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08172254.8 19 December 2008 (19.12.2008) EP(71) Applicant (for AE, AG, AU, BB, BH, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, KE, KN, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; a company registered in England and Wales under company no. 41424, Unilever House, 100 Victoria Embankment, London Greater London EC4Y 0DY (GB).(71) Applicant (for all designated States except AE, AG, AU, BB, BH, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, IN, KE, KN, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, US, VC, ZA, ZM, ZW): **UNILEVER N.V.** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).(71) Applicant (for IN only): **HINDUSTAN UNILEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, Mumbai 400 020 (IN).

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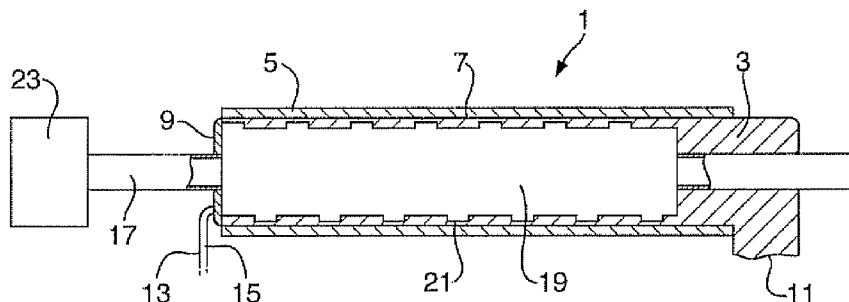
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(54) Title: EDIBLE GAS HYDRATE AND ITS PRODUCTION

Fig.2.



(57) Abstract: A method of producing an edible composite of gas hydrate and ice is provided, using an extruder (1) comprising a barrel (3) having an inlet (9) and an exit (11) and provided with cooling means (5), the method comprising: feeding an aqueous gas solution at a n elevated pressure into the barrel of the extruder via the inlet; cooling the barrel to form a frozen plug within the extruder so that the pressure inside the barrel is at or above the minimum pressure required for gas hydrate formation; freezing the gas solution inside the barrel to form the composite; and extruding the frozen composite from the extruder exit. A process for producing a frozen confection containing such a composite is also provided.

EDIBLE GAS HYDRATE AND ITS PRODUCTION

Field of the Invention

The present invention relates to a method of producing an edible composite of gas hydrate and ice, and products obtainable by that method, for example a frozen confection.

Background to the Invention

Frozen confections which contain a hydrate of a gas such as carbon dioxide give a pleasant 'sparkling' or fizzy sensation when consumed. Gas hydrates are also known as clathrates. US 5 538 745 discloses a process for producing frozen confections by mixing particles of sugar encapsulated in fat into a frozen aerated solution of milk protein. It is stated that clathrate ice crystals can be formed by adding CO₂, N₂, N₂O or mixtures thereof to the protein solution. These gases can comprise up to 100% of the gases used to aerate the solution. However no information is given about the process by which the clathrate crystals are formed.

It is known to produce gas hydrates by various batch processes, as disclosed for example in US-A-4 398 394, and WO 94 / 02414. Typically water is contacted with the gas under high pressure for a certain time to form the gas hydrate, and the resulting suspension of gas hydrate is then frozen. Generally, an excess of water is used so that a composite consisting of gas hydrate crystals in ice is formed. The required high pressure is usually achieved in a sealed pressure vessel. For this reason the known methods are batch processes. However, production efficiency could be significantly improved if the production could be effected in a continuous process.

Summary of the Invention

We have now found that such products may be continuously produced by using an extrusion apparatus. Accordingly, in a first aspect the present invention provides a method of producing an edible composite of gas hydrate and ice using an extruder comprising a barrel having an inlet and an exit and provided with cooling means, the method comprising:

- (a) feeding an aqueous gas solution at an elevated pressure into the barrel of the extruder via the inlet;

- (b) cooling the barrel to form a frozen plug within the extruder so that the pressure inside the barrel is at or above the minimum pressure required for gas hydrate formation;
- (c) freezing the gas solution inside the barrel to form the composite; and
- 5 (d) extruding the frozen composite from the extruder exit.

The present invention also extends to an extruded edible composite of gas hydrate and ice obtained by, or obtainable by the method of the invention. The product retains the gas so that when consumed, it produces an effervescent effect upon the tongue.

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In another aspect, the present invention provides a process for producing a frozen confection, the process comprising producing a composite according to the method of the invention; and then combining the composite with the remaining ingredients of the frozen confection.

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Detailed Description of the Invention

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art (e.g. in frozen confectionery manufacture). Definitions and descriptions of various terms and techniques used in frozen confectionery manufacture are found in Ice Cream, 6th Edition, Robert T. Marshall, H. Douglas Goff and Richard W. Hartel (2003), Kluwer Academic/Plenum Publishers. All percentages, unless otherwise stated, refer to the percentage by weight based on the frozen confection.

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- 25 Composites of gas hydrate and ice consist of gas hydrate crystals trapped within an ice structure. A gas hydrate is a crystalline solid which consists of a gas molecule surrounded by a cage of water molecules. Thus it is similar to ice, except that the crystalline structure has a guest gas molecule within the cage of water molecules. Many gases have molecular sizes suitable to form hydrates, including carbon dioxide
- 30 (CO₂) and nitrous oxide (N₂O). In the context of the present invention, gases comprising or consisting of carbon dioxide and/or nitrous oxide are preferred.

Suitable temperature and pressure conditions for the formation of carbon dioxide or nitrous oxide gas hydrates can be derived from the phase diagrams of the respective gas-aqueous liquid combination, which are available in the literature. For example, the phase diagram for carbon dioxide gas hydrates is given in Figure 1.

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Gas hydrates have a particular stoichiometric formula: for carbon dioxide gas hydrate it is $\text{CO}_2 \cdot 5.75\text{H}_2\text{O}$. However, gas hydrate crystals are unstable at atmospheric pressure (even at typical cold store temperatures). Therefore, when gas hydrates are prepared for use in frozen confections, an excess of water (i.e. more water than prescribed by the stoichiometric ratio) is typically used so that a composite of gas hydrate crystals in ice is formed. The ice around the hydrate crystals is essential in order to prevent the decomposition of the hydrates during manufacture and storage. In effect, the ice acts as a microscopic pressure vessel. On warming (e.g. in the mouth when consumed), the ice layer around the gas hydrate crystals melts, and the gas hydrate decomposes releasing the gas. This provides a "fizzing" sensation similar to that of carbonated drinks.

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The applicants have sought to devise a process whereby composites of gas hydrate and ice can be produced by a continuous extrusion process. We have found that this is made possible if an aqueous solution of gas is produced and then fed to an extruder. The barrel of the extruder is cooled in order to freeze the solution inside it. Pressure in the extruder is created by feeding the solution into the extruder, and can be maintained by the formation of a frozen plug of product within the extruder, preferably at or near the extruder exit. Thus the extruder allows the temperature and pressure conditions required for the formation of gas hydrate to be created. Since steps (a) – (d) of the method of the invention are effected using an extruder, the method provides a continuous process.

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The gas solution is conveniently formed by mixing the gas and water at elevated pressure and reduced temperature and may be performed in batch, continuous or continuous batch manner. Optionally, the water may be de-oxygenated before mixing with the gas. Pressurisation and/or cooling of the gas solution prior to it being fed to the extruder may be effected in the associated ducting and/or in any batch or semi-

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batch mixer(s) where the solution is prepared. In the case of a mixer, a pressurised gas (e.g. air) may be applied above the body of the liquid. Additionally or alternatively, an in-line pump may be used.

- 5 The gas solution (including any optional additional ingredients therein) is preferably fed to the extruder inlet at a pressure of at least 10 bar (10^6 Pa). The pressure is preferably at least 15 bar and preferably at most 45 bar, more preferably from 20 to 40 bar. Preferably the gas solution is at a reduced temperature, i.e. below ambient temperature. Preferably the temperature of the solution is as low as possible without
10 entering the part of the phase diagram where gas hydrate is formed. Thus, particularly for carbon dioxide, the temperature is preferably from 0°C to 20°C, more preferably from 0°C to 15°C, for example about 5 to 10°C.

- In its simplest product form, the liquid used to form the aqueous gas solution consists
15 substantially only of water so that the final product consists substantially of only ice and gas hydrate. However, one or more optional other ingredients may be added to the aqueous gas solution; and / or converge with the gas solution feed before entering the extruder; and / or be introduced to the extruder as one or more separate product streams. Preferably the solution comprises at least 90%, more preferably at least 95%,
20 most preferably at least 99% by weight of water.

- Preferably the solution contains one or more sweeteners. Sweeteners are standard ingredients in frozen confections since they provide sweetness and control the ice content via freezing point depression. Moreover, we have found that when added in
25 relatively small amounts, they act as process aids in the extruder. It is believed that their presence results in a more gradual change in the mechanical properties of the solution as ice is formed in the extruder because of the freezing point depression that they provide. Therefore the aqueous solution preferably comprises (in addition to the gas) at least 0.01%, preferably at least 0.1%, more preferably at least 0.2% but also
30 preferably at most 20%, more preferably less than 10%, even more preferably less than 5%, most preferably less than 1% by weight of one or more sweeteners. Sweeteners include mono- and disaccharides sugars, such as dextrose, fructose, sucrose and lactose; oligosaccharides containing from 3 to ten monosaccharide units joined in

glycosidic linkage; corn syrups and maltodextrins; sugar alcohols (also known as polyols or polyhydric alcohols), such as erythritol, arabitol, glycerol, xylitol, sorbitol, mannitol, lactitol, maltitol, hydrogenated starch hydrolysate (HSH) – also known as polyglycitol, isomalt and palatinit.

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Optionally, the solution comprises fat, preferably in the form of an oil in water emulsion, containing up to 10 wt% fat and an emulsion stabilizer, for example Tween 20, whey protein isolate or sodium caseinate. We have found that small amounts of emulsions also act as process aids in the extruder. This is believed to be because they

10 replace ice and weaken the structure of the frozen solution. Optionally, the solution may also comprise other ingredients typically used in frozen confections, such as stabilisers, colours and flavours.

Optionally, the product contains a surface active substance, such as dairy proteins, soy

15 proteins, egg protein, and hydrophobins, especially class II hydrophobins such as HFB I and HFB II from *Trichoderma reesei*; protein hydrolysates (often based on soy protein or dairy protein); non-ionic surfactants and anionic surfactants. Suitable substances include hydrolysed milk proteins such as Hygel™ and Hyfoama™ (available from Kerry Biosciences); or hydrolysed soya proteins such as Versawhip (available from Kerry

20 Biosciences) and D-100™ (available from Gunter Industries); Tweens, sucrose esters, diacetyl tartaric acid esters of monoglycerides (such as DATEM), citric acid esters of monoglycerides, polyglycerol esters (such as PGE 55, a polyglycerol ester of fatty acids, available from Danisco), stearyl lactylates, lactic acid esters, acetic acid esters, propylene glycol esters and mono-/di-glycerides (such as Myverol 18-04K, a distilled

25 95% monoglyceride prepared from vegetable oils, available from Quest International); biosurfactants such as glycolipids; lipopeptides and lipoproteins, fatty acids, neutral lipids, and phospholipids; polymeric biosurfactants.

The amount of surface active substance in the aqueous solution is preferably at least

30 0.01 wt%, more preferably at least 0.05 or 0.1 wt%, most preferably at least 0.2 wt%. Preferably the amount of aerating agent is less than 5 wt%, more preferably less than 2 wt% or 1 wt%, most preferably less than 0.5 wt%.

In the extruder, the temperature is reduced to below 0°C (e.g. -10 or -20°C), thus forming the frozen gas hydrate / ice composite. Many forms of extruder may be used but in a preferred class of embodiments, the extruder is screw barrel extruder. We have found that adding small amounts of ingredients such as sweeteners and surface
5 active substances can reduce the torque on the screw compared to when water alone is used, i.e. they act as process aids.

The extruder barrel is provided with cooling means, usually a cooling jacket, to cool the solution inside the barrel to a desired temperature. It is preferred that the barrel
10 cooling is performed such that at least over a portion of the length of the barrel and most preferably, near the exit end, the temperature of coolant is maintained at a temperature of from -50°C to -10°C, more preferably from -35°C to -10°C, still more preferably from -30°C to -10°C. However, the temperature in the exit region could in principle be higher, lower or substantially the same as that in the preceding part(s) of
15 the extruder.

A number of factors will determine the preferred or optimum temperature(s) of the barrel coolant. One is the amount(s) and kind(s) of material other than water which are used in the composition. For example, generally speaking the more sweetener present, the lower the coolant temperature needs to be. Some polyols are very
20 effective freezing point depressants. Therefore, the presence of even small amounts of these may require much lower temperatures. The thickness and thermal conductivity of the material(s) from which the barrel is formed will also have an effect. Finally, the torque and operating speed of the motor driving the screw, as well as the desired final product consistency and/or storage temperature will also influence the choice of
25 coolant temperature at each stage.

The screw may have one or more starts. The screw may have one or more differing profiles along the axis of the extruder. The screw angle is typically in the range normally used for solid transport e.g. less than 25°. The screw angle in the entrance section could be in range typically used for transport of viscous fluids e.g. 30 – 50°. The
30 entrance section of the screw may be designed so as to maximise heat transfer to fluid. The exit section may be designed so as to compact ice and transport out of

extruder. The screw may be cooled separately, for example by passing a cooling fluid through a hollow shaft in the centre of the screw.

The production rate of gas hydrate / ice composite is determined by the screw speed.

- 5 The screw speed must be adjusted to give good extrusion conditions: if the speed is too high, then the product will not be fully frozen within the extruder exit section and unfrozen material will be forced out due to the raised inlet pressure. If the speed is too low, the frozen material becomes too hard and brittle, fractures will occur within the barrel causing material to rotate within the barrel rather than being pushed
10 forward and extruded. The optimum screw speed will depend on the extruder configuration, the barrel temperature and the composition of the solution.

- Preferably, the extruder has a barrel which is grooved on its internal surface along at least part of its length, preferably at the exit section. A grooved barrel is a cylindrical
15 tube which has a scored internal surface, preferably along the entire length thereof. Preferably, this scoring is in the form of internal grooves which may have any particular geometry, for example grooves parallel to the main axis of the barrel. Optionally, a die may be used at the extruder exit to assist in maintaining the required pressure.

- 20 The composite of gas hydrate and ice leaves the extruder as a relatively hard extrudate having a high ice content. The gas hydrate / ice composite is generally intended as an additive to frozen confections to make them fizzy in the mouth. Thus after production, the extrudate is typically broken or cut into pieces of any desired size (for example approximately 1-5mm). The pieces may be packaged directly, or they may be mixed
25 with a sauce or incorporated into a frozen confection such as ice cream, sorbet or water ice to form a final product.

- The term "frozen confection" means a sweet-tasting fabricated foodstuff intended for consumption in the frozen state (i.e. under conditions wherein the temperature of the
30 foodstuff is less than 0°C, and preferably under conditions wherein the foodstuff comprises significant amounts of ice). Frozen confections include ice cream, sorbet, sherbet, frozen yoghurt, water ice, milk ice and the like. Frozen confections such as ice cream and frozen yoghurt typically contain fat, protein (such as milk protein) sugars,

together with other minor ingredients such as stabilisers, emulsifiers, colours and flavourings. Water ice typically contains, by weight of the composition 15–25% sugars together with stabilisers, colours and flavourings.

- 5 Typically the other ingredients have already been combined to produce a frozen confection (e.g. ice cream) or a sauce / syrup, into which the gas hydrate / ice pieces are mixed. Preferably the edible gas hydrate / ice composite constitutes from 5 to 50 wt%, preferably 10 to 20 wt% of the total frozen confection After combining the gas hydrate / ice composite with the other ingredients, the frozen confection may be
10 subjected to a further freezing step (e.g. hardening), and may then be packaged.

The invention will now be explained in more detail by way of the following description of a preferred embodiment and with reference to the accompanying drawings.

15 **Brief Description of the Drawings**

Figure 1 shows the phase diagram for carbon dioxide hydrates;

Figure 2 shows a screw barrel extruder for effecting a method according to the present invention; and

Figure 3 shows a block diagram of a complete apparatus for carrying out a method
20 according to the invention.

Description of Preferred Embodiments

As shown in Figure 2, there is provided an extruder 1 which comprises a main barrel 3 surrounded by a cooling jacket 5. The barrel 3 is substantially cylindrical in interior
25 profile and has grooves along the length of its interior wall 7. The barrel 3 has an inlet end 9 and an outlet end 11. The inlet end 9 is provided with a feed pipe 13 through which a solution 15 is introduced.

Along the axis of symmetry of the barrel 3 is situated a rotatable shaft 17 having a
30 screw transporter 19 attached thereto. The outer edge 21 of the screw transporter 19 runs close to the inside surface 7 of the barrel. The rotatable shaft 17 is rotated by means of a motor 23. As the shaft 17, and therefore, the screw transporter, 19, rotates, the solution 15 is transported from the inlet end 9 of the barrel to the outlet

end 11 where it is extruded after having been frozen during its transit through the barrel 3.

Figure 3 shows a block diagram of the overall apparatus. Reference numeral 41 denotes the extruder shown in Figure 2. A feed tank 43 contains water which is pumped by means of a pump 45, via flow meter 47 to join with a gas flow from a supply 49 which is fed via gas flow meter 51. A static mixer 53 forms the aqueous gas solution which is fed to the extruder 41.

Example

A single screw extruder of length 1.7m, internal diameter 137mm, screw angle 17° and 4mm flight height was used to make carbonated water ice. For start up, the barrel exit was closed to allow it to fill with the solution. The cooling was turned on whilst the screw was rotated so that ice began to form. After a few minutes, a substantial amount of ice had formed within the extruder and the torque on the screw began to increase. The increase in torque indicated that the screw had begun to transport ice along the barrel and that a plug of ice had formed at the exit. The extruder exit was then opened and ice began to be extruded from it. Once the temperature of the extruded ice reached approximately -5°C, the inlet pressure was increased and carbon dioxide gas was injected into the solution feed stream. Carbonated ice was produced under the following set of conditions: feed stream: 8°C, 25 bar, containing 3.3wt% CO₂; screw speed 1.5rpm, barrel jacket coolant -16.5°C. The product left the extruder at approximately -7°C, at a rate of 17kg/h and contained 17mlCO₂/g (measured at STP).

The various features and embodiments of the present invention, referred to in individual sections above apply, as appropriate, to other sections, mutatis mutandis. Consequently features specified in one section may be combined with features specified in other sections, as appropriate.

CLAIMS

1. A method of producing an edible composite of gas hydrate and ice using an extruder comprising a barrel having an inlet and an exit and provided with cooling means, the method comprising:
 - (a) feeding an aqueous gas solution at an elevated pressure into the barrel of the extruder via the inlet;
 - (b) cooling the barrel to form a frozen plug within the extruder so that the pressure inside the barrel is at or above the minimum pressure required for gas hydrate formation;
 - (c) freezing the gas solution inside the barrel to form the composite; and
 - (d) extruding the frozen composite from the extruder exit.
2. A method according to claim 1, wherein the gas comprises or consists of carbon dioxide, nitrous oxide or a mixture thereof.
3. A method according to claim 1 or claim 2, wherein the elevated pressure is from 10 to 45 bar, preferably from 15 to 40 bar.
4. A method according to any of claims 1 to 3, wherein the gas solution is fed to the extruder at reduced temperature.
5. A method according to claim 4, wherein the reduced temperature is from 0°C to 20°C, preferably from 0°C to 15°C.
6. A method according to any of claims 1 to 5, wherein the aqueous solution comprises from 0.01% to 20% by weight of sweetener, preferably from 0.1 to 1%.
7. A method according to any of claims 1 to 6, wherein the aqueous solution comprises from 0.01% to 5% by weight of a surface active substance, preferably from 0.1 to 1%.

8. A method according to any of claims 1 to 5, wherein the solution consists substantially of water.
9. A method according to any preceding claim, wherein the extruder is a screw
5 extruder.
10. A method according to claim 9, wherein the barrel is grooved on at least part of its internal surface.
- 10 11. A process for producing a frozen confection, the process comprising producing a composite by the method of any of claims 1 to 10; and then combining the composite with the remaining ingredients of the frozen confection

Fig.1.

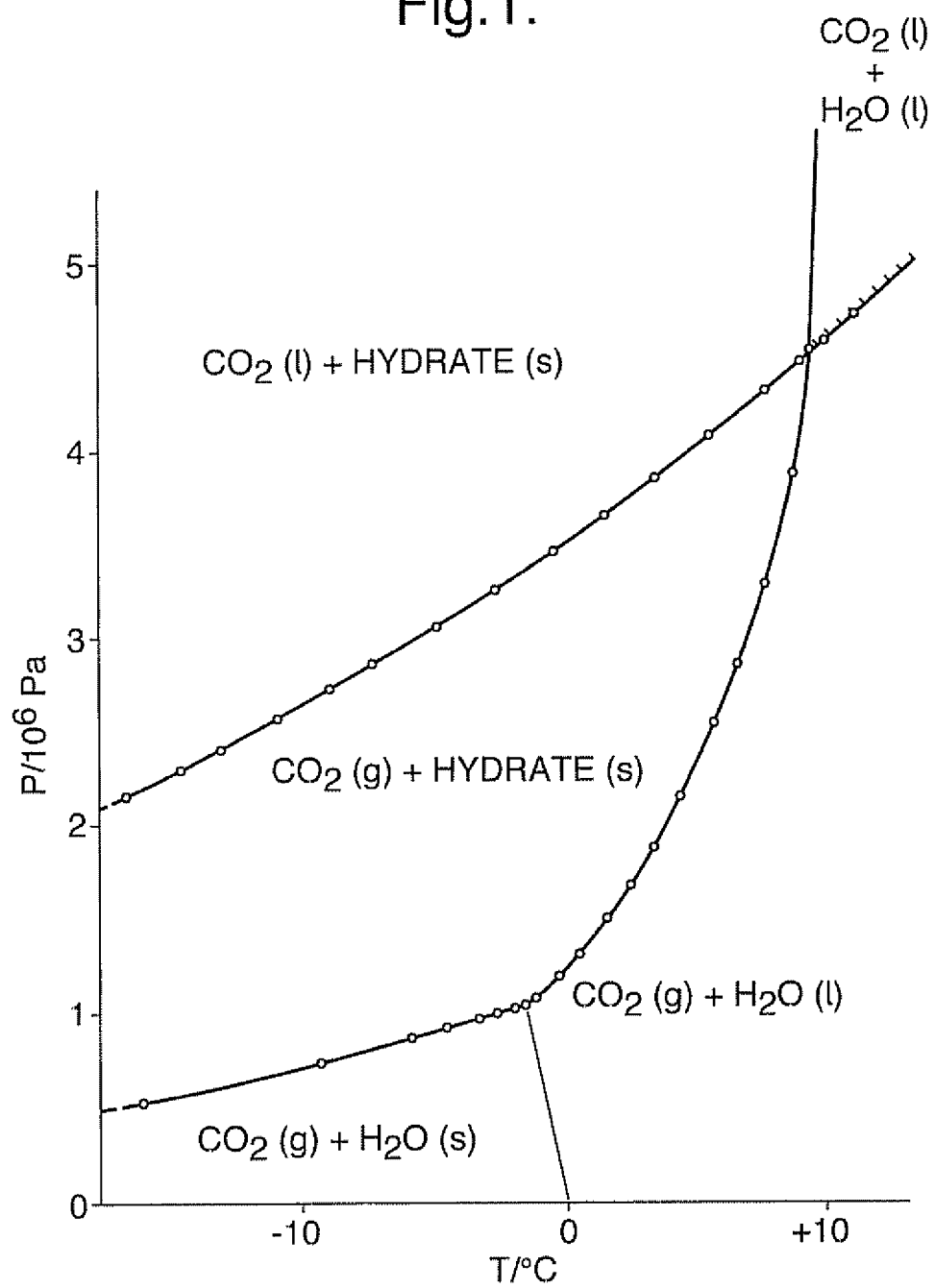


Fig.2.

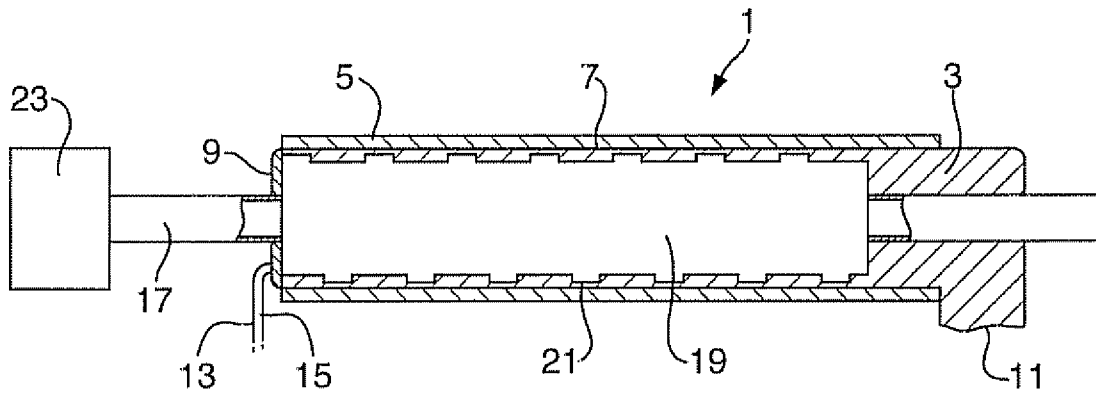
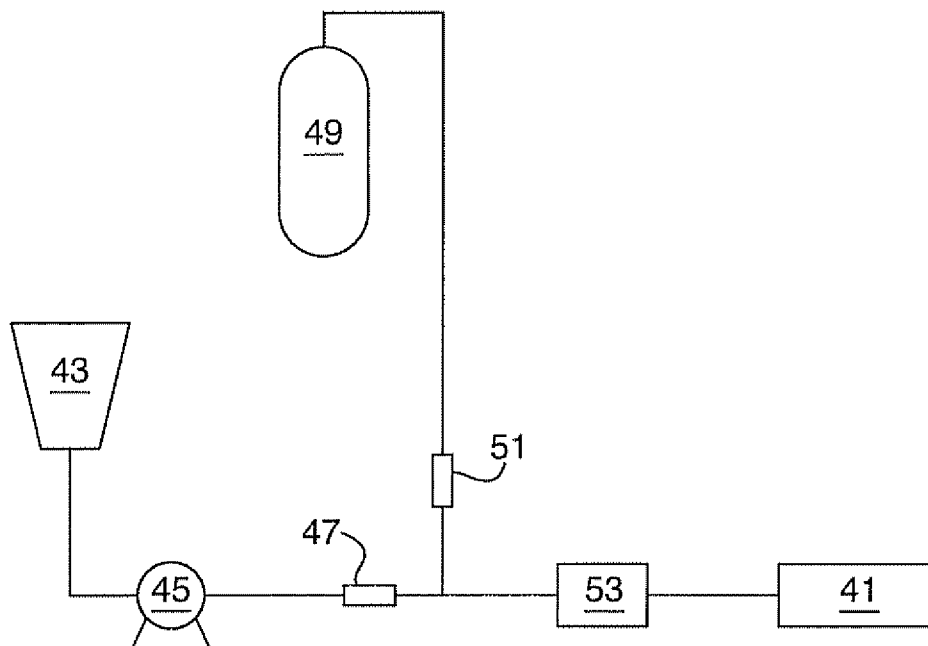


Fig.3.



INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. A23G9/46 A23G9/20
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)
A23G

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 practical, search terms used)

EPO-Internal, WPI Data

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Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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