Uı	nited S	tates Patent [19]	[11] E Re. 30,88				
Arn	nbruster		[45] Reissued Mar. 9, 198				
[54] [75]	PRODUC	. STARCH CONVERSION TS Frederick C. Armbruster, La Grange, Ill.	2,965,520 12/1960 Snyder et al				
[73]	Assignee:	Grain Processing Corporation, Muscatine, Iowa	OTHER PUBLICATIONS				
[21]	Appl. No.:	327,335	Wallerstein Technical Bulletin No. 236 (4 pp.), Ap 1964.				
[22]	Filed:	Jan. 29, 1973 ted U.S. Patent Documents	Primary Examiner—Lionel M. Shapiro Attorney, Agent, or Firm—Neuman, Williams, Anderson & Olson				
Reiss	sue of:						
[64]	Patent No	o.: 3,560,343	[57] ABSTRACT				
Issued: Feb. 2, 1971 Appl. No.: 625,584 Filed: Mar. 24, 1967			The present invention provides a process for preparing low D.E. starch hydrolysates and low D.E. starch con version syrup products which are both liquid and solid				
[51] [52] [58]	U.S. Cl	C12P 19/14 	Starch is treated with acid to a D.E. less than 15 and then converted with a bacterial alpha-amylase to a D.E between 10 and 25. From the resulting hydrolysate				
[56]		References Cited	product is obtained a non-hazing syrup which is almost				
	U.S.	PATENT DOCUMENTS	completely water-soluble.				

17 Claims, No Drawings

LOW D.E. STARCH CONVERSION PRODUCTS

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

The present invention relates to a process for preparing low D.E. starch hydrolysates and low D.E. starch 10 conversion syrups. The present invention also relates to the resulting products. D.E. is an abbreviation for dextrose equivalent which is a common expression in the art for describing the total reducing sugars content of a material calculated as dextrose, and expressed as per-15 cent dry basis.

Conventionally, low D.E. starch conversion syrups have been produced by the hydrolysis of starch with acids. The primary emphasis in the preparation of commercial starch hydrolysate syrups has been on attaining 20 stability, clarity and non-crystallizing characteristics.

There is a large potential market for syrups and syrup solids with bland taste, low sweetness and low hygroscopicity at a low D.E. level. Such syrups, hydrolysates and syrup solids are useful as basis for the preparation of 25 food items as well as for bodying agents and as additives having non-sweet, water holding, non-hygroscopic characteristics. Other applications include use as a carrier for synthetic sweeteners, as a flavor enhancer, as an additive for coloring agents, as a spray drying adjunct 30 for coffee extracts or tea extracts, as a bulking, bodying, or dispersing agent in synthetic creams or coffee whiteners, as a moisture holding agent in breads, pastries, meats and as a bodying and smoothing agent in puddings, soups, and frozen iced desserts.

Low D.E. syrups having a D.E. less than 28 to 30 are not practical to produce from starches by the process of the prior art. Previous attempts to produce low D.E. syrups from starches by prior art processes have failed by way of extremely poor filtration rates, yield losses 40 and substantial insolubility of syrup solids.

One object of the present invention is to provide a novel low D.E. starch hydrolysate product.

Another object of the present invention is to provide a low D.E. syrup that is clear and stable.

A further object of the present invention is to provide a bland tasting, low sweetness, non-hygroscopic, low D.E. starch hydrolysate product.

Still another object of the present invention is to provide a syrup solids product with improved charac- 50 teristics with respect to hygroscopicity and water-solubility.

Another object of the present invention is to provide syrups and syrup solids for use in food products, the syrup products having a minimum effect on flavors 55 while providing bulk, viscosity, body, and stability to the food products.

A related object of the invention is to provide new practical processes for the manufacture of syrups and syrup solids and starch hydrolysate products of the 60 character described.

A similar object of the invention is to provide new practical processes for the manufacture of starch hydrolysates that may be clarified and will remain clear at high solids concentration.

Other objects of the present invention will be apparent hereinafter from the following description and from the recitals of the appended claims.

The present invention provides a process for preparing a novel low D.E. starch hydrolysate. This process comprises subjecting a mixture of starch and water, having a solids content of less than about 50%, to the hydrolytic action of acid to obtain a starch hydrolysate having a D.E. between about 5 and about 15, subjecting the acid hydrolysate to the hydrolytic action of bacterial alpha-amylase to a D.E. between about 10 and about 25, the increase in D.E. being at least about 5, to produce a starch hydrolysate having a dextrose content of less than 4%, and that is also characterized by having a sum of the percentages of saccharides therein, dry basis, having a degree of polymerization of 1 to 6, divided by the D.E., provide a ratio greater than about 2.0. This ratio is referred to hereinafter as the characteristic or descriptive ratio.

The present invention also provides a process for preparing a novel low D.E. syrup by the concentration of the starch hydrolysate produced in accordance with this invention, to produce a syrup having a solids content greater than 50%. The syrup, i.e. concentrated hydrolysate, may or may not be refined by conventional means.

The present invention also provides a process for preparing syrup solids by reducing the moisture content of either a starch hydrolysate or a syrup produced in accordance with this invention to a moisture content of less than 15%.

It has been discovered that syrup and starch hydrolysate products may be obtained from starches by application in sequence of acid to the starch to yield a starch hydrolysate having a D.E. between about 5 and about 15 and subsequently applying a hydrolytic enzyme to the acid starch hydrolysate to yield a starch hydrolysate having a D.E. between about 10 and about 25 and having a descriptive ratio of at least about 2.0.

One preferred method of practicing the present invention involves the steps of slurrying corn starch in water to a density between 5° and 30° Baume, adjusting the pH of the slurry to between 1 and 3 and raising the temperature of the starch slurry to between 70° C. and 160° C. to solubilize and hydrolyze the starch to a D.E. between 5 and 15. The pH is adjusted to between 6 and 8 and the hydrolysate is dosed with bacterial alpha-45 amylase. The mixture is then hydrolyzed under the proper conditions to a D.E. between 10 and 25, preferably between about 15 and about 25 when it is desired that the final product be a haze-free syrup. The enzyme conversion step is carried out at a temperature in the range between about 50° and about 95° C. The mixture is held at the conversion temperature for a period of time ranging from a few minutes to as long as 1 or 2 hours or perhaps more.

The resulting hydrolysate may be concentrated and/or refined by conventional procedures to yield a stable
corn syrup, which is substantially haze-free and highly
soluble in water. The syrup may be spray dried to yield
corn syrup solids with low hygroscopicity and high
water solubility.

Suitable starches include cereal starches such as corn, grain sorghum and wheat, waxy starches such as, waxy milo and waxy maize, and root starches, such as potato starch and tapioca starch.

The initial step, i.e. mild acid hydrolysis of starch, 65 places the starch in proper condition for further hydrolysis by the hydrolytic enzyme. In order for acid hydrolysis to take place, it is necessary that starch solubilization be effected either simultaneously with acid treat-

ment or prior to acid treatment. Starch solubilization may be accomplished, for example, by heating the starch water slurry above the gelatinization temperature of the starch or by adding dry starch to heated water or by other similar means. Similarly, the acid may 5 be added to the starch before, during or after the starch is gelatinized.

Acid hydrolysis is carried out at a pH less than 4, preferably between about 1 and about 3 at a temperature sufficiently high to gelatinize the starch. The hy- 10 drolysis is continued to a D.E. of at least 5 and less than 16.

The acid hydrolysate is then neutralized and subjected to further conversion with a suitable enzyme preparation to increase the reducing sugar content by at 15 least 5 D.E.

The pH of the enzyme conversion medium is preferably that which is suitable for the optimum activity of the bacterial alpha-amylase. Generally, this pH range is between about 6 and about 8. The most suitable temper- 20 ature range lies between that required for gelatinizing starch which is at least 60° C. and that at which the enzyme will lose a large portion of its activity, which is about 95° C. It has been found that the preferred temperature range is between about 80° C. and about 92° C. 25

The preferred enzyme used for the conversion of the acid hydrolysate to low D.E. hydrolysates in accordance with the present invention is the type commonly referred to in the art as bacterial alpha-amylase. It is a starch liquefying, heat resistant, hydrolytic alpha-amy- 30 lase. Suitable bacterial alpha-amylase may be produced by certain strains of Bacillus subtilis, Bacillus mesentericus and the like by conventional fermentation methods. HT-1000, the proprietary name of a bacterial alphaamylase preparation produced and marketed by the 35 Miles Chemical Laboratories, is an example of an enzyme preparation that is suitable for use in the present invention. Other suitable bacterial alpha-amylase include Rhozyme, H39, manufactured and sold by Rohm & Haas, CPR-8 manufactured and sold by the Waller- 40 stein Division of Baxter Laboratories, Inc.

The time required for the solubilization and acid hydrolysis step depends upon the amount of acid used and the reaction temperature. The more acid used and the higher the temperature, the less time required for 45 the reaction. The same is true for the enzyme hydrolysis relative to the amount of enzyme employed and the reaction temperature selected. Optimum conditions for hydrolysis of starch with bacterial alpha-amylase are known.

When the desired D.E. is reached, conversion action may be stopped by adjusting the pH to 4.5 or below or by heating the conversion mixture to a temperature above the inactivation temperature of the enzyme, or the conversion may be effected at temperatures sufficiently high that the enzyme has been substantially inactivated by the time the final D.E. is reached.

It is desirable to operate at relatively high dry substance levels up to about 50% and preferably in the range of between about 20% and about 40%, i.e. about 60

10° to about 20° Baumé. When operating at a high dry substance level, the required tank volume for conversion is reduced as are evaporation costs. However, the process is suitably operated at dry substance concentration outside of this range.

The acid hydrolysis and saccharifying conditions may be varied within certain limits dictated by the stability and activity characteristics of the enzyme and the gelatinization and acid hydrolysis properties of the starch.

After termination of the enzyme conversion, the resulting starch hydrolysate has a solids content less than 50%. It may be used in unaltered form as a desirable product for the uses suggested heretofore. In addition, the starch hydrolysate may be concentrated and/or refined to yield a syrup having a solids content greater than 50%. Generally, industry prefers use of a syrup of high solids content both because it is advantageous in shipping and in applications.

The syrup may be dried by conventional means to yield syrup solids high in water solubility and stability as well as low in hygroscopicity.

The refining of the hydrolysate is achieved by conventional refining methods. These include treating with vegetable carbon, ion exchange resins, filtration, centrifugation and the like.

The invention will now be further described in detail by means of several exemplary demonstrations thereof.

EXAMPLE I

Several samples of corn starch (A, B and C) were slurried in water providing slurries having Baume's ranging from 14° to 22°. These slurries were partially acid hydrolyzed to a maximum of 15 D.E. The particular D.E. achieved by acid hydrolysis in each of the samples is set forth in the Table I below. After acid hydrolysis, the slurry was neutralized to a pH between 6 and 7. The neutralized liquor was cooled to between 80° and 85° C., and dosed with bacterial alpha-amylase (HT-1000) in the quantity set forth below. A final D.E. of 19 to 21 was obtained in each of the samples in a period of time between 1 and 3 hours. The final conversion liquors are low in color. These liquors are easily refined and evaporated to about 42° Baume to provide syrups. Sample D was a conventionally acid hydrolyzed starch conversion product. Acid hydrolysis was carried out to reach a D.E. of 20. Tables I and II below set forth the reaction conditions for conversion and the product analyses respectively.

TABLE I

	ENZ	ZYME CON	IVERSI(ON C	CONDITIO	NS	
Sam- ple	D.E. of acid hydrol-ysate	Percent dry substance	Temp. °C.	pН	Enzyme dose	Time, hours	Final D.E.
A	15.2	38	80	6.5	0.01	1	19.7
В	12.9	37.5	85	6.5	0.05	2	20.2
C	10.3	38.1	85	6.5	0.1	2	21.8
D	20.0						

TABLE II

			_ P	RODU	CT ANA	LYSE	<u>S_</u>			
Sample	Final D.E.	Percent dry sub- stance	DP ₁	DP ₂	DP ₃	DP ₄	DP ₅	DP_6	DP ₇₊	Descrip- tive ratio
A	19.7	72	3.9	5.8	8.2	7.2	7.3	10.2	57.4	2.1
В	20.2	72	2.3	5.9	8.5	6.4	6.6	12.6	57.7	2.1
C	21.8	75	2.3	8.3	10.9	8.1	9.2	16.9	44.3	2.5

TABLE II-continued

·			, <u>P</u> l	RODU	CT ANA	LYSE	<u>S</u>			
Sample		Percent dry sub- stance	DP_1	DP_2	$\mathbf{DP_3}$	DP ₄	1		DP7+	Descrip- tive ratio
D	20.0		5.5	5.9	5.8	5.8	5.5	4.3	67.2	1.6

The descriptive ratios of each of samples A-C were greater than 2. The descriptive ratio of sample D (con- 10 ventional acid hydrolysate) was 1.6.

After refining, typical analyses of the syrups were as follows: substantially colorless, clarity greater than 90%, sulfated ash 0.42% dry basis, protein 0.03% dry basis. The refined syrups were allowed to stand at room 15 temperature and at the end of a one month period remained haze-free.

EXAMPLE II

Waxy milo starch was slurried in water to a Baumé of 20 about 20°. The slurry was then partially hydrolyzed by acid to a D.E. of about 6.5 and then neutralized to a pH between 6 and 7. The acid hydrolyzed product was then dosed with bacterial alpha-amylase (HT-1000) in the amount of 0.02%. The temperature of the dosed liquor 25 was between 80° and 85° C. Conversion was allowed to proceed for about $1\frac{1}{2}$ hours until a D.E. of about 21 was obtained. Analysis of the product obtained appears in Table III below.

TABLE III

	Sample	G			
]	Final D.E.	·	·•	21.4	
	Dry substance percent			75	
	DP_1			2.3	
	DP_2	: :		5.9	35
	DP_3^{-}		• ,	8.4	
	DP ₄			7.3	
·	DP_5			8.0	
•	DP_6		. :	11.3	
	DP ₇ ↓	:		56.8	
	, r 1				40

It may be noted that in Examples I and II the descriptive ratio exceeds 2.0, i.e. the sum of the percentages of degree of polymerization from 1 to 6 divided by the D.E. provides a ratio in excess of 2. If the descriptive ratio is at least about 2, the product is highly water-soluble and exhibits almost no haze formation. If the descriptive ratio of syrups in the range of 15-25D.E. is substantially below 2, e.g. 1.6 or less, the products exhibit haze formation and are less water-soluble than products with a ratio of at least 2.

EXAMPLE III

Tapioca starch was slurried in water to a Baume of about 20°. The slurry was then partially hydrolyzed by acid to a D.E. of about 8, and then neutralized to a pH between about 6 and 7. The acid hydrolyzed product was then dosed with bacterial alpha-amylase (HT-1000) in a small quantity of about 0.02%. the temperature of the dosed liquor was raised to between 80° and 85° C. and conversion was allowed to proceed for a period of time sufficient to achieve a D.E. of about 20. Analysis of the product obtained appears in Table IV below.

TABLE IV

	*	. ·
Sample H	-	
Final D.E.		18.1
Dry substance percent	•	75
 $\mathbf{DP_i}$		2.5

TABLE IV-continued

DE IV-COmmucu
Sample H
5.0
7.5
7.4
7.5
10.5
59.6

EXAMPLE IV

A water slurry of waxy maize starch was prepared to about 20° Baumé. The slurry was acid hydrolyzed to a D.E. of 5. The acid hydrolysate was neutralized to a pH between 6 and 7 and a small quantity of bacterial alphaamylase (HT-1000) was added (about 0.01%). Hydrolysis was carried out under the temperature and time conditions discussed above to reach a D.E. of 10, at which time hydrolysis was terminated.

The hydrolysate product was concentrated and refined to obtain a syrup. The syrup was then spray dried to obtain syrup solids having a moisture content of about 4%. The syrup solids were substantially completely water soluble.

The product analyses appear in Table V below.

TABLE V

	·					
Sample J						
Final D.E.	10					
DP_1	1.4					
\mathbf{DP}_2	2.4					
\mathbf{DP}_{3}^{-}	4.0					
DP ₄	3.4					
DP_5	3.0					
$\mathbf{DP_6}$	6.0					
$\mathbf{DP}_{7.+}$	79.8					

Haze development in starch conversion syrups will vary considerably in prior art low D.E. hydrolysates depending upon the temperature at which the hydrolysates are held, the solids concentration, and the degree of the hydrolysis as reflected by the D.E. value, as well as other factors. In extreme cases, the hydrolysate can become completely opaque, or even set up to a solid or pasty mass. In less extreme cases, haze particles may be found to agglomerate and settle toward the bottom of the liquor resembling sludge. In lesser instances, haze particles appear too fine and too dispersed to agglomerate to a marked degree. They therefore remain in suspension lending the hydrolysate a cloudy appearance. In each of these cases, the optical clarity of the liquors is adversely effected.

Haze formation may therefore conveniently be determined by measuring the amount of light passing through a sample of the hydrolysate as compared to that passing through a blank of distilled water. This is used as a test for determining the clarity and solubility of hydrolysates prepared in accordance with the invention. The hydrolysates of the examples in the invention were concentrated to 65% solids, held for 3 days at 5° C., and examined spectrophotometrically by measuring

the light transmittance percent at 600 mµ through 4 centimeter cells, each containing portions of the hydrolysates respectively which had first been held three days at 5° C. The relative stability of low D.E. hydrolysates prepared by the acid-enzyme sequence taught in the 5 present invention is indicated by the very high light transmittance values observed. These are presented in the following table.

TABLE VI

_	PERCENT LI	GHT TRANS	SMITTANO	CE
D.E. value	Conventional Acid corn starch	Waxy milo starch	Tapioca starch	Hydrolyzed Corn Starch
15	92	93	66	0
20	96	93	68	1
25	96	94	70	6

In contrast, hydrolysates prepared by acid hydrolysis alone either failed to furnish clear haze-free hydrolysates because they could not be filtered in any appreciable rate after conversion, particularly from the low D.E. range or after filtration was achieved, or the clarified hydrolysates soon exhibited haze formation, often becoming completely opaque by exhibiting 0% light 25 transmittance within three days at 5° C.

The hydrolysate product of the present invention may be concentrated and/or refined to produce syrups or syrup solids. If the D.E. of the hydrolysate is substantially below 15, e.g. 10, the syrup products obtained will exhibit some haze formation. It is therefore advantgaeous to produce syrup solids from starch hydrolysates having a D.E. substantially below 15. The syrup solids are obtained by reducing the moisture content of the syrup to less than 15%, preferably about 4%. The syrup solids exhibit 100° water solubility, the solution being completely free of haze if the D.E. is 15-25.

The descriptive ratio

$$[DP_{1\rightarrow 6}/D.E.]$$

is a convenient method for the determining of the characteristics of the hydrolysate or syrup. If the descriptive ratio is at least about 2, the product is highly water soluble and exhibits almost no haze formation. If the 45 descriptive ratio is substantially below 2, e.g. 1.6 or less, the products exhibit haze formation and are less water soluble than products with a ratio of at least 2.

The hydrolysates of this invention, whether in the form of dilute or concentrated syrups, or in the form of 50 dry solids, are characterized by blandness of taste and low sweetness and they are non-hygroscopic. They are fully and readily soluble in water. When used in food products, they have a minimal effect upon the flavor while providing bulk and stability.

These characteristics make the products of the invention particularly suitable for applications such as, for example, carriers for synthetic sweeteners, flavors, coloring agents and essences; spray drying adjuncts for coffee extracts and tea extracts; bulking, bodying and 60 dispersing agents in synthetic creams or coffee whiteners; ingredients promoting moisture retention in bread, pastries, and meats; and as components of dry soap mixes, bakery mixes, frosting mixes, spice mixes, and blends, beverage powders, condiments, gravy mixes, 65 sauce mixes and frozen dairy foods. In addition, they are useful in the formulation of anti-caking agents, tabletting compounds, whipped products, protective coat-

ings, agglomeration aids and low or reduced calorie foods and beverages.

When the starch hydrolysate products or syrups or syrup solids of the invention are used as solutions at a high solids concentration of less than 40% by weight, they are particularly attractive because of their bland flavor, low hygroscopicity, low sweetness, and ready solubility. They impart density and good mouthing characteristics without appreciably affecting viscosity or flavor. At solids concentrations above about 40%, the solutions contribute significantly to the viscosity characteristics of any system in which they are employed.

While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modifications and this application is intended to cover any variations or adaptations of the invention, following in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice in the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth and as fall within the scope of the invention and the limits of the appended claims.

We claim:

- [1. A process for preparing a starch hydrolysate having
 - (A) a D.E. between about 10 and about 25 and
 - (B) a descriptive ratio greater than 2.0 said descriptive ratio being the quotient obtained by dividing the sum of the percentages of saccharide, dry basis, having a degree of polymerization of 1 to 6 by the D.E., which comprises
 - (1) subjecting the mixture of starch and water having a solids content of less than about 50% to the hydrolytic action of the acid to attain a D.E. between about 5 to about 15, and
 - (2) subjecting the resulting acid hydrolysate to sufficient hydrolytic action of bacteria alphaamylase to increase the D.E. by at least 5 and to obtain the starch hydrolysate.
- [2. A process in accordance with claim 1 wherein the starch is corn starch.]
- [3. A process in accordance with claim 1 wherein the starch is a waxy cereal starch.]
- [4. A process in accordance with claim 1 wherein the acid hydrolysis takes place at a pH between about 1 and about 3.]
 - [5. A process for preparing a syrup having
 - (A) A D.E. between about 10 and about 25.
 - (B) a solids content greater than about 50%, and
 - (C) a descriptive ratio greater than 2.0, said descriptive ratio being the quotient obtained by dividing the sum of the percentages of saccharides, dry basis, having a degree of polymerization of 1 to 6 by the D.E., which comprises
 - (1) subjecting a mixture of starch and water having a solids content less than about 50% to the hydrolytic action of acid to obtain a hydrolysate having a D.E. between about 5 and about 15.
 - (2) subjecting the resultant hydrolysate to the hydrolytic action of bacterial alpha-amylase to increase the D.E. by at least 5, and
 - (3) concentrating the resulting starch hydrolysate to a solids content greater than 50% thereby obtaining the syrup.
- [6. A process in accordance with claim 5 wherein the starch is corn starch.]

[7. A process in accordance with claim 5 wherein the starch is a waxy cereal starch.]

[8. A process in accordance with claim 5 wherin the pH during acid hydrolysis is between about 1 and about 3.]

19. A process for preparing low D.E. dry syrup solids comprising

(1) preparing a syrup in accordance with the process of claim 5 and then

(2) reducing the moisture content of said syrup to less than 15%.

10. A process for preparing a starch hydrolyzate having (A) a dextrose equivalent value between about 10 and about 25 and

(B) a descriptive ratio greater than 2.0 said descriptive ratio being the quotient obtained by dividing the sum 15 of the percentages of saccharide, dry basis, having a degree of polymerization of 1 to 6 by the dextrose equivalent value, which comprises:

(1) subjecting the mixture of starch and water having a solids content of less than about 50% to the hy-20 drolytic action of an acid to attain a dextrose equivalent value between about 5 and about 15, and

(2) subjecting the resulting acid hydrolyzate to sufficient hydrolytic action of bacterial alpha-amylase to increase the dextrose equivalent value by at least 5 to obtain the starch hydrolyzate.

11. A process in accordance with claim 10 wherein the starch is corn starch.

12. A process in accordance with claim 10 wherein the starch is a waxy cereal starch.

13. A process in accordance with claim 10 wherein the 30 acid hydrolysis takes place at a pH between about 1 and about 3.

14. A process for producing a starch hydrolyzate which comprises:

(1) treating a starch water slurry with an acid above the 35 gelatinization temperature of the starch to solubilize and hydrolyze the starch to a dextrose equivalent value no greater than about 15,

(2) treating the acid hydrolyzed starch with bacterial alpha-amylase to obtain a starch hydrolyzate product having a dextrose equivalent no greater than about 25,

(3) stopping the conversion action of the bacterial alphaamylase, and

(4) recovering the hydrolyzate so produced.

15. A process in accordance with claim 14, wherein said treatment with bacterial alpha-amylase is conducted at a 45 temperature from about 50° C. to about 95° C. and at a pH of from about 6 to 8.

16. A process in accordance with claim 14, which includes treatment with bacterial alpha-amylase at a temperature from about 60° C. to about 95° C.

17. A process in accordance with claim 14 wherein the starch is solubilized and hydrolyzed with an acid by raising the temperature of the starch slurry to between about 70° C. and about 160° C. at a pH between 1 and 3.

18. A process in accordance with claim 14 wherein the 55 starch is a non-waxy cereal starch.

19. A process in accordance with claim 14 wherein the starch is a waxy cereal starch.

20. A process in accordance with claim 14 wherein the starch is corn starch.

21. A process for producing a starch hydrolyzate which ⁶⁰ comprises:

(1) treating a starch-water slurry with an acid above the gelatinization temperature of the starch to solubilize and hydrolyze the starch to a dextrose equivalent value of about 5,

(2) treating the acid hydrolyzed starch with bacterial alpha-amylase to increase the dextrose equivalent value by at least about 5 and to obtain a starch hydro-

lyzate product having a dextrose equivalent value in the range of from about 10 to about 25,

(3) stopping the conversion action of the bacterial alphaamylase, and

(4) recovering the hydrolyzate so produced.

22. A process in accordance with claim 21 wherein the treatment with bacterial alpha-amylase is carried out at a pH range between about 6 and 8 and at a temperature between about 80° C. and about 92° C.

23. A process for producing a corn starch hydrolyzate which comprises:

(1) slurrying corn starch in water to a density between 5° and 30° Baumé.

(2) adjusting the pH of the slurry to between about 1 and about 3 with an acid and raising the temperature of the starch slurry to between 70° C. and 160° C. to solubilize and hydrolyze the starch to a dextrose equivalent value not greater than about 15,

(3) adjusting the pH of the acid hydrolyzed starch to between 6 and 8.

(4) treating the acid hydrolyzed starch mixture with bacterial alpha-amylase at a temperature in the range between 50° C. and about 95° C. to increase the dextrose equivalent value by at least about 5,

(5) stopping the conversion action of bacterial alphaamylase, and

(6) recovering the hydrolyzate so produced.

24. A process for producing a starch hydrolyzate which comprises:

(1) treating a starch-water slurry with an acid above the gelatinization temperature of the starch to solubilize and hydrolyze the starch to a dextrose equivalent value less than about 15,

(2) treating the acid hydrolyzed starch with bacterial alpha-amylase to increase the dextrose equivalent value by at least about 5 and to obtain a starch hydrolyzate product having a dextrose equivalent value in the range of from about 10 to about 25,

(3) stopping the conversion action of the bacterial alphaamylase, and

(4) recovering the hydrolyzate so produced.

25. A process for producing a starch hydrolyzate which comprises treating an aqueous slurry of starch with an acid at a temperature above 70° C. to liquefy and hydrolyze the starch to a dextrose equivalent of less than about 15, then treating the said hydrolyzed starch with a saccharifying enzyme at a temperature below 95° C. to achieve a hydrolyzate product having a dextrose equivalent value not substantially above about 25, stopping the saccharification reaction and recovering the hydrolyzate so produced.

26. A process for preparing a syrup having

(A) a dextrose equivalent value between about 10 and about 25,

(B) a solids content greater than about 50%, and

(C) a descriptive ratio greater than 2.0, said descriptive ratio being the quotient obtained by dividing the sum of the percentages of saccharides, dry basis, having a degree of polymerization of 1 to 6 by the dextrose equivalent value, which comprises

(1) subjecting a mixture of starch and water having a solids content less than about 50% to the hydrolytic action of acid to obtain a hydrolyzate having a dextrose equivalent value between about 5 and about 15,

(2) subjecting the resultant hydrolyzate to the hydrolytic action of bacterial alpha-amylase to increase the dextrose equivalent value by at least 5, and

(3) concentrating the resulting starch hydrolyzate to a solids content greater than 50% thereby obtaining the syrup.

UNITED STATES PATENT AND TRADEMARK OFFICE CERTIFICATE OF CORRECTION

PATENT NO. : Re. 30,880

DATED: March 9, 1982

INVENTOR(S): Frederick C. Armbruster

It is certified that error appears in the above—identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, Table VI, second column heading "Conventional Acid corn starch" should read -- Corn Starch --

> Table VI, fifth column heading "Hydrolyzed Corn Starch" should read -- Conventional Acid Hydrolyzed Corn Starch --

> > Bigned and Sealed this

Fisteenth Day of June 1982

[SEAL]

Attest:

GERALD J. MOSSINGHOFF

Attesting Officer

Commissioner of Patents and Trademarks