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[Continued on next page]

(54) Title: APPARATUS FOR STORING AND TRANSPORTING GASEOUS HYDROCARBONS

(57) Abstract: The invention discloses an apparatus for forming hydrocarbon gas hydrate in porous media, comprising injecting an aqueous solution of one or more of thermodynamic promoters, kinetic promoters, or ionic liquid into porous media, and injecting natural gas form semi-clathrate hydrate. The invention further discloses apparatus for efficient and safe storage of hydrocarbon gas such as natural gas or methane-rich gas in stationary or portable facilities.

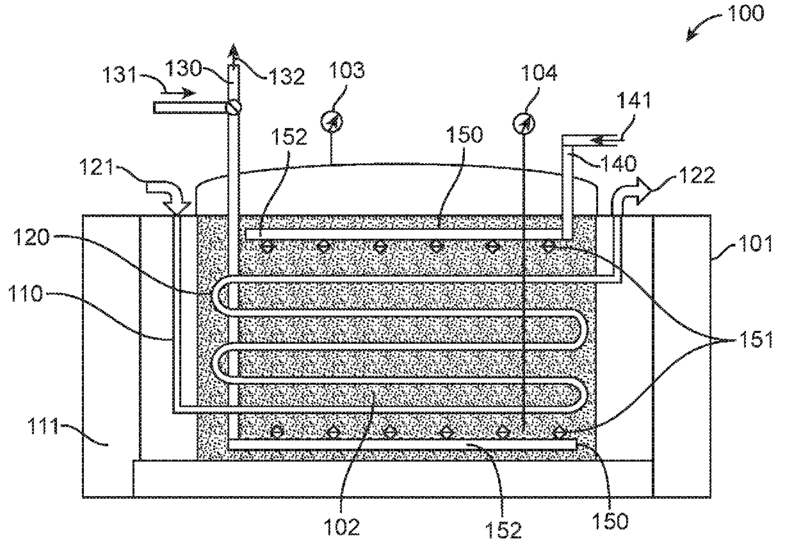

FIG. 1

WO 2015/101923 A1

GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

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APPARATUS FOR STORING AND TRANSPORTING GASEOUS HYDROCARBONS

CROSS-REFERENCES TO RELATED APPLICATIONS

This application claims priority to Indian provisional patent application 6199/CHE/2013 entitled METHOD AND APPARATUS TO STORE AND TRANSPORT GASEOUS HYDROCARBONS IN POROUS MEDIA filed on December 31, 2013, which is incorporated herein by reference.

FIELD OF THE INVENTION

The disclosure relates generally to an apparatus for storing gaseous hydrocarbons and in particular an apparatus for efficient and safe storage of hydrocarbon gas such as natural gas or methane-rich gas in stationary or portable facilities.

DESCRIPTION OF THE RELATED ART

[0001] The global energy demand is witnessing significant increase in the recent past due to increased population, growth in economy and increased industrial activities. Moreover, there has been a phenomenal shift towards use of oil and natural gas (NG) in the overall energy basket. The situation in India is also similar. The increased consumption has led to greater demand, necessitating action on increasing indigenous production and higher sourcing from abroad. Within the oil and gas basket, the demand growth for natural gas is higher than oil due to its benign characteristics. Increasing NG consumption also calls for increasing the infrastructure for its transportation and distribution besides storage to provide a buffer to meet seasonal demand shifts, and unexpected disruptions.

[0002] Natural Gas is transported primarily through pipelines or in the form of liquefied natural gas (LNG). Natural gas can be stored in the form of LNG or as compressed natural gas (CNG). Although pipeline transportation has been found to be the most reliable and cost-effective method of NG transportation, pipeline projects have a high gestation period, besides being cost intensive. Natural gas storage as LNG or CNG is very costly and not energy efficient. Natural gas can also be stored in depleted reservoirs, salt caverns, or aquifers but these have not developed so far in India. In addition, in case of emergency situations, such as war, gas pipeline failures, etc., safety and uninterrupted supply are a major concern. It is thus required to develop alternative technologies in the area of NG Storage and transportation that are safe and cost-efficient.

[0003] Natural gas hydrates (NGH) are of great interest to the scientific community for their potential to store large amounts of natural gas. Natural gas hydrates are crystalline solids that are formed from water and light hydrocarbons such as methane, ethane, in which the molecules of natural gas are trapped inside a 3- dimensional lattice structure (cage) made by the water molecules. The NGH are formed at high pressure and low temperature conditions (e.g. at 13°C, a minimum pressure of 100 bar is necessary to form NGH). It is reported that one m^3 of gas hydrate can store about 160 m^3 of natural gas at atmospheric conditions. As gas hydrates can store large amounts of natural gas, these also have a potential for use in storage and transportation of natural gas.

[0004] US20090035627 discloses a semi-clathrate hydrate compositions formed from water, a semi-clathrate hydrate forming compound and a gas used for energy storage and separation of gases. US5787605 discloses a method of storing and transporting gases by bringing the gas into contact with a porous material in presence of water at room temperature. Gholinezhad experimentally investigated the semi-clathrate hydrates in a micromodels comprising porous structure etched in the glass, towards the application of gas storage, transportation and separation.

[0005] Further, existing apparatus and methods have some shortcomings. The natural gas can first be converted to gas hydrates (solid form) which can then be used for storage and/or transportation. Thereafter the gas hydrate is dissociated to natural gas by destabilizing the phase equilibrium condition, typically, either by raising the temperature or decreasing the pressure or both. Chemical inhibitors can also be used in this process. However, the process of hydrate formation is slow due to slow nucleation even in the presence of vigorous stirring which requires large amount of energy. Moreover, the gas hydrates once formed are stable at high pressure and low temperature conditions and may not dissociate rapidly at the required rate.

[0006] The invention addresses some of the drawbacks of conventional apparatus and satisfies the need of an apparatus for storage and transport of natural gas in the form of gas hydrates in porous media with or without further additives, with further related advantages as set forth here.

SUMMARY OF THE INVENTION

[0007] In one embodiment, an apparatus for storing and transporting gaseous hydrocarbons comprises a tank filled with porous media comprising a sparger system configured for introducing pressurized gas and liquid through the porous media. The tank is provided with insulated jacket and heat exchanger means for regulating temperature within the tank. In one embodiment, the tank is configured for promoting the formation of a gas hydrates on infusion of pressurized gas and liquid into the porous media. In another embodiment, the tank is configured with means for facilitating decomposition of the gas hydrate to release the gas. In one embodiment, the gas is selected from one of natural gas, biogas or a methane-rich gas, and the gas hydrate is a semi-clathrate hydrate. The porous media in various embodiments is silica sand or a silica gel or activated carbon or a zeolite or a bed of carbon nanotubes.

[0008] In an embodiment, the sparger system comprises piping with nozzles located at various levels within the porous media. In various embodiments, the heat exchanger means comprises piping distributed within the porous media or enclosing the tank or a combination thereof.

[0009] In various aspects of the invention, the liquid comprises an aqueous solution of one or more of a thermodynamic promoter, a kinetic promoter, surfactants or an ionic liquid. The thermodynamic promoter is tetra-n-butyl-ammonium halides or a tetrahydrofuran (THF) or a combination thereof and inorganic salts such as chlorides of sodium or potassium or magnesium or calcium or a combination thereof. The tetra-n-butyl-ammonium halide of various embodiments is selected from tetra-n-butyl-ammonium bromide (TBAB) or tetra-n-butyl-ammonium chloride (TBAC) or tetra-n-butyl-ammonium fluoride (TBAF) or a combination thereof.

[0010] In one embodiment, the decomposition of the gas hydrate is carried out by chemical inhibition, depressurization or thermal stimulation or a combination thereof. In various embodiments the apparatus is a stationary installation, an underground installation or a portable kit.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The invention has other advantages and features which will be more readily apparent from the following detailed description of the invention and the appended claims, when taken in conjunction with the accompanying drawings, in which:

[0012] FIG. 1 shows an apparatus for storing natural gas or other hydrocarbons in porous media.

[0013] FIG. 2 shows a flow chart for the method of storing natural gas or other hydrocarbons in porous media.

[0014] FIG. 3 shows underground depleted reservoir for hydrocarbon gas semiclathrate hydrate storage.

[0015] FIG. 4 and FIG. 5 show the number of moles of gas consumed per mole of water molecule in gas hydrate system for the initial pressure at 7.5 MPa and for different temperatures.

[0016] FIG. 6 and FIG. 7 show the number of moles of gas consumed per mole of water molecule in gas hydrate for the initial pressure at 5.5 MPa and for different temperatures.

[0017] FIG. 8 and FIG. 9 shows the comparison has been made on methane gas consumption in gas hydrate for pure water in silica sand bed for methane hydrate system.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0018] While the invention has been disclosed with reference to certain embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the scope of the invention. In addition, many modifications may be made to adapt to a particular situation or material to the teachings of the invention without departing from its scope.

[0019] Throughout the specification and claims, the following terms take the meanings explicitly associated herein unless the context clearly dictates otherwise. The meaning of "a", "an", and "the" include plural references. The meaning of "in" includes "in" and "on." Referring to the drawings, like numbers indicate like parts throughout the views. Additionally, a reference to the singular includes a reference to the plural unless otherwise stated or inconsistent with the disclosure herein.

[0020] The proposed invention relates to apparatus for forming, storage and transportation of hydrocarbon gas hydrate, comprising porous media. The apparatus is provided with sparger system for injecting an aqueous solution of one or more of thermodynamic promoters, kinetic promoters, or ionic liquid into the porous media, along with natural gas to form the gas hydrate. The apparatus is intended to serve as efficient and safe storage of hydrocarbon gas such as natural gas or methane-rich gas in stationary or portable facilities as further described with reference to the embodiments to follow with reference to the sequentially numbered figures.

[0021] An apparatus **100** for storing and transporting gaseous hydrocarbons according to one embodiment of the invention shown in FIG. 1 comprises a tank **101** filled with porous media **102.** In various embodiments, a pressure sensor **103** and temperature sensor **104** are inserted into the hydrate formation tank **101** for measuring the variation in pressure and temperature respectively.

[0022] In one embodiment, the tank **101** is provided with a jacket **110** with thermal insulation **111**. In addition, heat exchanger **120** is provided, with inlet **120** and outlet **122** for regulating temperature within the tank **101**. In one embodiment, the tank **101** is configured for promoting the formation of a gas hydrate on infusion of pressurized gas and liquid into the porous media **102**. In some embodiments, the pressurized gas may be introduced into the tank through a gas piping system **130** comprising an inlet **131** and outlet **132**. In various embodiments, the liquid may be introduced into the tank by means of liquid piping system **140** with inlet **141**. The tank **101** with gas piping **130** and liquid piping **140** may connected to sparger system **150** comprising nozzles **151** and pipes **152** for introducing and uniformly distributing the pressurized gas and liquid throughout the porous media **102**. In various embodiments, the tank **101** is configured with means for facilitating decomposition of the gas hydrate to release the gas.

[0023] In some embodiment of the invention the gas is selected from one of natural gas, or biogas or a methane-rich gas and the gas hydrate is a semi-clathrate hydrate. In one embodiment of the apparatus **100**, the porous media **102** is silica sand or a silica gel or activated carbon or a zeolite or a bed of carbon nanotubes. In various embodiments, sparger system **150** comprises piping **152** with nozzles **151** located at various levels within the porous media **102**. In an embodiment, the heat exchanger **120** comprises piping **121** distributed within the porous media **102** or enclosing the tank **101** or a combination thereof, so as to maintain uniform temperature during formation or decomposition of gas hydrate.

[0024] In one embodiment, the liquid comprises an aqueous solution of one or more of a thermodynamic promoter, a kinetic promoter, surfactants or an ionic liquid. The thermodynamic promoter comprises one or more of a tetra-n-butyl-ammonium halide, a tetrahydrofuran (THF), chlorides of sodium, potassium, magnesium, or calcium. The tetra-n-butyl-ammonium halide is selected from tetra-n-butyl-ammonium bromide (TBAB) or tetra-n-butyl-ammonium chloride (TBAC) or tetra-n-butyl-ammonium fluoride (TBAF) or a combination thereof.

[0025] In an embodiment, the decomposition of the gas hydrate is carried out by chemical addition, depressurization or thermal stimulation or a combination thereof. In various embodiments, the apparatus **100** is a stationary facility or an underground facility or a portable kit.

[0026] In another embodiment of the invention, a system **200** for underground storage, retrieval and transportation is disclosed as shown in FIG. 2. The system comprises an underground depleted reservoir **201**storage and transportation apparatus **100** for natural gas semi-clathrate hydrate is disclosed. The depleted reservoir **201** can be an oil or a gas reservoir. In various embodiments a combination of vertical **202** and horizontal **203** wells may provide access for injection of liquid and gas to one or more apparatus **100A** located within the system **200**. As disclosed earlier in embodiments introduced through FIG. 1, apparatus **100A** comprises porous media and piping system for forming, storage and retrieval of hydrocarbon gas hydrate. In one embodiment the system further comprises transport vehicle **204** fitted with a portable storage apparatus **100B** for storage and transportation of gas as hydrate. Transport vehicle **204** provides safe means for transporting hydrocarbon gas under pressure, while enabling retrieval from **100B** at the desired destination, as earlier disclosed with reference to system **100**.

[0027] In some embodiments as disclosed with reference to FIG. 1 and 2, an aqueous solution of promoters is first injected into the apparatus **100**, **100A** or **100B**, followed by the injection of natural gas. In alternative embodiments the aqueous spraying may be carried out concurrently with pressurization. Absorption of the aqueous liquid with promoters and interaction of the gas with the liquid in the porous media enables easy formation of semi-clathrate gas hydrate. Since hydrate formation is exothermic, heat is liberated, which is drawn away by the heat exchange system **120**.

[0028] While the invention has been disclosed with reference to certain embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the scope of the invention. In addition, many modifications may be made to adapt to a particular situation or material the teachings of the invention without departing from its scope as further explained in the following examples, which however, are not to be construed to limit the scope of the invention as delineated by the claims.

EXAMPLES

Example – 1

[0029] The hydrate formation storage apparatus is shown in FIG. 3. The main part of the apparatus is made of stainless steel (SS-316). A pressure transducer and platinum resistance thermometer (Pt-100) are inserted into the hydrate formation apparatus. A dead weight pressure testing apparatus is used for calibration of the pressure transducer in the range of 1 to 7 MPa. The uncertainty in the pressure and temperature sensor is ± 0.005 MPa and ± 0.05 K, respectively. A syringe pump with a capacity of 507.38 ml is used to compress and transfer gas from a cylinder to the apparatus with a flow rate range from 0.001 ml/min to 204 ml/min for any pressure up to 25.86 MPa with a flow accuracy of +0.5% (maximum 1.0μl/min seal leakage).

[0030] A jacket is surrounded to the hydrate formation apparatus through which a cooling agent, such as water, glycol, alcohol, or any refrigerant can be used to maintain the temperature by using a heat exchanger. In this study, we use glycol solution to circulate through the jacket of the hydrate formation apparatus to maintain the temperature of the porous media inside the apparatus.

Example - 2

[0031] The storage vessel is filled with porous media such as silica sand of 0.16 mm size particle up to a bed height of 7 cm. A temperature sensor (Pt-100) is inserted into the bed properly so as to avoid temperature fluctuation. The bed of silica sand is made with a height of 7 cm and having a pore volume of 15 cm^3/gm. For kinetic measurements, the conditions at which experiments are carried out are initial pressures of 7.5 and 5.5 MPa and temperatures at 273.65 K and 276.15 K. The silica sand bed is having pore volume of 15 cm^3/gm which accounts for about 88.09 mL of distilled water to attain water saturation of 75% in the given bed of height. Pure water and with different concentration of TBAB and SDS have been used for making the bed by uniform layering of sand and aqueous solutions in order to remove any air pockets. The pressure transducer and temperature sensor are inserted properly at a suitable depth inside the porous bed and by closing the storage vessel from top to align properly to avoid any leakage.

[0032] As shown in FIG. 3, the methane gas from gas cylinder is charged to the storage vessel through a syringe pump. Before pressurising the storage vessel, the pure water and/or of TBAB with SDS aqueous solution is taken from liquid solution tank with the help of a liquid pump. The heat exchanger is connected to a jacket which is surrounded to the hydrate apparatus storage vessel. The temperature of the apparatus is maintained at a suitable hydrate formation temperature (in this case at 273.65 K or 276.15 K) throughout the hydrate formation process. The heat exchanger is used for reducing the temperature of the storage vessel as desired before injecting the methane gas.

[0033] As soon as the temperature is reached up to 273.65 K or 276.15 K (±1K) as per experimental requirement and stabilised at the same temperatures, the methane gas is injected in the storage vessel through nozzle from the gas cylinder up to a desired hydrate formation pressure conditions (in this case 5.5 MPa or 7.5 MPa). The pressure and temperature sensors are connected to a data acquisition board in order to record the pressure and temperature data at every 30s interval for about 12 h. The storage vessel is charged up to desired initial pressures (7.5 and 5.5 MPa). During the process of gas injection and hydrate formation, an increase in temperature indicates the onset of the nucleation of hydrate formation inside the storage vessel.

Example - 3

[0034] To support the invention, a kinetic study has been conducted for pure methane hydrate and methane hydrate with different concentration of tetra-*n*-butyl ammonium bromide (TBAB) and sodium dodecyl sulphate (SDS) using silica sand as a porous media. The kinetic study has been conducted in which gas uptake measurements have been done where the curves are plotted between number of moles of gas consumed per mole of water and time (hour). In FIG. 4 and 5, the kinetic measurements have been done with different concentration of TBAB and SDS in methane hydrate system for different pressures which is listed in Table 1. For example, the hydrate formation experiment was carried out for porous media in silica sand at initial pressure 7.5 MPa, and maintaining two different temperatures individually at 273.65 K and 276.15 K for 12 hrs. It is observed from FIG. 4 and 5, that the number of moles of gas consumed per mole of water molecule in gas hydrate system for the initial pressure at 7.5 MPa and for different temperatures 273.65 K and 276.15 K is more for 0.1 mass fraction TBAB+600 ppm SDS as compared to 0.1 mass fraction TBAB+0 ppm SDS and 0.2 mass fraction TBAB+0 ppm SDS in silica sand.

Table 1. Methane hydrate formation experiment in porous media

Experiment No.	TBAB conc.(mass fraction)	SDS conc. (ppm)	Temperature (K)	Pressure (MPa)
1	0.1	0	273.65	7.5
			276.15	
			273.65	5.5
			276.15	
2	0.1	600	273.65	7.5
			276.15	
			273.65	5.5
			276.15	
3	0.2	0	273.65	7.5
			276.15	

			273.65	5.5
			276.15	

[0035] In a similar way, as shown in FIG. 6 and 7, the number of moles of gas consumed per mole of water molecule in gas hydrate for 5.5 MPa at 273.65 K and 276.15 K is observed to be more for 0.1 mass fraction TBAB+600 ppm SDS as compared to 0.1 mass fraction TBAB+0 ppm SDS and 0.2 mass fraction TBAB+0 ppm SDS in silica sand. It is observed that with decrease in initial pressure for hydrate formation from 7.5 MPa to 5.5 MPa, the cumulative number of moles of methane gas consumption per mole of water in gas hydrate is also decreased for both the temperatures 273.65 K and 276.15 K.

[0036] In FIG. 8 and 9, the comparison has been made on methane gas consumption in gas hydrate for pure water, 0.1 mass fraction TBAB, 0.2 mass fraction TBAB and 0.1 mass fraction TBAB+600 ppm SDS in silica sand bed for methane hydrate system for initial pressures of 7.5 MPa and 5.5 MPa and temperature at 273.65 K. It is observed that the gas uptake for 0.1 mass fraction TBAB+600 ppm SDS is more with respect to time for initial pressure at 7.5 and 5.5 MPa as compared to other cases without SDS. It is observed that the gas consumption in hydrate of pure water in porous media is lower as compared to the hydrate of TBAB and hydrate of TBAB in the presence of SDS. Also, the induction time, at which hydrate formation start is reduced in the presence of TBAB at different concentrations of 0.1 and 0.2 mass fractions as compared to pure methane hydrate. However, the gas uptake is concerned, since TBAB alone with different concentration 0.1 and 0.2 mass fractions is not so much helpful for increasing the gas uptake with respect to time. The addition of surfactant, SDS along with TBAB have provide to provide significant increase in methane gas uptake in hydrate in the porous media, thereby indicating the combination of promoter of TBAB along with SDS for efficient storage of natural gas in porous media.

[0037] Here, the TBAB is a sample semiclathrate hydrate system taken along with sample surfactant SDS system for the hydrate formation of methane in porous media. The invention, in general, is applied to all the possible combinations of promoters such as, tetra-*n*-butyl ammonium bromide (TBAB), tetra-*n*-butyl ammonium chloride (TBAC), tetra-*n*-butyl ammonium fluoride (TBAF), tetrahydrofuran (THF), tetra-n-butyl ammonium nitrate ($TBANO_3$) along with all possible surfactant, for ex., anionic types - sodium dodecyl sulphate (SDS), sodium dodecyl benzene sulfonate (SDBS), cationic types - quaternary ammonium salts, polycyclic alkyl and amines and nonionic type - ethoxylated aliphatic alcohol, carboxylic esters.

[0038] While the invention has been disclosed with reference to certain embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the scope of the invention. In addition, many modifications may be made to adapt to a particular situation or material the teachings of the invention without departing from its scope.

WE CLAIM:

1. An apparatus for storing and transporting gaseous hydrocarbons comprising:

a tank filled with a porous media comprising a sparger system configured for introducing pressurized gas and liquid through the porous media, wherein,

the tank is provided with insulated jacket and heat exchanger means for regulating temperature within the tank;

the tank being configured for promoting the formation of a gas hydrate on infusion of pressurized gas and liquid into the porous media and

wherein the tank is configured with means for facilitating decomposition of the gas hydrate to release the gas.

2. The apparatus of claim 1, wherein the gas is selected from one of natural gas, or biogas or a methane-rich gas and the gas hydrate is a semi-clathrate hydrate.

3. The apparatus of claim 1, wherein the porous media is silica sand or a silica gel or activated carbon or a zeolite or a bed of carbon nanotubes.

4. The apparatus of claim 1, wherein the sparger system comprises piping with nozzles located at various levels within the porous media.

5 The apparatus of claim 1, wherein the heat exchanger means comprises piping distributed within the porous media or enclosing the tank or a combination thereof.

6. The apparatus of claim 1, wherein the liquid comprises an aqueous solution of one or more of a thermodynamic promoter, a kinetic promoter, surfactants or an ionic liquid.

7. The apparatus of claim 6, wherein the thermodynamic promoter comprises one or more of a tetra-n-butyl-ammonium halide, a tetrahydrofuran (THF), chlorides of sodium, potassium, magnesium, or calcium.

8. The apparatus of claim 7, wherein the tetra-n-butyl-ammonium halide is selected from tetra-n-butyl-ammonium bromide (TBAB) or tetra-n-butyl-ammonium chloride (TBAC) or tetra-n-butyl-ammonium fluoride (TBAF) or a combination thereof.

9. The apparatus of claim 1, wherein the decomposition of the gas hydrate is carried out by chemical inhibition, depressurization or thermal stimulation or a combination thereof.

10. The apparatus of claim 1, wherein the apparatus is a stationary facility or an underground facility or a portable kit.

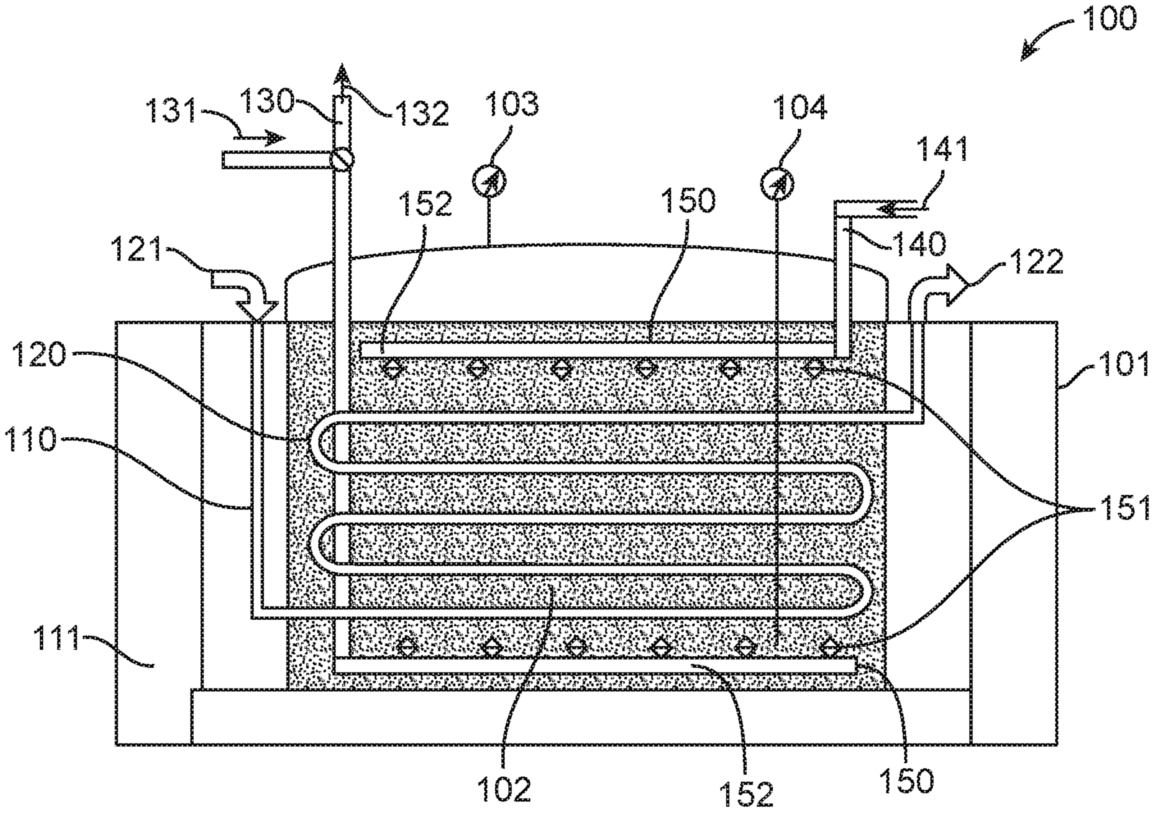
100
131
130
132
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FIG. 1

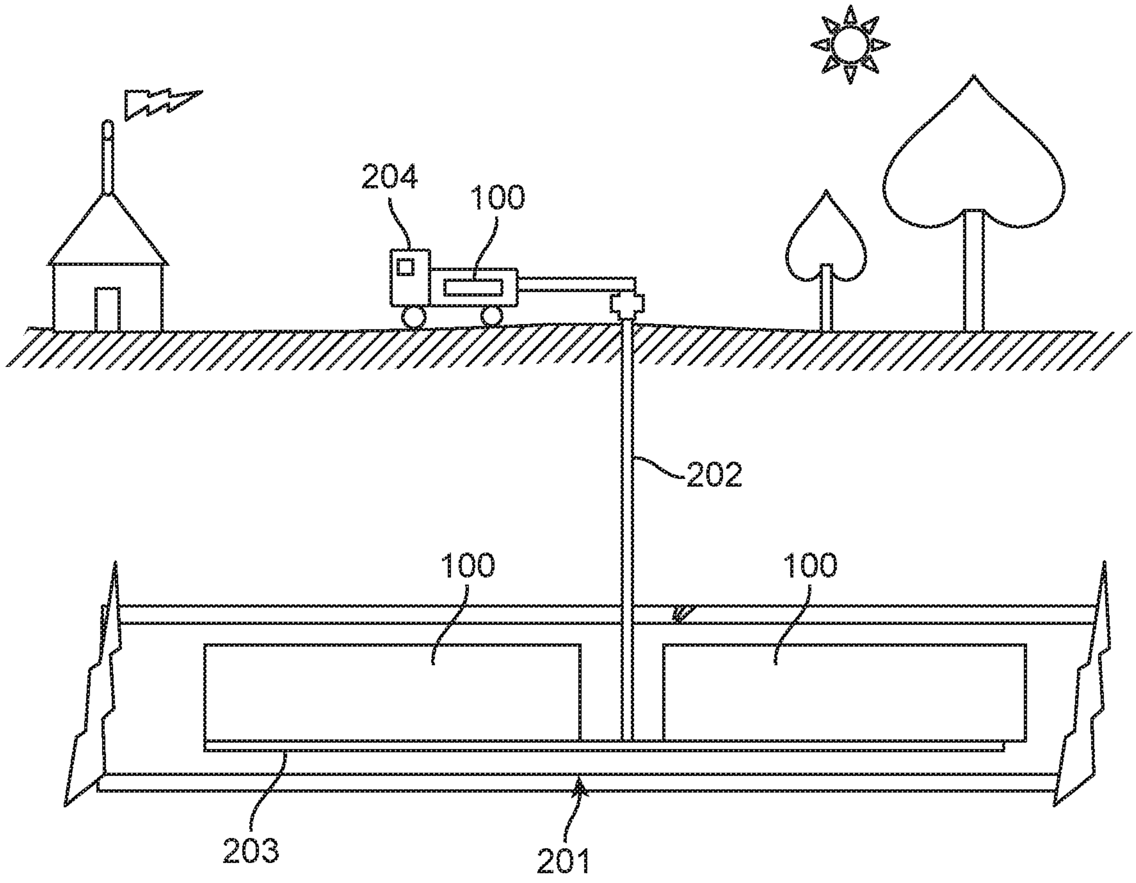

FIG. 2

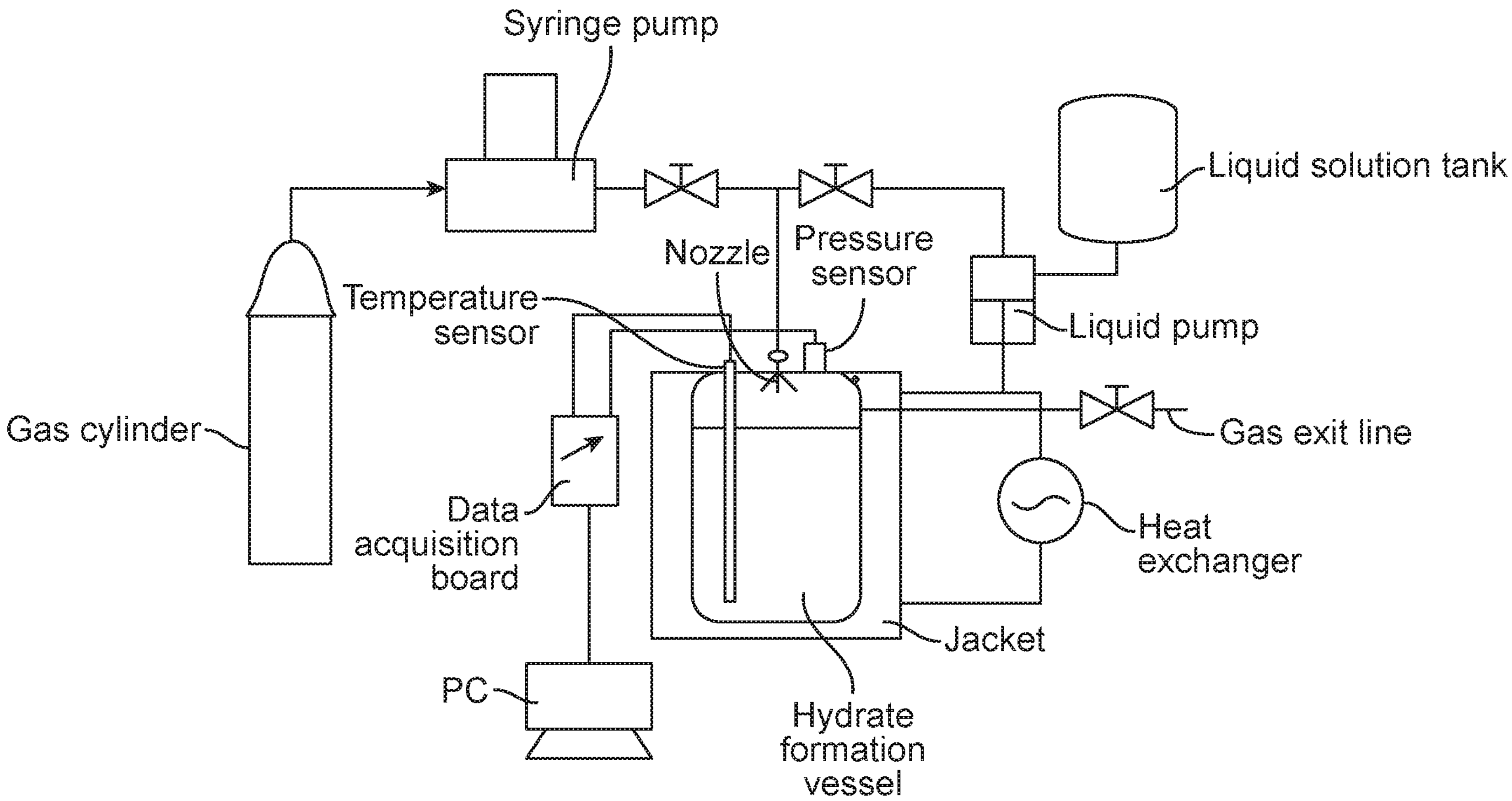
Syringe pump
Liquid solution tank
Nozzle
Pressure sensor
Temperature sensor
Liquid pump
Gas cylinder
Gas exit line
Data acquisition board
Heat exchanger
Jacket
PC
Hydrate formation vessel

FIG. 3

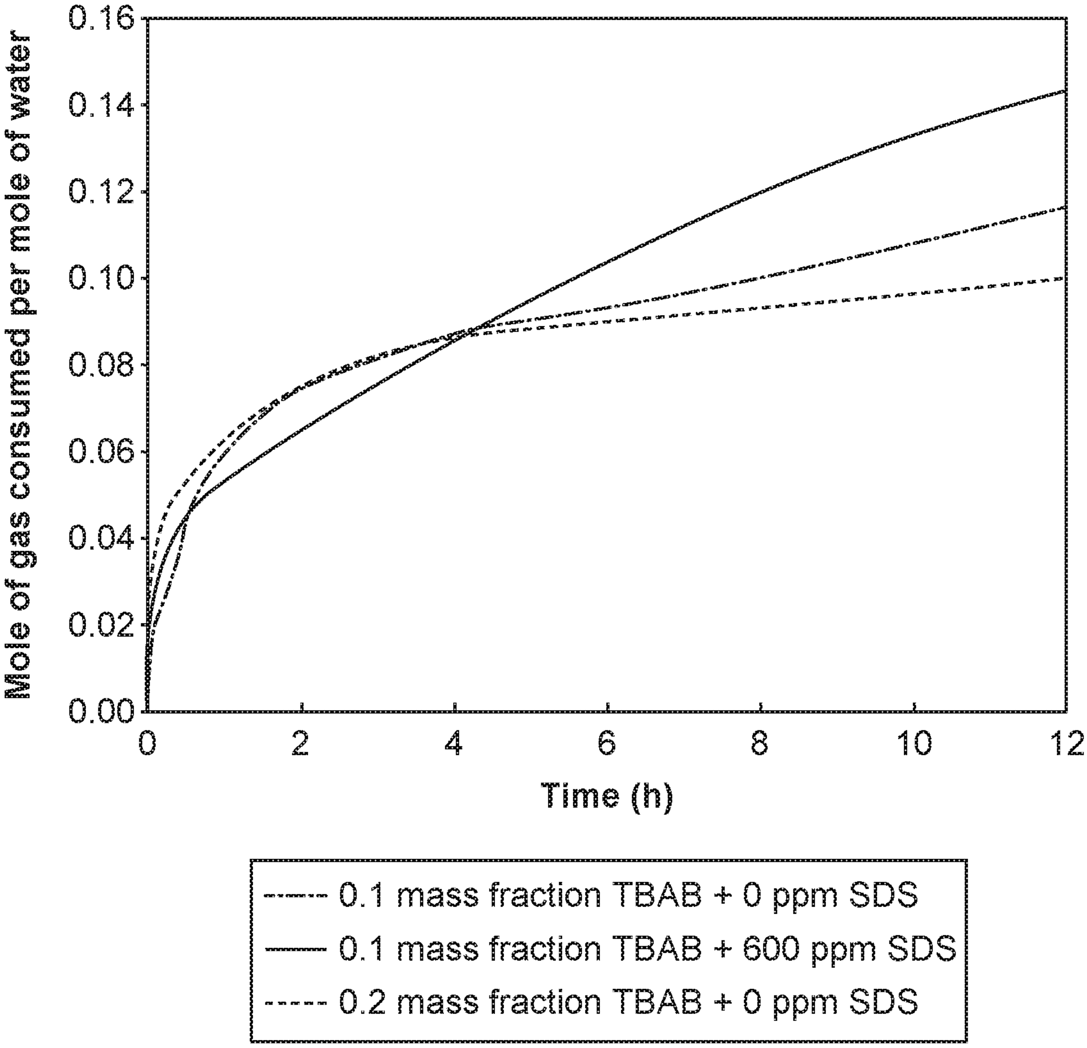
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Mole of gas consumed per mole of water
0
2
4
6
8
10
12
Time (h)
0.1 mass fraction TBAB + 0 ppm SDS
0.1 mass fraction TBAB + 600 ppm SDS
0.2 mass fraction TBAB + 0 ppm SDS

FIG. 4

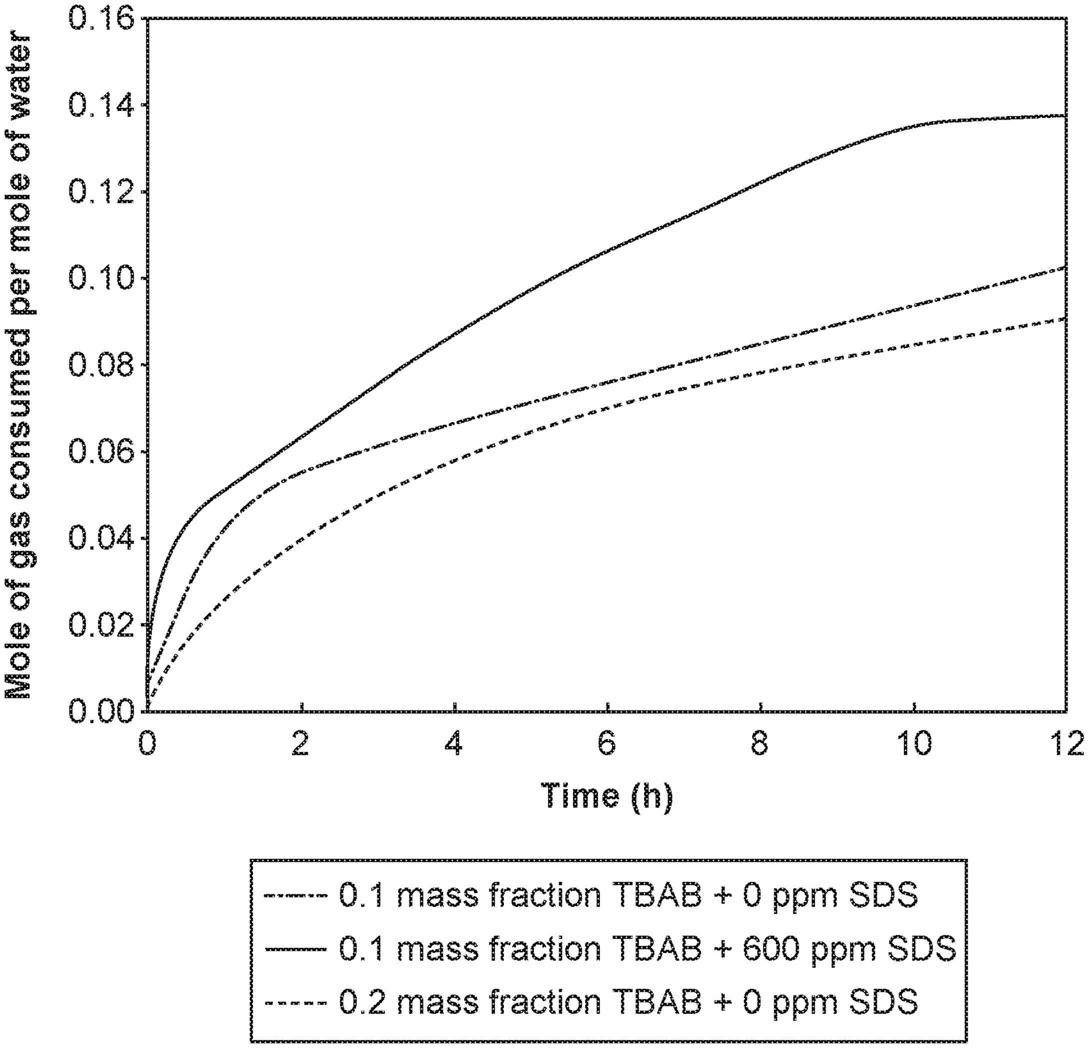
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Mole of gas consumed per mole of water
0
2
4
6
8
10
12
Time (h)
0.1 mass fraction TBAB + 0 ppm SDS
0.1 mass fraction TBAB + 600 ppm SDS
0.2 mass fraction TBAB + 0 ppm SDS

FIG. 5

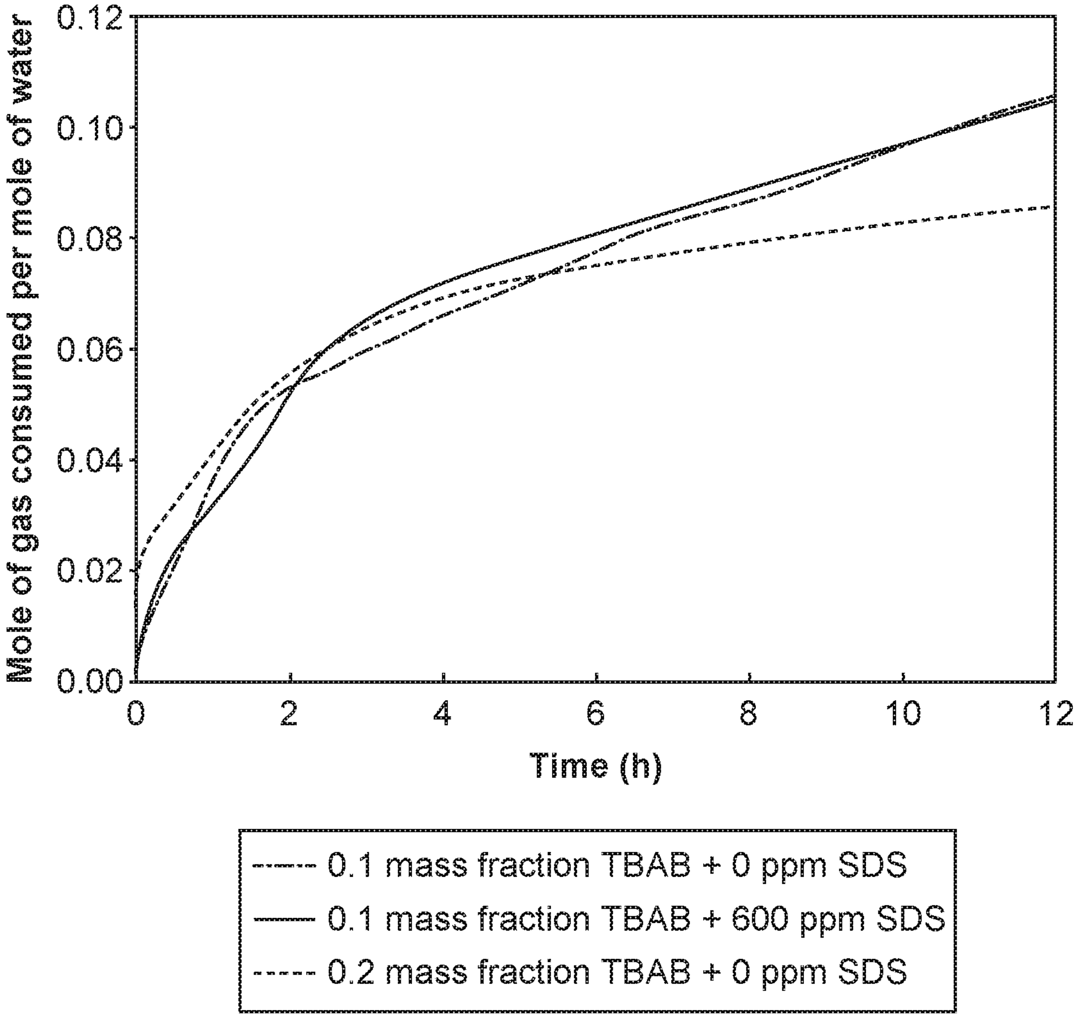
Mole of gas consumed per mole of water
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
2
4
6
8
10
12
Time (h)
0.1 mass fraction TBAB + 0 ppm SDS
0.1 mass fraction TBAB + 600 ppm SDS
0.2 mass fraction TBAB + 0 ppm SDS

FIG. 6

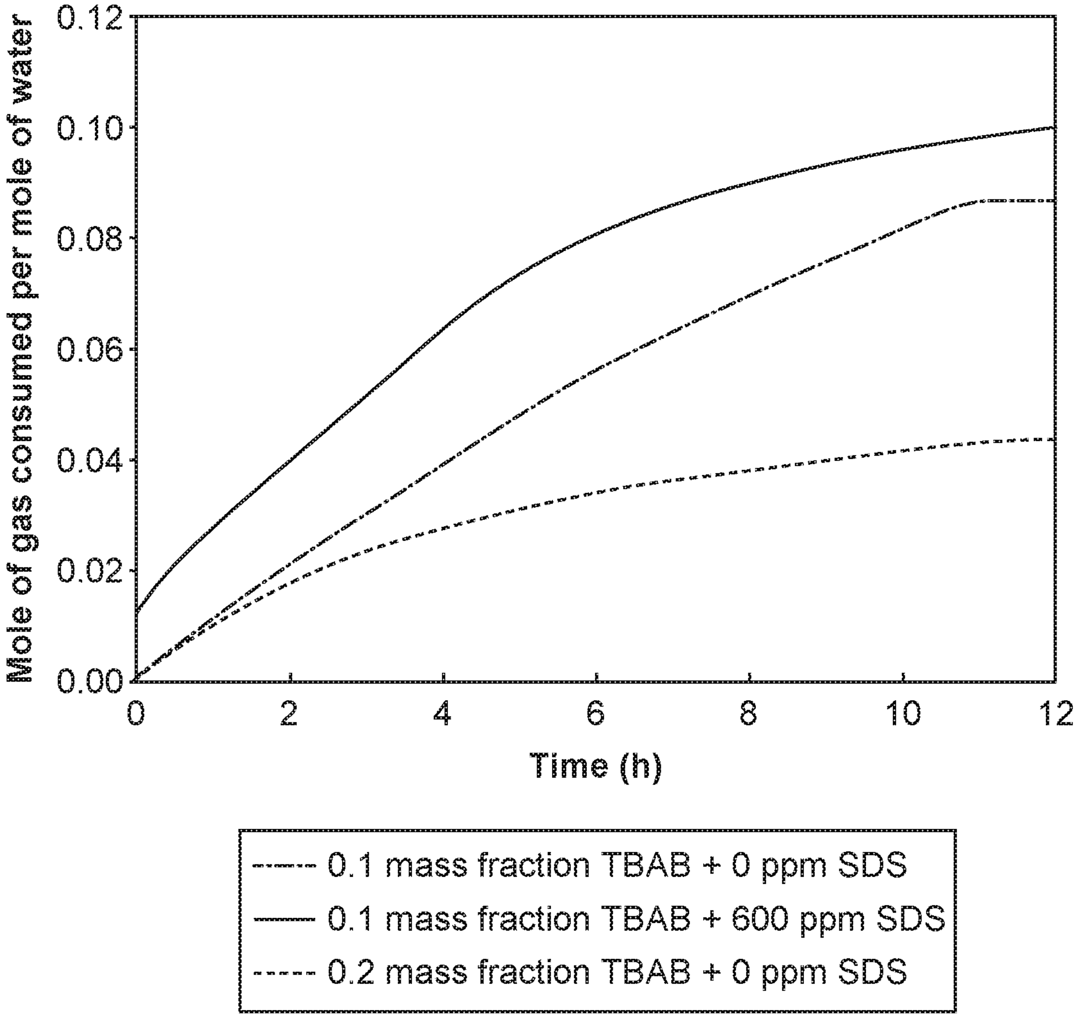
Mole of gas consumed per mole of water
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0
2
4
6
8
10
12
Time (h)
0.1 mass fraction TBAB + 0 ppm SDS
0.1 mass fraction TBAB + 600 ppm SDS
0.2 mass fraction TBAB + 0 ppm SDS

FIG. 7

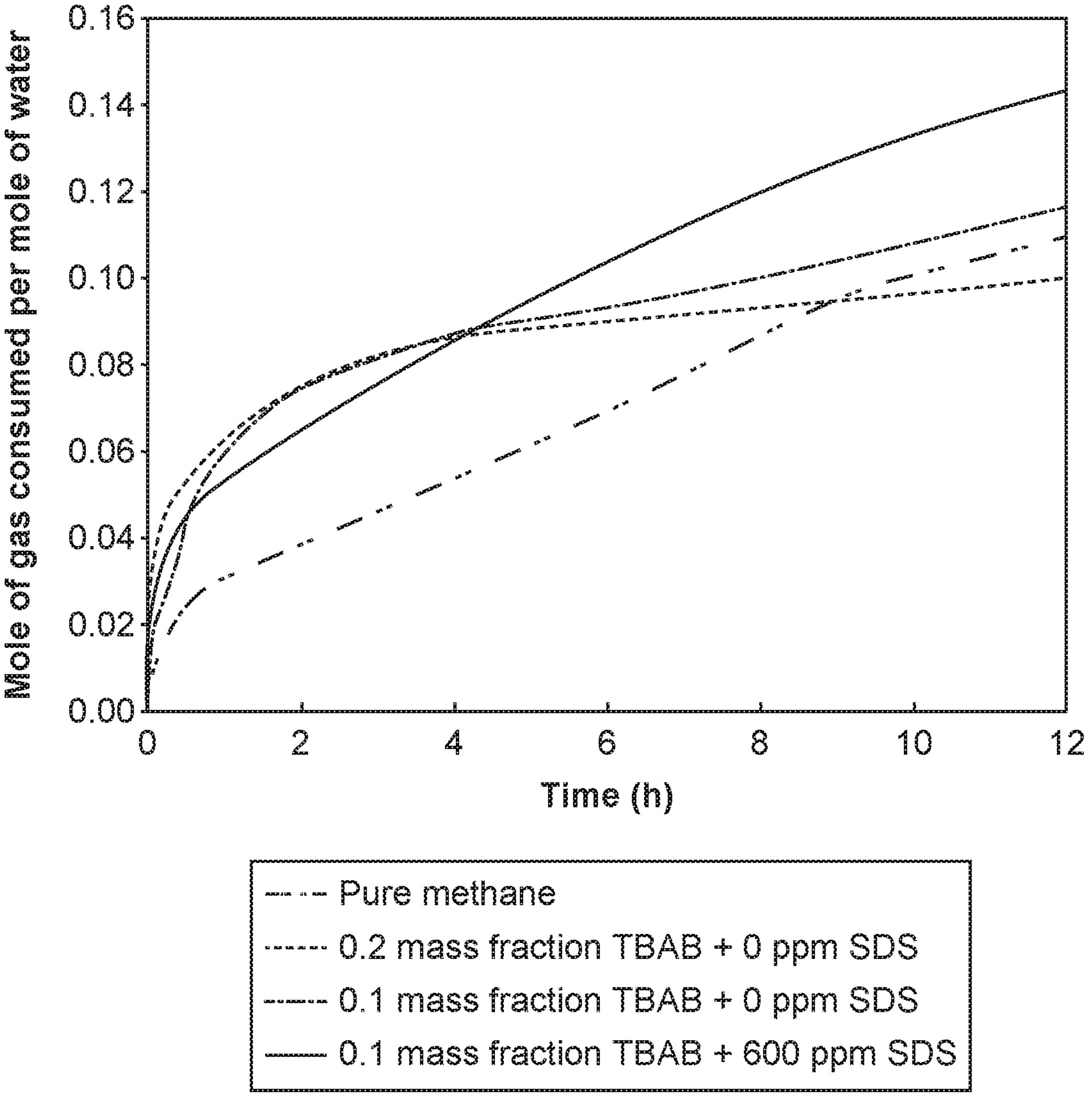
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Mole of gas consumed per mole of water
0
2
4
6
8
10
12
Time (h)
Pure methane
0.2 mass fraction TBAB + 0 ppm SDS
0.1 mass fraction TBAB + 0 ppm SDS
0.1 mass fraction TBAB + 600 ppm SDS

FIG. 8

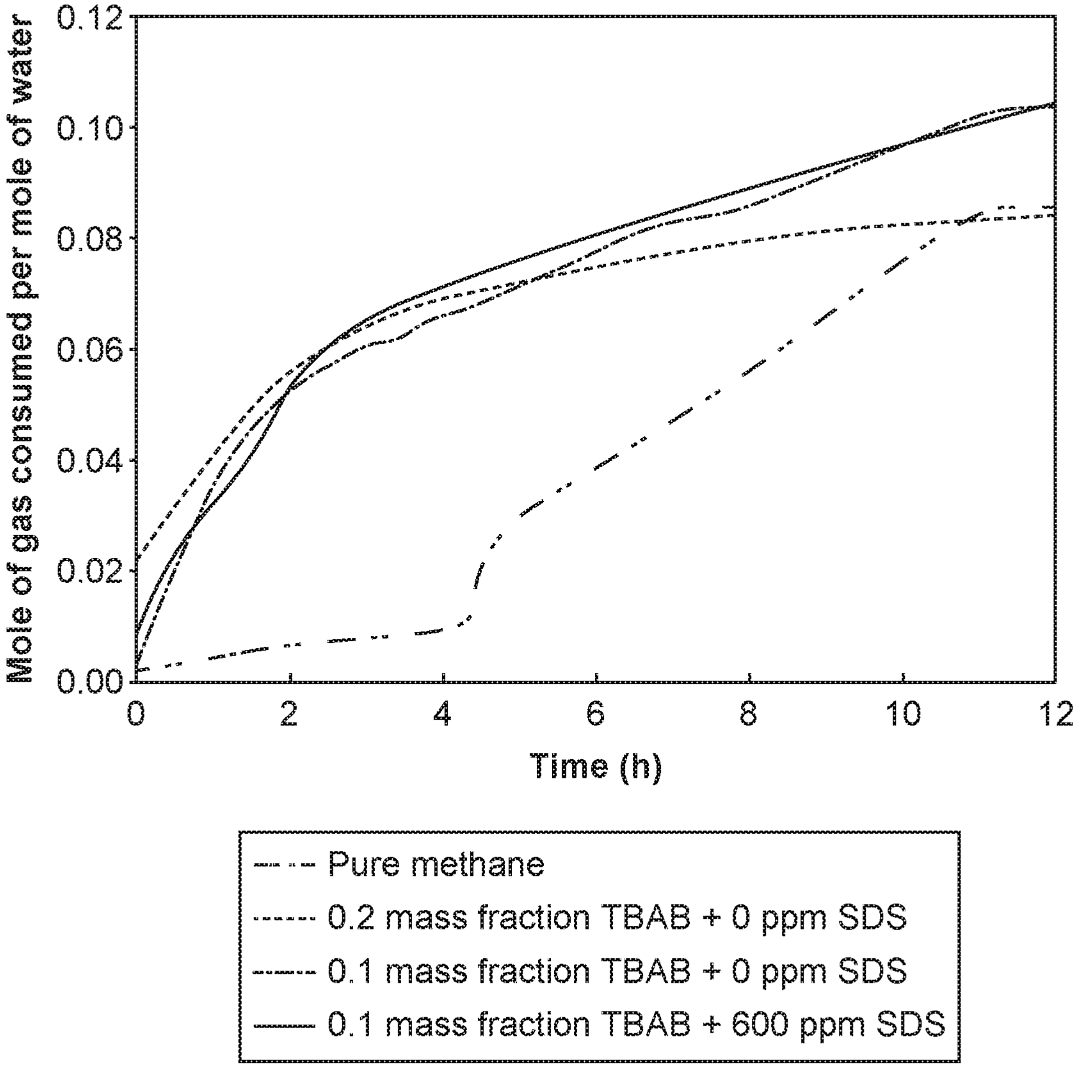
Mole of gas consumed per mole of water
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
2
4
6
8
10
12
Time (h)
Pure methane
0.2 mass fraction TBAB + 0 ppm SDS
0.1 mass fraction TBAB + 0 ppm SDS
0.1 mass fraction TBAB + 600 ppm SDS

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2014/067398

A. CLASSIFICATION OF SUBJECT MATTER
F17C5/00 Version=2014.01

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

F17C5/00

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

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

IPO internal database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3583351 A (Paul T Gorman) 8 Jun 1971 FIG. 01-07,WHOLE DOCUMENT	1-10
Y	US 5473904 A (Boyun Guo, Robert E. Bretz, Robert L. Lee) 12 Dec 1995 FIG. 01-03,WHOLE DOCUMENT, ABSTRACT	1-10
A	JP2004307300 A(HAYASHI TAKAHIRO; SUGIYAMA MASAHIKO; SUZUKI HIROSHI; SHINAGAWA TOMOHIRO) 2004-11-04 FIG. 01-02, ABSTRACT	1-10
A	JP2004051391 A (HAYASHI TAKAHIRO) 2004-02-19 FIG. 01-02, ABSTRACT	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier application or patent but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 25-05-2015	Date of mailing of the international search report 25-05-2015
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