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[Continued on next page]

(54) **Title:** METHOD OF DESULPHITATION OF CARBOHYDRATES

(57) **Abstract:** The present disclosure relates to methods of desulphitation of carbohydrates, particularly sucrose, by treatment using mild oxidizing agent in an effort to produce low sulfite sugar with substantially no inversion of sugar.

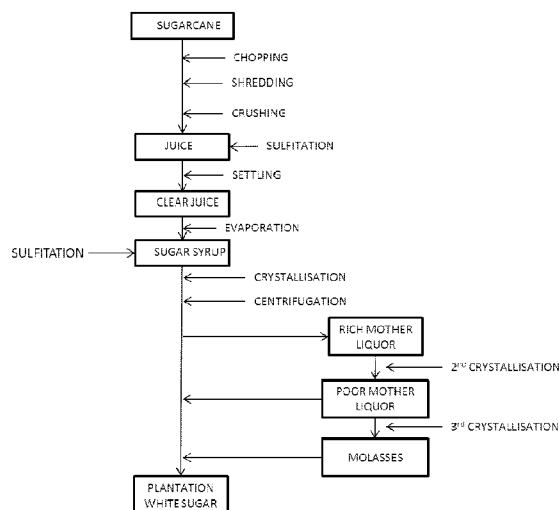


Fig 1



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METHOD OF DESULPHITATION OF CARBOHYDRATES

CROSS REFERENCE TO RELATED APPLICATIONS

- 5 This application claims the benefit of India Patent Application No. 3557/DEL/2014, filed December 5, 2014, which is incorporated by reference in its entirety.

FIELD OF THE INVENTION

- 10 The present disclosure relates to methods of desulphitation of carbohydrates. The present disclosure particularly relates desulphitation of carbohydrates, particularly sucrose containing carbohydrates by treatment with suitable chemical agents.

15 BACKGROUND OF THE INVENTION

The carbohydrates (saccharides) are divided into four chemical groups: monosaccharides, disaccharides, oligosaccharides, and polysaccharides. In general, the monosaccharides and disaccharides, which are smaller (lower molecular weight) carbohydrates, are commonly referred to as sugars.

- 20 Sucrose (sugar), is the organic compound commonly known as table sugar, cane sugar, beet sugar or, usually, just sugar. Sugar is a white, odorless, crystalline powder with a sweet taste, it is best known for its role in food, sweets, confectionaries and beverages. The molecule is a disaccharide composed of the monosaccharides glucose and fructose with the molecular formula $C_{12}H_{22}O_{11}$.

- The world demand for sugar is the primary driver of sugarcane agriculture. Sugarcane accounts for 80% of sugar produced. Sugar is produced by
30 subjecting the sugarcane, to operations such as crushing, clarification, and evaporation to produce the concentrated syrups and further crystallization to obtain the sugar crystals.

Plantation white or mill white sugar, commonly known as PWS is a white sugar commonly produced for local consumption in certain sugarcane-growing countries such as India. It is produced at the factory without remelting and refining of the raw sugar. Instead, sulfur dioxide gas is injected into
5 extracted juice, where it bleaches juice colorants, is oxidized to sulfate, and then is neutralized by the addition of lime. Sulfite salts are sometimes substituted for sulfur dioxide. The resulting PWS is suitable for table use but not for food processing, because it contains all the non-sugars (including bleached or reduced colorant) present in raw sugar. This sugar also contains
10 certain percentages of sulphites in the juices, concentrates and sugar crystals.

Sulphites in foods are known to cause certain allergic reactions. Sulphites as additives can cause an asthmatic reaction; presence of excessive amounts of
15 sulphites is considered responsible for off flavour in food products (McFeeters and Barish, 2003; Machado et al., 2008). Since Sugar is a major additive in a number of foods such as bakery items, confectionaries, beverages etc., it could be a potential problem if sulphite content was higher than tolerance levels of individuals.

20 Some of the suspected side effects / responses to sulphite intolerance could be
allergic reactions on face, eyes and also trouble with breathing, speaking or swallowing, increased anxiety, distress, cramps, diarrhea, vomiting
Other possible reactions could be drop in blood pressure, rapid heartbeat and
25 loss of consciousness.

“Plantation white sugar (PWS)” contributes to about 95% of total available sugar in India. There is a second grade which is termed as “Refined sugar” where the above mentioned PWS is subjected to operations such as
30 affination, filtration and carbonation to remove the slightest of the impurities and produce an extra white and fine granule sugar. This contributes to 5% of the market and is used by a select group of end users. The industry uses double-sulphitation route to produce sugar and molasses. This results in sugar containing residual sulfur as sulfite, which is not recommended for

human consumption. Currently the residual sulfur in form of sulfite can be removed by evaporation and double distillation method, which not only add to the operational costs but also lead to loss of yield while altering desirable parameters such as color and unwanted impurities such as sulphite residues.

5

United States issued patent US8394202 discloses a method of manufacturing low microbial count and substantially zero sulfur content sugar. The zero sulfur content is achieved by removing at least one sulphitation step by using neutralization by CO₂ gas instead of second sulphitation. The low microbial content is achieved by method comprising steps of dosing biocides on sugarcane during cane preparation, followed by heating and neutralizing the juice, sulphitation, clarification, evaporation to obtain syrup, crystallization of syrup, separation, washing and drying of sugar.

10

15 In a report titled, "Cane sugar manufacture in India" authored by D.P Kulkarni and published by "The Sugar Technologist's Association of India", in 1995, discloses that inversion of sugar is a function of pH and the reasons for inversion are low pH, high temperature and time. It has been described in this report that resin treatment has been used to remove the acidity by which inversion can be avoided. But it has also been mentioned that it is impractical to be used in PWS process. Also it is mentioned that differently designed evaporator tubes have been used to reduce the contact time at high temperature hence leading to less inversion.

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United States issued patent US4992288 discloses use of hydrogen peroxide as oxidizing compound for reduction of sulfite content in sulfite-containing sugarbeet pulp.

25

The solutions provided in the art however do not address reduction of sulfite in sugar without impacting yield of sugar due to inversion.

30 Thus, there is a need for better method of sulphite removal which can be used in place of the evaporation and double distillation method in the sugar processing and which causes minimal or no inversion without impacting yield.

SUMMARY OF THE INVENTION

An aspect of the present disclosure is a method of manufacturing a carbohydrate having reduced sulfite content, comprising one or more of the following steps:

- 5 (i) processing a carbohydrate source in order to extract a juice;
- (ii) sulphitation of the juice;
- (iii) settling to obtain a clear juice;
- (iv) concentrating the clear juice to obtain syrup;
- (v) treating the syrup with stabilized chlorine dioxide;
- 10 (vi) allowing the treated syrup to precipitate to yield one or more reduced sulfite content carbohydrate products selected from the group consisting of crystals of a carbohydrate, massecuite, and molasses; wherein the reduced sulfite content carbohydrate comprises less than 10 ppm sulfite.

- 15 Another aspect of the disclosure is a method of treating a carbohydrate having sulfite content in the range of about 10 ppm to 100 ppm, comprising treating the carbohydrate with stabilized chlorine dioxide in a proportion ranging from about 25 ppm to 500 ppm, wherein the pH of the treated carbohydrate is in the range of about 7 to 8, and wherein the treatment with
- 20 stabilized chlorine dioxide results in the reduction of sulfite content by about 40-100%.

BRIEF DESCRIPTION OF THE DRAWINGS

- The present invention should become apparent from the following description
- 25 when considered in conjunction with the accompanying drawings, in which:

Figure 1 represents the flow chart of a conventional double sulphitation method of manufacturing PWS sugar.

- 30 Figure 2 represents the flow chart for a method of manufacturing PWS sugar according to the present disclosure where one sulphitation step is removed and instead SCD is introduced.

Figure 3 represents the flow chart for a method of manufacturing refined sugar from PWS sugar

DETAILED DESCRIPTION OF THE INVENTION

5

DEFINITIONS

As used in the present disclosure, the term "syrup" represents the liquid obtained after concentrating a juice.

10 The term "liquor" refers to sugar dissolved in water during a refining process.

The term "massecuite" refers to the mixture of crystals and mother liquor resulting from the crystallization process.

15 The term "carbohydrate" as used herein is a monosaccharide, a disaccharide, an oligosaccharide, or a polysaccharide or mixtures or combinations thereof. Examples of monosaccharides, disaccharides, oligosaccharides, and polysaccharides are known to those skilled in the art. The carbohydrate is preferably a naturally-occurring carbohydrate. The naturally-occurring
20 carbohydrate may or may not have a reducing end group. Such carbohydrates are more readily metabolized, and therefore more susceptible to deterioration by microorganisms. Generally, a carbohydrate comprises between 1% and 70% carbohydrate based on the total weight of the feedstock, and also between 2 and 40%. The amount and composition of the
25 carbohydrates in the feedstock can vary depending on the intended end use.

The term "molasses" refers to the mother liquor which is collected during the final stages of processing, and separates out upon centrifugation of and separation of sugar crystals.

30 The term "raw sugar" refers to sugar that is obtained after centrifugation from a sugar syrup. The raw sugar may be subjected to further processing based on end use or impurity profile.

The term "refined sugar" refers to raw sugar which has subsequently been refined by methods such as crystallization.

5 The term "mother liquor" is term used to denote residual liquid resulting from crystallization and remaining after the sugar crystals have been removed

The term "sugar" denotes either or both, raw sugar and refined sugar unless indicated otherwise.

10 The term "inversion" refers to the breakdown of sugar or sucrose into glucose or fructose both in varying proportions.

The term "sugar solution" denotes solutions of sugar in water. This could be either raw or refined sugar or may be both.

15

The term "Stabilized chlorine dioxide" otherwise referred to herein as "SCD" means one or more chlorine dioxide containing oxy-chlorine complexes, one or more chlorite containing compounds, one or more other entities capable of forming chlorine dioxide when exposed to acid, and combinations thereof and
20 includes at least one buffering agent wherein the pH of the SCD is below about 10.5 to 11, more preferably in the range of about 8.5 to 9.5. SCD as defined herein could also include commercially available products.

Various embodiments of this disclosure provide methods for manufacturing
25 sugar from sugarcane. However, these embodiments are non-limiting and may be used in connection with various applications that will be described in later part of this specification.

In general, the present disclosure provides an efficient method for
30 manufacturing sugar with reduced sulphite content which includes the step of addition of stabilized chlorine dioxide (SCD) during the step of sugar crystallization from sugar syrup and optionally replacing at least one sulphitation step of the conventional double sulphitation process.

The carbonation process used in the prior art as an alternative to second sulphitation using carbon dioxide in conjunction with lime has the primary purpose of enhancing color of sugar solution i.e. It is predominantly used in refining process and not in Plantation white sugar (PWS) process. This is because CO₂ is a low solubility gas and would require large quantities when applied in PWS where the scales are very high. It also requires higher quantities of lime (10x compared to sulphitation) to function. Due to use of such high quantities of lime, the pH of the stream has to be adjusted with an acid. It can eliminate the use of second sulphitation, but cannot remove the incoming sulfite after the evaporation step which is in the tune of 1000-3000ppm.

The Stabilized chlorine dioxide (SCD) used in present disclosure has the advantage of high solubility due to which it dissolves immediately in the stream and can be applied to preparation of PWS as well as in the further refining process of PWS.

The use of SCD can not only eliminate the step of second sulphitation but can also reduce the level of sulfite introduced during the first sulphitation process to substantially zero levels.

Conventional methods of processing include addition of lime for settling after the first sulphitation step. In the current process since lime is not added, the second sulphitation step is not required. The remaining sulphite in the current process is removed using SCD,

This process however doesn't require any lime which is used in conventional methods as SCD can function independently to reduce sulphite. As there is no use of lime, adjustment of pH is not needed.

An aspect of the present disclosure is a method of manufacturing a carbohydrate having reduced sulfite content, comprising one or more of the following steps:

- (i) processing a carbohydrate source in order to extract a juice;
- (ii) sulphitation of the juice;
- (iii) settling to obtain a clear juice;

- (iv) concentrating the clear juice to obtain syrup;
- (v) treating the syrup with stabilized chlorine dioxide;
- (vi) allowing the treated syrup to precipitate to yield one or more reduced sulfite content carbohydrate products selected from the group consisting of crystals of a carbohydrate, massecuite, and molasses; wherein the reduced sulfite content carbohydrate comprises less than 10 ppm sulfite.

In one embodiment of the present disclosure, the reduced sulfite content carbohydrate product is carbohydrate crystals and wherein the crystals are isolated by a separation technique selected from filtration and/or centrifugation, and wherein carbohydrate crystals are processed.

In another embodiment, the processing comprises redissolving/ remelting, grinding, sifting, filtration and carbon treatment.

Another aspect of this disclosure is a method of treating a carbohydrate having sulfite content in the range of about 10 ppm to 100 ppm, comprising treating the carbohydrate with stabilized chlorine dioxide in a proportion ranging from about 25 ppm to 500 ppm, wherein the pH of the treated carbohydrate is in the range of about 7 to 8, and wherein the treatment with stabilized chlorine dioxide results in the reduction of sulfite content by 40-100%.

In one embodiment, the carbohydrate is selected from the group consisting of a monosaccharide, disaccharide, oligosaccharide, polysaccharide or mixtures or combinations thereof.

In another embodiment, the carbohydrate is selected from the group consisting of a solution, suspension, syrup, and a crystalline form of a sugar.

In still another embodiment, the carbohydrate is in a form of sugar and/or a sugar solution.

In yet another embodiment, treating the syrup in step (v) comprises contacting the syrup with stabilized chlorine dioxide in a proportion ranging from 250 ppm to 5000 ppm, and wherein the pH of the treated sugar syrup ranges between 4 and 7.

5

In yet another embodiment, the stabilized chlorine dioxide is a chlorine dioxide-containing oxy-chlorine complex selected from the group consisting of a complex of chlorine dioxide with carbonate, a complex of chlorine dioxide with bicarbonate or mixtures or combinations thereof.

10

In still another embodiment, the sulfite reduction in the carbohydrate is achieved without substantial inversion.

In yet another embodiment, the reduced sulfite carbohydrate is used in the manufacture of products for human and/or animal consumption.

15

In another embodiment, the products for human consumption are selected from the group consisting of sugar crystals, juices, alcoholic beverages, non-alcoholic beverages, carbonated beverages, confectionaries, sweets, desserts, baked foods, preserves, canned foods, frozen foods and other cooked foods and infant formulas.

20

In yet another embodiment, the products for animal consumption are including but not limited to sugar containing edible foods, nutritional diets, supplements, animal treat, a toy, kibble and a chew.

25

"Stabilized chlorine dioxide" otherwise referred to herein as "SCD" means one or more chlorine dioxide-containing oxy-chlorine complexes, one or more chlorite-containing compounds, one or more other entities capable of forming chlorine dioxide when exposed to acid, and combinations thereof and at least one buffering agent wherein the pH is below 10.5 to 11, more preferably 8.5 to 9.5.. SCD as defined herein are commercially available products.

30

A preferred chlorine dioxide-containing oxy-chlorine complex is selected from the group consisting of a complex of chlorine dioxide with carbonate, a complex of chlorine dioxide with bicarbonate and mixtures thereof. Examples of chlorite-containing compounds include metal chlorites, and in particular
5 alkali metal and alkaline earth metal chlorites. A specific example of a chlorite-containing compound that is useful as SCD (a chlorine dioxide precursor) is sodium chlorite, which can be used as technical grade sodium chlorite.

SCD is preferably used in the form of an aqueous solution, such as that of an
10 alkali metal or alkaline earth metal chlorite, typically sodium chlorite (NaClO_2).

Sodium chlorite in solution is generally stable at pH above 7, but releases the active chlorine dioxide (ClO_2), when the pH is lowered below neutral (pH 7). The rate of activation of SCD, that is, the rate at which the active ClO_2 is
15 released from the stable form, increases as pH decreases.

The exact chemical composition of many of SCD compositions, and in particular, chlorine dioxide-containing oxy-chlorine complexes, is not completely understood. The manufacture or production of certain chlorine
20 dioxide precursors is described by Gordon, U.S. Patent 3,585,147 and Lovely, U.S. Patent 3,591,515.

Specific examples of commercially available and useful stabilized chlorine dioxide include, for example, ANTHIUM DIOXCIDE® and FERMASURE® XL,
25 available from E. I. du Pont de Nemours and Company; OXINE® and PUROGENE®, available from Bio-Cide International, Inc., Norman, OK. SCD may be provided as a solution of the one or more chlorine dioxide-containing oxy-chlorine complexes, one or more chlorite-containing compounds, or one or more other entities capable of forming chlorine dioxide when exposed to
30 acid, and combinations thereof. The solution provides SCD in a liquid medium at a predetermined concentration of "available chlorine dioxide". The concentration of "available chlorine dioxide" is based on complete (100%) release of chlorine dioxide from the one or more chlorine dioxide-containing oxy-chlorine complexes and/or complete (100%) conversion of the one or

more chlorite-containing compounds to chlorine dioxide and/or complete (100%) formation of chlorine dioxide from the one or more other entities capable of forming chlorine dioxide.

- 5 Preferably, the SCD solution has sufficient SCD to have an available chlorine dioxide concentration in the range of about 0.002% to about 40% by weight, preferably, in the range of about 2% to about 30% by weight, more preferably in the range of about 5% to about 15% by weight, based on the total weight of the SCD solution.

10

SCD may be provided as a solid material, either as tablets or sachets (powdered material in pouches) as a composition comprising an alkali or alkaline earth metal chlorite inert ingredients, and optionally including a dry activator such as a dry acid.

15

Dry acid as used herein, refers to dry citric acid or anhydrous sulphuric acid.

The disclosed embodiments are hereinafter described in terms of SCD as stabilized alkali metal chlorite, more specifically sodium chlorite (NaClO_2).

- 20 Typically sodium chlorite is used as an aqueous solution comprising 5 - 22% by weight, based on weight of the solution. Hereinafter SCD concentrations are described in terms of the concentration of chlorine dioxide available when the chlorite is stoichiometrically converted to chlorine dioxide, "available ClO_2 ", in mg/L or ppm or Trade %, where Trade % = $\text{g/L} / 10$ The content of potential chlorine dioxide in 1 g of sodium chlorite is 0.597 g when acidified. Sodium chlorite solutions comprising 5 - 22% by weight of sodium chlorite thus contain approximately 3 - 13 wt. % available chlorine dioxide. The generation of ClO_2 is illustrated by the following equation (2):

- 30 $5 \text{ NaClO}_2 + 4 \text{ H}^+ \rightarrow 4 \text{ ClO}_2 + 2 \text{ H}_2\text{O} + \text{Cl}^- + 5 \text{ Na}^+$ (2) wherein one mole of NaClO_2 provide 0.8 mole of ClO_2 (5:4 ratio). (See for example, Ullmann's Encyclopedia of Industrial Chemistry, Wiley Online Library, http://onlinelibrary.wiley.com/doi/10.1002/14356007.a06_483.pub2/pdf, as accessed September 30, 2010.)

**Application using Stabilized Chlorine dioxide (SCD, commercial
FermaSure® XL)**

The present disclosure employs stabilized chlorine dioxide to remove undesired sulfite from sugar without employing any refining process. Testing
5 has shown that FermaSure® XL oxidizes sulfites at 1:1 stoichiometric ratio and converts 90-95% of sulfites to sulfates. In India, it is understood that Indian sugar may contain 70-150ppm of sulfite which is measured as sulfur dioxide for which 100-200ppm of FermaSure® XL is capable of oxidizing 80-100% of the sulfite.

10 Additionally, testing has also revealed that at the same dosage of FermaSure® XL, the inversion of the sugar solution, which is also a quality parameter for sugar, is reduced by 95-100%. Therefore reduced level of inversion is achieved while sulphite removal is also accomplished.

TEST METHODS

15 Sulfite reduction was determined by the Pararosaniline dye method. [EQS-0775-002]

0.2% pararosaniline hydrochloride solution was prepared in water, to which 0.1% formaldehyde solution was mixed at 1:1 ratio. 1ml of this mixture of pararosaniline and formaldehyde was mixed with 1ml of sulfite containing
20 sample.

The mixture was allowed to react for 30 minutes at room temperature after which absorbance was measured at 575nm. A liner absorbance curve of different known concentration of sulfite in water (0, 10, 20, 30ppm) was first determined before testing the actual samples.

25

Inversion of sugar was measured by the following instruments and conditions:

Instrument: BIO-RAD HPLC instrument

Column: AMINEX HPX-87N carbohydrate analysis column

30 Dimensions: 300 x 7.8 mm, cat No 125-0143 (serial no 427911)

HPLC Detector: WATERS 2414 RID detector (Refractive index detector)

Mobile phase: Isocratic system of prepared by dissolving 2.84 g of Sodium phosphate dibasic (CALBIOCHEM, cat no 567550) and in 2 L milliQ water (ultrapure water prepared by successive steps of filtration and deionization, supplied by Millipore Corporation, Massachusetts, USA)

5

Sample preparation:

a) Standard solution: Standard solution was prepared. 685 mg/ml sugar solution containing 640 mg/ml sucrose, 23 mg/ml glucose and 22 mg/ml fructose was prepared as a standard solution.

10

b) From this standard solution, a sample solution was made by 20 fold dilution.

c) 5 microliter of this sample solution and the test sugar solution of examples provided below was injected to check the retention times of individual sugars.

15

d) The flow rate was 0.6 ml/min; the column temperature was 50 °C and the injection volume 5 microliter.

e) The concentration of the products was determined from the peak area under the curve using the HPLC computer software. Peak identification was based on retention times t_R .

20

f) Identification of the three sugars was confirmed with known standards injected individually through the HPLC.

The following retention times were observed:

a) sucrose ($t_R = 8.7$ min),

25

b) glucose ($t_R = 10.8$ min) and

c) fructose ($t_R = 12.0$ min).

A calibration curve was plotted using 1, 10, 20, 40 and 50 mg/ml of sucrose; 0.10, 1, 2, 4 and 5 mg/ml of glucose and 0.10, 1, 2, 4, and 5 mg/ml of fructose.

30

EXAMPLES

The present disclosure will now be further explained in the following Examples. However, the present disclosure should not be construed as limited thereby. One of ordinary skill in art will understand how to vary the exemplified preparation to obtain the desired results.

COMPARITIVE EXAMPLE A

Sugar syrup obtained after first sulphitation and concentration of sugar cane juice contains sucrose in the range of about 60-65%, sulfite content in the range of about 500-3000ppm and has pH in the range of about 6.25-6.75.

- 10 This syrup is subjected to second sulphitation which increases the sulfite content to about 1500-4000ppm and reduces the pH to about 4.25-4.50. Due to lowering of pH there is also inversion of sucrose into glucose and fructose which is undesirable as they impact the overall yield of the final sugar.

15 COMPARITIVE EXAMPLE B

Sugar syrup obtained after first sulphitation and concentration of sugar cane juice, contains sucrose in the range of 60-65%, sulfite content in the range of about 500-3000ppm and has pH in the range of 6.25-6.75.

- The sugar solution can be treated with generated chlorine dioxide (GCD), which is produced by acidifying sodium chlorite with acids. When GCD is added to a sugar solution in the range of 250-3000ppm, it oxidizes 80-90% of sulfite to sulfate along with reduction in pH of syrup below 5.0. This treatment method eliminates or significantly reduces sulfite but does not address the inversion caused due to low pH. Reduction in pH below 5.0 causes inversion of sucrose to glucose and fructose. This is not desirable as this will reduce the yield of sugar formation. Table 1 shows the inversion of sugar (sucrose breaking down to glucose and fructose) below pH 5.

Table 1

pH of sugar solution	Sucrose%	Glucose%	Fructose%
6.5	69.8	0.01	0.01
5.0	71.0	0.01	0.01
3.0	71.0	0.14	0.16

5 EXAMPLE 1

Sugar syrup obtained after first sulphitation and concentration of sugar cane juice contains sucrose in the range of 60-65%, sulfite content in the range of 500-3000ppm and has pH in the range of 6.25-6.75, which when treated with stabilized chlorine dioxide in the dosage range of 250-3000ppm, wherein the pH of the resultant treated syrup solution was between 6.0 and 6.5 and oxidizes 25-90% of sulfite to sulfate.

Table 2 shows the reduction in sulfite content in syrup sample after treatment with stabilized chlorine dioxide.

Table 2

Dosage of stabilized chlorine dioxide	Sulfite content (ppm)	% Reduction	Glucose/Fructose
Control (0 ppm)	2833		
250ppm	2040	28%	0.01
1000ppm	1595	44%	0.01
2000ppm	426	85%	0.01

As can be seen from table 2, treatment of sugar syrup with 250-2000 ppm of SCD, reduced the sulfite content in the range of 28% to 85%. Also the SCD treatment was done in a pH range of 6.0-6.5 and it was observed that

there was very low conversion (inversion) to glucose and fructose, indicating that the pH was favorable for substantially minimal or no inversion.

EXAMPLE 2

5 A sugar solution was prepared by dissolving 100 g commercial grade PWS sugar crystals in 100 ml water (the PWS sugar was procured from retail market). The pH of this sugar solution was 6.32. This solution was divided into two equal portions. To one of the sugar solutions, 31 ppm of sodium sulfite (S.D. fine chemicals, LR grade, and 99 % purity) was added from a 1000 ppm
10 stock solution; and to other portion 38 ppm sodium sulfite (S.D. fine chemicals, LR grade, and 99 % purity) was added. The pH of the resulting sugar solution spiked with sodium sulfite was 7.38.

These two sulfite spiked sugar solution (spiked sugar solution 1 and 2)
15 were treated with 50ppm, 100ppm and 150 ppm of stabilized chlorine dioxide respectively in three different experiments and the corresponding reduction in the sulfite content was measured. The resultant pH of the SCD treated solution was 7.32.

20 Table 3, below shows the percentage reduction in sulfite content after SCD treatment.

Table 3

	Sulphite (ppm)	SCD (ppm)	Sulphite content after SCD treatment (ppm)	Reduction in sulphite (%)
Spiked sugar solution 1	38	50	21	45
		100	0	100
		150	0	100
Spiked sugar solution 2	31	50	10	60
		100	0	100
		150	0	100

As observed from results depicted from Table 3, treatment of a sugar solution having 30-40 ppm of sulfite with increasing concentration of SCD (50 to 100 ppm) reduced the sulfite content from 45 to 100%. Also since this treatment maintained the pH of the treated solution to 7.32, which was above
5 the critical pH where inversion takes place (pH of less than 5.0), the treatment process was favorable for sulphite reduction with minimal or substantially no inversion.

The sugar produced by using conventional evaporation and double distillation
10 method contains 500-3000 ppm of sulfite, and sugar produced by a process using SCD reduces the sulfite content by 80-95%. While the present embodiments have been disclosed in connection with certain aspects, this description should not be taken as limiting the embodiments to all of the provided details. Modifications and verifications of the described embodiments
15 may be made without departing from the scope and spirit of the invention. Various multiple alternate embodiments are encompassed in the present invention disclosure would be understood by one of ordinary skill in the art. The scopes of the embodiments are to be limited only by the following claims:

We Claim

1. A method of manufacturing a carbohydrate having reduced sulfite content, comprising one or more of the following steps :
 - (i) processing a carbohydrate source in order to extract a juice;
 - (ii) sulfitation of the juice;
 - (iii) settling to obtain a clear juice;
 - (iv) concentrating the clear juice to obtain syrup;
 - (v) treating the syrup with stabilized chlorine dioxide;
 - (vi) allowing the treated syrup to precipitate to yield one or more reduced sulfite content carbohydrate products selected from the group consisting of crystals of a carbohydrate, massecuite, and molasses; wherein the reduced sulfite content carbohydrate comprises less than 10 ppm sulfite.
2. The method as claimed in claim 1 wherein the reduced sulfite content carbohydrate product is carbohydrate crystals and wherein the crystals are isolated by a separation technique selected from filtration and/or centrifugation, and wherein carbohydrate crystals are processed.
3. The method as claimed in claim 2 wherein the processing comprises redissolving, remelting, grinding, sifting, filtration and carbon treatment.
4. A method of treating a carbohydrate having sulfite content in the range of 10 ppm to 100 ppm, comprising treating the carbohydrate with stabilized chlorine dioxide in a proportion ranging from 25 ppm to 500 ppm, wherein the pH of the treated carbohydrate is in the range of 7 to 8, and wherein the treatment with stabilized chlorine dioxide results in the reduction of sulfite content by 40-100%.
5. The method as claimed in claims 1 or 2 wherein the carbohydrate is selected from the group consisting of a monosaccharide, disaccharide, oligosaccharide, polysaccharide or mixtures or combinations thereof.

6. The method as claimed in any of claims 1-3 wherein the carbohydrate is selected from the group consisting of a solution, suspension, syrup, and a crystalline form of a sugar.
- 5 7. The method as claimed in claim 3 wherein the carbohydrate is in a form of sugar and/or a sugar solution.
8. The method of manufacturing carbohydrate as claimed in claims 1 or 2, wherein treating the syrup in step (v) comprises contacting the syrup with stabilized chlorine dioxide in a proportion ranging from 250 ppm to 5000 ppm, and wherein the pH of the treated sugar syrup ranges between 4 and 7.
- 10 9. The method of claims 1 or 2 wherein the stabilized chlorine dioxide is a chlorine dioxide-containing oxy-chlorine complex selected from the group consisting of a complex of chlorine dioxide with carbonate, a complex of chlorine dioxide with bicarbonate or mixtures or combinations thereof.
- 15 10. The method as claimed in any of claims 1-3 wherein the sulfite reduction in the carbohydrate is achieved without substantial inversion.
- 20 11. The method as claimed in Claim 1 and 2, wherein the reduced sulfite carbohydrate is used in the manufacture of products for human and/or animal consumption.
- 25 12. The method as claimed in claim 11, wherein the products for human consumption are selected from the group consisting of sugar crystals, juices, alcoholic beverages, non -alcoholic beverages, carbonated beverages, confectionaries, sweets, desserts, baked foods, preserves, canned foods, frozen foods and other cooked foods and infant formulas.
- 30

13. The method as claimed in claim 11, wherein the products for animal consumption are selected from the group consisting of food, a nutritional diet, a supplement, an animal treat, a toy, kibble and a chew

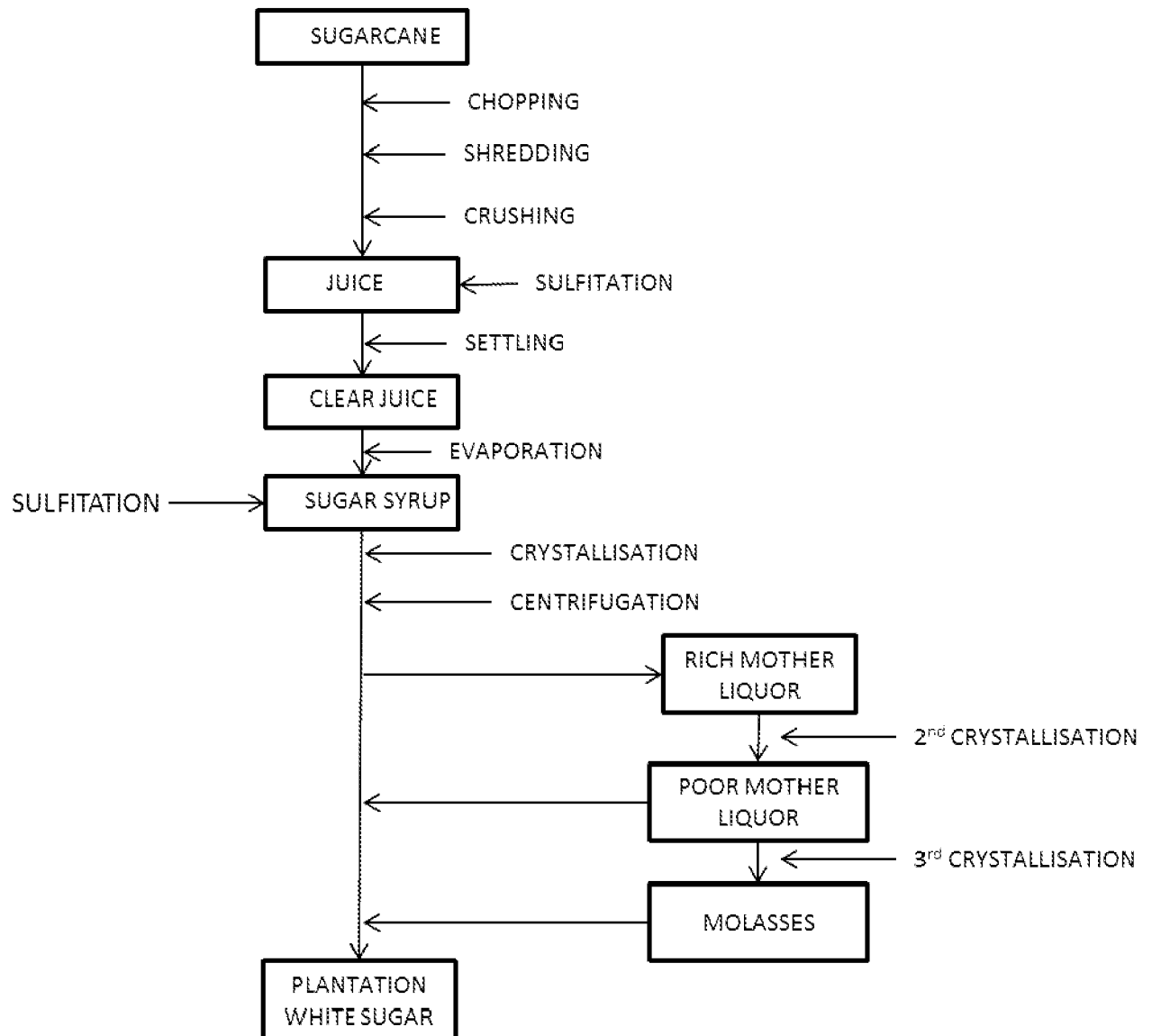


Fig 1

2/3

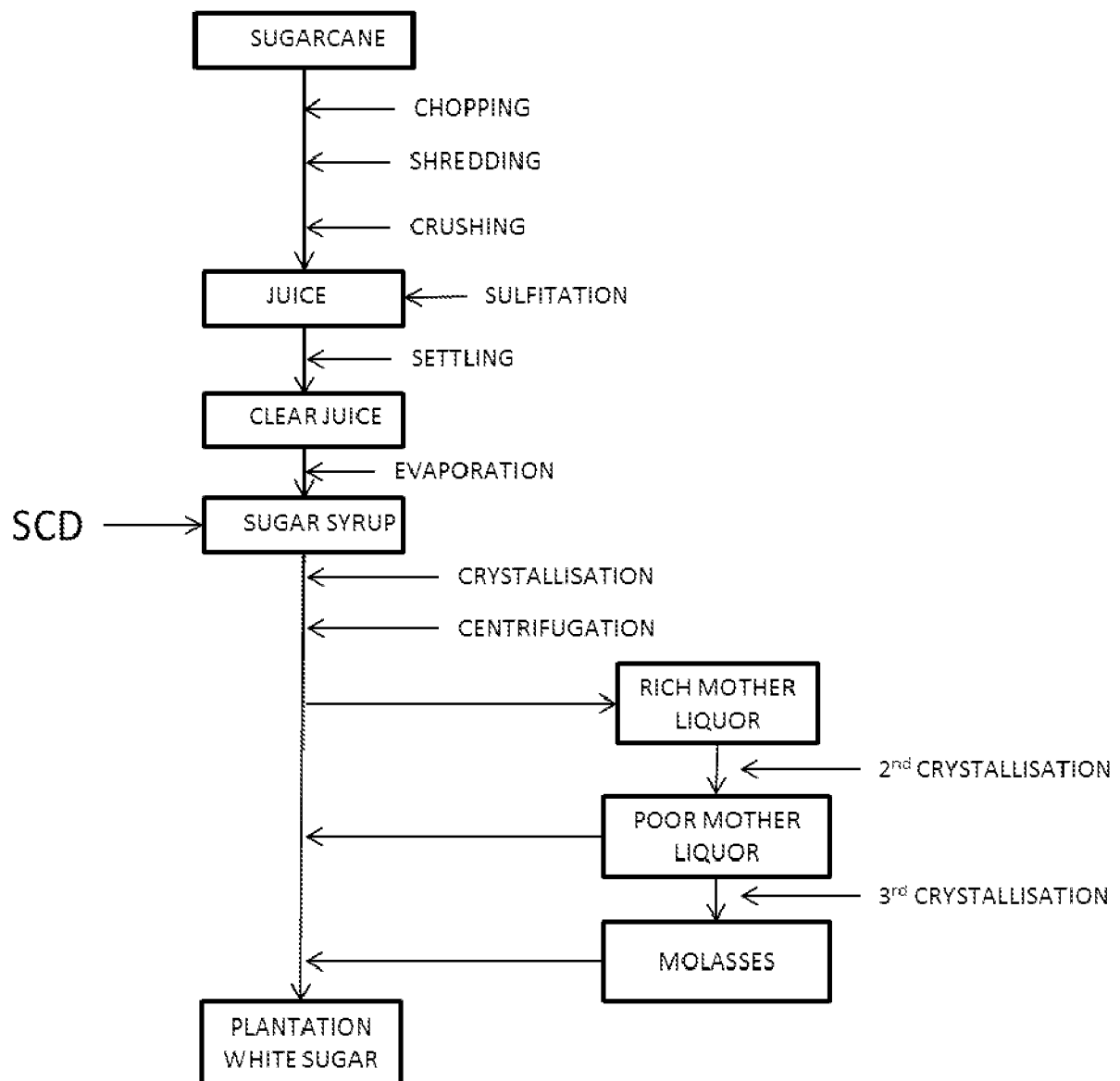


Fig 2

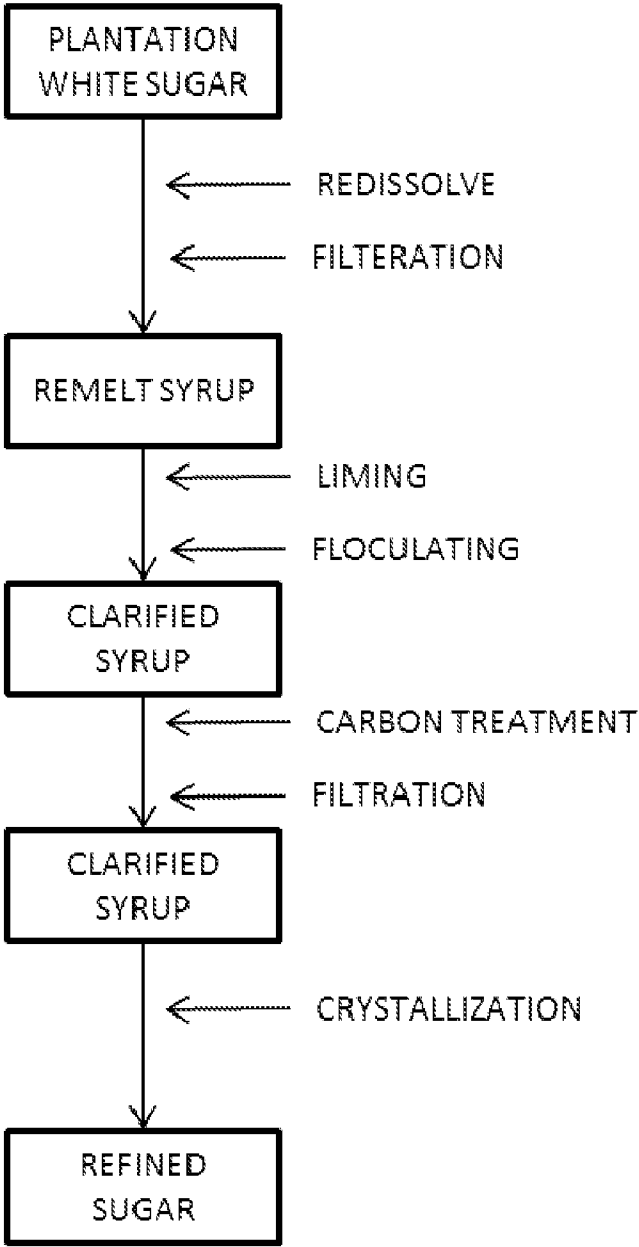


Fig 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/063915

A. CLASSIFICATION OF SUBJECT MATTER
INV. C13B20/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C13B C13K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, BIOSIS, FSTA, WPI Data, EMBASE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 200950 Thomson Scientific, London, GB; AN 2009-L83758 XP002755241, -& CN 101 481 746 A (UNIV GUANGXI) 15 July 2009 (2009-07-15) abstract page 4 -page 5: Beneficial effect N°2 and N°4 page 5 - page 6: Embodiments 1, 2, 3 and 4 ----- -/-	1-13

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

9 March 2016

Date of mailing of the international search report

04/04/2016

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/063915

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 200951 Thomson Scientific, London, GB; AN 2009-L83759 XP002755242, -& CN 101 481 745 A (UNIV GUANGXI) 15 July 2009 (2009-07-15) abstract page 6 to page 7: Beneficial effect N°3 and N°5	1-13
A	----- XIN-YUAN PENG ET AL: "Effect of SO₂-ClO₂ treatment on postharvest quality of "Munage" grape.", FOOD SCIENCE, vol. 35, no. 18, 1 April 2014 (2014-04-01) , pages 178-186, XP002755243, INSTITUTE OF AGRO-PRODUCTS STORAGE AND PROCESSING, XINJIANG ACADEMY OF AGRICULTURAL SCIENCES, CHINA. abstract; figure 1	1-13
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2015/063915

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			KR 20120094919 A 27-08-2012
			RU 2012116511 A 27-10-2013
			US 2011236257 A1 29-09-2011
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			WO 2011038317 A1 31-03-2011