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(71) Applicant: BAKER HUGHES INCORPORATED
[US/US]; P.O. Box 4740, Houston, TX 77210-4740 (US).

(72) Inventors: AGRAWAL, Devesh Kumar; 14990 Yorktown Plaza Drive, Houston, TX 77040 (US). MURUGESAN, Sankaran; 28702 Maple Red Drive, Katy, TX 77494 (US). KHABASHESKU, Valery N.; 2421B Dorrington Street, Houston, TX 77030 (US).

(74) Agents: RIDDLE, J. Albert et al.; Baker Hughes Incorporated, P.O. Box 4740, Houston, TX 77210-4740 (US).

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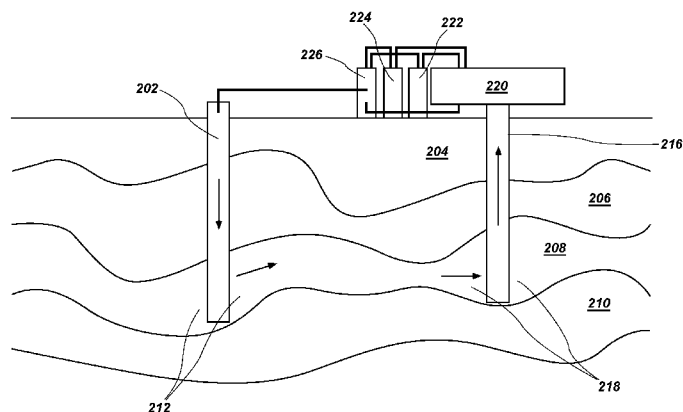


FIG. 2

(57) Abstract: A suspension for removing hydrocarbons from a subterranean formation includes a fluid comprising at least one of water, brine, steam, carbon dioxide, a light hydrocarbon, and an organic solvent; and a plurality of nanoparticles dispersed with the fluid. Nanoparticles of the plurality comprise silica and carbon. A method includes forming a plurality of nanoparticles and dispersing the plurality of nanoparticles with a fluid to form a suspension comprising the nanoparticles. A method of recovering a hydrocarbon material includes introducing a suspension into a subterranean formation containing hydrocarbons, forming a stabilized emulsion of the suspension and the hydrocarbons within the subterranean formation; and removing the emulsion from the subterranean formation. The suspension comprises a plurality of nanoparticles, and at least some nanoparticles of the plurality comprise silica and carbon.



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TITLE

METHODS AND SUSPENSIONS FOR RECOVERY OF HYDROCARBON
MATERIAL FROM SUBTERRANEAN FORMATIONS

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PRIORITY CLAIM

This application claims the benefit of the filing date of United States Patent Application Serial No. 14/744,520, filed June 19, 2015, for “METHODS AND SUSPENSIONS FOR RECOVERY OF HYDROCARBON MATERIAL FROM SUBTERRANEAN FORMATIONS,” the entire disclosure of which is hereby incorporated
10 by reference.

TECHNICAL FIELD

Embodiments of the present disclosure relate generally to methods of recovering a hydrocarbon material from a subterranean formation. More particularly, embodiments of
15 the disclosure relate to methods of forming a suspension including nanoparticles comprising silica and carbon, methods of recovering hydrocarbons using the nanoparticles, and to suspensions including the nanoparticles.

BACKGROUND

20 Water flooding is a conventional process of enhancing the extraction of hydrocarbon materials (*e.g.*, crude oil, natural gas, *etc.*) from a subterranean formation. In this process, an aqueous fluid (*e.g.*, water, brine, *etc.*) is injected into the subterranean formation through injection wells to sweep a hydrocarbon material contained within interstitial spaces (*e.g.*, pores, cracks, fractures, channels, *etc.*) of the subterranean
25 formation toward production wells. One or more additives may be added to the aqueous fluid to assist in the extraction and subsequent processing of the hydrocarbon material.

For example, in some approaches, a surfactant, solid particles (*e.g.*, as colloids), or both, are added to the aqueous fluid. The surfactant and/or the solid particles can adhere to or gather at interfaces between a hydrocarbon material and an aqueous material to form a
30 stabilized emulsion of one of the hydrocarbon material and the aqueous material dispersed in the other of the hydrocarbon material and the aqueous material. Surfactants may decrease the surface tension between the hydrocarbon phase and the water phase, such as in an emulsion of a hydrocarbon phase dispersed within an aqueous phase. Stabilization by the surfactant, the solid particles, or both, lowers the interfacial tension between the

hydrocarbon and water and reduces the energy of the system, preventing the dispersed material (*e.g.*, the hydrocarbon material, or the aqueous material) from coalescing, and maintaining the one material dispersed as units (*e.g.*, droplets) throughout the other material. Reducing the interfacial tension increases the permeability and the flowability of the hydrocarbon material. As a consequence, the hydrocarbon material may be more easily transported through and extracted from the subterranean formation as compared to water flooding processes that do not employ a surfactant and/or solid particles. The effectiveness of the emulsion is determined in large part by the ability of the emulsion to remain stable and ensure mixing of the two phases.

However, application of surfactants is usually limited by the ability of the surfactant to sufficiently contact a large portion of a volume of hydrocarbons located within the subterranean formation and form an emulsion containing the hydrocarbons and the aqueous material carrying the surfactants. For example, the surfaces of the hydrocarbon-containing reservoir may not be sufficiently contacted by the surfactants, or the surfactants may not sufficiently adhere to hydrocarbon-bearing surfaces of the subterranean formation.

DISCLOSURE

In some embodiments, a suspension for removing hydrocarbons from a subterranean formation includes a fluid comprising at least one of water, brine, steam, carbon dioxide, a light hydrocarbon, and an organic solvent; and a plurality of nanoparticles dispersed within the fluid. At least some nanoparticles of the plurality comprise both silica and carbon.

In other embodiments, a method includes forming a plurality of nanoparticles to comprise silica and carbon, and dispersing the plurality of nanoparticles with a fluid to form a suspension comprising the nanoparticles.

In certain embodiments, a method of recovering a hydrocarbon material includes introducing a suspension into a subterranean formation containing hydrocarbons, forming a stabilized emulsion of the suspension and the hydrocarbons within the subterranean formation; and removing the emulsion from the subterranean formation. The suspension comprises a plurality of nanoparticles, and at least some nanoparticles of the plurality comprise silica and carbon.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a simplified side view illustrating an embodiment of a suspension according to the present disclosure.

FIG. 2 is a simplified schematic showing how the suspension shown in FIG. 1 may
5 be used for recovering hydrocarbons from subterranean formations.

MODE(S) FOR CARRYING OUT THE INVENTION

The following description provides specific details, such as material types, compositions, material thicknesses, and processing conditions in order to provide a
10 thorough description of embodiments of the disclosure. However, a person of ordinary skill in the art will understand that embodiments of the disclosure may be practiced without employing these specific details. Indeed, embodiments of the disclosure may be practiced in conjunction with conventional techniques employed in the industry. In addition, the description provided below does not form a complete process flow for recovering
15 hydrocarbons from a hydrocarbon-bearing subterranean formation. Only those process acts and structures necessary to understand the embodiments of the disclosure are described in detail below. A person of ordinary skill in the art will understand that some process components (*e.g.*, pipelines, line filters, valves, temperature detectors, flow detectors, pressure detectors, *etc.*) are inherently disclosed herein and that adding various
20 conventional process components and acts would be in accord with the disclosure. Additional acts or materials to extract a hydrocarbon material from a subterranean formation or from bitumen may be performed by conventional techniques.

As used herein, the singular forms “a,” “an,” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise.

25 As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

As used herein, relational terms, such as “first,” “second,” “top,” “bottom,” “upper,” “lower,” “over,” “under,” *etc.*, are used for clarity and convenience in understanding the disclosure and accompanying drawings and do not connote or depend on
30 any specific preference, orientation, or order, except where the context clearly indicates otherwise.

As used herein, the term “substantially,” in reference to a given parameter, property, or condition, means to a degree that one of ordinary skill in the art would

understand that the given parameter, property, or condition is met with a small degree of variance, such as within acceptable manufacturing tolerances.

As used herein, the term “nanoparticle” means and includes particles having a mean diameter of less than about 1,000 nm (nanometers).

5 As used herein, the term “suspension” means and includes a material including at least one carrier material with which a material of a different phase is dispersed. A suspension of solid particles in a gaseous carrier fluid may also be referred to in the art as an aerosol or particulate. A suspension can also include a foam, in which a liquid or solid material forms discrete or connected pockets of a gas, or an aerosol, in which solid or
10 liquid particles are dispersed in a gas.

As used herein, “mean diameter” refers to the number average particle size based on the largest linear dimension of the particle (sometimes referred to as “diameter”), whether the particle is spherical or not. Diameters, including average, maximum, and minimum particle sizes, may be determined by an appropriate method of sizing particles
15 such as, for example, static or dynamic light scattering (SLS or DLS) using a laser light source.

Methods of recovering hydrocarbons from a subterranean formation using a suspension including nanoparticles of silica and carbon are described. In particular, nanoparticles that include carbon attached to or bonded to silica appear to have beneficial
20 properties in excess of the properties of either silica or carbon alone. The suspension including such nanoparticles is introduced into the subterranean formation and contacts the hydrocarbons within the formation. Upon contacting the hydrocarbons, the suspension appears to reduce an interfacial tension between an aqueous phase and the hydrocarbon phase. For example, without being bound by any particular theory, it appears that
25 nanoparticles enable a mechanism of separation based on “disjoining pressure.” That is, nanoparticles adjacent interfaces between the aqueous phase, the hydrocarbon phase, and the surface of the formation may tend to form a wedge-like structure and between the hydrocarbon phase and the formation. Thus, the attraction between the hydrocarbon phase and the formation may be decreased, and the hydrocarbon may be more easily swept away
30 from the formation. Such a process is described in Paul McElfresh, *et al.*, “Application of Nanofluid Technology to Improve Oil Recovery in Oil and Gas Wells,” in SPE International Oilfield Nanotechnology Conference 2012, pp. 46-51, SPE 154827. The nanoparticles stabilize an emulsion of the hydrocarbon phase dispersed within the aqueous phase of the suspension or an emulsion of the aqueous phase dispersed within the

hydrocarbon phase. The stabilized emulsion is transported to the surface where the emulsion may be destabilized and the hydrocarbons recovered therefrom.

FIG. 1 is a simplified side view illustrating a suspension 100 within a container 101 having a plurality of nanoparticles 102a, 102b, 102c, 102d (referred to generally herein as
5 “nanoparticles 102”) dispersed within a fluid 104. The fluid 104 may include, for example, water, brine, steam, an organic solvent, carbon dioxide, light hydrocarbons (e.g., propane, butane, *etc.*), or any combination thereof. The pH or other properties of the fluid 104 may be selected to control the distribution of the nanoparticles 102 in the fluid 104.

At least some nanoparticles 102 may include both silica 106 and carbon 108 in the
10 same particle. For example, nanoparticles 102a may include nanoparticles of silica 106 bonded to or attached to nanoparticles of carbon 108. Some nanoparticles 102b may include a mixture of silica and carbon. Other nanoparticles 102c may include silica 106 coated or otherwise treated with carbon 108 or a carbon-containing compound, such as graphite, graphene, graphene oxide, carbon nanotubes, carbon nanodots (or quantum dots),
15 nanodiamonds (*i.e.*, nanoparticles of carbon having sp^3 hybridization), fullerenes, *etc.* Certain nanoparticles 102d may include carbon 108 coated or otherwise treated with silica 106 or another silicon-containing compound. In embodiments in which the nanoparticles 102 include carbon nanotubes, the carbon nanotubes may be single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), or
20 combinations thereof. The carbon 108 and/or the silica 106 may be functionalized with one or more functional groups.

For example, surfaces of the silica 106 may be functionalized with one or more functional groups to impart desired physical and chemical properties to the surface of the nanoparticles 102, such as to improve reaction with the carbon 108 or carbon-containing
25 compound. In some embodiments, the silica 106 may be fumed silica nanoparticles, amorphous silica nanoparticles, or any other type or morphology of silica. For example, the silica 106 may be colloidal silica made by growing mono-dispersed, negatively charged, amorphous silica particles in water. Such colloidal silica is sold by Nissan Chemical America Corporation, of Houston, Texas, under the trade name SNOWTEX®.
30 Surfaces of the silica 106 may include hydroxyl (OH^-) ions, and the silica 106 may be stabilized in a suspension by repulsion between negatively charged particles. Functionalization of silica particles is described in U.S. Patent Application 14/169,432, filed January 31, 2014, titled “Nano-Surfactants for Enhanced Hydrocarbon Recovery, and

Methods of Forming and Using Such Nano-Surfactants,” the entire disclosure of which is hereby incorporated herein by reference.

The carbon 108 may be deposited or attached to the silica 106 by physical or chemical bonds. For example, hydroxyl groups on the surfaces of the silica 106 may bond
5 with the carbon 108.

The nanoparticles 102 may be structured and formulated to react with hydrocarbons and other carbon-containing materials present within a subterranean formation. By way of non-limiting example, contacting a porous, hydrocarbon-containing material with a suspension 100 including the nanoparticles 102 may form an emulsion at locations where
10 the suspension 100 contacts the porous material. The nanoparticles 102 may stabilize the emulsion during transportation of the emulsion to the surface of the subterranean formation.

The nanoparticles 102 may include one or more functional groups configured and formulated to increase an interaction between the nanoparticles 102 and at least one of the
15 subterranean formation, hydrocarbons within the subterranean formation, and other nanoparticles (if any) within the suspension 100. Functionalization of nanoparticles is described in, for example, U.S. Patent Application Publication 2014/0187449, titled “Functionalized Silicate Nanoparticle Composition, Removing and Exfoliating Asphaltenes with Same,” published July 3, 2014, the entire disclosure of which is hereby incorporated
20 herein by reference.

In some embodiments, the suspension 100 may include a mixture of nanoparticles 102 having different properties. For example, a mixture of nanoparticles 102 may include a portion of nanoparticles 102 with at least one type of functional group and at least another portion of nanoparticles 102 with at least another type of functional group. In
25 certain embodiments, each of the nanoparticles 102 may include more than one type of functional group.

In some embodiments, silica nanoparticles may be coated with graphene or another carbon-containing material by functionalizing outer surfaces of the silica nanoparticles with a charged species (*e.g.*, cationic functional groups or anionic functional groups) and then
30 immersing the functionalized silica nanoparticles in a solution containing an oppositely charged species, such as a graphene species having a charge opposite to the charged species on the surfaces of the silica nanoparticles.

In other embodiments, at least one type of nanoparticle (*e.g.*, containing silica 106) may be attached to at least another type of nanoparticle (*e.g.*, containing carbon 108) by at

least one covalent bond. Such nanoparticles may be bonded to each other by coupling reactions to form the nanoparticles 102.

In some embodiments, the nanoparticles 102 may exhibit a mean diameter from about 1 nm to about 100 nm, such as from about 5 nm to about 50 nm. For example, the nanoparticles 102 may exhibit a mean diameter of about 40 nm. The nanoparticles 102 may have any selected particle-size distribution (*i.e.*, any selected distribution of particle diameters). For example, the nanoparticles 102 may be monomodal (*i.e.*, having diameters clustered around a single mode), bi-modal, *etc.*

The nanoparticles 102 may be hydrophilic or may contain a hydrophilic material. For example, if the nanoparticles 102 have one or more functional groups attached thereto, a functional group may be selected to make the nanoparticles 102 more hydrophilic.

In addition to the nanoparticles 102, the suspension 100 may include at least one additive. By way of non-limiting example, the additive may be at least one of a surfactant, a catalyst, a dispersant, a scale inhibitor, a scale dissolver, a defoamer, a biocide, or another additive used in the well-service industry. The suspension 100 may be substantially homogeneous (*e.g.*, the nanoparticles 102 and the additive, if present, may be uniformly dispersed throughout the suspension 100), or may be heterogeneous (*e.g.*, the nanoparticles 102 and the additive, if present, may be non-uniformly dispersed throughout the suspension 100).

The suspension 100 may be formed by dispersing the nanoparticles 102 in the fluid. In some embodiments, the nanoparticles 102 may be formed by mixing solid carbon 108 with nanoparticles comprising silica 106 in a liquid medium, then evaporating the liquid. As the liquid evaporates, the nanoparticles 102 may form from the silica 106 and carbon 108. At least some of the nanoparticles 102 may include both silica 106 and carbon 106. The solid carbon 108 and the silica 106 may be mixed in an acidic or basic medium. For example, a basic medium may promote dispersion of particles due to interactions between hydroxyl groups of the solid with hydroxyl groups of the liquid. As the liquid evaporates, the carbon 108 may become bonded to the silica 106. In some embodiments, the carbon 108 and/or the silica 106 may be in the form of nanoparticles, and the nanoparticles may bond to one another during evaporation of the liquid to form the nanoparticles 102.

The nanoparticles 102 may then be dispersed in any appropriate fluid 104, such as those fluids conventionally used for enhanced oil recovery (EOR) processes. For example, the nanoparticles 102 may be dispersed in water, brine, steam, carbon dioxide, a light

hydrocarbon, (*e.g.*, propane, butane, *etc.*) an organic solvent (*e.g.*, methanol, ethanol, propanol, hexane, heptane, toluene, benzene, *etc.*), or any combination thereof.

In some embodiments, the nanoparticles 102 may be formed by chemical reaction. For example, reaction of functionalized carbon 108 with hydroxyl groups of silica 108 may
5 form nanoparticles 102 having covalent bonds. Functionalization of carbon 108 may be either hydrophilic or hydrophobic.

The nanoparticles 102 may be formulated to be compatible with other components (*e.g.*, materials, constituents, *etc.*) of the suspension 100. As used herein, the term
“compatible” means that a material does not impair the functionality of another material
10 used in conjunction therewith.

The suspension 100 may be formulated to include a concentration of the nanoparticles 102 ranging from about 10 ppm to about 10,000 ppm. For example, the suspension 100 may have a concentration of the nanoparticles 102 ranging from about 10
ppm to about 100 ppm, from about 100 ppm to about 500 ppm, from about 500 ppm to
15 about 1,000 ppm, from about 1,000 ppm to about 2,000 ppm, from about 2,000 ppm to about 5,000 ppm, or from about 5,000 ppm to about 10,000 ppm.

The suspension 100 may be introduced into a subterranean formation to detach a hydrocarbon material from surfaces of the subterranean formation and form a stabilized emulsion containing the hydrocarbon material. The suspension 100 may be provided into
20 the subterranean formation through conventional processes. For example, pressurized steam may be pumped into an injection well extending to a desired depth in the subterranean formation, and may infiltrate (*e.g.*, permeate, diffuse, *etc.*) into interstitial spaces of the subterranean formation. The extent to which the suspension 100 infiltrates the interstitial spaces of the subterranean formation at least partially depends on the
25 properties of the suspension 100 (*e.g.*, density, viscosity, material composition (*e.g.*, properties of the nanoparticles 102), *etc.*), and the hydrocarbon materials (*e.g.*, molecular weight, density, viscosity, *etc.*) contained within interstitial spaces of the subterranean formation, as well as on the nature of the hydrocarbons within the formation and formation porosity.

30 The nanoparticles 102 may be structured and formulated to facilitate formation of a stabilized emulsion containing a hydrocarbon material. For example, the nanoparticles 102 may be structured and formulated to gather (*e.g.*, agglomerate) at, adhere to, and/or absorb to interfaces of a hydrocarbon material and an aqueous material (*e.g.*, the fluid 104 or another fluid) to form an emulsion comprising units (*e.g.*, droplets) of one of the

hydrocarbon material and the aqueous material dispersed in the other of the hydrocarbon material and the aqueous material. The nanoparticles 102 may prevent the dispersed material (*e.g.*, the hydrocarbon material or the aqueous material) from coalescing, and may thus maintain the dispersed material as units throughout the other material.

5 The emulsion including the nanoparticles and hydrocarbons may include the same, a higher, or a lower concentration of the nanoparticles than the suspension 100. Furthermore, in some embodiments, the suspension 100 may be diluted or otherwise mixed with another fluid before injection into a well.

 Due to the particle-size distribution of the nanoparticles 102, the suspension 100
10 may be particularly useful for contacting hydrocarbons disposed within pores defined by the subterranean formation, particularly within nanopores (*i.e.*, pores having a maximum opening of about 1 micron or less). That is, the nanoparticles 102 and the fluid 104 may penetrate into pores and voids in the formation, and may promote separation of hydrocarbons from such pores and voids. Without being bound to any particular theory, it
15 appears that the relatively large specific surface area of nanoparticles 102, the ability of the nanoparticles 102 to travel into small volumes, and the possibility of better interaction with the oil in pore bodies and on pore surfaces improve the effectiveness of oil recovery from porous formations.

 The surface-to-volume ratio is higher for smaller particles than for larger particles.
20 Thus, results based on surface interactions can be achieved at relatively lower solids concentrations when the solids are provided as nanoparticles 102. This may assist in keeping the materials and process costs low.

 The silica 106 may help to “peel off” crude oil or other hydrocarbon-based material deposited on rock surfaces. A theory of “disjoining pressure,” which appears to at least
25 partially characterize this effect is described in, for example, U.S. Patent Application Publication 2010/0096139, titled “Method for Intervention Operations in Subsurface Hydrocarbon Formations,” published April 22, 2010, the entire disclosure of which is hereby incorporated herein by reference. The carbon 108 may help exfoliate bitumen and improve flow through throats of the pores. Stabilization of emulsion droplets by the
30 nanoparticles 102 appears to depend upon the particle-particle interactions. Thus, the combination of the carbon 108 and the silica 106 may simultaneously improve oil removal from rock surfaces and exfoliation.

 In some embodiments, the nanoparticles 102 may include both hydrophobic and hydrophilic domains. The hydrophilic domain may improve dispersion in water and

improve compatibility with water-based fluids. The hydrophobic domain may trap organic compounds and stabilize the organic compounds, allowing the organic compounds to be removed from the formation.

The process of extracting hydrocarbons from subsurface formations may include
5 flowing (*e.g.*, driving, sweeping, forcing, *etc.*) the stabilized emulsion from the subterranean formation to the surface. The nanoparticles 102 prevent the dispersed material from coalescing and enable substantial removal of hydrocarbons from the subterranean formation.

FIG. 2 is a simplified schematic showing how the suspension 100 shown in FIG. 1
10 may be used for recovering hydrocarbons from subterranean formations. A first well 202 may traverse subterranean formations 204 and 206, and may have openings at a formation 208. Portions 212 of the formation 208 may be optionally fractured and/or perforated. A second well 216 may traverse the subterranean formations 204 and 206, and may have openings at the formation 208. Portions 218 of the formation 406 may be
15 optionally fractured and/or perforated.

The suspension 100 (FIG. 1) may be introduced into the formation 208. A stabilized emulsion of the suspension 100 and hydrocarbons within the formation 208 may form, and may be removed from the formation 208 through the portions 218 thereof. The emulsion may travel up the second well 216 to a production facility 220. The production
20 facility 220 at the surface may include pumps, filters, storage tanks, and other equipment for recovering hydrocarbons. The production facility 220 may separate the recovered hydrocarbons from at least a portion of the suspension 100. For example, gases may be stored in a first tank 222, liquid hydrocarbons may be stored in a second tank 224, and the portion of the suspension 100 may be stored in a third tank 226. The suspension 100 may
25 be reintroduced to the formation 208 through the first well 202.

Once the hydrocarbons are removed from the subterranean formation, at least a portion of the emulsion may be destabilized to form distinct, immiscible phases including an aqueous phase and a hydrocarbon phase. One or more properties (*e.g.*, temperature, pH, material composition, pressure, *etc.*) of the stabilized emulsion or the aqueous phase may
30 be modified (*e.g.*, altered, changed) to at least partially destabilize the emulsion. For example, the pH of the aqueous phase may be modified to increase the solubility of the nanoparticles 102 within the aqueous phase and destabilize the emulsion, forming distinct, immiscible phases. In some embodiments, the aqueous phase may be separated from the hydrocarbon phase by decreasing a pH of the emulsion. The pH of the emulsion may be

decreased by adding hydrochloric acid, phosphoric acid, acetic acid, another acid, or combinations thereof to the emulsion.

A demulsifier may be added to the emulsion to destabilize the emulsion and form distinct, immiscible phases including an aqueous phase and the hydrocarbon phase. In some embodiments, the emulsion is destabilized by adjusting the pH of at least one of the aqueous phase and the emulsion and by adding a demulsifier to the emulsion. In some embodiments, at least a portion of the nanoparticles 102 may be recovered and recycled for use in subsequent operations.

10

EXAMPLES

Example 1: Oil recovery from Canadian Oil Sand from Athabasca

Commercially available silica nanoparticle dispersions were obtained from Nissan Chemical America Corporation, of Houston, Texas. The silica nanoparticles had a mean particle diameter from about 5 nm to about 40 nm, and the particles were dispersed in water (product numbers for each sample are shown in Table 1, below). The silica nanoparticles were coated with carbon quantum dots by mixing carbon particles into the dispersions. The liquid phase was then evaporated, leaving particles of silica and carbon.

The particles were redispersed in deionized water and mixed with Canadian oil sands in glass vials. The vials were heated to approximately 80°C for 10 days, and the color of the liquid phase was observed (with darker color corresponding to more oil removed from the sand). The liquid phase was then removed and the sand was dried and analyzed with an optical microscope (with lighter sand color corresponding to more oil removed from the sand). The sand was analyzed by thermogravimetric analysis (TGA) to determine differences in materials that decompose at elevated temperatures. Table 1 shows the results of the tests, with oil recovery determined by the change in color of the liquid phase, the change in color of the dried sand, and the TGA curves.

Table 1

Sample #	Nissan Chemical America product number	Mean particle diameter of silica (before adding carbon)	Oil recovery
Water	n/a	n/a	No
1	250624	5 nm	Yes
2	210818	8 nm	Yes
3	240707	40 nm	Yes
4	131204	12 nm	Yes
5	LB130410	50 nm	Yes

Example 2: Oil Dispersion

A commercially available silica nanoparticle dispersion was obtained from Nissan Chemical America Corporation, of Houston, Texas (240707). The silica nanoparticles had a mean particle diameter of about 40 nm, and the particles were dispersed in water. One portion of the silica nanoparticles was coated with carbon quantum dots by mixing carbon particles into the dispersions. The liquid phase was then evaporated, leaving particles of silica and carbon. The particles were redispersed in deionized water. Another portion of the silica particles was used without the carbon modification.

Both portions were mixed with oil in glass vials. The vials were heated to approximately 60°C, and the color and consistency of the liquid phases were observed (with darker color corresponding to more oil in a phase). Table 2 shows the results of the tests, with oil dispersion determined by the change in color of the liquid phases and the separation of the phases.

15

Table 2

Sample #	Composition of particles	Oil dispersion
Water	n/a	No—water phase remained almost entirely clear while oil phase was dark
6	Silica only	Some—two phases were present and water phase was lighter than oil phase (but appreciably darker than the control sample)
7	Silica and carbon	Yes—the oil and water appeared to form a single liquid phase

Additional non limiting example embodiments of the disclosure are described below.

Embodiment 1: A suspension for removing hydrocarbons from a subterranean formation, comprising a fluid comprising at least one of water, brine, steam, carbon dioxide, a light hydrocarbon, and an organic solvent; and a plurality of nanoparticles dispersed with the fluid. At least some nanoparticles of the plurality comprise both silica and carbon.

Embodiment 2: The suspension of Embodiment 1, wherein the at least some nanoparticles of the plurality comprise a silica nanoparticle attached to at least one material selected from the group consisting of carbon nanodots, graphene, graphene oxide, carbon nanotubes, and functionalized carbon nanotubes.

Embodiment 3: The suspension of Embodiment 1 or Embodiment 2, wherein the at least some nanoparticles of the plurality of nanoparticles exhibit a mean diameter from about 1 nm to about 100 nm.

Embodiment 4: The suspension of any of Embodiments 1 through 3, wherein the at least some nanoparticles of the plurality are hydrophilic.

Embodiment 5: The suspension of any of Embodiments 1 through 4, wherein the at least some nanoparticles of the plurality comprise silica and carbon bonded by hydroxyl groups.

Embodiment 6: The suspension of any of Embodiments 1 through 5, further comprising a surfactant.

Embodiment 7: The suspension of any of Embodiments 1 through 6, wherein at least some nanoparticles of the plurality comprise carbon coated with silica.

Embodiment 8: The suspension of any of Embodiments 1 through 7, wherein at least one of the silica and the carbon is functionalized with at least one functional group.

Embodiment 9: The suspension of any of Embodiments 1 through 8, wherein the silica comprises at least one material selected from the group consisting of colloidal silica.

Embodiment 10: The suspension of any of Embodiments 1 through 9, wherein the fluid comprises a basic medium.

Embodiment 11: The suspension of any of Embodiments 1 through 10, wherein the silica and carbon are attached to one another by chemical bonds.

Embodiment 12: The suspension of any of Embodiments 1 through 11, wherein the silica and carbon are attached to one another by physical bonds.

Embodiment 13: A method of recovering a hydrocarbon material, the method comprising introducing the suspension of any of Embodiments 1 through 12 into a subterranean formation containing hydrocarbons; forming a stabilized emulsion of the suspension and the hydrocarbons within the subterranean formation; and removing the emulsion from the subterranean formation.

Embodiment 14: The method of Embodiment 13, further comprising introducing the at least some nanoparticles into voids defined by the subterranean formation.

Embodiment 15: The method of Embodiment 13 or Embodiment 14, wherein forming a stabilized emulsion of the suspension and the hydrocarbons within the subterranean formation comprises contacting hydrocarbons within the subterranean formation with the suspension to form an emulsion comprising the nanoparticles, an aqueous phase, and a hydrocarbon phase dispersed within the aqueous phase.

Embodiment 16: The method of Embodiment 15, wherein contacting the subterranean formation with the suspension comprises contacting hydrocarbons within nanopores of the subterranean formation.

Embodiment 17: The method of Embodiment 16, further comprising:
5 transporting the emulsion to a surface of the subterranean formation; and separating hydrocarbons from the emulsion.

Embodiment 18: A method comprising forming a plurality of nanoparticles to comprise silica and carbon, and dispersing the plurality of nanoparticles with a fluid to form a suspension comprising the nanoparticles.

10 Embodiment 19: The method of Embodiment 18, further comprising introducing the suspension into a subterranean formation and contacting hydrocarbons within the subterranean formation with the suspension to form an emulsion comprising the nanoparticles, an aqueous phase, and a hydrocarbon phase dispersed within the aqueous phase.

15 Embodiment 20: The method of Embodiment 19, wherein contacting the subterranean formation with the suspension comprises contacting hydrocarbons within nanopores of the subterranean formation.

Embodiment 21: The method of Embodiment 19 or Embodiment 20, further comprising transporting the emulsion to a surface of the subterranean formation and
20 separating hydrocarbons from the emulsion.

Embodiment 22: The method of any of Embodiments 18 through 21, wherein forming a plurality of nanoparticles comprises forming nanoparticles comprising silica and at least one material selected from the group consisting of carbon nanodots, graphene, graphene oxide, carbon nanotubes, and functionalized carbon nanotubes.

25 Embodiment 23: The method of any of Embodiments 18 through 22, wherein forming a plurality of nanoparticles comprises reacting carbon with nanoparticles comprising silica.

Embodiment 24: The method of Embodiment 23, wherein reacting carbon with nanoparticles comprising silica comprises reacting carbon with nanoparticles comprising
30 silica in a liquid medium and evaporating the liquid.

Embodiment 25: The method of Embodiment 24, wherein reacting carbon with nanoparticles comprising silica in a liquid medium comprises reacting carbon with nanoparticles comprising silica in a basic medium.

Embodiment 26: The method of any of Embodiments 18 through 25, wherein forming a plurality of nanoparticles comprises bonding carbon to silica.

Embodiment 27: The method of Embodiment 26, wherein bonding carbon to silica comprises bonding nanoparticles comprising carbon to nanoparticles comprising silica.

5 Embodiment 28: A method of recovering a hydrocarbon material, the method comprising introducing a suspension into a subterranean formation containing hydrocarbons, forming a stabilized emulsion of the suspension and the hydrocarbons within the subterranean formation; and removing the emulsion from the subterranean formation. The suspension comprises a plurality of nanoparticles, and at least some nanoparticles of
10 the plurality comprise silica and carbon.

Embodiment 29: The method of Embodiment 28, wherein introducing a suspension into a subterranean formation comprises introducing the at least some nanoparticles comprising silica and at least one material selected from the group consisting of carbon nanodots, graphene, graphene oxide, carbon nanotubes, and functionalized carbon
15 nanotubes.

Embodiment 30: The method of Embodiment 28 or Embodiment 29, wherein introducing a suspension into a subterranean formation comprises introducing the at least some nanoparticles having a mean diameter from about 5 nm to about 50 nm.

Embodiment 31: The method of any of Embodiments 28 through 30, further
20 comprising introducing the at least some nanoparticles into voids defined by the subterranean formation.

While the present disclosure has been described herein with respect to certain illustrated embodiments, those of ordinary skill in the art will recognize and appreciate that it is not so limited. Rather, many additions, deletions, and modifications to the illustrated
25 embodiments may be made without departing from the scope of the invention as hereinafter claimed, including legal equivalents thereof. In addition, features from one embodiment may be combined with features of another embodiment while still being encompassed within the scope of the disclosure as contemplated by the inventors. Further, embodiments of the disclosure have utility with different and various particle types and
30 formulations.

CLAIMS

What is claimed is:

- 5 1. A suspension for removing hydrocarbons from a subterranean formation, the suspension comprising:
a fluid comprising at least one of water, brine, steam, carbon dioxide, a light hydrocarbon,
and an organic solvent; and
a plurality of nanoparticles dispersed with the fluid, at least some nanoparticles of the
10 plurality comprising both silica and carbon.
2. The suspension of claim 1, wherein the at least some nanoparticles of the plurality comprise a silica nanoparticle attached to at least one material selected from the group consisting of carbon nanodots, graphene, graphene oxide, carbon nanotubes, and
15 functionalized carbon nanotubes.
3. The suspension of claim 1, wherein the at least some nanoparticles of the plurality of nanoparticles exhibit a mean diameter from about 1 nm to about 100 nm.
- 20 4. The suspension of any of claims 1 through 3, wherein the at least some nanoparticles of the plurality are hydrophilic.
5. The suspension of any of claims 1 through 3, wherein the at least some nanoparticles of the plurality comprise silica and carbon bonded by hydroxyl groups.
25 6. The suspension of any of claims 1 through 3, further comprising a surfactant.
7. The suspension of any of claims 1 through 3, wherein at least some
30 nanoparticles of the plurality comprise carbon coated with silica.
8. The suspension of any of claims 1 through 3, wherein at least one of the silica and the carbon is functionalized with at least one functional group.

9. The suspension of any of claims 1 through 3, wherein the silica comprises at least one material selected from the group consisting of colloidal silica.

10. The suspension of any of claims 1 through 3, wherein the fluid comprises a
5 basic medium.

11. The suspension of any of claims 1 through 3, wherein the silica and carbon are attached to one another by chemical bonds.

10 12. The suspension of any of claims 1 through 3, wherein the silica and carbon are attached to one another by physical bonds.

13. A method of recovering a hydrocarbon material, the method comprising:
introducing the suspension of any of claims 1 through 3 into a subterranean formation
15 containing hydrocarbons;
forming a stabilized emulsion of the suspension and the hydrocarbons within the
subterranean formation; and
removing the emulsion from the subterranean formation.

20 14. The method of claim 13, further comprising introducing the at least some nanoparticles into voids defined by the subterranean formation.

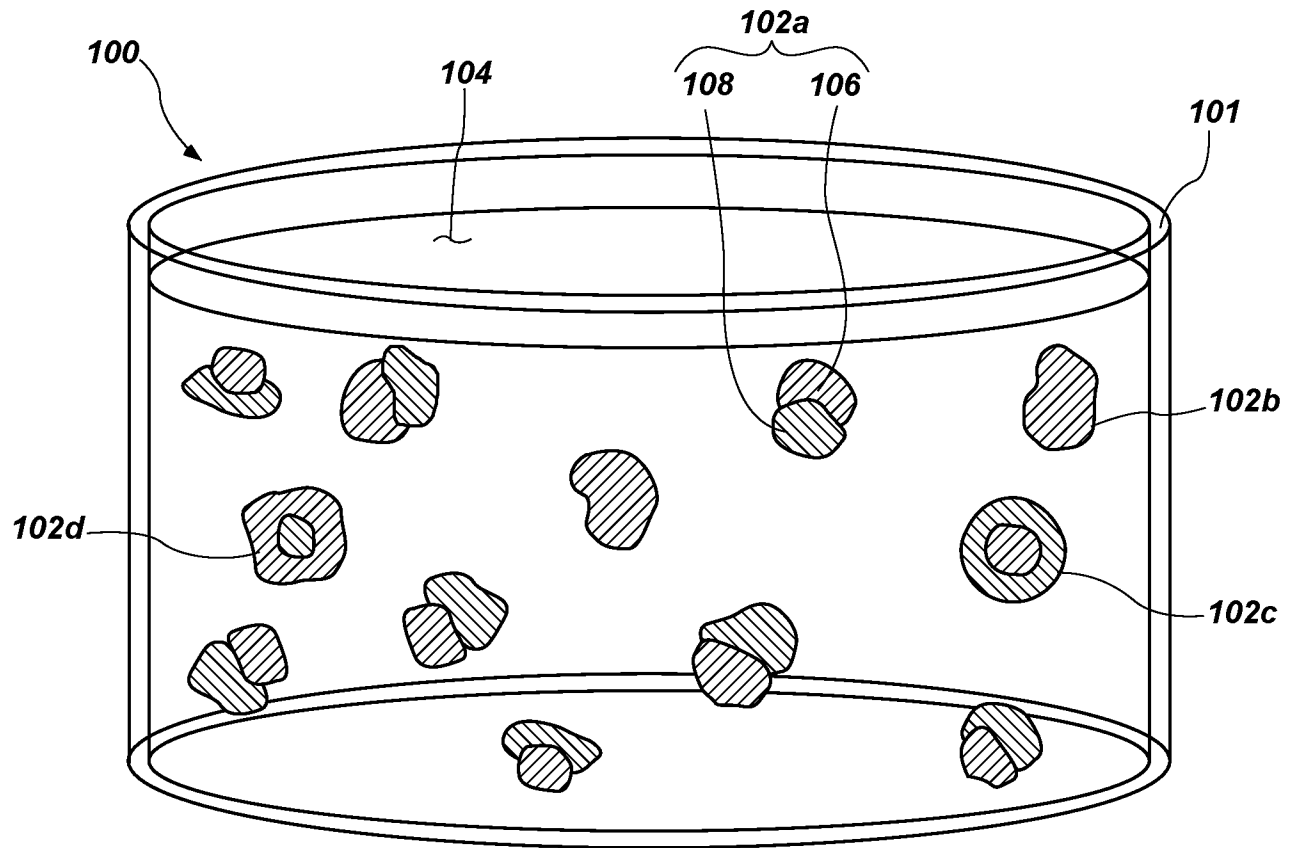
15. The method of claim 13, wherein forming a stabilized emulsion of the
suspension and the hydrocarbons within the subterranean formation comprises contacting
25 hydrocarbons within the subterranean formation with the suspension to form an emulsion
comprising the nanoparticles, an aqueous phase, and a hydrocarbon phase dispersed within
the aqueous phase.

16. The method of claim 15, wherein contacting the subterranean formation
30 with the suspension comprises contacting hydrocarbons within nanopores of the
subterranean formation.

17. The method of claim 16, further comprising:
transporting the emulsion to a surface of the subterranean formation; and
separating hydrocarbons from the emulsion.

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**FIG. 1**

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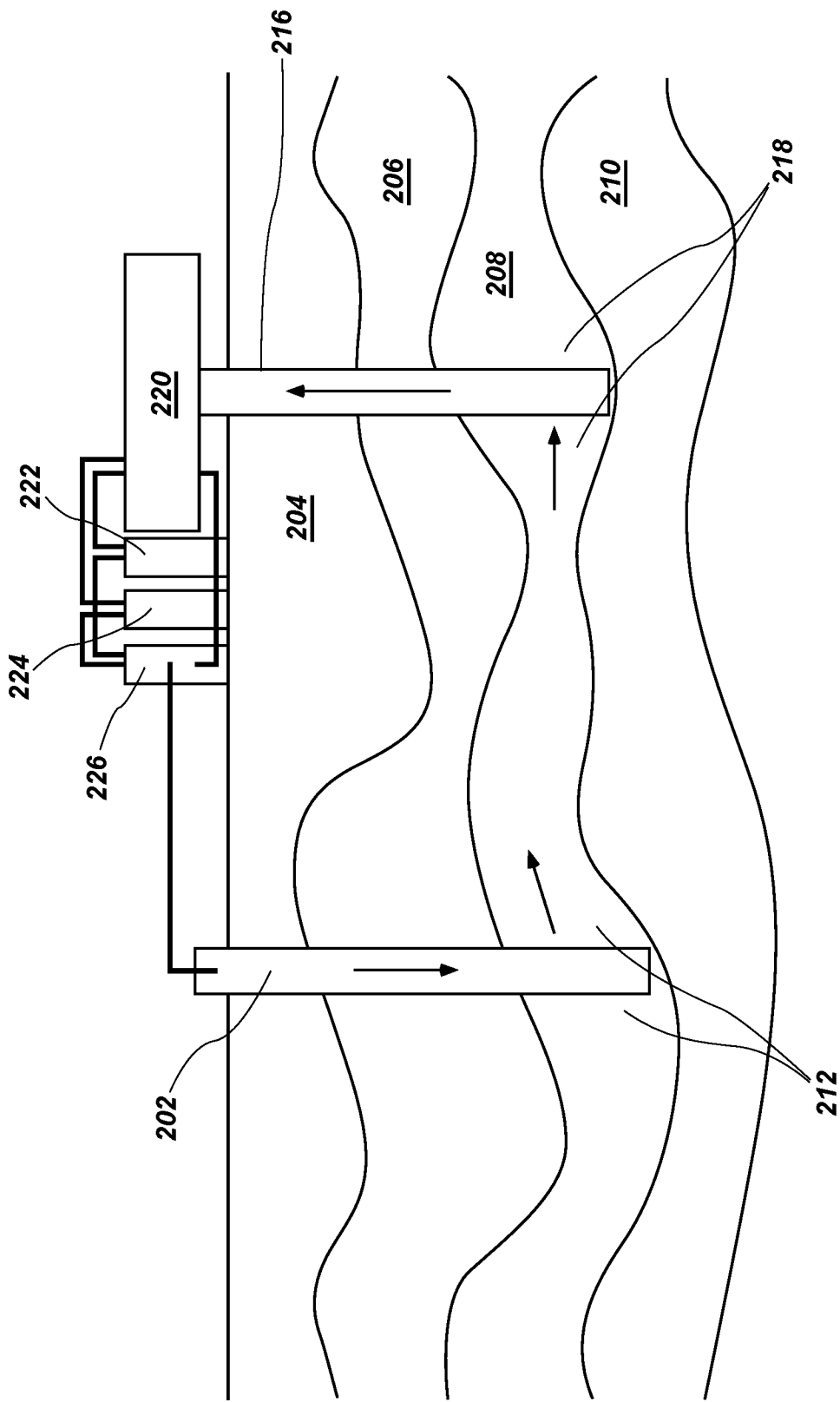


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/037516**A. CLASSIFICATION OF SUBJECT MATTER****C09K 8/58(2006.01)I, C09K 8/84(2006.01)I, C09K 8/86(2006.01)I, C09K 8/26(2006.01)I**

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)

C09K 8/58; E21B 1/00; C09K 8/035; E21B 43/22; E21B 43/16; C07C 53/00; C09K 8/84; C09K 8/86; C09K 8/26

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: suspension, hydrocarbon, nanoparticles, silica, carbon, fluid

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2013-0045897 A1 (CHAKRABORTY, S. et al.) 21 February 2013 See paragraphs [0012], [0022] and [0025]; and claims 1-18.	1-17
A	US 2003-0220204 A1 (BARAN, JR., J. R. et al.) 27 November 2003 See claims 1-6.	1-17
A	US 2010-0243248 A1 (GOLOMB, D. S. et al.) 30 September 2010 See claims 1-12.	1-17
A	US 2013-0341022 A1 (NGUYEN, P. D. et al.) 26 December 2013 See claims 1-12.	1-17
PX	WO 2016-064568 A1 (BAKER HUGHES INCORPORATED) 28 April 2016 See page 4, lines 6-12; page 12, lines 14-22; and claims 1-15.	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"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

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Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

Facsimile No. +82-42-481-8578

Authorized officer

CHO, KI YUN

Telephone No. +82-42-481-5655



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/037516

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WO 2016-064568 A1	28/04/2016	None	