(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 November 2017 (23.11.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/201016 A1

(51) International Patent Classification:
B01D 17/04 (2006.01) ***B01D 17/05*** (2006.01)
B01D 17/00 (2006.01) ***C10G 33/00*** (2006.01)
B01D 17/02 (2006.01)

(21) International Application Number:
PCT/US2017/032858

(22) International Filing Date:
16 May 2017 (16.05.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/337,431 17 May 2016 (17.05.2016) US

(71) Applicant: NANO GAS TECHNOLOGIES, INC. [US/US]; 655 Deerfield Rd, Suite 100-140, Deerfield, IL 60015 (US).

(72) Inventors: FOLDS, Rudy, M.; 655 Deerfield Rd, Suite 100-140, Deerfield, IL 60015 (US). **FIEDLER, Scott, A.**; 655 Deerfield Rd, Suite 100-140, Deerfield, IL 60015 (US). **HARDIN, Jeffrey, K.**; 655 Deerfield Rd, Suite 100-140, Deerfield, IL 60015 (US).

(74) Agent: GOODMAN, Jonathan; Synthesis Intellectual Property, LLC, 1740 Ridge Ave., Suite 300, Evanston, IL 60201 (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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, 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).

Declarations under Rule 4.17:

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

— *of inventorship (Rule 4.17(iv))*

Published:

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

WO 2017/201016 A1

(54) Title: METHODS OF AFFECTING SEPARATION

(57) Abstract: Herein is provided processes for affecting the separation of oil from emulsions by the addition of nanogas solutions. For example, the nanogas solutions can be used to affect the viscosity and/or density of oil droplets in oil-in-water emulsions, break the oil-in-water emulsion; and form an oil phase floating on a water phase. In another example, the nanogas solutions can be used in conjunction with a floatation tank to separate oil from, for example, produced water. In other examples selection of the gasses in the nanogas solution can be used to affect reactions and/or separation.

METHODS OF AFFECTING SEPARATION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This disclosure claims the benefit of priority to US Appl. No. 62/337,431, filed 17 May, 2016, the disclosure of which is incorporated herein in its entirety.

FIELD OF THE INVENTION

[0002] This disclosure is directed to methods of affecting the viscosities of oils for the separation of these oils from emulsions.

BACKGROUND

[0003] Subsurface geological operations such as mineral mining, oil well drilling, natural gas exploration, and induced hydraulic fracturing generate wastewater contaminated with significant concentrations of impurities. These impurities vary widely in both type and amount depending on the type of geological operation, the nature of the subsurface environment, and the type and amount of soluble minerals present in the native water source. The contaminated water is eventually discharged into surface waters or sub-surface aquifers. In some cases, wastewater generated from drilling and mining operations have resulted in making regional water supplies unusable. Induced hydraulic fracturing in particular is a highly water-intensive process, employing water pumped at pressures exceeding 3,000 psi and flow rates exceeding 85 gallons per minute to create fractures in subsurface rock layers. These created fractures intersect with natural fractures, thereby creating a network of flow channels to a well bore. These flow channels allow the release of petroleum and natural gas products for extraction. The flow channels also allow the injected water plus additional native water to flow to the surface along with the fuel products once the fractures are created.

[0004] Flowback water, and produced water, from subsurface geological operations contains a variety of contaminants. Often, produced water is “hard” or brackish and further includes dissolved or dispersed organic and inorganic materials. Produced water can include chemicals used in the mining operation, such as hydrocarbons that are injected along with water to facilitate fracture formation in hydrofracturing. One common type of contaminant present in produced water from hydrofracturing is a mixture of free and emulsified oil together with gel-like accumulations of hydrocarbons. In most cases, this oily mixture further contains silt, sand,

and/or clay particulates gathered by the produced water as it travels to the surface. These oily mixtures are neutrally buoyant—that is, they neither sink nor float, or they require extended times to sink or float—in produced water. While in some cases these oily mixtures are visible as agglomerated, black, and tarry-looking residues, in other cases the oily mixtures, or some portion thereof, are finely divided dispersed liquids or liquid/solid droplets or particles present throughout the water phase.

[0005] Conventional oil separation processes relying on density differences are incapable of effectively separating this oily mixture from produced water. Conventional filtering methods employ screen or filter media that are quickly clogged by the oily mixture. Gravity separation is not only slow but also requires the use of large tanks and low flow rates in order to provide the long residence times needed to achieve an effective separation. Even with very long residence times, very well dispersed, fine oily mixture droplets are sometimes inseparable from the water phase. Methods such as evaporation of water from the mixture are not only time intensive, but highly energy intensive as well, and impractical for mining operations where large volumes of produced water are generated in short periods of time. Thus, current processes for removing such material suffer many drawbacks.

[0006] Further remediation of produced water is only possible once this oily mixture is removed. Therefore, there is a need for a process for effectively removing neutrally buoyant materials from water. For example, in the mining industry, there is a need for a process to effectively remove an oily mixture from produced water in an efficient manner to result in produced water that is substantially free of emulsified petroleum, sand, silt, clay, and gel-like hydrocarbons. There is a need to remove neutrally buoyant materials other than such oily mixtures from water. There is a need for these processes to operate without undue energy expenditure. There is a need for these processes to operate at a rate that is commensurate with water-intensive applications such as hydrofracturing.

SUMMARY

[0007] One embodiment is a process that includes admixing a nanogas solution and an oil-in-water emulsion; breaking the oil-in-water emulsion; and forming an oil phase floating on a water phase; wherein the nanogas solution is a homogeneous mixture of nanobubbles and water.

[0008] Another embodiment is a process that includes providing a floatation tank having an inlet end and an outlet end; the floatation tank including an oil-in-water emulsion inlet and a first nanogas inlet proximal to the inlet end, and having an underflow baffle proximal to the outlet end; providing an oil-in-water emulsion to the floatation tank via the oil-in-water emulsion inlet; providing a nanogas solution to the floatation tank via the first nanogas inlet thereby admixing the nanogas solution with the oil-in-water emulsion; breaking the oil-in-water emulsion and forming an oil phase floating on a water phase; separating the water phase from the oil phase by carrying the water phase under the underflow baffle.

[0009] Still Another embodiment is a process that includes admixing a nanogas solution an oil sand tailings; breaking the oil sands tailings into an oil phase, a water phase, and a solids phase; and separating the phases.

[0010] Yet another embodiment is a process that includes shearing a first nanogas solution into an oil-in-water micro emulsion; breaking the oil-in-water micro emulsion and forming a water-in-oil macro emulsion, a water phase, and a solids phase, where the water-in-oil macro emulsion is carried on the water phase; and collecting oil from the water-in-oil macro emulsion; wherein the nanogas solution consists essentially of a homogeneous mixture of nanobubbles and water.

[0011] Yet still another embodiment is a process that includes providing a floatation tank having an inlet end and an outlet end; the floatation tank including an oil-in-water emulsion inlet and a first nanogas inlet, both, proximal to the inlet end, and having an underflow baffle proximal to the outlet end; providing an oil-in-water emulsion to the floatation tank via the oil-in-water emulsion inlet; providing a nanogas solution to the floatation tank via the first nanogas inlet thereby admixing the nanogas solution with the oil-in-water emulsion without the formation of macrobubbles; breaking the oil-in-water emulsion and forming an oil phase floating on a water phase; and separating the water phase from the oil phase by carrying the water phase under the underflow baffle.

[0012] Still yet another embodiment is a method that includes admixing a nanogas solution with oil sands tailings; and separating materials including silts, residual bitumen, and organic compounds from water in the oil sands tailings; wherein the nanogas solution is a nitrogen-nanogas solution or an ON-nanogas solution.

[0013] Another embodiment is a method that includes admixing an oxygen-nanogas solution or an ON-nanogas solution with an aqueous solution that includes hydrogen sulfide; and oxidizing the hydrogen sulfide.

[0014] Yet another embodiment is a method that includes admixing an oxygen-nanogas solution or an ON-nanogas solution with a slurry of iron sulfide and water; and oxidizing the iron sulfide to iron oxide.

BRIEF DESCRIPTION OF THE FIGURES

[0015] For a more complete understanding of the disclosure, reference should be made to the following detailed description and accompanying drawing figures wherein:

[0016] Figure 1 is a process diagram of a process described herein; and

[0017] Figure 2 is a cross section of a separation tank showing the inflow and outflow of agents.

[0018] While specific embodiments are illustrated in the figures, with the understanding that the disclosure is intended to be illustrative, these embodiments are not intended to limit the invention described and illustrated herein.

DETAILED DESCRIPTION

[0019] A first embodiment is a process of breaking an oil-in-water emulsion. As used throughout, emulsions are oil-in-water emulsions. The process can include admixing a nanogas solution and an emulsion; breaking the emulsion; and forming an oil phase floating on a water phase. Preferably, the emulsion can be flow back water, produced water, or oil sands tailing water. In other examples, the emulsion can be mayonnaise, butter, or a palm oil-in-water emulsion.

[0020] Notably, the nanogas solution is a homogeneous mixture of nanobubbles and water. As used herein, the term “nanobubbles” means bubbles of a gas within a liquid, wherein the bubbles having an average diameter of about 10 nm to 100 nm; preferably, wherein there are no bubble having a diameter of greater than about 500 nm, about 400 nm, about 300 nm, about 250 nm, or about 200 nm, more preferably, there are no microbubbles. The herein utilized nanobubbles can be formed in or by a nanogas solution generator, one example of which is provided in US 9,586,176 which is incorporated herein in its entirety. Additional means for forming the herein utilized nanobubbles include those machines and methods described in 8,500,104.

[0021] The nanogas solution is preferably homogeneous, that is, the nanobubbles are evenly distributed throughout the solution and appear as a suspended “particulate” in the liquid. Notably, the liquid may further be saturated with or near saturation with the gas that comprises the nanobubbles. A mixture of bubbles and liquid wherein the bubbles coalesce and/or rise to the surface and break is not a homogeneous mixture of nanobubbles and the liquid.

[0022] The homogeneous mixture can include nanobubbles that include, consist essentially of, or consist of oxygen (O_2), nitrogen (N_2), carbon dioxide (CO_2), or a mixture thereof; and can include a liquid that is water, for example, distilled water, di-water, ground water, municipal water, collected water, or recycled water. As used herein, the terms oxygen and nitrogen refer to the gasses O_2 and N_2 whether or not the term oxygen gas or nitrogen gas is used.

[0023] In one instance, the homogeneous mixture includes collected water; as used herein collected water means the water that has been used in the oil industry for the hydraulic fracturing of subterranean formations, well stimulation or treatment, specifically water that has been collected from a subterranean use. In another instance, the homogeneous mixture includes recycled water, as used herein recycled water means the water has been passed through the herein disclosed process of breaking an emulsion. Fig 1 shows a schematic of a general process of breaking the emulsion. Notably, the dashed lines denote the optional use of the water separated from the emulsion as the feed water or generator water for the nanogas solution (feeding into a nanogas solution generator).

[0024] In yet another instance the homogeneous mixture (i.e., the nanogas solution) includes oxygen, nitrogen, carbon dioxide, or a mixture thereof. In one example, the nanogas solution is a nitrogen-nanogas solution wherein the solution includes, consists essentially of, or consists of nitrogen (N_2) and the water. Herein, the term consists essentially of refers to the inclusion of salts, gases, or solutes that may occur in the water (liquid) but have no effect on the performance of the nanogas solution in the herein disclosed processes. Notably, unless rigorously cleaned and degassed, water will always include some concentration of contaminants (solutes and gases). Furthermore, the term consisting essentially of includes the use of recycled water for the formation of the nanogas solution; in this instance, the solution will consist of the gas, water (H_2O), and minor concentrations of compounds found in the emulsion from which the recycled water was obtained. Herewith, the nanogas solution preferably consists essentially of the gas and water, wherein the contaminants in the water do not affect the performance of the solution. In another example, the nanogas solution is an oxygen-nanogas solution wherein the solution includes, consists essentially of, or consists of oxygen and water. In still another example, the nanogas solution is a ON-nanogas solution wherein the solution includes, consists essentially of, or consists of oxygen, nitrogen, and water. Herein, an ON-nanogas includes molar ratios of oxygen to nitrogen of 99:1 to 1:99, for example 99:1, 90:1, 80:1, 70:1, 60:1, 50:1, 40:1, 30:1, 20:1, 10:1, 1:1, 1:10, 1:20, 1:30, 1:40, 1:50, 1:60, 1:70, 1:80, 1:90, and 1:99. Preferred molar ratios include about 18:82, 21:79, 28:72, 30:70, 32:68, 35:65, 40:60, 42:58, and 50:50. Other particularly relevant molar ratios can be selected from 50:50; 60:40; 70:30; and 80:20. In yet still another example, the nanogas solution includes carbon dioxide wherein the solution includes, consists essentially of, or consists of carbon dioxide and water, more preferably a mixture of carbon dioxide, nitrogen, and water.

[0025] In one example, the process includes admixing a nitrogen-nanogas solution with the emulsion. Preferably, the process includes breaking the emulsion and forming (and separating) a water phase and a nitrogen-oil phase. Herein, the term nitrogen-oil phase is a designation of source for the material coming from the treatment of the emulsion with the nanogas solution. In some examples, the nitrogen-oil phase includes nitrogen gas. In one example, the emulsion is an emulsion of a crude oil and water (e.g., a produced water, flow back water, or oil sands tailing water) and, from the admixing of this emulsion with the nitrogen nanogas solution is, preferably, separated a light crude oil (a crude oil having a API gravity of higher than 31.1°). More preferably, the emulsion is an emulsion of heavy (API gravity of less than 22.3°) and/or medium (22.3° to 31.1°) crude oil in water and the process provides a water phase and a nitrogen-oil phase. The nitrogen-oil phase can be a light oil phase, a medium oil phase, or a heavy oil phase; notably, the nitrogen-oil phase is preferably an admixture of water, oil, and gas that floats on the water phase. In specific examples, the nitrogen-oil can be separated from the water phase (for example, by overflow of a separation weir). The water retained in the nitrogen oil phase can then be removed (e.g., by cyclone separation, emulsion breaking, or absorption) leaving the oil phase. The isolated oil phase can be a heavy or medium oil. That is, the admixing of the nitrogen-nanogas solution with the emulsion, breaks the emulsion and carries a nanogas-oil phase on a water phase, the nanogas-oil phase can be separated and dried to leave a heavy oil. Unexpectedly, the nitrogen-oil phase has been separated and dried of residual water, leaving an oil having an API gravity of about 8-10. That is, the process can separate carry and separate very heavy oil from produced water or oil sands tailings.

[0026] In one example, the nitrogen-nanogas solution can include, consist essentially of, consist of nanobubbles that include at least 80%, 90%, or 95% nitrogen and water. Preferably, the nitrogen-nanogas solution consists of nitrogen nanobubbles and water wherein the nitrogen nanobubbles include at least 90%, or at least 95% nitrogen gas. The process, preferably, further includes separating an underlying water phase and the nitrogen-oil phase (which floats on the water phase). The underlying water phase can be recycled for the preparation of a nanogas solution; the nitrogen-oil phase is, preferably, recovered and can be processed (e.g., pumped to storage facilities).

[0027] The process can further include separating a precipitate or solid from the water phase. In one example, the addition of the nitrogen-nanogas solution to the emulsion provides a tri-phase or three component mixture of a nitrogen-oil phase, a water phase, and a precipitate. For example, emulsion can include bitumen, iron sulfide, shale, sand, and/or other subterranean component (herein subterranean components means materials other than water and oil that are carried to the surface during hydrocarbon extraction). In this example, the subterranean component (including bitumen, iron sulfide, shale, sand, and other materials) is the precipitate. That is, the process can break both the emulsion (separating oil and water) but can contemporaneously separate solid subterranean components from the oil droplet.

[0028] In another example, the process includes admixing an oxygen-nanogas solution with the emulsion providing an oxygen-oil phase. Preferably, the oxygen-nanogas solution includes oxygen nanobubbles composed of at least 80%, 90%, or 95% oxygen. Preferably, the nanogas solution consists essentially of, more preferably consists of oxygen nanobubbles and water wherein the oxygen nanobubbles includes at least 90%, or at least 95% oxygen. Preferably, the process includes breaking the emulsion and forming (and separating) a water phase and an oxygen-oil phase. Herein, the term oxygen-oil phase is a designation of source for the material coming from the treatment of the emulsion with the nanogas solution, in some examples the oxygen-oil phase includes oxygen gas (O_2). In one example, the emulsion is an emulsion of a crude oil and water (e.g., a produced water, flow back water, or oil sands tailing water) and, from the admixing of this emulsion with the oxygen nanogas solution is, preferably, separated a crude oil. As distinct from the addition of the nitrogen-nanogas solution as described above, the addition of the oxygen-nanogas solution to the emulsion provides the separation of a medium or heavy crude oil. Even more typically, the addition of the oxygen-nanogas solution provides the separation of an agglomerated oil mixture (which can include water) that does not freely flow but can float on water.

[0029] In one example, the oxygen-nanogas solution can include, consist essentially of, consist of nanobubbles that include at least 80%, 90%, or 95% oxygen and water. Preferably, the oxygen-nanogas solution consists of oxygen nanobubbles and water wherein the oxygen nanobubbles include at least 90%, or at least 95% oxygen gas. The process, preferably, further includes separating an underlying water phase and the oxygen-oil phase (which floats on the water phase). The underlying water phase can be recycled for the preparation of a nanogas solution; the oxygen-oil phase is, preferably, recovered and can be processed (e.g., pumped to storage facilities).

[0030] In another preferable instance, the process includes reducing a concentration of hydrogen sulfide in the emulsion or in a separated water phase. Preferably wherein the hydrogen sulfide concentration is reduced to a level below about 10 ppm, 5 ppm, or 1 ppm. The reduction of the hydrogen sulfide concentration can include the formation of sulfite and sulfate species in the water. In one example, the addition of the oxygen-nanogas solution to the emulsion or the separated water provides a sufficient concentration of oxygen that the hydrogen sulfide is oxidized. In another example, the addition of the oxygen-nanogas solution to a mixture of hydrogen sulfide and water oxidizes the sulfide to a sulfite and/or sulfate. Preferably, the sulfide (S^{2-}) is oxidized to sulfite (SO_3^{2-}) and/or sulfate (SO_4^{2-}) in water (e.g., the H_2S or X(SH) oxidized to hydrogen sulfite, hydrogen sulfate, or the salts thereof). In certain examples, the emulsion (or the water solution) includes ions or agents that react with and/or bind the sulfite or sulfate and precipitate this sulfur species from the solution.

[0031] In yet another preferable instance, the process can include reducing a concentration of iron in the emulsion; affecting the separation of iron from water; and/or oxidizing iron sulfide (e.g., FeS), for example, to reduce any likelihood pyrophoric actions upon removal. Notably, flow back water, produced water, or oil sands tailing water can include a concentration of iron sulfide, typically FeS. In one example, the majority (preferably all) of the iron sulfide can be separated from an emulsion by the addition of a nitrogen nanogas solution; this process breaks the emulsion and precipitates the iron sulfide. In some instances, portions of the iron sulfide may stay suspended in the water phase; in these instances, the addition of an oxygen nanogas solution provides an admixture that can be filtered without irreversibly clogging filter membranes or screens. In another example, the iron sulfide concentration in the water phase is reduced to a level below about 10 ppm, 5 ppm, or 1 ppm. Preferably, the addition of the oxygen nanogas solution provides an admixture that can be filtered and the filter screen back washed. Notably, the iron sulfide suspended in the solution without the addition of the oxygen-nanogas solution is an admixture capable of filtration but clogs the screens and cannot be backwashed. In one example, the addition of an oxygen-nanogas solution or an ON-nanogas solution to an admixture of iron sulfide and water (obtained from an emulsion) partially oxidizes the surface of the iron sulfide, decreases the adhesion of oil to the surface of this oxidized material, and permits for the more facile filtration. In another example, the iron sulfide can be oxidized to iron oxide (Fe_2O_3 or FeO). Herein, an oxygen-nanogas solution can be added to an admixture of water and iron sulfide; in one example the admixture of water and iron sulfide is selected from the emulsion (unseparated), a separated water phase that includes iron sulfide, or a slurry of iron sulfide and water (for example, a slurry that was previously separated from the emulsion by the addition of a nitrogen-nanogas solution; or a slurry that is the resuspension of separated iron sulfide, and optionally other materials, in water)). Preferably, the iron sulfide is quantitatively converted to an iron oxide.

[0032] In still another instance, the process can include admixing an ON-nanogas solution with the emulsion. In this instance, the addition can afford the reduction of the sulfide concentration in the separated water, the reduction of the iron sulfide concentration in the separated water, a lightening of the separated oil phase, and or a mixture thereof. In one example, the nanogas solution is a ON-nanogas solution wherein the solution includes, consists essentially of, or consists of oxygen (O_2), nitrogen (N_2), and water. Herein, an ON-nanogas includes molar ratios of oxygen to nitrogen in the range of 99:1 to 1:99; examples include 99:1, 90:1, 80:1, 70:1, 60:1, 50:1, 40:1, 30:1, 20:1, 10:1, 1:1, 1:10, 1:20, 1:30, 1:40, 1:50, 1:60, 1:70, 1:80, 1:90, and 1:99. Preferred molar ratios include about 18:82, 21:79, 28:72, 30:70, 32:68, 35:65, 40:60, 42:58, and 50:50. One particularly relevant molar ratio is 21:79 (air). Other particularly relevant molar ratios can be selected from 50:50; 60:40; 70:30; and 80:20. In particular, the amount of oxygen (relative to the amount of nitrogen) can be varied to achieve different results (oxidation vs separation), and the higher the concentration of the composition that is desired to be oxidized (e.g., a sulfide) the higher the oxygen concentration can be.

[0033] In yet another instance, the process can include admixing the emulsion with a first nanogas solution. The process can then include either (A) separating the admixture into components (i.e., oil phase, water phase, and possibly solid phase) and then admixing the water phase with a second nanogas solution, or (B) prior to separating the components, adding a second nanogas solution to the first admixture. When the first admixture is a heterogeneous admixture (having at least an oil phase and a water phase), the second nanogas solution is preferably added to the water phase. In one example, the first nanogas solution is a nitrogen-nanogas solution and the second nanogas solution is an oxygen nanogas solution. In a second example, the first nanogas solution is an oxygen nanogas solution or an ON-nanogas solution and the second nanogas solution is a nitrogen-nanogas solution. In a third example the first nanogas solution is selected from the group consisting of a nitrogen-, an oxygen-, and a ON-nanogas solution; and the second nanogas has a composition that is different from the first nanogas solution and is selected from the group consisting of a nitrogen-, an oxygen-, and a ON- nanogas solution.

[0034] Preferably, the addition of the nitrogen-nanogas to the water phase forms a nitrogen-oil phase which has a viscosity that is lower than a viscosity of the oxygen-oil phase. That is, the addition of the nitrogen-nanogas solution (e.g., to the broken emulsion formed by the admixing of the oxygen-nanogas solution and an emulsion) affects a change in the oil-phase carried on the water, thereby reducing the viscosity of the oil-phase and preferably furthering a separation of the oil and water. In one instance, this can be understood as a further lightening of the oil. In another instance, the addition of the nitrogen-nanogas solution affects a separation of the oil and any subterranean components (e.g., solids). In one unexpected instance, the addition of the oxygen-nanogas solution did not affect or affected to a minor extent the separation of the subterranean components and the addition of the nitrogen-nanogas solution afforded separation or enhanced separation (beyond what is achievable with just the oxygen nanogas solution). Still further, the nitrogen-oil phase is, preferably, separated from the underlying water phase and the oil is recovered and can be processed.

[0035] Another example of the process described herein includes shearing a first nanogas solution into an oil-in-water micro emulsion, and breaking the oil-in-water micro emulsion and forming a water-in-oil macro emulsion, a water phase, and a solids phase, where the water-in-oil macro emulsion is carried on the water phase. The process can also include collecting oil from the water-in-oil macro emulsion. Here, the nanogas solution consists essentially of a homogeneous mixture of nanobubbles and water.

[0036] In one instance, shearing means contacting the nanogas solution and the oil-in-water micro emulsion in such a way that the oil droplets in the emulsion are disrupted, in one case made even smaller. In another instance, shearing means injecting the nanogas solution between a double layer boundary of the oil droplets in the micro emulsion. The shearing can involve providing a flow of the oil-in-water micro emulsion and injecting a stream of the first nanogas solution into the micro emulsion flow at a direction that is 90° to 180° from the flow, preferably 115° to 180°, more preferably 135° to 180°. Preferably, the nanogas solution is injected as a stream with sufficient pressure to provide turbulence and shear in the micro emulsion flow. In one preferable instance, a plurality of nanogas solution streams are injected into the micro emulsion flow path at angles ranging from 115° to 180° using a nozzle or tube. Preferably, the nozzle or tube does not constrict at its termination as this constriction can disrupt the nanogas solution and promote macrobubble formation. In another preferable instance, the plurality of nanogas solution streams intersect in the micro emulsion flow path. In another instance, the nanogas solution and the micro emulsion can be intermixed in a volume ("mixer") that can carry both materials. Examples of a mixer can include a pipe carrying the micro emulsion or can include shearing mixers or mixing containers (e.g., rotostator mixers). This sheared admixture is then preferably ejected (transferred) into a separation container (e.g., a floatation tank, a drum, a pond).

[0037] The process can also include separating the water phase from the water-in-oil macro emulsion and the solids. Notably, the separated water phase can include nanobubbles; that is, the concentration of nanobubbles in the sheared admixture is sufficiently high that the nanobubbles are not consumed or absorbed into the water-in-oil emulsion. This separated water, if containing a sufficient concentration of nanobubble can be used as a nanogas solution (e.g., sheared into an oil-in-water emulsion to provide the benefits described herein). Preferably, a portion of the separated water is recycled and used to provide the first nanogas solution (e.g., by addition to a machine or process for the manufacture of a nanogas solution).

[0038] In another instance, the oil-in-water micro emulsion can include a number of emulsifiers that promote or stabilize the emulsion. Notably, when the emulsion is the result of, for example, the petroleum industry, the micro emulsion can include emulsifiers selected from solids, asphaltenes, paraffins, resins, and mixtures thereof. Typically, these emulsifiers are distributed at the interface between the oil droplets and the water, stabilizing the oil droplets, preventing them from agglomerating, and thereby stabilizing the emulsion. Notably, these emulsifiers increase the zeta-potential of the oil droplets to prevent the agglomeration and separation of the oil. In one case, where the first nanogas solution is an oxygen-nanogas solution; the process involves absorbing oxygen nanobubbles into the emulsifiers, reducing the zeta potential of an oil droplet, and forming an admixture that includes a coagulum. Herein, the coagulum is an oil-in-water macro emulsion; that is, the oxygen nanobubbles act as a chemical coagulant without the addition of traditional coagulants. In this case, the macro-emulsion may float or separate from the water but generally includes a high proportion of water to oil. Accordingly, the process preferably also includes admixing a second nanogas solution with the admixture that includes the coagulum. Here, this second nanogas solution is a nitrogen-nanogas solution which dissociates the emulsifiers from a surface of oil droplets in the oil-in-water macro emulsion, breaks the oil-in-water emulsion, and forms the water-in-oil macro emulsion.

[0039] Notably, the addition of a nitrogen-nanogas solution in the current process has been found to support a process that includes dissociating the emulsifiers from a surface of oil droplets in the oil-in-water macro emulsion; breaking the oil-in-water emulsion; and forming the water-in-oil macro emulsion. In one case, the nitrogen nanobubbles disrupt the emulsifiers from the oil droplets and allow the oil to demulsify (e.g., group into larger drops). Notably, the addition of the nitrogen-nanogas solution in the current process separates a large percentage (e.g., greater than 50 wt.%) of solids from the oil droplets causing these solids to precipitate or settle from the solutions.

[0040] In one preferable case, the first nanogas solution can include carbon dioxide and nitrogen; that is, nanobubbles of carbon dioxide and nitrogen (either as admixtures or separate nanobubbles). This case can include the absorption of the carbon dioxide (from the nanobubbles) into oil droplets (e.g., providing an oil-carbon dioxide composition). Preferably, the oil-carbon dioxide composition (carbon dioxide absorbed oil droplet) has a density that is less than the density of the oil droplet without the carbon dioxide. In this case, the separation of the components of the emulsion can provide an water-in-oil macro emulsion which includes carbon dioxide in the oil.

[0041] In another case, the oil-in-water micro emulsion might include a concentration of sulfides greater than 50 ppm, the sulfides selected from iron sulfide, hydrogen sulfide, and a mixture thereof. This process can include either (a) the first nanogas solution includes a sufficient quantity of oxygen nanobubbles to react completely with the concentration of sulfides in the oil-in-water emulsion, thereby reducing the sulfide concentration to less than 10 ppm, or (b) the process further includes admixing a second nanogas solution with the water phase, wherein the sulfides of the oil-in-water micro emulsion are carried into the water phase, and where the second nanogas solution includes a sufficient quantity of oxygen nanobubbles to react completely with the concentration of sulfides in the water phase, thereby reducing a sulfide concentration to less than 10 ppm.

[0042] Notably, the embodiments provided herein proceed without the formation of macrobubbles. In one case, the first nanogas solution does not form macrobubbles. Preferably, none of the nanogas solutions utilized herein form or include macrobubble (i.e., any bubble larger than a nanobubble). Preferably, the water-in-oil macro emulsion (separated from the micro emulsion) further does not include macrobubbles. In one instance, the water-in-oil macro emulsion includes greater than about 50 wt.% oil, less than about 50 wt.% water, and further includes nanobubbles.

[0043] In another embodiment, the process of breaking the emulsion can be utilized to continuously or batch wise separate oil from water. For example, the process can be used to separate oil from water in oil field produced water, collected water, or catch basins. More preferably, the process can be used to reduce the hydrocarbon content of a water and facilitate reuse or disposal. In one instance (e.g., as shown in Fig 2) the process can utilize a floatation tank 100 for the oil and water separation. The floatation tank 100 can have an inlet end 101 and an outlet end 102; an emulsion inlet 103 and a first nanogas inlet 104 proximal to the inlet end 101 and an underflow baffle 105 proximal to the outlet end 102. Examples of floatation tanks include DAF tanks and API tanks. Preferably, the floatation tank is a circular or rectangular DAF tank; more preferably the floatation tank is a rectangular tank that provides at least 5 minutes, 10 minutes, 15 minutes, or 20 minutes of residency time in the tank.

[0044] The process can include providing an emulsion to the floatation tank 100 via the emulsion inlet 103. The emulsion can be a produced water or collected water from a well operation. The process can additionally include providing a nanogas solution to the floatation tank via the first nanogas inlet 104. The process further includes admixing the nanogas solution with the emulsion. The admixing can be facilitated by the hydraulic flow within the floatation tank or can be further facilitated by the operation of a mixer (e.g., a paddle or propeller) within the floatation tank.

[0045] The process preferably includes breaking the emulsion and forming an oil phase 106 floating on a water phase 107. Herein, breaking the emulsion includes the coalescence of the oil “droplets” to form an oil phase (e.g., an water-in-oil emulsion) carried by the water phase.

[0046] The process can then include separating the water phase from the oil phase. Preferably, the water phase is separated by carrying the water phase 107 under the underflow baffle 105. In this instance, the oil phase is retained on the surface of the water phase. The oil phase can further be removed by an overflow or oil skimmer that can conduct the oil phase to a collection or storage apparatus.

[0047] In another instance, the floating tank 100 can include a second nanogas inlet 108 down steam from the first nanogas inlet and upstream from the underflow baffle. Herein, downstream means a position closer to the outlet end than the first nanogas inlet. Preferably, the second nanogas inlet is upstream of a midpoint between the inlet end and the outlet end. Still more preferably, the second nanogas inlet is upstream of the first quarter point between the inlet end and the outlet end. In this instance, the process can further include providing a second nanogas solution to the floatation tank via the second nanogas inlet. Thereby, the second nanogas solution is preferably admixed with the water phase carrying the oil phase, that is, the second nanogas solution is added to the floatation tank at a position or time after the emulsion breaks. Preferably, the second nanogas solution is a homogeneous mixture of nitrogen nanobubbles Yet another embodiment is a method of treating tailing water from oil sands production processes. The method can include admixing a nanogas solution and oil sands tailings; and then separating materials including silts, residual bitumen, and organic compounds from water in the oil sands tailings. As described above, the nanogas solution is a homogeneous mixture of nanobubbles and water. In one instance, the nanogas solution is a nitrogen-nanogas solution and, preferably, the nitrogen-nanogas solution affects the viscosity of materials in the oil sands tailings. In another instance, the nanogas solution is an oxygen-nanogas solution and, preferably, oxidizes volatile materials in the oil sands tailings. In still another instance, the method includes admixing a second nanogas solution with the admixture of the nanogas solution and the oil sands tailings; wherein the nanogas solution is an oxygen-nanogas solution and the second nanogas solution is a nitrogen-nanogas solution.

[0048] In one example, a nanogas solution is directly added to the tailings, preferably directly added to a tailings pond. For example, the nanogas solution can be injected or added to the tailing by subsurface injection, that is, injection of the nanogas solution into the tailings below the surface of the tailings pond. Recognizing the enormity of tailings ponds (e.g., those associated with tar sands recovery) the nanogas solution can be poured, sprayed, or distributed over the pond. In another example, the nanogas solution is added to the tailings prior to the addition of the tailings to the ponds; that is, at the end of the hydrocarbon recovery process. Preferably, the nanogas solution is mixed with the tailings prior to addition of the tailings to the tailings pond. In yet another example, the nanogas solution can be mixed with tailings by pumping tailings from the tailings pond, admixing with the nanogas solution, and then returning the mixture to the tailings pond.

[0049] In a preferable example, the addition of the nanogas solution (e.g., a nitrogen-nanogas solution) to the tailings pond increases the rate of separation of the oils, water, and solids contained in the tailings. In another preferable example, the addition of a nanogas solution that includes oxygen (e.g., an oxygen-nanogas solution or an ON-nanogas solution) and oxidizes hydrogen sulfide and/or other oxidizable components of the tailings solution. In one example, the addition of an oxygen including nanogas solution additionally causes hydrocarbon materials to agglomerate and increase separation; in another example, the addition of a nitrogen nanogas solution separates and lightens the oil(s) and allows for more facile removal of the hydrocarbons from the surface of the tailings pond. Preferably, the addition of the nanogas solution increases the settling rate by a factor of 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, or 2.0. More preferably, the addition of the nanogas solution increases the settling rate by at least 2 times.

[0050] In a particular instance, the method can include admixing a nanogas solution with oil sands tailings and then separating materials including silts, residual bitumen, and organic compounds from water in the oil sands tailings. In this instance, the nanogas solution includes nitrogen nanobubbles, oxygen nanobubbles, carbon dioxide nanobubbles or a mixture thereof. In one case, the nanogas solution is a nitrogen-nanogas solution. In another case, the viscosity of oil in the tailings is reduced as an effect of the addition of the nanogas solution. In yet another case includes further admixing an oxygen-nanogas solution with the oil sands tailings; and oxidizing a sulfide. The process can includes admixing the nanogas solution with the tailings and then adding the admixture to a tailings pond; can include subservice injection and admixing of the nanogas solution and the tailings, for example the subsurface injection of the nanogas solution into tailings held in a tailings pond.

[0051] Still another embodiment is a method for oxidizing sulfides. In one instance this method can include admixing an oxygen-nanogas solution or an ON-nanogas solution with an aqueous solution that includes hydrogen sulfide and oxidizing the hydrogen sulfide. In another instance this method can include admixing an oxygen-nanogas solution or an ON-nanogas solution with a slurry of iron sulfide and water and oxidizing the iron sulfide to iron oxide.

WHAT IS CLAIMED:

1. A process comprising:

shearing a first nanogas solution into an oil-in-water micro emulsion;

breaking the oil-in-water micro emulsion and forming a water-in-oil macro emulsion, a water phase, and a solids phase, where the water-in-oil macro emulsion is carried on the water phase; and

collecting oil from the water-in-oil macro emulsion;

wherein the nanogas solution consists essentially of a homogeneous mixture of nanobubbles and water.

2. The process of claim 1 further comprising separating the water phase from the water-in-oil macro emulsion and the solids; wherein the separated water phase includes nanobubbles.

3. The process of claim 2 further comprising recycling a portion of the water phase; and using the recycled portion of the water phase to provide the first nanogas solution.

4. The process of claim 1, wherein the oil-in-water micro emulsion includes emulsifiers selected from solids, asphaltenes, paraffins, resins, and mixtures thereof.

5. The process of claim 4, wherein the first nanogas solution is an oxygen-nanogas solution; the process further comprising absorbing oxygen nanobubbles into the emulsifiers, reducing the zeta potential of an oil droplet, and forming an admixture that includes a coagulum; wherein the coagulum comprises an oil-in-water macro emulsion.

6. The process of claim 5, further comprising admixing a second nanogas solution with the admixture that includes the coagulum, where the second nanogas solution is a nitrogen-nanogas solution; dissociating the emulsifiers from a surface of oil droplets in the oil-in-water macro emulsion; breaking the oil-in-water emulsion; and forming the water-in-oil macro emulsion.

7. The process of claim 4, wherein the first nanogas solution is a nitrogen-nanogas solution; the process further comprising dissociating the emulsifiers from a surface of oil droplets in the oil-in-water macro emulsion; breaking the oil-in-water emulsion; and forming the water-in-oil macro emulsion.

8. The process of claim 1, wherein the first nanogas solution includes carbon dioxide and nitrogen; the process further comprising absorbing the carbon dioxide into an oil

droplet; and reducing the density of the oil droplet; wherein the water-in-oil macro emulsion includes carbon dioxide in the oil.

9. The process of claim 1, wherein the oil-in-water micro emulsion includes a concentration of sulfides greater than 50 ppm, the sulfides selected from iron sulfide, hydrogen sulfide, and a mixture thereof; wherein either (a) the first nanogas solution includes a sufficient quantity of oxygen nanobubbles to react completely with the concentration of sulfides in the oil-in-water emulsion, thereby reducing the sulfide concentration to less than 10 ppm, or (b) the process further includes admixing a second nanogas solution with the water phase, wherein the sulfides of the oil-in-water micro emulsion are carried into the water phase, and where the second nanogas solution includes a sufficient quantity of oxygen nanobubbles to react completely with the concentration of sulfides in the water phase, thereby reducing a sulfide concentration to less than 10 ppm.

10. The process of claim 1 further comprising providing a flow of the oil-in-water micro emulsion; wherein shearing the first nanogas solution into the oil-in-water micro emulsion includes injecting a stream of the first nanogas solution into the micro emulsion flow at a direction that is 90° to 180° from the flow, preferably 115° to 180°, more preferably 135° to 180°.

11. The process of claim 1, wherein shearing the first nanogas solution into the oil-in-water micro emulsion includes admixing the first nanogas solution and the micro emulsion in a mixer; the process further including ejecting this admixture into a separation container.

12. The process of claim 1, wherein the first nanogas solution does not form macrobubbles.

13. The process of claim 1, wherein the water-in-oil macro emulsion does not include macrobubbles.

14. The process of claim 1, wherein the water-in-oil macro emulsion includes greater than about 50 wt.% oil and less than about 50 wt.% water; wherein the water-in-oil macro emulsion further includes nanobubbles.

15. A process comprising:

providing a floatation tank having an inlet end and an outlet end; the floatation tank including an oil-in-water emulsion inlet and a first nanogas inlet, both, proximal to the inlet end, and having an underflow baffle proximal to the outlet end;

providing an oil-in-water emulsion to the floatation tank via the oil-in-water emulsion inlet;

providing a nanogas solution to the floatation tank via the first nanogas inlet by injecting a stream of a nanogas solution into a flow path of the oil-in-water emulsion at a direction that is 90° to 180° from the flow path, preferably 115° to 180°, more preferably 135° to 180°, thereby admixing the nanogas solution with the oil-in-water emulsion without the formation of macrobubbles;

breaking the oil-in-water emulsion and forming an oil phase floating on a water phase;

separating the water phase from the oil phase by carrying the water phase under the underflow baffle.

16. The process of claim 15,

wherein the floatation tank includes a second nanogas inlet down steam from the first nanogas inlet and upstream from the underflow baffle;

the process further including

providing a second nanogas solution to the floatation tank via the second nanogas inlet thereby admixing the second nanogas solution with the water phase carrying the oil phase.

17. A method comprising:

admixing a nanogas solution with oil sands tailings;

separating materials including silts, residual bitumen, and organic compounds from water in the oil sands tailings;

wherein the nanogas solution includes nitrogen nanobubbles, oxygen nanobubbles, carbon dioxide nanobubbles or a mixture thereof.

18. The method of claim 17, wherein the nanogas solution is a nitrogen-nanogas solution.

19. The method of claim 17, wherein the viscosity of oil in the tailings is reduced as an effect of the addition of the nanogas solution.

20. The method of claim 17 further comprising admixing an oxygen-nanogas solution with the oil sands tailings; and oxidizing a sulfide.

21. The method of claim 17 further comprising admixing the nanogas solution with the tailings and then adding the admixture to a tailings pond.

22. The method of claim 17, wherein admixing the nanogas solution and the tailings includes subsurface injection of the nanogas solution into tailings held in a tailings pond.

23. A method comprising:

admixing an oxygen-nanogas solution or an ON-nanogas solution with an aqueous solution that includes hydrogen sulfide; and

oxidizing the hydrogen sulfide.

24. A method comprising:

admixing an oxygen-nanogas solution or an ON-nanogas solution with a slurry of iron sulfide and water; and

oxidizing the iron sulfide to iron oxide.

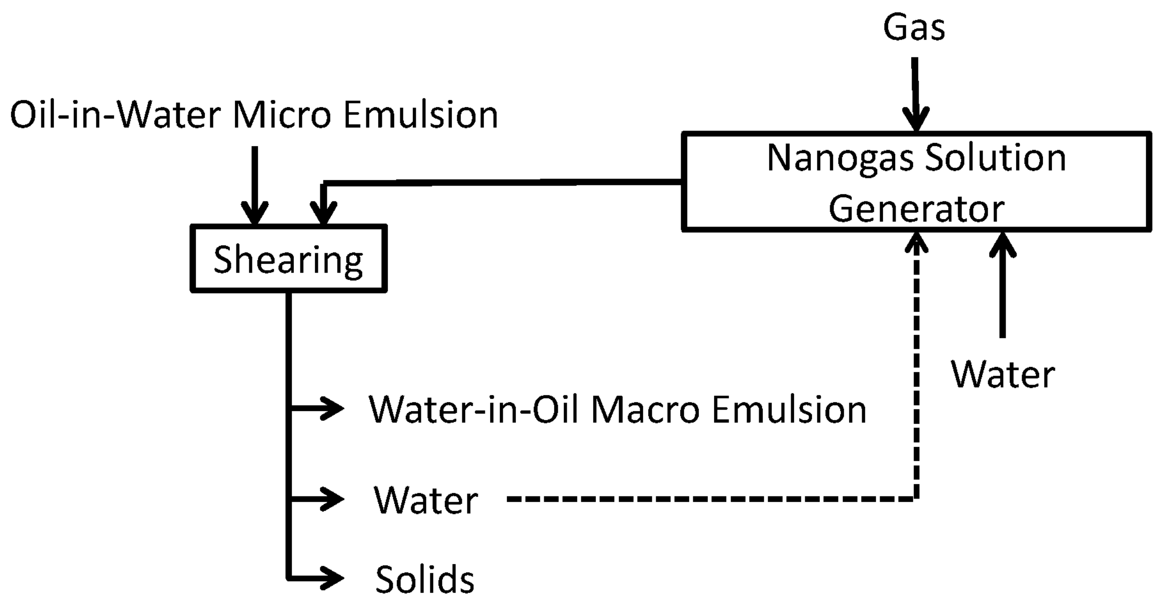
Gas
Oil-in-Water Micro Emulsion
Nanogas Solution Generator
Shearing
Water
Water-in-Oil Macro Emulsion
Water
Solids

FIG. 1

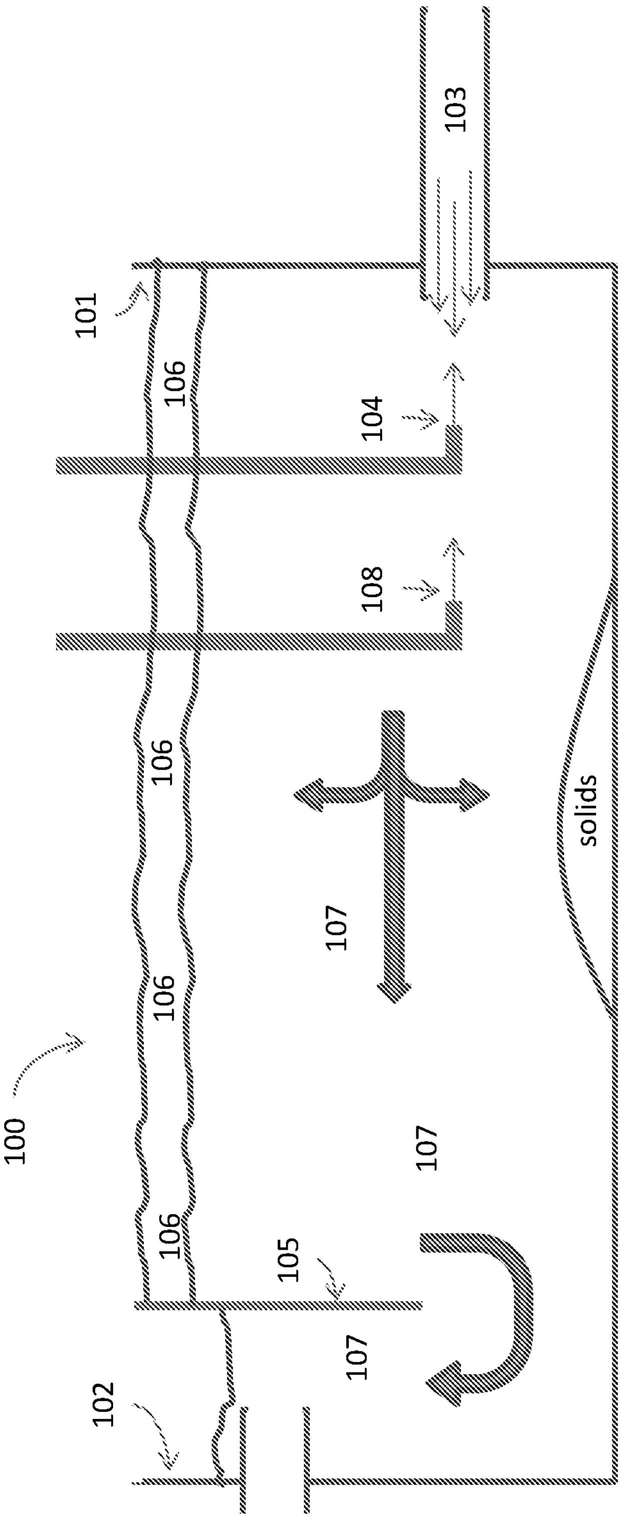
100
101
102
103
104
105
106
106
106
106
106
107
107
107
107
108
solids

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/032858

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01D 17/04; B01D 17/00; B01D 17/02; B01D 17/05; C10G 33/00 (2017.01)
CPC - B01D 17/0205; B01D 17/00; B01D 17/02; B01D 17/04; C10G 33/00 (2017.05)

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)
See Search History document

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)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010/0104744 A1 (MOFFETT) 29 April 2010 (29.04.2010) entire document	17, 18, 20
Y	US 4,783,268 A (LEUNG) 08 November 1988 (08.11.1988) entire document	17, 18, 20
Y	US 3,913,673 A (BARBER) 21 October 1975 (21.10.1975) entire document	20, 23
Y	CN 102218275 B (DAQING XINYU TECHNOLOGY) 24 April 2013 (24.04.2013) see machine translation	23, 24
Y	US 2,503,528 A (WALKER et al) 11 April 1950 (11.04.1950) entire document	24
A	US 5,935,447 A (FEBRES et al) 10 August 1999 (10.08.1999) entire document	1-24

☐ 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 14 July 2017	Date of mailing of the international search report 31 JUL 2017
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774