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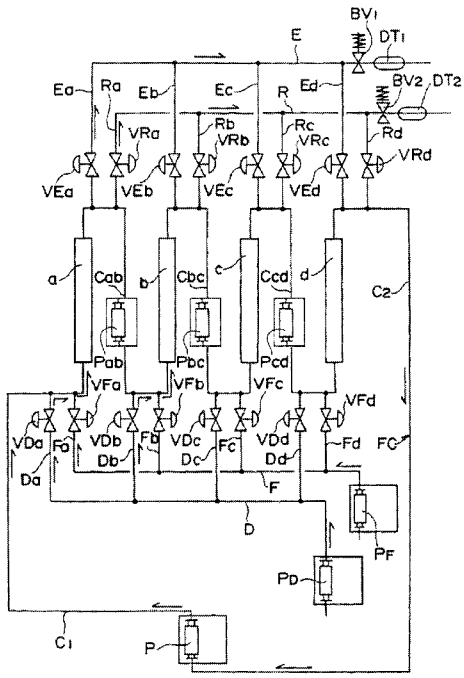
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(54) **Title**: METHOD OF PRODUCING A SUGAR PRODUCT FROM FRUIT

FIG. 1



(57) **Abstract**: A method of producing a sugar -product from fruit, the method including the steps of : a) providing a fruit juice containing glucose and fructose; b) demineralizing and decolouring the fruit juice to obtain a clarified, demineralized fruit juice; c) concentrating the clarified, demineralized fruit juice to obtain a concentrated clarified, demineralized fruit juice; and d) separating the concentrated demineralized, clarified fruit juice by chromatography to obtain at least a glucose-enriched fraction and at least a fructose-enriched fraction,- the method including, after step d), a step e) of filtering the glucose-enriched fraction and fructose- enriched fraction on a carbon filter; and steps d) and e) being performed at a temperature of 50-70°C.

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METHOD OF PRODUCING A SUGAR PRODUCT FROM FRUIT

TECHNICAL FIELD

The present invention relates to a method of producing a liquid or solid sugar product, in particular glucose and fructose, from fruit.

BACKGROUND ART

Producing sugar, such as glucose and fructose, from fruit juice, in particular grape juice, is known.

The juice, obtained for example by pressing the fruit, is normally processed first to eliminate non-sugar components, and then by chromatography to separate the sugars, mainly glucose from fructose. The resulting products, in liquid form or later crystallized, are normally used in the food industry or consumed as they are, for example, as sweeteners.

EP1734108 and EP2425723 describe a method of producing sugar products from grapes, in which a concentrated rectified must solution is chromatography processed to obtain a glucose solution and a fructose solution, which are then crystallized.

Prior to the chromatography stage, the juice obtained from crushing the grapes is clarified and demineralized, and then concentrated to the right concentration for chromatography processing. The EP1734108 and EP2425723 method, however, has the

drawback of including no treatment to reduce the colour of the sugar solutions, and no control of the hydroxymethylfurfurol (HMF) content, which has crystallization inhibiting properties. Also, the chromatography process fails to provide for complete, satisfactory separation, and more specifically for correct, uniform extraction, of the glucose and fructose. Demand therefore exists for a method of separating sugars, particularly glucose and fructose, from fruit juices, designed to eliminate the above drawbacks, and which, in particular, provides for controlling hydroxymethylfurfurol levels; correct, uniform extraction of sugars from fruit, while at the same time safeguarding the integrity of the sugars; and low energy consumption.

DESCRIPTION OF THE INVENTION

It is an object of the present invention to provide a method of producing a sugar product from fruit, designed to permit hydroxymethylfurfurol level control; correct uniform sugar extraction from fruit, while at the same time safeguarding the integrity of the sugars; lower energy consumption than known methods; and product purity comparable with that of known methods.

According to the present invention, there is provided a method as claimed in Claim 1.

BRIEF DESCRIPTION OF THE DRAWINGS

A non-limiting embodiment of the invention will be described by way of example, with particular reference to grapes and to the attached drawing, in which :

Figure 1 shows a chromatography system for separating a glucose solution and fructose solution in accordance with the present invention.

BEST WAY OF IMPLEMENTING THE INVENTION

In the present invention, the term 'juice' refers to grape juice, and in particular to juice obtained from crushing grapes.

After being filtered to remove any remaining solids, the juice so formed is clarified, e.g. by adding gelatine, bentonite and carbon, and demineralized, e.g. on ion resins. Alternatively, clarification and demineralization may be performed as described in EP2425723.

This stage produces a clarified, demineralized fruit juice with a sugar, in particular glucose and fructose, percentage of over 98%, e.g. 98.5%, with reference to the dry substance.

Next, the clarified, demineralized fruit juice is concentrated to reduce its water content, but without altering the composition of its solid portion. The obtained concentrated juice, also known as rectified concentrated must, is a colourless solution containing over 98%, with reference to the dry substance, of

fructose and glucose, and the rest of which is made up of components such as alcohol, flavonoids and other polyphenols.

The concentrated concentrated rectified must is then heated to a temperature of 50-70°C, in particular 57-65°C, e.g. 60°C. Advantageously, at these temperatures, the concentrated concentrated rectified must has a viscosity (<10 mPa*s) allowing an uniform leading front during chromatography process.

At these temperatures, the glucose and fructose in the juice can be separated effectively with no need for a high-pressure eluent, and above all without altering the stability of the sugars and/or deteriorating the chromatography resins.

So, despite operating at higher than the ambient temperature of known methods, improved sugar separation allows a considerable reduction in total energy consumption of the method according to the invention as a whole.

The concentrated concentrated rectified must is then subjected to chromatographic separation, in particular on ion-exchange resins, more specifically on cation resins, and preferably on styrene-divinylbenzene resins derivatized with sulphone groups. The resins used may have the characteristics described in EP2425723.

Chromatographic separation is performed in a

simulated fluid-bed system as shown in Figure 1.

The Figure 1 system comprises four columns : *a*, *b*, *c* and *d*, each with a pump (P, Pab, Pbc, Pcd) for pumping the circulating fluid, i.e. the eluent, through the columns.

The four columns are filled with a cation resin, preferably styrene-divinylbenzene resin derivatized with sulphone groups.

The outlet of column *a* is connected to the inlet of column *b* by a line Cab fitted with pump Pab; the outlet of column *b* is connected to the inlet of column *c* by a line Cbc fitted with pump Pbc; the outlet of column *c* is connected to the inlet of column *d* by a line Ccd fitted with pump Pcd; the outlet of column *d* is connected to the inlet of pump P by a line C_2; and the outlet of pump P is connected to the inlet of column *a* by a line C_1. Columns *a-d*, lines C_1, C_2, Cab, Cbc, Ccd and pumps P, Pab, Pbc, Pcd thus form a separation circuit FC, through which the circulating fluid, i.e. the eluent, e.g. deionized water, circulates in the direction of the arrows in Figure 1.

Eluent feed lines Da-Dd and concentrated rectified must feed lines Fa-Fd into separation circuit FC are connected to separation circuit FC close to the respective inlets of columns *a-d*.

Glucose extraction lines Ea-Ed, for extracting a

glucose-enriched fraction from separation circuit FC, and fructose extraction lines Ra-Rd, for extracting a fructose-enriched fraction from separation circuit FC, are connected to separation circuit FC close to the respective outlets of columns *a-d*.

Eluent feed lines Da-Dd branch off from an eluent feed pipe D connected at one end to an eluent pump P_D; and concentrated rectified must feed lines Fa-Fd branch off from a concentrated rectified must feed pipe F connected at one end to a concentrated rectified must pump P_F.

Open-close valves VDa-VDd are installed along respective eluent feed lines Da-Dd; and open-close valves VFa-VFd are installed along respective concentrated rectified must feed lines Fa-Fd.

Open-close valves VEa-VEd are installed along respective glucose extraction lines Ea-Ed; and open-close valves VRa-VRd are installed along respective fructose extraction lines Ra-Rd.

Glucose extraction lines Ea-Ed are connected to a glucose extraction pipe E.

Fructose extraction lines Ra-Rd are connected to a fructose extraction pipe R.

The Figure 1 system operates as follows.

After initiating the system by filling it with eluent - preferably deionized water or at any rate water

with a low calcium content, which acts as the circulating fluid - one of eluent feed lines Da-Dd, one of glucose extraction lines Ea-Ed, one of concentrated rectified must feed lines Fa-Fd and one of fructose extraction lines Ra-Rd are connected so as to be positioned in the following order: eluent feed line, glucose extraction line, concentrated rectified must feed line, fructose extraction line along the direction of the circulation fluid in the separation circuit FC, through opening and closing of valves VDa-VDd, VEa-VEd, VFa-VFd and VRa-VRd.

For example, eluent feed line Da, glucose extraction line Ea, concentrated rectified must feed line Fc and fructose extraction line Rc are connected to separation circuit FC by opening valves VDa, VEa, VFc, VRc and closing all the other valves.

This results in the formation of an elution zone IV in column *a*, between eluent feed line Da and glucose extraction line Ea; a concentration zone III in column *b*, between glucose extraction line Ea and concentrated rectified must feed line Fc; a refining zone II in column *c*, between concentrated rectified must feed line Fc and fructose extraction line Rc; and an adsorption zone I in column *d*, between fructose extraction line Rc and eluent feed line Da.

In column *a* containing the elution zone, the resin-

retained glucose is eluted by the eluent from line Da, and is transferred to the circulating fluid in separation circuit FC. At the inlet of column *a*, the circulating fluid therefore contains roughly no glucose. This concentration increases as the circulating fluid flows through column *a*, and, at the outlet of column *a*, the circulating fluid contains a large amount of glucose (glucose-enriched fraction), part of which is extracted from the separation circuit by glucose extraction line Ea and collected in a glucose tank, and the rest of which is fed into column *b*.

In column *b* containing concentration zone III, the glucose in the circulating fluid from column *a* is retained by the resin as the circulating fluid flows through column *b*. In the meantime, the fructose in column *b*, retained by the resin to a lesser degree than the glucose, is transferred to the circulating fluid, so the glucose concentration in the circulating fluid flowing through column *b* decreases, while the fructose concentration increases. The circulating fluid from column *b* is then fed into column *c* together with a portion of concentrated rectified must from line Fc.

In column *c* containing refining zone II, the glucose in the concentrated rectified must from line Fc and in the circulating fluid is retained by the resin, and the fructose previously retained by the resin in

column *c* is transferred to the circulating fluid. At the inlet of column *c*, the circulating fluid therefore contains roughly no glucose, whereas the fructose concentration increases as the circulating fluid flows through column *c*. The circulating fluid from column *c* and containing a large amount of fructose (fructose-enriched fraction) is partly extracted by fructose extraction line Rc and collected in a fructose tank, and partly fed into column *d*.

In column *d* containing adsorption zone I, the large amount of fructose in the circulating fluid from column *c* is retained by the resin, so, at the outlet of column *d*, the circulating fluid contains practically no glucose and no fructose, and is fed back into column *a* along lines C_1 and C_2.

After a given time interval (6.5 minutes), valves VDa, VEa, VFc, VRc are closed and valves VDb, VEb, VFd, VRd are opened. Opening and closing the valves above determines a transfer of the elution zone IV from column *a* to column *b*, of the concentration zone III from column *b* to column *c*, of the refining zone II from column *c* to column *d*, and of the adsorption zone I from column *d* to column *a*.

In column *b*, the resin-retained glucose is therefore eluted by the eluent from line Db; and the circulating fluid from column b (glucose-enriched

fraction) is partly extracted by glucose extraction line Eb and collected in a glucose tank, and the rest fed into column *c* along line Cbc.

In column *c*, the glucose in the circulating fluid from column *b* is retained by the resin, and the fructose, retained by the resin to a lesser degree, is transferred to the circulating fluid, so the glucose concentration in the circulating fluid decreases, while the fructose concentration increases as the circulating fluid flows through column *c*.

The circulating fluid from column *c* is fed into column *d* together with the concentrated rectified must from concentrated rectified must feed line Fd. In column *d*, the glucose in the concentrated rectified must and in the circulating fluid is retained by the resin, and the fructose is transferred to the circulating fluid. And, at the outlet of column *d*, part of the circulating fluid (fructose-enriched fraction) is extracted by fructose extraction line Rd and collected in a fructose tank, and the rest is fed into column *a*.

In column *a*, the glucose and fructose in the circulating fluid are retained by the resin, so the circulating fluid from column *a* has no glucose and no fructose, and is fed back into column *b*.

After a given time interval (6.5 minutes), valves VDb, VEb, VFd, VRd are closed and valves VDc, VEc, VFa,

VRa are opened. Opening and closing the valves above determines a transfer of the elution zone IV from column *b* to column *c*, of the concentration zone III from column *c* to column *d*, of the refining zone II from column *d* to column *a*, and of the adsorption zone I from column *a* to column *b*; and the process is repeated as described above.

Chromatographic separation is performed at a temperature of 50-70°C, and more specifically of 57-65°C, e.g. 60°C.

At these temperatures, the glucose and fructose in the juice can be separated effectively with no need for a high-pressure eluent, and above all without altering the stability of the sugars and/or deteriorating the chromatography resins.

On the other hand, these temperatures greatly increase the amount of hydroxymethylfurfurol (HMF) derived from thermal decomposition of the sugars.

In the production method according to the invention, the concentrated rectified must and the sugars in it are kept several days in the system. Before it is crystallized, the sugar molecule remains in the process solutions in the system for a period of 5-10 days, and at temperatures of 70-28°C, so a certain amount of HMF, however small, is inevitably produced.

excessive amounts of hydroxymethylfurfurol may

render the crystallization stage ineffective and greatly reduce crystallization efficiency. In fact, hydroxymethylfurfurol is a known fructose crystallization inhibitor.

Excessive amounts of hydroxymethylfurfurol have the following effect on fructose crystallization :

20 ppm of HMF in the fructose syrup - 60% crystallization efficiency

50 ppm of HMF in the fructose syrup - 55% crystallization efficiency

200 ppm of HMF in the fructose syrup - 45% crystallization efficiency

The chromatographic separation stage is therefore followed by a filtration stage using carbon filters (e.g. active-carbon - 3 micron filtration BECODISC Filters ®) which, in addition to reducing the colour of the chromatography eluate, also retains the HMF contained in it, to achieve a high degree of crystallization efficiency.

Temperature is preferably maintained constant at both the chromatographic and filtration stages.

The post-filtration fructose- and glucose-enriched fractions are then concentrated, e.g. in steam concentrators, to the Brix required to produce liquid sugar products for consumption or crystallization - roughly 88° Brix for fructose and 75° Brix for glucose.

After chromatography and filtration, the glucose-enriched fraction is over 86% pure, and the fructose-enriched fraction over 96% pure.

Chromatographic separation, filtration and concentration are performed at a preferably constant temperature of 50-70°C, and more specifically 57-65°C, e.g. 60°C.

The liquid sugar products obtained may then be crystallized by cooling - and possibly inseminating fructose or glucose crystals - from a temperature of 50-70°C to a temperature of 25-30°C. These crystallization temperatures, as opposed to the 12-13°C temperatures used in known methods, have the advantage of improving sugar crystallization efficiency and greatly reducing energy consumption.

The crystallized end products obtained are over 99% pure.

All the documents mentioned in the above disclosure are incorporated by way of reference.

CLAIMS

1) A method of producing a sugar product from fruit, the method comprising the steps of :

a) providing a fruit juice comprising glucose and fructose;

b) demineralizing and decolouring said fruit juice to obtain a clarified, demineralized fruit juice;

c) concentrating said clarified, demineralized fruit juice to obtain a concentrated clarified, demineralized fruit juice; and

d) separating said concentrated demineralized, clarified fruit juice by chromatography to obtain at least a glucose-enriched fraction and at least a fructose-enriched fraction;

the method being characterized by comprising, after said step d), a step e) of filtering said glucose-enriched fraction and said fructose-enriched fraction on a carbon filter; and in that said steps d) and e) are performed at a temperature of 50-70°C.

2) A method as claimed in Claim 1, characterized in that said temperature is between 57°C and 65°C.

3) A method as claimed in Claim 1 or 2, characterized in that said temperature is maintained constant at steps d) and e).

4) A method as claimed in any one of Claims 1 to 3,

characterized by comprising, after step e), a step f) of crystallizing said glucose-enriched fraction and said fructose-enriched fraction.

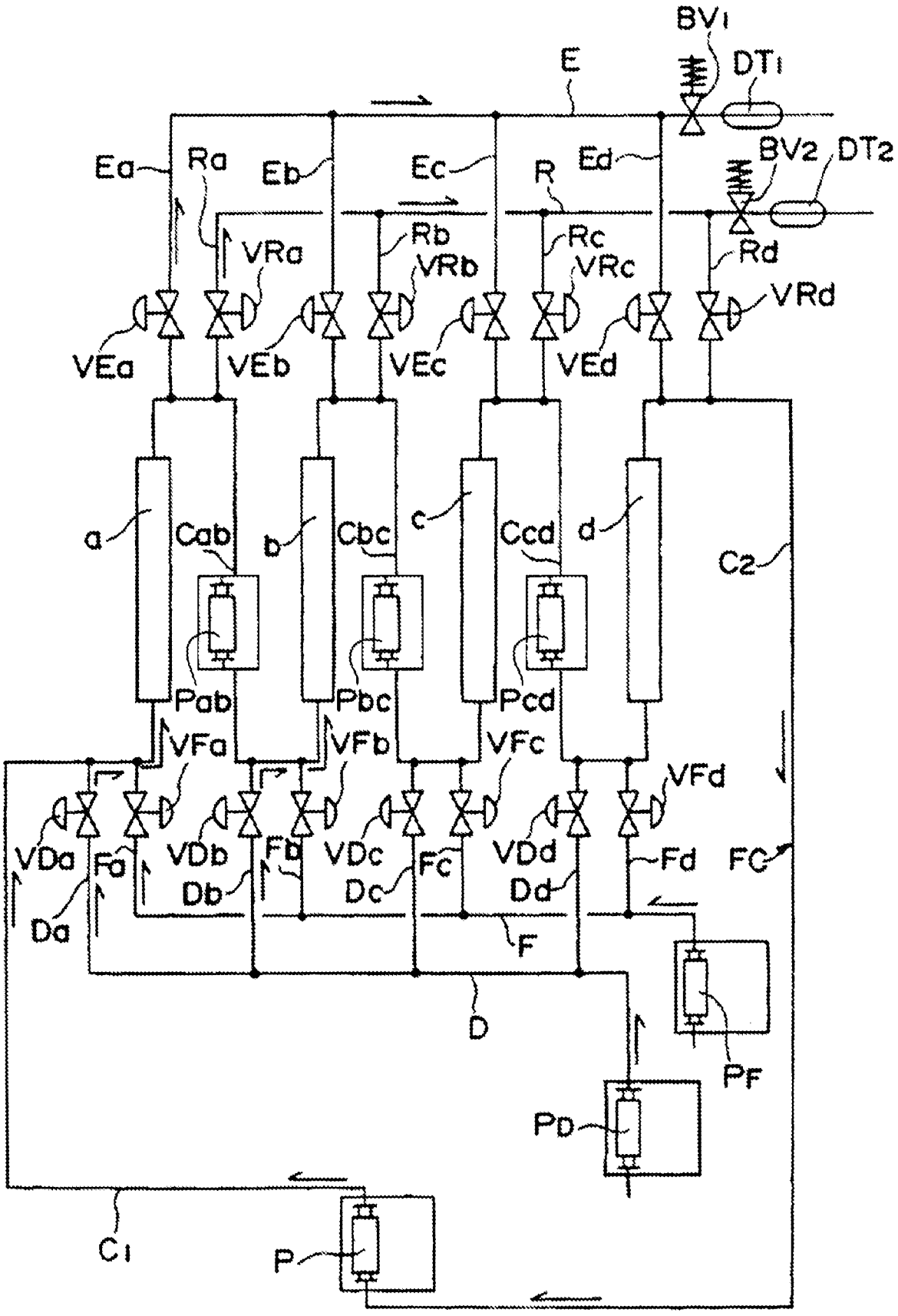
5) A method as claimed in Claim 4, characterized in that said crystallization step f) is performed with a temperature gradient of 70 to 25°C.

6) A method as claimed in any one of Claims 1 to 5, characterized in that said chromatographic separation step d) is performed on ion-exchange resins.

7) A method as claimed in Claim 6, characterized in that said ion-exchange resins are cation resins.

8) A method as claimed in Claim 7, characterized in that said cation resins are styrene-divinylbenzene resins derivatized with sulphone groups.

FIG. 1


BV1
DT1
E
Ea
Ra
Eb
Ec
R
Ed
BV2
DT2
Rb
Rc
Rd
VRa
VRb
VRc
VRd
VEa
VEb
VEc
VEd
a
Cab
b
Cbc
c
Ccd
d
C2
Pab
Pbc
Pcd
VFa
VFb
VFc
VFd
VDa
Fa
VDb
Fb
VDc
Fc
VDd
Fd
FC
Da
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P

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
INV. A23L2/78 C12G1/02 C13K1/00 C13K3/00 C13K11/00
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A23L C12G C13K

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, BIOSIS, EMBASE, FSTA, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	FR 2 912 036 A1 (NUTRITIS [FR]; INST NAT SCIENCES APPLIQ [FR]) 8 August 2008 (2008-08-08) the whole document	1-8
Y	WO 2006/125286 A1 (GETEC GUANABARA QUIMICA IND S [BR]; FERREIRA JOAO AFONSO [BR]; TEIXEIR) 30 November 2006 (2006-11-30) page 4, line 15 - line 22; figure 1 page 7, line 13 - page 8, line 25	1-8
Y	WO 03/016577 A1 (GETEC GUANABARA QUIMICA IND S [BR]; DE MENDONCA FERREIRA JOAO AFON [BR]) 27 February 2003 (2003-02-27) page 17, line 26 - page 18, line 27	1-8

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

"&" document member of the same patent family

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 292 803 A1 (DANISCO [DK] DUPONT NUTRITION BIOSCI APS [DK]) 9 March 2011 (2011-03-09) paragraph [0043]; examples 1-8 -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2012/054210

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2912036 A1	08-08-2008	AR 065101 A1	13-05-2009
		AT 487801 T	15-11-2010
		CA 2676989 A1	12-09-2008
		CL 2252008 A1	02-05-2008
		CN 101668867 A	10-03-2010
		DK 2126142 T3	21-02-2011
		EP 2126142 A2	02-12-2009
		ES 2356175 T3	05-04-2011
		FR 2912036 A1	08-08-2008
		IL 200133 A	28-02-2013
		JP 2010517522 A	27-05-2010
		KR 20090116770 A	11-11-2009
		MA 31230 B1	01-03-2010
		PT 2126142 E	09-02-2011
		US 2010006091 A1	14-01-2010
		WO 2008107560 A2	12-09-2008
		ZA 200905961 A	26-05-2010
WO 2006125286 A1	30-11-2006	BR PI0520266 A2	28-04-2009
		WO 2006125286 A1	30-11-2006
WO 03016577 A1	27-02-2003	BR 0103406 A	04-05-2004
		EP 1417354 A1	12-05-2004
		JP 2004537326 A	16-12-2004
		US 2004231662 A1	25-11-2004
		WO 03016577 A1	27-02-2003
EP 2292803 A1	09-03-2011	NONE	

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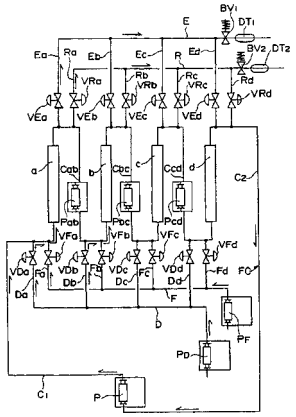
权利要求书1页 说明书4页 附图1页

(54)发明名称

从水果中制备糖产品的方法

(57)摘要

一种从水果中制备糖产品的方法，该方法包括步骤：a)提供含有葡萄糖和果糖的果汁；b)去除果汁的矿物质并脱色，获得澄清、脱矿物质果汁；c)对澄清、脱矿物质果汁进行浓缩，获得浓缩澄清脱除矿物质果汁；以及d)通过色谱法将浓缩、澄清脱矿物质果汁分离，获得至少富含葡萄糖部分和至少富含果糖部分；所述方法包括在步骤d)后，在碳过滤器上过滤富含葡萄糖的部分和富含果糖的部分的步骤e)；步骤d)和e)在50-70℃的温度下进行。



CN 104837376 A

1. 一种从水果中制备糖产品的方法，所述方法包括步骤：

a) 提供含葡萄糖和果糖的果汁；

b) 将所述果汁去除矿物质和脱色以获得澄清脱矿物质果汁；

c) 浓缩所述澄清脱矿物质果汁以获得浓缩的澄清脱矿物质果汁；以及

d) 通过色谱法将所述浓缩的澄清脱矿物质果汁分离，获得至少富含葡萄糖部分和至少富含果糖部分；

所述方法的特征在于，在步骤 d) 之后，含有在碳过滤器上过滤所述富含葡萄糖部分和所述富含果糖部分的步骤 e)；以及所述步骤 d) 和 e) 在 50-70℃的温度下进行。

2. 如权利要求 1 所请求保护的方法，其特征在于，所述温度为 57℃ -65℃之间。

3. 如权利要求 1 或 2 请求保护的方法，其特征在于，步骤 d) 和 e) 中所述温度维持恒温。

4. 如权利要求 1 至 3 任一项请求保护的方法，其特征在于，在步骤 e) 之后，含有结晶所述富含葡萄糖部分和所述富含果糖部分的步骤 f)。

5. 如权利要求 4 请求保护的方法，其特征在于，所述结晶步骤 f) 以 70-25℃的温度梯度进行。

6. 如权利要求 1 至 5 任一项请求保护的方法，其特征在于，所述色谱分离步骤 d) 在离子交换树脂上进行。

7. 如权利要求 6 请求保护的方法，其特征在于，所述离子交换树脂是阳离子树脂。

8. 如权利要求 7 请求保护的方法，其特征在于，所述阳离子树脂是衍生有砜基的苯乙烯 - 二乙烯苯树脂。

从水果中制备糖产品的方法

技术领域

[0001] 本发明涉及一种从水果中制备液态或固态糖产品，特别是葡萄糖和果糖的方法。

背景技术

[0002] 从果汁，特别是葡萄汁中制备如葡萄糖和果糖的糖已是已知的。

[0003] 果汁，如通过压榨水果获得，通常先加工去除非糖成分，随后通过色谱法将糖（主要葡萄糖）与果糖分离。由此得到的液态或随后结晶状的产品通常用于食品工业或直接食用，例如，作为甜味剂。

[0004] EP1734108 和 EP2425723 描述了一种由葡萄制备糖产品的方法，其中浓缩精馏葡萄汁溶液经色谱处理，以得到随后结晶的葡萄糖溶液和果糖溶液。

[0005] 在色谱阶段之前，通过破碎葡萄而获得的果汁被澄清和去除矿物质，随后浓缩到适于色谱处理的合适浓度。然而，EP1734108 和 EP2425723 的方法具有不包括降低糖溶液颜色的处理和没有控制具有抑制结晶性质的羟甲基糠醛 (HMF) 含量的缺点。此外，色谱处理无法提供完全的、令人满意的葡萄糖和果糖的分离，尤其是准确、均匀提取。因此，存在对意在消除上述缺点的、从果汁中分离糖，尤其葡萄糖和果糖的方法的需求，所述方法尤其提供控制羟甲基糠醛 (HM) 水平、准确、均匀地从水果中提取糖，同时保护糖的完整性，并且能量损耗低。

发明内容

[0006] 本发明的目标是提供一种从水果中制备糖的方法，该方法意在允许控制羟甲基糠醛水平，从水果中准确均匀地提取糖，同时保护糖的完整性，比已知方法能量损耗低，且产品纯度与已知方法可比。

[0007] 根据本发明，提供如权利要求 1 所请求保护的方法。

附图说明

[0008] 通过实施例以及特别参考葡萄 (grape) 和附图描述本发明非限制性的实施方式，其中：

[0009] 附图 1 显示根据本发明的分离葡萄糖溶液和果糖溶液的色谱系统。

具体实施方式

[0010] 在本发明中，术语“果汁”指的是葡萄汁，具体而言是从破碎葡萄中获得的果汁。

[0011] 过滤除去任意剩余固体后，例如通过加入明胶、膨润土和碳来澄清以形成果汁，同时去除矿物质，例如在离子树脂上。可选的，根据 EP2425723 所述进行澄清和去除矿物质。

[0012] 该阶段制备了以干物质计含糖（特别是葡萄糖和果糖）百分比高于 98％，例如 98.5％的澄清、脱矿物质果汁。

[0013] 然后，浓缩澄清脱矿物质果汁以降低其水分含量，但不改变其固体部分的组成。所

获得的浓缩果汁，也被称为精馏浓缩葡萄汁，是一种包含以干物质计高于 98％的果糖和葡萄糖的无色溶液，而其剩余部分由例如乙醇、黄酮和其他多酚的组分构成。

[0014] 所述浓缩精馏葡萄汁随后被加热到 50-70℃的温度，特别是 57-65℃，例如 60℃。有利的是，在这些温度下，浓缩精馏葡萄汁具有能在色谱处理中给予均匀前沿的粘度系数（＜ 10mPa*s）。

[0015] 在这些温度下，果汁中的葡萄糖和果糖可被有效分离而无需高压洗脱剂，且最为重要的是无需改变糖的稳定性和 / 或使色谱树脂劣化。

[0016] 因此，尽管在比已知方法的室温更高的温度下操作，总的来说，改善后的糖分离使得根据本发明方法的总能耗显著降低。

[0017] 随后对浓缩精馏葡萄汁进行色谱分离，尤其是在离子交换树脂上，更具体的是在阳离子树脂上，并且优选在衍生有砜基的苯乙烯 - 二乙烯苯树脂上。所用树脂可具有 EP2425723 中所述的特征。

[0018] 色谱分离在如附图 1 所示的模拟流化床系统中进行。

[0019] 图 1 的系统包含四个柱子 :a、b、c 和 d，各带有一用于泵入过柱的循环流体（例如洗脱剂）的泵 (P、Pab、Pbc、Pcd)。

[0020] 四个柱子被阳离子树脂填充，优选砜基衍生的苯乙烯 - 二乙烯苯树脂。

[0021] 柱 a 的出口通过与泵 Pab 匹配的线 Cab 连接到柱 b 的入口 ;柱 b 的出口通过与泵 Pbc 匹配的线 Cbc 连接到柱 c 的入口 ;柱 c 的出口通过与泵 Pcd 匹配的线 Ccd 连接到柱 d 的入口 ;柱 d 的出口通过线 C_2连接到泵 P 的入口 ;以及泵 P 的出口通过线 C_1连接到柱 a 的入口。柱 a-d、线 C_1、C_2、Cab、Cbc、Ccd 和泵 P、Pab、Pbc、Pcd 如此组成分离回路 FC，循环流体即洗脱剂（例如去离子水），沿图 1 中箭头方向循环。

[0022] 洗脱剂供料液管线 Da-Dd 和进入分离回路 FC 的浓缩精馏葡萄汁供料液管线 Fa-Fd 连接到接近柱 a-d 各自出口的分离回路 FC。

[0023] 用于从分离回路 FC 中提取富含葡萄糖部分的葡萄糖提取线 Ea-Ed，以及用于从分离回路 FC 中提取富含果糖部分的果糖提取线 Ra-Rd 连接到接近柱 a-d 各自出口的分离回路 FC。

[0024] 洗脱剂供料液管线 Da-Dd 从与洗脱剂泵 P_D末端相连的洗脱剂进料管 D 分支出来 ;且浓缩精馏葡萄汁供料液管线 Fa-Fd 从与浓缩精制葡萄汁泵 P_F末端相连的浓缩精制葡萄汁进料管 F 分支出来。

[0025] 开关阀门 VDa-VDd 分别沿着洗脱剂供料液管线 Da-Dd 安装 ;而开关阀门 VFa-VFd 分别沿着浓缩精馏葡萄汁供料液管线 Fa-Fd 安装。

[0026] 开关阀门 VEa-VEd 分别沿着葡萄糖提取线 Ea-Ed 安装 ;而开关阀门 VRa-VRd 分别沿着果糖提取线 Ra-Rd 安装。

[0027] 葡萄糖提取线 Ea-Ed 与葡萄糖提取管 E 相连。

[0028] 果糖提取线 Ra-Rd 与果糖提取管 R 相连。

[0029] 所述附图 1 的系统操作如下。

[0030] 洗脱剂优选去离子水或至少具有低钙含量的任意级别的水，用洗脱剂作为循环液体填充系统以启动系统后，洗脱剂供料液管线 Da-Dd 的其中一个，葡萄糖提取线 Ea-Ed 的其中一个，浓缩精制葡萄汁供料液管供料液管线 Fa-Fd 的其中一个和果糖提取线 Ra-Rd 的其

中一个连接以按下列顺序放置：洗脱剂供料液管线、葡萄糖提取线、浓缩精馏葡萄汁供料液管线、果糖提取线通过阀门 VDa-VDd、VEa-VEd、VFa-VFd 和 VRa-VRd 的开启和闭合，在分离回路 FC 中沿着循环液体的方向。

[0031] 例如，洗脱剂供料液管线 Da、葡萄糖提取线 Ea、浓缩精制葡萄汁供料液管线 Fc 以及果糖提取线 Rc 通过开启阀门 VDa、VEa、VFc、VRc 和关闭所有其他阀门被连接到分离回路 FC 中。

[0032] 这导致形成柱 a 中位于洗脱剂供料液管线 Da 和葡萄糖提取线 Ea 之间的洗脱区 IV，柱 b 中位于葡萄糖提取线 Ea 和浓缩精制葡萄汁供料液管线 Fc 之间的浓缩区 III，柱 c 中位于浓缩精制葡萄汁供料液管线 Fc 和果糖提取线 Rc 之间的精制区 II，以及柱 d 中位于果糖提取线 Rc 和洗脱剂供料液管线 Da 之间的吸收区 I。

[0033] 在包含洗脱区的柱 a 中，被树脂保留的葡萄糖被来自线 Da 的洗脱剂洗脱，且转移至分离回路 FC 的循环液体中。因此，在柱 a 的入口处，循环液体几乎不含葡萄糖。所述葡萄糖的浓度随着循环液体流经柱 a 而提高，且柱 a 出口处的循环液体包含大量葡萄糖（富含葡萄糖部分），其部分被葡萄糖提取线 Ea 从分离循环中提取并收集于葡萄糖罐，而剩余部分则被注入柱 b 中。

[0034] 在包含浓缩区 III 的柱 b 中，随着循环液体流经柱 b，来自柱 a 循环液体的葡萄糖被树脂保留。同时，柱 b 中被树脂保留至低于葡萄糖浓度的果糖被转移到循环液体中，因此在流经柱 b 的循环液体中的葡萄糖浓度降低，而果糖浓度则升高。来自柱 b 的循环液体与来自线 Fc 的部分浓缩精制葡萄汁随后被一同注入柱 c 中。

[0035] 在包含精制区 II 的柱 c 中，在来自线 Fc 的浓缩精制葡萄汁和循环液体中的葡萄糖被树脂保留，柱 c 中之前被树脂保留的果糖转移至循环液体。因此，柱 c 入口，循环液体几乎不包含葡萄糖，而果糖浓度却随着循环液体流经柱 c 而提高。来自柱 c 且包含大量果糖（富含果糖部分）的循环液体经果糖提取线 Rc 被部分提取并被收集于果糖罐，部分则被注入柱 d。

[0036] 在包含吸收区 I 的柱 d 中，来自柱 c 的循环液体中的大量果糖被树脂保留，因此在柱 d 出口，循环液体实际上不包含葡萄糖和果糖，且沿着线 C_1和 C_2反馈至柱 a。

[0037] 在给定时间间隔 (6.5 分钟）后，关闭阀门 VDa、VEa、VFc、VRc 并开启阀门 VDb、VEb、VFd、VRd。开启和关闭上述阀门决定了洗脱区 IV 从柱 a 转移到柱 b，浓缩区 III 从柱 b 转移到柱 c，精制区 II 从柱 c 转移到柱 d，以及吸收区 I 从柱 d 转移到柱 a。

[0038] 在柱 b 中，被树脂保留的葡萄糖因此被来自线 Db 的洗脱剂洗脱；柱 b 的循环液体（富含葡萄糖部分）被葡萄糖提取线 Eb 部分提取且被收集于葡萄糖罐中，剩余部分沿线 Cbc 被反馈到柱 c。

[0039] 在柱 c 中，柱 b 循环液体中的葡萄糖被树脂保留，被树脂保留至较低程度的果糖转移至循环液体中，因此随着循环液体流经柱 c，循环液体中的葡萄糖浓度降低，果糖浓度升高。

[0040] 柱 c 的循环液体与浓缩精制葡萄汁供料液管线 Fd 中的浓缩精制葡萄汁一同被注入到柱 d。在柱 d 中，浓缩精制葡萄汁和循环液体中的葡萄糖被树脂保留，而果糖被转移到循环液体中。以及在柱 d 的出口处，部分循环液体（富含果糖部分）被果糖提取线 Rd 提取并收集于果糖罐，剩余部分注入柱 a 中。

[0041] 在柱 a 中，循环液体的葡萄糖和果糖被树脂保留，因此来自柱 a 的循环液体不含葡萄糖和果糖，且被反馈到柱 b。

[0042] 在给定的时间间隔 (6.5 分钟) 后，关闭阀门 VDb、VEb、VFd、VRd 而开启阀门 VDc、VEc、VFa、VRa。开启和关闭上述阀门决定了洗脱区 IV 从柱 b 转移洗脱区 IV 到柱 c，浓缩区 III 从柱 c 转移浓缩区 III 到柱 d，精制区 II 从柱 d 转移精制区 II 到柱 a，以及吸收区 I 从柱 a 转移吸收区 I 到柱 b 的转移 ；且如上所述重复所述过程。

[0043] 色谱分离在温度 50-70℃下，更具体的在 57-65℃下，例如 60℃下进行。

[0044] 这些温度下，果汁中的葡萄糖和果糖可被有效分离而无需高压洗脱剂，且尤其是不会改变糖的稳定性和 / 或劣化色谱树脂。

[0045] 另一方面，这些温度极大地提高源自糖的热分解的羟甲基糠醛 (HMF) 的量。

[0046] 在根据本发明的制造方法中，浓缩精制葡萄汁和其中的糖在系统中被保存数日。在其结晶之前，糖分子在温度 70-28℃下在系统过程溶液中保留 5-10 天的时间段，因此，尽管很少，必然会产生一定量的 HMF。

[0047] 过量的羟甲基糠醛可能会致使结晶阶段无效和大大降低结晶效率。事实上，羟甲基糠醛是一种公知的果糖结晶抑制剂。

[0048] 过量的羟甲基糠醛对果糖结晶具有以下作用 ：

[0049] 含 20ppm HMF 的果糖糖浆 -60％结晶效率

[0050] 含 50ppmHMF 的果糖糖浆 -55％结晶效率

[0051] 含 200ppmHMF 的果糖糖浆 -45％结晶效率

[0052] 因此色谱分离阶段随后是使用碳过滤器 (例如活性碳 -3- 微米过滤 BECODISC Filters®) 的过滤阶段，该过滤阶段除了减少色谱洗脱物的颜色外，还截留包含在其中的 HMF 以获得高效的结晶效率。

[0053] 在色谱和过滤阶段，温度均优选维持恒温。

[0054] 过滤后的富含果糖的部分和富含葡萄糖的部分随后，例如在蒸汽浓缩器中，浓缩到制备消费用液态糖产品或结晶品所需的白利糖度 (Brix)，对于果糖大致为 88° 白利糖度和对于葡萄糖为 75° 白利糖度。在色谱和过滤之后，富含葡萄糖部分的纯度高于 86％，富含果糖部分的纯度高于 96％。

[0055] 色谱分离、过滤和浓缩优选在 50-70℃恒温下，更具体地在 57-65℃恒温下，例如 60℃恒温下进行。

[0056] 获得的液态糖产品可随后通过从温度 50-70℃到温度 25-30℃冷却而被结晶，且可能诱导果糖或葡萄糖晶体。与已知方法中使用的 12-13℃温度相反，这些结晶温度具有提高糖结晶效率和大大降低能耗的优势。

[0057] 获得的结晶终产物纯度高于 99％。

[0058] 上述说明中提及的所有文献以参考方式被引入。

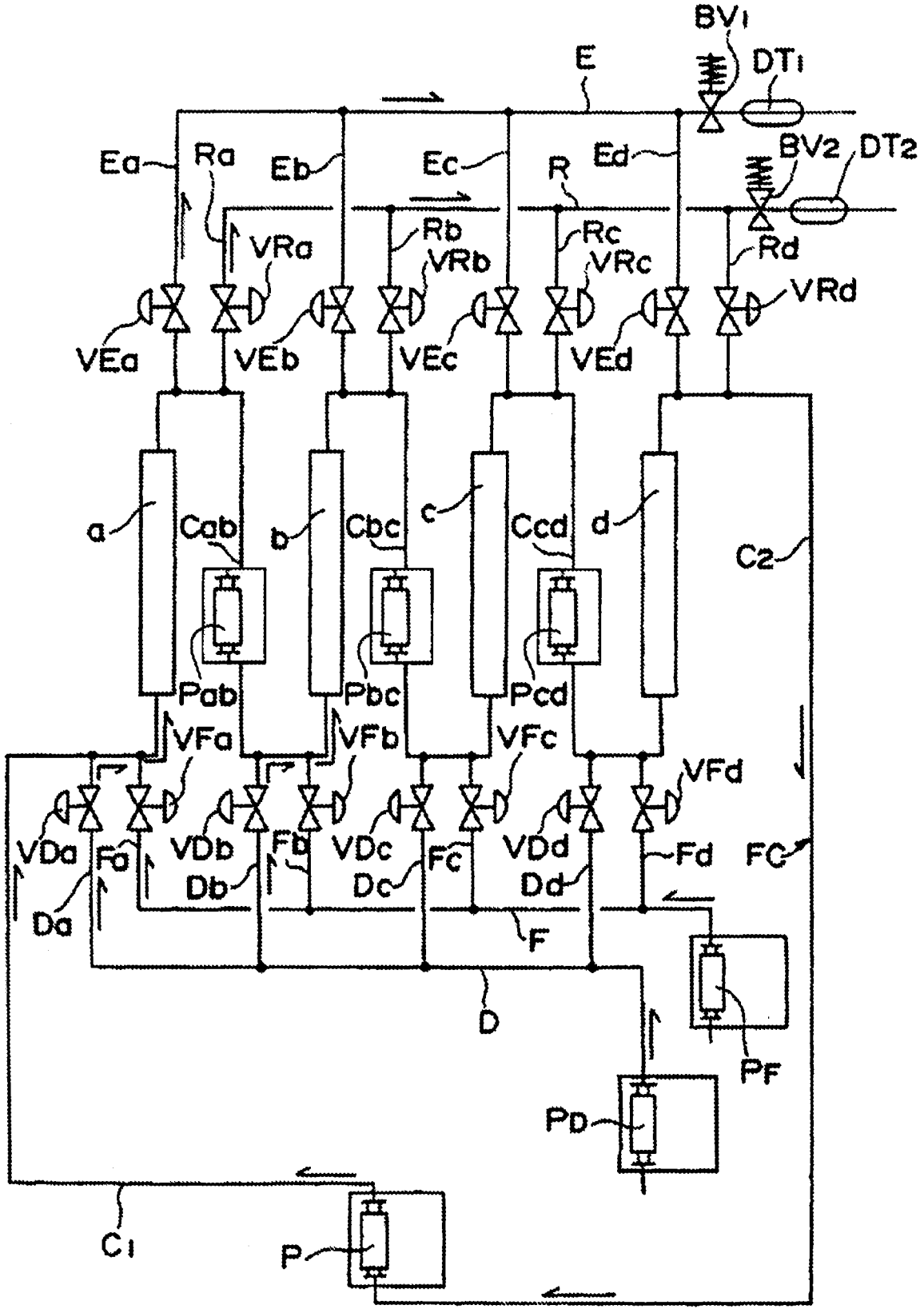

BV1
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VEa
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VEd
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Cab
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图 1