acid radical except chloride or other known catalyst poison which exerts a specific hindering effect on the reduction. Generally, then, any non-hindering radical can be the anion of the accelerator salt.

The accelerating salts can be used singly as in the examples or two or more can be mixed if desired.

Preferably the accelerating salts are used in the proportion of from 1 to 5 mols of the cation in the salt to 100 mols of the sugar being reduced.

The accelerating salts can be added as such to the sugar solution before hydrogenation or the elements of the salts may be added and the salts thereafter formed in the mixture. Thus, a base having the proper cation to form an accelerator salt can be added along with an acid which will furnish one of the permissible anions and the reaction of these two will form the accelerator salt.

The invention is not to be taken as limited to the examples given, nor to the specific conditions of catalyst, pressure, temperature and the like set out above for the purpose of illustration, but the invention is limited only by the scope of the following claims.

I claim:

1. In the process of reducing a reducible sugar to a product containing a substantial amount of polyhydric alcohol with the same number of carbon atoms as said sugar in a solution at a pH less than 7.0 by the action of hydrogen at pressures of from 500 to 2000 pounds per square inch and at temperatures of from 140 to 160° C. in the presence of a supported reduced nickel catalyst, the improvement which consists in adding to the sugar before reduction an accelerator comprising a salt having a cation selected from the group consisting of alkali metals, ammonium, magnesium and alkaline earth metals, and said salt having a non-hindering anion.

2. In the process of catalytically reducing a reducible sugar to a product containing a substantial amount of polyhydric alcohol with the same number of carbon atoms as said sugar in an acid medium with hydrogen at superatmospheric pressure and at a temperature below that at which cracking of the carbon-carbon bond occurs; the improvement which consists in adding to the sugar before reduction a small amount of an accelerator salt having a cation selected from

the group consisting of alkali metals, ammonium, magnesium, and alkaline earth metals, said salt having a non-hindering anion, said accelerator salt being added independently of the catalyst, and reducing the sugar in the presence of said accelerator salt.

3. In the process of catalytically reducing a reducible sugar to a product containing a substantial amount of a polyhydric alcohol with the same number of carbon atoms as said sugar in an acid medium with hydrogen at superatmospheric pressure and at a temperature below that at which cracking of the carbon-carbon bond occurs; the improvement which consists in adding to the sugar before reduction and independently of the catalyst an accelerator salt having a cation selected from the group consisting of alkali metals, ammonium, magnesium, and alkaline earth metals, said salt having a non-hindering anion, and said salt being added in the quantity of from 1 to 5 mols of the cation per 100 mols of sugar, and thereafter reducing the sugar in the presence of said accelerator salt.

4. The process for producing a product comprising a substantial amount of sorbitol from glucose which comprises subjecting an acid solution of glucose to the action of hydrogen at superatmospheric pressure and at a temperature below that at which cracking of the carbon-carbon bond occurs, in the presence of a hydrogenating catalyst, and an accelerator salt added independently of the catalyst and having a cation selected from the group consisting of alkali metals, ammonium, magnesium and alkaline earth metals, said salt having a non-hindering anion.

5. In the process for producing a product comprising a substantial amount of sorbitol from glucose by catalytic pressure hydrogenation in acid medium at a temperature below that at which cracking of the carbon-carbon bond occurs; the improvement which consists in adding to the glucose before reduction from 1 to 5 mols of an accelerating cation per 100 mols of glucose, said cation being selected from the group consisting of alkali metals, ammonium, magnesium, and alkaline earth metals, said cation being added independently of the catalyst, and reducing the glucose in the presence of said accelerating cation.

6. In the process of catalytically reducing a reducible sugar to a product containing a substantial amount of a polyhydric alcohol with the same number of carbon atoms as said sugar in an acid medium with hydrogen at superatmospheric pressure and at a temperature below that at which cracking of the carbon-carbon bond occurs; the improvement which consists in adding to the sugar before reduction and independently of the catalyst an accelerator comprising an acetate salt with a cation selected from the group consisting of alkali metals, ammonium, magnesium, and alkaline earth metals, and reducing the sugar in the presence of said accelerator.

7. In the process of catalytically reducing a reducible sugar to a product containing a substantial amount of a polyhydric alcohol with the same number of carbon atoms as said sugar in an acid medium with hydrogen at superatmospheric pressure and at a temperature below that at which cracking of the carbon-carbon bond occurs; the improvement which consists in adding to the sugar before reduction an accelerator comprising an acetate salt with a cation selected from the group consisting of alkali metals, am-

monium, magnesium, and alkaline earth metals, said accelerator being added independently of the catalyst and in amount sufficient to give 1 to 5 mols of the cation per hundred mols of sugar and reducing the sugar in the presence of said accelerator.

8. In the process of catalytically reducing glucose to a product comprising a substantial quantity of sorbitol in an acid medium with hydrogen at superatmospheric pressure and at a temperature below that at which cracking of the carbon-carbon bond occurs; the improvement which consists in adding to the glucose before reduction an accelerator comprising an acetate salt with a cation selected from the group consisting of alkali metals, ammonium, magnesium, and alkaline earth metals, said salt being added independently of the catalyst in amount sufficient to give substantially 1 mol of the cation per hundred mols of glucose, and reducing the glucose in the presence of said accelerator.

9. In the process of catalytically reducing a reducible sugar to a product containing a substantial amount of a polyhydric alcohol with the same number of carbon atoms as said sugar in an acid medium with hydrogen at superatmospheric pressure and at a temperature below that at

which cracking of the carbon-carbon bond occurs; the improvement which consists in adding to the sugar before reduction and independently of the catalyst and accelerator salt having a cation selected from the group consisting of alkali metals, ammonium, magnesium, and alkaline earth metals, and having a non-hindering anion, and reducing the sugar in the presence of said accelerator salt.

10. In the process of reducing a reducible sugar to a product containing a substantial amount of a polyhydric alcohol with the same number of carbon atoms as said sugar in a solution at a pH less than 7.0 by the action of hydrogen at pressures of from 500 to 2000 pounds per square inch and at temperatures of from 140 to 160° C. in the presence of a supported reduced nickel catalyst; the improvement which consists in adding to the sugar before reduction and independently of the catalyst an accelerator comprising a salt having an alkaline earth metal cation and a non-hindering anion, and reducing the sugar in the presence of said accelerator.

11. The process of claim 10 wherein the cation of the said accelerator salt is calcium.

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