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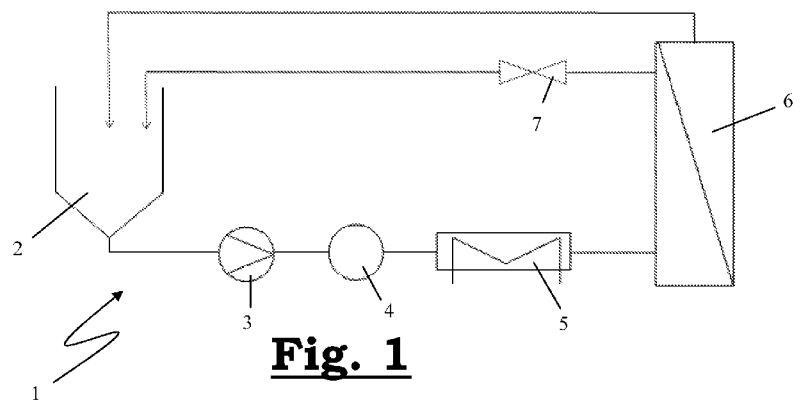

Fig. 1

(57) Abstract: The invention concerns a process for the preparation of a sorbitol rich syrup having less than 0.2% on ds of total reducing sugars, wherein said process comprises the following steps: (i) hydrogenation of a glucose syrup having a glucose content of 94% to 97% on dry substance (d.s.), (ii) separation step of the hydrogenated glucose syrup by at least one membrane nanofiltration stage to obtain a permeate and a retentate, wherein the permeate is a sorbitol rich syrup having at least 99.2% by weight on ds of hexitol, less than 0.2% by weight on ds of total reducing sugars and less than 0.3% by weight on ds of sugar alcohols having a molecular mass higher than hexitols. The invention also concerns a sorbitol rich syrup having at least 99.2% by weight on ds of hexitol, less than 0.1% by weight of total reducing sugars on ds and less than 0.2% by weight on ds of sugar alcohols having a molecular mass higher than hexitols.

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PROCESS FOR PREPARING A SORBITOL RICH SYRUP OF HIGH PURITY

This invention relates to a process for the preparation of a sorbitol rich syrup of high purity, with less than 0.2% total reducing sugars on ds and the sorbitol syrup thus obtained.

In the prior art several processes are described for the preparation of sorbitol rich syrups among which, the hydrogenation of a solution of crystalline dextrose monohydrate such as illustrated in the International Patent Application WO 2012/045985 (Example 2). The syrup obtained contains 98.6% of sorbitol, a limited number of by-products, and 0.18% total reducing sugars at 70% dry substance (thus 0.26% on ds), as determined by means of Bertrand method. The dextrose syrup used is a highly pur syrup obtained by use of crystalline dextrose, that means after a purification step via a crystallization process of high-Dextrose (D-glucose) syrup.

An alternative method for the preparation of a sorbitol rich syrup, involves performing a purification step via a nanofiltration treatment of a high Dextrose starch hydrolyzate in order to obtain in this way a so-called D99 syrup (a syrup which contains more than 99% glucose). The D99 syrup is then hydrogenated to obtain a sorbitol rich syrup. Such a process is described in the American Patent Application U.S. 5,869,297.

The Chinese Patent Application CN 1928121 discloses a method in which a glucose syrup with a high Dextrose is purified by using the "simulated moving bed chromatography" technology, whereby a fraction with more than 99.0% glucose is obtained. The glucose syrup is then hydrogenated to a high sorbitol syrup.

The above-mentioned processes for preparing high sorbitol syrups have a number of drawbacks with regard to the substrate or with respect to the operations that are carried out in order to obtain such a high purity substrate.

Firstly, the prior art methods use expensive substrates. Indeed, Dextrose monohydrate is a rather expensive substrate which can be better exploited in other applications. The inventors envisaged the use of less expensive products such as glucose-rich products having a reduced purity. For example, the mother liquor

obtained during dextrose crystallization, or, changeover losses when using a single sugar alcohol production line for making various products. The use of glucose-rich products having a reduced purity increases the productivity of such facilities.

Concerning the purification of the substrate before hydrogenation, if nanofiltration is used to purify high Dextrose syrups into glucose fractions with a high purity (i.e. glucose concentration> 99%), then relatively low fluxes are obtained. Higher fluxes can be obtained by increasing the pH at which the nano-filtration is done but this is at the cost of purity. Relatively low fluxes are also obtained during nanofiltration of "changeover losses" and "mother liquors" (hereafter retentates), as when crystalline dextrose is used. The prior art does not provide solution to this problem.

Besides, using another purification process such as chromatographic separation does not provide a relevant solution. Indeed, compared to the use of nanofiltration, chromatographic separation is technically more complicated, and requires a higher investment and a higher operational cost. Moreover, similar drawbacks with respect to the formation of the "mother liquors", and "changeover losses" are also observed.

The German Patent Application DE19612826 discloses a process for the preparation of highly pure sorbitol. Thereby, an intermediate of sorbitol syrup containing more than 98% of sorbitol is further chromatographed, whereby a high-purity sorbitol syrup, containing more than 99% sorbitol, and 0.15% of total reducing sugars is obtained. The sorbitol syrup thus obtained is color stable during acidic and /or alkaline heat treatment.

However, this process is quite complicated. Indeed, the glucose substrate which is hydrogenated contains more than 99% glucose and is obtained by a first purification step such as a crystallization, nanofiltration or chromatography.

From the above description of the state of the art it is clear that there is a need for a simpler and therefore less costly process, having a good productivity and which uses a low value substrate as glucose-rich products having a reduced purity such as mother liquors or changeover losses, for the preparation of a sorbitol syrup of high purity which contains less than 0.2% total reducing sugars. Besides, prior art does not provide a highly heat stable sorbitol syrup that means a syrup which is

stable during one hour at 200°C. Such stability is particularly relevant for a number of chemical applications such as for example polyurethane foams, anhydrohexitol based surfactants (TWEEN, SPAN surfactants...).

After an extensive research, the inventors were able to develop a low cost, unique, stable and reproductive process for producing with a high yield, sorbitol rich syrups of high purity by using low commercial value substrates. The invention is achieved by providing a **process for the preparation of a sorbitol rich syrup** having less than 0.2% total reducing sugars, wherein said process comprises the following steps:

- hydrogenation of a glucose syrup having a glucose content of 94% to 97% on dry substance (d.s.),

- separation step of the hydrogenated glucose syrup by at least one membrane nanofiltration stage to obtain a permeate and a retentate, wherein the permeate is a sorbitol rich syrup having at least 99.2% by weight of hexitol, less than 0.2% by weight of total reducing sugars and less than 0.3% by weight of sugar alcohols having a molecular mass higher than hexitols.

Indeed, the inventors have shown a surprising improvement of productivity of a process for obtaining a high sorbitol syrup by applying i) a hydrogenation step on a moderate glucose content syrup and ii) a separation step by membrane nanofiltration after the hydrogenation step. By proposing a hydrogenation of a moderate glucose content syrup instead of hydrogenation of a high glucose content syrup, the process of the invention avoids a two-step purification needed for removal of by-products such as DP2 formed during hydrogenation. Moreover, the hydrogenation is applied on a low cost substrate which has no incidence on the productivity of this step but which also reduces the costs related to losses in change-overs from high purity dextrose into other, lower purity feedstocks hydrogenated in the same line. In addition, nanofiltration of dextrose syrup compared to nanofiltration of sorbitol syrup results in a higher volume of retentate having a reduced purity and thus, a higher volume of low-value syrup.

Typically, the "**glucose syrup**" according to the invention is a high dextrose glucose syrup which is well known in the prior art. Nowadays, such a glucose syrup can be prepared by the enzymatic liquefaction and saccharification of starch. In the

present invention, a glucose level as high as possible is desirable, because such syrups may also be used as a substrate for the production of crystalline dextrose, sorbitol or isoglucose. In one embodiment, the glucose concentration may vary between 92 and 98%, preferably, 94 and 97% on dry substance (d.s.). The process for obtaining such dextrose syrup is extensively described in the patent and technical literature. (eg *" Starch Hydrolysis Products " by W. Schenk and RE Hebeda -1992, p.110*).

According to the invention, the hydrogenation may be performed as described in prior art and notably in *Roland Albert et al, Chem Ing Tech 52 (1980) Nr 7 S. 582 – 587*.

In one embodiment, the hydrogenation may be performed by known catalysts such as Raney Ni or Ru/C.

The sorbitol syrup thus obtained has typically about 92-96% sorbitol on d.s., preferably 94-95%, typically, a small amount of other hexitols such as mannitol and iditol, maltitol (2.5-3.5% d.s.), a minor amount of hydrogenated oligosaccharides and some of the lower MW degradation products. The maltitol and hydrogenated oligosaccharides fractions present in the syrup are responsible for color formation during thermal treatment under acidic conditions, because of the release of reducing sugars and their thermal decomposition.

The removal of these components will then greatly reduce the level of color-forming compounds.

The inventors have shown that surprisingly, a separation by membrane nanofiltration of the hydrogenated glucose syrup of reduced purity provides also an unexpected improvement of the yield and selectivity of said nanofiltration comparing with prior art processes to obtain sorbitol rich syrups of high purity using a nanofiltration on the glucose syrup of reduced purity. Indeed, during nanofiltration, of said hydrogenated high glucose syrup of reduced purity, an increasing flow rate can be observed without reducing subsequently the purity of the permeate obtained.

Hereby, the inventors have unexpectedly shown that by applying the nanofiltration in the conditions of the invention, compared with the non-hydrogenated equivalent, and notably with corresponding glucose syrup, that the sorbitol syrup, when administered under the same conditions of pressure and

temperature to the nanofiltration system, exhibited an increased flux at the permeate side that was 50 to 100% higher than the one obtained with the corresponding glucose syrup.

Moreover, the inventors have demonstrated that despite their similar molecular masses and similar characteristics, a separation step by membrane nanofiltration applied to said hydrogenated high glucose syrup of reduced purity shows a surprising increase in selectivity compared to a separation step by membrane nanofiltration under the same conditions of a high glucose syrup of reduced purity. This means that a higher purity and at the same time a higher productivity is reached with a sorbitol rich substrate comparing with an equivalent glucose rich composition, if the same conditions are used.

According to the invention, the expression "**separation by membrane nanofiltration**" or "**Nanofiltration**" refers to a pressure-driven membrane filtration process, situated between reverse osmosis and ultrafiltration. Nanofiltration typically retains large and organic molecules with a molar mass of more than 300-500g/mol. Suitable nanofiltration membranes are composite membranes, notably polymeric and/or organic membrane, such as those made by interfacial polymerisation.

According to the invention the membrane nanofiltration stage means one nanofiltration module or several nanofiltration modules in parallel.

The inventors have found that a great improvement is observed when the process of the invention comprises a separation step having two membrane nanofiltration stages. Typically, wherein the permeate of the first membrane nanofiltration stage is then applied on the second membrane nanofiltration stage and wherein the permeate of the second membrane nanofiltration stage is the sorbitol rich syrup, preferably, the retentate of the second membrane nanofiltration stage is recycled in the first membrane nanofiltration stage.

The nanofiltration membranes which may be used in the process according to the invention typically have a Molecular Weight Cut Off (MWCO) of 300 or less. Molecular weight cut-off or MWCO refers to the lowest molecular weight solute (in daltons) in which 90% of the solute is retained by the membrane or the molecular weight of the molecule (e.g. globular protein) that is 90% retained by the membrane. Typical polymeric nanofiltration membranes which are used in the present invention

include, for example, aromatic polyamide membranes, polysulfone membranes, sulfonated polysulfone membranes, polyether sulfone membranes, polyester membranes, and combinations of the membranes listed. The polyamide membranes and polysulfone membranes are prefered. Typical inorganic membranes are, for example, zirconium oxide and aluminum oxide membranes.

The typical shape of the nanofiltration membrane is in the form of spiral wound elements. However, other shapes for the membrane are also possible, for example, tubular, flat and hollow fiber membranes.

In one embodiment, the separation by membrane nanofiltration is carried out with a hydrogenated glucose syrup having a hydrogenated glucose content comprised between 30 and 60% preferably 40% and 50% on cp.

Nanofiltration is typically carried out at a pH of from 4 to 8, preferably from 4.5 to 7.

In one embodiment, said separation by membrane nanofiltration is performed at a temperature between 20 and 80°C, preferably 25°C to 75°C, more preferably, 30°C to 45°C, or 32°C to 40°C.

In one embodiment, said separation by membrane nanofiltration is performed at a pressure between 15 to 75 bar, preferably 25 to 70 bar, more preferably 55 to 40 bar or 50 to 38 bar.

Typically, said nanofiltration may be carried out at a temperature between 20 and 80°C and at a pressure of 15 to 75 bar, preferably, at a temperature of about 25°C to 75°C and a pressure between 25 to 70 bar, more preferably, at a temperature of about 30°C to 45°C and a pressure of about 55 to 40 bar, and even more preferably, at a temperature of about 30°C to 40°C and a pressure of about 50 to 40 bar.

Preferably said separation by membrane nanofiltration is performed at a temperature between 20 and 80°C and at a pressure between 15 to 75 bar, wherein said hydrogenated glucose syrup has a dry substance (d.s.) content comprised between 30% and 60%.

Typically, said separation by membrane nanofiltration is performed at a temperature of about 30°C to 45°C and at a pressure of about 55 to 40 bar, or at a

temperature of about 30°C to 40°C and at a pressure of about 50 to 40 bar wherein said hydrogenated glucose syrup has a dry substance (d.s.) content comprised between 40% and 50%.

During nanofiltration separation two fractions are provided one that is called the permeate and the other, the retentate. The "**permeate**" refers to the fraction of the liquid that passes through the membrane while the "retentate" refers to the fraction that does not pass through the membrane.

According to the process of the invention, the permeate refers to the sorbitol rich syrup according to the invention.

In the context of the invention, the expression "**sorbitol rich syrup**" means a sorbitol syrup having a high purity and which consists essentially of sorbitol. More particularly, said sorbitol rich syrup has a sorbitol content of more than 97.5% on dry substance (d.s), preferably more than 98% on dry substance (d.s.).

Indeed, said sorbitol rich syrup obtained according to the process of the invention has less than 3%, and preferably less than 2% on dry substance (d.s.) of sugar alcohols other than sorbitol. Said sugar alcohols other than sorbitol are typically isomeric hexitols and sugar alcohols having a molecular mass higher than hexitols (DP2 and higher hydrogenated oligosaccharides). Isomeric hexitols are for example mannitol and iditol. DP2 are typically maltitol and isomaltitol. In one embodiment, said sorbitol rich syrup has a fraction of sugar alcohols having a molecular mass higher than hexitols (DP2 and higher) of less than 0.3%, preferably less than 0.2%, more preferably, less than 0.15% on d.s. Hence, the sorbitol rich syrup according to the invention may have a content of hexitols (DP1-ol) of more than 99.3%, preferably, more than 99.4%, more preferably, more than 99.5%, even more preferably, more than 99.55% or more than 99.85%.

Accordingly, such sorbitol rich syrups exhibit a high chemical stability against acids and bases, as well as against thermal stresses.

The remaining part of the permeate obtained, is composed of fractions with a similar or lower molecular weight than the hexitols such as mannitol, iditol, arabitol glycerol and erythritol.

Improved membrane selectivity between the hydrogenated glucose and high molecular weight compounds was observed, as compared to this between the non-

hydrogenated glucose and high molecular weight counterparts, despite of the similar molecular weight of hydrogenated and non-hydrogenated counterparts. The selectivity has been measured for a hydrogenated glucose syrup by the “maltitol reduction factor" (MRF '), or the equivalent thereof during nanofiltration of a non-hydrogenated glucose syrup, the "maltose reduction factor" (MRF). This "maltitol reduction factor" or its equivalent, the "maltose reduction factor", is the expression of the ratio maltitol (maltose) present in the retentate and the permeate. The higher this value, the better the separation selectivity is between DP1 and DP2-sugars or sugar alcohols.

The inventors have demonstrated that this "maltitol reduction factor", is higher compared to the "maltose reduction factor" for nanofiltration of a non-hydrogenated glucose syrup in the same conditions, with a percentage ranging between 10% and 200% (as will be explained further in the examples), and results in a higher purity at a higher flux. The combination of both factors is thus resulting in a sharp increase in the efficiency of the nanofiltration separation process during the treatment of the sorbitol syrup, in comparison with the corresponding glucose syrup.

The inventors have also demonstrated that the processing of such sorbitol syrup by means of nanofiltration makes it possible to reduce in a very efficient way sugar alcohols having a molecular mass higher than hexitols in the permeate, whereby a high-purity sorbitol syrup is obtained with less than 0.2% total reducing sugars. Examples of sugar alcohols having a molecular mass higher than hexitols is DP2 and higher hydrogenated oligosaccharides such as maltitol, isomaltitol and maltotriitol. According to the invention, the total reducing sugars is determined by the Bertrand method (*BERTRAND, G. (1906) Bull. Soc. Chim. ser.3, 35: 1285-1299*). Typically, the sorbitol rich syrup obtained has less than 0.15%, preferably less than 0.1% (wt) total reducing sugars.

According to one embodiment, said permeate is a sorbitol rich syrup having at least 99.3% by weight of hexitol, preferably, 99.4% more preferably at least 99.5% even more preferably at least 99.6% or of about 99.7% by weight of hexitol on ds, less than 0.1 wt% of total reducing sugars on ds and less than 0.15% on ds (wt) of sugar alcohols having a molecular mass higher than hexitols.

The invention is also about **a sorbitol syrup** preferably, susceptible to be obtained by the process according to the invention, said sorbitol syrup having at least 99.2% preferably, 99.3%, more preferably, 99.5%, even more preferably at least 99.6% or of about 99.7% by weight of hexitol on ds, less than 0.2%, preferably less than 0.15%, more preferably less than 0.1% by weight of total reducing sugars on ds and less than 0.3%, preferably less than 0.2%, more preferably, less than 0.15% by weight on ds of sugar alcohols having a molecular mass higher than hexitols.

Typically, said sorbitol syrup has a sorbitol content of at least 97.5%, preferably at least 98% on dry substance (d.s.), preferably, between 97.5 and 99.9%, more preferably, between 97.8 and 99.8, even more preferably between 97.9 and 99.7%. According to one embodiment, said sorbitol syrup has less than 1% by weight of hexitol other than sorbitol.

According to one embodiment, said sorbitol syrup has a total reducing sugars of less than 0.09% on ds, preferably less than 0.08% (wt) on ds, more preferably of about 0.07 on ds.

According to one embodiment, said sorbitol syrup has less than 1% by weight of mannitol and iditol content, preferably less than 0.99%, more preferably of about 0.98% on ds.

According to one embodiment, said sorbitol syrup has less than 0.15% by weight on ds of sugar alcohols having a molecular mass higher than hexitols, preferably about 0.14% by weight on ds of sugar alcohols having a molecular mass higher than hexitols.

Typically, said sorbitol syrup shows, when measured in a 1 cm cuvet, a coloration of less than 0.1, preferably, of less than 0.07, more preferably, of less than 0.06, even more preferably of less than or equal to 0.04 at 420 nm when subjected to a temperature of 200°C during 1hour, more preferably said sorbitol syrup shows a coloration of less than 0.1, preferably, of less than 0.07, more preferably, of less than 0.06, even more preferably of less than or equal to 0.04 when subjected to a heat stability test according to test A. It should be noted that said sorbitol syrup according to the invention is uncolored at 420 nm before said heat stability test.

Indeed, as a result of the low content of total reducing sugars, of DP2 and higher hydrogenated oligosaccharides, sorbitol rich syrups according to the invention have excellent properties with regard to heat stability and are particularly adapted to be used for a number of chemical applications such as for example polyurethane foams, anhydrohexitol based surfactants (TWEEN, SPAN surfactants...).

The test A of evaluating the heat stability of a syrup comprises the step of:

a) concentrating said syrup to be evaluated by evaporation typically, under vacuum, to reach a dry substance of 79% or more
b) heating the concentrated syrup during 1 hour at 200°C, preferably in an oil bath, typically, 30ml of the syrup obtained is heated in a test tube that is immersed in the oil bath
c) cooling the syrup to about 80°C under gentle agitation
d) measuring the absorption *of the heat treated syrup at 420 nm in a 1 cm cuvet*

The absence of color of the syrup to be tested is confirmed (by measurement as step d)) before applying test A, preferably at a dry substance of about 79%. The test tube has typically an internal diameter of 3 cm. and 20 cm height; said test tube is a glass tube. According to one embodiment, the liquid level in the test tube is at the same height as the oil level in the bath.

By heating at 200°C, DP2 and higher polyols start hydrolysing. The released sugars on their turn quickly degrade and create coloration of the syrup.

This confirms the test A is really suited for the evaluation of sorbitol stability in high temperature conditions

Although having distinct meanings, the terms “comprising”, “having”, “containing’ and “consisting of” may be replaced with one another throughout the above description of the invention.

The invention will now be further illustrated by a number of examples, which should not considered as limiting the scope of the invention

BRIEF DESCRIPTION OF THE FIGURES

By means of reference numbers to the figures attached hereto, whereby in this specification:

- **Figure 1** shows a schematic representation of a nanofiltration set-up;

- **Figure 2** is a schematic representation of an alternative nanofiltration set-up;

- **Figure 3** shows a graphical representation of the results of Tables 1 and 2.

Detailed description of the invention

The nanofiltration process may be carried out in an **installation** as shown in **Figures 1** and 2, or a combination of both systems. The installation (1) shown in Figure 1 comprises a feed tank (2), a frequency-controlled high-pressure metering pump (3), a flow rate meter (4), a heat exchanger (5), a spiral-wound nanofiltration element (6), a back-pressure valve (7) and the necessary connections for the power supply, permeate and retentate streams.

When using an installation (1) according to Figure 1, a syrup from the feed tank (2) is applied to the spiral wound filter element (6) with a high pressure pump (3). The pressure is controlled by adjusting a back pressure valve. The temperature of the feed is controlled by the use of hot or cold water in the heat exchanger (5).

The installation (8) shown in **Figure 2** comprises a feed tank (2), a frequency-controlled high-pressure metering pump (3), a frequency-controlled retentate recycle pump (9), a heat exchanger (5), a spiral-wound nanofiltration element (6), a retentate pressure control valve (10), a flow rate meter for retentate (4) and a flow meter for permeate (4'), the necessary pressure and temperature probes for PLC controlled operation and the necessary connections for feed, permeate and retentate streams.

When using an installation (8) according to Figure 2, a syrup in the feed tank (2) is fed by a high pressure pump (3) in the retentate circuit. This retentate loop is composed of a recycle pump (9), a heat exchanger (5), and a spiral nanofiltration element (6). The pressure drop across the retentate side of the spirally wound element is controlled by the recycle pump. The retentate control valve (10) will control the pressure in the retentate circuit. The temperature of the feed is controlled

by the use of hot or cold water to the heat exchanger. Both the permeate and the retentate are continuously withdrawn from the system and collected separately.

EXAMPLES

EXAMPLE 1:

In this example, a number of settings for dilution, temperature, and pressure are tested with the aid of a high glucose syrup (SIRODEX® 431 from TEREOS SYRAL) (Table 1) and its hydrogenated counterpart (MERITOL® 130 from TEREOS SYRAL) (Table 2).

A new NF3A-2540-46N spiral-wound nanofiltration element from SEPRO MEMBRANES INC. is used in a membrane filtration pilot plant as shown in Figure 1.

The commercial syrups are diluted with demineralized water and fed into the feed tank (2) of the installation (1). With the aid of the high-pressure pump, the diluted syrup was fed at 600 l/h to the nanofiltration element (6). Both the permeate and the retentate are fed back to the feed tank (2). The pressure in the system is controlled by adjusting a back-pressure valve. The temperature is controlled by supplying hot or cold water to the heat exchanger (5). Every time when one of the settings is changed, the system is allowed to re-equilibrate over a period of 15 minutes. At the end of this equilibration period and before proceeding to the new setting, samples of permeate and retentate are taken and the flow rate of the permeate is measured.

The samples are analyzed for % d.s. and also for the content of the monosaccharides and disaccharides (DP1 and DP2), or the content of their hydrogenated counterparts, via HPLC analysis. DP1 and DP2 content is expressed as a percentage on d.s. of the treated syrup. For each set of parameters, a maltose or maltitol reduction factor (hereinafter abbreviated as respectively MRF or MRF') calculated by dividing the figure for the retentate DP2 by the DP2 figure for the permeate. The MRF and MRF' factors provide information about the resolution of the process with respect to the DP1 and DP2 fractions, under the conditions used.

The following settings are used:

Temperature (T) in combination with the pressure:

- 40°C and 40 bar ;

- 45°C and 32 bar ;

- 50°C and 25 bar

Each setting was tested on three different concentration levels: ~ 58% d.s., ~ 52% and ~ 42% d.s..The results are shown in Tables 1 and 2.

The results of Tables 1 and 2 are shown graphically in Figure 3, and clearly demonstrate the benefits of applying nanofiltration on a sorbitol syrup instead of on its non-hydrogenated counterpart. At similar conditions of temperature, pressure and concentration, the permeate flux for the hydrogenated syrup is always significantly higher than the one for the non-hydrogenated syrup. The permeate ds flux is doubled to more than tripled. Despite of the much higher flux, also the selectivity is significantly improved. At similar conditions of temperature, pressure and concentration, the MRF' is 1.4 up to 2.4 times higher than the corresponding MRF.

Membrane working conditions		Retentate			Permeate				
		HPLC% on d.s			HPLC% on d.s.				
T(°C)	P (bar)	DP1	DP2	% d.s.	DP1	DP2	% d.s.	Flux kg d.s./h/ m²	MRF
40	40	95.6	3.0	57.6	98.9	0.77	53.5	0.20	3.9
45	32	95.6	3.0	57.6	99.1	0.68	54.4	0.21	4.5
50	25	95.6	3.0	57.6	99.0	0.74	55.5	0.23	4.1
40	40	95.6	3.1	51.6	99.2	0.58	45.6	0.26	5.2
45	32	95.6	3.1	51.6	99.2	0.53	47.7	0.27	5.8
50	25	95.5	3.1	51.6	99.3	0.55	47.8	0.29	5.6
40	40	95.5	3.1	41.6	99.5	0.40	32.8	0.40	7.8
45	32	95.5	3.1	41.6	99.5	0.40	33.7	0.38	7.8
50	25	95.4	3.1	41.6	99.4	0.42	35.9	0.42	7.4

Table 1: nanofiltration of high glucose syrup, membrane: NF3A-2540-540 46 M (Sepro Membrane Inc.)

Membrane working conditions		Retentate			Permeate				
		HPLC% on d.s.			HPLC% on d.s.				
T(°C)	P (bar)	DP1	DP2	% d.s.	DP1	DP2	% d.s.	Flux kg d.s./h/m²	MRF'
40	40	95.2	2.9	58.0	99.6	0.31	55.1	0.63	9.4
45	32	95.2	2.9	58.2	99.6	0.30	55.6	0.69	9.7
50	25	95.1	3.0	58.1	99.6	0.35	56.2	0.66	8.5
40	40	95.3	2.9	52.4	99.7	0.27	47.4	0.77	10.6
45	32	95.2	2.9	52.3	99.6	0.31	49.3	0.76	9.3
50	25	95.1	2.9	52.2	99.6	0.29	49.3	0.76	10.1
40	40	95.1	2.9	42.4	99.6	0.27	33.8	0.88	10.9
45	32	95.0	3.0	42.7	99.7	0.25	35.6	0.94	12.0
50	25	94.9	3.1	42.8	99.7	0.26	37.1	0.96	11.8

Table 2: nanofiltration of hydrogenated high glucose syrup, membrane: NF3A-2540-540 46 M (Sepro Membrane Inc.)

EXAMPLE 2:

In this example, a practically worn-out spiral wound membrane DESAL DL2540F1073 was used in the membrane filtration system, as shown in Figure 1.

Once again, a high-glucose syrup (SIRODEX® 431) and a high sorbitol syrup (MERITOL® 130) are compared with each other.

Here, the syrup was diluted to 40% d.s. and fed at a flow rate of 600l / h to the nano- filtration membrane. In both cases a temperature of 40°C and a pressure of 40 bar was applied.

The results in table 3 show an improved flux value and higher MRF ' - value for the sorbitol syrup. The relative flux improvement for the sorbitol syrup is a bit less important, at 1.6 times the flux for the non-hydrogenated counterpart, compared to the flux increase observed in example 1. In absolute terms however (kg ds / m2 / h) the flux increase is even more important.

The improvement in selectivity, at ~ 24%, also is less important compared to the increase observed in example 1. Nevertheless, this example demonstrates that, by applying nanofiltration on a sorbitol syrup instead of its non-hydrogenated counterpart, one can obtain, even with used membranes, a huge increase in productivity without sacrifying on purity.

It also demonstrates that the improvements are not restricted to the use of a specific membrane from a specific membrane supplier.

	Retentate			Permeate				
	HPLC% on d.s.			HPLC% on d.s.				
	DP1(ol)	DP2(ol)	% d.s.	DP1(ol)	DP2(ol)	% d.s.	Flux (kg d.s./h/m²)	MRF(')
SIRODEX 431	95.6	3.0	40.3	99.3	0.55	31.9	3.2	5.5
MERITOL 130	95.1	2.9	41.8	99.4	0.48	34.2	5.2	6.0

Table 3: Results Test Example 2

EXAMPLE 3:

In this example, a membrane filtration plant is used as shown in Figure 2. The system (8) consists of a feed tank (2), a high pressure feed pump, a retentate recycle pump, a heat exchanger (5), a housing for the spiral wound filter element, a retentate pressure control valve, a flow meter for retentate and a flow meter for permeate. The spiral wound membrane for nanofiltration is a new NF3A-4040-46N spiral wound nano-filtration element from Sepro Membranes Inc. The diluted syrup is fed at about 150 liters / hour in the retentate circuit, composed of the recycle pump, the filter housing for the spiral wound membrane and the heat exchanger. The recycle pump is set to maintain a pressure drop of 0,5 bar on the retentate side of the spiral wound element. Cooling water is fed to the heat exchanger to maintain a temperature of 40°C in the retentate circuit. The retentate control valve is set to maintain a pressure of 40 bar in the retentate circuit. Both permeate and retentate are continuously withdrawn from the system and collected separately. The system is provided in order to equilibrate for 30 minutes prior to sampling.

Because of the different set-up of the nanofiltration plant, DP2 (ol) and highers are more concentrated in the retentate streams of this example 3 compared to in the retentate streams of example 1. Nevertheless, when comparing the results in table 4 below with the results in table 1, an increase of the flux and an improvement of selectivity are clearly observed in this test for sorbitol syrup compared with its non-hydrogenated counterpart. Those improvements are similar than the ones obtained in example 1 at comparable temperature, pressure and concentration.

The results are presented in Table 4:

	Retentate			Permeate				
	HPLC% on d.s.			HPLC% on d.s.				
	DP1(ol)	DP2(ol)	% d.s.	DP1(ol)	DP2(ol)	% d.s.	Flux (kg d.s./h/m²)	MRF(')
IRODEX® 31	95.1	3.3	39.9	99.4	0.31	32.5	0.33	10.7
ERITOL® 30	95.9	2.7	40.0	99.7	0.18	33.2	0.66	14.8

Table 4: Results Test Example 3

EXAMPLE 4:

Here is a "double pass" nanofiltration process of a sorbitol syrup described.

MERITOL 130, a starch derived sorbitol syrup commercialized by TEREOS SYRAL, is diluted with demineralized water and supplied to the feed tank of the membrane filtration skid 2 described in figure 2. The spiral wound filter element mounted in the system is the one that has been used before for example 3

Using the high pressure pump, the diluted syrup is fed at ~150 l/h into the retentate loop consisting of the recycle pump, the filter housing with the spiral wound filter element and the heat exchanger. The frequency of the recycle pump is adjusted to maintain a pressure drop of 0.5 bar over the retentate side of the spiral wound element. Cooling water is supplied to the heat exchanger to maintain a temperature of 40°C in the retentate loop. The retentate control valve is adjusted to maintain a pressure of 25 bar in the retentate loop. Both permeate as well as retentate are continuously withdrawn from the system and send to the sewer.

The system is allowed to equilibrate for 30 minutes. After that time, the permeate is sent to the feed tank of the membrane filtration skid 1 described in figure 1 equipped with the spiral wound filter element that has been used before for example 1. Using the high pressure pump of skid 1, the permeate A of skid 2 is fed at 600 l/h to the spiral wound filter element. The retentate of skid 1 is returned to the suction of the high pressure pump of skid 2. The permeate B of skid 1 is partially recycled to the feed tank of skid 1, to maintain the level in this feed tank, and partially collected. The pressure in the system is controlled at 25 bar by adjusting of the back pressure valve; the temperature is controlled at 40°C by applying cold water on the heat exchanger.

The combined systems are allowed to equilibrate for 4 hours. After that time, samples are taken of both permeates and analyzed against the feed for % DP1, total sugars and heat stability. The heat stability of permeates A and B have been evaluated by measuring the color of the permeates after a heating treatment according to the following test. The absence of color of permeate A and B are checked before starting the evaluation of their heat stability. The syrup to be evaluated is concentrated by evaporation under vacuum to about 79% d.s. Then, 30 ml of the concentrated syrup is introduced in a test tube with an internal diameter of 3 cm. and 20 cm height. The test tube is placed in an oil bath heated to 200°C for 1 hour, whereby the liquid level in the test tube is at the same height as the oil level in the bath. The syrup is then cooled to about 80°C. The color of the heat treated syrup is measured in a cuvette of 1 cm. at 420 nm.

The results for this test are resumed in table 5.

	DP1(ol) on d.s.	Total reducing sugars % on d.s.	Colour after heating
feed	95.1		
Permeate A	99.6	0.18	0.09
Permeate B	99.9	0.07	0.04

Table 5: Results Test Example 4

Table 5 clearly shows that by applying the process of the invention comprising a two pass nanofiltration , a very high purity sorbitol is produced. Indeed, the process according to the invention provides a sorbitol syrup having a very high hexitol content of 99.9%, an extremely low total reducing sugars content and an extremely high color stability

EXAMPLE 5

In order to compare heat stability and total reducing sugar content of sorbitol syrups according to the invention and sorbitol syrups obtained by hydrogenation of highly pure dextrose syrup, three sorbitol syrups are produced by the hydrogenation of three batches of highly pure dextrose syrup (D99 dextrose syrup).

The hydrogenated syrups are then passed through three parallel columns at 0,33 BV/hour. Said columns are filled with 100 ml of a strong base anionic exchange resin in the hydroxide form. The resin used is Amberlite FPA 90. The operating temperature for the columns containing Amberlite FPA90 is 60 C.

The processed sorbitol syrup is collected and hexitol content and total reducing sugars are measured (see table 2).

Product	DP1-ol % / ds	Total Reducing Sugars % / ds	Heat Stability color after heating
Sorbitol Syrup (batch 1)	99.6	0.17	0.07
Sorbitol Syrup (batch 2)	99.4	0.22	0.09
Sorbitol Syrup (batch 3)	99.5	0.19	0.08

Table 6

Comparing to table 5, the sorbitol syrups obtained by hydrogenation of highly pure dextrose syrup have reduced heat stability (twice less than the syrups according to the invention) and a total reducing sugar content clearly above 0.1%. This is observed even after the second purification step on a strong base anionic resin.

EXAMPLE 6

Permeate B of example 4 is further analyzed in order to define the nature and content of sugar alcohols of this sorbitol syrup.

Sugar alcohol		% / ds
DP2+	maltotriitol:	0.02
	maltitol:	0.09
	isomaltitol:	0.03

hexitols	mannitol:	0.75
	iditol:	0.18
	sorbitol	98.65
other	erytritol:	0.11
	glycerol:	0.13

By using the method of the invention, a highly pure sorbitol syrup having 99.58% by weight on ds of hexitol among which a sorbitol content of 98.65%, 0.07 wt% of total reducing sugars (see table 5) and 0.14% (wt) maltitol plus higher hydrogenated oligosaccharides.

CLAIMS

1. A process for the preparation of a sorbitol rich syrup having less than 0.2% total reducing sugars, wherein said process comprises the following steps:

   - hydrogenation of a glucose syrup having a glucose content of 94% to 97% on dry substance (d.s.),

   - separation step of the hydrogenated glucose syrup by at least one membrane nanofiltration stage to obtain a permeate and a retentate, wherein the permeate is a sorbitol rich syrup having at least 99.2% by weight on ds of hexitol, less than 0.2% by weight on ds of total reducing sugars and less than 0.3% by weight on ds of sugar alcohols having a molecular mass higher than hexitols.

2. The process according to claim 1, wherein said process comprises a separation step by two membrane nanofiltration stages, wherein the permeate of the first membrane nanofiltration stage is then applied on the second membrane nanofiltration stage and wherein the permeate of the second membrane nanofiltration stage is the sorbitol rich syrup, preferably, the retentate of the second membrane nanofiltration stage is recycled in the first membrane nanofiltration stage.

3. The process according to claim 1 or 2, wherein said permeate is a sorbitol rich syrup having having at least 99.3% by weight on ds of hexitol, less than 0.1 wt% of total reducing sugars on ds and less than 0.15% by weight on ds of sugar alcohols having a molecular mass higher than hexitols.

4. The process according to any one of claim 1 to 3, wherein said hydrogenated glucose syrup has a dry substance (d.s.)of 30% to 60% and/or wherein the nanofiltration separation is carried out at a temperature of about 25°C to 75°C and a pressure of 25 to 70 bar.

5. The process according to any one of the preceding claims, wherein said hydrogenated glucose syrup has a dry substance (d.s.) of 40% to 50% and/or wherein the nanofiltration separation is carried out at a temperature of about 30°C to 45°C and a pressure of 40 to 55 bar.

6. The process according to any one of the preceding claims, wherein said hydrogenated glucose syrup has a dry substance (d.s.)of 40% to 50%, and/or

wherein the nanofiltration separation is carried out at a temperature of about 30°C to 40°C and a pressure of 40 to 50 bar.

7. The process according to any one of the preceding claims, wherein the membranes used in the nanofiltration separation, having a MWCO of 300 or less.

8. A sorbitol rich syrup having at least 99.2% by weight on ds of hexitol, less than 0.1% by weight of total reducing sugars on ds and less than 0.2% by weight on ds of sugar alcohols having a molecular mass higher than hexitols.

9. The sorbitol syrup according to claim 9 wherein said sorbitol syrup has a sorbitol content of at least 97.5%, preferably at least 98% on dry substance (d.s.).

10. The sorbitol syrup according to claim 8 or 9 wherein said sorbitol syrup has less than 1% by weight on ds of hexitol other than sorbitol.

11. The sorbitol syrup according to any one of the preceding claims, wherein said sorbitol syrup has a total reducing sugars of less than 0.09% on ds, preferably less than 0.08% (wt) on ds.

12. The sorbitol syrup according to any one of the preceding claims, wherein said sorbitol syrup has less than 1% by weight of mannitol and iditol content on ds.

13. The sorbitol syrup according to any one of the preceding claims, wherein said sorbitol syrup has less than 0.15% by weight on ds of sugar alcohols having a molecular mass higher than hexitols.

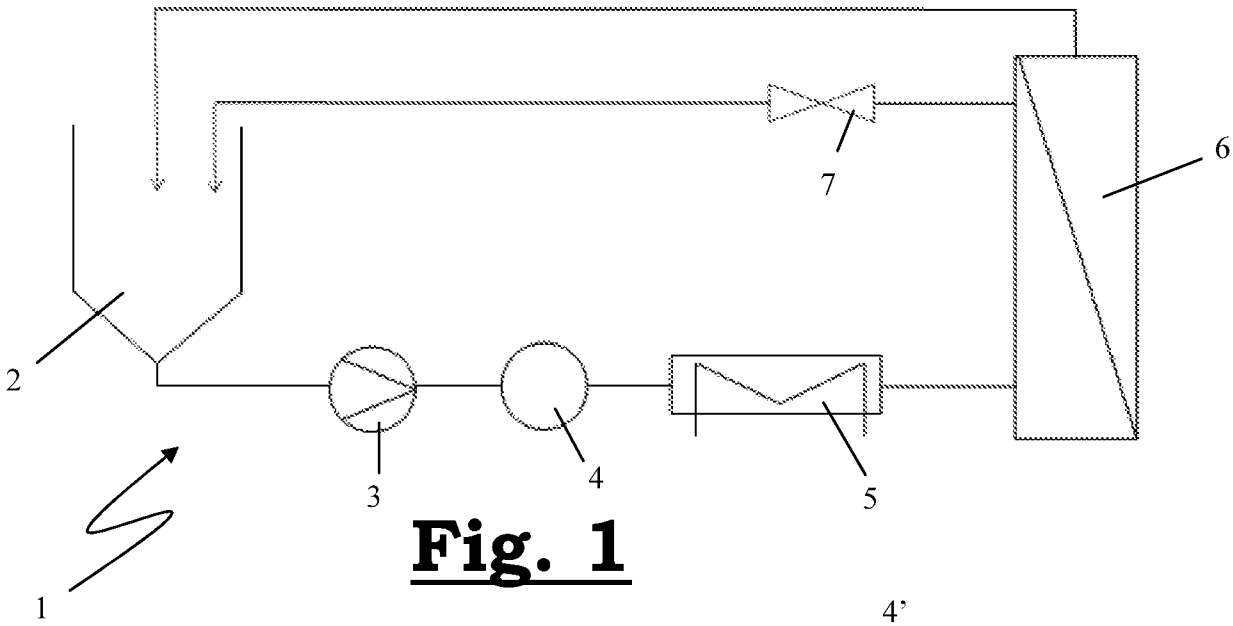

Fig. 1

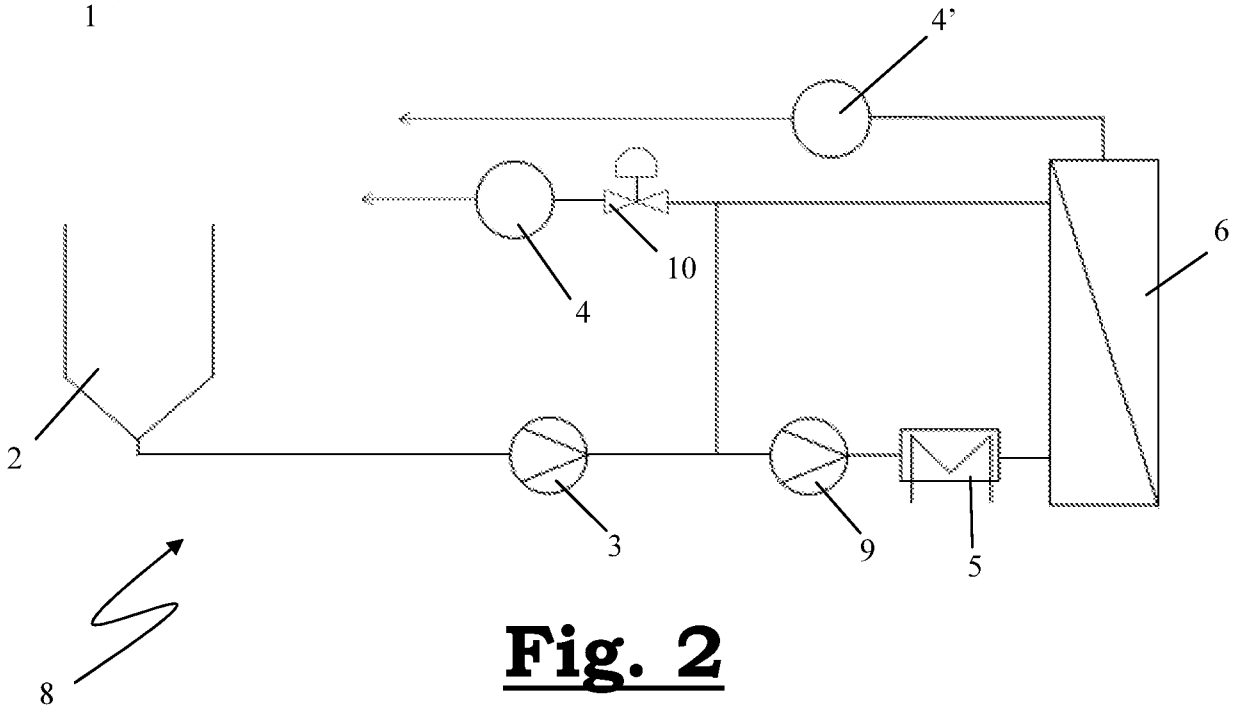

Fig. 2

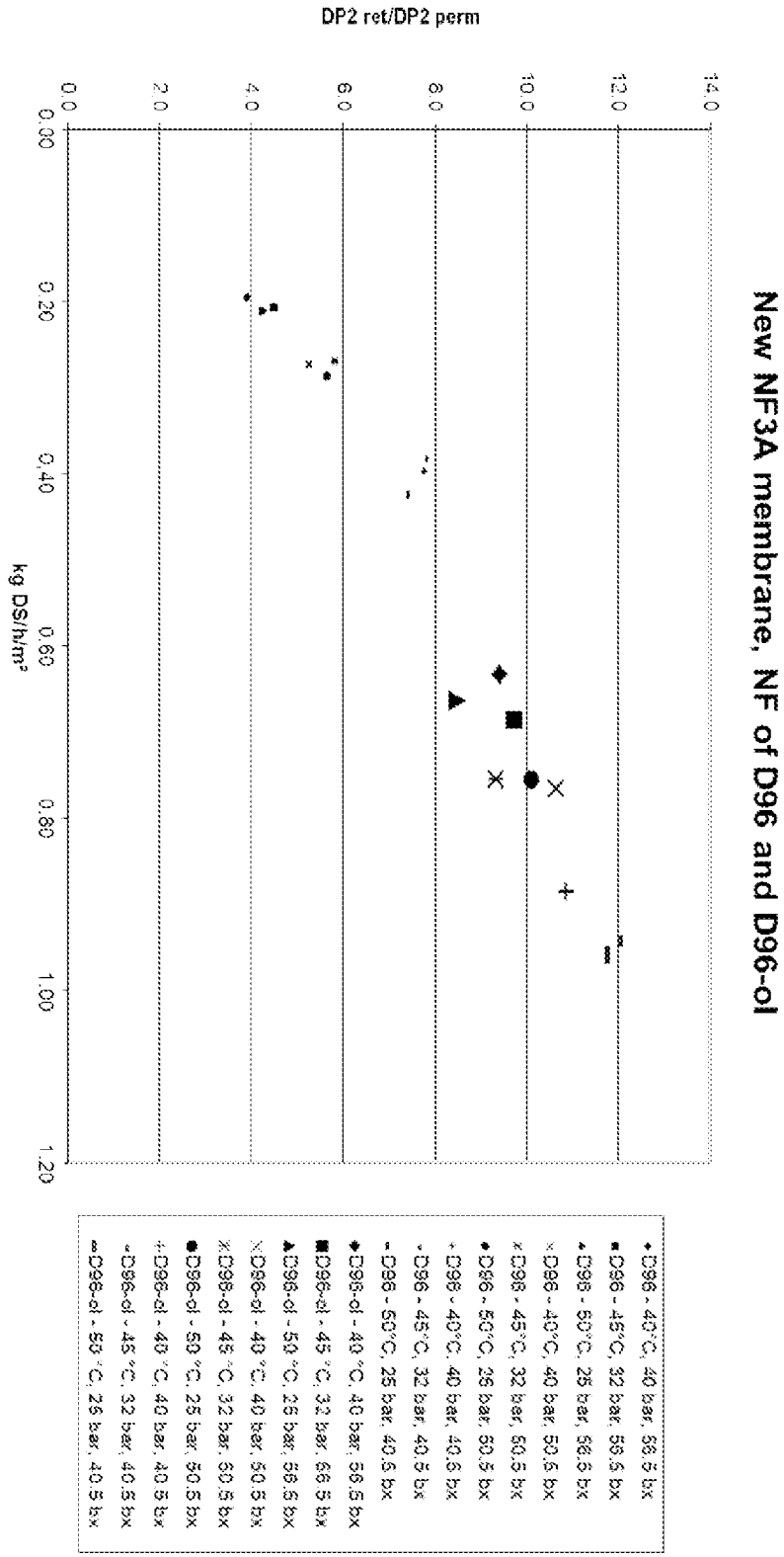
New NF3A membrane, NF of D96 and D96-ol
DP2 ret/DP2 perm
kg DS/h/m²
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
0.00
0.20
0.40
0.60
0.80
1.00
1.20
D96 - 40°C, 40 bar, 56.5 bx
D96 - 45°C, 32 bar, 56.5 bx
D96 - 50°C, 25 bar, 56.5 bx
D96 - 40°C, 40 bar, 50.5 bx
D96 - 45°C, 32 bar, 50.5 bx
D96 - 50°C, 25 bar, 50.5 bx
D96 - 40°C, 40 bar, 40.5 bx
D96 - 45°C, 32 bar, 40.5 bx
D96 - 50°C, 25 bar, 40.5 bx
D96-ol - 40 °C, 40 bar, 56.5 bx
D96-ol - 45 °C, 32 bar, 56.5 bx
D96-ol - 50 °C, 25 bar, 56.5 bx
D96-ol - 40 °C, 40 bar, 50.5 bx
D96-ol - 45 °C, 32 bar, 50.5 bx
D96-ol - 50 °C, 25 bar, 50.5 bx
D96-ol - 40 °C, 40 bar, 40.5 bx
D96-ol - 45 °C, 32 bar, 40.5 bx
D96-ol - 50 °C, 25 bar, 40.5 bx

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2015/050392

A. CLASSIFICATION OF SUBJECT MATTER
INV. A23L1/09 A23L1/236 C12P7/18
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A23L C12P C13B C13K

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

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

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

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
18 March 2015	25/03/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Tallgren, Antti

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