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Description

FIELD OF THE INVENTION

[0001] The present invention relates to an improved process of producing crystalline fructose. The process is based on chromatographic fractionation of fructose crystallization run-offs with cation exchange resins in two different ion forms and introduction of the fructose fractions thus obtained into further crystallization for the production of crystalline fructose.

BACKGROUND OF THE INVENTION

[0002] US Patent 3 692 582, Melaja, A.J. (publ. 19 September 1972) discloses a chromatographic process of separating fructose from an invert sugar solution with a cation exchange resin in an alkaline earth metal salt form, such as a calcium form. A glucose-rich fraction, a fraction containing glucose and fructose as well as a fructose-rich fraction are recovered. The fraction containing glucose and fructose may be returned to the feed for diluting the invert sugar feed solution. It is recited that the purity of the fructose fraction may be 95-97%. It is also recited that the fructose fraction may be evaporated and fructose crystallized therefrom.

[0003] US Patent 3 883 365, Suomen Sokeri Osakeyhtiö, Forsberg, H. *et al.* (publ. 13 May 1975) relates to a method of crystallizing fructose at a pH in the range of 4.5 to 5.5 from an aqueous solution containing glucose as an impurity. The solution to be crystallized contains at least about 90% dry substance, the fructose content of the dry substance being at least about 90% by weight. The crystallization may be carried in two or more steps. It is also recited in the reference that difructoses and difructose anhydrides are believed to be actual crystallization inhibitors.

[0004] US Patent 3 928 062, Daiichi Kogyo Seiayku Co., Ltd (publ. 23 December 1975) discloses a process for obtaining anhydrous fructose crystals without the formation of fructose hemihydrate or fructose dihydrate crystals from an aqueous fructose solution, whereby it is essential that the crystallization is carried out within a certain range of fructose concentration and temperature. The starting fructose solutions include those obtained from the inversion of sucrose or from the isomerization of glucose, optionally pretreated by concentration, dilution, heating or cooling. It is recited that the starting fructose solution may also be a mother liquor from a previous crystallization cycle.

[0005] US Patent 4 634 472, A.E. Staley Manufacturing Co. (publ. 6 January 1987) discloses a process for manufacturing an enriched fructose syrup. In this process, dextrose is crystallized from a relatively high solids feed syrup (a dry solids content between about 75 and 89 percent) containing fructose and dextrose. Then another relatively dilute (or low solids) fructose containing diluent syrup is added to enhance separation of the dextrose crystals from the mother liquor.

[0006] US Patent 5 230 742, A.E. Staley Manufacturing Co. (publ. 27 July 1993) and US Patent 5 234 503, A.E. Staley Manufacturing Co. (publ. 10 August 1993) disclose an integrated process for producing crystalline fructose and high-fructose liquid-phase sweetener (such as a high fructose corn syrup) from a feed stream comprising dextrose. A portion of the dextrose in the feed stream is isomerized to fructose and the resulting dextrose/fructose stream is fractionated to produce a high fructose stream. A portion of the fructose in the high fructose stream is crystallized out and the mother liquor remaining after crystallization is blended with dextrose-containing streams to produce the liquid-phase sweetener. It is recited that the fractionation may be carried out in a chromatographic column with a polystyrene sulfonate cation resin using calcium as the preferred salt form.

[0007] US 4 938 804, Suomen Sokeri Oy, Heikkilä *et al.* (publ. 3 July 1990) relates to a process of producing crystalline fructose by adding ethanol to a concentrated fructose syrup to form an ethanol-water azeotrope, supersaturating the solution, seeding the solution with fructose seed crystals and removing the ethanol-water azeotrope under reduced pressure to crystallize fructose. The crystalline fructose is separated from the crystallization mother liquor. The spent mother liquor is recovered and distilled to recover ethanol.

[0008] WO 92/07097, Suomen Xyrofin Oy, Heikkilä *et al.* (publ. 30 April 1992) (= EP 553 126 B1) discloses a process for producing glucose and fructose from sucrose by enzymatic hydrolysis. The hydrolysis is carried out by an invertase enzyme immobilized on a solid carrier, followed by separating a glucose fraction and a fructose fraction from the hydrolysis product by chromatographic simulated moving-bed process. The chromatographic separation is typically carried out with a strongly acid cation exchange resin, which is preferably in calcium form. Fructose and glucose may then be crystallized from the fructose and glucose fractions obtained from the separation.

[0009] US Patent 6 206 977 B1, Danisco Finland Oy, Heikkilä *et al.* (publ. 27 March 2001) relates to a method of crystallizing anhydrous fructose from water by a cooling crystallization process, where the temperature difference between the solution and the cooling elements is maintained at a value of less than about 10°C and the supersaturation of the solution with respect to saturated fructose is maintained at a ratio between 1.1. and 1.25. The crystallization is carried out from an aqueous solution containing at least about 90% dry substance, which has a fructose content of at least about 90% by weight.

[0010] US Patent 6 607 603 B1, Warcoing S.A. (published 20 January 2000) discloses a process for manufacturing crystallized fructose by preparing a pure fructose syrup by melting fructose dihydrate crystals, concentrating the melt to

a dry matter content above 96% by weight, seeding the concentrated syrup with fructose seed crystals and solidifying the seeded syrup. The crystallization mother liquor may be submitted to a new crystallization stage.

[0011] US 6 924 371 B2, Danisco Sweeteners Oy (published 8 January 2004) relates to a chromatographic process of separating hydrophilic carbohydrates from hydrophobic carbohydrates with a weak acid cation exchange resin. Example 7 of the reference discloses chromatographic separation of a fructose crystallization run-off with a weak acid cation exchange resin in Na^+-form. It is recited in the reference that the resin separates well fructose and oligosaccharides formed in thermal acid breakdown of fructose. It is also recited that oligosaccharides are eluted from the column faster than fructose.

[0012] US 7 150 794 B2, Getec Guanabara Quimica Industrial S.A. (published 25 November 2004) discloses a process for the production of crystalline fructose, comprising (a) hydrolysis of an aqueous solution of sucrose to produce a solution of fructose and glucose, (b) chromatographing the solution of fructose and glucose to yield a solution having a fructose content between 84% and 90% and concentrating the solution to a dry solids concentration of at least 92% by weight, (c) rapidly cooling the syrup thus obtained and seeding the syrup with fructose seed crystals to obtain a massecuite, (d) subjecting the massecuite to controlled slow cooling, (e) adding absolute ethanol, (f) subjecting the massecuite to slow cooling and (g) separating the fructose crystals. The chromatographic separation step is carried out with a cation exchange resin. The ethanol-containing crystallization mother liquor is subjected to evaporation, until complete removal of ethanol is achieved. The mother liquor thus obtained is a valuable fructose-containing by-product and can be used for example as a fructose-rich syrup or for the production of mannitol and sorbitol.

[0013] US Patent 7 314 528, Danisco Sweeteners (published 8 January 2004) discloses a process of removing crystallization inhibitors from a solution comprising one or more reducing sugars, such as fructose, by subjecting the solution to one or more purification steps selected from nanofiltration, hydrolysis and chromatography. After the purification, the solution is subjected to crystallization. It is recited in the reference that the starting solution may also be a mother liquor obtained from the crystallization of fructose. Furthermore, Example 5 discloses the purification of a fructose run-off by nanofiltration to provide a purified fructose-rich nanofiltration permeate, followed by crystallization of fructose from the purified nanofiltration permeate.

[0014] US 5 730 877, Xyrofin Oy (publ. 24 March 1998) discloses a method for fractionating a solution by a simulated moving bed chromatographic separation system comprising at least two packing material beds in different ionic forms. One of the ion forms may be a divalent cation, such as Ca^{2+}, and the other may a monovalent cation, such as Na^+. Example 6 discloses two-phase separation of maltose, glucose and fructose with a five-column system where the first column is in Na^+ form and the next four columns are in Ca^{2+} form. A maltose fraction was withdrawn from the first column and a glucose fraction and a fructose fraction were withdrawn from the third and fifth column. Crystallization of the fructose fraction is not disclosed.

[0015] US 6 896 811 B2, Danisco Sweeteners Oy (published 9 January 2003) discloses a chromatographic SMB fractionation process, where the separation profile passes more than once or less than once through the separation loop during each separation cycle. The solution to be separated may be a fructose syrup, for example. Example 4 of the US patent discloses separation of fructose syryp by a separation system, which comprised two columns containing a strong acid cation exchange resin in a Ca^{2+} form as the column filling material. One fructose-containing fraction was drawn from both columns. Crystallization of the fructose fractions is not disclosed.

[0016] One of the problems associated with conventional fructose crystallization methods relates to the presence of crystallization inhibitors, especially dimeric sugars of fructose, in the crystallization. The formation of dimeric sugars is especially accelerated in prolonged heating of a concentrated fructose solution in an acidic environment. Dimeric sugars having an inhibiting effect on the crystallization of fructose are formed in the enzymatic or acid inversion of sucrose to a mixture of fructose and glucose, in the enzymatic isomerization of glucose to fructose and in the crystallization process itself especially during evaporation. The presence of dimeric sugars and other impurities in the crystallization of fructose leads to lower process yields. The presence and formation of dimeric sugars in the crystallization of fructose is discussed for example in the Example at columns 17 and 18 of US 5 234 503 (see especially Table III).

[0017] Another problem associated with conventional fructose crystallization methods relates to a low overall yield of crystalline fructose from the fructose feed solution for the reason that fructose has not as a rule been recovered by crystallization from crystallization run-offs because of a low yield due to dimeric crystallization inhibitors such as difructose dianhydrides, which are concentrated into the run-offs. Instead, the run-offs have conventionally been used for preparing liquid fructose syrups, for example.

BRIEF DESCRIPTION OF THE INVENTION

[0018] It is thus an object of the present invention to provide a process of producing crystalline fructose so as to alleviate the above disadvantages, such as an insufficient yield of crystalline fructose due to the presence and formation of crystallization inhibitors in the fructose crystallization leading to inefficient crystallization of fructose from crystallization run-offs. The object of the invention is achieved by a process which is characterized by what is stated in the independent

claim. The preferred embodiments of the invention are disclosed in the dependent claims.

[0019] The invention is based on the treatment of fructose crystallization run-offs by a chromatographic fractionation with cation exchange resins in two different ion forms and introduction of the fructose fractions thus obtained into further crystallization for the production of further crystalline fructose. The process of the invention provides an improved overall yield of crystalline fructose calculated on the basis of the fructose source as well as on the basis of fructose in the crystallization batch.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] The following drawings are illustrative embodiments of the invention and are not meant to limit the scope of the invention as defined in the claims in any way.

Figure 1 is a process scheme showing one embodiment of the invention, including two crystallization steps and chromatographic separation with a combination of resins in Ca^{2+} form and Na^{+} form.

Figure 2 is a graphical representation of the separation profile obtained from chromatographic separation of a fructose run-off with a Na^{+} form resin.

Figure 3 shows a HPLC-diagram of a residual fraction defined in claim 8, identifying the location of the peaks for disaccharides A and B.

DETAILED DESCRIPTION OF THE INVENTION

[0021] The present invention relates to a process of producing crystalline fructose with a high overall yield of crystalline fructose from the starting material of a fructose process and from the crystallization feed.

[0022] The process of the invention comprises, as characteristic elements, the following steps:

one or more crystallization steps for producing crystalline fructose and one or more crystallization run-offs,
chromatographic fractionation of at least part of said one or more crystallization run-offs in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to produce a fructose fraction and optionally at least one other fraction, and
introduction of said fructose fraction to at least one of said one or more crystallization steps for the production of crystalline fructose.

[0023] The crystallization as such is carried out by conventional methods known in the art for the crystallization of fructose, advantageously by cooling crystallization or by other methods such as boiling crystallization, or precipitation crystallization, or a combination thereof. Seeding of the crystallization mass may be used, if desired. The crystallization may be carried out in water, but an alcohol, such as ethanol, or a mixture of water and alcohol, can also be used. The crystallization is preferably carried out at a pH in the range of 4.5 to 5.5. The crystals are separated from the crystallization massecuite for instance by centrifugation or filtering to provide crystalline fructose and a fructose run-off.

[0024] Said one or more crystallization steps provide crystalline fructose and a fructose run-off, which can be crystallized to provide further crystalline fructose and a further fructose run-off.

[0025] The crystallization run-offs contain high amounts of fructose as well as reasonable amounts of glucose and disaccharides. In a typical embodiment of the invention, the crystallization run-offs may contain 88 to 96% of fructose, 2 to 5% of disaccharides and 1 to 8% of glucose, based on the dry substance content (DS) of the run-offs.

[0026] Disaccharides, especially fructose dimers, act as crystallization inhibitors in the crystallization of fructose, whereby they should be removed as efficiently as possible from the crystallization run-offs before subsequent recovery of fructose by further crystallization.

[0027] Consequently, in a further step of the process of the invention, at least part of said fructose crystallization run-offs are subjected to chromatographic fractionation in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form.

[0028] The resin in a monovalent cation form may be in a Na^{+} form or K^{+} form, for example.

[0029] In a preferred embodiment of the invention, the chromatographic fractionation by the separation system described above provides from the fructose run-off a fructose fraction, which contains 94 to 98% of fructose, less than 3%, preferably less than 2% of disaccharides and less than 1.5%, preferably less than 1.0% of glucose on DS.

[0030] Said disaccharides existing in the fructose run-offs may be fructose dimers, degradation products of starch, such as maltose or isomaltose or a residue of raw material such as saccharose. In connection with the present invention, said disaccharides are especially selected from disaccharides A and disaccharides B, which are mainly composed of

fructose dimers, such as difructose dianhydrides. Fructose dimers have been formed in acidic conditions, in a concentrated fructose solution in enzymatic conversions (inversion, isomerization), in acidic inversion of saccharose and during the crystallization process of fructose. Fructose dimers such as difructose dianhydrides include various difructose anhydrides and various diheterolevulosans, which have been formed from the polymerization of fructose during a prolonged treatment of fructose in a concentrated form in acid or alkaline conditions.

[0031] Disaccharides may be analyzed by HPLC with a Na^+ -form resin using water as an eluant. The elution order of disaccharides in the HPLC-diagram is saccharose (similar retention time also for maltose and isomaltose), disaccharides B, disaccharides A, glucose and fructose. Disaccharides A and B show two separate peaks in the HPLC diagram. HPLC-peaks for disaccharides A and B mainly consist of different difructose dianhydrides, which are considered to be more harmful crystallization inhibitors than the other type of disaccharides such as saccharose, maltose or isomaltose.

[0032] The disaccharide A type of difructose dianhydrides is more difficult to remove from a fructose run-off solution by chromatographic separation than disaccharides B. Inventors have surprisingly discovered that the disaccharide A type of difructose dianhydrides can be efficiently separated from fructose solution using a cation exchange resin in a monovalent form in the chromatographic separation. The cation exchange resin may be a strong or weak cation exchange resin. Especially advantageous removal of disaccharides A, disaccharides B and glucose and low loss of fructose can been achieved when using cation exchange resin beds in Ca^{2+}- form and Na^+ -form consecutively. The accumulation of crystallization inhibitors to the fructose run-off will be prevented and the separated fructose fraction depleted in fructose dimers can be recycled back to the crystallization to obtain a total yield of crystalline fructose up to 93 to 97% based on the fructose feed to crystallization or 93 to 98% based on the sucrose used for the inversion and isomerization, if sucrose has been used as a basic source of fructose.

[0033] The fructose fraction obtained from the chromatographic fractionation of the invention typically comprises less than 1.5%, preferably less than 1.0% of disaccharides A and less than 1.5%, preferably less than 0.8% of disaccharides B on DS. A typical range for disaccharides A is 0.5 to 1% on DS and for disaccharides B 0.5 to 0.8% on DS.

[0034] The separation of disaccharides A and disaccharides B from fructose can be seen from Figure 2, which shows the separation profile obtained from the chromatographic separation of a fructose run-off with a Na^+ form resin. It can be seen from Figure 2 that efficient separation of disaccharides A and B from fructose was achieved with a Na^+ form resin. On the other hand, a Ca^{2+} form resin is effective to separate glucose from fructose solutions.

[0035] Said at least one other fraction in the chromatographic fractionation of fructose run-off may be a residue fraction enriched in fructose dimers. Consequently, in addition to the fructose fraction, which is depleted in fructose dimers (disaccharides A and B), a residue fraction can be obtained, which is enriched in fructose dimers (disaccharides A and B). The fructose fraction depleted in fructose dimers (disaccharides A and B) typically comprises less than 1.5%, preferably less than 1.0% disaccharides A and less than 1.5%, preferably less than 0.8% disaccharides B on DS. The residue fraction enriched in fructose dimers typically contains 2 to 8%, preferably 4 to 8% disaccharides A and 3 to 10%, preferably 8 to 10% disaccharides B on DS.

[0036] The chromatographic separation system used in the process of the present invention comprises two or more cation exchange resin beds, whereby at least one of the resin beds in a Ca^{2+} form and at least one of the resin beds is in a monovalent cation form.

[0037] In one embodiment of the invention, at least 20% of the total length of the resin beds of the separation system is in a Ca^{2+} form. In another embodiment of the invention, at least 20% of the total length of the resin beds of the separation system is in a monovalent cation form.

[0038] The relation between the length of the Ca^{2+} resin bed/beds and the other resin bed/beds may be adjusted depending on the content of disaccharides A and B and glucose in the fructose crystallization run-off used as the feed for the chromatographic fractionation. Consequently, in a further embodiment of the invention, when the feed contains less than 2% disaccharides A and B on DS and more than 3% glucose on DS, 60 to 80% of the total length of the resin beds of the separation system may be in a Ca^{2+} form. In another embodiment of the invention, when the feed contains more than 3% disaccharides on DS and less than 2% glucose on DS, 60 to 80% of the total length of the resin beds may be in a monovalent cation form.

[0039] Said two or more cation exchange resin beds of the separation system are preferably composed of strongly acid cation exchange resins. The resins have typically a styrene skeleton, which is preferably cross-linked with divinylbenzene.

[0040] Said two or more cation exchange resin beds may also comprise a weakly acid cation exchange resin. The weakly acid cation exchange resin may be in a free acid form, for example.

[0041] Said two or more cation exchange resin beds may be arranged in series or in parallel.

[0042] The chromatographic fractionation in accordance with the present invention may be carried out with a batch process or a simulated moving bed process (SMB process). The simulated moving bed process may be continuous or sequential.

[0043] The temperature of the chromatographic fractionation is typically in the range of 20 to 90°C, preferably 40 to 65°C. The pH of the solution to be fractionated is typically in the range of pH 3 to pH 6, preferably in the range of pH 4

to pH 5 to minimize further formation of fructose-based disaccharides.

[0044] The chromatographic fractionation provides the fructose fraction with a fructose yield of more than 80%, preferably more than 90% and with an especially preferred fructose yield of more than 95% based on fructose in the fructose crystallization run-off used as the feed in the chromatographic fractionation. In the fructose fraction, the amount of disaccharides A is reduced to a level of less than 60% and the amount of disaccharides B is reduced to a level less of than 40% based on the disaccharide A or B content in the fructose run-off.

[0045] The fructose fraction obtained from the chromatographic fractionation has a typical fructose purity of more than 93%, preferably more than 95% and more preferably more than 97%, based on dissolved dry substance (DS). The removal of disaccharides B is as a rule more efficient than the removal of disaccharides A.

[0046] The residue fraction obtained from the chromatographic fractionation of the fructose crystallization run-off with the process of the invention contains fructose in an amount of 45 to 65% on DS, glucose in an amount of 10 to 30% on DS, preferably 20 to 30% on DS, disaccharides A in an amount of 2 to 8% on DS, preferably 4 to 8% on DS, disaccharides B in an amount of 3 to 10% on DS, preferably 8 to 10% on DS. The dry substance yield to the residue fraction represents 5 to 15 weight-%, preferably 5 to 8 weight-% of the run-off.

[0047] Typical yield of crystalline fructose in a single pass (no previous crystallizations) in the crystallization of a solution containing over 95% fructose on DS is in the range of 40-55%, normally about 45% of the fructose in the feed. Generally the yield of crystalline fructose in a second pass (crystallization of a run-off from a previous crystallization) is less than 90% of the yield of the first pass. Also a much longer time is required for the crystallization of the second pass due to the crystallization inhibitors.

[0048] The efficient removal of the crystallization inhibitors with the method of the invention facilitates the overall crystallization yield of the crystalline fructose to be more than 90%, preferably more than 93% and most preferably over 95%, based on the fructose in the crystallization feed.

[0049] The fructose fraction depleted in fructose dimers, obtained from the fractionation of the fructose run-off is then introduced into at least one of said one or more crystallization steps for the production of crystalline fructose. This step may be realized in different ways.

[0050] In one embodiment of the present invention, the process may comprise the following steps:

chromatographic fractionation of a fructose crystallization run-off by a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to obtain a fructose fraction,
introducing said fructose fraction to crystallization to obtain crystalline fructose and a further crystallization run-off, and returning at least part of said further crystallization run-off to the chromatographic fractionation.

[0051] In another embodiment of the present invention, the process may comprise the following steps:

crystallization of a fructose crystallization run-off to obtain crystalline fructose and a further crystallization run-off,
chromatographic fractionation of at least part of said further crystallization run-off by a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to obtain a fructose fraction,
returning said fructose fraction to the crystallization.

[0052] Conventional sources for obtaining fructose are as a rule mixtures of glucose and fructose, such as solutions of inverted sucrose, solutions of isomerized glucose (starch based) and mixtures thereof. The fructose source may also be a fructose solution obtained by hydrolysing inulin.

[0053] The solution of inverted sucrose is typically obtained by enzymatic or acidic inversion of sucrose to a mixture of fructose and glucose. One process for enzymatic inversion is described in WO 92/07057 (EP 553 126 B1). Small amounts of dimeric sugars are formed in the inversion process, especially at lower pH values. The acidic inversion processes catalyze the formation of dimers, leading into small amounts of dimeric sugars. Such dimeric sugars comprise for example difructose anhydrides, fructose dianhydrides, and diheterolevulosans. These inversion by-products act as crystallization inhibitors in the subsequent crystallization of fructose.

[0054] The solution of isomerized glucose is obtained from starch-based glucose syrup, which is isomerized with an isomerase enzyme to a mixture of glucose and fructose. The enzymatic isomerization is preferably carried out at the optimum pH range for the enzyme, i.e. at a pH of about 8. One process for the isomerization is disclosed in US 4 411 996. The isomerization is carried out at a higher pH than the inversion of glucose. Consequently, the fructose solution from isomerized glucose includes less fructose dimers than the fructose solution from inverted sucrose. Before and after the isomerization, ion exchange is as a rule used for removing ions.

[0055] Even mixtures of inverted sucrose and isomerized glucose can be used as a source in the production of

crystalline fructose.

[0056] Consequently, the first step in the fructose process typically comprises separation of these mixtures of glucose and fructose into a glucose fraction and a fructose fraction. To achieve a high process yield of crystalline fructose especially from sucrose, the crystallization inhibitors, such as dimeric sugars formed either in the inversion or isomerization process or during the crystallization, should be removed as efficiently as possible by various separation techniques.

[0057] In a further embodiment of the present invention, the process may thus also comprise, as a preceding step, chromatographic fractionation of a solution containing glucose and fructose to obtain a glucose fraction and a fructose fraction for producing crystalline fructose.

[0058] In a still further embodiment of the invention, the process may also comprise the following steps:

subjecting the glucose fraction to isomerization to obtain a solution containing glucose and fructose, and feeding the solution containing glucose and fructose to chromatographic fractionation.

[0059] The chromatographic separation of glucose and fructose is typically carried out with a cation exchange resin, preferably with a strongly acid cation exchange resin. The resin is preferably in a divalent cation form, whereby the divalent cation is typically selected from Ca^{2+}, Mg^{2+} or Sr^{2+}, especially Ca^{2+}. The resin has typically a styrene skeleton, which is preferably cross-linked with divinylbenzene.

[0060] In a typical embodiment of this latter embodiment of the invention, the starting solution containing glucose and fructose is selected from inverted sucrose, converted and isomerized starch and isomerized glucose.

[0061] In a still further embodiment of the invention, the process may com-comprise the following steps:

(a) providing a solution containing glucose and fructose,
(b) subjecting the solution containing glucose and fructose to chromatographic fractionation to obtain a glucose fraction and a fructose fraction,
(c) subjecting the fructose fraction to crystallization to obtain crystalline fructose and a fructose crystallization run-off,
(d) subjecting at least part of the fructose crystallization run-off to chromatographic fractionation in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to obtain a further fructose fraction,
(e) introducing said further fructose fraction to crystallization to obtain further crystalline fructose and a further crystallization run-off, and
(f) returning at least part of said further crystallization run-off to chromatographic fractionation in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form.

[0062] In a still further embodiment of the invention, the process may comprise the following steps:

(a) providing a solution containing glucose and fructose,
(b) subjecting the solution containing glucose and fructose to chromatographic fractionation to obtain a glucose fraction and a fructose fraction,
(c) subjecting the fructose fraction to crystallization to obtain crystalline fructose and a fructose crystallization run-off,
(d) subjecting the fructose crystallization run-off to crystallization to obtain further crystalline fructose and a further crystallization run-off,
(e) subjecting at least part of said further crystallization run-off to chromatographic fractionation in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to obtain a further fructose fraction,
(f) returning said fructose fraction to the crystallization.

[0063] One further embodiment of the process of the invention comprises, as characteristic elements, the following steps:

(a) providing a solution containing fructose and glucose,
(b) subjecting the solution containing fructose and glucose to chromatographic fractionation to obtain a fructose fraction and a glucose fraction,
(c) subjecting the fructose fraction to crystallization to obtain a first crop of crystalline fructose and a crystallization run-off,
(d) recovering the first crop of crystalline fructose,

followed by the following further steps:

(e)(1) at least one further chromatographic fractionation of the crystallization run-off from step (c) in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to obtain a further fructose fraction or (e)(2) at least one further crystallization of the crystallization run-off from step (c) to obtain a further crop/crops of crystalline fructose and a further crystallisation run-off/run-offs,
(f)(1) at least one further crystallization of said further fructose fraction from step (e)(1) to obtain a further crop/crops of crystalline fructose and a fruther crystallisation run-off/run-offs or (f)(2) at least one further chromatographic fractionation of said further crystallization run-off/run-offs from step (e)(2) in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to obtain a further fructose fraction,

(g) optionally returning said further crystallization run-off/run-offs from step (f)(1) and/or said further fructose fractions from step (f)(2) to any earlier chromatographic step of the process or any earlier crystallization step of the process, and
(h) recovering said further crop/crops of crystalline fructose, and
(i) optionally combining the first crop of crystalline fructose with said further crop/crops of crystalline fructose.

[0064] In a still further embodiment of the process of invention, where the further steps (e) to (i) comprise the following:

(e)(1) chromatographic fractionation of the crystallization run-off in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to obtain a further fructose fraction,
(f)(1) crystallization of said further solution enriched in fructose to obtain a further crop of crystalline fructose, and
(h) recovering said further crop of crystalline fructose.

[0065] In another embodiment of the process of the invention, where the further steps (e) to (i) comprise the following:

(e)(1) chromatographic fractionation of the crystallization run-off in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to obtain a further solution enriched in fructose,
(f)(1) crystallization of said further solution enriched in fructose to obtain a further crop of crystalline fructose and a further crystallization run-off,
(g) returning said further crystallization run-off to the chromatographic fractionation in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, and
(h) recovering said further crop of crystalline fructose.

[0066] In a still further embodiment of the process of the invention, steps (e) to (i) comprise the following:

(e)(2) crystallization of the crystallization run-off to obtain a further crop of crystalline fructose and a further crystallization run-off,
(f)(2) chromatographic fractionation of said further crystallization run-off in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to obtain a further fructose fraction,
(g)(2) returning said further solution enriched in fructose to the crystallization of step (e)(2), and
(h) recovering said further crop of crystalline fructose.

[0067] Furthermore, the fructose fraction obtained from the chromatographic fractionation of a fructose crystallization run-off in accordance with the present invention is as a rule subjected to decolorization before the next crystallization.

[0068] Figure 1 shows one preferred embodiment of carrying out the present invention. In the process of Figure 1, a fructose fraction (1) obtained from chromatographic fractionation of a glucose/fructose solution is introduced into a first crystallization (crystallization 1), which provides fructose crystals (a first batch of crystalline fructose) and a first fructose run-off (run-off 1). The first fructose run-off is introduced into a second crystallization (crystallization 2), which provides fructose crystals (a second batch of crystalline fructose) and a second run-off (run-off 2). The second run-off is introduced into chromatographic fractionation, which is carried out with a combination of a Ca^{2+} form resin and a Na^{+} form resin.

The chromatographic fractionation provides a fructose fraction (2), which is returned to crystallization 2, and a residual fraction containing most of the crystallization inhibitors (disaccharides A and B).

[0069] The embodiment is especially efficient, if the source of glucose/fructose solution is sucrose, because the feed to the second crystallization is a mixture of fructose run-off (1) and fructose fraction (2) containing a low amount of crystallization inhibitors and a high amount of fructose to facilitate an overall yield of crystalline fructose of up to 98% of the sucrose. The process schema is also advantageous in respect to the required chromatographic system, because the volume of the fructose run-off (2) to be separated is significantly lower (30-40%) than if the total volume of run-off (1) would be separated.

[0070] The following examples represent illustrative embodiments of the invention without limiting the scope of the invention in any way.

[0071] In the examples and throughout the specification and claims, the following definitions have been used:

DS refers to the dry substance content measured by refractometric index expressed as % by weight.

[0072] The content of fructose and glucose was measured as follows: Liquid chromatography HPLC, Na^+ form cation exchange column at a temperature of 85°C with a flow rate of 0.8 ml/min using water as the eluent.

[0073] The content of disaccharides A and disaccharides B was measured by HPLC (liquid chromatography) in the following conditions:

1) Na^+ form cation exchange column at a temperature of 85°C with a flow rate of 0.8 ml/min using water as the eluent, whereby the elution order of glucose and fructose and disaccharides in HPLC-diagram is saccharose (or maltose, isomaltose), disaccharides B, disaccharides A, glucose and fructose.
2) Pb^{2+} form cation exchange column at a temperature of 65°C with a flow rate of 0.4 ml/min using water as the eluent.

[0074] The abbreviation "tn" refers to 1000 kg.
"Mother liquor" refers to a fructose crystallization run-off.

EXAMPLE 1. CHROMATOGRAPHIC SEPARATION OF INVERTED SUCROSE WITH CA^{2+}-ION FORM RESIN

[0075] The process equipment included four columns connected in series, feed pump, recycling pumps, eluent water pump, heat exchangers, flow control means for the out-coming liquids as well as inlet and product valves for the various process streams. The height of each column was 4.0 m and each column had a diameter of 3.1 m. The columns were packed with a strong acid gel type cation exchange resin (manufactured by Finex) in Ca^{2+}-form. The divinylbenzene content of the resin was 5.5% and the mean bead size of the resin was 0.36 mm.

[0076] As a feed, enzymatically inverted sucrose (obtained by a process described in US 4 411 996) was used and the aim was to separate glucose and fructose to different fractions.

[0077] The liquor concentration was 67.5 g/100 ml and the pH was 4.1. The fructose syrup was composed as set forth below, whereby the percentages are given on a dry substance weight basis.

TABLE E1-1

Composition of Feed	
Fructose, % on DS	49.6
Glucose, % on DS	49.4
Disaccharides A, % on DS	0.5
Disaccharides B, % on DS	0.1
Others, % on DS	0.4

[0078] The fractionation was performed by way of a 12-step SMB sequence as set forth below. The feed and the eluent were used at a temperature of 65°C and water was used as an eluent.

[0079] Step 1: 3.5 m^3 of feed solution were pumped into the first column at a flow rate of 25 m^3/h and a glucose fraction was collected from the same column. Simultaneously 4.45 m^3 of water were pumped into the third column at a flow rate of 35 m^3/h and fructose fraction was collected from the same column.

[0080] Step 2: 2.85 m^3 of water were pumped into the third column at a flow rate of 28 m^3/h and glucose fraction was collected from the first column.

[0081] Step 3: 15.6 m^3 were circulated in the column set loop, formed with all columns, at a flow rate of 30 m^3/h.

[0082] Step 4: 3.5 m^3 of feed solution were pumped into the second column at a flow rate of 25 m^3/h and a glucose

fraction was collected from the same column. Simultaneously 4.45 m^3 of water were pumped into the fourth column at a flow rate of 35 m^3/h and fructose fraction was collected from the same column.

[0083] Step 5: 2.85 m^3 of water were pumped into the fourth column at a flow rate of 28 m^3/h and glucose fraction was collected from the second column.

[0084] Step 6: 15.6 m^3 were circulated in the column set loop, formed with all columns, at a flow rate of 30 m^3/h.

[0085] Step 7: 3.5 m^3 of feed solution were pumped into the third column at a flow rate of 25 m^3/h and a glucose fraction was collected from the same column. Simultaneously 4.45 m^3 of water were pumped into the first column at a flow rate of 35 m^3/h and fructose fraction was collected from the same column.

[0086] Step 8: 2.85 m^3 of water were pumped into the first column at a flow rate of 28 m^3/h and glucose fraction was collected from the third column.

[0087] Step 9: 15.6 m^3 were circulated in the column set loop, formed with all columns, at a flow rate of 30 m^3/h.

[0088] Step 10: 3.5 m^3 of feed solution were pumped into the fourth column at a flow rate of 25 m^3/h and a glucose fraction was collected from the same column. Simultaneously 4.45 m^3 of water were pumped into the second column at a flow rate of 35 m^3/h and fructose fraction was collected from the same column.

[0089] Step 11: 2.85 m^3 of water were pumped into the second column at a flow rate of 28 m^3/h and glucose fraction was collected from the fourth column.

[0090] Step 12: 15.6 m^3 were circulated in the column set loop, formed with all columns, at a flow rate of 30 m^3/h.

[0091] After equilibration of the system, the following fractions were drawn from the system: one glucose-enriched fraction from each column and one fructose-enriched fraction from each column. The results including HPLC analyses for the combined fractions are set forth in the table below.

TABLE E1-2

	Fructose	Glucose
Volume, m^3	17.8	25.4
Dry solids, g/100ml	27.3	19.8
Fructose, % on DS	97.5	4.8
Glucose, % on DS	0.8	93.5
Disaccharides A, % on DS	0.4	0.8
Disaccharides B, % on DS	0.3	0.2
Others, % on DS	1.0	0.7

[0092] The overall fructose yield calculated from these fractions was 95.2%.

EXAMPLE 2. CHROMATOGRAPHIC SEPARATION OF ISOMERIZED GLUCOSE WITH CA^{2+}-ION FORM RESIN

[0093] The process equipment included four columns connected in series, feed pump, recycling pumps, eluent water pump, heat exchangers, flow control means for the out-coming liquids as well as inlet and product valves for the various process streams. The height of each column was 4.0 m and each column had a diameter of 0.2 m. The columns were packed with a strong acid gel type cation exchange resin (manufactured by Finex) in Ca^{2+}-form. The divinylbenzene content of the resin was 5.5% and the mean bead size of the resin was 0.36 mm.

[0094] As a feed, an enzymatically isomerized glucose solution (US 4 411 996) was used and the aim was to separate glucose and fructose to different fractions.

[0095] The liquor concentration was 64.2 g/100 ml and the pH was 4.0. The fructose syrup was composed as set forth below, whereby the percentages are given on a dry substance weight basis.

TABLE E2-1

Composition of Feed	
Fructose, % on DS	47.5
Glucose, % on DS	49.5
Disaccharides A, % on DS	1.7
Disaccharides B, % on DS	1.2
Others, % on DS	0.1

[0096] The fractionation was performed by way of a 12-step SMB sequence as set forth below. The feed and the

eluent were used at a temperature of 65°C and water was used as an eluent.

[0097] Step 1: 17.9 l of feed solution were pumped into the first column at a flow rate of 110 l/h and a glucose fraction was collected from the same column. Simultaneously 17.4 l of water were pumped into the third column at a flow rate of 110 l/h and fructose fraction was collected from the same column.

[0098] Step 2: 17.4 l of water were pumped into the third column at a flow rate of 120 l/h and glucose fraction was collected from the first column.

[0099] Step 3: 59.5 l were circulated in the column set loop, formed with all columns, at a flow rate of 125 l/h.

[0100] Step 4: 17.9 l of feed solution were pumped into the second column at a flow rate of 110 l/h and a glucose fraction was collected from the same column. Simultaneously 17.4 l of water were pumped into the fourth column at a flow rate of 110 l/h and fructose fraction was collected from the same column.

[0101] Step 5: 17.4 l of water were pumped into the fourth column at a flow rate of 120 l/h and glucose fraction was collected from the second column.

[0102] Step 6: 59.5 l were circulated in the column set loop, formed with all columns, at a flow rate of 125 l/h.

[0103] Step 7: 17.9 l of feed solution were pumped into the third column at a flow rate of 110 l/h and a glucose fraction was collected from the same column. Simultaneously 17.4 l of water were pumped into the first column at a flow rate of 110 l/h and fructose fraction was collected from the same column.

[0104] Step 8: 17.4 l of water were pumped into the first column at a flow rate of 120 l/h and glucose fraction was collected from the third column.

[0105] Step 9: 59.5 l were circulated in the column set loop, formed with all columns, at a flow rate of 125 l/h.

[0106] Step 10: 17.9 l of feed solution were pumped into the fourth column at a flow rate of 110 l/h and a glucose fraction was collected from the same column. Simultaneously 17.4 l of water were pumped into the second column at a flow rate of 110 l/h and fructose fraction was collected from the same column.

[0107] Step 11: 17.4 l of water were pumped into the second column at a flow rate of 120 l/h and glucose fraction was collected from the fourth column.

[0108] Step 12: 59.5 l were circulated in the column set loop, formed with all columns, at a flow rate of 125 l/h.

[0109] After equilibration of the system, the following fractions were drawn from the system: one glucose-enriched fraction from each column and one fructose-enriched fraction from each column. The results including HPLC analyses for the combined fractions are set forth in the table below.

TABLE E2-2

	Fructose	Glucose
Volume, l	69.6	141.2
Dry solids, g/100ml	29.8	17.9
Fructose, % on DS	97.8	4.7
Glucose, % on DS	0.5	88.7
Disaccharides A, % on DS	0.3	2.6
Disaccharides B, % on DS	0.7	1.5
Others, % on DS	0.7	2.3

The overall fructose yield calculated from these fractions was 94.4%.

EXAMPLE 3. CHROMATOGRAPHIC BATCH SEPARATION OF FRUCTOSE MOTHER LIQUOR WITH NA^+-ION FORM RESIN

[0110] The process equipment included a separation column, feed pump, eluent water pump, heat exchangers, flow control means for the out-coming liquid as well as inlet and product valves for the various process streams. The height of the column was 3.3 m and column had a diameter of 2.76 m. The column was packed with a strong acid gel type cation exchange resin (manufactured by Finex) in Na^+-form. The divinylbenzene content of the resin was 5.5% and the mean bead size of the resin was 0.35 mm.

[0111] As a feed, a fructose crystallization run-off was used and the aim was to separate fructose contained therein

[0112] The liquor concentration was 41.9 g/100 ml and the pH was 4.0. The fructose run-off was composed as set forth below, whereby the percentages are given on a dry substance weight basis.

TABLE E3-1

Composition of Feed	
Fructose, % on DS	92.4
Glucose, % on DS	3.2
Disaccharides A, % on DS	1.6
Disaccharides B, % on DS	2.0
Others, % on DS	0.8

[0113] The feed and the eluent were used at a temperature of 65°C and water was used as the eluent. The feed volume was 2.6 m^3 and the flow rate for the feed and elution was 3.2 m^3/h. Feed interval for the separation was 9.0 m^3.
[0114] After equilibration of the system with several feeds, the following fractions were drawn from the separation column product valves: residual fraction, two recycle fractions (both sides of the fructose peak) and fructose product fraction. The results including HPLC analyses for the residual fraction, combined recycle fractions and the fructose fraction are set forth in the table below.

TABLE E3-2

	Residual	Recycle	Fructose
Volume, m^3	4.67	1.10	3.19
Dry solids, g/100ml	1.6	12.1	29.3
Fructose, % on DS	65.9	86.2	95.5
Glucose, % on DS	13.2	8.8	1.4
Disaccharides A, % on DS	2.1	1.9	0.9
Disaccharides B, % on DS	3.5	2.1	1.0
Others, % on DS	15.3	1.0	1.2

[0115] The overall fructose yield calculated from these fractions was 94.7%. In the fructose product fraction, the glucose content was reduced to 43.8%, the content of disaccharides A to 56.3% and the content of disaccharides B content to 50.0% compared to the content in the feed.

EXAMPLE 4. CHROMATOGRAPHIC BATCH SEPARATION OF FRUCTOSE MOTHER LIQUOR WITH CA^{2+}-ION FORM RESIN

[0116] The process equipment included a separation column, feed pump, eluent water pump, heat exchangers, flow control means for the out-coming liquid as well as inlet and product valves for the various process streams. The height of the column was 3.7 m and column had a diameter of 2.76 m. The column was packed with a strong acid gel type cation exchange resin (manufactured by Finex) in Ca^{2+}-form. The divinylbenzene content of the resin was 5.5% and the mean bead size of the resin was 0.35 mm.
[0117] As a feed, a fructose crystallization run-off was used and the aim was to separate fructose contained therein.
[0118] The liquor concentration was 41.9 g/100 ml and the pH was 4.0. The fructose run-off was composed as set forth below, whereby the percentages are given on a dry substance weight basis.

TABLE E4-1

Composition of Feed	
Fructose, % on DS	92.4
Glucose, % on DS	3.2
Disaccharides A, % on DS	1.6
Disaccharides B, % on DS	2.0
Others, % on DS	0.8

[0119] The feed and the eluent were used at a temperature of 65°C and water was used as the eluent. The feed volume was 2.5 m^3 and the flow rate for the feed and elution was 3.2 m^3/h. Feed interval for the separation was 9.0 m^3.
[0120] After equilibration of the system with several feeds, the following fractions were drawn from the separation

column product valves: residual fraction, two recycle fractions (both sides of the fructose peak) and fructose product fraction. The results including HPLC analyses for the residual fraction, combined recycle fractions and the fructose fraction are set forth in the table below.

TABLE E4-2

	Residual	Recycle	Fructose
Volume, m^3	4.41	1.3	3.24
Dry solids, g/100ml	1.8	12.8	25.2
Fructose, % on DS	52.3	86.5	95.2
Glucose, % on DS	22.1	6.3	0.6
Disaccharides A, % on DS	3.5	2.1	1.2
Disaccharides B, % on DS	10.6	2.5	0.7
Others, % on DS	11.5	2.6	2.3

[0121] The overall fructose yield calculated from these fractions was 94.8%. In the fructose product fraction, the glucose content was reduced to 18.8%, the content of disaccharides A to 75.0% and the content of disaccharides B to 35.0% compared to the content in the feed.

EXAMPLE 5. CHROMATOGRAPHIC SMB SEPARATION OF FRUCTOSE RUN-OFF WITH CA^{2+}-ION FORM RESIN

[0122] The process equipment included two columns connected in series, feed pump, recycling pumps, eluent water pump, heat exchangers, flow control means for the out-coming liquids as well as inlet and product valves for the various process streams. The height of both columns was 4.3 m and both columns had a diameter of 2.76 m. The columns were packed with a strong acid gel type cation exchange resin (manufactured by Finex) in Ca^{2+}-form. The divinylbenzene content of the resin was 5.5% and the mean bead size of the resin was 0.36 mm.

[0123] As a feed, a fructose crystallization run-off was used and the aim was to separate the fructose contained therein.

[0124] The liquor concentration was 65.5 g/100 ml and the pH was 4.0. The fructose crystallization run off was composed as set forth below, whereby the percentages are given on a dry substance weight basis.

TABLE E5-1

Composition of Feed	
Fructose, % on DS	94.3
Glucose, % on DS	2.8
Disaccharides A, % on DS	1.3
Disaccharides B, % on DS	1.5
Others, % on DS	0.1

[0125] The fractionation was performed by way of a 16-step SMB sequence as set forth below. The feed and the eluent were used at a temperature of 65°C and water was used as an eluent.

[0126] Step 1: 1.8 m^3 of feed solution were pumped into the first column at a flow rate of 9 m^3/h and a recycle fraction was collected from the second column.

[0127] Step 2: 0.2 m^3 of feed solution were pumped into the first column at a flow rate of 9 m^3/h and a fructose fraction was collected from the second column.

[0128] Step 3: 4,8 m^3 of feed solution were pumped into the first column at a flow rate of 9,5 m^3/h and a residual fraction was collected from the same column. Simultaneously 12,3 m^3 of water were pumped into the second column at a flow rate of 20 m^3/h and fructose fraction was collected from the same column.

[0129] Step 4: 12.5 m^3 were circulated in the column set loop, formed with all columns, at a flow rate of 12 m^3/h.

[0130] Step 5: 5.7 m^3 of water were pumped into the first column at a flow rate of 12 m^3/h and a residual fraction was collected from the second column.

[0131] Step 6: 12.5 m^3 were circulated in the column set loop, formed with all columns, at a flow rate of 12 m^3/h.

[0132] Step 7: 5.7 m^3 of water were pumped into the second column at a flow rate of 12 m^3/h and a residual fraction was collected from the first column.

[0133] Step 8: 9.4 m^3 were circulated in the column set loop, formed with all columns, at a flow rate of 12 m^3/h.

[0134] Step 9: 1.8 m^3 of feed solution were pumped into the second column at a flow rate of 9 m^3/h and a recycle

fraction was collected from the first column.

[0135] Step 10: 0.2 m^3 of feed solution were pumped into the second column at a flow rate of 9 m^3/h and a fructose fraction was collected from the first column.

[0136] Step 11: 4.8 m^3 of feed solution were pumped into the second column at a flow rate of 9.5 m^3/h and a residual fraction was collected from the same column. Simultaneously 12.3 m^3 of water were pumped into the first column at a flow rate of 20 m^3/h and fructose fraction was collected from the same column.

[0137] Step 12: 12.5 m^3 were circulated in the column set loop, formed with all columns, at a flow rate of 12 m^3/h.

[0138] Step 13: 5.7 m^3 of water were pumped into the second column at a flow rate of 12 m^3/h and a residual fraction was collected from the first column.

[0139] Step 14: 12.5 m^3 were circulated in the column set loop, formed with all columns, at a flow rate of 12 m^3/h.

[0140] Step 15: 5.7 m^3 of water were pumped into the first column at a flow rate of 12 m^3/h and a residual fraction was collected from the second column.

[0141] Step 16: 9.4 m^3 were circulated in the column set loop, formed with all columns, at a flow rate of 12 m^3/h.

[0142] After equilibration of the system, the following fractions were drawn from the system: three residual fractions from both columns, one fructose-containing fraction and one recycle fraction from both columns. The results including HPLC analyses for combined fractions are set forth in the table below.

TABLE E5-2

	Fructose	Residual	Recycle
Volume, m^3	25.0	32.4	3.6
Dry solids, g/100ml	28.3	2.2	37.0
Fructose, % on DS	97.8	45.5	96.7
Glucose, % on DS	0.5	24.7	1.4
Disaccharides A, % on DS	1.1	3.2	1.0
Disaccharides B, % on DS	0.6	9.0	0.9
Others, % on DS	0.0	17.6	0.0

[0143] The overall fructose yield calculated from these fractions was 95.5%. In the fructose product fraction, the glucose content was reduced to 17.9%, the content of disaccharides A to 84.6% and the content of disaccharides B to 40.0% compared to the content in the feed.

EXAMPLE 6. CHROMATOGRAPHIC SMB SEPARATION OF FRUCTOSE RUN-OFF WITH NA^+-ION FORM RESIN

[0144] The process equipment included two columns connected in series, feed pump, recycling pumps, eluent water pump, heat exchangers, flow control means for the out-coming liquids as well as inlet and product valves for the various process streams. The height of both columns was 3.95 m and both columns had a diameter of 0.2 m. The columns were packed with a strong acid gel type cation exchange resin (manufactured by Finex) in Na^+-form. The divinylbenzene content of the resin was 5.5% and the mean bead size of the resin was 0.36 mm.

[0145] As a feed, a fructose crystallization run-off was used and the aim was to separate the fructose contained therein.

[0146] The liquor concentration was 66.1 g/100 ml and the pH was 3.8. The fructose crystallization run-off was composed as set forth below, whereby the percentages are given on a dry substance weight basis.

TABLE E6-1

Composition of Feed	
Fructose, % on DS	92.0
Glucose, % on DS	2.7
Disaccharides A, % on DS	1.9
Disaccharides B, % on DS	1.7
Others, % on DS	1.7

[0147] The fractionation was performed by way of a 14-step SMB sequence as set forth below. The feed and the eluent were used at a temperature of 65°C and water was used as an eluent.

[0148] Step 1: 13 l of feed solution were pumped into the first column at a flow rate of 90 l/h and a recycle fraction was collected from the second column.

[0149] Step 2: 22 l of feed solution were pumped into the first column at a flow rate of 90 l/h and a residual fraction was collected from the same column. Simultaneously 47 l of water were pumped into the second column at a flow rate of 190 l/h and fructose fraction was collected from the same column.

[0150] Step 3: 54 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0151] Step 4: 28 l of water were pumped into the first column at a flow rate of 90 l/h and a residual fraction was collected from the second column.

[0152] Step 5: 57 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0153] Step 6: 25 l of water were pumped into the second column at a flow rate of 90 l/h and a residual fraction was collected from the first column.

[0154] Step 7: 44 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0155] Step 8: 13 l of feed solution were pumped into the second column at a flow rate of 90 l/h and a recycle fraction was collected from the first column.

[0156] Step 9: 22 l of feed solution were pumped into the second column at a flow rate of 90 l/h and a residual fraction was collected from the same column. Simultaneously 47 l of water were pumped into the first column at a flow rate of 190 l/h and fructose fraction was collected from the same column.

[0157] Step 10: 54 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0158] Step 11: 28 l of water were pumped into the second column at a flow rate of 90 l/h and a residual fraction was collected from the first column.

[0159] Step 12: 57 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0160] Step 13: 25 l of water were pumped into the first column at a flow rate of 90 l/h and a residual fraction was collected from the second column.

[0161] Step 14: 44 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0162] After equilibration of the system, the following fractions were drawn from the system: three residual fractions from both columns, one fructose-containing fraction and one recycle fraction from both columns. The results including HPLC analyses for combined fractions are set forth in the table below.

TABLE E6-2

	Fructose	Residual	Recycle
Volume, l	94.0	150.0	26.0
Dry solids, g/100ml	38.8	1.7	28.2
Fructose, % on DS	94.9	55.4	91.3
Glucose, % on DS	1.3	19.6	3.9
Disaccharides A, % on DS	0.6	8.7	1.5
Disaccharides B, % on DS	0.7	8.7	1.3
Others, % on DS	2.5	7.6	2.0
PH	4.5	4.4	4.7

[0163] The overall fructose yield calculated from these fractions was 96.1%. In the fructose product fraction, the glucose content was reduced to 48.1%, the content of disaccharides A to 36.1% and the content of disaccharides B to 41.2% compared to the content in the feed.

EXAMPLE 7. CHROMATOGRAPHIC SMB SEPARATION OF FRUCTOSE RUN-OFF WITH A WEAKLY ACID CATION EXCHANGE RESIN

[0164] The process equipment included two columns connected in series, feed pump, recycling pumps, eluent water pump, heat exchangers, flow control means for the out-coming liquids as well as inlet and product valves for the various process streams. The height of both columns was 3.9 m and both columns had a diameter of 0.2 m. The columns were packed with a weakly acid gel type cation exchange resin (manufactured by Finex). The divinylbenzene content of the resin was 8% and the mean bead size of the resin was 0.31 mm. The resin was balanced to pH 4.5 with 5-% Na-acetate solution and HCl by circulating solution through the resin bed until the outflow pH was 4.5.

[0165] As a feed, fructose crystallization run-off was used and the aim was to separate the fructose contained therein.

[0166] The liquor concentration was 68.1 g/100ml and the pH was 3.9. The fructose crystallization run-off was composed as set forth below, whereby the percentages are given on a dry substance weight basis.

TABLE E7-1

Composition of Feed	
Fructose, % on DS	90.3
Glucose, % on DS	2.5
Disaccharides A, % on DS	1.6
Disaccharides B, % on DS	2.0
Others, % on DS	3.6

[0167] The fractionation was performed by way of a 16-step SMB sequence as set forth below. The feed and the eluent were used at a temperature of 65°C and water was used as an eluent.

[0168] Step1: 8 l of feed solution were pumped into the first column at a flow rate of 90 l/h and a recycle fraction was collected from the second column.

[0169] Step 2: 22 l of feed solution were pumped into the first column at a flow rate of 90 l/h and a residual fraction was collected from the same column. Simultaneously 37 l of water were pumped into the second column at a flow rate of 143 l/h and first 3 l of recycle fraction and then 34 l of fructose fraction were collected from the same column.

[0170] Step 3: 5 l of feed solution were pumped into the first column at a flow rate of 90 l/h and a fructose fraction was collected from the second column.

[0171] Step 4: 50 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0172] Step 5: 24 l of water were pumped into the first column at a flow rate of 90 l/h and a residual fraction was collected from the second column.

[0173] Step 6: 55 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0174] Step 7: 24 l of water were pumped into the second column at a flow rate of 90 l/h and a residual fraction was collected from the first column.

[0175] Step 8: 48 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0176] Step 9: 8 l of feed solution were pumped into the second column at a flow rate of 90 l/h and a recycle fraction was collected from the first column.

[0177] Step 10: 22 l of feed solution were pumped into the second column at a flow rate of 90 l/h and a residual fraction was collected from the same column. Simultaneously 37 l of water were pumped into the first column at a flow rate of 143 l/h and first 3 l of recycle fraction and the 34 l of fructose fraction were collected from the same column.

[0178] Step 11: 5 l of feed solution were pumped into the second column at a flow rate of 90 l/h and a fructose fraction was collected from the first column.

[0179] Step 12: 50 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0180] Step 13: 24 l of water were pumped into the second column at a flow rate of 90 l/h and a residual fraction was collected from the first column.

[0181] Step 14: 55 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0182] Step 15: 24 l of water were pumped into the first column at a flow rate of 90 l/h and a residual fraction was collected from the second column.

[0183] Step 16: 48 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0184] After equilibration of the system, the following fractions were drawn from the system: three residual fractions from both columns, one fructose-containing fraction and one recycle fraction from both columns. The results including HPLC analyses for combined fractions are set forth in the table below.

TABLE E7-2

	Fructose	Residual	Recycle
Volume, l	78.0	140.0	22.0
Dry solids, g/100ml	43.1	2.6	41.2
Fructose, % on DS	94.6	53.8	91.5
Glucose, % on DS	1.2	14.1	2.9
Disaccharides A, % on DS	0.5	7.4	1.5
Disaccharides B, % on DS	0.5	8.0	1.6
Others, % on DS	3.2	16.7	2.5
pH	3.6	3.8	3.7

[0185] The overall fructose yield calculated from these fractions was 94.2%. In the fructose product fraction, the glucose

content was reduced to 48.0%, the content of disaccharides A to 31.3% and the content of disaccharides B to 25.0% compared to the content in the feed.

EXAMPLE 8. CHROMATOGRAPHIC SMB SEPARATION OF FRUCTOSE RUN-OFF WITH NA^+ AND CA^{2+}-ION FORM RESINS

[0186] The process equipment included two columns connected in series, feed pump, recycling pumps, eluent water pump, heat exchangers, flow control means for the out-coming liquids as well as inlet and product valves for the various process streams. The height of both columns was 3.95 m and both columns had a diameter of 0.2 m. The columns were packed with a strong acid gel type cation exchange resin (manufactured by Finex) and first column was in Na^+-ion form and second column in Ca^{2+}-ion form. The divinylbenzene content of the resin was 5.5% and the mean bead size of the resin was 0.36 mm.

[0187] As a feed, a fructose crystallization run-off was used and the aim was to separate the fructose contained therein.

[0188] The liquor concentration was 66.1 g/100 ml and the pH was 3.8. The fructose crystallization run-off was composed as set forth below, whereby the percentages are given on a dry substance weight basis.

TABLE E8-1

Composition of Feed	
Fructose, % on DS	91.6
Glucose, % on DS	2.7
Disaccharides A, % on DS	2.0
Disaccharides B, % on DS	1.8
Others, % on DS	1.9

[0189] The fractionation was performed by way of a 14-step SMB sequence as set forth below. The feed and the eluent were used at a temperature of 65°C and water was used as an eluent.

[0190] Step 1: 10 l of feed solution were pumped into the first column at a flow rate of 90 l/h and a recycle fraction was collected from the second column.

[0191] Step 2: 25 l of feed solution were pumped into the first column at a flow rate of 90 l/h and a residual fraction was collected from the same column. Simultaneously 45 l of water were pumped into the second column at a flow rate of 190 l/h and fructose fraction was collected from the same column.

[0192] Step 3: 58 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0193] Step 4: 30.5 l of water were pumped into the first column at a flow rate of 90 l/h and a residual fraction was collected from the second column.

[0194] Step 5: 55 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0195] Step 6: 27.5 l of water were pumped into the second column at a flow rate of 90 l/h and a residual fraction was collected from the first column.

[0196] Step 7: 48 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0197] Step 8: 13 l of feed solution were pumped into the second column at a flow rate of 90 l/h and a recycle fraction was collected from the first column.

[0198] Step 9: 22 l of feed solution were pumped into the second column at a flow rate of 90 l/h and a residual fraction was collected from the same column. Simultaneously 45 l of water were pumped into the first column at a flow rate of 190 l/h and fructose fraction was collected from the same column.

[0199] Step 10: 55 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0200] Step 11: 28 l of water were pumped into the second column at a flow rate of 90 l/h and a residual fraction was collected from the first column.

[0201] Step 12: 58 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0202] Step 13: 30.5 l of water were pumped into the first column at a flow rate of 90 l/h and a residual fraction was collected from the second column.

[0203] Step 14: 49 l were circulated in the column set loop, formed with all columns, at a flow rate of 90 l/h.

[0204] After equilibration of the system, the following fractions were drawn from the system: three residual fractions from both columns, one fructose containing fraction and one recycle fraction from both columns. The result including HPLC analyses for combined fractions are set forth in the table below.

TABLE E8-2

	Fructose	Residual	Recycle
Volume, l	90.0	163.5	23.0
Dry solids, g/100ml	39.8	1.9	34.7
Fructose, % on DS	96.3	48.8	93.2
Glucose, % on DS	0.6	30.0	2.3
Disaccharides A, % on DS	1.1	3.6	1.7
Disaccharides B, % on DS	0.7	7.9	1.4
Others, % on DS	1.3	9.7	1.4
pH	4.1	4.3	4.2

[0205] The overall fructose yield calculated from these fractions was 95.8%. The dry substance yield to the residue fraction was 6.6%. In the fructose product fraction, the glucose content was reduced to 22.2%, the content of disaccharides A to 55.0% and the content of disaccharides B to 38.9% compared to the content in the feed.

EXAMPLE 9. CRYSTALLIZATION OF FRUCTOSE FROM A PRODUCT FRACTION MIXTURE OBTAINED FROM CA^{2+}-ION FORM INVERT SEPARATION OF EXAMPLE 1 AND CA^{2+}-ION FORM ISOMEROSE SEPARATION OF EXAMPLE 2

[0206] Approximately 18.1 tn of crystalline fructose was recovered in 36.4 hours from a fructose feed liquid containing 97.2% fructose, 0.8% glucose and 1.3% disaccharides on DS. The crystallization was performed in a cylindrical cooling crystallizer (30 m^3).

[0207] Seed crystal magma was prepared in 10 m^3 cooling crystallizer by filling the crystallizer with evaporated 90.5% w/w feed liquid, seeding at 57.1°C temperature by adding 1.5 kg seed crystals and cooling the suspension to 40.4°C in 32 hours. The average size of the seed crystals was about 0.03 mm and 90% of the crystals were between 0.02-0.08 mm as analyzed by a PMT-PAMAS particle analyzing system.

[0208] About 9 m^3 of the seed crystal magma, which had a mean crystal size about 0.2 mm, was placed in the 30 m^3 cooling crystallizer. Next about 92 w/w % fructose syrup was added to the crystallizer and mixed with the seed magma. When the crystallizer was filled, the temperature of the mass in the crystallizer was adjusted to 56°C and a total concentration of 91.2% w/w was measured. A crystal yield of about 5-10% of dry substance was obtained. The mass was then cooled to 24.3°C over 26 hours. After cooling, the crystals were separated and washed by a conventional centrifuge, dried in a drum drier, sieved and packed. The fructose yield after cooling was about 58% of the dry substance. The product yield was about 44.5% of dry substance (45.7% of fructose), with a mean crystal size of 0.53 mm and purity of 99.9%.

EXAMPLE 10. CRYSTALLIZATION OF FRUCTOSE FROM A PRODUCT FRACTION OBTAINED FROM CA^{2+}/NA^{+} -ION FORM FRUCTOSE MOTHER LIQUOR SEPARATION OF EXAMPLE 8

[0209] Approximately 17.5 tn of crystalline fructose was recovered in 45.8 hours from the fructose feed liquid containing 96.7% fructose, 0.5% glucose and 1.9% disaccharides on DS. The crystallization was performed in a 30 m^3 cylindrical cooling crystallizer.

[0210] Seed crystal magma was prepared in a 10 m^3 cooling crystallizer by filling the crystallizer with evaporated 91.0% w/w feed liquid, seeding at 58.1°C temperature by adding 1.5 kg seed crystals and cooling the suspension to 42.2°C in 39 hours. About 9 m^3 of the seed crystal magma, which had a mean crystal size about 0.2 mm, was placed in the 30 m^3 cooling crystallizer. Next about 92 w/w % fructose syrup was added to the crystallizer and mixed with the seed magma. When the crystallizer was filled, the temperature of the mass in the crystallizer was adjusted to 56°C and a total concentration of 91.8% w/w was measured. The mass was then cooled to 30.0°C over 36 hours. After cooling, the crystals were separated and washed by a conventional centrifuge, dried in a drum drier, sieved and packed. The fructose yield after cooling was about 57% of the dry substance. The product yield was about 43.2% of dry substance with a mean crystal size of 0.51 mm and a purity of 99.9%.

EXAMPLE 11. CRYSTALLIZATION OF FRUCTOSE FROM A PRODUCT FRACTION MIXTURE OBTAINED FROM CRYSTALLIZATION RUN-OFF OF EXAMPLE 9 AND CA^{2+}/NA^{+} -ION FORM FRUCTOSE MOTHER LIQUOR SEPARATION OF EXAMPLE 8

[0211] Approximately 16.8 tn of crystalline fructose was recovered in 54.1 hours from a fructose feed liquid containing 96.0% fructose, 1.0% glucose and 2.1% disaccharides on DS. The crystallization was performed in a 30 m^3 cylindrical cooling crystallizer.

[0212] Seed crystal magma was prepared in 10 m^3 cooling crystallizer by filling the crystallizer with evaporated 90.5% w/w feed liquid, seeding at 56.2°C temperature by adding 1.0 kg seed crystals and cooling the suspension to 38.6°C in 47 hours. About 9 m^3 of the seed crystal magma, which had a mean crystal size about 0.2 mm, was placed in the 30 m^3 cooling crystallizer. Next about 92 w/w % fructose syrup was added to the crystallizer and mixed with the seed magma. When the crystallizer was filled, the temperature of the mass in the crystallizer was adjusted to 56°C and a total concentration of 91.7% w/w was measured. The mass was then cooled to 26.5°C over 44 hours. After cooling, the crystals were separated and washed by a conventional centrifuge, dried in a drum drier, sieved and packed. The fructose yield after cooling was about 53% of the dry substance. The product yield was about 41.4% of dry substance with a mean crystal size of 0.52 mm and a purity of 99.7%.

EXAMPLE 12. CRYSTALLIZATION OF FRUCTOSE FROM A PRODUCT FRACTION MIXTURE OBTAINED FROM CA^{2+} -ION FORM INVERT SEPARATION OF EXAMPLE 1, CA^{2+} -ION FORM ISOMEROSE SEPARATION OF EXAMPLE 2 AND CA^{2+} -ION FORM FRUCTOSE MOTHER LIQUOR SEPARATION OF EXAMPLE 5

[0213] Approximately 17.7 tn of crystalline fructose was recovered in 41.4 hours from a fructose feed liquid containing 97.2% fructose, 0.5% glucose and 1.7% disaccharides on DS. The crystallization was performed in a 30 m^3 cylindrical cooling crystallizer.

[0214] Seed crystal magma was prepared in 10 m^3 cooling crystallizer by filling the crystallizer with evaporated 91.0% w/w feed liquid, seeding at 58.6°C temperature by adding 1.5 kg seed crystals and cooling the suspension to 40.4°C in 39 hours. About 9 m^3 of the seed crystal magma, which had a mean crystal size about 0.2 mm, was placed in the 30 m^3 cooling crystallizer. Next about 92 w/w % fructose syrup was added to the crystallizer and mixed with the seed magma. When the crystallizer was filled, the temperature of the mass in the crystallizer was adjusted to 56°C and a total concentration of 91.6% w/w was measured. The mass was then cooled to 28.2°C over 31 hours. After cooling, the crystals were separated and washed by a conventional centrifuge, dried in a drum drier, sieved and packed. The fructose yield after cooling was about 58% of the dry substance. The product yield was about 43.5% of dry substance with a mean crystal size of 0.45 mm and a purity of 99.8%.

EXAMPLE 13. PRODUCTION OF CRYSTALLINE FRUCTOSE WITH ONE CRYSTALLIZATION STEP (YIELD 46.7%)

[0215] Crystalline sucrose (57.0 tn/d) is first dissolved and inverted enzymatically (EP 553 126). Inverted sucrose dry substance is adjusted and invert separation is performed with Ca^{2+} -ion form strongly acidic cation exchange resin as descript in the example 1. Glucose fraction is evaporated and subjected to the isomerization (US 4 411996) and further to the isomerose separation. Isomerose separation is performed with Ca^{2+} -ion form strongly acidic cation exchange resin as described in Example 2. Glucose fractions from the invert and isomerose separation are combined, evaporated and subjected back to the enzymatic isomerization and further to the isomerose separation. Fructose fractions from both separations are combined, evaporated and subjected to the crystallization. Purity for the combined fraction is 97.2% on dry solids and amount 59.9 tn/d.

[0216] Fructose is crystallized (feed purity 97.2% and the mass amount of 59.9 tn/d) with 45.7% fructose yield as described in Example 9. Total fructose process yield calculated from sucrose is 46.7% and the fructose yield calculated from fructose entering the crystallization (fructose in the crystallization feed) is 45.9%. Production volume for fructose is 26.7 tn/d. In this option total mass amount to be crystallized is 59.9 tn/d and no mother liquor separation is used.

EXAMPLE 14. PRODUCTION OF CRYSTALLINE FRUCTOSE WITH FIRST CRYSTALLIZATION STEP, CA^{2+}/NA^{+} -ION FORM MOTHER LIQUOR SEPARATION AND SECOND CRYSTALLIZATION STEP (YIELD 70.8%)

[0217] Crystalline sucrose (57.0 tn/d) is first dissolved and inverted enzymatically (EP 553 126). Inverted sucrose dry substance is adjusted and invert separation is performed with Ca^{2+} -ion form strongly acidic cation exchange resin as described in Example 1. Glucose fraction is evaporated and subjected to the isomerization (US 4 411 996) and further to the isomerose separation. Isomerose separation is performed with Ca^{2+} -ion form strongly acidic cation exchange resin as described in Example 2. Glucose fractions from the invert and isomerose separation are combined, evaporated and subjected back to the enzymatic isomerization and further to the isomerose separation. Fructose fractions from both

separations are combined, evaporated and subjected to the crystallization. Purity for the combined fraction is 97.2% on dry solids and the amount 59.9 tn/d.

[0218] Fructose is crystallized (feed purity 97.2% and the mass amount 59.9 tn/d) with 45.7% fructose yield as described in Example 9. Mother liquor (amount 33.2 tn/d) is subjected to the chromatographic separation using Na^+ and Ca^{2+} resins and fractionated with 94% fructose yield as described in example 8. Fructose fraction from the mother liquor separation (amount 30,4 tn/d) is crystallized (feed purity 97.7% and mass amount 30.4 tn/d) with 46% fructose yield. Total fructose process yield calculated from sucrose is 70.8% and the fructose yield calculated from fructose in the crystallization feed is 69.4%. Production volume is 40.4 tn/d. In this option mother liquor amount to be separated is 33.2 tn/d and the total mass amount to be crystallized is 90.3 tn/d.

EXAMPLE 15. PRODUCTION OF CRYSTALLINE FRUCTOSE WITH FIRST CRYSTALLIZATION STEP, CA^{2+}/NA^+ -ION FORM MOTHER LIQUOR SEPARATION AND SECOND CRYSTALLIZATION STEP FROM WHERE THE MOTHER LIQUOR IS SUBJECTED BACK TO THE MOTHER LIQUOR SEPARATION (YIELD 95.5%)

[0219] Crystalline sucrose (57.0 tn/d) is first dissolved and inverted enzymatically (EP 553 126). Inverted sucrose dry substance is adjusted and invert separation is performed with Ca^{2+} -ion form strongly acidic cation exchange resin as described in Example 1. Glucose fraction is evaporated and subjected to the isomerization (US 4 411996) and further to the isomerose separation. Isomerose separation is performed with Ca^{2+} -ion form strongly acidic cation exchange resin as described in Example 2. Glucose fractions from the invert and isomerose separation are combined, evaporated and subjected back to the enzymatic isomerization and further to the isomerose separation. Fructose fractions from both separations are combined, evaporated and subjected to the crystallization. Purity for the combined fraction is 97.2% on dry solids and amount 59.9 tn/d.

[0220] Fructose is crystallized (feed purity 97.2% and mass amount 59.9 tn/d) with 45.7% fructose yield as described in Example 9. Mother liquor (amount 33.2 tn/d) is subjected to the chromatographic separation using Na^+ and Ca^{2+} resins and fractionated with 94% fructose yield as described in Example 8. Fructose fraction (61.7 tn/d) from the mother liquor separation is crystallized (feed purity 97.9% and the mass amount 61.7 tn/d) with 46% fructose yield and second crystallization mother liquor (amount 33.9 tn/d) is also subjected back to the mother liquor separation. Total fructose process yield calculated from sucrose is 95.5% and the fructose yield calculated from fructose in the crystallization feed is 93.6%. Production volume is 54.5 tn/d. In this option the mother liquor amount to be separated is 67.1 tn/d and total mass amount to be crystallized is 121.6 tn/d.

EXAMPLE 16. PRODUCTION OF CRYSTALLINE FRUCTOSE WITH FIRST CRYSTALLIZATION STEP, SECOND CRYSTALLIZATION STEP AND USING CA^{2+} AND NA^+ -ION FORM MOTHER LIQUOR SEPARATION FROM WHERE THE FRUCTOSE FRACTION IS SUBJECTED BACK TO SECOND CRYSTALLIZATION (YIELD 98.3%).

[0221] Crystalline sucrose (57.0 tn/d) is first dissolved and inverted enzymatically (EP 553 126). Dry substance of the the inverted sucrose solution is adjusted and the separation is performed using Ca^{2+} -ion form strongly acidic cation exchange resin bed as described in Example 1. Glucose fraction is evaporated and subjected to the isomerization (US 4 411 996) and further to the isomerose separation. Isomerose separation is performed using a Ca^{2+} -ion form strongly acidic cation exchange resin bed as described in Example 2. Glucose fractions from the invert and isomerose separation are combined, evaporated and subjected back to the enzymatic isomerization and further to the isomerose separation. Fructose fractions from both separations are combined, evaporated and subjected to the crystallization. Purity for the combined fructose fraction is 97.2% on dry solids and the amount 59.9 tn/d.

[0222] Fructose is crystallized (feed purity 97.2% and mass amount 59.9 tn/d) with 45.7% fructose yield as described in Example 9. Mother liquor (amount 33.2 tn/d) is subjected to the second crystallization step and 43% fructose yield (feed purity 96.0% and mass amount 71 tn/d) is obtained like described in Example 11. Mother liquor (purity 93.4% and amount 41.6 tn/d) from the second crystallization step is subjected to the chromatographic separation using Na^+ and Ca^{2+} resin beds like described in Examples 5, 6 and 8. Fructose fractions from the mother liquor separation are combined (purity 96.7% and amount 37.8 tn/d) and subjected back to the second crystallization step. Total fructose process yield calculated from sucrose is 98.3% and the fructose yield calculated from fructose in the crystallization feed is 96.4%. Production volume is 56.1 tn/d. In this option mother liquor (=run-off) amount to be separated is 41.6 tn/d and total mass amount to be crystallized is 130.9 tn/d.

[0223] The results of Example 16 show that a very high yield of crystalline fructose (98.3% on the basis of sucrose) is achieved by introducing a reasonably low amount of fructose mother liquor (41.6 tn/d) from the second crystallization step to chromatographic fractionation using a combination of Na^+ and Ca^{2+} resins. Consequently, the chromatographic fractionation improves the crystallization.

EXAMPLE 17. PRODUCTION OF CRYSTALLINE FRUCTOSE WITH ONE CRYSTALLIZATION STEP, CA^{2+} -ION FORM MOTHER LIQUOR SEPARATION AND MOTHER LIQUOR SEPARATION FRUCTOSE FRACTION SUBJECTED BACK TO CRYSTALLIZATION (YIELD 95.2%) (REFERENCE EXAMPLE)

[0224] Crystalline sucrose (57.0 tn/d) is first dissolved and inverted enzymatically (EP 553 126). Inverted sucrose dry substance is adjusted and invert separation is performed with Ca^{2+} -ion form strongly acidic cation exchange resin as described in Example 1. Glucose fraction is evaporated and subjected to the isomerization (US 4 411 996) and further to the isomerose separation. Isomerose separation is performed with Ca^{2+} -ion form strongly acidic cation exchange resin as described in Example 2. Glucose fractions from the invert and isomerose separation are combined, evaporated and subjected back to the enzymatic isomerization and further to the isomerose separation. Fructose fractions from both separations are combined, evaporated and subjected to the crystallization. Purity for the combined fraction is 97.2% on dry solids and the amount 59.9 tn/d.

[0225] Fructose is crystallized (feed purity 97.2% and the mass amount 124.8 tn/d) with 44.7% fructose yield as described in Example 12 and mother liquor (amount 70.4 tn/d) is subjected to the chromatographic separation using Ca^{2+} resin with 94% fructose yield as described in Example 5. Fructose fraction from the mother liquor separation (purity 97.2% and the amount 64.9 tn/d) is subjected back to crystallization. Total fructose process yield calculated from sucrose is 95.2% and the fructose yield calculated from fructose in the crystallization feed is 93.3%. Production volume is 54.3 tn/d. In this option the mother liquor amount to be separated is 70.4 tn/d and the total mass amount to be crystallized is 124.8 tn/d.

[0226] In this example (separation with Ca^{2+} form resin), a high fructose process yield is achieved, but a large amount of mother liquor (70.4 tn/d) must be subjected the chromatographic separation to ensure a high purity of the crystallization mass and a relatively good crystallization yield.

[0227] For comparison purposes, the process of this example was modified by using a Na^{+} form resin and the Ca^{2+} form resin in the chromatographic separation in consecutive beds (columns) and by returning 50% of the mother liquor from the crystallization directly to the same crystallization step (with a the feed purity of 96.0% and a mass amount of 135.7 tn/d). In this process modification, the need for the mother liquor separation (the amount of the mother liquor to be introduced into the chromatographic separation) can be reduced significantly (to an amount of 39.7 tn/d with a purity of 93.4%), while a relatively high crystallization yield (fructose yield of 43%) is still maintained and the total process yield was improved (the total fructose process yield from sucrose was 98.5% and the fructose yield from fructose in the crystallization feed was 96.5%.

[0228] It will be obvious to a person skilled in the art that, as the technology advances, the inventive concept can be implemented in various ways. The invention and its embodiments are not limited to the examples described above but may vary within the scope of the claims.

Claims

1. A process of producing crystalline fructose with improved yield, charact**e**rized in that it comprises:

   one or more crystallization steps for producing crystalline fructose and one or more fructose crystallization run-offs, which contain 88 to 96% fructose, 2 to 5% disaccharides and 1 to 8% glucose on DS, whereby said disaccharides comprise fructose dimers,
   chromatographic fractionation of at least part of said one or more fructose crystallization run-offs in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to produce a fructose fraction depleted in fructose dimers and optionally at least one other fraction, and
   introduction of said fructose fraction to at least one of said one or more crystallization steps for the production of crystalline fructose.

2. A process as claimed in claim 1, **characterized in that** the fructose fraction obtained from the chromatographic fractionation contains 94 to 98% fructose, less than 3%, preferably less than 2% fructose dimers and less than 1.5%, preferably less than 1.0% glucose on DS.

3. A process as claimed in claim 1, **characterized in that** said fructose dimers are selected from disaccharides A and/or disaccharides B.

4. A process as claimed in claim 1, **characterized in that** fructose dimers comprise difructose dianhydrides.

5. A process as claimed in claim 1, **characterized in that** said at least one other fraction is a residue fraction enriched in fructose dimers.

6. A process as claimed in claim 1 and 5, **characterized** that a fructose fraction depleted in fructose dimers and a residue fraction enriched in fructose dimers are obtained.

7. A process as claimed in claim 4, **characterized in that** said the fructose fraction comprises less than 1.5%, preferably less than 1.0% disaccharides A and less than 1.5%, preferably less than 0.8% disaccharides B on DS.

8. A process as claimed in claim 1, **characterized in that** the chromatographic fractionation provides a fructose yield of more than 80%, preferably more than 90% and more preferably more than 95% based on fructose in the fructose crystallization run-off used as the feed in the chromatographic fractionation.

9. A process as claimed in claim 1, **characterized in that** said monovalent cation is selected from Na^+ and K^+.

10. A process as claimed in claim 1, **characterized in that** said cation exchange resins in the separation system are strongly acid cation exchange resins.

11. A process as claimed in claim 1, **characterized in that** at least 20% of the total length of the resin beds of the separation system is in a Ca^{2+} form.

12. A process as claimed in claim 1, **characterized in that** at least 20% of the total length of the resin beds of the separation system is in a monovalent cation form.

13. A process as claimed in claim 1, **characterized in that** the fructose crystallization run-off used as the feed in the chromatographic fractionation contains disaccharides in an amount of less than 2% on DS and glucose in a amount of more than 3% on DS, whereby 60 to 80% of the total length of the resin bed of the separation system is in Ca^{2+} form.

14. A process as claimed in claim 1, **characterized in that** the fructose crystallization run-off used as the feed in the chromatographic fractionation contains disaccharides in an amount of more than 3% on DS and glucose in an amount of less than 2% on DS, whereby 60 to 80% of the total length of the resin beds of the separation system is in a monovalent cation form.

15. A process as claimed in claim 1, **characterized in that** said two or more cation exchange resin beds in a monovalent cation form comprise a weakly acid cation exchange resin.

16. A process as claimed in claim 15, **characterized in that** said weakly acid cation exchange resin is in a free acid form.

17. A process as claimed in claim 1, **characterized in that** said two or more cation exchange resin beds are arranged in series or in parallel.

18. A process as claimed in claim 1, **characterized in that** said chromatographic fractionation is carried out with a batch process or a simulated moving bed process.

19. A process as claimed in claim 18, **characterized in that** said simulated moving bed process is continuous or sequential.

20. A proces as claimed in claim 1, **characterized in that** the chromatographic fractionation is carried out at a pH of 3 to 6, preferably at a pH in the range of 4 to 5.

21. A process as claimed in claim 1, **characterized in that** said fructose fraction to be introduced into the crystallization has a fructose purity of more than 93%, preferably more than 95% and more preferably more than 97%, based on dissolved dry substance.

22. A process as claimed in claim 1, **characterized** the process provides an overall crystallization yield of crystalline fructose of more than 90%, preferably more than 93% and most preferably more than 95%, based on the fructose in the crystallization feed.

23. A process as claimed in claim 1, **characterized in that** the chromatographic fractionation provides a fructose yield of more than 90%, preferably more than 95% based on fructose in the fructose crystallization run-off used as the feed in the chromatographic fractionation and that the process provides an overall yield of crystalline fructose of more than 90% and preferably more than 95% based on fructose in the crystallization feed.

24. A process as claimed in claim 1, **characterized by** the following steps:

chromatographic fractionation of at least part of said one or more fructose crystallization run-offs in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to produce a fructose fraction depleted in fructose dimers,
introducing said fructose fraction to crystallization to obtain crystalline fructose and a further crystallization run-off, and
returning at least part of said further crystallization run-off to the chromatographic fractionation.

25. A process as claimed in claim 1, **characterized by** the following steps:

crystallization of a fructose crystallization run-off to obtain crystalline fructose and a further crystallization run-off, which contains 88 to 96% fructose, 2 to 5% disaccharides and 1 to 8% glucose on DS, whereby said disaccharides comprise fructose dimers,
chromatographic fractionation of at least part of said further crystallization run-off in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to produce a fructose fraction depleted in fructose dimers,
returning said fructose fraction to the crystallization.

26. A process as claimed in claim 1, **characterized in that** the process also comprises, as a preceding step, chromatographic fractionation of a solution containing glucose and fructose to obtain a glucose fraction and a fructose fraction for producing crystalline fructose.

27. A process as claimed in claim 26, **characterized in that** the solution containing glucose and fructose is selected from inverted sucrose and isomerized glucose.

28. A process as claimed in claim 26, **characterized in that** the process also comprises
subjecting the glucose fraction to isomerization to obtain a solution containing glucose and fructose, and
returning the solution containing glucose and fructose to chromatographic fractionation.

29. A process as claimed in claim 26, **characterized in that** it comprises the following steps:

(a) providing a solution containing glucose and fructose,
(b) subjecting the solution containing glucose and fructose to chromatographic fractionation to obtain a glucose fraction and a fructose fraction,
(c) subjecting the fructose fraction to crystallization to obtain crystalline fructose and a fructose crystallization run-off, which contains 88 to 96% fructose, 2 to 5% disaccharides and 1 to 8% glucose on DS, whereby said disaccharides comprise fructose dimers.
(d) subjecting at least part of the fructose crystallization run-off to chromatographic fractionation in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in a monovalent cation form, to obtain a further fructose fraction depleted in fructose dimers,
(e) introducing said further fructose fraction to crystallization to obtain further crystalline fructose and a further crystallization run-off, which contains 88 to 96% fructose, 2 to 5% disaccharides and 1 to 8% glucose on DS, whereby said disaccharides comprise fructose dimers, and
(f) returning at least part of said further crystallization run-off to the chromatographic fractionation of step (d).

30. A process as claimed in claim 26, **characterized in that** it comprises the following steps:

(a) providing a solution containing glucose and fructose,
(b) subjecting the solution containing glucose and fructose to chromatographic fractionation to obtain a glucose

fraction and a fructose fraction,
(c) subjecting the fructose fraction to crystallization to obtain crystalline fructose and a fructose crystallization run-off,
(d) subjecting the fructose crystallization run-off to crystallization to obtain further crystalline fructose and a further crystallization run-off, which contains 88 to 96% fructose, 2 to 5% disaccharides and 1 to 8% glucose on DS, whereby said disaccharides comprise fructose dimers,
(e) subjecting at least part of said further crystallization run-off to chromatographic fractionation in a separation system, which comprises two or more cation exchange resin beds, whereby at least one of said cation exchange resin beds is in a Ca^{2+} form and at least one of said cation exchange resin beds is in other than Ca^{2+} form, to obtain a further fructose fraction depleted in fructose dimers,
(f) returning said further fructose fraction to the crystallization.

Patentansprüche

1. Verfahren zur Herstellung kristalliner Fructose mit verbesserter Ausbeute, **dadurch gekennzeichnet, dass** es umfasst:

   eine oder mehrere Kristallisationsschritte zur Herstellung kristalliner Fructose und einen oder mehrere Fructose-Kristallisationsabläufe, die 88 bis 96% Fructose, 2 bis 5% Disaccharide und 1 bis 8% Glucose bezogen auf die Trockensubstanz enthalten, wobei die Disaccharide Fructose-Dimere umfassen,
   chromatographische Fraktionierung mindestens eines Teils des einen oder der mehreren Fructose-Kristallisationsabläufe in einem Trennungssystem, das zwei oder mehr Kationenaustauscherharzbetten umfasst, wobei mindestens einer der Kationenaustauscherharzbetten in einer Ca^{2+}-Form vorliegt und mindestens einer der Kationenaustauscherharzbetten in einer monovalenten Kationenform vorliegt, um eine an Fructose-Dimeren abgereicherte Fructose-Fraktion und gegebenenfalls mindestens eine andere Fraktion zu erzeugen, und
   Einführen der Fructose-Fraktion in mindestens eine der einen oder mehreren Kristallisationsschritte zur Herstellung kristalliner Fructose.

2. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die aus der chromatographischen Fraktionierung erhaltene Fructose-Fraktion 94 bis 98% Fructose, weniger als 3%, vorzugsweise weniger als 2% Fructose-Dimere und weniger als 1,5%, vorzugsweise weniger als 1,0% Glucose bezogen auf die Trockensubstanz enthält.

3. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die Fructose-Dimere aus Disacchariden A und/oder Disacchariden B ausgewählt sind.

4. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die Fructose-Dimere DiFructose Dianhydride umfassen.

5. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die mindestens eine andere Fraktion eine mit Fructose-Dimeren angereicherte Rückstandsfraktion ist.

6. Verfahren gemäß Anspruch 1 und 5, **dadurch gekennzeichnet, dass** eine an Fructose-Dimeren abgereicherte Fructose-Fraktion und eine mit Fructose-Dimeren angereicherte Rückstandsfraktion erhalten werden.

7. Verfahren gemäß Anspruch 4, **dadurch gekennzeichnet, dass** die Fructose-Fraktion weniger als 1,5%, vorzugsweise weniger als 1,0% Disaccharide A und weniger als 1,5%, vorzugsweise weniger als 0,8% Disaccharide B bezogen auf die Trockensubstanz umfasst.

8. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die chromatographische Fraktionierung eine Fructose Ausbeute von mehr als 80%, vorzugsweise mehr als 90% und besonders bevorzugt mehr als 95% bezogen auf die Fructose in dem in der chromatographischen Fraktionierung als Zulauf verwendeten Fructose-Kristallisationsablauf bereitstellt.

9. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** das einwertige Kation aus Na^+ und K^+ ausgewählt ist.

10. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die Kationenaustauscherharze im Trennungssystem stark saure Kationenaustauscherharze sind.

11. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** mindestens 20% der Gesamtlänge der Harzbetten des Trennungssystems in einer Ca^{2+}-Form vorliegen.

12. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** mindestens 20% der Gesamtlänge der Harzbetten des Trennungssystems in einer monovalenten Kationenform vorliegen.

13. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** der als Zulauf in der chromatographischen Fraktionierung verwendete Fructose-Kristallisationsablauf Disaccharide in einer Menge von weniger als 2% bezogen auf die Trockensubstanz und Glucose in einer Menge von mehr als 3% bezogen auf die Trockensubstanz enthält, wobei 60 bis 80% der Gesamtlänge des Harzbettes des Trennungssystems in Ca^{2+}-Form vorliegen.

14. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** der als Zulauf in der chromatographischen Fraktionierung verwendete Fructose-Kristallisationsablauf Disaccharide in einer Menge von mehr als 3% bezogen auf die Trockensubstanz und Glucose in einer Menge von weniger als 2% bezogen auf die Trockensubstanz enthält, wobei 60 bis 80% der Gesamtlänge der Harzbetten des Trennungssystems in einer monovalenten Kationenform vorliegen.

15. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die zwei oder mehreren Kationenaustauscherharzbetten in einer monovalenten Kationenform ein schwach saures Kationenaustauscherharz umfassen.

16. Verfahren gemäß Anspruch 15, **dadurch gekennzeichnet, dass** das schwach saure Kationenaustauscherharz in einer freien Säureform vorliegt.

17. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die zwei oder mehreren Kationenaustauscherharzbetten in Reihe oder parallel angeordnet sind.

18. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die chromatographische Fraktionierung mit einem diskontinuierlichen Verfahren oder einem simulierten Wanderbett-Verfahren durchgeführt wird.

19. Verfahren gemäß Anspruch 18, **dadurch gekennzeichnet, dass** das simulierte Wanderbett-Verfahren kontinuierlich oder sequentiell ist.

20. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die chromatographische Fraktionierung bei einem pH von 3 bis 6, vorzugsweise bei einem pH im Bereich von 4 bis 5 durchgeführt wird.

21. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die Fructose-Fraktion, die in die Kristallisation eingeführt werden soll, eine Fructose-Reinheit von mehr als 93%, vorzugsweise mehr als 95% und besonders bevorzugt mehr als 97%, bezogen auf die gelöste Trockensubstanz aufweist.

22. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** das Verfahren eine Gesamtkristallisationsausbeute an kristalliner Fructose von mehr als 90%, vorzugsweise mehr als 93% und am meisten bevorzugt mehr als 95% bezogen auf die Fructose im Kristallisationszulauf bereitstellt.

23. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die chromatographische Fraktionierung eine Ausbeute an Fructose von mehr als 90%, bevorzugt mehr als 95% bezogen auf die Fructose in dem als Zulauf in der chromatographischen Fraktionierung verwendeten Fructose-Kristallisationsablauf bereitstellt und dass das Verfahren eine Gesamtausbeute an kristalliner Fructose von mehr als 90% und vorzugsweise mehr als 95% bezogen auf die Fructose im Kristallisationszulauf bereitstellt.

24. Verfahren gemäß Anspruch 1, **gekennzeichnet durch** folgende Schritte:

chromatographische Fraktionierung mindestens eines Teils des einen oder der mehreren Fructose-Kristallisationsabläufe in einem Trennungssystem, das zwei oder mehr Kationenaustauscherharzbetten umfasst, wobei mindestens einer der Kationenaustauscherharzbetten in einer Ca^{2+}-Form vorliegt und mindestens einer der Kationenaustauscherharzbetten in einer monovalenten Kationenform vorliegt, um eine an Fructose-Dimeren abgereicherte Fructose-Fraktion zu erzeugen,
Einführen der Fructose-Fraktion in die Kristallisation, um kristalline Fructose und einen weiteren Kristallisationsablauf zu erhalten, und

Rückführen mindestens eines Teils des weiteren Kristallisationsablaufs in die chromatographische Fraktionierung.

25. Verfahren gemäß Anspruch 1, **gekennzeichnet durch** folgende Schritte:

Kristallisation eines Fructose-Kristallisationsablaufs um kristalline Fructose und einen weiteren Kristallisationsablauf zu erhalten, der 88 bis 96% Fructose, 2 bis 5% Disaccharide und 1 bis 8% Glucose bezogen auf die Trockensubstanz enthält, wobei die Disaccharide Fructose-Dimere umfassen,
chromatographische Fraktionierung mindestens eines Teils des weiteren Kristallisationsablaufs in einem Trennungssystem, das zwei oder mehr Kationenaustauscherharzbetten umfasst, wobei mindestens einer der Kationenaustauscherharzbetten in einer Ca^{2+}-Form vorliegt und mindestens einer der Kationenaustauscherharzbetten in einer monovalenten Kationenform vorliegt, um eine an Fructose-Dimeren abgereicherte Fructose-Fraktion zu erzeugen,
Rückführen der Fructose-Fraktion in die Kristallisation.

26. Verfahren gemäß Anspruch 1, **dadurch gekennzeichnet, dass** das Verfahren auch, als vorangehenden Schritt, eine chromatographische Fraktionierung einer Lösung umfasst, die Glucose und Fructose enthält, um eine Glucose-Fraktion und eine Fructose-Fraktion zur Herstellung kristalliner Fructose zu erhalten.

27. Verfahren gemäß Anspruch 26, **dadurch gekennzeichnet, dass** die Lösung, die Glucose und Fructose enthält, ausgewählt ist aus invertierter Saccharose und isomerisierter Glucose.

28. Verfahren gemäß Anspruch 26, **dadurch gekennzeichnet, dass** das Verfahren auch umfasst
Unterwerfen der Glucose-Fraktion einer Isomerisierung, um eine Lösung zu erhalten, die Glucose und Fructose enthält, und
Rückführen der Lösung, die Glucose und Fructose enthält, in die chromatographische Fraktionierung.

29. Verfahren gemäß Anspruch 26, **dadurch gekennzeichnet, dass** es die folgenden Schritte umfasst:

(a) Bereitstellen einer Lösung, die Glucose und Fructose enthält,
(b) Unterwerfen der Lösung, die Glucose und Fructose enthält, der chromatographischen Fraktionierung, um eine Glucose-Fraktion und eine Fructose-Fraktion zu erhalten,
(c) Unterwerfen der Fructose-Fraktion der Kristallisation, um kristalline Fructose und einen Fructose-Kristallisationsablauf zu erhalten, der 88 bis 96% Fructose, 2 bis 5% Disaccharide und 1 bis 8% Glucose bezogen auf die Trockensubstanz enthält, wobei die Disaccharide Fructose-Dimere umfassen,
(d) Unterwerfen mindestens eines Teils des Fructose-Kristallisationsablaufs der chromatographischen Fraktionierung in einem Trennungssystem, das zwei oder mehr Kationenaustauscherharzbetten umfasst, wobei mindestens einer der Kationenaustauscherharzbetten in einer Ca^{2+}-Form vorliegt und mindestens einer der Kationenaustauscherharzbetten in einer monovalenten Kationenform vorliegt, um eine weitere an Fructose-Dimeren abgereicherte Fructose-Fraktion zu erhalten,
(e) Einführen der weiteren Fructose-Fraktion in die Kristallisation, um weitere kristalline Fructose und einen weiteren Kristallisationsablauf zu erhalten, der 88 bis 96% Fructose, 2 bis 5% Disaccharide und 1 bis 8% Glucose bezogen auf die Trockensubstanz enthält, wobei die Disaccharide Fructose-Dimere umfassen, und
(f) Rückführen mindestens eines Teils des weiteren Kristallisationsablaufs in die chromatographische Fraktionierung des Schrittes (d).

30. Verfahren gemäß Anspruch 26, **dadurch gekennzeichnet, dass** es die folgenden Schritte umfasst:

(a) Bereitstellen einer Lösung, die Glucose und Fructose enthält,
(b) Unterwerfen der Lösung, die Glucose und Fructose enthält, der chromatographischen Fraktionierung, um eine Glucose-Fraktion und eine Fructose-Fraktion zu erhalten,
(c) Unterwerfen der Fructose-Fraktion der Kristallisation, um kristalline Fructose und einen Fructose-Kristallisationsablauf zu erhalten,
(d) Unterwerfen des Fructose-Kristallisationsablaufs der Kristallisation, um weitere kristalline Fructose und einen weiteren Kristallisationsablauf zu erhalten, der 88 bis 96% Fructose, 2 bis 5% Disaccharide und 1 bis 8% Glucose bezogen auf die Trockensubstanz enthält, wobei die Disaccharide Fructose-Dimere umfassen,
(e) Unterwerfen mindestens eines Teils des weiteren Kristallisationsablaufs der chromatographischen Fraktionierung in einem Trennungssystem, das zwei oder mehr Kationenaustauscherharzbetten umfasst, wobei min-

destens einer der Kationenaustauscherharzbetten in einer Ca^{2+}-Form vorliegt und mindestens einer der Kationenaustauscherharzbetten in einer anderen als einer Ca^{2+}-Form vorliegt, um eine weitere an Fructose-Dimeren abgereicherte Fructose-Fraktion zu erhalten,
(f) Rückführen der weiteren Fructose-Fraktion in die Kristallisation.

Revendications

1. Procédé de production de fructose cristallin à rendement amélioré, **caractérisé en ce qu'**il comprend :

   une ou plusieurs étapes de cristallisation afin de produire du fructose cristallin et un ou plusieurs égouts de cristallisation du fructose contenant 88 à 96 % de fructose, 2 à 5 % de disaccharides et 1 à 8 % de glucose, rapportés à la MS, lesdits disaccharides comprenant des dimères de fructose,
   le fractionnement chromatographique d'au moins une partie desdits un ou plusieurs égouts de cristallisation du fructose dans un système de séparation, lequel comprend deux lits de résine échangeuse de cations ou plus, au moins un desdits lits de résine échangeuse de cations étant sous forme Ca^{2+} et au moins un desdits lits de résine échangeuse de cations étant sous forme de cation monovalent, pour produire une fraction de fructose appauvrie en dimères de fructose et éventuellement au moins une autre fraction, et
   l'introduction de ladite fraction de fructose lors d'au moins l'une desdites une ou plusieurs étapes de cristallisation destinées à la production de fructose cristallin.

2. Procédé selon la revendication 1, **caractérisé en ce que** la fraction de fructose obtenue par fractionnement chromatographique contient 94 à 98 % de fructose, moins de 3 %, de préférence moins de 2 % de dimères de fructose et moins de 1,5 %, de préférence moins de 1,0 % de glucose, rapportés à la MS.

3. Procédé selon la revendication 1, **caractérisé en ce que** lesdits dimères de fructose sont choisis parmi les disaccharides A et/ou les disaccharides B.

4. Procédé selon la revendication 1, **caractérisé en ce que** lesdits dimères de fructose comprennent des dianhydrides de difructose.

5. Procédé selon la revendication 1, **caractérisé en ce que** ladite au moins une autre fraction est une fraction résiduelle enrichie en dimères de fructose.

6. Procédé selon la revendication 1 et la revendication 5, **caractérisé en ce que** l'on obtient une fraction de fructose appauvrie en dimères de fructose et une fraction résiduelle enrichie en dimères de fructose.

7. Procédé selon la revendication 4, **caractérisé en ce que** ladite fraction de fructose comprend moins de 1,5 %, de préférence moins de 1,0 % de disaccharides A et moins de 1,5 %, de préférence moins de 0,8 % de disaccharides B, rapportés à la MS.

8. Procédé selon la revendication 1, **caractérisé en ce que** le fractionnement chromatographique permet un rendement en fructose supérieur à 80 %, de préférence supérieur à 90 % et de préférence encore supérieur à 95 % à partir du fructose contenu dans l'égout de cristallisation du fructose utilisé pour alimenter le fractionnement chromatographique.

9. Procédé selon la revendication 1, **caractérisé en ce que** ledit cation monovalent est choisi entre Na^+ et K^+.

10. Procédé selon la revendication 1, **caractérisé en ce que** lesdites résines échangeuses de cations du système de séparation sont des résines échangeuses de cations fortement acides.

11. Procédé selon la revendication 1, **caractérisé en ce qu'**au moins 20 % de la longueur totale des lits de résine du système de séparation est sous forme Ca^{2+}.

12. Procédé selon la revendication 1, **caractérisé en ce qu'**au moins 20 % de la longueur totale des lits de résine du système de séparation est sous forme de cation monovalent.

13. Procédé selon la revendication 1, **caractérisé en ce que** l'égout de cristallisation du fructose utilisé pour alimenter

le fractionnement chromatographique contient des disaccharides en quantité inférieure à 2 % de la MS et du glucose en quantité supérieure à 3 % de la MS, 60 à 80 % de la longueur totale du lit de résine du système de séparation étant sous forme Ca^{2+}.

14. Procédé selon la revendication 1, **caractérisé en ce que** l'égout de cristallisation du fructose utilisé pour alimenter le fractionnement chromatographique contient des disaccharides en quantité supérieure à 3 % de la MS et du glucose en quantité inférieure à 2 % de la MS, 60 à 80 % de la longueur totale des lits de résine du système de séparation étant sous forme de cation monovalent.

15. Procédé selon la revendication 1, **caractérisé en ce que** lesdits deux lits de résine échangeuse de cations ou plus sous forme de cation monovalent comprennent une résine échangeuse de cations faiblement acide.

16. Procédé selon la revendication 15, **caractérisé en ce que** ladite résine échangeuse de cations faiblement acide est sous forme d'acide libre.

17. Procédé selon la revendication 1, **caractérisé en ce que** lesdits deux lits de résine échangeuse de cations ou plus sont disposés en série ou en parallèle.

18. Procédé selon la revendication 1, **caractérisé en ce que** ledit fractionnement chromatographique est réalisé selon un procédé discontinu (batch) ou un procédé à lit mobile simulé.

19. Procédé selon la revendication 18, **caractérisé en ce que** ledit procédé à lit mobile simulé est continu ou séquentiel.

20. Procédé selon la revendication 1, **caractérisé en ce que** le fractionnement chromatographique est réalisé à un pH de 3 à 6, de préférence à un pH de 4 à 5.

21. Procédé selon la revendication 1, **caractérisé en ce que** ladite fraction de fructose à introduire dans la cristallisation a une pureté en fructose supérieure à 93 %, de préférence supérieure à 95 % et de préférence encore supérieure à 97 %, rapportée à la matière sèche dissoute.

22. Procédé selon la revendication 1, **caractérisé en ce que** le processus permet un rendement global de cristallisation en fructose cristallin supérieur à 90 %, de préférence supérieur à 93 % et idéalement supérieur à 95 %, rapporté au fructose alimentant la cristallisation.

23. Procédé selon la revendication 1, **caractérisé en ce que** le fractionnement chromatographique permet un rendement en fructose supérieur à 90 %, de préférence supérieur à 95 %, rapporté au fructose contenu dans l'égout de cristallisation du fructose utilisé pour alimenter le fractionnement chromatographique et **en ce que** le procédé permet un rendement global en fructose cristallin supérieur à 90 % et de préférence supérieur à 95 %, rapporté au fructose alimentant la cristallisation.

24. Procédé selon la revendication 1, **caractérisé par** les étapes suivantes :

fractionnement chromatographique d'au moins une partie desdits un ou plusieurs égouts de cristallisation du fructose dans un système de séparation, lequel comprend deux lits de résine échangeuse de cations ou plus, au moins un desdits lits de résine échangeuse de cations étant sous forme Ca^{2+} et au moins un desdits lits de résine échangeuse de cations étant sous forme de cation monovalent, pour produire une fraction de fructose appauvrie en dimères de fructose,
introduction de ladite fraction de fructose dans la cristallisation pour obtenir du fructose cristallin et un autre égout de cristallisation, et
renvoi d'au moins une partie dudit autre égout de cristallisation vers le fractionnement chromatographique.

25. Procédé selon la revendication 1, **caractérisé par** les étapes suivantes :

cristallisation d'un égout de cristallisation du fructose pour obtenir du fructose cristallin et un autre égout de cristallisation du fructose contenant 88 à 96 % de fructose, 2 à 5 % de disaccharides et 1 à 8 % de glucose, rapportés à la MS, lesdits disaccharides comprenant des dimères de fructose,
fractionnement chromatographique d'au moins une partie dudit autre égout de cristallisation dans un système de séparation, lequel comprend deux lits de résine échangeuse de cations ou plus, au moins un desdits lits de

résine échangeuse de cations étant sous forme Ca^{2+} et au moins un desdits lits de résine échangeuse de cations étant sous forme de cation monovalent, pour produire une fraction de fructose appauvrie en dimères de fructose,
renvoi de ladite fraction de fructose vers la cristallisation.

26. Procédé selon la revendication 1, **caractérisé en ce que** le procédé comprend également, à titre d'étape préalable, le fractionnement chromatographique d'une solution contenant du glucose et du fructose pour obtenir une fraction de glucose et une fraction de fructose destinée à la production de fructose cristallin.

27. Procédé selon la revendication 26, **caractérisé en ce que** la solution contenant du glucose et du fructose est choisie entre le saccharose inverti et le glucose isomérisé.

28. Procédé selon la revendication 26, **caractérisé en ce que** le procédé comprend également les étapes consistant à soumettre la fraction de glucose à une isomérisation pour obtenir une solution contenant du glucose et du fructose, et renvoyer la solution contenant du glucose et du fructose vers le fractionnement chromatographique.

29. Procédé selon la revendication 26, **caractérisé en ce qu'**il comprend également les étapes suivantes :

(a) prévoir une solution contenant du glucose et du fructose,
(b) soumettre la solution contenant du glucose et du fructose à un fractionnement chromatographique pour obtenir une fraction de glucose et une fraction de fructose,
(c) soumettre la fraction de fructose à la cristallisation pour obtenir du fructose cristallin et un égout de cristallisation du fructose contenant 88 à 96 % de fructose, 2 à 5 % de disaccharides et 1 à 8 % de glucose, rapportés à la MS, lesdits disaccharides comprenant des dimères de fructose,
(d) soumettre au moins une partie de l'égout de cristallisation du fructose à un fractionnement chromatographique dans un système de séparation, lequel comprend deux lits de résine échangeuse de cations ou plus, au moins un desdits lits de résine échangeuse de cations étant sous forme Ca^{2+} et au moins un desdits lits de résine échangeuse de cations étant sous forme de cation monovalent, pour obtenir une autre fraction de fructose appauvrie en dimères de fructose,
(e) introduire ladite autre fraction de fructose dans la cristallisation pour obtenir de nouveau du fructose cristallin et un autre égout de cristallisation contenant 88 à 96 % de fructose, 2 à 5 % de disaccharides et 1 à 8 % de glucose, rapportés à la MS, lesdits disaccharides comprenant des dimères de fructose, et
(f) renvoyer au moins une partie dudit autre égout de cristallisation vers le fractionnement chromatographique de l'étape (d).

30. Procédé selon la revendication 26, **caractérisé en ce qu'**il comprend les étapes suivantes :

(a) prévoir une solution contenant du glucose et du fructose,
(b) soumettre la solution contenant du glucose et du fructose à un fractionnement chromatographique pour obtenir une fraction de glucose et une fraction de fructose,
(c) soumettre la fraction de fructose à la cristallisation pour obtenir du fructose cristallin et un égout de cristallisation du fructose,
(d) soumettre l'égout de cristallisation du fructose à la cristallisation pour obtenir de nouveau du fructose cristallin et un autre égout de cristallisation contenant 88 à 96 % de fructose, 2 à 5 % de disaccharides et 1 à 8 % de glucose, rapportés à la MS, lesdits disaccharides comprenant des dimères de fructose,
(e) soumettre au moins une partie dudit autre égout de cristallisation à un fractionnement chromatographique dans un système de séparation, lequel comprend deux lits de résine échangeuse de cations ou plus, au moins un desdits lits de résine échangeuse de cations étant sous forme Ca^{2+} et au moins un desdits lits de résine échangeuse de cations étant sous une forme autre que Ca^{2+}, pour obtenir une autre fraction de fructose appauvrie en dimères de fructose,
(f) renvoyer ladite autre fraction de fructose vers la cristallisation.

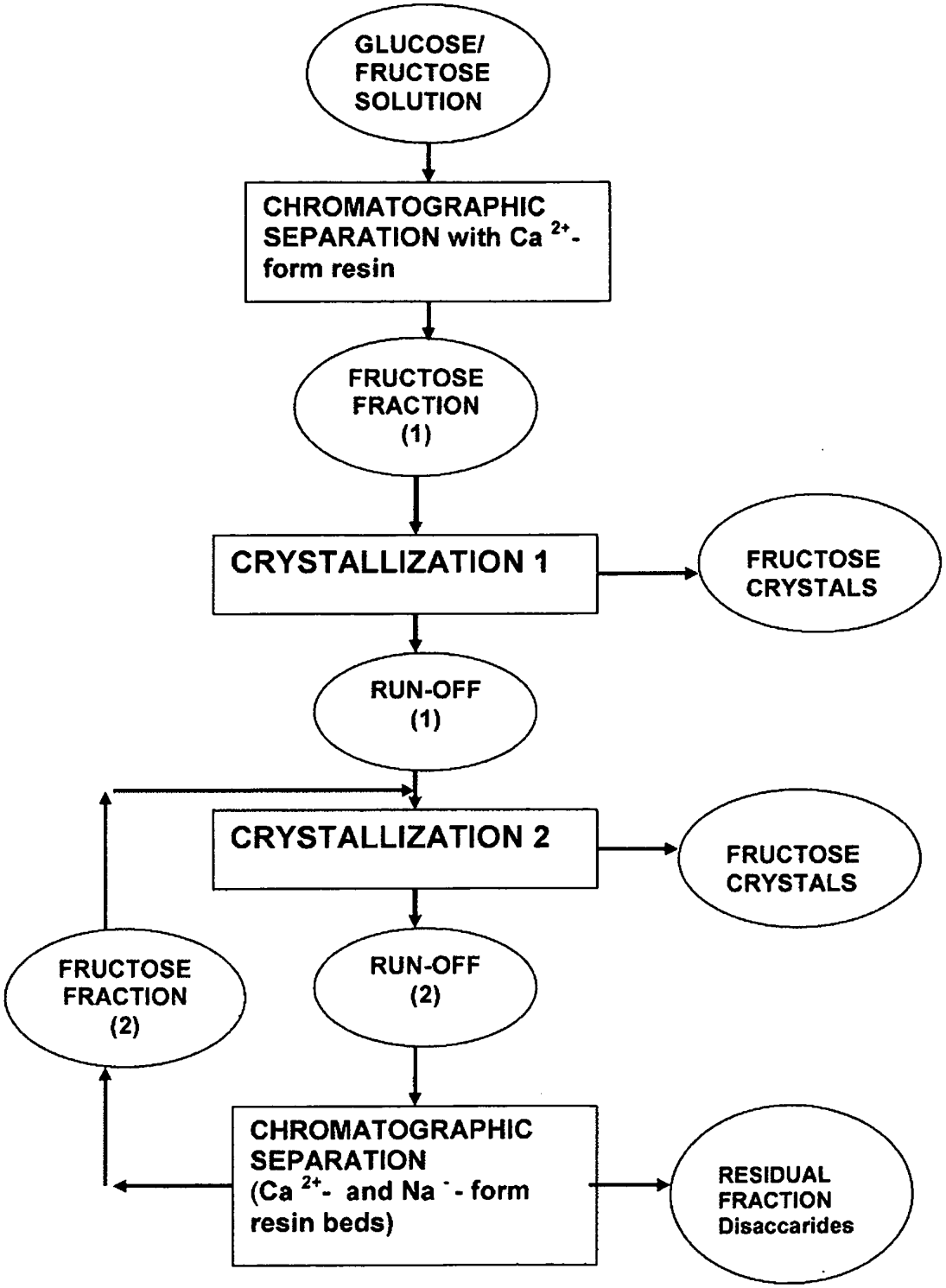
GLUCOSE/ FRUCTOSE SOLUTION
CHROMATOGRAPHIC SEPARATION with Ca 2+- form resin
FRUCTOSE FRACTION (1)
CRYSTALLIZATION 1
FRUCTOSE CRYSTALS
RUN-OFF (1)
CRYSTALLIZATION 2
FRUCTOSE CRYSTALS
FRUCTOSE FRACTION (2)
RUN-OFF (2)
CHROMATOGRAPHIC SEPARATION (Ca 2+- and Na +- form resin beds)
RESIDUAL FRACTION Disaccarides

FIGURE 1

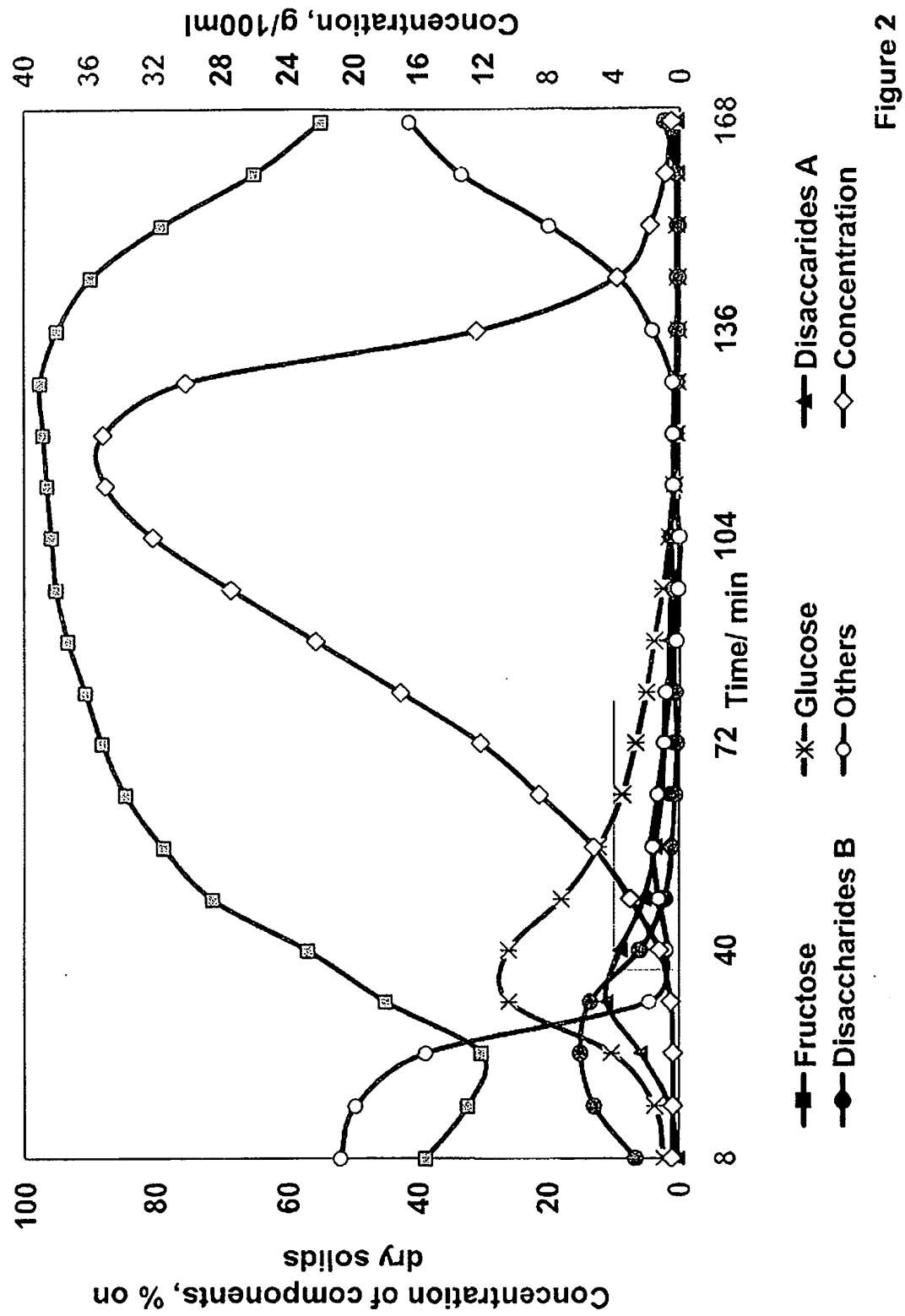
Concentration of components, % on dry solids
Concentration, g/100ml
Time/ min
Fructose
Disaccharides B
Glucose
Others
Disaccarides A
Concentration

Figure 2

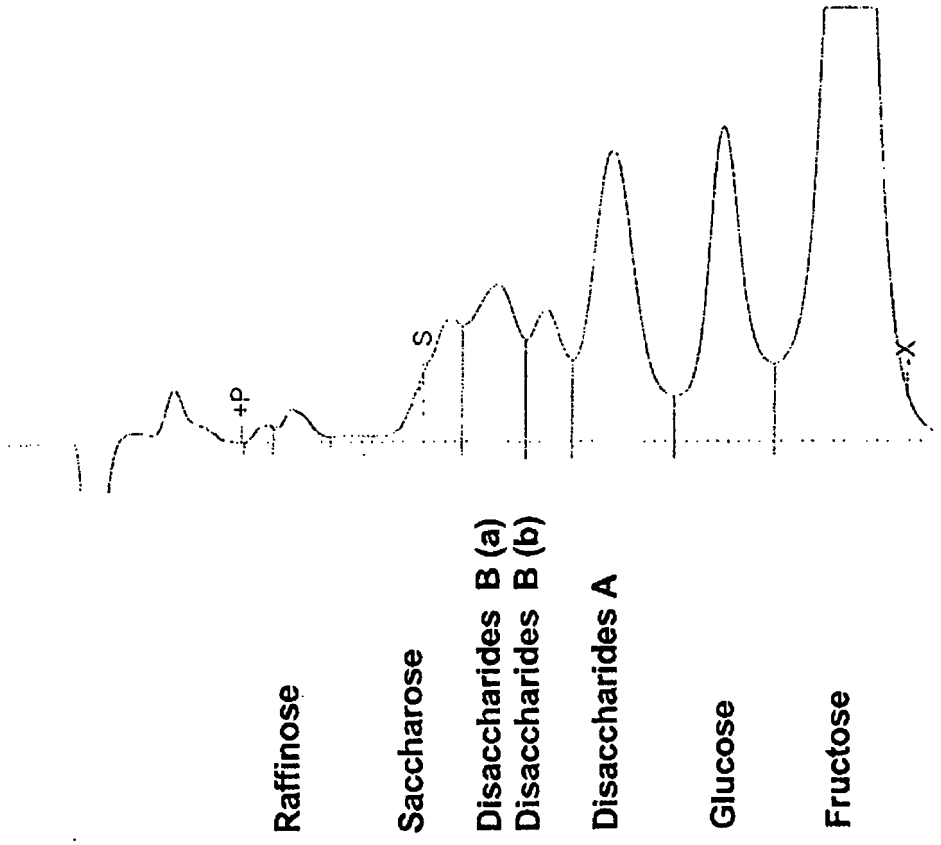
+p
S
X
Raffinose
Saccharose
Disaccharides B (a)
Disaccharides B (b)
Disaccharides A
Glucose
Fructose

Figure 3

REFERENCES CITED IN THE DESCRIPTION

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