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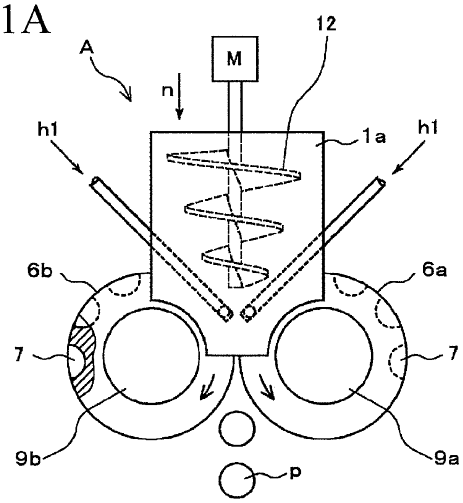
(54) **Apparatus for producing gas hydrate pellet and process for producing gas hydrate pellet with the same**

(57) In producing gas hydrate pellets by compression-molding a gas hydrate powder, heat generated in a compressing part is removed with a simple method so as to reduce the degree of gas hydrate decomposition, and a gas hydrate aggregate blocking the compressing part is promptly and easily removed. A gas-hydrate-pellet production apparatus A is characterized by including: a roll-cooling mechanism which causes cooling water to flow through outer peripheral portions and/or insides of rolls 6a and 6b, thereby cooling the rolls 6a and 6b, and also cools the cooling water 43 discharged after the flow and supplies the cooled cooling water 43 to the outer peripheral portion and/or the inner portion of each of the rolls 6a and 6b; and/or heating means provided in a part of a hopper chamber 5 from which the gas hydrate powder n is fed to the rolls 6a and 6b.

Fig.1A



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Description

TECHNICAL FIELD

[0001] The present invention relates to an apparatus for producing gas hydrate pellets and a process for producing gas hydrate pellets with the same. More specifically, the present invention relates to: an apparatus for producing gas hydrate pellets that is designed to promptly remove a blockage formed of a gas hydrate aggregate generated between rolls used for compression molding; an apparatus for producing gas hydrate pellets that is designed to reduce the degree of decomposition in pelletizing a gas hydrate powder; and a process for producing gas hydrate pellets with the same.

BACKGROUND ART

[0002] In these days, natural gases, which are mainly composed of methane, propane, and the like, have attracted attention as clean energy sources. Such natural gases are liquefied into liquefied natural gases (LNGs) for the transportation and storage of the natural gases. However, the transportation and storage of gases in the form of LNGs need to be conducted under very low temperature conditions (at -162°C or below); accordingly, the transport system and the storage system therefor are expensive.

[0003] A gas hydrate is an ice-like solid substance composed of water molecules and raw-material gas molecules, and is a kind of stable clathrate compound in which the raw-material gas molecule is included inside a three-dimensional cage-like structure formed of the water molecules. The gas hydrate has a relatively large gas content and has characteristic properties such as large generation/decomposition energies and a high selectivity of gas to be hydrated. For these reasons, the gas hydrates have a variety of possible applications including transportation/storage means for natural gases and the like, heat storage systems, actuators, separation and recovery of specific component gases, for example, and have been actively studied.

[0004] Gas hydrates are generally generated under high pressure and low temperature conditions. As generating means for gas hydrates, a so-called "water spray system" and a so-called "bubbling system" are known, for example. In the water spray system, cooled raw-material water is sprayed within a generating vessel that is filled with a raw-material gas at a high pressure from the top thereof, whereby gas hydrates are generated in the surfaces of water droplets while the water droplets are falling down in the raw-material gas. In the bubbling system, a raw-material gas is introduced as bubbles (is bubbled) into raw-material water, whereby gas hydrates are generated in the surfaces of the bubbles of the raw-material gas while the bubbles are rising in the water.

[0005] The gas hydrate thus produced is in the form of a so-called powder like a powder snow or a crushed ice. The gas hydrate powder has been proposed to be transported and stored while being maintained at a temperature (for example, approximately -20°C) at which the gas hydrate effects the self-preservation. The filling fraction of the gas hydrate powder in a storage tank ((the volume of the gas hydrate powder) / (the volume of the container)) is small. For this reason, the transportation or storage of the gas hydrate powder require a tank or the like having a large volume. Moreover, there is a problem in that the gas hydrate powder has a large surface area because of its powder form, and thus is decomposed into the natural gas and water at a very high decomposition rate. There is also a problem in that, if a large amount of the gas hydrate powder is stored, lower part of the powder is hardened into a bedrock-like form, thus becoming difficult to take out.

[0006] In this regard, the present inventors have proposed so far a technique in which the powdery gas hydrate powder is compression-molded into a product in the form of pellets of a substantially spherical shape or the like by using a molding apparatus, and then the gas hydrate pellets are transported or stored (refer to, for example, Patent Document 1).

[0007] An apparatus F for producing gas hydrate pellets of this technique is configured as follows, as illustrated in Fig. 8. A gas hydrate powder n supplied into a hopper chamber 30 is fed to a pair of rolls 33a and 33b having facing pockets 34 (molding concave portions). The gas hydrate powder n filled in the pockets 34 is then compressed and molded along with the rotations of the rolls 33a and 33b. In addition, a screw-type push-in device 31 for filling the gas hydrate powder n into the pockets 34 is disposed in the hopper chamber 30, and the gas hydrate powder receives, in addition to its own weight, a predetermined pressure applied by the push-in device 31.

[0008] Meanwhile, according to the observation of the inventors, it has been found that, in the above-described production apparatus F, water may exude from the snow-powder-form gas hydrate powder n if the compression molding is conducted under conditions similar to those for generating the powder n (for example, approximately at 4 to 6 MPa and 2 to 5°C). The following facts have also been found: since having a specific gravity smaller than that of water, the gas hydrate powder n has a nature to float up as the exuding water is accumulated in the hopper chamber 30; and the higher the molding pressure, the larger the amount of water to exude.

[0009] In the compression molding with the production apparatus F using the gas hydrate powder n as a raw material, pellets p can be steadily produced in the initial stage of the operation because no exuding water has been accumulated. However, since the gas hydrate that has been pressed and consolidated is filled in a gap between the rolls 33a and 33b, water squeezed out by the rolls 33a and 33b (squeezed water) is not discharged through the gap but accumulated in the hopper chamber 30.

[0010] As the operation continues in such a state, the water level keeps rising in the hopper chamber 30. Buoyancy is provided to the gas hydrate powder along with the rise of the water level. Consequently, the gas hydrate powder n pushed in by the push-in device 31 and the gas hydrate powder n floating up are successively accumulated near the tip of the screw of the push-in device 31, and are thus compressed into an aggregate.

[0011] Then, the powder n fed by the push-in device 31 causes the aggregate having a substantially wedge-shaped cross section and extending in the axial direction of the rolls 33a and 33b to grow to be an aggregate b of a substantial size. The aggregate b acts like a blockage in an opening portion 35 of the hopper chamber 30 and between the rolls 33a and 33b, so that the gas hydrate powder n cannot be fed to the rolls 33a and 33b, causing a problem in that the gas hydrate pellets p cannot be produced.

[0012] Moreover, operating the production apparatus F at normal pressure (atmospheric pressure) also brings about a similar problem. When the pressurizing force of the push-in device 31 is increased for securing the filling into the pockets 34, the particles of the powder n are fixed together to form the aggregate b, eventually acting like a blockage.

[0013] Once the aggregate b is generated as described above, the operation of the production apparatus F has to be interrupted for removal of the gas hydrate aggregate b, requiring works such as disassembly, reassembly, and adjustment of the apparatus F. As a result, the operating efficiency of the gas-hydrate-powder production apparatus is significantly deteriorated. In particular, when the production apparatus F produces the gas hydrate pellets p through compression molding in a high-pressure atmosphere (4 to 6 MPa) that is conditions similar to those for generating the gas hydrate powder, the following problems occur. In this case, the work for removing the gas hydrate aggregate b is extremely difficult because the entire apparatus is accommodated in a robust pressure-tight container having a thickness of 200 mm or more. It takes a long time (for example, 24 hours) for the aggregate b to be dissolved, and the production apparatus F has to stop the operation for such a long time. Eventually, the production amount of the production apparatus for the gas hydrate powder n, which is the raw material, has to be considerably reduced, or the production has to be stopped.

[0014] On the other hand, another problem would occur in pelletizing a gas hydrate powder through compression molding. Specifically, the surface temperature of the rotating rolls 33a and 33b increases accompanying the compression work in the pelletization. If the surface temperature reaches the decomposition temperature of the gas hydrate, the gas hydrate powder is decomposed. For example, after a gas hydrate powder is generated under conditions of a pressure of 5.4 MPa and a temperature of 2 to 3°C, if the gas hydrate powder is continuously formed into pellets through compression molding by using a rotating-roll-type pelletizer, the surface temperature of the rolls increases. Then, if the atmosphere reaches conditions of a pressure of 5.4 MPa and a temperature of 8°C, the gas hydrate is decomposed. The decomposition of the gas hydrate reduces the concentration, in turn causing a problem in that the advantages of the gas hydrate cannot sufficiently be exerted.

[0015] As a countermeasure to this problem, the temperature of the gas hydrate powder may be lowered in advance prior to the supply thereof to the pelletizer. However, this approach requires another cooling device to be disposed between the gas hydrate generator and the pelletizer. Thus, there is a concern that the number of manufacturing processes increases, leading to an increase in producing cost.

[0016] Accordingly, no process for producing gas hydrate pellets has been established yet, the process being capable of pelletizing a gas hydrate powder while suppressing the decomposition of the powder by a method that is simple and does not lead to a cost increase.

Patent Document 1: Japanese patent application *Kokai* publication No. 2002-220353

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0017] The present invention has been made for solving the above-described problems. A first object of the present invention is to provide an apparatus for producing gas hydrate pellets which is designed to promptly melt a blockage formed of a gas hydrate aggregate generated between rolls when gas hydrate pellets are produced by compression-molding a gas hydrate powder by using a rotating-roll-type pellet production apparatus. A second object thereof is to provide: an apparatus for producing gas hydrate pellets which is designed to reduce the degree of decomposition of a gas hydrate by removing, with a simple method, heat generated in a compressing part on a roll surface; and a process for producing gas hydrate pellets with the same.

MEANS FOR SOLVING THE PROBLEMS

[0018] An apparatus for producing gas hydrate pellets of a first invention for achieving the above object is a production apparatus which compression-molds a powdery gas hydrate powder into gas hydrate pellets of a substantially spherical shape or the like, the gas hydrate powder being generated by contacting and reacting a raw-material gas and raw-material water with each other. The production apparatus is characterized as follows. The production apparatus includes: a hopper chamber which houses the gas hydrate powder; a pair of compression rolls which are disposed below an opening portion of the hopper chamber; and a push-in device which feeds the gas hydrate powder in the hopper chamber to the compression rolls. Heating means is provided on at least one side of the hopper chamber.

[0019] The heating means preferably supplies hot water to the pair of compression rolls from a lower portion of the at least one side of the hopper chamber, and discharges the water from a lower portion of another side thereof. Moreover, a nozzle for jetting the hot water or water is preferably provided in the lower portion of the at least one side of the hopper chamber.

[0020] An apparatus for producing gas hydrate pellets of a second invention is a roll-type gas-hydrate-pellet production apparatus which compression-molds a gas hydrate powder to produce gas hydrate pellets, the gas hydrate powder being generated by contacting and reacting a raw-material gas and raw-material water with each other. The gas-hydrate-pellet production apparatus is characterized as follows. The gas-hydrate-pellet production apparatus includes: a hopper chamber which houses the gas hydrate powder; a pair of compression rolls which are disposed below an opening portion of the hopper chamber; and a push-in device which supplies the gas hydrate powder in the hopper chamber to the compression rolls. The gas-hydrate-pellet production apparatus further includes a roll-cooling mechanism which causes cooling water to flow through an outer peripheral portion and/or an inside of each roll so as to cool the roll, and which cools the cooling water discharged after the flow by use of a cooler.

[0021] Furthermore, the apparatus for producing gas hydrate pellets of the first invention may include a roll-cooling mechanism which causes cooling water to flow through an outer peripheral portion and/or an inside of each roll so as to cool the roll, and which cools the cooling water discharged after the flow by use of a cooler.

[0022] A process for producing gas hydrate pellets of the present invention is a process for producing gas hydrate pellets by contacting and reacting a raw-material gas and raw-material water with each other so as to generate a gas hydrate powder, and by compression-molding the gas hydrate powder with a roll-type gas-hydrate-pellet production apparatus. The process is characterized by including: causing cooling water to flow through an outer peripheral portion and/or an inside of a roll of the gas-hydrate-pellet production apparatus so as to cool the roll; cooling the cooling water discharged after the flow by use of a cooler; and supplying the cooled cooling water to the outer peripheral portion and/or the inner portion of the roll.

[0023] In the production process, preferably, the cooling water is supplied to a hopper chamber from which the gas hydrate powder is fed to the roll, the cooling water is thereby brought into contact with the outer peripheral portion of the roll, and the cooling water is discharged from a cooling-water outlet of the hopper chamber. A cooling bath may be disposed below the roll. The cooling water may be supplied to the cooling bath. The cooling water may be brought into contact with the outer peripheral portion of the roll. Additionally, the cooling water may be supplied to a cooling-water jacket provided inside the roll so as to cool the roll.

[0024] The temperature difference T - To between the temperature T of the gas hydrate pellets and the temperature To of the gas hydrate powder is preferably set to be below 3°C. The amount of heat removed by the cooler is preferably set to be not less than the amount of heat Q1 obtained by the following expression (I):

$$Q1 = (T - T_0)\, cM + qM\beta / 100 \ldots (I),$$

(in the expression (I), Q1 is the amount of heat [w] which the gas hydrate powder receives in the pelletization, c is the specific heat [kJ/kgK], q is the decomposition heat [kJ/kg], M is the pelletization speed [kg/s] for the gas hydrate powder, and β is the degree of decomposition [%] in the pelletization of the gas hydrate powder).

EFFECTS OF THE INVENTION

[0025] According to the apparatus for producing gas hydrate pellets of the first invention, a substantially wedge-shaped aggregate (blockage) of a gas hydrate powder, which is formed between the compression rolls, is directly melted with the hot water, so that the aggregate is melted at a high melting rate. Accordingly, the time for which the pellet production is interrupted by the clogging in the production apparatus is shortened. In particular, the operation for removing a blockage is significantly improved in producing pellets at a high pressure under conditions similar to those for generating a gas hydrate powder. As a result, the production amount of gas hydrate pellets is prevented from being deteriorated.

[0026] Moreover, since the hot water or water is jetted, such hot water or the like collides intensively against a gas hydrate aggregate at a high pressure. Accordingly, the aggregate can be further efficiently melted.

[0027] The apparatus for producing gas hydrate pellets of the second invention includes the roll-cooling mechanism which causes the cooling water to flow through the outer peripheral portion and/or the inside of each roll so as to cool the rolls, which cools the cooling water discharged after the flow by use of the cooler, and which circulates the cooled cooling water so as to again flow through the outer peripheral portion and/or the inside of the roll. Accordingly, the temperatures of the gas hydrate and the roll surfaces are prevented from reaching the decomposition temperature of the gas hydrate. As a result, the degree of decomposition of the gas hydrate can be reduced.

[0028] The process for producing gas hydrate pellets of the present invention uses the roll-type gas-hydrate-pellet production apparatus. In producing gas hydrate pellets by compression-molding a gas hydrate powder, the cooling water is circulated to flow through the outer peripheral portion and/or the inside of the roll of the gas-hydrate-pellet production apparatus so as to cool the roll surface. Accordingly, even when heat is generated by the compression work in the pelletization of the gas hydrate powder, the cooling water removes the heat, so that the temperatures of the gas hydrate and the roll surfaces are prevented from reaching the decomposition temperature of the gas hydrate. As a result, the degree of decomposition of the gas hydrate can be reduced.

[0029] In addition, after the cooling water flows through the outer peripheral portion and/or the inside of the roll so as to cool the roll surface, the discharged cooling water is cooled to a predetermined temperature, and then, is circulated again through the outer peripheral portion and/or the inner portion of the roll. This securely prevents the temperature of the roll surface from increasing. Accordingly, it is possible to produce firmly compacted gas hydrate pellets while removing generated heat and suppressing an increase in production cost with a simple method.

BRIEF DESCRIPTION OF THE DRAWINGS

[0030]

[Fig. 1] Part a of Fig. 1 and Part b of Fig. 1 are schematic configuration views of an embodiment of an apparatus for producing gas hydrate pellets of a first invention, and Part a of Fig. 1 is a side view while Part b of Fig. 1 is a top view.

[Fig. 2] Fig. 2 is a perspective view of Fig. 1.

[Fig. 3] Fig. 3 is an explanatory view illustrating the overview of a gas-hydrate-pellet production apparatus of a rotating roll type that is an embodiment of an apparatus for producing gas hydrate pellets of a second invention.

[Fig. 4] Fig. 4 is a block flow diagram showing an example of processes in a process for producing gas hydrate pellets of the present invention.

[Fig. 5] Fig. 5 is an explanatory view schematically showing an example of processes according to a first embodiment of the production process of the present invention.

[Fig. 6] Fig. 6 is an explanatory view schematically showing an example of processes according to a second embodiment of the production process of the present invention.

[Fig. 7] Fig. 7 is an explanatory view schematically showing an example of processes according to a third embodiment of the production process of the present invention.

[Fig.8] Fig. 8 is a schematic configuration view of a conventional apparatus for producing gas hydrate pellets.

EXPLANATION OF REFERENCE SIGNS

[0031]

1, 1a, 1b	side plate
2	heat-transfer-medium line
3	ejecting nozzle
4	water pipe (cooling-water outlet)
5	hopper chamber
6a, 6b	molding roll
7	pocket
9a, 9b	roll shaft
10a, 10b	feeder base
12	push-in device
21	generator
22	gas-hydrate-pellet production apparatus (pelletizer)
41, 42	cooling water
43	discharged cooling water
57	cooler
58	cooling bath
A	production apparatus
h1	hot water
h2	discharged water
h3	squeezed water
g	raw-material gas
w	raw-material water
n	gas hydrate powder
p	gas hydrate pellets

BEST MODES FOR CARRYING OUT THE INVENTION

[0032] Hereinafter, an embodiment of a production apparatus A according to a first invention will be described with reference to Fig. 1 and Fig. 2.

[0033] As illustrated in Parts a and b of Fig. 1 as well as Fig. 2, the production apparatus A includes: a hopper chamber 5 for storing a gas hydrate powder n; a pair of compression rolls 6a and 6b disposed below an opening portion 5a of the hopper chamber 5; and a push-in device 12 for feeding the gas hydrate powder n in the hopper chamber 5 to the compression rolls 6a and 6b. The hopper chamber 5 is formed of: side plates 1 a and 1 b that are disposed on side surfaces of the rolls 6a and 6b in such a way as to face each other; and feeder bases 10a and 10b that are disposed to face each other while being inclined to extend toward a gap between the roll 6a and the roll 6b. Note that the illustration of the screw-type push-in device 12 disposed in the hopper chamber 5 is omitted in Part b of Fig. 1 and Fig. 2.

[0034] Hot water h1 is supplied to the pair of compression rolls 6a and 6b through a lower portion of the side plate 1a of the hopper chamber 5, and is discharged through a lower portion of the other side plate 1 b. Further, nozzles 3 for ejecting the hot water are provided to the lower portion of the side plate 1 a.

[0035] As the hot water h1, water such as discharged water h2 discharged from a water pipe 4, squeezed water h3 from the gas hydrate powder, or unreacted water in a gas-hydrate-powder production apparatus; or water such as ion-exchange water or pure water may be used with control of the temperature. The hot water h1 is maintained at a predetermined temperature (for example, in a range of 60 to 80°C) in a thermostatic chamber (not illustrated) formed of a temperature control unit, a transfer pump, a water storage tank, and a heat exchanger. The hot water h1 is supplied into the hopper chamber 5 through the nozzles 3 from heat-transfer-medium lines, and the squeezed water h3 and the discharged water h2 resulting from the supplied hot water are circulated back to the thermostatic chamber through the water pipe 4.

[0036] In addition, the side plate 1a as well as the rolls 6a and 6b can be cooled by causing cooling water (for example, pure water at approximately 1°C) to flow through the heat-transfer-medium line 2 in the side plate 1a as necessary during the compression molding of gas hydrate pellets p.

[0037] The compression production apparatus A for the gas hydrate pellets p, which has the above-described structure, operates as follows. The gas hydrate powder n supplied from the unillustrated gas-hydrate-powder production apparatus is once retained in the hopper chamber 5 under the conditions similar to those for generating the gas hydrate powder (for example, approximately at 5 MPa and 3°C). Then, the powder n is fed to the pair of rolls 6a and 6b disposed below the opening portion 5a of the hopper chamber 5 by the action of the screw-type push-in device 12. The gas hydrate powder n is securely filled in pockets 7 formed in the rolls 6a and 6b, and is compressed along with the rotation of the rolls 6a and 6b, so that the pellets p are produced.

[0038] In the compressing part between the rolls 6a and 6b, water (unreacted water) contained in the gas hydrate powder n exudes out as if being squeezed out. The squeezed water h3 is not discharged to the outside through the gap between the rolls 6a and 6b because the gas hydrate has been pressed and consolidated in the gap. Instead, the squeezed water h3 is discharged all the time through the water pipe 4 provided in the lower portion of the side plate 1 b of the hopper chamber 5.

[0039] When the pellets p are produced using the apparatus A, the aforementioned substantially wedge-shaped aggregate b (blockage) is generated in some cases between the rolls 6a and 6b and in the opening portion 5a of the hopper chamber 5. Such generation of the aggregate is caused due to variations in the pressing force of the push-in device 12, the property of the gas hydrate powder n, which is the raw material, and the like.

[0040] In such a case, the hot water h1 (for example, at 60°C) is supplied from the thermostatic chamber into the hopper chamber 5 through the heat-transfer-medium line 2 in the side plate 1a. The supply amount and temperature of the hot water h1 are preferably adjusted as appropriate in accordance with the interior size of the hopper chamber, the length of the rolls in the axial direction thereof, the temperature of the gas hydrate powder to be supplied, and the like.

[0041] With the supply of the hot water h1, the aggregate b (blockage) of the gas hydrate powder receives the heat of the hot water h1, and is thereby melted (decomposed) in a short time period (for example, 3 to 6 minutes) while emitting a gas (a natural gas such as methane or propane). Then, the hot water h1 which has given the heat to the aggregate b (blockage) is discharged as the discharged water h2 through the water pipe 4. The gas generated in the melting of the aggregate b (blockage) is recovered through a gas recovery conduit so as to be reused as a raw-material gas for the gas-hydrate-powder production apparatus or the like.

[0042] The production apparatus A according to the first invention significantly reduces the burden on the operation of removing the substantially wedge-shaped aggregate (blockage) generated in the hopper chamber 5 of the production apparatus, and also shortens the time taken for the removal from several hours to several minutes.

[0043] It should be noted that, although the configuration to supply the hot water into the hopper chamber 5 has been described in the embodiment illustrated in Figs. 1 and 2, it is also possible to cause a highly-pressurized jet flow to collide against the aggregate b through the nozzle 3, and hot water or cool water (for example, approximately at 1 to 4°C) may be used as the jet flow.

[0044] Moreover, it is possible that a plurality of movable nozzles are provided in the lower portions of the side plates 1a and 1b of the hopper chamber 5, and thus a highly-pressurized jet flow is caused to collide intensively against a predetermined part by these movable nozzles. This configuration makes it possible to further effectively dissolve the aggregate b.

[0045] Furthermore, in order to prevent the gas hydrate powder from clogging the inside and the opening portion of the water pipe 4 on the hopper chamber 5 side, a conduit may be provided through which the hot water h1 is caused to flow in a side portion of the opening portion in the side plate 1 b and around the water pipe.

[0046] Fig. 3 is a perspective view illustrating an example of an embodiment of a production apparatus of a second invention.

[0047] In Fig. 3, a production apparatus A is a rotating-roll-type gas-hydrate-pellet production apparatus, and is a so-called briquetting-roll-type gas-hydrate-pellet production apparatus including a hopper chamber 5 above a pair of rotating rolls 6a and 6b. As has already been illustrated in Part a of Fig. 1, the hopper chamber 5 includes a screw-type push-in device (not illustrated) for pushing a gas hydrate powder to the rotating rolls with increased pressure while the gas hydrate powder is supplied to the inside of the hopper chamber 5. The gas hydrate powder is taken in by pockets 7 formed in the roll surfaces of the rotating rolls 6a and 6b, and is pelletized through compression molding between the rolls. The shape of each pocket 7 is not particularly limited, and preferably is a semi-spherical shape, a semi-oval shape, a semi-columnar shape, a rectangular shape, an almond shape, or a pillow shape. It is particularly preferable that the pockets 7 have the semi-spherical shape, the pillow shape, or the semi-oval shape, and are arranged in such a way that the longitudinal directions thereof are substantially parallel to the circumferential directions (rotating directions) of the rolls. This is because the formed pellets are easily removed off the pockets 7, in other words, provides a better releasability.

[0048] In the production apparatus A, the pressure to be applied between the pair of rotating rolls 6a and 6b is preferably 5 MPa to 200 MPa. Compression-molding with a pressure within this range enables the pelletization while suppressing the decomposition of the gas hydrate powder as much as possible. On the other hand, the amount of heat generated from the gas hydrate powder due to the compression work and friction acting between the rotating rolls as described above is approximately 1 kJ/kg to 100 kJ/kg. Along with the heat generation, the temperature of the roll surfaces is increased, in turn increasing also the temperatures of the gas hydrate powder and the pellets, which are in contact with the roll surfaces. If the temperature of the gas hydrate powder or the pellets reaches the decomposition temperature of the gas hydrate, part thereof is decomposed.

[0049] In the second invention, the production apparatus A includes a roll-cooling mechanism. The roll-cooling mechanism cools the rolls 6a and 6b by causing cooling water to flow through the outer peripheral portions and/or the insides of the respective rolls 6a and 6b. Accordingly, the temperatures of the gas hydrate and the roll surfaces can be prevented from reaching the decomposition temperature of the gas hydrate. As a result, the degree of gas hydrate decomposition can be reduced. In addition, the roll-cooling mechanism is configured as follows. The cooling water 43 that has flowed through the outer peripheral portions and/or the insides of the rolls is discharged from a cooling-water outlet 4 and recovered to a cooling-water tank; thereafter, the cooling water 43 is cooled and circulated again through the outer peripheral portions and/or the inner portions of the rolls.

[0050] The roll-cooling mechanism may be installed in the production apparatus of the aforementioned first invention. The installation makes it possible to reduce the degree of gas hydrate decomposition by removing, with a simple method, the heat generated in the compressing part in producing the gas hydrate pellets by compression-molding the gas hydrate powder. As a result, high-quality gas hydrate pellets can be stably produced. In addition, consider a case where an aggregate (blockage) of the gas hydrate powder has been generated between the compression rolls due to disturbance or the like. In this case, supplying hot water instead of the cooling water makes it possible to promptly melt the aggregate (blockage), to shorten the time for which the production apparatus is stopped, and thus to prevent the production efficiency of the gas hydrate pellets from being deteriorated.

[0051] Fig. 4 is a block flow diagram showing an example of processes in a process for producing gas hydrate pellets of the present invention. In Fig. 4, reference numeral 21 denotes a generator; 22 denotes a gas-hydrate-pellet production apparatus (hereinafter, sometimes called a "pelletizer"); 23 denotes a chilling machine; 24 denotes a depressurizer; and 25 denotes a storage tank. In the generator 21, a raw-material gas g and raw-material water w are brought into contact with each other, so that a powdery gas hydrate powder n is generated under predetermined low-temperature, high-pressure conditions. The gas hydrate powder n is supplied to the pelletizer 22, which thus produces gas hydrate pellets p. The gas hydrate pellets p are cooled to a further low temperature by the chilling machine 23. After the high pressure is released by the depressurizer 24, the gas hydrate pellets p are stored at a low temperature in the storage tank 25. In addition, cooling water 41 is supplied to the pelletizer 22 for cooling. Discharged cooling water 43 after the cooling is cooled and circulated as cooling water 42. Moreover, part of the discharged cooling water may be supplied to the generator 21 as raw-material water 45.

[0052] The conditions for generating the gas hydrate powder n in the generator 21 are given as follows. When methane hydrate is taken as an example, what is generally required is a pressure higher than or a temperature lower than a temperature/pressure curve that connects points of 253 K/2 MPa, 273 K/3.5 MPa, and 284 K/8 MPa, of (generating temperature)/(generating pressure). By contrast, if exposed to a pressure lower than or a temperature higher than the temperature/pressure curve, the gas hydrate powder is decomposed into the raw-material gas and water. The generator 21 may be formed of a single unit or a plurality of units. In particular, it is preferable to increase the gas hydrate concentration by using a generator formed of two units. In addition, the generator may include dewatering means (not illustrated) to increase the gas hydrate concentration.

[0053] The process for producing gas hydrate pellets of the present invention includes cooling the rolls 6a and 6b by causing the cooling water to flow through the outer peripheral portions and/or the insides of the rolls. The cooling water set at a predetermined temperature is brought into direct contact with the roll surfaces and is further caused to coexist with the gas hydrate powder, whereby the amount of heat generated by the compression work and friction can be directly removed and the temperatures of the gas hydrate and the roll surfaces are thus prevented from increasing. Moreover, the cooling water is caused to flow in the insides of the rolls and is further circulated, whereby the roll surfaces can be set at a predetermined temperature without reduction of the cooling water.

[0054] In the present invention, the cooling water that has flowed through the outer peripheral portions and/or the insides of the rolls is recovered to the cooling-water tank; thereafter, the cooling water is cooled and is circulated again through the outer peripheral portions and/or the inner portions of the rolls. The cooling-water tank may be supplied with new water in addition to the recovered cooling water. In addition, the water pooled in the cooling-water tank may be not only used as the cooling water but also supplied to the generator as the raw-material water of the gas hydrate.

[0055] In a first embodiment of the production process of the present invention, as illustrated in Fig. 5, a gas hydrate powder n is fed to the rolls 6a and 6b from a hopper chamber 5, and is formed into gas hydrate pellets p through compression molding, which are transferred to the chilling machine 23 to be cooled. In this event, the cooling water 42 is supplied to the hopper chamber 5, the cooling water is brought into contact with the outer peripheral portions of the rolls 6a and 6b, and then, the discharged cooling water 43 after the cooling process is discharged through a cooling-water outlet 4 of the hopper chamber 5. In other words, the cooling water 42 supplied to the hopper chamber 5 is brought into contact with the outer peripheral portions of the rolls, and thereby removes heat generated due to the compression work and friction and cools the roll surfaces. Part of the cooling water after the cooling process is consumed as a binder for the gas hydrate powder n, and the rest thereof is discharged through the cooling-water outlet 4 provided to the hopper chamber. The discharged cooling water 43 is recovered to a cooling-water tank 55. The cooling-water tank 55 is supplied as necessary with the new cooling water 41 and/or water that is obtained through dewatering of the gas hydrate by the dewatering means of the generator, or the like. With a pump 56, cooling water 44 pooled in the cooling-water tank 55 is cooled to a predetermined temperature by a cooler 57 and is circulated as the cooling water 42 to the hopper chamber 5. Note that, part of the cooling water 44 may be supplied to the generator as the raw-material water 45. With this configuration, the heat generated due to the compression work and friction in the compression molding of the gas hydrate pellets can be efficiently removed, so that the gas hydrate can be prevented from being decomposed.

[0056] In the production process of the present invention, the temperature difference T - To between the temperature T of the gas hydrate pellets p and the temperature To of the gas hydrate powder n is set to be preferably below 3°C, and more preferably below 0°C, that is, it is preferable that the temperature T of the pellets p be set to be lower than the temperature To of the powder n. Setting the temperature difference T - To in such a range makes it possible to securely suppress the decomposition of the gas hydrate. Here, the amount of removed heat Q2 removed by the cooler 57 may be set to be equal to or more than the amount of heat Q1 which the gas hydrate powder receives in the pelletization, whereby an increase in temperatures of the rotating rolls and the gas hydrate can be suppressed.

[0057] It should be noted that setting the temperature of the cooling water too low is not preferable because the cooling water is frozen and thus does not function as the binder in the compression molding of the gas hydrate powder as described above. Specifically, the gas hydrate powder having a high concentration is dry and unlikely to be hardened like a loose snow even being compressed. For this reason, the cooling water is supplied to the gas hydrate powder, so that part of the cooling water functions as the binder for the particles of the gas hydrate powder. The gas hydrate powder, thus, can be compression-molded into firmly compacted gas hydrate pellets. Note that the surplus of the cooling water is removed upward with the gap between the pair of rotating rolls becoming narrower, and no excessive amount of water is contained in the gas hydrate pellets. In addition, the water serving as the binder is further cooled to be frozen by the chilling machine 23 provided downstream of the pelletizer 22, and thus the gas hydrate pellets can be further firmly compacted.

[0058] In the production process of the present invention, the degree of decomposition β in the pelletization of the gas hydrate powder is set to be ideally 0%, but preferably not more than 10%, and more preferably 0% to 5%. Note that the degree of decomposition β is determined as follows. Each of the gas hydrate powder and the gas hydrate pellet is sampled, and each sample is decomposed into water and the raw-material gas. Then, the gas content [% by weight] of each sample is measured. The ratio [%] of the gas content of the gas hydrate pellets to the gas content of the gas hydrate powder is obtained as the degree of decomposition β.

[0059] Moreover, it is preferable that the amount of heat removed by the cooler 57 be set to be not less than the amount of heat Q1 obtained in accordance with the following expression (I).

$$Q1 = (T - T_0)\, cM + qM\beta / 100 \ldots \text{(I)}$$

[0060] Here, Q1 is the amount of heat [w] which the gas hydrate powder receives in the pelletization, and c is the specific heat [kJ/kgK], which is, for example, 1.8 to 2.0 kJ/kgK in the case of natural gas hydrates. q is the decomposition heat [kJ/kg], which is, for example, approximately 440 kJ/kg in the case of natural gas hydrates. M is the pelletization speed [kg/s] for the gas hydrate powder. The temperature T of the gas hydrate pellets p, the temperature To of the gas hydrate powder n before supplied to the pelletizer, and the degree of decomposition β are actual measurement values.

[0061] To be specific, the temperature To of the gas hydrate powder n before supplied to the pelletizer and the temperature T of the gas hydrate pellets p are measured. The degree of decomposition β is obtained by measurement according to the above-described method. The amount of heat Q1 is calculated in accordance with the expression (I). Then, the coolant temperature of the cooler 57 and the flow rate of the pump 56 may be adjusted so that the amount of heat Q2 removed by the cooler should be not less than the amount of heat Q1.

[0062] A second embodiment of the production process of the present invention is, as illustrated in Fig. 6, a process in which: cooling baths 58 are arranged respectively below the rolls 6a and 6b; the cooling water 42 is circulated to the cooling baths 58; and gas hydrate pellets are produced while the cooling water 42 is brought into contact with the outer peripheral portions of the rolls 6a and 6b to thereby cool the roll surfaces. When the lower portions of the rolls are dipped into the cooling water 42 supplied to the cooling baths 58, water films are formed on the roll surfaces, whereby the roll surfaces are effectively cooled. In addition, the compression molding is carried out while the rolls are rotated with the roll surfaces being wet and thus catch the gas hydrate powder in the hopper chamber 5. Accordingly, the cooling water appropriately functions as the binder in the same manner as the above-described first embodiment of the production process.

[0063] Instead of the dipping of the lower portions of the rolls in the cooling baths, the cooling water may be sprayed onto the roll surfaces for the heat removal. It is preferable that a cooling bath be disposed in a lower portion for recovering the surplus of the cooling water thus sprayed. Further, both of the cooling by dipping the lower portions of the rolls in the cooling bath and the cooling by spraying may be employed in combination. These methods are also preferable because the methods make it possible to effectively remove the heat of the roll surfaces and to supply a proper amount of water as the binder.

[0064] It should be noted that it is preferable to perform the treatment process for the discharged cooling water 43 after the cooling process as well as the removal of heat in amount Q2 by the cooler 57 in the same manner as the first embodiment of the production process of the present invention. Moreover, it is preferable to set the temperature difference T - To between the temperature To of the gas hydrate powder n before supplied to the pelletizer and the temperature T of the gas hydrate pellets p as well as the degree of gas hydrate decomposition β in the same manner as the first embodiment.

[0065] A third embodiment of the production process of the present invention is, as illustrated in Fig. 7, a process for producing gas hydrate pellets while cooling the rolls 6a and 6b from the insides thereof with the cooling water 42 supplied to cooling-water jackets provided respectively inside the rolls 6a and 6b. The cooling water is introduced to the insides through roll shafts 59, and flows through the cooling-water jackets provided inside the rolls. The temperature of the roll surfaces can be set at a predetermined temperature with no decrease of the cooling water by causing the cooling water to flow into the insides of the rolls and then to circulate while being cooled to a predetermined temperature by the cooler.

[0066] It should be noted that it is preferable to perform the treatment process for the discharged cooling water 43 after the cooling process as well as the removal of heat in amount Q2 by the cooler 57 in the same manner as the first embodiment. Moreover, it is preferable to set the temperature difference T - To between the temperature To of the gas hydrate powder n before supplied to the pelletizer and the temperature T of the gas hydrate pellets p as well as the degree of gas hydrate decomposition β in the same manner as the first embodiment.

[0067] In each of the above-described embodiments, the gas hydrate powder n is formed into the gas hydrate pellets p while the cooling water is supplied at the stage before the pressure release to atmospheric pressure conducted by the depressurizer 24. The process for producing gas hydrate pellets of the present invention is not limited to the embodiments, and is also effective in producing gas hydrate pellets, for example, at atmospheric pressure, after depressurization. Specifically, consider a case where an atmosphere that does not allow a gas hydrate to be decomposed is set for production of gas hydrate pellets. Even in this case, the production process of the present invention makes it possible to produce firmer gas hydrate pellets with the degree of gas hydrate decomposition reduced by preventing the set atmospheric conditions, from being changed by heat generated due to the compression work and friction, and thus from being converted into a state where the gas hydrate is likely to be decomposed.

[0068] Hereinafter, although the present invention will be further described by giving an example, the scope of the present invention is not limited to the example.

EXAMPLE

[Comparative Example]

[0069] In accordance with the gas hydrate pellet production processes illustrated in Fig. 5, a gas hydrate powder having a temperature To of 6°C (with an equilibrium temperature of 7°C) was generated from a natural gas as a raw-material gas. The gas hydrate powder was compression-molded at a pelletization speed M of 0.06 kg/s, with no supply of cooling water. The temperature T of gas hydrate pellets thus produced was 7°C, that is, the temperature difference T - To was 1°C. The degree of decomposition β measured by the aforementioned method was 3.2%. In the production, the amount of heat Q1 calculated in accordance with the expression (I) was 1.8 kw, where the specific heat was set at 1.6 kJ/kgK and the decomposition heat q was set at 440 kJ/kg.

[Example]

[0070] In accordance with the gas hydrate pellet production processes illustrated in Fig. 5, gas hydrate pellets were produced in the same manner as Comparative Example except that cooling water was circulated to the hopper chamber of the rotating-roll-type pelletizer while being cooled so that the amount of heat Q2 removed by the cooler should be 1.8 kw. As a result, the temperature difference T - To between the gas hydrate powder before the pelletization and the pellets after the pelletization was 0°C, and the degree of gas hydrate decomposition β was 0%. In addition, the gas hydrate pellets obtained in Example were more firmly compacted than those obtained in Comparative Example.

Claims

1. A roll-type gas-hydrate-pellet production apparatus which compression-molds a gas hydrate powder to produce gas hydrate pellets, the gas hydrate powder being generated by contacting and reacting a raw-material gas and raw-material water with each other, the gas-hydrate-pellet production apparatus comprising:

   a hopper chamber which houses the gas hydrate powder;
   a pair of compression rolls which are disposed below an opening portion of the hopper chamber; and
   a push-in device which supplies the gas hydrate powder in the hopper chamber to the compression rolls,
   the gas-hydrate-pellet production apparatus further comprising a roll-cooling mechanism which causes cooling water to flow through an outer peripheral portion and/or an inside of each roll so as to cool the roll, and which cools the cooling water discharged after the flow by use of a cooler.

2. A process for producing gas hydrate pellets by contacting and reacting a raw-material gas and raw-material water with each other so as to generate a gas hydrate powder, and by compression-molding the gas hydrate powder with a roll-type gas-hydrate-pellet production apparatus,
   the process comprising:

   causing cooling water to flow through an outer peripheral portion and/or an inside of a roll of the gas-hydrate-pellet production apparatus so as to cool the roll;
   cooling the cooling water discharged after the flow by use of a cooler; and
   supplying the cooled cooling water to the outer peripheral portion and/or the inner portion of the roll.

3. The process for producing gas hydrate pellets according to claim 2, wherein
   the cooling water is supplied to a hopper chamber from which the gas hydrate powder is fed to the roll,
   the cooling water is thereby brought into contact with the outer peripheral portion of the roll, and
   the cooling water is discharged from a cooling-water outlet of the hopper chamber.

4. The process for producing gas hydrate pellets according to any one of claims 2 and 3, wherein
   a cooling bath is disposed below the roll,
   the cooling water is supplied to the cooling bath, and the cooling water is brought into contact with the outer peripheral portion of the roll.

5. The process for producing gas hydrate pellets according to any one of claims 2, 3, and 4, wherein the cooling water is supplied to a cooling-water jacket provided inside the roll so as to cool the roll.

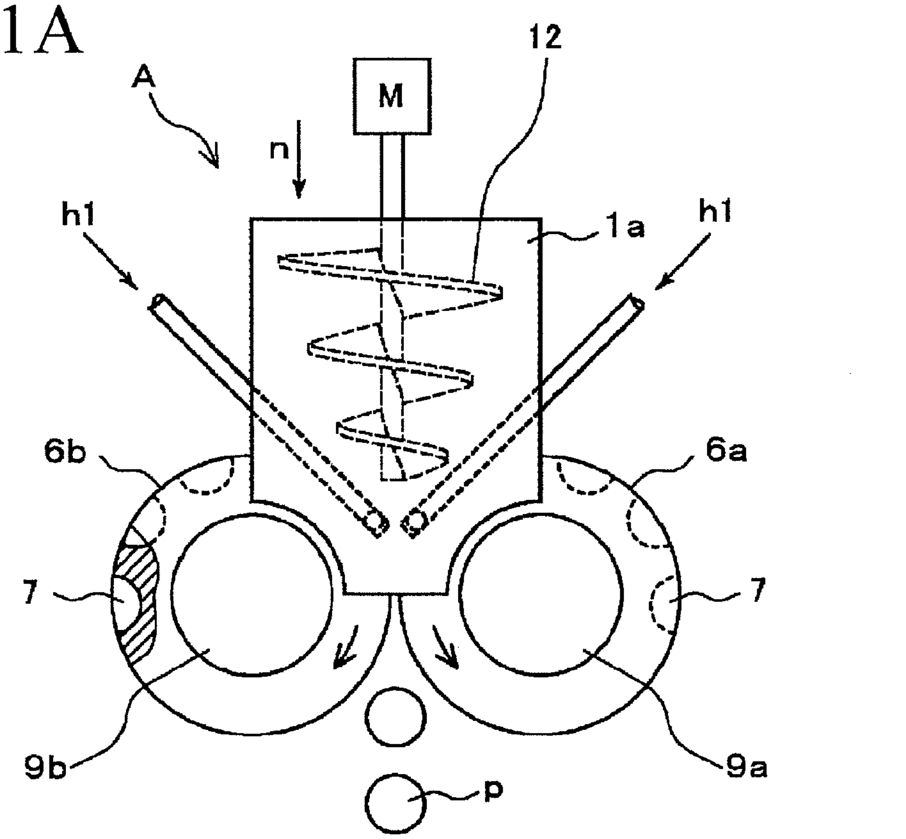
6. The process for producing gas hydrate pellets according to any one of claims 2 to 5, wherein
   the temperature difference T - To between the temperature T of the gas hydrate pellets and the temperature To of the gas hydrate powder is set to be below 3°C.

7. The process for producing gas hydrate pellets according to any one of claims 2 to 6, wherein
   the amount of heat removed by the cooler is set to be not less than the amount of heat Q1 obtained by the following expression (I):

$$Q1 = (T - T_0)\, cM + qM\beta / 100 \ldots (I),$$

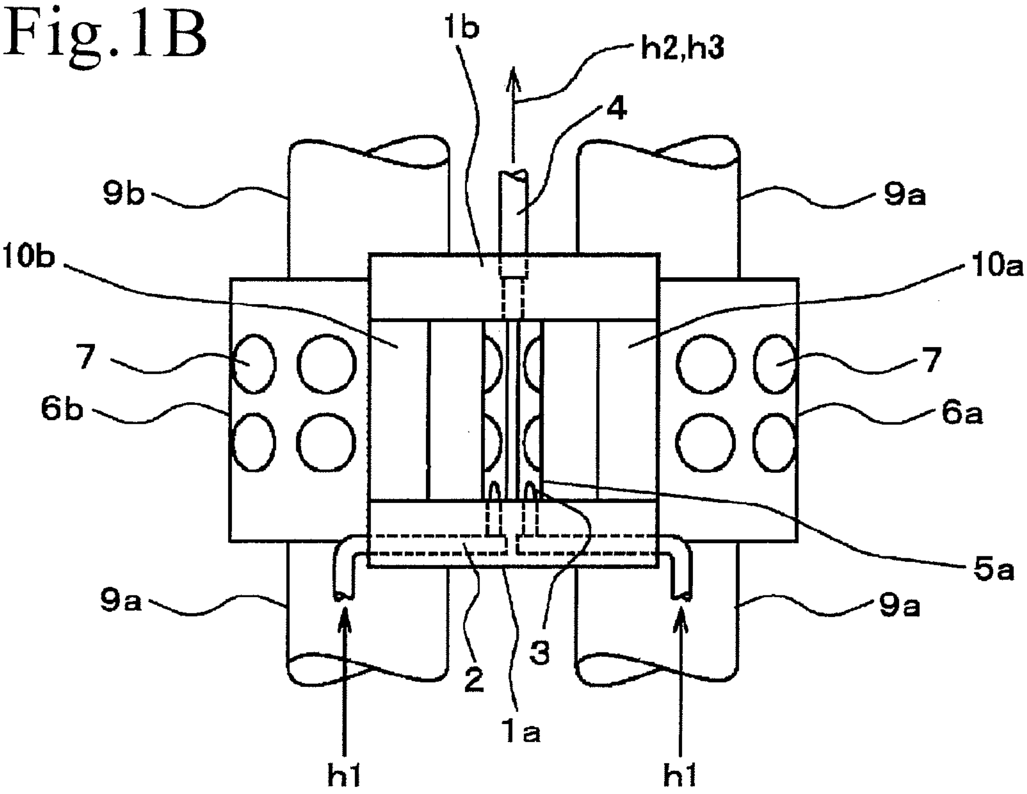
   (in the expression (I),
   Q1 is the amount of heat [w] which the gas hydrate powder receives in the pelletization,
   c is the specific heat [kJ/kgK],
   q is the decomposition heat [kJ/kg],
   M is the pelletization speed [kg/s] for the gas hydrate powder, and
   β is the degree of decomposition [%] in the pelletization of the gas hydrate powder).

Fig.1A



A
n
M
12
h1
h1
1a
6b
6a
7
7
9b
9a
p

Fig.1B



1b
h2,h3
4
9b
9a
10b
10a
7
7
6b
6a
5a
9a
9a
3
2
1a
h1
h1

Fig.2

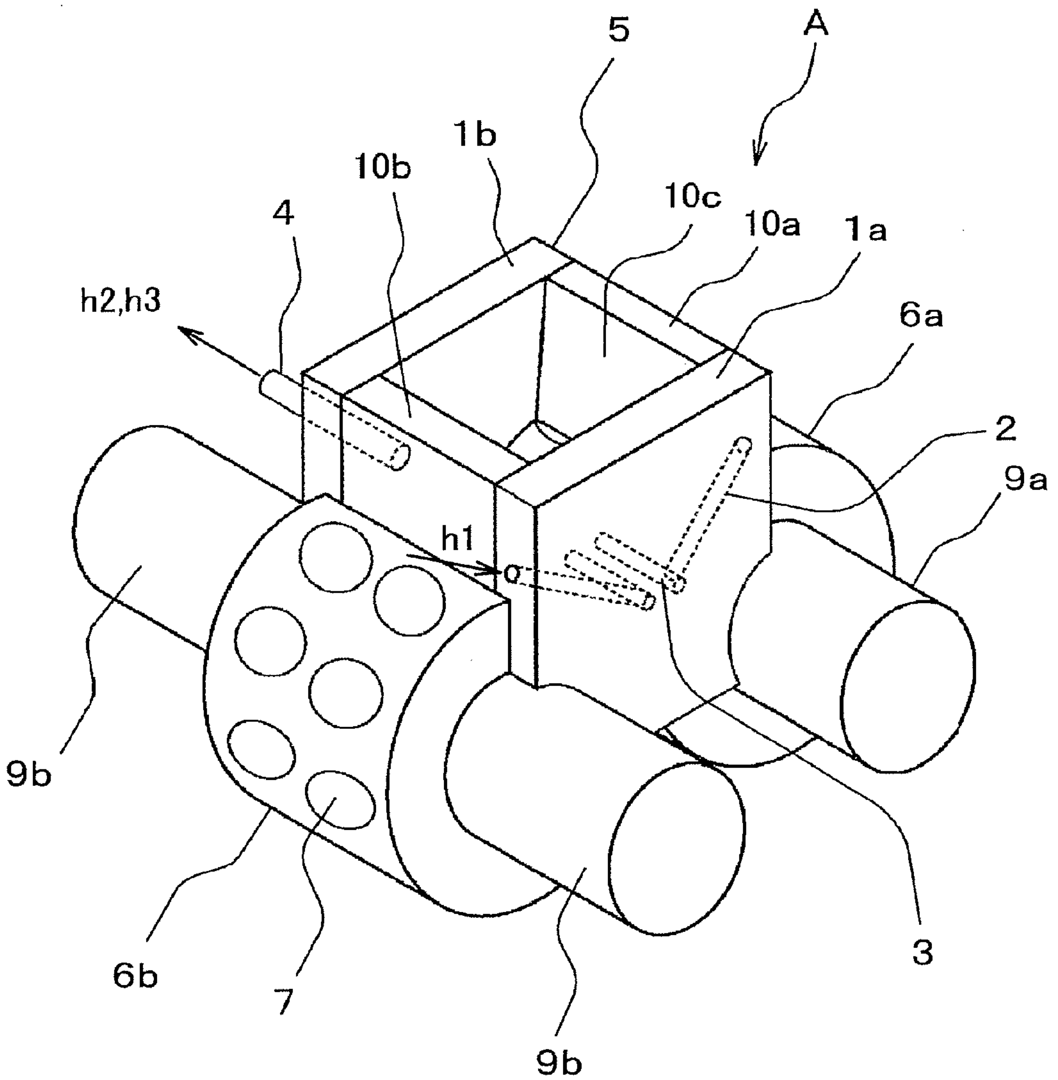


Fig.3

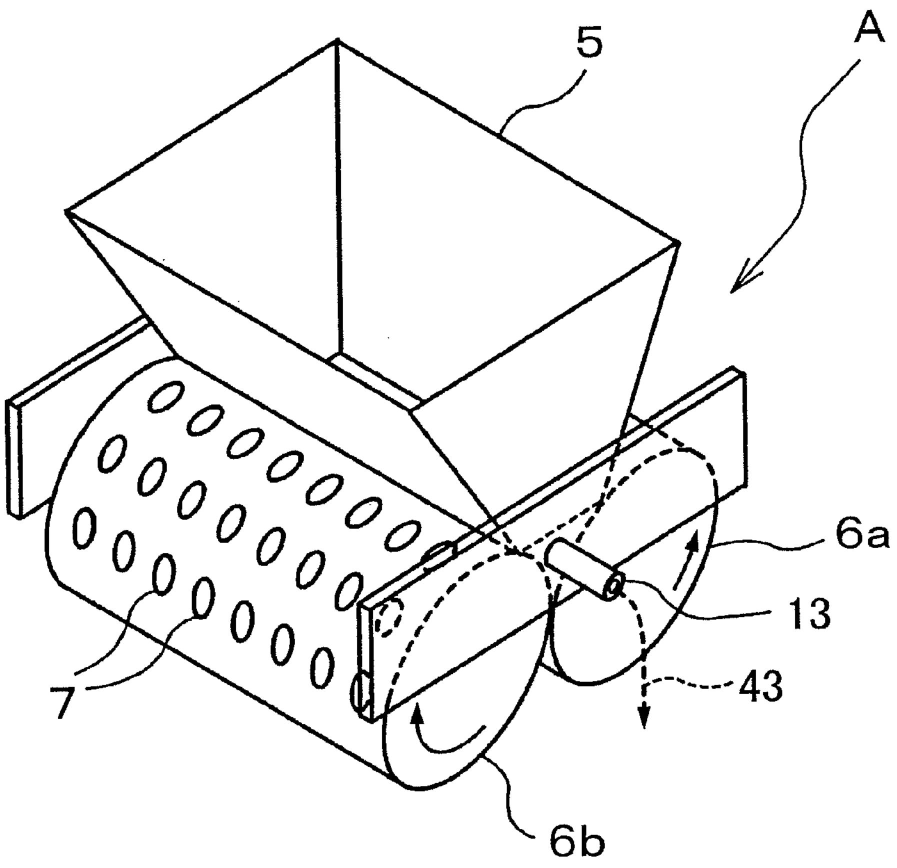


Fig.4

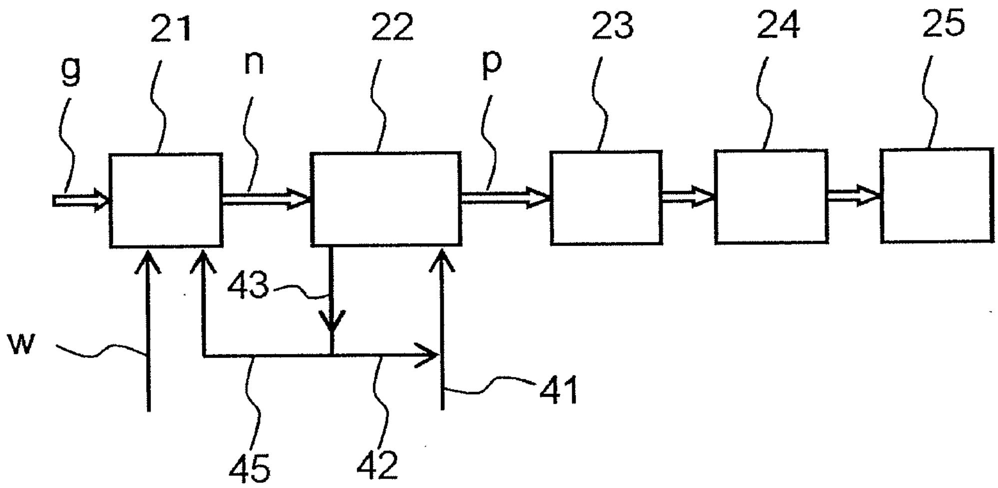


Fig.5

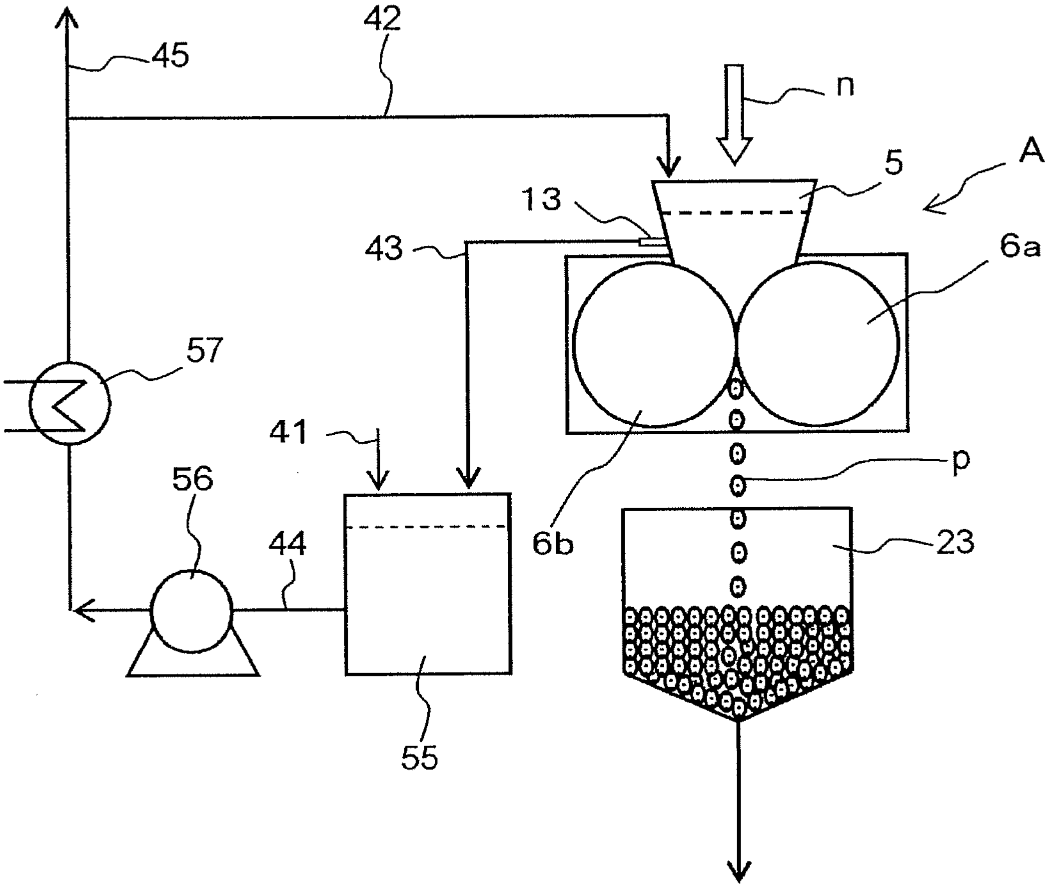


Fig.6

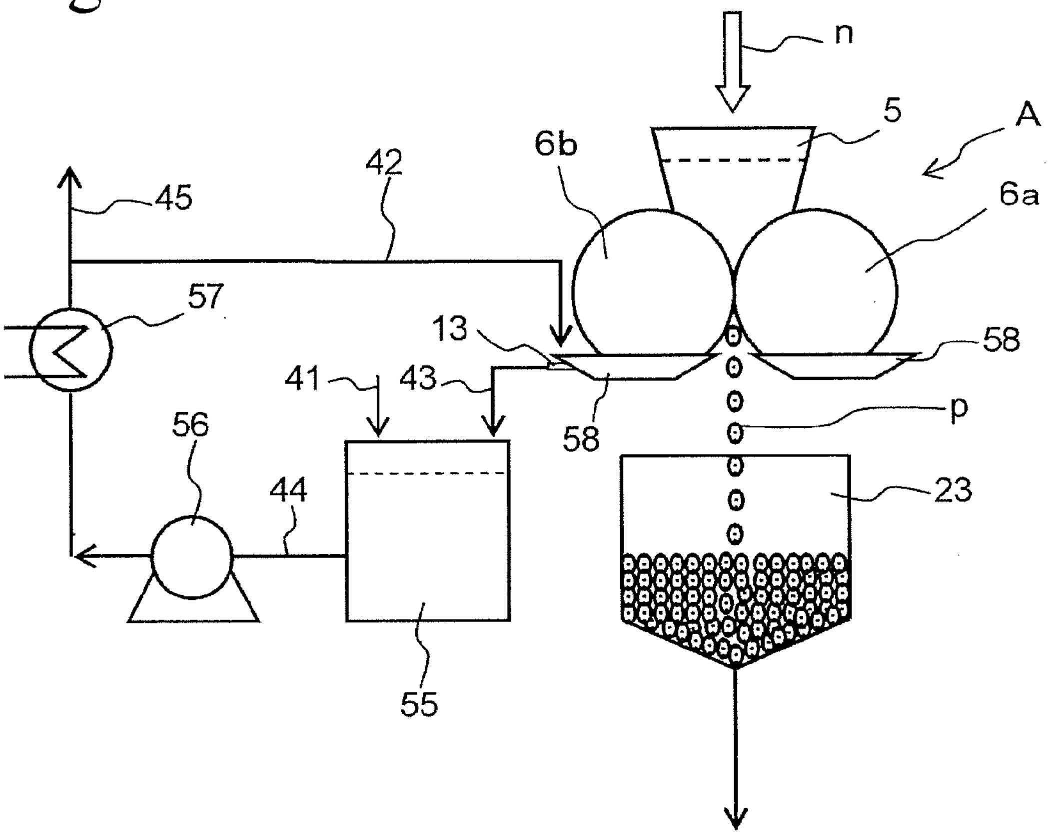


Fig.7

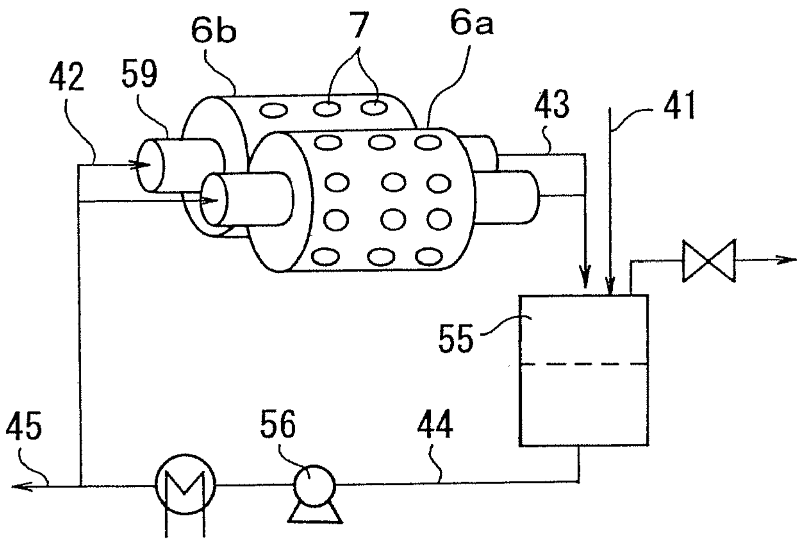
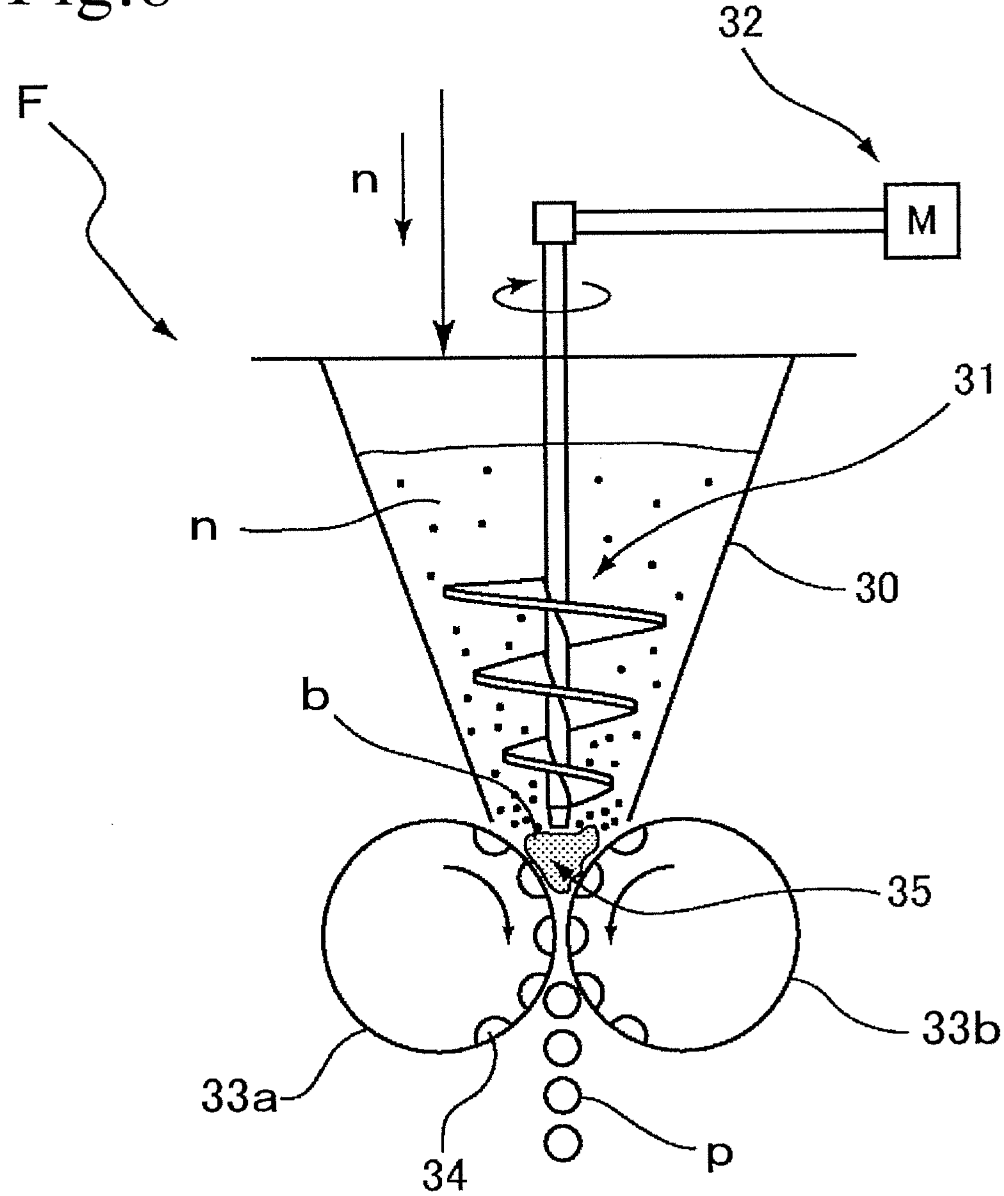


Fig.8



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EUROPEAN SEARCH REPORT

Application Number
EP 13 17 8339

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	JP 2007 224249 A (MITSUI SHIPBUILDING ENG) 6 September 2007 (2007-09-06) * abstract; figure 1 * -----	1-7	INV. C10L3/06
Y	WO 01/43959 A1 (ALEXANDERWERK AG [DE]; EGGERT AXEL [DE]) 21 June 2001 (2001-06-21) * claim 1; figures 1,2 * -----	1,2,5-7	
Y,D	AU 2002 306 357 B2 (MITSUI SHIPBUILDING ENG) 9 March 2006 (2006-03-09) * page 5; figures 1,2 * & JP 2002 220353 A (MITSUI SHIPBUILDING ENG) 9 August 2002 (2002-08-09) * abstract; figures 1,2 * -----	3,4,6,7	
A	DATABASE WPI Week 200767 Thomson Scientific, London, GB; AN 2007-713888 XP002659814, & JP 2007 246642 A (MITSUI ENG & SHIPBUILDING CO LTD) 27 September 2007 (2007-09-27) * abstract * -----	1-7	

TECHNICAL FIELDS SEARCHED (IPC)

C10L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	19 August 2013	Pöllmann, Klaus

2

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19-08-2013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2007224249 A	06-09-2007	NONE	
WO 0143959 A1	21-06-2001	NONE	
AU 2002306357 B2	09-03-2006	AU 2002306357 B2	09-03-2006
		JP 4167977 B2	22-10-2008
		RU 2276128 C2	10-05-2006
		WO 03006589 A1	23-01-2003
JP 2007246642 A	27-09-2007	NONE	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2002220353 A **[0016]**