

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
9 September 2011 (09.09.2011)

PCT

(10) International Publication Number
WO 2011/109118 A1

(51) International Patent Classification:
E21B 43/25 (2006.01)

(21) International Application Number:
PCT/US2011/020383

(22) International Filing Date:
6 January 2011 (06.01.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/311,034 5 March 2010 (05.03.2010) US

(71) Applicant (*for all designated States except US*):
EXXONMOBIL UPSTREAM RESEARCH COMPANY [US/US]; CORP-URC-SW-359, P.O.Box 2189,
Houston, TX 77252-2189 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **LACHANCE, Jason, W.** [US/US]; 3401 Klebery Court, Pearland, TX 77584 (US). **TURNER, Douglas, J.** [US/US]; 3614 Village Pine Drive, Humble, TX 77339 (US).

(74) Agents: **TIMMINS, Stephen** et al.; ExxonMobil Upstream Research Company, CORP-URC-SW-359, P.O.Box 2189, Houston, TX 77252-2189 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, 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, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

(54) Title: SYSTEM AND METHOD FOR CREATING FLOWABLE HYDRATE SLURRIES IN PRODUCTION FLUIDS

(57) Abstract: Methods and systems are provided for producing hydrocarbons from production fluids that have water as an external phase. An exemplary embodiment provides a method that comprises producing a production fluid having water as the external phase and injecting an amount of a thermodynamic hydrate inhibitor into the production fluid, wherein the amount is adjusted to allow hydrate formation to occur while retaining liquid water as the external phase. The water and thermodynamic hydrate inhibitor may be separated from the production fluid and a purified hydrocarbon stream may be produced.



WO 2011/109118 A1

SYSTEM AND METHOD FOR CREATING FLOWABLE HYDRATE SLURRIES IN PRODUCTION FLUIDS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the priority benefit of U.S. Provisional Patent Application
5 61/311,034 filed 5 March 2010 entitled SYSTEM AND METHOD FOR CREATING
FLOWABLE HYDRATE SLURRIES IN PRODUCTION FLUIDS, the entirety of which is
incorporated by reference herein.

FIELD

[0002] Exemplary embodiments of the present techniques relate to increasing the
10 flowability of hydrocarbons in an external water phase by allowing the formation of hydrates
to occur.

BACKGROUND

[0003] The presence of water in production fluids may cause problems while transporting
a hydrocarbon due to the formation of clathrate hydrates with the hydrocarbons. Clathrate
15 hydrates (commonly called hydrates) are weak composites formed from a water matrix and a
guest molecule, such as methane or carbon dioxide, among others. Hydrates may form, for
example, at the high pressures and low temperatures that may be found in pipelines and other
hydrocarbon equipment. While forming, the hydrates can agglomerate, leading to plugging
or fouling of the equipment. Various techniques have been used to lower the ability for
20 hydrates to form or cause plugging or fouling. Exemplary, but non-limiting techniques
include insulation of lines, dehydration of the hydrocarbon, and the adding of thermodynamic
hydrate inhibitors (THIs), kinetic hydrate inhibitors (KHIs), and/or anti-agglomerates (AAs).

[0004] Insulation, active heating, and dehydration can be expensive, especially for subsea
systems. Even with insulation, cool-down of production fluids can limit the distance of a
25 producing pipeline. For example, the contents of the pipeline may cool down during shut-in
periods and form a hydrate plug. If a hydrate blockage does occur, insulation can be
detrimental by preventing heat transfer from the surroundings that is needed for hydrate
melting.

[0005] Thermodynamic hydrate inhibitors, such as methanol, monoethylene glycol,
30 diethylene glycol, triethylene glycol, and potassium formate, among others, lower the hydrate

formation temperature, which may inhibit the formation of the hydrate under the conditions found in a particular process. Thermodynamic inhibitors can be very effective at hydrate prevention, but the quantities required for total inhibition are large and proportional to the amount of water produced, leading to increasing and even prohibitive quantities late in field life. *See* Valberg, T., "Efficiency of Thermodynamic Inhibitors for Melting Gas Hydrates," Master's Thesis, Norwegian University of Science and Technology, Trondheim, Norway (2006). Low dosage hydrate inhibitors (LDHIs) exist, including kinetic hydrate inhibitors (KHIs) and anti-agglomeration agents (AAs).

[0006] KHIs slow the formation of hydrates, but not by changing the thermodynamic conditions. Instead, KHIs inhibit the nucleation and growth of the hydrate crystals. Such materials may include, for example, Poly(2-alkyl-2-oxazoline) polymers (or poly(N-acylalkylene imine) polymers), poly(2-alkyl-2-oxazoline) copolymers, and others. *See* Urdahl, Olav, et al., "Experimental testing and evaluation of a kinetic gas hydrate inhibitor in different fluid systems," Preprints from the Spring 1997 Meeting of the ACS Division of Fuel Chemistry, 42, 498-502 (American Chemical Society, 1997).

[0007] For example, U.S. Patent No. 6,359,047 discloses a gas hydrate inhibitor. The inhibitor includes, by weight, a copolymer including about 80 to about 95% of polyvinyl caprolactam (VCL) and about 5 to about 20% of N,N-dialkylaminoethyl(meth)acrylate or N-(3-dimethylaminopropyl) methacrylamide. As another example, U.S. Patent No. 5,874,660 discloses a method for inhibiting hydrate formation. The method is used in treating a petroleum fluid stream, such as natural gas conveyed in a pipe, to inhibit the formation of a hydrate restriction in the pipe. The hydrate inhibitor used for practicing the method is selected from the family of substantially water soluble copolymers formed from N-methyl-N-vinylacetamide (VIMA) and one of three comonomers, vinylpyrrolidone (VP), vinylpiperidone (VPip), or vinylcaprolactam (VCap). VIMA/VCap is the preferred copolymer. These copolymers may be used alone or in combination with each other or other hydrate inhibitors. Preferably, a solvent, such as water, brine, alcohol, or mixtures thereof, is used to produce an inhibitor solution or mixture to facilitate treatment of the petroleum fluid stream.

[0008] Another type of low dosage hydrate inhibitor (LDHI) uses surface active agents (surfactants) that may function both as KHIs and as AAs. AAs may prevent the agglomeration, or self-sticking, of small hydrate crystals into larger hydrate crystals or groups

of crystals. For example, U.S. Patent Nos. 5,841,010 and 6,015,929 disclose the use of surface active agents as gas hydrate inhibitors for inhibiting the formation (nucleation, growth and agglomeration) of clathrate hydrates. The methods comprise adding into a mixture comprising hydrate forming substituents and water, an effective amount of a hydrate inhibitor selected from the group consisting of anionic, cationic, non-ionic and zwitterionic hydrate inhibitors. The hydrate inhibitor has a polar head group and a nonpolar tail group not exceeding 12 carbon atoms in the longest carbon chain. The AAs may allow for the formation of a flowable slurry, i.e., hydrates that can be carried by a flowing hydrocarbon without sticking to each other.

[0009] Although smaller dosages of LDHIs are generally used to manage hydrates than for THIs, LDHIs may be expensive. At high water quantities, these inhibitors may be uneconomical. Further, AAs begin to lose their effectiveness at moderate water volumes (greater than about 50 vol. %) because there is not enough liquid hydrocarbon remaining in the system to transport the particles. Further, research studies on system containing water in an oil-external phase indicate that the addition of too low an amount of inhibitor, either THI or KHI, may actually increase the likelihood of plugging. See Hemmingson, P.V., Li, X. and Kinnari, K, "Hydrate Plugging Potential in Underinhibited Systems", Proc. of the 6th ICGH, Vancouver, Canada, July 6-10, 2008. In the Hemmingson system, the aqueous phase was about 20 volume % of the liquids in liquid hydrocarbon. The results showed an increase in the plugging potential for under-inhibited system which was attributed to increased hydrate formation rates.

[0010] Related information may be found in U.S. Patent Nos. 6,957,146; 5,936,040; 5,841,010; and 5,744,665. Further information may be found in: U.S. Patent Application Publication Nos. 2004/0133531, 2006/0092766, 2008/0312478 and 2007/0129256; Sloan, E.D., "Gas Hydrate Tutorial," Preprints from the Spring 1997 Meeting of the ACS Division of Fuel Chemistry, 42(2), 449-56 (American Chemical Society, 1997); and in Talley, L.D. and Edwards, M., "First Low Dosage Hydrate Inhibitor is Field Proven in Deepwater," Pipeline and Gas Journal 44, 226 (1999).

[0011] An alternative to the use of THIs and KHIs is cold flow technology, in which hydrate can be formed in a manner that prevents hydrate particles from sticking to each other without the use of chemical inhibitors. International Patent Application Publication No. WO 2007/095399 discloses a method of generating a non-plugging hydrocarbon slurry. In one

aspect, the method includes seeding a cold-flow reactor before startup operation with dry hydrate particles, creating a dry hydrate sidestream by diverting a portion of wellstream of hydrocarbons into the reactor, wherein the wellstream hydrocarbons contain water, and feeding the dry hydrate sidestream into the main pipeline to be transported to a destination with the full wellstream.

[0012] As another example, International Patent Application Publication No. WO 2007/025062 discloses a method and system for transporting a flow of fluid hydrocarbons containing water. In the method and system, a pump is used to recycle a fluid containing hydrate particles in a line back to a reactor. The pump may advantageously be of a type which crushes the hydrate particles into more and smaller particles.

[0013] Cold flow has been demonstrated to be successful in systems where oil is the external phase in a water-oil system. The external oil phase is important to this process since cold flow depends on the generation of small water droplets that can be converted to hydrate particles. Following hydrate formation sufficient liquid should be present to mobilize the hydrate particles. Therefore, at high water cuts, current cold flow strategies may be inadequate.

[0014] At high water cuts, where the water phase is external, uninhibited hydrate will continue to form until the water or the gas is exhausted, which may lead to plugging. International Patent Application Publication No. WO 2005/058450 discloses a method and system for preventing clathrate hydrate blockage formation in flow lines by adding water. In this method, water is added to a hydrocarbon containing fluid to produce a water cut enhanced hydrocarbon containing fluid. Sufficient water may be added such that the hydrocarbon containing fluid is converted from a water in oil emulsion to a water continuous emulsion. However, at large gas production rates, the amount of water injected may be significant, for example, similar to production rates. This may require the use of large pumps and extra pipelines, as well as the production of large quantities of additional water that would require treating and disposal.

[0015] Hydrate formation is one of the most common flow assurance issues. Hydrates that form in production pipelines can cause blockages that shut-in production. As deepwater production increases, the need to adequately handle hydrates is consequently increasing. Also, as a field matures, it will produce more water. A field may eventually produce primarily water which can limit hydrate remediation strategies and often dictates the end of

profitable field production. Thus, research is continuing to identify techniques for preventing hydrate plugging during hydrocarbon transport.

SUMMARY

5 [0016] An exemplary embodiment of the present techniques provides A method for forming a flowable hydrate slurry in a production fluid that has water as an external phase. The method includes injecting an amount of a thermodynamic hydrate inhibitor (THI) into the production fluid, wherein the amount of the THI added is controlled to allow a formation of a hydrate while retaining the water as the external phase.

10 [0017] The method may also include monitoring a phase behavior of the production fluid after the hydrate forms to determine that the water is the external phase. The amount of the THI injected into the production fluid may be adjusted to select the water as the external phase. An anti-agglomerate agent (AA) may be added to the production fluid. Further, a kinetic hydrate inhibitor (KHI) may be added to the production fluid.

15 [0018] The THI may include glycols, alcohols, salts, or any combinations thereof. The production fluid may be passed through a static mixer after injecting the THI. The amount of the THI injected into the production fluid may be less than about 5 % by wt. in the water phase before the formation of the hydrate.

20 [0019] Another exemplary embodiment provides a system for producing a production fluid in which water is an external phase. The system includes a pipeline configured to carry the production fluid and an injector configured to inject an amount of a THI into the production fluid, wherein the amount of the THI added will allow the formation of the hydrate while retaining the water as the external phase.

25 [0020] The system may include a static mixer in the pipeline downstream of the injector. The system may also include an analyzer to determine a phase behavior of the production fluid. An addition system may be configured to change the amount of the THI added in order to select the water as the external phase. A processing facility may be configured to remove the water and the THI from the production fluid. A processing facility configured to process the hydrocarbon for shipping in a pipeline.

30 [0021] The system may include a hydrocarbon field configured to produce the production fluid. The production fluid may include natural gas. Further, the production fluid may include oil.

[0022] Another exemplary embodiment provides a method for producing a hydrocarbon. The method includes producing a production fluid having water as an external phase, and injecting an amount of a THI into the production fluid, wherein the amount is adjusted to allow hydrate formation to occur while retaining water as the external phase. The method
5 also includes separating out the water and the THI from the production fluid and producing a purified hydrocarbon stream.

[0023] The method may include monitoring a phase behavior of the production fluid after the injection of the THI. Producing the purified hydrocarbon stream may include producing a liquefied natural gas. The THI may be separated from the water and reinjected into a
10 production fluid.

DESCRIPTION OF THE DRAWINGS

[0024] The advantages of the present techniques are better understood by referring to the following detailed description and the attached drawings, in which:

[0025] Fig. 1 is a diagram of a subsea natural gas field that can be protected from hydrate
15 plugging;

[0026] Fig. 2A is a diagram of THI molecules in a production fluid having water as the external phase;

[0027] Fig. 2B is a diagram showing the increase in concentration of the THI molecules as a hydrate forms;

[0028] Fig. 3 is a process flow diagram of a method for producing a production fluid that
20 has water as the external phase;

[0029] Fig. 4 is a graph of calculated equilibrium curves for a hydrate formation at a series of THI levels; and

[0030] Fig. 5 is a graph that shows how the equilibrium temperature changes as a
25 function of the quantity of hydrate formed for the system that is initially under-inhibited with 5 wt. % of THI.

DETAILED DESCRIPTION

[0031] In the following detailed description section, specific embodiments of the present techniques are described. However, to the extent that the following description is specific to

a particular embodiment or a particular use of the present techniques, this is intended to be for exemplary purposes only and simply provides a description of the exemplary embodiments. Accordingly, the techniques are not limited to the specific embodiments described below, but rather, include all alternatives, modifications, and equivalents falling within the true spirit and scope of the appended claims.

[0032] At the outset, for ease of reference, certain terms used in this application and their meanings as used in this context are set forth. To the extent a term used herein is not defined below, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Further, the present techniques are not limited by the usage of the terms shown below, as all equivalents, synonyms, new developments, and terms or techniques that serve the same or a similar purpose are considered to be within the scope of the present claims.

[0033] As used herein, "clathrate" is a weak composite made of a host compound that forms a basic framework and a guest compound that is held in the host framework by inter-molecular interaction, such as hydrogen bonding, Van der Waals forces, and the like. Clathrates may also be called host-guest complexes, inclusion compounds, and adducts. As used herein, "clathrate hydrate" and "hydrate" are interchangeable terms used to indicate a clathrate having a basic framework made from water as the host compound. A hydrate is a crystalline solid which looks like ice, and forms when water molecules form a cage-like structure around a "hydrate-forming constituent."

[0034] A "hydrate-forming constituent" refers to a compound or molecule in petroleum fluids, including natural gas, that forms hydrate at elevated pressures and/or reduced temperatures. Illustrative hydrate-forming constituents include, but are not limited to, hydrocarbons such as methane, ethane, propane, butane, neopentane, ethylene, propylene, isobutylene, cyclopropane, cyclobutane, cyclopentane, cyclohexane, and benzene, among others. Hydrate-forming constituents can also include non-hydrocarbons, such as oxygen, nitrogen, hydrogen sulfide, carbon dioxide, sulfur dioxide, and chlorine, among others.

[0035] "Exemplary" is used exclusively herein to mean "serving as an example, instance, or illustration." Any embodiment described herein as "exemplary" is not to be construed as preferred or advantageous over other embodiments.

[0036] A "facility" as used herein is a representation of a tangible piece of physical equipment through which hydrocarbon fluids are either produced from a reservoir or injected

into a reservoir. In its broadest sense, the term facility is applied to any equipment that may be present along the flow path between a reservoir and the destination for a hydrocarbon product. Facilities may comprise production wells, injection wells, well tubulars, wellhead equipment, gathering lines, manifolds, pumps, compressors, separators, surface flow lines and delivery outlets. In some instances, the term "surface facility" is used to distinguish those facilities other than wells. A "facility network" is the complete collection of facilities that are present in the model, which would include all wells and the surface facilities between the wellheads and the delivery outlets.

[0037] A "formation" is any finite subsurface region. The formation may contain one or more hydrocarbon-containing layers, one or more non-hydrocarbon containing layers, an overburden, and/or an underburden of any subsurface geologic formation. An "overburden" and/or an "underburden" is geological material above or below the formation of interest.

[0038] The term "FSO" refers to a Floating Storage and Offloading vessel. A floating storage device, usually for oil, is commonly used where it is not possible or efficient to lay a pipe-line to the shore. A production platform can transfer hydrocarbons to the FSO where they can be stored until a tanker arrives and connects to the FSO to offload it. A FSO may include a liquefied natural gas (LNG) production platform or any other floating facility designed to process and store a hydrocarbon prior to shipping.

[0039] The term "gas" is used interchangeably with "vapor," and means a substance or mixture of substances in the gaseous state as distinguished from the liquid or solid state. Likewise, the term "liquid" means a substance or mixture of substances in the liquid state as distinguished from the gas or solid state. As used herein, "fluid" is a generic term that may include either a gas or vapor.

[0040] A "hydrocarbon" is an organic compound that primarily includes the elements hydrogen and carbon although nitrogen, sulfur, oxygen, metals, or any number of other elements may be present in small amounts. As used herein, hydrocarbons generally refer to organic materials that are transported by pipeline, such as any form of natural gas or oil. A "hydrocarbon stream" is a stream enriched in hydrocarbons by the removal of other materials such as water and/or THI.

[0041] "Kinetic hydrate inhibitor" refers to a molecule and/or compound or mixture of molecules and/or compounds capable of decreasing the rate of hydrate formation in a petroleum fluid that is either liquid or gas phase. A kinetic hydrate inhibitor can be a solid or

liquid at room temperature and/or operating conditions. The hydrate formation rate can be reduced sufficiently by a kinetic hydrate inhibitor such that no hydrates form during the time fluids are resident in a pipeline at temperatures below the hydrate formation temperature.

[0042] For the inhibition of hydrate formation by thermodynamic or kinetic hydrate inhibitors, the term "minimum effective operating temperature" refers to the temperature above which hydrates do not form in fluids containing hydrate forming constituents during the time the fluids are resident in a pipeline. For thermodynamic inhibition only, the minimum effective operating temperature is equal to the thermodynamically inhibited hydrate formation temperature. For kinetic hydrate inhibitors, the minimum effective operating temperature is lower than the thermodynamically inhibited hydrate formation temperature. For a combination of thermodynamic and kinetic inhibition, the minimum effective operating temperature may be even lower than the thermodynamically inhibited hydrate formation temperature by itself.

[0043] "Liquefied natural gas" or "LNG" is natural gas that has been processed to remove impurities (for example, nitrogen, water and/or heavy hydrocarbons) and then condensed into a liquid at almost atmospheric pressure by cooling and depressurization.

[0044] The term "natural gas" refers to a multi-component gas obtained from a crude oil well (termed associated gas) or from a subterranean gas-bearing formation (termed non-associated gas). The composition and pressure of natural gas can vary significantly. A typical natural gas stream contains methane (CH_4) as a significant component. Raw natural gas will also typically contain ethylene (C_2H_4), ethane (C_2H_6), other hydrocarbons, one or more acid gases (such as carbon dioxide, hydrogen sulfide, carbonyl sulfide, carbon disulfide, and mercaptans), and minor amounts of contaminants such as water, nitrogen, iron sulfide, wax, and crude oil.

[0045] "Pressure" is the force exerted per unit area by the gas on the walls of the volume. Pressure can be shown as pounds per square inch (psi). "Atmospheric pressure" refers to the local pressure of the air. "Absolute pressure" (psia) refers to the sum of the atmospheric pressure (14.7 psia at standard conditions) plus the gage pressure (psig). "Gauge pressure" (psig) refers to the pressure measured by a gauge, which indicates only the pressure exceeding the local atmospheric pressure (i.e., a gauge pressure of 0 psig corresponds to an absolute pressure of 14.7 psia).

[0046] "Production fluid" refers to a liquid and/or gaseous stream removed from a subsurface formation, such as an organic-rich rock formation. Produced fluids may include both hydrocarbon fluids and non-hydrocarbon fluids. For example, production fluids may include, but are not limited to, oil, natural gas and water.

5 [0047] "Substantial" when used in reference to a quantity or amount of a material, or a specific characteristic thereof, refers to an amount that is sufficient to provide an effect that the material or characteristic was intended to provide. The exact degree of deviation allowable may in some cases depend on the specific context.

[0048] "Thermodynamic hydrate inhibitor" refers to compounds or mixtures capable of
10 reducing the hydrate formation temperature in a petroleum fluid that is either liquid or gas phase. For example, the minimum effective operating temperature of a petroleum fluid can be reduced by at least 1.5 °C, 3 °C, 6 °C, 12 °C, or 25 °C, due to the addition of one or more thermodynamic hydrate inhibitors. Generally the THI is added to a system in an amount sufficient to prevent the formation of any hydrate.

15 [0049] "Well" or "wellbore" refers to a hole in the subsurface made by drilling or insertion of a conduit into the subsurface. The terms are interchangeable when referring to an opening in the formation. A well may have a substantially circular cross section, or other cross-sectional shapes (for example, circles, ovals, squares, rectangles, triangles, slits, or other regular or irregular shapes). Wells may be cased, cased and cemented, or open-hole
20 well, and may be any type, including, but not limited to a producing well, an experimental well, an exploratory well, or the like. A well may be vertical, horizontal, or any angle between vertical and horizontal (a deviated well), for example a vertical well may comprise a non-vertical component.

Hydrate Inhibition in a Production System by Limited THI addition

25 [0050] As previously noted, the formation of hydrates can be a problem in the harvesting and transportation of hydrocarbons. For example, production fluids harvested from a formation may contain a substantial amount of water, which may increase over time as the hydrocarbons in the formation are produced. A production fluid containing a high amount of water may be termed a high water cut, and may have water as the continuous, or external,
30 phase, with hydrocarbons forming droplets or bubbles in the water phase. The production fluid from the formation may be at a sufficiently high temperature that hydrate formation is

not favored, but cooling of the production fluid during production or shipping may allow formation of hydrates and plugging of lines.

[0051] An exemplary embodiment of the present techniques provides a method for generating a flowable hydrate slurry in a water external mixture of water and hydrocarbon, such as at a high water cut. This can be performed by controlling the hydrate concentration through a limited addition of thermodynamic hydrate inhibitor (THI). During formation, the hydrate incorporates a host molecule, such as a hydrocarbon or other molecule, but may exclude impurities that may be dissolved in the water. As the THI is an impurity in the water with respect to the hydrate, formation of the hydrate increases the concentration of the THI in the remaining water. When the concentration of the THI in the water reaches a sufficient quantity, further hydrate formation will be inhibited. In a water external system, this may result in the formation of a flowable slurry of hydrates in water, carrying the hydrocarbon droplets to the destination.

[0052] Fig. 1 is an illustration of a subsea natural gas field 100 that can be protected from hydrate plugging. However, the present techniques are not limited to subsea fields or natural gas harvesting, but may be used for the mitigation of plugging in the production or transportation of oil, oil from oil sands, natural gas, or any number of liquid or gaseous hydrocarbons from any number of sources.

[0053] As shown in Fig. 1, the natural gas field 100 can have a number of wellheads 102 coupled to wells 104 that harvest natural gas from a formation (not shown). As shown in this example, the wellheads 102 may be located on the ocean floor 106. Each of the wells 104 may include single wellbores or multiple, branch wellbores. Each of the wellheads 102 can be can be coupled to a central pipeline 108 by gathering lines 110. The central pipeline 108 may continue through the field 100, coupling to further wellheads 102, as indicated by reference number 112. A flexible line 114 may couple the central pipeline 108 to a collection platform 116 at the ocean surface 118. The collection platform 116 may, for example, be a floating processing station, such as a floating storage and offloading unit (or FSO), that is anchored to the sea floor 106 by a number of tethers 120. The collection platform 116 may have equipment for dehydration, purification, and other processing, such as liquefaction equipment to form liquefied natural gas (LNG) for storage in vessels 122. The collection vessel 116 may transport the processed gas to shore facilities by pipeline (not shown).

[0054] Prior to processing of the natural gas on the collection platform 116, the collected gas may cool and form hydrates in various locations, such as the collection pipeline 108, the gathering lines 110, or the flexible line 114, among others. The formation of the hydrates may lead to partial or even complete plugging of the lines 108, 110, and 114. Similarly, in on-shore fields, hydrates can plug wells, gathering lines, and collection lines. A THI may be added to mitigate the formation of hydrates, for example, from the collection vessel 116 by a line 124 to one or more injection points, such as at injector 126. Although the line 124 is shown as being independent of the flexible line 114, the line 124 may be incorporated along with the flexible line 114 and any other utility or sensor lines into a single piping bundle. In various embodiments, the injector 126 may be located on the collection pipeline 108, the gathering lines 110, the flexible line 114, or on any combinations thereof.

[0055] In an exemplary embodiment, the THI is injected into the collection line 108 in an amount that is less than required to completely inhibit the formation of hydrates. For example, although the amount needed to fully inhibit hydrate formation may be 10 %, 20 %, 30 %, 50 %, or higher, by weight of the water phase in the production fluid, depending on the water cut, the amount of THI injected in embodiments may be only 15 %, 10 %, 5 %, or lower, by weight of the water phase in the production fluid. As discussed below, the formation of hydrates concentrates the THI, which remains in the water phase.

[0056] The amount of THI to be used may be determined by analyzing or monitoring the water content of the production fluid. The amount may be controlled so that the production fluid is still in a water external condition at the point where the THI is concentrated enough to inhibit further formation of hydrates. One or more static mixers 128 can be placed in the lines, for example, in the collection line 108 downstream of the entry points 130 for each of the gathering lines 110. The placement of the static mixers 128 is not limited to the collection line 108, as static mixers 128 may be placed in the flexible line 114, the gathering lines 110, the wellheads 102, or even down the wells 104. Placing a THI line 124 and an injector 126 down a well, for example, upstream of a static mixer 128, may be useful for mitigating hydrate formation in wellbores.

[0057] The phase behavior of the production fluid brought up the flexible line 114 from the connection pipe 108 may be monitored, for example, by an analyzer 132 located at the collection vessel 116 or at any number of other points in the natural gas field 100. The analyzer 132 may determine the concentration of the hydrate, the concentration of the

external phase in the production fluid, the amount of hydrocarbon present, or any combinations of these parameters. For example, a particle size analyzer may be included to analyze the different refracting items in the production fluid, such as the hydrate particles and the hydrocarbon droplets. The output from the analyzer 132 may be used to control an addition system 134, which may be used to adjust the amount of THI, as well as other additives, sent to the injector 126. In an exemplary embodiment, the configuration discussed above may be used to control the phase behavior by controlling the amount of THI injected in order to select the water as the external phase. The arrangement of the facility network is not limited to that shown in Fig. 1, as any number of configurations may be used.

10 *Hydrate Formation Concentrating a Thermodynamic Hydrate Inhibitor*

[0058] Fig. 2A is an illustration 200 of THI molecules 202 in a production fluid having water as the external phase. In the illustration 200, the THI molecules 202, such as methanol, are dissolved in a water phase 204. A hydrocarbon phase 206 can be carried as droplets or bubbles in the water phase 204.

15 [0059] Fig. 2B is an illustration 208 showing the increase in concentration of the THI molecules 202 as a hydrate forms. The THI molecules 202 may be excluded from the hydrate particle 210 as it forms, and, thus, the THI molecules 202 may consequently be concentrated in the water phase 204. As the concentration of the THI molecules 202 increases, the hydrate subcooling may be decreased, eventually preventing additional growth or formation of hydrate particles 210. As nucleation time can be inversely correlated with subcooling, the residence time prior to hydrate nucleation will also be increased. Accordingly, the THI may also be performing as a weak KHI.

25 [0060] Under certain concentration conditions, such as in an external water phase 204, the hydrate particles 210 may be flowable, since capillary attractive forces between hydrate particles 210 may not be present in a dispersion in the water phase 204. Flowloop tests have indicated that rapid hydrate formation without sufficient shear may cause increased potential for blockages, possibly due to the formation of water bridges between hydrate particles 210. The water bridges may be converted to hydrate, which can cementing the bridged hydrate particles 210 together. In an external water phase 204, these water bridges may not occur.

30 [0061] However, the hydrocarbon phase 206 is also concentrated by the formation of hydrate particles 210 in the water phase 204. In an exemplary embodiment of the present techniques, the phase behavior of the system is monitored and controlled to keep an external

water phase 204, as a phase inversion to an oil external phase may lead to formation of hydrate agglomerates and the plugging of lines.

[0062] In an exemplary embodiment, the use of limited thermodynamic inhibitors can be combined with limited amounts of anti-agglomerate (AA) to aid in keeping the hydrate particles 210 separated. Smaller quantities of each class of inhibitor may be needed as a result of the concentration by the formation of the hydrate particles 210.

[0063] Fig. 3 is a flow chart of a method 300 for producing a production fluid that has water as an external phase. The method 300 begins at block 302 with the production of a production fluid having water as the external phase. Such a stream may result late in the life of a hydrocarbon field, when high water cuts (such as 20 %, 40 %, 50 %, 60 %, 80 %, or more, by weight of the production fluid) may be produced. Depending on the chemical composition of the hydrocarbon, a water external phase may result even at relatively low water concentrations, such as at 20 % by weight of the production fluid or even lower. At block 304, a thermodynamic hydrate inhibitor can be injected into the production fluid. As discussed above, the amount of THI injected may be determined by an analysis of the water and hydrocarbon amounts in the production fluid, so that water remains as the external phase. For example, the amount injected may be about 5 %, 10 %, 15 %, or more, by weight of the water phase in the production fluid.

[0064] At block 306, the concentration of the phases and hydrate particles in the production fluid may be monitored by an analyzer. At block 308, the amount of THI added to the stream can be adjusted based on the results from the analysis. This control may be used, for example, to prevent phase inversion of the system into an oil external phase, which may result in plugging of the lines. At block 310, the water, which generally includes the hydrophilic THI is separated from the hydrocarbon, and any further processing of the hydrocarbon is performed, such as the purification, cooling, and condensation used to produce LNG.

Example of Concentration of THI Limiting Further Hydrate Formation

[0065] Fig. 4 is a graph 400 of calculated equilibrium curves for a hydrate formation at a series of THI levels. The x-axis 402 represents the temperature of the composition in degrees Fahrenheit, while the y-axis 404 represents the pressure of the system in psia. The calculations were performed for a gas with composition of 90% CH₄, 5% C₂H₆, 4% C₃H₈,

and 1% n-C₄H₁₀, which is in a hydrate stable region 406 at about 900 psia and about 50 °F (assuming less than about 16 % methanol), as indicated at point 408. In the graph 400, the gas is assumed to be in contact with any amount of water containing the weight percentage amount of methanol shown.

[0066] Equilibrium curves for four different concentrations of the THI, methanol, are shown in the graph 400: 0 wt. % 410 in the water phase, 10 wt. % 412 in the water phase, 20 wt. % 414 in the water phase, and 30 wt. % 416 in the water phase. As can be seen from these curves, thermodynamic inhibition of the formation of hydrate at point 408 would require a concentration of methanol greater than about 16 wt % in the water phase. As the concentration of thermodynamic inhibitor in water increases, the hydrate subcooling is more significant such as is shown in Fig. 5 for a gas composition of 90% CH₄, 5% C₂H₆, 4% C₃H₈, and 1% n-C₄H₁₀.

[0067] Fig. 5 is a graph 500 that shows how the equilibrium temperature changes as a function of the quantity of hydrate formed for the system that is initially under-inhibited with 5 wt. % THI. In the graph 500, the x-axis 502 represents the fraction of hydrate formed. The first y-axis 504 shows the hydrate equilibrium temperature, i.e., the temperature below which the formation of hydrate is favored. The second y-axis 506 shows the amount of subcooling in the system, i.e., the difference between the hydrate equilibrium temperature 504 and the ambient temperature 508. The third y-axis 510 shows the methanol concentration in the water phase as hydrate is formed.

[0068] As shown in the graph 500, the hydrate subcooling temperature 512 (read on the second y-axis 506) decreases as hydrate is formed. This is caused by the concurrent increase in the methanol concentration 514 (read on the third y-axis 510) in the water phase as the hydrate forms. As discussed previously, the increase in concentration is caused by the exclusion of methanol from the hydrate particles. When the hydrate fraction reaches 11 wt. %, as indicated at reference number 516, the hydrate subcooling temperature 512 reaches zero, and no additional hydrate is formed. As indicated by dotted line 518, this is the point at which the inhibitor concentration in the water phase reaches 16 wt. %, which inhibits further hydrate formation.

[0069] While the present techniques may be susceptible to various modifications and alternative forms, the exemplary embodiments discussed above have been shown only by way of example. However, it should again be understood that the techniques are not intended

to be limited to the particular embodiments disclosed herein. Indeed, the present techniques include all alternatives, modifications, and equivalents falling within the true spirit and scope of the appended claims.

CLAIMS

What is claimed is:

1. A method for forming a flowable hydrate slurry in a production fluid that has
5 water as an external phase, comprising:
injecting an amount of a thermodynamic hydrate inhibitor (THI) into the production
fluid, wherein the amount of the THI added is controlled to allow formation of
a hydrate while retaining the water as the external phase.
- 10 2. The method of claim 1, further comprising monitoring a phase behavior of the
production fluid after the hydrate forms to determine that the water is the external phase.
3. The method of claim 2, further comprising adjusting the amount of the THI
injected into the production fluid to select the water as the external phase.
15
4. The method of claim 1, further comprising adding an anti-agglomerate agent
(AA) to the production fluid.
5. The method of claim 1, further comprising adding a kinetic hydrate inhibitor
20 to the production fluid.
6. The method of claim 1, wherein the THI comprises glycols, alcohols, salts, or
any combinations thereof.
- 25 7. The method of claim 1, further comprising passing the production fluid
through a static mixer after injecting the THI.
8. The method of claim 1, wherein the amount of the THI injected into the
production fluid is less than about 5 % by wt. in the water phase before the formation of the
30 hydrate.
9. A system for producing a production fluid in which water is an external phase,
comprising:

a pipeline configured to carry the production fluid; and
an injector configured to inject an amount of a thermodynamic hydrate inhibitor (THI)
into the production fluid, wherein the amount of the THI added will allow
formation of a hydrate while retaining the water as the external phase.

5

10. The system of claim 9, further comprising a static mixer in the pipeline
downstream of the injector.

11. The system of claim 9, further comprising an analyzer to determine a phase
10 behavior of the production fluid.

12. The system of claim 11, further comprising an addition system configured to
change the amount of the THI added in order to select the water as the external phase.

13. The system of claim 9, comprising a processing facility configured to remove
15 the water and the THI from the production fluid.

14. The system of claim 9, comprising a processing facility configured to process
the hydrocarbon for shipping in a pipeline.

20

15. The system of claim 9, comprising a hydrocarbon field configured to produce
the production fluid.

16. The system of claim 15, wherein the production fluid comprises a natural gas.

25

17. The system of claim 15, wherein the production fluid comprises an oil.

18. A method for producing a hydrocarbon, comprising:

producing a production fluid having water as an external phase;

30 injecting an amount of a thermodynamic hydrate inhibitor (THI) into the production
fluid, wherein the amount is adjusted to allow hydrate formation to occur
while retaining water as the external phase;

separating out the water and the THI from the production fluid; and

producing a purified hydrocarbon stream.

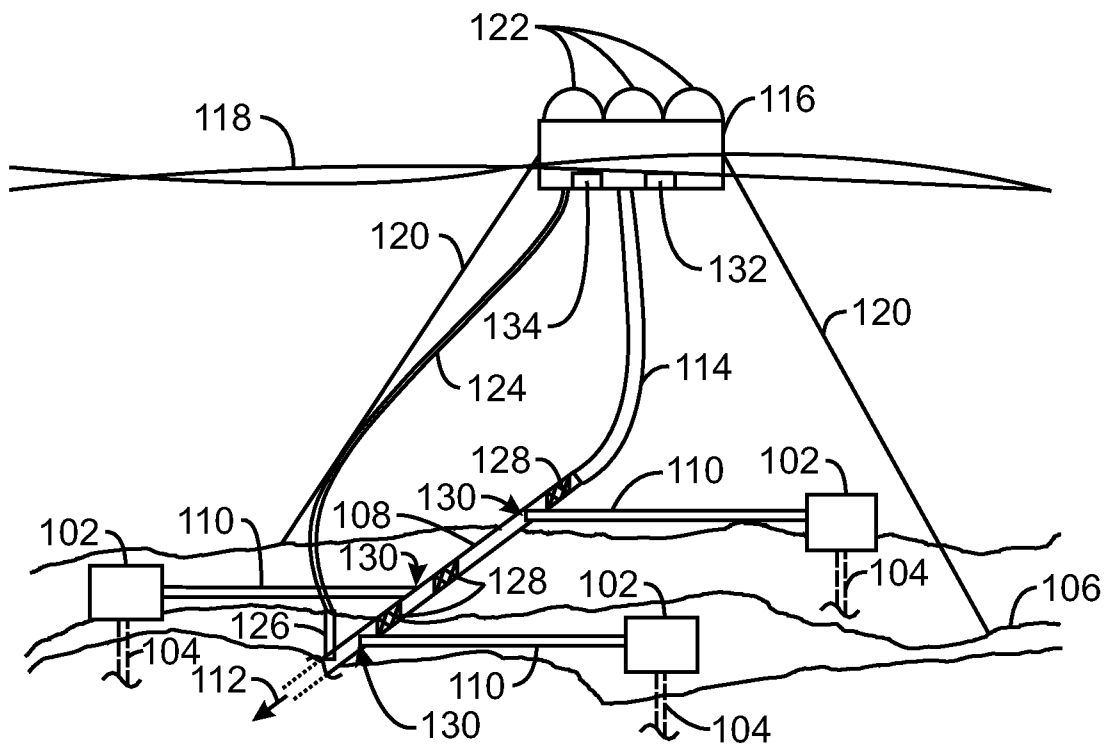
19. The method of claim 18, further comprising monitoring a phase behavior of the production fluid after the injection of the THI.

5

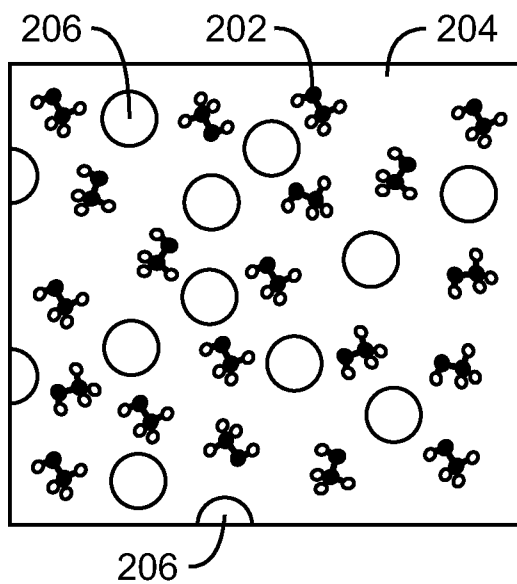
20. The method of claim 18, wherein producing the purified hydrocarbon stream comprises producing a liquefied natural gas.

21. The method of claim 18, further comprising separating the THI from the water
10 and reinjecting the THI into the production fluid.

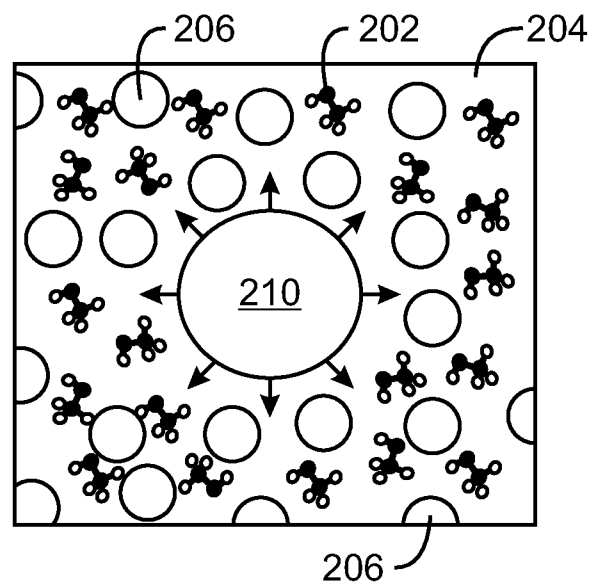
1/4



100
FIG. 1

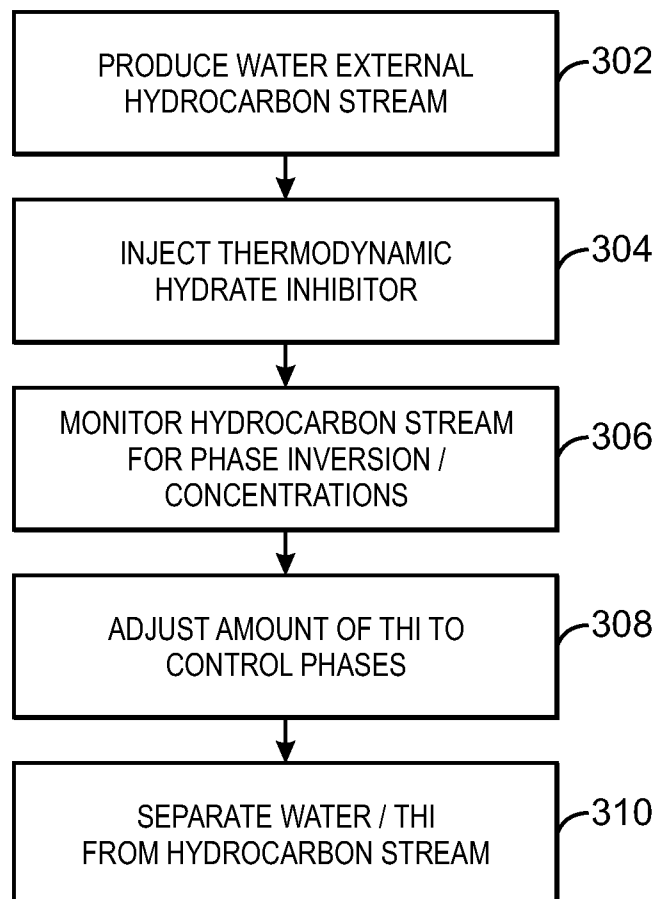


200
FIG. 2A



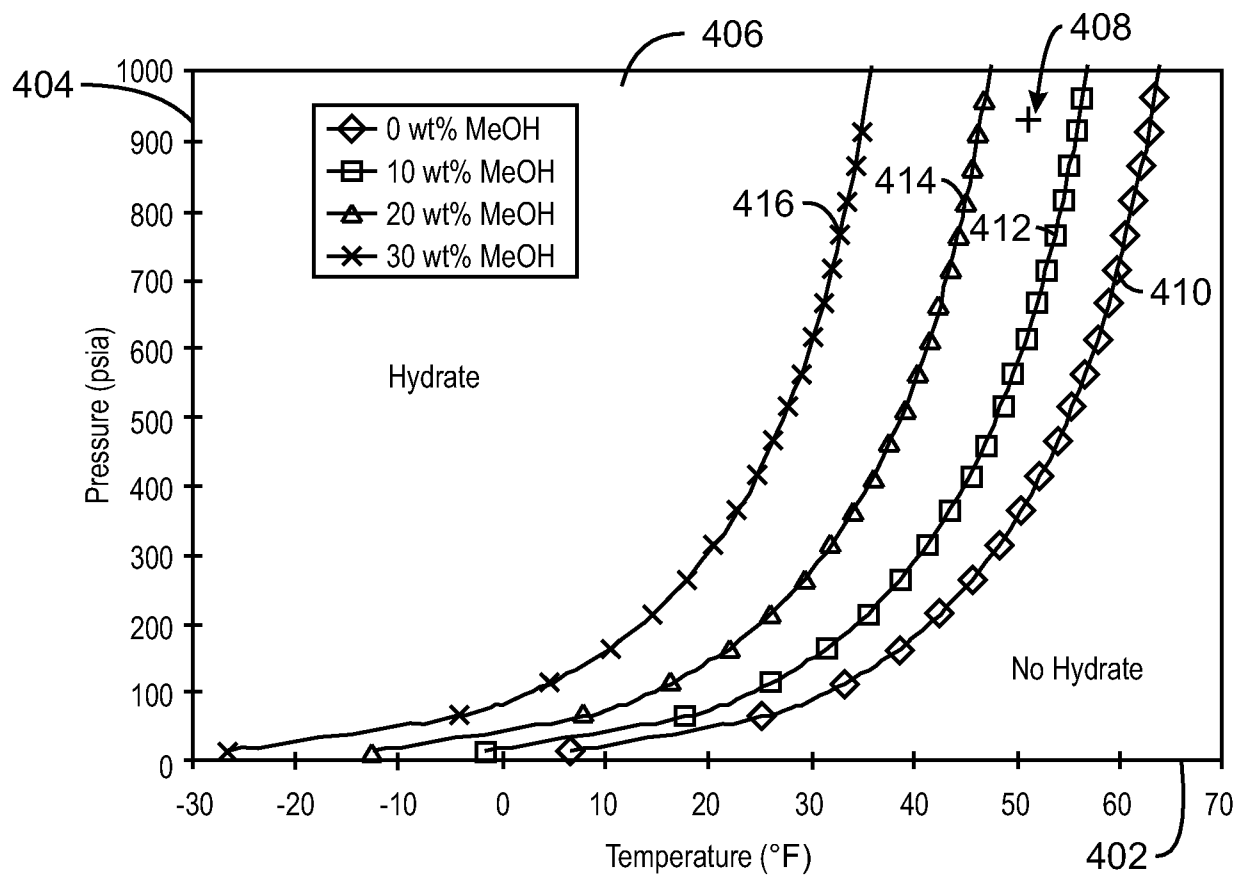
208
FIG. 2B

2/4



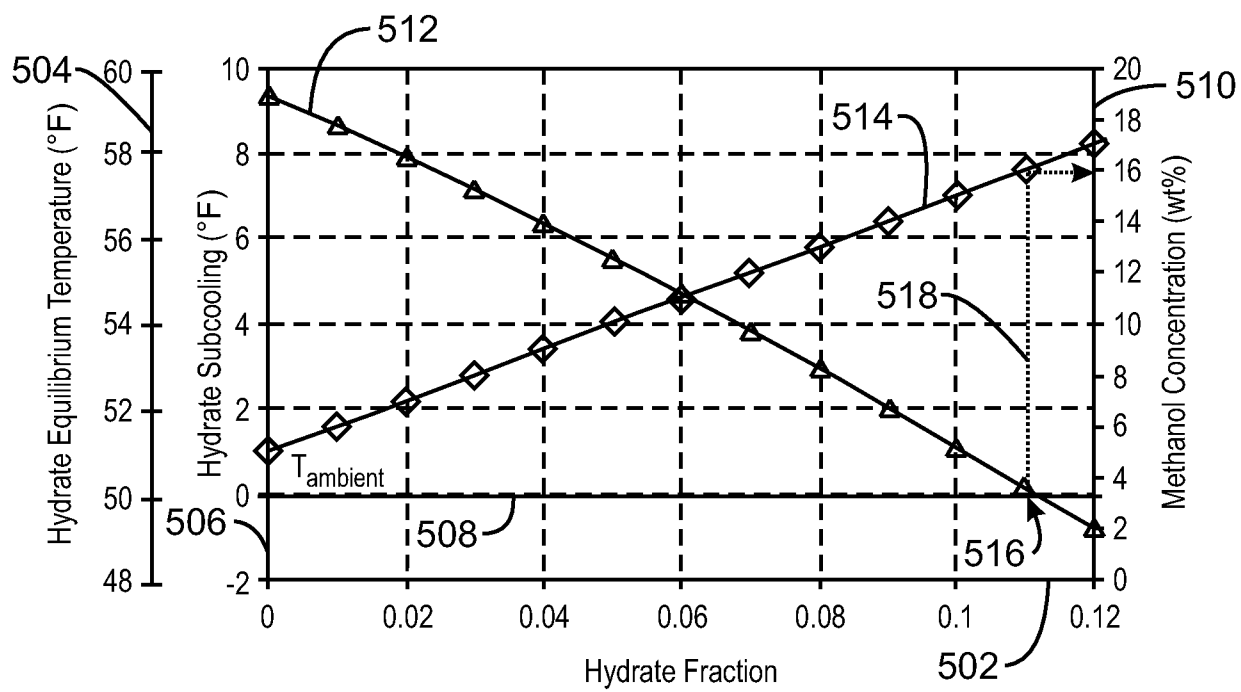
300
FIG. 3

3/4



400
FIG. 4

4/4



500
FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 11/20383

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - E21B 43/25 (2011.01)

USPC - 507/90

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)

IPC(8) - E21B 43/25 (2011.01)

USPC - 507/90

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
E21B 43/28; C09K 8/52; 137/13,1; 166/310; E21B\$; C09K\$; 137/\$; 166/\$; 507/\$ and (text search - see terms below)Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST(USPT,PGPB,USOCT, EPAB,JPAB); Google Patent and Google Scholar. Search terms: hydrate, clartrate, slurry, solid, suspension, mixture, external, water, aqueous, aqua, moisture, external, continuous, carrier, phase, thermodynamic, inhibitor, thi, methanol, salt, glycol, kinetic, limit, control, adjust, maintain, limit, monitor, measure, determ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009/0124520 A1 to (Tohidi) 14 May 2009 (14.05.2009) Entire document, especially para [0003], [0006], [0012], [0014], [0019]-[0022], [0035], [0048], [0073] [0089].	1-21
Y	US 2005/0137432 A1 (Matthews et al.) 23 June 2005 (23.06.2005) Entire document, especially [0003], [0007], [0033], [0034] and [0043]	1-21
Y	US 5,741,758 A (Pakulski) 21 April 1998 (21.04.1998) Entire document, especially col 4, ln 58-63	7 and 10

☐ Further documents are listed in the continuation of Box C.

* 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

17 February 2011 (07.02.2011)

Date of mailing of the international search report

08 MAR 2011

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774