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(54) **SUCCESSIVE GAS HYDRATE
MANUFACTURING METHOD**

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(57) **ABSTRACT**

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Embodiments of the inventive concept provide a successive gas hydrate manufacturing method, without hydration after generating gas hydrate slurry, capable of operating with a higher conversion rate and relatively low hydrate generation pressure and reducing a product cost by decreasing the number of processing steps for removing heat of reaction, for which the total exothermic value downs due to no need of latent heat according to a phase change rather than the case of generating a gas hydrate directly from a water solution, as well as making gas diffusion easier during reaction of generation and maximizing a contact area between water and gas to increase a gas capture rate and shorten the total hydrate generation time.

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FIG. 1

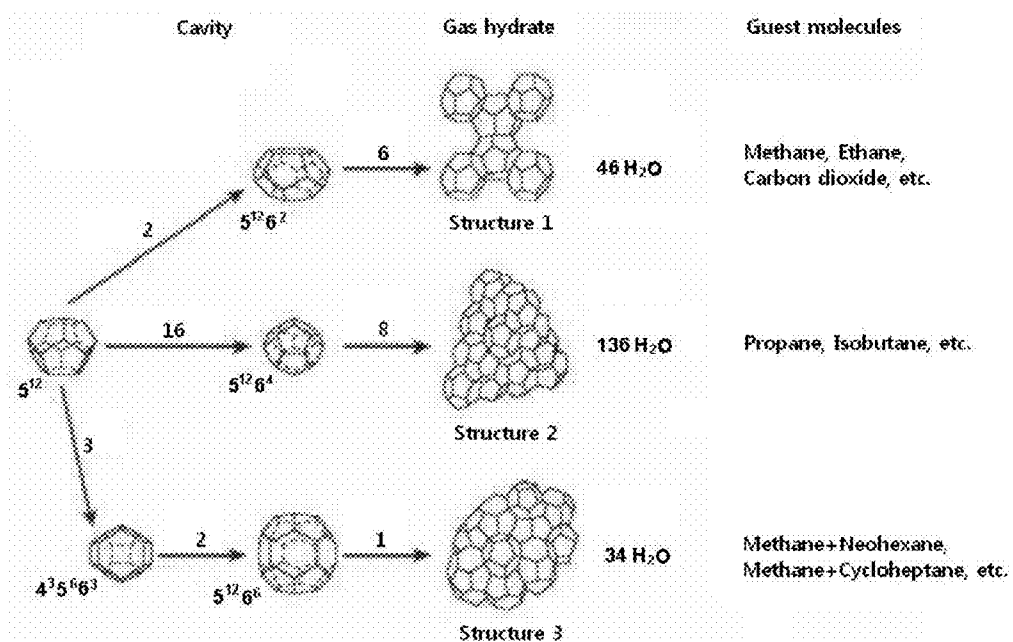


FIG. 2

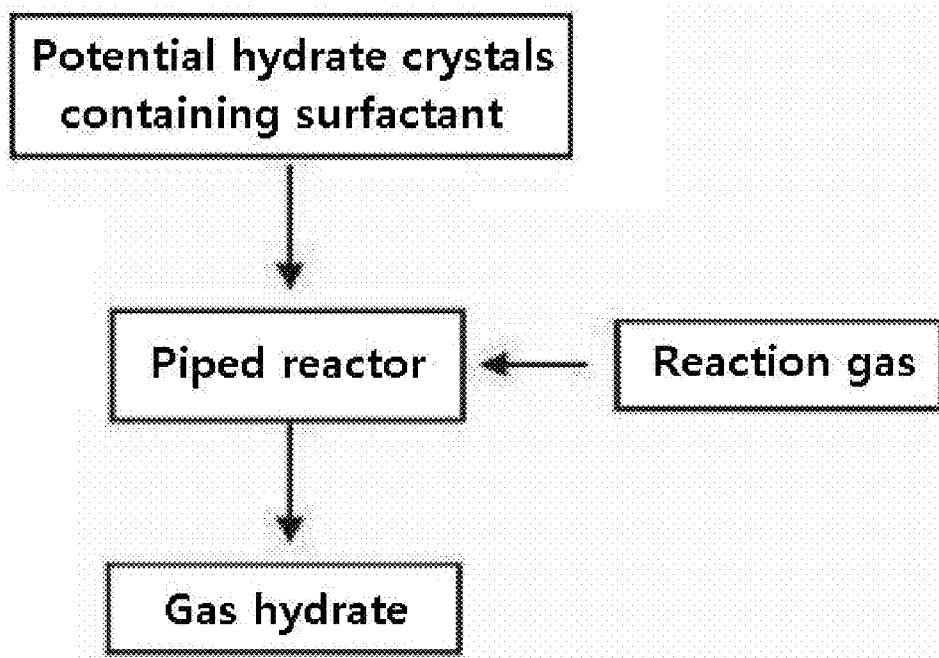


FIG. 3

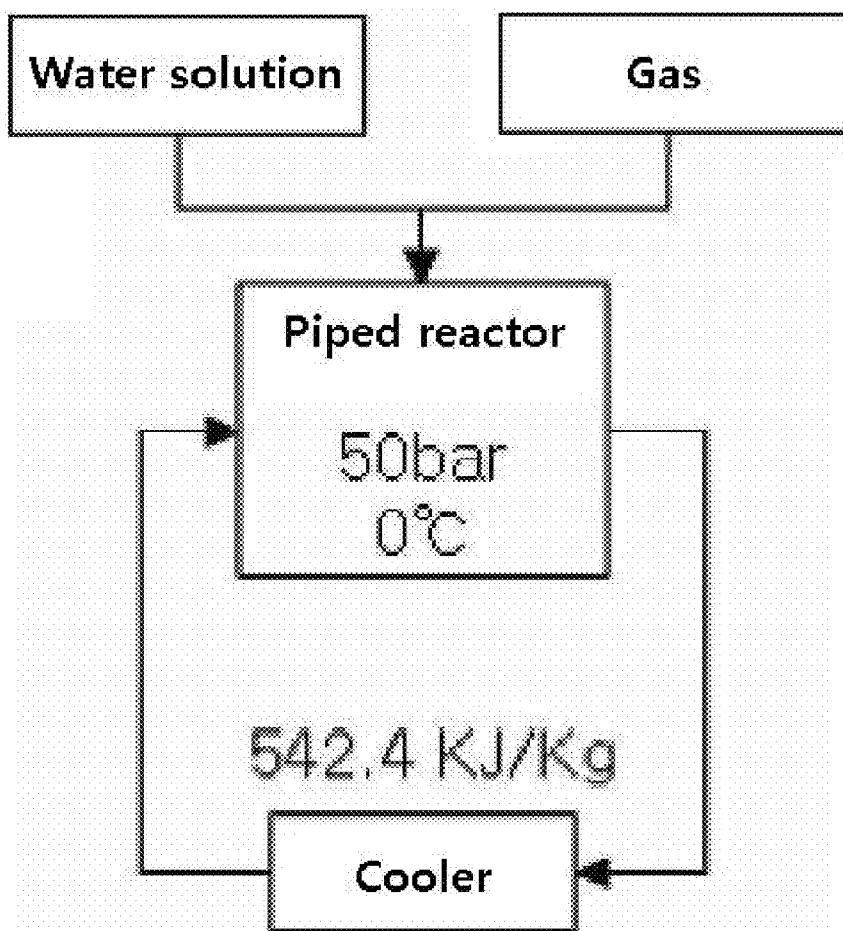


FIG. 4

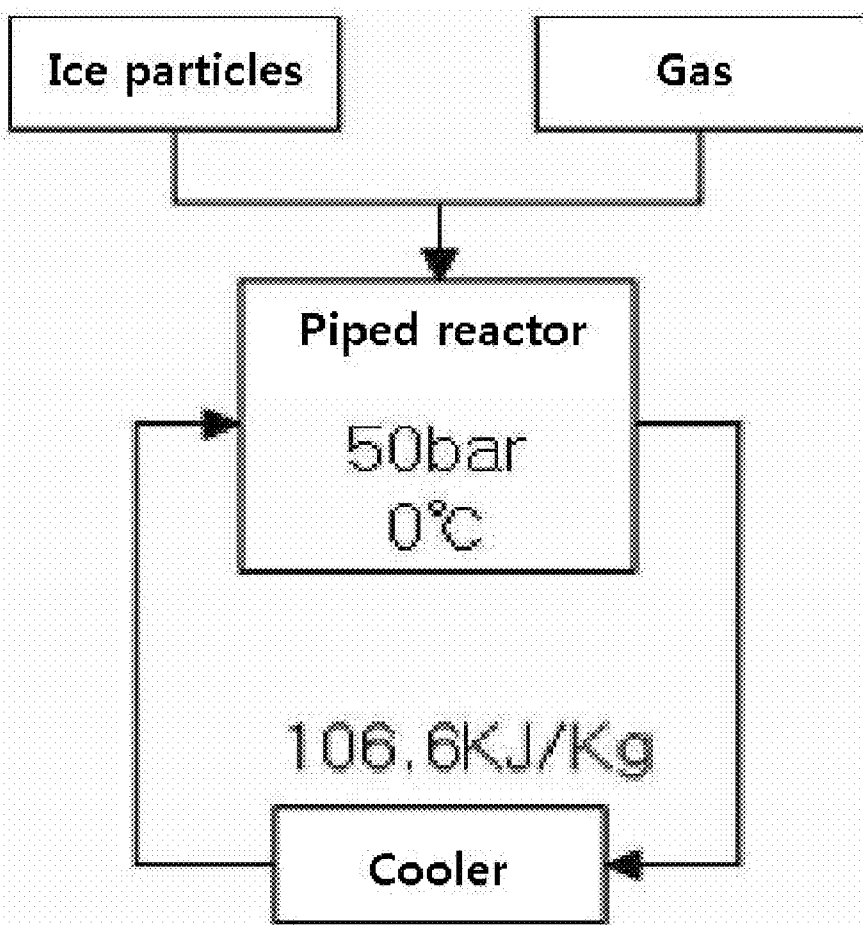


FIG. 5

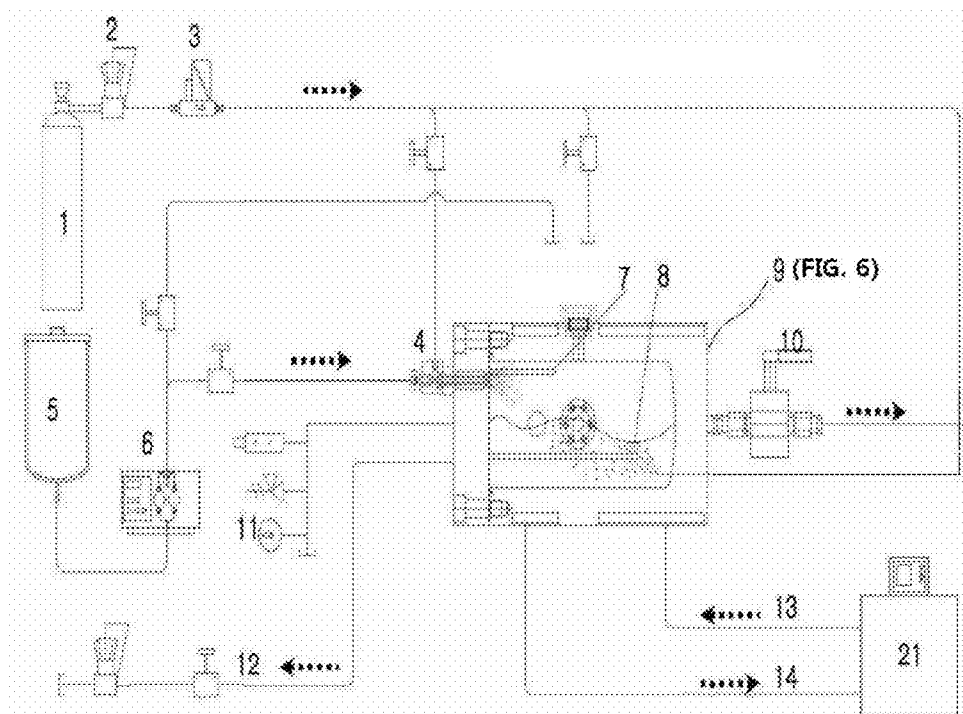


FIG. 6

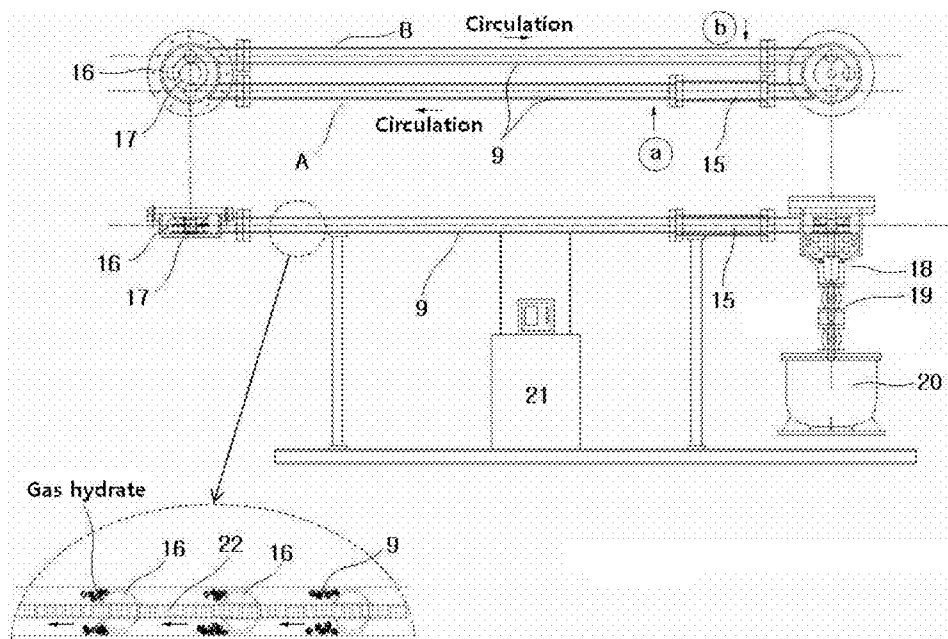
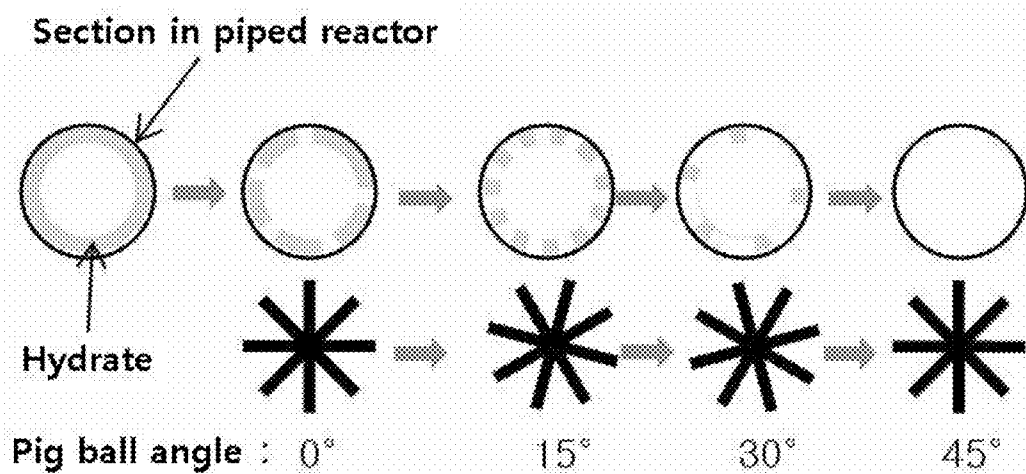


FIG. 7



SUCCESSIVE GAS HYDRATE MANUFACTURING METHOD

BACKGROUND

[0001] 1. Field

[0002] Embodiments of the inventive concept relate to a successive gas hydrate manufacturing method using potential hydrate crystals. More particularly, embodiments of the inventive concept relates to a successive gas hydrate manufacturing method including the steps of: injecting potential hydrate crystals of water solution, which include a surfactant, into a piped reactor; generating a gas hydrate by pressurizing a gas to the piped reactor in which the potential hydrate crystals are injected; and circularly transporting the gas hydrate through the full length of the piped reactor in the piped reactor to maximize a conversion rate. Circularly transporting the gas hydrate is carried out by means of pig-balls connected to each other with a constant interval in multiplicity.

[0003] 2. Description of Related Art

[0004] Natural gas is a kind of fuel having purity, stability and convenience, being sprightly interested as alternative energy capable of replacing the traditional solid fuel such as petroleum and coal. The use of natural gas has been gradually increasing in a variety of fields, e.g. home, commerce, transportation, industry, striking the keynote of worldwide energy industry, along with the solid fuel of petroleum and coal, as an energy resource taking charge of about a quarter of the total global energy consumption.

[0005] As natural gas transported in its crude gaseous state, after mining the natural gas from a gas field, is too large in bulk and explosive, there has been generally adopted a transporting way of cooling the natural gas down to liquefied temperature to generate Liquefied Natural Gas (LNG) and then storing the LNG in a specific tank equipped in a transport ship. LNG usually contains 600 times of natural gas per unit bulk.

[0006] In the meantime, methane gas, which is a main ingredient of LNG, can be liquefied at extremely low temperature about -162°C . so it takes much cost for manufacturing an LNG transporting device in the sea and land as well as for preparing production facilities.

[0007] While another way for storing and transporting LNG is to use gas compression, it also has problems such as technical difficulty in manufacturing a huge container due to high storage pressure, high cost, and low stability due to high pressure explosion.

[0008] On the other hand, a natural gas hydrate can be made under relatively moderate pressure and temperature while providing 170 times of gas per unit bulk, and stored at the condition of -20°C . and 1 air pressure after generation. These conditions of pressure and temperature are much moderate than those for LNG or compressed gas.

[0009] Additionally, a natural gas hydrate is profitable to safety because it is less explosive, even if exposed to normal temperature and pressure, to secure a more sufficient time for coping with systemic leakage and destruction. That is, such a natural gas hydrate is more safe and economic in storage and transportation than LNG or Compressed Natural Gas (CNG).

[0010] A natural gas hydrate, a compound generated like dry ice by means of physical combination, not chemical combination, with gas and water under low temperature and high pressure, has an exothermic value of 1 m^2 that is similar to that of natural gas of 180 m^2 . The gas hydrate is naturally buried

in the form of crystals, which is made of water and gas, in the bottom of the sea or the frozen earth with low temperature and high pressure, and easily dissolved into water and gas if it is conditioned on dissociation.

[0011] The natural gas hydrate is classified into I, II and III types in accordance with molecular structure, and structured similar to, but different from ice. While ice has a planar structure at low temperature around 0°C ., water molecules forms three-dimensional cavities structure if a natural gas hydrate is situated under an appropriate pressure (see FIG. 1).

[0012] Assuming that the cavity is a sphere, its size is about 1 nanometer and the unit cell size is about 2 nanometers. Natural gas enters the inside of the cavities. In other words, water molecules coupled by hydrogen bond becomes 'host' and gas molecules becomes 'guest'. A general formula of gas hydrate is represented in $\text{Gas}(\text{H}_2\text{O})_n$, where n denotes a hydration number that ranges from about 5 to 8. Between a non-polar gas molecule and a water molecule, van der Waals force acts.

[0013] In manufacturing a natural gas hydrate, generally used is a bubbling method of generating the natural gas hydrate by contacting a highly pressurized cooled natural gas, which is supplied through a gas nozzle placed at the top of a reactor, with water ejected through a nozzle leveled lower or through a porous plate placed at the bottom of the reactor. As the whole procedure of the bubbling method is an exothermic reaction, removing heat generated during the reaction needs a cooling system in the reactor or requires an external system for dropping temperature of the reactor.

[0014] However, such a natural gas hydrate generated by such a method may cause a plugging effect to nozzles for raw water or natural gas. If an ejection plate is employed, raw water particles with a large diameter meet large material transfer resistance during the reaction of generation. Furthermore, it is difficult to separate the generated natural gas hydrate and unreacted water from each other. And its low conversion rate may result in a large amount of unreacted materials, consuming a lot of energy for separating and recycling the remnant of the reaction.

[0015] On the other hand, a traditional method of generating a natural gas hydrate is disadvantageous to industrialization because of a long hydrate induction period and a low hydrate crystallization rate. The hydrate induction period may be defined as a period of maintaining a state of liquid hydrate before generating solid hydrate crystals. An induction period for methane is usually about several days.

[0016] For mass production, it is necessary to reduce such a long hydrate induction period and low hydrate crystallization rate. To reduce a hydrate induction time, it needs a wider reaction area capable of allowing a reaction under an appropriate condition of temperature and pressure. In extending a reaction area, there have been being used different methods such as nozzle ejection, microscopic bubbling, agitation, etc., but limited to conversion rate and highly cost for manufacturing equipment.

[0017] It is important to regulate a condition of temperature and pressure in generating a hydrate. Most portion of process for generating a hydrate is carried out by a cooling system for removing heat arising from the reaction. While at present there is being used a manner of supplying cool water and removing heat of reaction by means of a heat exchanger, internal heat of hydrate reaction can be removed through heat exchange by way of a high pressure reactor. Thus, it is difficult to manufacture such a heat exchange system and impos-

sible to conduct uniform heat exchange within the reactor when an amount of hydrate generated increases, which makes mass production harder.

[0018] Moreover, since a hydrate begins to be generated from a cooled surface of the heat exchanger, absorption (like an effect that ice is attached to the inside of a cold/freezing room) between the surface of the heat exchanger and the hydrate degrades heat conductivity to further restrain heat exchange in the reactor, also causing separation to be difficult and hence disturbing hydrate transportation.

[0019] In the meantime, for the purpose of successively manufacturing a gas hydrate, a gaseous charge rate in the hydrate becomes higher by eliminating moisture, which has not been yet reacted in the reactor, by way of a dehydration process after exhausting an internally generated hydrate as slurry. During this, since hydrate slurry is compressed by mechanical or centrifugal force for dehydration and thereby ice films are formed on a filtration net or filter to degrade the capability of dehydration, it is necessary to additionally prepare a device for periodically cleaning the filtration net or filter. Therefore, such a foregoing method makes it difficult to manufacture equipment thereof due to some restrictions involved in endurance of devices for cleaning the filtration net or filter, and structural availability that the dehydration should be carried out within the reactor, hence less suitable for mass production in commercialization because of enlargement of equipment.

[0020] Accordingly, in utilizing natural gas energy, there is a need of developing a device capable of successively manufacturing a gas hydrate, without dehydration after generating gas hydrate slurry, accompanying with the effects of overcoming the aforementioned problems, e.g. accomplishing a higher conversion rate even while increasing a gas hydrate crystallization rate owing to easy gaseous diffusion without a gas hydrate induction period, as well as minimizing the number of processing steps for removing heat of reaction to reduce a product cost thereof.

SUMMARY

[0021] Embodiments of the inventive concept provide a successive gas hydrate manufacturing method, without hydration after generating gas hydrate slurry, capable of operating with a higher conversion rate and relatively low hydrate generation pressure and reducing a product cost by decreasing the number of processing steps for removing heat of reaction, for which the total exothermic value downs due to no need of latent heat according to a phase change rather than the case of generating a gas hydrate directly from a water solution, as well as making gas diffusion easier during reaction of generation and maximizing a contact area between water and gas to increase a gas capture rate and shorten the total hydrate generation time.

[0022] The technical objectives of the inventive concept are not limited to the above disclosure; other objectives may become apparent to those of ordinary skill in the art based on the following descriptions.

[0023] In accordance with an aspect of the inventive concept, a successive gas hydrate manufacturing method includes the steps of: injecting potential hydrate crystals of water solution, which include a surfactant, into a piped reactor; generating a gas hydrate by pressurizing a gas to the piped reactor in which the potential hydrate crystals are injected;

and circularly transporting the gas hydrate through the full length of the piped reactor in the piped reactor to maximize a conversion rate.

[0024] In an embodiment, pig-balls connected to each other with a constant interval in multiplicity may act to circularly transport the gas hydrate in the piped reactor.

[0025] In an embodiment, the potential hydrate crystals may be porously structured.

[0026] In an embodiment, the porous potential hydrate crystals may be adopted from a material formed in (i) ice particles or (ii) slurry, or a material obtained by (iii) cooling after impregnating the water solution in a porous material or (4) cooling after making a highly absorbent resin absorb the water solution.

[0027] In some embodiments, the method may further include a step of cooling the piped reactor before injecting the potential hydrate crystals, which contain the surfactant, into the piped reactor.

[0028] In some embodiments, the method may further include a step of constantly maintaining internal temperature by additional gas supply after injecting a gas into the piped reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] The foregoing and other features and advantages of the inventive concepts will be apparent from the more particular description of preferred embodiments of the inventive concepts, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the inventive concepts. In the drawings:

[0030] FIG. 1 is a diagram illustrating a structure of a gas hydrate;

[0031] FIG. 2 is a schematic diagram showing an operating mechanism of the inventive concept;

[0032] FIG. 3 illustrates heat of reaction from a piped reactor using a general gas hydrate manufacturing method;

[0033] FIG. 4 illustrates heat of reaction from a piped reactor in accordance with embodiments of the inventive concept;

[0034] FIG. 5 illustrates a successive gas hydrate manufacturing method in accordance with embodiments of the inventive concept;

[0035] FIG. 6 illustrates the piped reactor of FIG. 5 in detail; and

[0036] FIG. 7 illustrates a state and effect of installing pig-balls to be adjacent to each other in different angles in accordance with embodiments of the inventive concept.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0037] Various embodiments will now be described more fully with reference to the accompanying drawings in which some embodiments are shown. These inventive concepts may, however, be embodied in different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure is thorough and complete and fully conveys the inventive concept to those skilled in the art. In the drawings, the sizes and relative sizes of layers and regions may be exaggerated for clarity.

[0038] Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning

as commonly understood by one of ordinary skill in the art to which this inventive concept belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

[0039] A successive gas hydrate manufacturing method according to embodiments of the inventive concept includes the steps of: injecting potential hydrate crystals of water solution, which include a surfactant, into a piped reactor; generating a gas hydrate by pressurizing a gas to the piped reactor in which the potential hydrate crystals are injected; and circularly transporting the gas hydrate through the full length of the piped reactor in the piped reactor to maximize a conversion rate. Hereinafter will be described embodiments of the inventive concept along the steps in conjunction mostly with FIGS. 5 and 6.

Injecting Potential Hydrate Crystals of Water Solution Containing Surfactant

[0040] In a successive gas hydrate manufacturing method according to embodiments of the inventive concept, potential hydrate crystals of a water solution containing a surfactant are first injected into a piped reactor 9.

[0041] Here, the piped reactor 9 is made in a shape of long pipe, as shown in FIG. 6, not in a cylinder (this will be detailed later).

[0042] Gas hydrate means a compound existing as solid crystals, like dry ice, by physical combinations similar to structural entanglement, not by chemical bonds, with gas of low molecular weight and water under low temperature and high pressure (see FIG. 1).

[0043] Potential hydrate crystals mean precursors of gas hydrate crystals that do not need an additional hydrate induction period in converting to gas hydrate crystals because they already have a porous structure.

[0044] Such potential hydrate crystals having a porous structure may be adopted from a material, by way of preliminarily cooling and smashing a water solution containing a surfactant, formed in (1) ice particles of solid state or (2) slurry of suspension state with insoluble solid particles.

[0045] Instead of directly cooling and smashing a water solution, a cooled water solution may be even injected directly into the piped reactor 9, without a pre-smashing process, by way of (3) cooling after impregnating the water solution in a porous material or (4) cooling after making a highly absorbent resin absorb the water solution.

[0046] During this, artificially separating particles of the water solution through a porous material or highly absorbent resin maximizes a contact area between the water solution and gas. While the porous material can be adopted from all commercially available kinds, it may be used with active carbon, silica gel, zeolite, etc. And, while the highly absorbent resin can be adopted from general kinds of resins, it may be used from polyacrylate, polyacryl amide, polyacryl acid, polymethacrylic acid, polyethylene oxide, polyvinyl alcohol, etc.

Generating as Hydrate in the piped reactor

[0047] If a reaction gas is injected into the piped reactor 9 containing the potential hydrate crystals aforementioned, the potential hydrate crystals reacts on the injected gas to immediately generate a gas hydrate (see FIG. 2).

[0048] During this, owing to the structural characteristics of the porous potential hydrate crystals, gas diffusion becomes easier in the potential hydrate crystals and a contact area between water and gas is maximized. Thus, it results in a higher conversion rate and a relatively low gas hydrate generation pressure, as well as increasing a gas capture rate and shortening a hydrate generation time.

[0049] Additionally, as latent heat according to a phase change is not needed relative to the case of generating a gas hydrate directly from a water solution, the total exothermic value can be reduced to lessen devices and processes for removing heat of reaction from the piped reactor 9, saving the whole product cost.

[0050] FIGS. 3 and 4 illustrate exothermic portions to be externally removed when generating a hydrate from a water solution and when generating a hydrate from potential hydrate crystals of ice particles in accordance with an embodiment of the inventive concept, respectively. As illustrated in FIGS. 3 and 4, while the exothermic value of generating a methane hydrate of 1 kg from the water solution is 542.4 KJ/kg, the exothermic value of generating a methane hydrate of 1 kg from the ice particles is 106.6 KJ/kg that is as much as being given by subtracting 435.8 KJ/kg, which is the exothermic value by a phase change of the ice particles of 1 kg, from 542.4 KJ/kg.

[0051] This is because since the water solution containing a surfactant has been already excluded from latent heat while turning to ice particles, the remaining exothermic portion to be removed from the piped reactor 9 during the reaction can be reduced to lessen the total capacity of a cooler 21 for removing heat of reaction from the reactor 9 and shorten a cooling time thereof

[0052] These potential hydrate crystals contain a surfactant. The surfactant can be adopted from all general kinds, but it may be used from sodium dodecyl sulfate (SDS), diisooctyl sodium sulfosuccinate (DSS), sodium tetradecyl sulfate, sodium hexadecyl sulfate, sodium dodecylbenzene sulfonate, xylenesulfonate, sodium oleate, 4-n-decylbenzenesulfonate, sodium laurate, 4-dodecylbenzenesulfonic acid, dodecylamine hydrochloride, dodecyltrimethylammonium chloride, 4-n-octylbenzenesulfonate, ethoxylated sulfonate, decylbenzenesulfonate, potassium oleate, n-decylbenzene sulfonate, alkyltrimethylammonium bromide (C10-C16 chains), dodecyl amine, tetradecyltrimethylammonium chloride, dodecyl polysaccharide glycoside, cyclodextrins, glycolipids, lipprotein-lipopeptides, para-toluene sulfonic acid, trisiloxane, riton X-100, and a mixture thereof

[0053] The surfactant aforementioned may be sufficient in an amount less than 0.5% of the total volume of the water solution, and may be ranged in concentration from 50 ppm to 1000 ppm.

[0054] In the meantime, it is preferred to preliminarily cool down the piped reactor 9 before injecting the hydrate crystals, which contain a surfactant, into the piped reactor 9. During this, the piped reactor 9 may be set in cooling temperature of -10°C . to 10°C .

[0055] Additionally, after injecting gas into the piped reactor 9, a gas may be further supplied to maintain internal pressure of the piped reactor 9. During this, the internal temperature of the piped reactor 9 may be ranged from 10 bars to 100 bars.

[0056] The gas injected into the piped reactor 9 may be adopted from methane, ethane, propane, carbon dioxide, butane, or a mixture thereof.

Circularly Transporting Gas Hydrate in the Piped Reactor

[0057] Although a gas hydrate generated in the piped reactor 9 has a high conversion rate through the step of generating the gas hydrate, it may not that of 100%. Rather, in a certain situation, the conversion rate would be less than a desired level.

[0058] With this condition, to successively manufacture a gas hydrate, moisture, which has not been yet reacted in the reactor, should be eliminated by way of a dehydration process after exhausting an internally generated hydrate as slurry. During this, since hydrate slurry is compressed by mechanical or centrifugal force for dehydration and thereby ice films are formed on a filtration net or filter to degrade the capability of dehydration, it is necessary to additionally prepare a device for periodically cleaning the filtration net or filter. Therefore, such a foregoing method makes it difficult to manufacture equipment thereof due to some restrictions involved in endurance of devices for cleaning the filtration net or filter, and structural availability that the dehydration should be carried out within the reactor, hence less suitable for mass production in commercialization because of enlargement of equipment.

[0059] Therefore, embodiments of the inventive concept provide the reactor in a form of pipe as shown in FIG. 6, different from a traditional cylinder type, in order to such problems (in this specification, this reactor is specifically referred to as 'piped reactor' for the purpose of representing the feature of the inventive concept).

[0060] The reason for using the piped reactor 9 instead of a cylindrical reactor is to maximize the conversion rate by way of circularly transporting a gas hydrate, which is first generated in the piped reactor 9, along the full length of the piped reactor 9 while staying within the piped reactor 9, not being immediately exhausted to the outside.

[0061] Now will be further detailed an operation of the piped reactor 8 in conjunction with FIGS. 5 and 6.

[0062] In embodiments of the inventive concept, after making ice particles by cooling and smashing a water solution containing a surfactant, the ice particles are injected into the piped reactor 9. Then, by supplying a reaction gas from a gas cylinder 1 through a nozzle 4 by way of a mass flowmeter 3 capable of measuring an amount of gas injection according to gas hydrate generation through a pipe, a gas hydrate is immediately generated at an outlet (a) of the piped ice maker 15 in the piped reactor 9.

[0063] During this, a gas regulator 2 sets pressure to maintain constant pressure in the piped reactor 9, and coolant lines 13 and 14 are connected to the piped reactor 9 in the cooler 21, to which a temperature controller is attached, to drop temperature of the piped reactor 9.

[0064] The conversion rate is maximized while the gas hydrate generated at the outlet of the piped ice maker 15 in the piped reactor 9 is circularly transported over the full length of the piped reactor 9, staying in the inside of the piped reactor 9, not being immediately exhausted to the outside.

[0065] As stated above, since the inside of the piped reactor 9 is maintained on appropriate pressure and temperature through the full length by means of the gas regulator 2 and the coolant lines 13 and 14, the gas hydrate generated at the outlet (a) of the piped ice maker 15 is conditioned to have a maximized conversion rate when it arrives at an end (b) of the piped reactor 9, being continuously exposed to an appropriate condition of pressure and temperature during the circulative transportation through the full length of the piped reactor 9, even though the conversion rate has been experienced to be

less than 100% at first or less than a desired level under circumstances. The gas hydrate exhausted from the end (b) of the piped reactor 9 becomes to be available at once without additional dehydration.

[0066] From the embodiment of FIG. 6, it can be seen that the piped reactor 9 is formed of two long bodies A and B. This is for elongating the full length of the piped reactor 9 to enhance the effect. After generated at the outlet (a) of the piped ice maker 15 in the piped reactor 9, the gas hydrate is transported by circulation and exhausted to arrive at a first tank 18 in the end (b), and then finally stored in a second tank 20 through a pelletizer 19 including a depressurizer. Needless to say, this procedure does not accompany with dehydration of the gas hydrate.

[0067] Additionally, in embodiments of the inventive concept, pig-balls 16 as means for circularly transporting the gas hydrate through the full length of the piped reactor 9, instead of a general screw type, are employed to prevent enlargement of equipment due to the screw types, reducing a product cost thereof.

[0068] By an action of the pig-balls 16, which are coupled with each other in multiplicity, circularly moving along the inside of the piped reactor 9, the gas hydrate is circularly transported in the piped reactor 9.

[0069] Referring to FIG. 6, a multiplicity of the pig-balls 16 are coupled with each other by means of a chain 22 in the piped reactor 9. In this structure, a diameter of the pig-balls 16 may be mostly close to a caliber of the piped reactor 9. The pig-balls 16 effectively scrape away the gas hydrate attached to the inner wall of the piped reactor 9, while moving along the inside of the piped reactor 9, and continuously push out toward their progress direction. Thus, the gas hydrate is forced to be transported from (a) toward (b) by the action of the pig-balls 16.

[0070] Here, the pig-balls 16 adjacent to each other may be installed to be different in angle. This arrangement of the pig-balls 16, as illustrated in FIG. 7, is helpful to scraping away the remnants of the gas hydrate, which have not been yet removed by the preceding pig-balls, without leaving any. Therefore, it prevents a loss in a product quantity of the gas hydrate and accumulative deposition on the inner wall of the piped reactor 9.

Without Potential Hydrate Crystals

[0071] In the meantime, according to embodiments of the inventive concept, it is still possible to achieve higher usefulness even without potential hydrate crystals such as the aforementioned.

[0072] Unless the potential hydrate crystals are used, the necessity of performing dehydration becomes inevitably higher in successively manufacturing a gas hydrate because a conversion rate of the hydrate generated from the reactor is much low. However, according to embodiments of the inventive concept, if the piped reactor is employed and the circular transportation of gas hydrate with the piped reactor is performed, it is possible to successively manufacture even without such a process of dehydration.

[0073] From this connection, there is also provided a successive gas hydrate manufacturing method including the steps of: generating a gas hydrate in a piped reactor; and circularly transporting the gas hydrate over the full length of the piped reactor in the piped reactor to maximize a conversion rate. The detailed procedure in the steps of generating

and circularly transporting the gas hydrate in the piped reactor is as same as the aforementioned, so will not be further described.

[0074] As can be seen from the forgoing, the embodiments of the inventive concept have advantageous effects as follows.

[0075] By using potential hydrate crystals such as ice particles or powder, which already have a porous structure and do not need an additional hydrate induction time, it is possible to increase a diffusion rate of the reaction gas and maximize a contact area between water and the gas, reducing a reaction time and maximizing reaction efficiency.

[0076] Additionally, since a gas hydrate is generated from potential hydrate crystals, latent heat according to a phase change is unnecessary relative to the case of generating a gas hydrate directly from a water solution, hence reducing a product cost and the number of processing steps for removing heat of reaction.

[0077] Moreover, as a gas hydrate is successively manufactured without dehydration that is carried out after generating gas hydrate slurry, it is permissible to allow mass production, for commercialization, that has been disturbed due to enlargement of equipment because an additional device was needed to clean a filtration net or filter or the dehydration was needed in the reactor.

[0078] The foregoing is illustrative of embodiments and is not to be construed as limiting thereof. Although a few embodiments have been described, those skilled in the art will readily appreciate that many modifications are possible in embodiments without materially departing from the novel teachings and advantages. Accordingly, all such modifications are intended to be included within the scope of this inventive concept as defined in the claims. In the claims, means-plus-function clauses are intended to cover the structures described herein as performing the recited function, and not only structural equivalents but also equivalent structures. Therefore, it is to be understood that the foregoing is illustrative of various embodiments and is not to be construed as limited to the specific embodiments disclosed, and that modifications to the disclosed embodiments, as well as other embodiments, are intended to be included within the scope of the appended claims.

1. A successive gas hydrate manufacturing method comprising:

injecting potential hydrate crystals of water solution, which include a surfactant, into a piped reactor;

generating a gas hydrate by pressurizing a gas to the piped reactor in which the potential hydrate crystals are injected; and

circularly transporting the gas hydrate through the full length of the piped reactor in the piped reactor to maximize a conversion rate.

2. The successive gas hydrate manufacturing method according to claim 1, wherein circularly transporting the gas hydrate is performed by pig-balls configured to circularly transport the gas hydrate in the piped reactor while connected to each other with a constant interval in multiplicity.

3. The successive gas hydrate manufacturing method according to claim 2, wherein a diameter of the pig-balls is conditioned to be close to a caliber of the piped reactor.

4. The successive gas hydrate manufacturing method according to claim 2, wherein a multiplicity of the pig-balls adjacent to each other are arranged to be different in angle.

5. The successive gas hydrate manufacturing method according to claim 1, wherein the potential hydrate crystals are porously structured.

6. The successive gas hydrate manufacturing method according to claim 5, wherein the porous potential hydrate crystals are formed in ice particles of the water solution.

7. The successive gas hydrate manufacturing method according to claim 5, wherein the porous potential hydrate crystals are formed in slurry of the water solution.

8. The successive gas hydrate manufacturing method according to claim 6, wherein the potential hydrate crystals are made by cooling and smashing the water solution.

9. The successive gas hydrate manufacturing method according to claim 5, wherein the porous potential hydrate crystals are made by impregnating a porous material in a water solution and cooling the impregnated porous material.

10. The successive gas hydrate manufacturing method according to claim 9, wherein the porous material is adopted from active carbon, silica gel and zeolite.

11. The successive gas hydrate manufacturing method according to claim 5, wherein the porous potential hydrate crystals are made by rendering a highly absorbent resin to absorb a water solution, which contains the surfactant, and cooling the highly absorbent resin in which the water solution is absorbed.

12. The successive gas hydrate manufacturing method according to claim 11, wherein the highly absorbent resin is adopted from polyacrylate, polyacryl amide, polyacryl acid, polymethacrylic acid, polyethylene oxide, and polyvinyl alcohol.

13. The successive gas hydrate manufacturing method according to claim 1, wherein the surfactant is adopted from sodium dodecyl sulfate (SDS), diisooctyl sodium sulfosuccinate (DSS), sodium tetradecyl sulfate, sodium hexadecyl sulfate, sodium dodecylbenzene sulfonate, xylenesulfonate, sodium oleate, 4-n-decylbenzenesulfonate, sodium laurate, 4-dodecylbenzenesulfonic acid, dodecylamine hydrochloride, dodecyltrimethylammonium chloride, 4-n-octylbenzenesulfonate, ethoxylated sulfonate, decylbenzenesulfonate, potassium oleate, n-decylbenzene sulfonate, alkyltrimethylammonium bromide (C10-C16 chains), dodecyl amine, tetradecyltrimethylammonium chloride, dodecyl polysaccharide glycoside, cyclodextrins, glycolipids, lipopeptides, lipopeptides, para-toluene sulfonic acid, trisiloxane, triton X-100, and a mixture.

14. The successive gas hydrate manufacturing method according to claim 13, wherein the volume of the surfactant is less than 0.5% of the total volume of the water solution.

15. The successive gas hydrate manufacturing method according to claim 13, wherein the surfactant is ranged from 50 ppm to 1000 ppm in concentration.

16. The successive gas hydrate manufacturing method according to claim 1, further comprising:

cooling the piped reactor before injecting the potential hydrate crystals, which contain the surfactant, into the piped reactor.

17. The successive gas hydrate manufacturing method according to claim 16, wherein the piped reactor is ranged from -10° C. to 10° C. in cooling temperature.

18. The successive gas hydrate manufacturing method according to claim 1, further comprising:

constantly maintaining internal temperature by additional gas supply after injecting a gas into the piped reactor.

19. The successive gas hydrate manufacturing method according to claim 18, wherein the piped reactor is ranged from 10 bars to 100 bars in internal pressure.

20. The successive gas hydrate manufacturing method according to claim 1, wherein the gas injected into the piped reactor is adopted from methane, ethane, propane, carbon dioxide, butane, and a mixture.

21. A successive gas hydrate manufacturing method comprising:

generating a gas hydrate in a piped reactor; and circularly transporting the gas hydrate through the full length of the piped reactor in the piped reactor to maximize a conversion rate.

22. The successive gas hydrate manufacturing method according to claim 21, wherein the piped reactor comprises pig-balls configured to circularly transport the gas hydrate in the piped reactor while connected to each other with a constant interval in multiplicity.

23. The successive gas hydrate manufacturing method according to claim 22, wherein a diameter of the pig-balls is conditioned to be close to a caliber of the piped reactor.

24. The successive gas hydrate manufacturing method according to claim 22, wherein a multiplicity of the pig-balls adjacent to each other are arranged to be different in angle.

25. The successive gas hydrate manufacturing method according to claim 7, wherein the potential hydrate crystals are made by cooling and smashing the water solution.

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