Sept. 4, 1951 G. C. DOCAL 2,567,060

SUGAR SEPARATION

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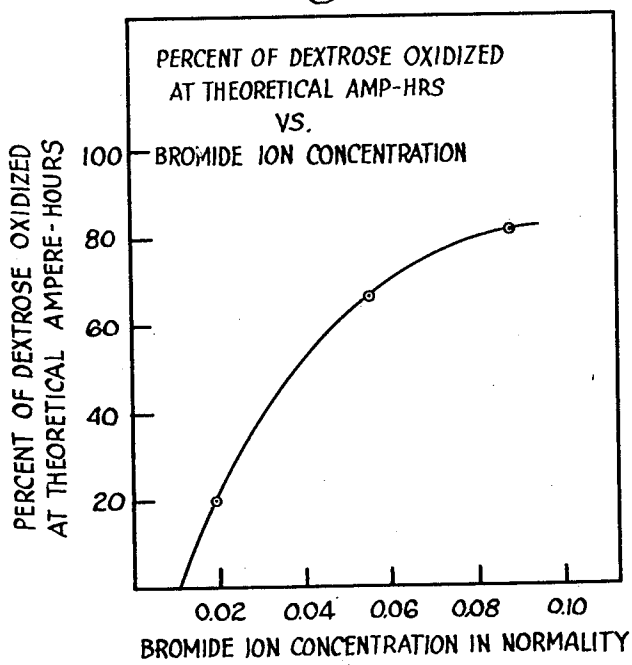
Fig. 1



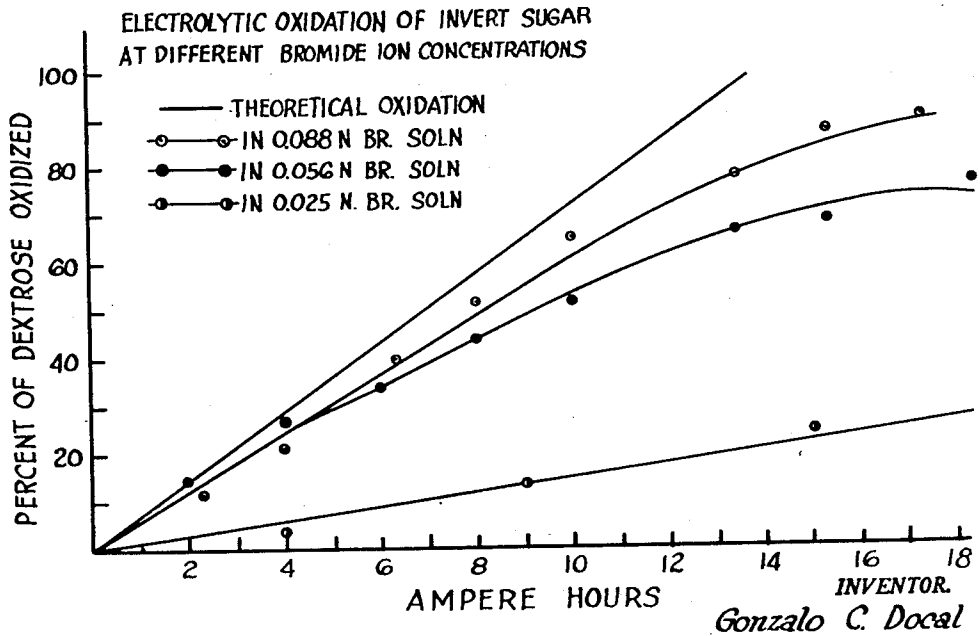


Fig. 2

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SUGAR SEPARATION

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3 Claims. (Cl. 127—53)

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This invention relates to electrolytically oxidized sugar liquors. More particularly, the invention relates to a method for electrolyzing sugar liquors consisting of mixtures of dextrose and fructose under conditions which result in substantially quantitative oxidation of the dextrose to gluconic acid, the removal of the gluconic acid in the form of calcium gluconate, and the subsequent isolation and recovery of non-modified fructose from the remaining crude electrolyte.

One object of the invention is to provide an electrolytic invert sugar oxidation process which enables maximum aldose oxidation with substantially no ketose decomposition.

Another object is to provide an electrolytic oxidation process for mixtures of dextrose and fructose which enables the production, in solution, of substantially theoretical amounts of calcium gluconate with substantially no fructose oxidation or modification.

A further object of the invention is to provide a selective solvent process which enables the solvent extraction of fructose from an invert sugar liquor which has had its dextrose oxidized to gluconic acid and the latter removed as calcium gluconate.

Another object of the invention is to provide a fructose solvent process that enables the production of substantially pure crystalline fructose from an invert sugar solution which has had its dextrose electrolytically oxidized to gluconic acid, in the presence of a bromide ion catalyst, and which has had the gluconic acid removed in the form of calcium gluconate.

Further objects of the invention will become apparent from the specification and the claims.

Certain features of the invention are illustrated in the drawings accompanying this specification, in which

Fig. 1 is a graph showing the percentage of dextrose oxidized, and

Fig. 2 is a graph showing the oxidation of dextrose in relation to current consumed.

I have discovered that when a solution containing a mixture of dextrose and fructose is subjected to electrolytic oxidation in the presence of a bromide ion catalyst, the degree of oxidation of the dextrose to gluconic acid and the accompanying degree of oxidative destruction of fructose to various breakdown products are a function of the concentration of the bromide ion catalyst in the invert sugar solution, as well as of the amount of ampere hours applied during the electrolysis.

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I have also discovered that the destructive oxidation or degradation of fructose becomes more pronounced after the dextrose has been oxidized to gluconic acid. It was found that when a mixture of dextrose and fructose is subjected to electrolytic oxidation, the rate of fructose degradation into non-reducing compounds is lower during the time when the dextrose is being oxidized to gluconic acid, and that when the theoretical amount of ampere hours required to oxidize the dextrose to gluconic acid had been consumed, the degree of fructose degradation increases. It has also been discovered that at proper bromide ion concentration, one may obtain optimum dextrose oxidation with little or no fructose degradation after the consumption of the theoretical amount of ampere hours or even after higher ampere hours.

By properly controlling the bromide ion concentration, and by introducing a sufficient amount of basic calcium compound, such as lime or calcium carbonate, to neutralize the gluconic acid as it is formed, one may subject an invert sugar solution or other mixtures of dextrose and fructose to electrolytic oxidation and obtain high yields of calcium gluconate with practically no accompanying fructose destruction.

It has also been found that the fructose remaining in the electrolyzed sugar liquor from which calcium gluconate has been separated, can be removed and obtained in substantially pure crystalline form by means of alkyl alcohols which are capable of directly solvent extracting the fructose out of the crude electrolyzed sugar liquor with minimum inorganic ion contamination.

Having now indicated in a general way the nature and purpose of this invention, I shall submit a more detailed description of the invention in the form of examples. Examples I through IV deal with the means for obtaining optimum dextrose oxidation with accompanying minimum fructose modification. Examples V through IX deal with means for directly removing and isolating fructose from the electrolyte subsequent to the removal of calcium gluconate.

Examples I through IV

The table below shows the operating conditions and the results obtained with each case. The procedure followed with each example was as follows:

A quarter of a mole (85.5 grams) of sucrose and a 40 per cent hydrobromic acid solution were mixed with water to form a liter of solution.

The amount of hydrobromic acid used was adjusted to give the final solution the bromide ion concentration shown in the table for each test. The acidified sucrose solution was then inverted by heating for two hours at between 70° and 80° C., after which the specific rotation reached a constant value. The invert sugar liquor was then neutralized with calcium carbonate and there was then added an additional 0.25 mole, or 25 grams of calcium carbonate to serve as a medium for neutralizing the gluconic acid as formed. The liquor was then brought again to one liter with water and electrolyzed in a glass electrolytic cell provided with four carbon electrodes at an average temperature of about 25° C. Electrolysis was allowed to proceed for the number of ampere hours shown in the table. The theoretical quantity of electricity needed to oxidize 0.25 mole of dextrose is 13.4 ampere hours, or 0.50 faraday. At intervals during the electrolysis, 2 cc. samples were taken and one analyzed for dextrose while the other was analyzed for total reducing sugar. The difference between the total reducing sugar and dextrose is taken to be fructose. The table follows:

Example No.	Moles of Invert	Moles of $CaCO_3$	Normality of Br Ion	Ampere Hours	Per Cent Dextrose Oxidized	Milligrams Dextrose in 2 cc. of Invert	Milligrams Fructose in 2 cc. of Invert	Milligrams Reducing Sugar in 2 cc. of Invert
I	0.25	0.25	0.01	0	0	98.0	69.2	167.2
				4	0	96.0	58.5	154.5
				13.4	0	98.6	45.4	144.0
II	0.25	0.25	0.02	0	0	98.6	45.4	144.0
				4	2	96.2	41.0	137.2
				9	10	88.0	34.6	122.6
				15	20	78.5	28.5	107.0
				29	28	70.8	11.2	82.0
III	0.25	0.25	0.056	0	0	101.7	67.9	169.6
				4	20	76.1	68.5	144.6
				8	43	58.2	66.0	124.2
				13.4	66	35.6	65.9	101.5
				18.4	77	25.0	62.3	87.3
IV	0.25	0.25	0.088	0	0	94.6	70.3	164.9
				4	21	75.0	67.9	142.9
				10.2	63	34.9	71.5	106.4
				15.4	88	11.3	71.7	83.0
				17.4	92	8.3	72.6	80.9

Referring now to the table, it will be seen from Examples I and II that when the bromide ion concentration is low, there is little or no dextrose oxidation and that this is accompanied by a large amount of fructose degradation. When the bromide ion concentration gets beyond about 0.06 normal, the per cent of dextrose oxidation reaches substantial amounts at the theoretical ampere hours of 13.4 with practically no accompanying fructose destruction. When the ampere hours are greater than the theoretical value, there is a slight increase of fructose destruction in the case of 0.056 N bromine ion concentration, and no fructose destruction in the case of 0.088 N bromine ion concentration. The latter, i. e., Example IV, shows a high degree of dextrose oxidation, namely, 92 per cent, and no fructose degradation with 17.4 ampere hours.

For the recovery of calcium gluconate, the electrolyte liquor, after the completion of the electrolysis, is heated on a steam bath at 60° to 70° C. to insure the solution of all the calcium gluconate formed. The mixture is filtered hot and the filtrate evaporated at 55° to 65° C. under reduced pressure until syrupy. It is then seeded and allowed to crystallize. The crystals are then filtered and, if desired, recrystallized from hot water. In the case of Example III, there was obtained 52 grams or an 89 per cent yield of crude calcium gluconate. In the case of Example IV, there was obtained 66 grams of crude calcium gluconate, or a crude yield of 113 per cent. The crude calcium gluconate was contaminated with fructose. Upon recrystallization from hot water, pure calcium gluconate was readily obtained.

Figure 1 in the drawing shows the curve obtained when plotting bromide ion concentration against the per cent of dextrose oxidized at the theoretical ampere hours of 13.4. It will be seen that the optimum concentration of bromide ion catalyst for maximum invert sugar oxidation is around 0.1 N.

Figure 2 is another series of curves showing the relationship between per cent of dextrose oxidized and ampere hours. It will be seen from these curves that as the bromide ion concentration approaches 0.1 normal, the curve approaches the straight line representing the theoretical oxidation conditions.

The above examples and data show that the best conditions for obtaining a maximum amount of calcium gluconate, accompanied by minimum fructose modification, is obtained when the bromide ion concentration is in the range of about 0.06 to 0.10 normal. The preferred operating conditions are those illustrated in Example IV.

The advantage of using sucrose liquor that has been inverted by means of hydrobromic acid is the fact that the introduction of additional ion impurities to the electrolyzed liquor is avoided. The presence of only bromide and calcium ions makes it easier to extract the fructose by solvent extraction after the removal of the calcium gluconate. However, one may, if one desires, carry out my process with other types of dextrose and fructose sugar solution mixtures. Thus the commercial invert sugar products, such as those produced by the hydrochloric or sulfuric acid inversion of sucrose or the invert sugar products obtained by means of invertase or other biochemical inversion means, may serve as raw materials for electrolytic oxidation and the subsequent separation and isolation of calcium gluconate and fructose. One may also use such products as honey, or mixtures of dextrose and fructose obtained by the lime conversion of dextrose solutions, or invert sugar liquor obtained by the inversion of c e cane or beet sugar liquors. When starting with commercial invert sugar solutions, the necessary bromide ion concentration for optimum dextrose oxidation may be introduced by any suitable means, such as the addition of the required amount of calcium bromide, sodium bromide, or any other soluble bromide salt which is

not deleterious to the electrolytic oxidizing reaction.

The electrolysis may be carried out by any suitable apparatus, such as a glass electrolytic cell provided with carbon electrodes, or between copper cathodes and rotating graphite anodes. The temperature during electrolysis may range from 10° to about 40° C.

After the removal of calcium gluconate from the electrolyzed liquor, the remaining electrolyte is ready to be treated for the removal of crude fructose and the isolation of pure fructose. I have found that the fructose in the crude electrolyte may be readily removed by means of certain organic solvents for fructose. In order that a solvent may serve as an efficient means for removing fructose from the electrolyte, it is necessary that such a solvent be capable of making some kind of separation between the aqueous fructose solution and the aqueous solution of ion impurities in the electrolyte. I have found that certain alkyl alcohols which are capable of forming a liquid-liquid phase separation with sugar solutions are particularly suitable for the extraction of sugars from impure sugar solutions contaminated with inorganic salts. Examples of preferred alcohols which fulfill the above-described requirements are isobutanol and propanol-2.

In general, the preferred alcohols are those which are either partly water-miscible or completely water-immiscible, which have little or no solvent power for inorganic salts in aqueous solution, and which have good solvent power for fructose. However, an alcohol which is completely water-miscible, but which is capable of forming liquid-liquid phase separations with sugar solutions wherein a substantial amount of sugar substance is dissolved in the aqueous alcoholic phase, is satisfactory for the purposes of this invention, provided the said aqueous alcoholic sugar solution is not excessively viscous, and provided the said alcohol does not readily dissolve inorganic salts.

The above operating conditions may be illustrated with methanol, ethanol, isopropanol, and isobutanol. The methanol forms no phase separation between aqueous alcoholic sugar solution and alcohol, and cannot, therefore, be used as a sugar extractant for the purposes of this invention. The ethanol does form a bottom sugar solution phase and a top aqueous alcohol phase, but is unsatisfactory because of the excessive viscosity and difficult crystallization of the sugar solution phase and because of the ready solubility of inorganic ion impurities, such as bromide or calcium ions, in the alcohol. The isopropanol, on the other hand, was found to have an unexpected comparatively high solvent power for fructose, a low solvent power for dextrose, and a low solvent power for inorganic ion impurities. It also readily forms two liquid phase layers when added to an aqueous sugar solution. Isopropanol, therefore, is a preferred fructose extractant of the completely water-miscible class. Isobutanol is an example of the partially water-miscible type alcohol. This partial water-miscibility enables two distinct liquid-liquid phases with resultant concentration of ion impurities in the predominantly aqueous liquid phase. Solutions of fructose in isobutanol have been found to be readily crystallizable upon cooling, and the fructose crystals readily filterable.

Having now indicated in a general way the nature and functional requirements of satisfactory solvent extractants of fructose from aqueous solution, there follow more detailed descriptions in the form of examples.

Example V

Extraction of aqueous fructose solution with isobutanol:

5.4 grams of pure fructose were dissolved in 300 cc. of water to make a 0.10 molar solution. The solution was continuously extracted with 150 cc. of isobutanol for 30 hours in a commercial extractor of the usual type with a spiral distributor. This particular extractor used was that of the Ace Glass Company, and designated by this company as No. 6835.

The specific rotation of fructose in an isobutanol solution saturated with water at the concentration of 0.22 gram fructose per 25 cc. of solution was determined at 23.6° C. to be −30.7°. With this value and the volume of isobutanol extract after extraction, it was possible to determine the amount of fructose dissolved in the isobutanol by measuring the angular rotation of the isobutanol extract. It was thus found that 15.2 per cent of the fructose had been extracted. Upon cooling the isobutanol extract, the fructose crystallized and was readily removed by filtration.

At room temperature an isobutanol-water mixture which is in equilibrium gives a water-rich layer containing 8 per cent isobutanol and an isobutanol-rich layer containing 83 per cent isobutanol. The solubility of fructose in water at room temperature is about 80 per cent. The solubility of fructose in a water-saturated isobutanol solution at room temperature was found to be 0.35 per cent or 2.5 grams of fructose per liter of water-saturated isobutanol solution.

Example VI

Extraction of aqueous fructose solution with isobutanol:

A volume of 400 cc. of 0.1 M fructose solution was extracted with 500 cc. of isobutanol for 42 hours with the same commercial extractor as that used in Example V. At intervals during the extraction 2 cc. samples were removed from the boiling flask of the extractor and analyzed for fructose. It was found that 40 per cent of the fructose had been extracted with most of this extraction taking place by the middle of the extraction period. Thus, after 16 hours, 35 per cent of the fructose in the aqueous fructose solution had been extracted by the isobutanol.

Example VII

Isobutanol extraction of fructose from glucose-free electrolyzed invert sugar:

A mole of sucrose (342 grams) was dissolved in water and sufficient hydrobromic acid added to give two liters of sugar solution having a bromide ion concentration of 0.32 N. The acidified sucrose solution was then inverted by heating for two hours at 80° C. The invert sugar was then neutralized with calcium carbonate and an additional mole or 100 grams of calcium carbonate added to serve as a means for neutralizing the gluconic acid as formed. The liquor was then diluted with water to its original two-liter volume and subjected to electrolytic oxidation for a period equivalent to 4.1 faradays of power consumption at a temperature of between 25 to 40° C. At this stage the dextrose in the electrolyte had been oxidized to gluconic acid, and the latter neutralized to calcium gluconate, while the fruc-

tose remained in the electrolyte in unmodified form. The electrolyzed liquor was then heated to 70° C. to insure the solution of all of the calcium gluconate, and then filtered. The filtrate was vacuum concentrated to a syrupy consistency, seeded with calcium gluconate, and allowed to crystallize. The crude calcium gluconate crystals were filtered and recrystallized from hot water. There was obtained 255 grams or a 55 per cent yeld of pure calcium gluconate.

The electrolyzed invert sugar solution from which the calcium gluconate had been removed was then subjected to isobutanol extraction from fructose removal. A volume of 150 cc. of this glucose-free electrolyte was diluted with 150 cc. of water and then continuously extracted with 150 cc. of isobutanol for 9.5 hours with the same commercial extractor used in Example V. At the end of this time the isobutanol extract, when placed in a 2 dm. polarimeter tube, gave an angular rotation of −5.87°. The extract also gave a negative bromide test. The lack of bromide contamination is of particular significance in view of the fact that in this batch the amount of bromide ion concentration was over three times the amount necessary for optimum dextrose oxidation.

Without further evaporation the isobutanol extract was cooled to 0° C. and the precipitate filtered, washed with isobutanol, and dried. The resulting product was white in color, gave a negative bromide test, and was identified as fructose.

Example VIII

Isbutanol extraction with renewal of solvent:

A 275 cc. portion of glucose-free syrup electrolyte was taken from the batch prepared in Example VII and extracted in the same commercial extractor with 300 cc. of isobutanol for 38.5 hours. At the end of this time there remained 230 cc. of isobutanol extract. This was poured out and 230 cc. of fresh isobutanol added. Extraction was then continued for 45 additional hours. The original glucose-free syrup contained 32 per cent reducing sugar.

Both isobutanol extracts were mixed, cooled, and filtered. The filtrate was decolorized, concentrated, seeded with fructose, and allowed to crystallize. There was obtained a batch of crystalline fructose which was then filtered and dried.

The above illustrates the use of isobutanol for the removal and isolation of fructose from inorganic ion-contaminated fructose solutions obtained subsequent to the removal of calcium gluconate from electrolytically oxidized invert sugar. Isobutanol may also be used for the extraction of dextrose from aqueous solution or for the extraction of sugars from commercial invert sugar or honey, or for the extraction of fructose from crude fructose liquors obtained by the hydrolysis of the inulin present in plants, such as dahlia, chicory, or Jerusalem artichoke.

Example IX

Isopropanol extraction of fructose from glucose-free electrolyzed invert sugar:

A 25 cc. portion of glucose-free electrolyzed invert sugar obtained from the batch prepared in Example VII was shaken for 58 hours with 25 cc. of isopropanol in a graduated separatory funnel placed in a wrist-action shaker. At the end of this time the volume of the syrup layer was 20 cc. and that of the propanol liquid-phase layer was 30 cc. Analysis of each layer for reducing sugar permitted the calculation of the fructose extracted. The original syrup contained 32 per cent fructose. Of this total fructose present 16 per cent was extracted by the isopropanol. Upon cooling the isopropanol extract, the liquid was crystallized, filtered, and dried. Small, fine crystals of fructose were obtained.

When it is desired to minimize bromide ion contamination of the alcoholic fructose extract, it is best to keep the bromide ion concentration below 0.1 N. Best results, from the standpoint of both calcium gluconate yields, fructose nonmodification, and alcoholic fructose purity, are obtained when the bromide ion concentration is about 0.09 N, such as, for instance, the extraction of glucose-free electrolyte obtained from Example IV with either isopropanol or isobutanol.

Although preferred methods of operating the process have been given, many variations in procedure or in the material processed will be apparent which may be made without departing from the spirit of the invention. The invention is not to be construed as being limited by such described procedure as herein taught, nor by the examples given, but is to be limited only as set forth in the accompanying claims forming a part of this specification.

I claim:

1. A method of obtaining substantially pure fructose from an electrolyticaliy oxidized, lime-neutralized invert sugar liquor free of calcium gluconate which comprises solvent-extracting a given volume of said liquor with about an equal volume of isobutanol and crystallizing fructose from the isobutanol extract.

2. A method of obtaining substantially pure fructose from an electrolytically oxidized, lime-neutralized invert sugar liquor free of calcium gluconate which comprises solvent-extracting a given volume of said liquor with about an equal volume of isopropanol and crystallizing fructose from the isopropanol extract.

3. Process of extracting fructose from aqueous solutions containing the same and dissolved inorganic salts which comprises repeatedly contacting a given volume of said solutions with about an equal volume of a partially water-miscible alcohol from the group consisting of isopropanol and isobutanol whereby said fructose will be selectively dissolved in said alcohol and hence removed from the aqueous solution; and recovering the fructose from its solution in said alcohol.

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