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54 Improved method of recovering sucrose.

57 An improved method of recovering sucrose from plant-derived aqueous solutions is provided. The method comprises contacting an aqueous sucrose-containing solution derived from plant juice, such as sugar cane or sugar beet juice, with aliphatic carboxylic acid having an average carbon chain length of about 2-6, in a concentration sufficient to selectively precipitate a substantial amount of sucrose from the solution. The precipitate is then separated and recovered and the depleted solution can be recycled. Preferably the sucrose-containing solution is concentrated to about 55-96 Brix before the contacting and the contacting is carried out by rapidly adding the sucrose-containing solution to the acid in order to assure rapid growth of large sucrose crystals for maximum sucrose recovery. The sucrose-containing solution before concentrating can be any solution obtained prior to molasses formation; e.g. untreated diffusion juice, pre-limed and/or predefecated diffusion juice, purified diffusion juice or even a solution formed by reconstituting from raw recovered sugar; alternatively, it can be a solution after molasses formation, in which event the selected acid, if it includes acetic acid, only includes it in a mixture with other aliphatic carboxylic acids. It may also be waste fluid from a canning operation or the like.

IMPROVED METHOD OF RECOVERING SUCROSE

The present invention generally relates to sugar refining and, more particularly, to an improved method of recovering sucrose from an aqueous solution.

In the conventional purification of sugar beet juices and
5 the recovery of sucrose contained in the juices, milk of lime is added to the diffusion juice from the beets and is then precipitated from the solution with carbon dioxide. The physical and chemical changes caused by the addition of milk of lime and carbon dioxide, and the subsequent settling or filtration of the precipitated
10 calcium carbonate, effect removal of between 20 and 40% of the impurities present in the juice. This purification step is known as first carbonation. The amount of carbon dioxide and lime used is selected to achieve an optimal removal of color and other impurities and achieve an optimal filterability of sludge produced. The usual
15 alkalinity range for this process is 0.065 to 0.140% CaO. First carbonation is followed by second carbonation. The purpose of second carbonation is to minimize the amount of dissolved calcium (lime salts) remaining in the juice. This is done to minimize scaling in the equipment and lines in the process, as well as to
20 remove the calcium ion which would otherwise contribute to the

formation of molasses.

There are many process variations known and practiced for the purification of sugar beet juices that employ lime and lime plus magnesium oxide or magnesium carbonate. These include variations
5 employed in both the first and second carbonation steps. Some of the process variations are:

- a) Preliming with carbonation;
- b) Preliming without carbonation;
- c) Defeco-carbonation;
- 10 d) Separation of prelime sludge;
- e) Separation of precarbonated sludge;
- f) Recycle of spent lime from first carbonation;
- g) Intermediate liming;
- h) Main liming;
- 15 i) Main carbonation;
- j) Over-carbonation prior to main liming;
- k) Over-carbonating second carbonation, followed by realkalization with magnesium oxide; and
- l) Carbonating second carbonation to its optimum
20 alkalinity, followed by the addition of freshly prepared magnesium carbonate.

The ability of the refining process to recover white sugar from sugar beets is dependent on the extent of process losses. These include pulp loss from diffusion, lime flume loss, inversion
25 in the process, uncontrolled leakage, and loss of the sugar contained in the molasses produced by the process. The largest loss is sucrose in the molasses and the amount of sugar contained in molasses is heavily dependent on the efficiency of impurity removal by carbonation in the process.

Several processes have been developed and employed to enhance the recovery of sucrose from sugar beets. The most common process for selectively recovering sucrose from molasses is the Steffens process, which employs lime at low temperatures to precipitate sucrose. A similar process employs barium hydroxide to precipitate sucrose. Sucrose may also be separated chromatographically on ion exchange columns. Another major technique involves the modification of the juice composition by ion exchange. One approach is the Quentin process, where cations are selectively exchanged for magnesium. Another approach is the partial or complete removal of ionic impurities to decrease or eliminate molasses production.

Another method of recovering sucrose from sugar beet molasses involves concentrating molasses to a very high dry substance and then mixing it with solvents. The result is a precipitation of sucrose, while essentially all impurities remain in solution. Work on this method continued through the 1920's, but commercial exploitation was never realized. The method was never applied to substrates other than molasses.

Two phase solvent extractor systems have also been devised to recover sucrose. For example, in one known process sugar juice is countercurrently contacted with an immiscible solvent comprising two mutually insoluble phases. Acid addition is required to control pH to 1.3-1.5, a range which greatly accelerates inversion of sucrose and thus reduces the amount of sucrose recovered. The process has never been commercially employed.

Juices extracted from sugar cane must also be treated with one, or a combination of several, processes for the production of either white or raw sugar. Lime or magnesia is a usual purification

agent used, and the treatment step is termed defecation. Other steps employed may include treatment with sulfurous acid (sulfitation), phosphoric acid (phosphatation), and carbon dioxide (carbonitiation). Processes are also employed that use flocculating
5 or foaming agents to remove coloring matter.

All of the methods employed for purification in the cane sugar industry are chemically gentle. This is required for economic and quality reasons, because the aggressive chemical conditions required for beet sugar production would lead to the destruction of
10 invert sugar and the creation of large quantities of colored impurities in the cane sugar refining process. Invert sugars in that process are beneficial because they lower the solubility of sucrose in the final molasses, and coloring matter is detrimental because it lowers the quality of sugar produced. However, the
15 gentle conditions are not capable of removing significant amounts of impurities and the improvement is generally in the range of .5 to 2 purity points. The recovery of sucrose from cane juices is thus limited. The removal of impurities in cane sugar processing is significantly less than the impurity removal in beet processing, but
20 the ability to crystallize sucrose to produce a low purity molasses in cane sugar processing compensates for the lower impurity removal.

The method of the present invention comprises contacting a concentrated (about 55-96 Brix) aqueous solution of sucrose with selected aliphatic carboxylic acid having an average carbon chain
25 length of about 2-6 preferably by rapidly adding the solution to and rapidly dispersing it in the acid, in order to assure rapid maximum growth of large sucrose crystals to facilitate their selective recovery. The weight ratio of water in the solution to acid is about 0.02-0.2:1. The solution also usually contains non-sugar

solids in a weight ratio to the acid of about 0.1-1:1. The sucrose precipitate is then separated from the solution, as by filtration, centrifugation or the like, and recovered in purified form. The sucrose-stripped carboxylic acid-containing solution can be recycled, if desired, or stripped of its carboxylic acid.

The fundamental principle of the present invention is the precipitation of sucrose by making a solvent change. Sucrose and the non-sugars present in sugar-containing juices have different solubilities in different solvents. In the normal aqueous system, all impurities, as well as the sucrose, are highly soluble. If a solvent change is made to sufficiently reduce the solubility of sucrose, sucrose will precipitate from solution. Aliphatic carboxylic acids having an average carbon chain of about 2-6 have excellent characteristics for this purpose in that sucrose has a very low solubility in them, while all impurities normally associated with sucrose-containing plant juices are highly soluble in such acids. In contrast, sucrose is highly soluble in formic acid. Co-precipitation of impurities with sucrose is undesirable because it results in a lowered recovery of the sucrose in subsequent steps in the refining process. In the case of the selected carboxylic acid, potentially saleable sucrose can be produced directly from the prelined concentrated diffusion juice.

The solvent change is accomplished in juice which first has been concentrated to a high solids content. The solvent system may consist of pure or somewhat diluted selected acid, a recycled solvent stream, or a mixture of the two. Such acid preferably is acetic acid, propanoic acid, butanoic acid, pentanoic acid, hexanoic acid or mixtures thereof, except where the solution is molasses or molasses derived, in which event if any acetic acid is present,

others of the aliphatic carboxylic acids are also present. It will also be understood that the selected acid can be a mixture which includes aliphatic carboxylic acids having a carbon chain length in excess of 6 or less than 2, provided that the average carbon chain
5 length of the mixture is about 2-6. Thus, formic acid can be present, but only in mixture with other aliphatic carboxylic acid so that the average sucrose solubility of the acid mixture is acceptably low.

The purity of the sucrose produced by the contacting of the
10 solution with the acid may be enhanced by pre-treatment steps such as those normally employed with sugar juices. The sucrose crystallization with selected acid solvent precipitation is greatly improved, compared to aqueous systems, and equilibrium is closely approached at room temperature in less than two hours under most
15 laboratory conditions.

In the case of a sugar juice purified by conventional techniques, as previously described, the juice is concentrated to a high percent of solids in the range of 55 to 96%. The concentrated aqueous solution is then fed into, for example, acetic acid or
20 recycled acetic acid-containing solution wherein the sucrose precipitates out in high yield and high purity. The slurry of crystals and solution is very low viscosity and the crystals may be recovered by conventional filtration techniques, such as a rotary vacuum filter. The mother liquor resulting from the separation
25 contains dissolved sucrose in low amounts, the sucrose concentration being a function of the water content, the impurity content, and the acetic acid concentration.

The weight ratio of the water to the selected carboxylic acid in the contact zone is usually in the range of .02 to .2:1 and

the non-sugar to selected acid weight ratio is usually in the range of .1 to 1.0:1.

The selected acid must be recovered for most economical operation of the sugar refining process. Care must be taken in the case of acetic acid because dehydration of the acetic acid solution by boiling tends to result in a significant loss of acetic acid by decomposition so that the process must operate under conditions insuring adequate water to minimize such loss. Alternative techniques may be employed, such as recovery via solvent extraction, utilizing liquid carbon dioxide or some other solvent in which the carboxylic acid has a high solubility.

Significantly more rapid and larger sucrose crystal growth control may be obtained by adding the aqueous sucrose-containing solution to the selected acid, followed by rapid dispersion into the acid. Slow dispersion of the sucrose-containing solution in the acid or addition of the acid to the aqueous solution will result in localized supersaturation and result in the formation of small crystals of sucrose, rendering sucrose recovery more difficult.

In the case where conventional solution purification is not practiced prior to the contacting, a significant economic gain is achieved for several reasons. First, the cost of conventional purification is eliminated from the economics of sugar production; second, the production of non-sugars for sale increases up to 50%; and third, the extraction is significantly improved because only low levels of sucrose remain in the resulting molasses.

Significant reductions in energy requirements are possible in the case where sucrose is sold as produced or where it is dissolved and sold as a liquid. If conventional granular sucrose is desired, the energy requirements are still diminished because the

intermediate and raw sides of the sugar refining process are not needed in their present form due to the high purity of the sugar and the ability to return to the processing plant low purity syrups that will eventually be produced to the solvent precipitation step.

5 The process may be applied at a variety of alternative points in a beet sugar factory, depending upon the grade of sugar desired and the impurity production desired. Examples of those possibilities are set forth below:

10 Alternative 1:

Conventional untreated beet sugar diffusion juice is concentrated to between 55 and 96 Brix, while controlling pH. The juice is then fed to the selected carboxylic acid contacting zone where the sucrose precipitates from solution. The sucrose is
15 separated and recovered by filtration or other solids separation techniques. The separated sugar contains suspended solids and some colloidal material present in the diffusion juice.

Alternative 2:

20 Conventional beet sugar juice is treated by a preliming technique or predefecation technique to remove suspended solids and proteinaceous material and to clarify and stabilize the juice. The juice is then concentrated under controlled pH conditions to 55 to 96 Brix and fed to the selected carboxylic acid-contacting zone
25 where the sucrose is separated from the mother liquor. In this case, with careful control of the conditions involved in solvent precipitation, a high purity sucrose can be produced for sale directly. The sucrose may be separated from the mother liquor by filtration or other techniques, and the residual acetic acid removed

by air drying, solvent extraction, or another technique.

Alternative 3:

Beet sugar diffusion juice is first purified by conventional means and then concentrated to 55 to 96% (Brix) solids. The resulting juice is fed to the selected carboxylic acid contacting zone where sucrose is separated from the mother liquor. In this case, with careful monitoring of the conditions involved in solvent precipitation, a high purity sucrose can be produced for sale. The sucrose may be separated from the mother liquor by filtration or another solid-liquid separation technique and the residual acetic acid removed by air drying, solvent extraction, or another technique.

15 Alternative 4:

The sugar factory may be run in a conventional fashion up to the raw side operation. In this case, the raw pan fillmass is concentrated to as high a Brix as can be handled and the material is subsequently fed to the selected carboxylic acid contacting zone where the sucrose is precipitated from the mother liquor. The precipitated sucrose is returned in a conventional fashion to the high melter where it is used in a conventional fashion to produce white sugar.

25 Alternative 5:

In production of cane sugar, the juice, at any stage of processing analogous to those listed in Alternatives 1, 2, 3 and 4, is concentrated to 55 to 96 Brix and fed to the selected carboxylic acid contacting zone, where sucrose precipitates from solution and

is recovered either for sale or for subsequent reprocessing.

Alternative 6:

Raw cane sugar is dissolved in water to produce a solution
5 of between 55 and 96 Brix and is subsequently fed to the selected
carboxylic acid contacting zone where sucrose is separated from the
mother liquor as previously described.

Alternative 7:

10 Certain waste flows containing sucrose, such as are involved
in canning operations, are concentrated with pH control to between
55 and 96 Brix and fed to the selected carboxylic acid contacting
zone as described above, to precipitate the sucrose therefrom.

15 Alternative 8:

Molasses can be contacted with the selected carboxylic acid
to remove available sucrose.

The following specific Examples further illustrate certain
20 features of the present invention:

Example 1 - Recovery of Sucrose from Diffusion (Raw) Juice

A 1,700 ml. sample of diffusion juice (13.87% by weight
solids, 86.7% by weight purity) was treated with 35 ml. of
25 approximately 30° Brix milk of lime so that the pH was brought to
10.3 at 50°C. The sludge that separated was removed by filtration
and the filtrate was conventionally carbonated to a pH of 7.6 at
35°C. The filtrate was then heated to 90° and filtered to remove
calcium carbonate.

A 745.0 g. sample of treated juice, obtained as described above, was placed in a tared 2 liter filter flask equipped with an air delivery tube and the water in the juice sample was evaporated under an air stream. Heat was provided by a water bath. After the residual syrup had reached 89.0% by weight solids, the flask was removed from the water bath, disconnected from the air supply and 127 ml. of glacial acetic acid was added to the hot syrup. Sucrose precipitated immediately. The solution was allowed to cool to room temperature and the product was collected by suction filtration. The filter cake was washed with three 30 ml. portions of glacial acetic acid and four 25 ml. portions of acetone and then dried at 80°C for one hour. The yield was 81.7 g. sucrose with a pol of 97.9°S. The yield, based on sucrose taken and corrected for product purity, was 89.3%. Accordingly, the present method was shown to be rapid, efficient and practical, providing for a large immediate recovery of sucrose from a sugar refining stream.

Example 2 - Recovery of Sucrose from Thin Juice

The apparatus employed in this run was identical to that used in Example 1. A 677.2 g. portion of thin juice (13.08% by weight solids, 88.8% by weight purity) was placed in a tared 2 liter filter flask and water was removed until the solids content of the syrup reached 89.9% by weight. A 110 ml. portion of glacial acetic acid was added to the hot syrup and sucrose precipitated promptly. Washing and drying were carried out as in Example 1. A total of 71.39 g. of 97.7°S pol sucrose was obtained. The yield, based on sucrose taken and corrected for product purity, was 88.6% by weight.

Example 3 - Recovery of Sucrose from Thick Juice

A 205.0 g. portion of thick juice (67.72% by weight solids, 87.4% by weight purity) was placed in the evaporation apparatus described in Example 1 and water was removed in the usual fashion.

5 When the solids content reached 91.0% by weight, acetic acid (170 ml.) was added to the hot syrup and sucrose precipitated promptly. Isolation of the product in a manner analogous to the procedure of Example 1 gave 112.61 g. of 98.0°S pol sucrose. The yield, based on sucrose taken and corrected for product purity, was 90.9% by weight.

10

Example 4 - Purification of Cane Raw Sugar

A 100.0 g. sample of cane raw sugar (96.3°S pol) was mixed with a 25.0 g. portion of water and water was evaporated until the solids content had reached 88.5% by weight. A 125 ml. portion of
15 glacial acetic acid was added to the hot slurry of crystals and syrup and the sucrose precipitated in the usual fashion. A total of 88.63 g. of 97.2°S pol sugar was obtained. The yield, based on sucrose taken and corrected for product purity, was 89.4% by weight.

20 Example 5 - Recovery of Sucrose from 55 Brix Carbonated Beet Juice

A 250.00 g. sample of carbonated beet juice (55.0% by weight solids, 87.0% by weight purity) was mixed at 25° C with a 1750 g. portion of glacial acetic acid and crystallization was allowed to proceed at 25° C. After an initial induction period of 0.5 hour,
25 sucrose precipitated as small crystals. The crystals were isolated, washed and dried in the usual fashion to give 83.22 g. of 97.6°S pol sugar (67.9% recovery corrected for pol).

Example 6 - Recovery of Sucrose from 96 Brix Massecuite (Mixture of Mother Liquor and Crystals)

A 100.20 g. portion of massecuite (96.0 weight percent solids, 89.6 weight percent purity) was heated on a water bath and
5 mixed with 129.00 g. of hot (approximately 100° C) glacial acetic acid. Sucrose precipitated promptly. After cooling, the product was collected and washed in the usual fashion to give 77.53 g. of 99.4°S pol sugar (88.2% recovery corrected for pol).

10 Example 7 - Recovery of Sucrose from Thick Juice with Propanoic Acid

A 200.13 g. portion of beet-derived juice (65.4% solids, 90.8% purity) was placed in a 1 liter flask and water was evaporated under an air stream until the solids content reached 88.4%. A
15 253.44 g. portion of n-propanoic acid was heated to about 100° C and then added all at once to the hot concentrated juice with stirring. Within 45 seconds sucrose began to crystallize. After cooling, filtration and washing with four 150 ml. portions of methanol, the product was dried in an oven. The yield was 109.0 g. (99.0°S pol)
20 sucrose (91.7% recovery corrected for pol).

Example 8 - Recovery of Sucrose from Thick Juice with n-Butanoic Acid

A 141.84 g. sample of thick juice (67.4% solids, 90.5%
25 purity) was treated in the same manner as in Example 7. A 193.00 g. portion of n-butanoic acid at 100° C was added all at once to the hot concentrated juice (90.0% solids). After cooling, filtration, washing and drying, the sucrose yield was 79.56 g. and the pol was 95.6°S (91.9% recovery corrected for pol).

In a parallel run, formic acid was substituted for the n-butanoic acid. However, no sucrose precipitated. The formic acid kept the sucrose in solution.

5 Example 9 - Recovery of Sucrose from Thick Juice with Mixed Acid.

A 200.00 g. sample of thick juice (68.06% solids, 90.0% purity) was heated on a water bath while water was evaporated under an air stream to reduce it to 150.41 g. (136.12 g. solids). It was then contacted with a 100° C mixture of 120.10 g. acetic acid and
10 144.16 g. n-propanoic acid (less a 15.00 g. portion of the acid mixture which had been discarded before the contacting), the acid being added all at once to the sugar solution, with stirring. The resulting mixture was then cooled to room temperature. The precipitated sucrose product was collected by filtration and was
15 washed with 75 ml. n-propanoic acid and then methanol and then was dried. The dried product weighed 105.40 g. to provide a 86.0% yield (99.0°S pol).

Examples 1 through 9 clearly illustrate that when a beet
20 sugar raw (diffusion) juice, thin juice or thick juice or a raw cane sugar solution is concentrated to about 55-96 Brix, then contacted with a selected aliphatic carboxylic acid of 2-6 carbon chain length, such as acetic acid, propanoic acid, butanoic acid or a mixture thereof, sucrose immediately precipitates in very high yield
25 therefrom and is recovered easily from the juice by filtration, centrifugation or the like. Similar results have been obtained with cane sugar juice. In contrast, formic acid solubilizes the sucrose.

Parallel tests have shown that juices and other solutions containing sucrose such as are described in Alternatives 1-7 above,

which solutions have been concentrated to about 55-96 Brix, can be readily precipitated by contacting with acetic acid, propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, or a mixture of aliphatic carboxylic acid having an average carbon chain length of about 2-6, in a concentration sufficient to provide a weight ratio of water to selected carboxylic acid of about 0.02-0.2:1. After precipitation and recovery of the sucrose, the selected carboxylic acid solution can be recycled per se or the selected carboxylic acid therein can be recovered by various means for reuse.

CLAIMS

1. A method of recovering sucrose from plant-derived aqueous solutions, which method comprises contacting an aqueous sucrose-containing solution comprising or derived from plant juice with aliphatic carboxylic acid
5 having an average carbon chain length of about 2-6, said acid being in an amount sufficient to selectively precipitate said sucrose; and separating and recovering said precipitated sucrose.
2. A method according to claim 1, wherein said
10 acid comprises acetic acid, preferably glacial acetic acid.
3. A method according to claim 1 or claim 2, wherein contact with the acid is effected prior to or after molasses formation, provided that if effected after
15 molasses formation and acetic acid is used, the acetic acid is in admixture with other carboxylic acids.
4. A method according to any one of claims 1 to 3, wherein the aqueous sucrose-containing solution comprises or is derived from sugar beet juice or sugar cane juice
20 or mixtures thereof.
5. A method according to any one of claims 1 to 4, wherein the weight ratio of water in said solution to said acid is about 0.02-0.2:1.

6. A method according to any one of claims 1 to 5, wherein the weight ratio of non-sugar solids in said solution to said acid is about 0.1-1:1.

7. A method according to any one of claims 1 to 6,
5 wherein the aqueous sucrose-containing solution has a concentration of from about 55 to 96 Brix.

8. A method according to any one of claims 1 to 7, wherein the aqueous sucrose-containing solution comprises untreated diffusion juice; diffusion juice which has been
10 prelined and/or predefecated to remove suspended solids and proteinaceous material and to clarify said juice; diffusion juice which has been conventionally purified; dissolved raw sugar; or a sugar-containing solution from a canning operation.

15 9. A method according to any one of claims 1 to 8, wherein the resulting sucrose-depleted solution, after precipitation, separation and recovery of said sucrose therefrom, is treated to recover said acid.

10. A method according to any one of claims 1 to 9,
20 wherein contact with the acid is effected by adding said sucrose-containing solution to said acid and dispersing said solution in said acid to promote rapid large sucrose crystal growth.