(19) DANMARK

(10) DK/EP 3351110 T3

(12) Oversættelse af europæisk patentskrift

Patent- og Varemærkestyrelsen

(51) Int.Cl.: *A 23 C 9/142 (2006.01)* *A 23 C 1/04 (2006.01)* *A 23 C 21/00 (2006.01)*
A 23 C 21/02 (2006.01) *A 23 J 1/08 (2006.01)* *A 23 J 1/20 (2006.01)*
B 01 D 61/02 (2006.01) *C 07 C 51/47 (2006.01)* *C 07 K 1/34 (2006.01)*
C 07 K 14/47 (2006.01)

(45) Oversættelsen bekendtgjort den: **2020-05-25**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2020-03-04**

(86) Europæisk ansøgning nr.: **17152543.9**

(86) Europæisk indleveringsdag: **2017-01-22**

(87) Den europæiske ansøgnings publiceringsdag: **2018-07-25**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

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(54) Benævnelse: **FREMGANGSMÅDE TIL KOMBINERET INDVINDING AF SØD VALLE OG MÆLKESYRE FRA SUR VALLE**

(56) Fremdragne publikationer:
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PROCESS FOR COUPLED PRODUCTION OF SWEET WHEY AND LACTIC ACID FROM ACID WHEY

FIELD OF THE INVENTION

The invention is in the field of dairy processing and relates to a process by means of which it is possible to convert acid whey into sweet whey, obtaining lactic acid as a valuable coupled product in the process.

STATE OF THE ART

Whey is the aqueous greenish-yellowish fluid obtained from the process of cheese making. It is the liquid portion which is separated after the curdling of milk to produce cheese or quark. There are two types of whey, which are distinguished depending on the production process: *sweet whey* (also referred to as *rennet whey*), which is formed when milk is coagulated with rennet to produce cheese, and *acid whey*, which is formed when milk is fermented by lactic acid bacteria. Whey consists of 94% by weight water, 4 to 5% by weight lactose and is virtually fat-free. It also contains lactic acid, vitamins B_1, B_2 (which causes the greenish colour) and B_6 as well as potassium, calcium, phosphorus and other minerals, but primarily 0.6 to 1% by weight whey protein. As a consequence, whey contains significantly less protein than milk. In particular, in contrast to milk, it does not contain any casein. Sweet whey has an almost neutral pH value, whereas acid whey has a pH value of 5 or less.

Sweet whey is considered to be the most important form of whey, serving as a source of raw material for other dairy products, especially for the so-called whey proteins, but it is also used in the food sector.

In contrast, acid whey is a waste product that is obtained in great quantities during the production of fresh cheese and of quark. As a result of the high lactic acid content and its associated low pH value, it can only be used with restrictions for human nutrition. Acid whey is also difficult to filter, and can only be spray-dried with great difficulty. As a result, this by-product of the production of cheese is usually disposed of, leading to additional environmental pollution and costs; this also constitutes a loss, as ingredients of the milk which are attractive per se, in particular whey proteins, lactose, and calcium phosphate, are lost.

BARRANTES L. D. et al. (J food science, Vol. 62, No. 2, 1997) discloses the deacidification and demineralisation of cottage cheese whey by means of nanofiltration and nanodiafiltration.

YEBO L. et al. (Appl. Biochem. and Biotech., Vol. 147, No. 1-3, 2007) discloses the separation and concentration of lactic acid from a fermented ultra-filtered cheese whey preparation by means of nanofiltration and reverse osmosis.

ROMAN A. et al. (Desalination, Vol. 241, No. 1-3, 2009) discloses the partial demineralisation and concentration of acid whey by means of nanofiltration and diafiltration.

The object of the invention was, therefore, to remove any undesired constituents of acid whey such that a commercially attractive and exploitable product is obtained. In particular, a product was required which is almost identical to sweet whey in terms of composition and pH value and which provides lactic acid as an attractive industrial raw material as a by-product in a form that is as highly concentrated and as pure as possible.

DESCRIPTION OF THE INVENTION

The subject matter of the invention relates to a process for the coupled production of sweet whey and lactic acid from acid whey, comprising the following steps:

(a) providing acid whey having a lactic acid content of about 0.1 to about 1% by weight;

(b) nanofiltration of the acid whey, obtaining a first permeate P1 and a first retentate R1;

(c) optionally, redilution of the first retentate R1 with water to reconstitute the initial dry matter content, and preparation of the second nanofiltration step;

(d) nanofiltration of the retentate R1, obtaining a second permeate P2 and sweet whey as a second retentate R2, wherein the nanofiltration step is performed using a closed membrane having a cut-off in the range of 150 to 300 Dalton;

(e) combining the two permeates P1 and P2 and subjecting the mixture to reverse osmosis, obtaining a third permeate P3 which, substantially, only contains water, and a concentrate of lactic acid as a third retentate R3.

Surprisingly, it was found that by a two-step nanofiltration process it is possible to convert acid whey into a product having the quality of sweet whey, whereby lactic acid in industrial grade purity is obtainable as a coupled product. The desired depletion of the whey in lactic acid and, naturally, also in the amount of the desired coupled product can be controlled in a targeted manner by selecting suitable membranes and filtration conditions. Within the scope of the process according to the invention, a partial demineralisation of the initial products also takes place simultaneously. The degree of demineralisation is between 50 and 70%. The salt content is transferred to the lactic acid solution.

ACID WHEY

As explained above, acid whey constitutes the liquid phase, which is produced when milk is coagulated to produce fresh cheese or quark using lactic acid bacteria. Preferably, qualities are used which have a lactic acid content in the range of about 0.1 to 1% by weight.

NANOFILTRATION

Nanofiltration is a filtration process from the field of membrane technology, by means of which macro-molecular substances and small particles may be separated from a medium and concentrated. A distinction is made between microfiltration, ultrafiltration and nanofiltration based on the degree of separation. If the cut-off limit (or also "*cut-off*") is 100 nm or more, the process is referred to as microfiltration. If the cut-off limit is in the range between 2-100 nm, this is referred to as ultrafiltration. In the case of nanofiltration, the cut-off limit is below 2 nm. Each of these cases is a purely physical, i.e. mechanical membrane separation process which applies the principle of mechanical size exclusion: all particles in the fluids which are larger than the membrane pores are retained by the membrane. The driving force in both separation methods is the differential pressure between the inlet and the outlet of the filter area, which is between 1 and 40 bar, in some cases up to 120 bar.

The cut-off limits of nanofiltration membranes are also indicated in form of the *NMWC* (nominal molecular weight cut-off, also referred to as *MWCO*, molecular weight cut off, unit: Dalton). This is defined as the minimal molecular mass of globular molecules, 90% of which are retained by the membrane. In practice, the NMWC should be at least 20% lower than the molar mass of the molecule to be separated. Further qualitative statements on filtration may be made using the *flux* (water value) (transmembrane flux or passage rate). Ideally, this is proportional to the transmembrane pressure and reciprocal to the membrane resistance. These sizes are determined both by the characteristics of the membrane used and by concentration polarisation and any fouling which occurs. The passage rate relates to 1 m^2 of membrane area. Its unit is l/(m^2h bar).

With respect to a separation of lactic acid in two steps which is as efficient as possible, it has proven to be advantageous to perform the second nanofiltration step using a membrane which has a greater cut-off than the membrane of the first nanofiltration step.

Specifically, it is recommended to perform the first nanofiltration step using an open membrane, preferably one having a cut-off in the range of about 500 to about 1,000 Dalton, and particularly of about 800 Dalton. It is also preferred to perform the nanofiltration step at a pressure

in the range of about 10 to about 15 bar. Under these combined conditions, a retentate is obtained which only has about 20% of the originally obtained lactic acid. If closed membranes with a higher cut-off and/or higher or lower pressures are used instead, only between about 25 and about 50% by weight of lactic acid are removed instead of 80, leading to the result that the second nanofiltration step will be initiated with higher lactic acid contents and a comparably lower separation performance will be correspondingly achieved.

Before the second nanofiltration step, it is recommended to add to the retentate 1 the amount of water which was previously removed with the permeate 1. This prevents the osmotic pressure from becoming too high at this point and prevents the filtration/purification performance from being insufficient. The amount of lactic acid within the retentate 2 can also be controlled by means of the amount of diafiltration water.

The second nanofiltration step is subsequently performed using a closed membrane which has a cut-off in the range of 150 to 300 Dalton. Here it is recommended to operate at a higher pressure in the range of about 30 to about 40 bar. Depending on the concentration of lactic acid in the applied retentate from the first nanofiltration, retentates are obtained from the second step which contain between 0.1 and 0.5% by weight residual lactic acid and thus practically correspond to sweet whey or at least come close.

The material of the nanofiltration membrane may be stainless steel, polymer materials, ceramics, aluminium oxide or textile fabrics. Filter elements appear in different forms: candle filters, flat membranes, spiral coil membranes, bag filters and hollow fibre modules, all of which are, in principle, suitable within the meaning of the present invention. However, spiral coil membranes made of polymer materials or candle filters made of ceramics or aluminium oxide are preferably used, the second embodiment having proven to be particularly preferred for nanofiltration.

Both nanofiltration steps within the meaning of the present invention may be performed "hot" or "cold", i.e., within the temperature range of about 10 to about 60°C. However, it is preferred to operate at temperatures in the range of about 10 to about 20°C.

REVERSE OSMOSIS

Reverse osmosis is a physical membrane process for concentrating substances dissolved in liquids, in which the natural osmotic process is reversed by means of pressure. In the present case, this step serves to concentrate the mixture of the two permeates P1 and P2 in order for less water to have to be removed in the following drying step.

The principle of the process is that the medium in which the concentration of a particular substance is to be reduced is separated by a semi-permeable membrane from the medium in which the concentration is to be increased. The latter is subjected to a pressure which must be higher than the pressure created by the osmotic desire to balance the concentration. As a result, the molecules of the solvent can migrate counter to their "natural" osmotic spreading direction. The process forces them into the compartment in which dissolved substances are present in a less concentrated form. Typical pressures for reverse osmosis are in the range of 3 to 30 bar (desalination of drinking water) or up to 80 bar (desalination of sea water).

The osmotic membrane, which only the carrier liquid (solvent) permeates and which retains the dissolved substances (solute), must be able to withstand these high pressures. If the pressure difference more than balances the osmotic gradient, the molecules of the solvent pass through the membrane just like in a filter, while the "contaminating molecules" are retained. In contrast to a classic membrane filter, osmotic membranes do not have through-pores. Rather, the ions and molecules migrate through the membrane by diffusing through the membrane material, as is described by the solution-diffusion model: the osmotic pressure rises as the concentration difference increases. If the osmotic pressure becomes equal to the applied pressure, the process ceases. An osmotic equilibrium is then present. A continuous discharge of concentrate may prevent this. During the discharge of concentrate, the pressure is either controlled by means of a pressure controller or used by a pressure exchanger to accumulate the pressure required at the inflow of the system.

DRYING

Finally, the lactic acid concentrates obtained from reverse osmosis as retentates can be dehydrated. Preferably, spray-drying is applied, wherein the temperature is typically about 180 to about 260°C at the inlet and about 80 to about 105°C at the outlet. The fraction therefore does not need any cooling before entering the spraying tower. Temperatures of 60 to 70°C are even preferred in this process, as this reduces the risk of the proteins being denatured. Alternatively, the products may also be dehydrated by freeze-drying. The yield, based on the lactic acid contained in the original acid whey, is about 70 to 90%, and the purity is 90 to 95%.

The invention is defined by claims 1-7 and is illustrated below by exemplary embodiments and by **Figure 1**, which provides a flowchart of the process.

EXAMPLES

EXAMPLE 1

100 kg acid whey having a lactic acid content of 0.45% by weight and a pH value of 4.9 was supplied to a nanofiltration step at a flow rate of 5 kg/min, where it was filtered through an open membrane having a cut-off of 800 Dalton at a temperature of 20°C and a pressure of 12 bar as well as a volume concentration factor (VCF) of 4. 75 kg of the first permeate P1 was obtained, which had 0.365% by weight lactic acid, and 25 kg of the retentate R1, which still contained 0.7% by weight lactic acid. Thus, 80% of the original amount of lactic acid were detected in the permeate. 75 kg water was added to the first retentate, which was then supplied to a further nanofiltration step, where it was filtered through a closed membrane with a cut-off of 200 Dalton at a temperature of 20°C and a pressure of 35 bar. A second permeate P2 was obtained, which had 0.18% by weight lactic acid, while the second retentate R2 was depleted to 0.2% by weight lactic acid and thus had the quality of sweet whey.

EXAMPLE 2

100 kg acid whey having a lactic acid content of 0.45% by weight and a pH value of 4.9 was supplied to a nanofiltration step at a flow rate of 5 kg/min, where it was filtered through an open membrane having a cut-off of 800 Dalton at a temperature of 20°C, a volume concentration factor of 4 and a pressure of 35 bar. A first permeate P1 was obtained, which had 0.23% by weight lactic acid, and a first retentate R1, which contained 1.1% by weight lactic acid. Thus, in this example only 50% of the original amount of lactic acid was detected in the permeate. 75 kg water (P3) was initially added to the first retentate, which was subsequently supplied to a further nanofiltration step, where it was filtered through a closed membrane having a cut-off of 200 Dalton, at a temperature of 20°C and a pressure of 35 bar. A second permeate P2 was obtained, which had 0.05% by weight lactic acid, while the second retentate R2 was depleted to 0.95% by weight lactic acid in the concentrate, which corresponds to about 0.27% by weight lactic acid in the initial solution, and thus has a similar quality to sweet whey.

EXAMPLE 3

100 kg acid whey having a lactic acid content of 0.45% by weight and a pH value of 4.9 was supplied to a nanofiltration step at a flow rate of 5 kg/min, where it was filtered through an closed membrane having a cut-off of 200 Dalton at a temperature of 20°C, a VCF of 4 and a pressure of 35 bar. 75 kg of the first permeate P1 was obtained, which had 0.11% by weight lactic acid, and 25 kg

of the first retentate R1, which still contained 1.47% by weight lactic acid. Thus, in this example, only 25% of the original amount of lactic acid was detected in the permeate. 75 kg water (P3) was added to the first retentate, which was supplied to a further nanofiltration step, where it was filtered through a closed membrane having a cut-off of 200 Dalton at a temperature of 20°C and a pressure of 35 bar. A second permeate P2 was obtained, which had 0.09% by weight lactic acid, while the second retentate R2 had 1.2% by weight lactic acid in the concentrate, which corresponds to 0.3% by weight in the initial concentration. A similar quality to sweet whey could thus be achieved to a limited extent.

EXAMPLE 4

The first and second permeates of examples 1 to 3 were supplied to a reverse osmosis unit, where they were concentrated up to a residual water content of 25% by weight. Subsequently, the concentrates were pre-heated to 90°C using a heat exchanger, supplied to a tower and spray-dried at 180°C. Lactic acid was obtained as a fine white crystal powder in a purity of about 85%. About 10-20% of the dry matter is formed by the mineral salts from the acid whey. As a result of the low pH value of the acid whey, these salts are also permeable at the NF membrane.

Patentkrav

1. Fremgangsmåde til kombineret fremstilling af sød valle og mælkesyre fra sur valle, omfattende følgende trin:

(a) tilvejebringelse af en sur valle med et mælkesyreindhold på ca. 0,1 til ca. 1 vægtprocent;

(b) nanofiltrering af den sure valle til indvinding af et første permeat P1 og et første retentat R1;

(c) eventuelt, genfortynding af det første retentat R1 med vand for at gendanne udgangstørmassen og forberedelse af det andet nanofiltreringstrin;

(d) nanofiltrering af retentatet R1 til indvinding af et andet permeat P2 og en sød valle som det andet retentat R2, idet der anvendes en lukket NF-membran med en adskillelsesgrænse i området fra 150 til 300 dalton;

(e) samling af de to permeater P1 og P2 og underkastelse af blandingen for omvendt osmose til fremstilling af et tredje permeat P3, som i alt væsentlig kun indeholder vand, og et mælkesyrekoncentrat som tredje retentat R3.

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** der anvendes sur valle, som har et mælkesyreindhold i området fra ca. 0,1 til 1 vægtprocent.

3. Fremgangsmåde ifølge mindst et af kravene 1 til 2, **kendetegnet ved, at** den første nanofiltrering udføres med en åben membran.

4. Fremgangsmåde ifølge krav 3, **kendetegnet ved, at** der anvendes en åben NF-membran med en adskillelsesgrænse i området fra ca. 500 til ca. 2,000 dalton.

5. Fremgangsmåde ifølge mindst et af kravene 1 til 4, **kendetegnet ved, at** den første nanofiltrering udføres ved et tryk i området fra ca. 10 til ca. 15 bar.

6. Fremgangsmåde ifølge mindst et af kravene 1 til 5, **kendetegnet ved, at** den anden nanofiltrering udføres ved et tryk i området fra ca. 30 til ca. 40 bar.

7. Fremgangsmåde ifølge mindst et af kravene 1 til 6, **kendetegnet ved, at** mælkesyrekoncentratet efterfølgende dehydreres.

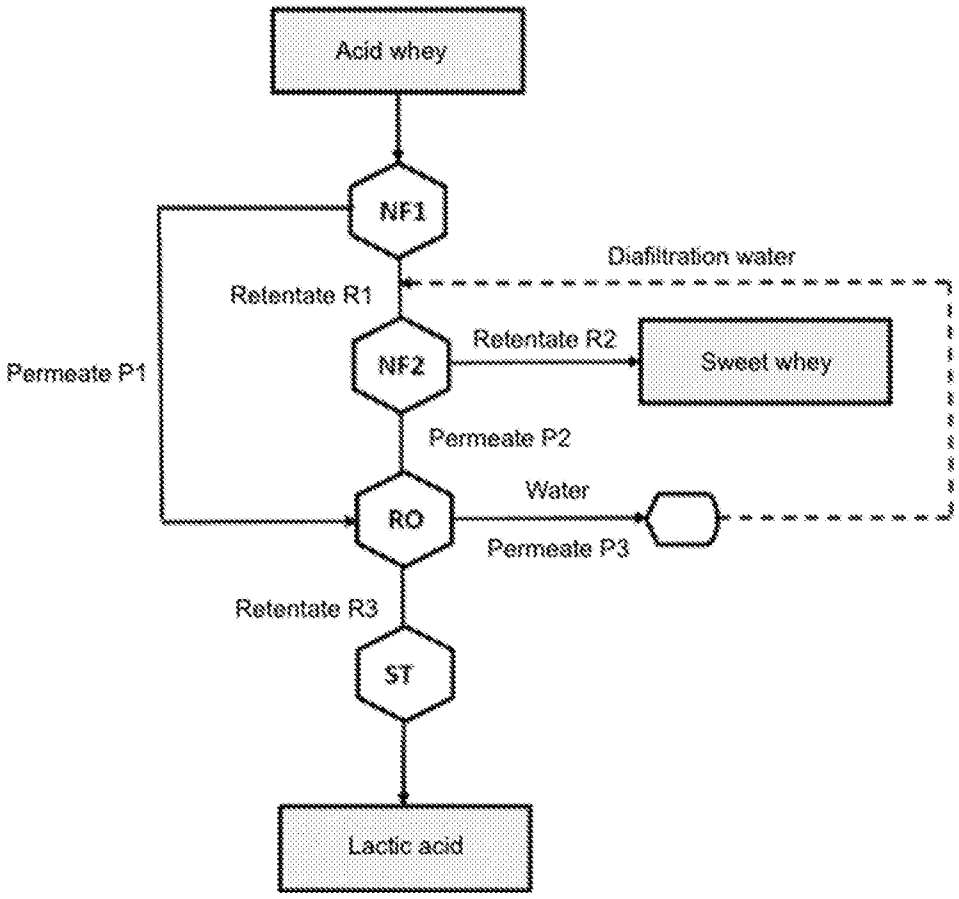
Acid whey
NF1
Diafiltration water
Retentate R1
Retentate R2
Sweet whey
NF2
Permeate P1
Permeate P2
Water
RO
Permeate P3
Retentate R3
ST
Lactic acid

Figure 1