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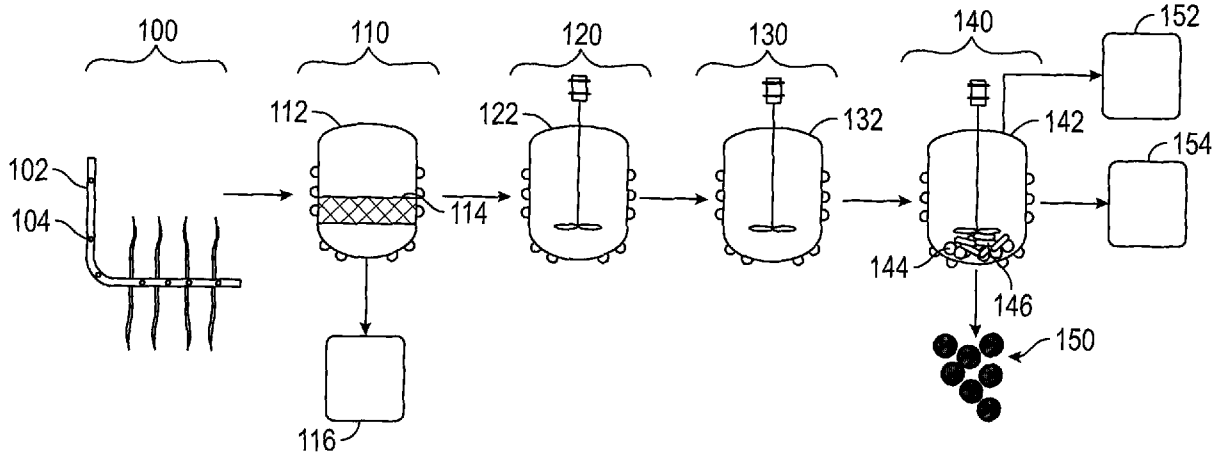


FIG. 1

(57) Abstract: A method for generating hydrogen includes oxidizing a natural polysaccharide included in a fracturing fluid in a subterranean formation, extracting the fracturing fluid from the subterranean formation, purifying the fracturing fluid, and treating the fracturing fluid. The method further includes introducing at least one additive into the fracturing fluid, introducing at least one microbial biomass into the fracturing fluid, and biodegrading the natural polysaccharide in the fracturing fluid with the at least one microbial biomass to produce hydrogen, reaction products and non-degrading products. A fluid composition includes a natural polysaccharide, at least one microbial biomass, an oxidizing agent, at least one additive, and a fluid medium. The microbial biomass includes a hydrogen-producing bacteria. A method for producing a fluid composition includes sequentially adding an oxidizing agent, an additive, and a microbial biomass to a source fracturing fluid. The source fracturing fluid includes a natural polysaccharide and a fluid medium.

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FLUID COMPOSITION AND METHOD FOR GENERATING HYDROGEN FROM FLOW-BACK HYDRAULIC FRACTURING FLUID

BACKGROUND

[0001] Hydraulic fracturing ("fracking") is a stimulation technique of oil and gas wells used to increase the permeability and conductivity of hydrocarbon reservoirs. In fracking, a fracturing fluid is introduced to the reservoirs through the wells to generate and maintain formation fractures, thereby increasing the amount of extracted oil and gas. The fracturing fluid generally includes water, a proppant, a viscosity modifier, and additional components to modify various properties of the fracturing fluid. A proppant is a solid material designed to be embedded in the formed fractures to keep the fractures open. In order to prevent clogging and settling, the proppant is suspended in the fracturing fluid, which may be accomplished by including a viscosity modifier to adjust the viscosity of the fracturing fluid to an appropriate range.

[0002] The viscosity modifier used to modify the fracturing fluid viscosity can be a polysaccharide derived from natural sources, and may be in a form of a gel. Once the proppant is delivered to the fractures, the viscosity modifier in the fracturing fluid is broken down to improve the flow of oil and gas. A portion of the fragmented viscosity modifier, such as 10 to 75%, may be recovered with the fracturing fluid, while the rest may remain in the reservoir. However, the fragmented viscosity modifier that is recovered with the fracturing fluid and that remains in the reservoir generally provide no additional purpose. Accordingly, there exists an opportunity to use the viscosity modifier as the source material to produce valuable products.

SUMMARY

[0003] This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.

[0004] In one aspect, embodiments disclosed herein relate to a method for generating hydrogen. The method includes oxidizing a natural polysaccharide included in a fracturing fluid in a subterranean formation, extracting the fracturing fluid from the subterranean formation, purifying the fracturing fluid, and treating the fracturing fluid. The method further includes introducing at least one additive into the fracturing fluid, introducing at least one microbial biomass into the fracturing fluid, and biodegrading the natural polysaccharide in the fracturing fluid with the at least one microbial biomass to produce hydrogen, reaction products and non-degrading products.

[0005] In another aspect, embodiments disclosed herein relate to a fluid composition including a natural polysaccharide, at least one microbial biomass, an oxidizing agent, at least one additive, and a fluid medium. The at least one microbial biomass includes a hydrogen-producing bacteria.

[0006] In another aspect, embodiments disclosed herein relate to a method for producing a fluid composition. The method includes sequentially adding an oxidizing agent, an additive, and a microbial biomass to a source fracturing fluid. The source fracturing fluid includes a natural polysaccharide and a fluid medium.

[0007] Other aspects and advantages of the claimed subject matter will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF DRAWINGS

[0008] FIG. 1 is a schematic diagram illustrating a method for generating hydrogen from a natural polysaccharide in accordance with one or more embodiments.

[0009] FIG. 2 is a schematic diagram illustrating a method for generating hydrogen from a natural polysaccharide in accordance with one or more embodiments.

DETAILED DESCRIPTION

FLUID COMPOSITION

[0010] In one aspect, embodiments disclosed herein relate to a fluid composition for biologically generating hydrogen. In one or more embodiments, the fluid composition

includes a natural polysaccharide, a microbial biomass, an oxidizer, an additive, and a fluid medium. The fluid composition may further include a modifier comprising at least one of biocide, neutralizing agent, and fragmentation agent.

[0011] In the present disclosure, a "microbial biomass" refers to living microorganisms capable of producing hydrogen from a natural polysaccharide, degrading a natural polysaccharide, or a combination thereof. The microbial biomass may be bacteria or fungi, and may be naturally-occurring microorganisms or artificially-synthesized microorganisms.

[0012] In one or more embodiments, the fluid composition includes a natural polysaccharide, a microbial biomass, an oxidizer, an additive, and a fluid medium. The fluid composition may further include a modifier. The fluid composition may be used to produce hydrogen and other reaction products through the degradation of the natural polysaccharide by the microbial biomass. In one or more embodiments, the fluid composition is produced from a fracturing fluid, such as a source fracturing fluid, as a base material. A "source fracturing fluid" refers to a fluid that is used or can be used in a hydraulic fracturing operation. A source fracturing fluid may include a viscosity modifier such as a natural polysaccharide, a fluid medium such as aqueous fluid including water, a proppant, and additional components known in the art, as described in the subsequent section.

[0013] In one or more embodiments, the fluid composition includes a natural polysaccharide. In the present disclosure, a "natural polysaccharide" refers to polysaccharides obtained from a biological source, such as plants, or microbes. Natural polysaccharides may be included in the fracturing fluid in order to increase the viscosity of the fracturing fluid. The natural polysaccharides may be guar-based fluids or cellulose-based fluids. Non-limiting examples of the natural polysaccharides include xanthan gum, guar gum, glycol, starch, hydroxyethyl cellulose, carboxymethyl cellulose, cellulose, gum Arabic, gum ghatti, karaya gum, locust bean gum, hydroxypropyl guar, maleic anhydride guar gum, sulfonated hydroxypropyl guar gum, tragacanth gum, welan gum, alginate,

agarose, gelatin, carboxymethyl hydroxypropyl guar, their derivatives and combinations thereof. The natural polysaccharide in the fracturing fluid may be in a form of a gel.

[0014] In one or more embodiments, the fluid composition includes a microbial biomass. The microbial biomass in the composition may degrade natural polysaccharides, in their original state, or fragmented state, into smaller molecules including hydrogen and other reaction products, such as acetic acid, butyric acid and ethanol.

[0015] The microbial biomass may be an aerobic strain, an anaerobic strain, or combinations thereof. In the present disclosure a "strain" refers to a type of microorganism, which may be bacteria or fungi.

[0016] As an example, in case both aerobic and anaerobic strains are used as the microbial biomass, the aerobic strain may be used to fragment the natural polysaccharides, while the anaerobic strain may be used to biodegrade the fragmented natural polysaccharides into hydrogen, reaction products and non-degrading products. In such a case, the aerobic strain may be present in a separate vessel than the anaerobic strain.

[0017] The microbial biomass may be a dark-fermentative strain, a photo-fermentative strain, or combinations thereof.

[0018] In one or more embodiments, the microbial biomass in the fluid composition includes hydrogen-producing bacteria. The hydrogen-producing bacteria may be any bacteria capable of producing hydrogen from the natural polysaccharides. Non-limiting examples of the hydrogen-producing bacteria include bacteria from the classes including *Clostridia*, *Gammaproteobacteria*, *Bacilli*, *Synergistia*, *Thermotogae*, *Alphaproteobacteria*, and combinations thereof.

[0019] In one or more embodiments, the microbial biomass in the fracturing fluid composition includes a degrader strain of natural polysaccharides. The degrader strain of natural polysaccharides may include a bacterial degrader, a fungal degrader of natural polysaccharides and combinations thereof. Non-limiting examples of the bacterial degrader include bacteria from the classes and phylum including *Actinobacteria*, *Bacteroidetes*, *Alphaproteobacteria*, *Betaproteobacteria*, *and Gammaproteobacteria*,

Clostridia, Bacilli, Epsilonproteobacteria, Bacteroidia, and *Fusobacteriia.* Non-limiting examples of the fungal degrader include fungi from *Basidiomycetes.*

[0020] In one or more embodiments, the microbial biomass in the fluid composition may be one type of the microbial biomass as described above. The fluid composition may include a plurality of the microbial biomass strains such as up to 4 strains. In one or more embodiments, the microbial biomass in the fluid composition includes any of the combinations of the microbial biomass as described above.

[0021] In one or more embodiments, the microbial biomass is immobilized onto a carrier. Immobilization of the microbial biomass may prevent microbial biomass cell losses during the biodegradation process or the separation of the microbial biomass from the generated products, which may improve the production efficiency of the generated products including hydrogen. The immobilization may occur on the outer surface of the carrier, inside of the carrier, if the carrier is porous or contains cavities/channels, or combinations thereof.

[0022] In one or more embodiments, a ratio of the weight of the microbial biomass immobilized onto a carrier, to the weight of the carrier is in in a range of from about 0.2 (e.g., 0.2 g of microbial biomass is immobilized onto 1.0 g of carrier) to about 2.0 (2.0 g of microbial biomass is immobilized onto 1.0 g of carrier), such as in a range of from a lower limit selected from any one of 0.2, 0.3, 0.4 and 0.5, to an upper limit selected from any one of 1.5, 1.6, 1.7, 1.8, 1.9 and 2.0, where any lower limit may be paired with any upper limit. 1 g of microbial biomass may contain at least 10^4 to 10^6 microbial biomass cells.

[0023] A carrier may be any material to which the microbial biomass can be attached and immobilized. In one or more embodiments, the carrier is a carbon-based carrier including coal-based carriers, such as biochar. Biochar refers to a carbon-rich solid product obtained by pyrolysis of organic matter, or biomass. The carrier may be derived from waste products generated in oil and gas production, or may be produced from non-degraded products generated in the presently-disclosed method for producing hydrogen, as described in the subsequent section.

[0024] In one or more embodiments, the microbial biomass may be immobilized onto the carrier through suitable processes such as chemical fixation, impregnation, and electrostatic immobilization.

[0025] In one or more embodiments, the amount of the microbial biomass in the fluid composition is in a range of from about 10^3 to about 10^9 CFU/mL, where CFU stands for "colony-forming units." The amount of microbial biomass in the fluid composition may be in a range of from a lower limit selected from any one of 10^3, 10^4, 10^5, 10^6 and 10^7 CFU/mL, to an upper limit selected from any one of 10^8 and 10^9 CFU/mL, where any lower limit may be paired with any upper limit.

[0026] In one or more embodiments, the fluid composition includes an oxidizer. The oxidizer may degrade the natural polysaccharide into oligomers and/or smaller fragments of simple sugars (monomers) such as glucose, mannose, and galactose, along with other molecules. In one or more embodiments, the oxidizer in the fluid composition includes a chemical oxidizer such as peroxydisulfate salts (persulfates), and a biological oxidizer such as enzymes. The oxidizer may be an encapsulated oxidizer which remains inactive and incapable of degrading the natural polysaccharide until it is activated (i.e., the encapsulation is broken/degraded). The encapsulated oxidizer may be activated chemically, physically, by time, or combinations thereof. A chemically-activated encapsulated oxidizer may include an encapsulant which degrades upon introduction of a specific chemical, which may be introduced to the fracturing fluid when the activation of the oxidizer is required. The encapsulant of a physically-activated encapsulated oxidizer may degrade upon exposure to the change in the external environment, such as a temperature or pressure change. A time-activated encapsulated oxidizer may include an encapsulant which degrades or dissolves at a specific rate such that the oxidizer becomes active after a predetermined time period.

[0027] Examples of a physically-activated encapsulated oxidizer may include, but are not limited to, an oxidizer encapsulated with a urea formaldehyde resin, and an oxidizer encapsulated in alginate beads. The oxidizer encapsulated with urea formaldehyde resin may be activated by an elevated temperature. The oxidizer encapsulated in alginate beads

may be activated by rupturing the encapsulant mechanically, such as by applying a force or pressure.

[0028] The oxidizer encapsulated in alginate beads may also be an exemplary encapsulated oxidizer that is activated by time (by diffusion).

[0029] An example of a chemically-activated encapsulated oxidizer may include, but is not limited to, an oxidizer encapsulated with poly(methacrylic anhydride-co-ethylene glycol dimethacrylate).

[0030] In one or more embodiments, the amount of the oxidizer in the fluid composition is about 2 wt% or less, or in a range from a lower limit selected from any one of 0.001, 0.01, and 0.1 wt%, to an upper limit selected from any one of 1, 1.5 and 2 wt %, where any lower limit may be paired with any upper limit.

[0031] In one or more embodiments, the fluid composition includes additives. The additives are used to adjust the properties of the fluid composition in order to provide suitable conditions for the growth of the microbial biomass. The types and amounts of additives may be adjusted based on the properties of the fluid composition and the types of microbial biomass used in the composition.

[0032] In one or more embodiments, the additive in the fluid composition includes nutrients (such as compounds containing nitrogen, phosphorus, or combinations thereof), proteins, glycoproteins, minerals, hydrolyzed proteins, peptides, polysaccharides, oligosaccharide, disaccharides, monosaccharides, fatty acids, ethers of fatty acids, their derivatives, combinations thereof, salts, pH modifier, enzymes, vitamins, growth factor, antibiotics, buffer salts, divalent salts, nitrogen salts, heat resistant proteins, enzyme stabilizers, and combinations thereof.

[0033] In one or more embodiments, the amount of the additive in the fluid composition is about 25 wt% or less, or in a range from a lower limit selected from any one of 0.01, 0.1 1, and 5 wt%, to an upper limit selected from any one of 10, 15, 20 and 25 wt %, where any lower limit may be paired with any upper limit.

[0034] In one or more embodiments, the fluid composition includes modifiers. The modifier in the fluid composition may include a biocide, a neutralizing agent for neutralizing (inactivating) biocides, and a fragmentation agent for fragmenting natural polysaccharide, such as bacterial and fungal enzymes.

[0035] In one or more embodiments, examples of the biocide include, but are not limited to, amines, such as quaternary and primary amines, acids, bases, glutaraldehyde, tetrakis hydroxymethyl phosphonium sulfate (THPS), and combinations thereof.

[0036] In one or more embodiments, examples of the neutralizing agent include, but are not limited to, acids (in case the biocide included in the composition is bases and/or amines), and bases (in case the biocide included in the composition is acids and/or THPS).

[0037] In one or more embodiments, examples of the fragmentation agent include, but are not limited to, enzyme, hydrogen peroxide, potassium persulfate, and ammonium persulfate.

[0038] The biocide may be included in the source fracturing fluid, or subsequently added after the fracking operation is complete in order to eliminate undesired microorganisms such as methanogens and hydrogen-consuming bacteria. However, the biocide included in the fluid composition may be in a neutralized (inactivated) form such that the growth of the added microbial biomass is not negatively affected by the biocide and prevent poor viability of the microbial biomass. In other words, the biocide comprised in the fluid composition may be a neutralized biocide neutralized by a neutralizing agent. The neutralizing agent may be added to neutralize the biocide prior to adding the microbial biomass.

[0039] In one or more embodiments, the amount of the modifiers in the fluid composition is about 2 wt% or less, or in a range from a lower limit selected from any one of 0.001, 0.01, and 0.1 wt%, to an upper limit selected from any one of 1, 1.5 and 2 wt %, where any lower limit may be paired with any upper limit.

[0040] In one or more embodiments, the fluid composition includes a fluid medium. The fluid medium in the fluid composition may be a fluid included in the source fracturing fluid, and may be an aqueous fluid including water.

[0041] In one or more embodiments, the fluid composition may further include other components. Examples of such additional components may include, but are not limited to, corrosion inhibitors, friction reducers, non-emulsification agents, anti-sludging agents, lost circulation materials, scale inhibitors, surfactants, clay stabilizers, paraffin inhibitors, asphaltene inhibitors, penetrating agents, clay control additives, reducers, oxygen scavengers, emulsifiers, foamers, gases, and combinations thereof.

[0042] In one or more embodiments, the fluid composition has a pH in a range of from about 5.5 to about 7.5, such as in a range having a lower limit selected from any one of 5.5, 5.6, 5.7, 5.8, 5.9 and 6.0 to an upper limit selected from any one of 7.0, 7.1, 7.2, 7.3, 7.4 and 7.5, where any lower limit may be paired with any upper limit.

[0043] In one or more embodiments, the fluid composition has a viscosity in a range of from about 10 to about 20 cP, when the fluid composition has a temperature in a range of from about 20 to about 40 °C.

METHOD FOR PRODUCING A FLUID COMPOSITION

[0044] In one aspect, embodiments disclosed herein relate to a method for producing the previously described fluid composition. In one or more embodiments, the method includes adding an oxidizing agent, an additive, and a microbial biomass to the source fracturing fluid in the sequential order. The method may further include adding a modifier prior to adding the additive. The source fracturing fluid may include a natural polysaccharide and a fluid medium. In other words, the method may include adding an oxidizing agent to the source fracturing fluid to degrade the natural polysaccharide included in the source fracturing fluid, then adding an additive such that the mixture is adjusted to have suitable conditions for the growth of the microbial biomass. Subsequently, a microbial biomass is added to biodegrade the natural polysaccharide, which may be a fragmented natural polysaccharide as a result of the addition of the oxidizing agent, into smaller molecules including hydrogen and reaction products.

[0045] The method may further include adding a modifier prior to the addition of the additive. The modifier may include a biocide, neutralizing agent and a fragmentation agent. The addition of the biocide may be conducted if the source fracturing fluid contains undesirable microorganisms. In case a biocide is added as the modifier, the method may further include adding a neutralizing agent after the biocide is added, in order to prevent the biocide from adversely affecting the microbial biomass.

[0046] A portion of the sequential addition of the aforementioned components may be conducted in the same vessel. For example, addition of the additive and the modifiers may be conducted in the same vessel, and the mixture may be then transferred to another vessel prior to adding the microbial biomass. In one or more embodiments, addition of the components is conducted separately in different vessels.

METHOD FOR PRODUCING HYDROGEN

[0047] In one aspect, embodiments disclosed herein relate to a method for generating hydrogen from a natural polysaccharide. In one or more embodiments, the method for generating hydrogen includes oxidizing a natural polysaccharide included in a fracturing fluid in a subterranean formation, extracting the fracturing fluid from the subterranean formation, purifying the fracturing fluid, treating the fracturing fluid, adjusting the fracturing fluid, biodegrading the natural polysaccharide in the fracturing fluid with a microbial biomass to produce hydrogen and reaction products. The method may provide sustainable hydrogen production by reusing the natural polysaccharide in the fracturing fluids.

[0048] FIG. 1 is a schematic diagram illustrating the method for generating hydrogen from a natural polysaccharide. In step 100, a natural polysaccharide 104 included in a fracturing fluid 102 is oxidized in a subterranean formation to degrade and fragment the natural polysaccharide 104. As shown in FIG. 1, the fracturing fluid 102 including the natural polysaccharide 104 to be oxidized is located in a subterranean formation. In the present disclosure, "located in a subterranean formation" means that the substance in question is located in or in the vicinity of any portion of the subsurface structure which includes, but are not limited to, a rock formation, a wellbore, a reservoir, and a cavity. The oxidation of

the natural polysaccharide 104 is conducted by injecting an oxidizer into the subterranean wellbore. The fracturing fluid 102 including the degraded natural polysaccharide 104 is then extracted from the subterranean formation prior to the purifying step.

[0049] In step 110, the fracturing fluid from the oxidation process (step 100) extracted from the subterranean formation, which includes the degraded natural polysaccharide 104, is purified. The purification process includes introducing the fracturing fluid 102 to a vessel 112, such as a purification tank, and then through a filter 114 included in the vessel 112 to separate suspended solids 116 in the fracturing fluid 102. The filtered suspended solids 116 are removed from the vessel 112 to provide a purified fracturing fluid.

[0050] In step 120, the purified fracturing fluid is introduced to a vessel 122 and treated. The treatment process is conducted to remove any undesired microorganisms from the fracturing fluid, to further reduce the size of the natural polysaccharide 104, and to modify the properties of the fracturing fluid to be suitable for the growth of the microbial biomass. The treatment process may be conducted chemically, physically, enzymically, or combinations thereof. Chemical/enzymic treatment of the fracturing fluid may include introducing a modifier into the fracturing fluid. The modifier may be at least one selected from the group consisting of a biocide, a neutralizing agent, and a fragmentation agent. The physical treatment of the fracturing fluid may include subjecting the fracturing fluid to a condition under which the undesired microorganisms in the fracturing fluid is eradicated. The details of chemical, enzymic and physical treatment of the fracturing fluid are described in the subsequent section. The treatment process produces a treated fracturing fluid.

[0051] The physical treatment in step 120, such as a treatment with elevated temperature or a radiation such as ultraviolet (UV) rays, may eliminate undesired microorganism from the fracturing fluid and reduce polymer fragmentation due to the expose to the radiation or elevated temperatures. The chemical treatment in step 120 may provide effective microbial control and natural polysaccharide fragmentation. The chemical treatment may require assessment and mitigation regarding the impact of the added chemicals on culture viability

and the extent of the polysaccharide fragmentation. The enzyme treatment in step 120 provides no adverse effects on cell viability and may be effective under specific conditions.

[0052] In step 130, the treated fracturing fluid from the treating step 120 is introduced to a vessel 132 to undergo an adjustment process. The adjustment process includes introducing at least one additive into the fracturing fluid.

[0053] In step 140, the adjusted fracturing fluid from the adjusting step 130 is introduced to a vessel 142 to undergo a biodegradation process. A microbial biomass 144 is introduced to the vessel 142 which is capable of biodegrading the natural polysaccharide 104 included in the fracturing fluid. The microbial biomass 144 may be immobilized on a carrier 146. The biodegradation of the natural polysaccharide 104 by the microbial biomass 144 results in generation of hydrogen 152 and other reaction products 154, which are separated from the fracturing fluid and collected from the vessel 142. Components in the adjusted fracturing fluid 102 that are not degraded by the microbial biomass 144 are collected from the vessel 142 as a non-degraded product 150. The non-degraded product 150 may be used as an input material to produce the carrier 146 to which the microbial biomass 144 is attached and immobilized.

[0054] In one or more embodiments, the oxidizing of the natural polysaccharide (step 100) is conducted to degrade the natural polysaccharide, which may be in a gel form, into smaller fragments ("fragmented natural polysaccharide," "fragmented polysaccharide") which may include simple sugars (monomers) such as glucose, mannose and galactose, oligomers, fragmented starch, fragmented cellulose, fragmented guar gum, and fragmented xanthan gum, or combinations of any of the oligomers and monomers.

[0055] The oxidation of the natural polysaccharide 104 may reduce the viscosity of the fracturing fluid. The fracturing fluid prior to the oxidation step 100 may have a viscosity in a range of from about 60 to 500 cP. The oxidation step 100 may reduce the viscosity of the fracturing fluid to a range from about 10 to 20 cP. The viscosity for fracturing fluid before and after the oxidation step 100 may vary depending on the condition of the fluid, such as temperature.

[0056] The fracturing fluid may be a source fracturing fluid which is used for a fracking operation in a subterranean formation. The oxidation step 100 of the natural polysaccharide 104 may be conducted chemically using an oxidizing chemical, or biologically using oxidizing enzymes. A non-limiting example of the oxidizing chemical includes peroxydisulfate salts (persulfates). Non-limiting examples of the oxidizing enzymes include xanthanase, endo-1,4-beta-xylanase, cellulase, guaranase, mannase, xylanase, amylase, glucoamylase, and combinations thereof. Each of the oligomer and monomer may be produced by the oxidizing chemical, oxidizing enzymes or combinations of the oxidizing chemical and the oxidizing enzymes.

[0057] The oxidation process 100 may be conducted by injecting the oxidizer into the subterranean formation. The injection of the oxidizer may be conducted after the source fracturing fluid is injected to the subterranean formation to generate fractures, and proppants contained in the source fracturing fluid is delivered to the fractures in the subterranean formation. In one or more embodiments, the oxidizer may be introduced to the subterranean formation before or while the proppants are being delivered to the fractures, provided that the oxidizer is an encapsulated oxidizer which remains inactive until an activation process is conducted. In case an encapsulated oxidizer is used, the oxidation step may include introducing the encapsulated oxidizer into the subterranean formation, and activating the encapsulated oxidizer. As previously described, the encapsulated oxidizer may be configured to be activated chemically, physically, by time or combinations thereof.

[0058] In one or more embodiments, the fragmented polysaccharide has a molecular weight in a range of from about 150 to about 250 g/mol, such as in a range of from a lower limit selected from any one of 150, 160 and 170 g/mol, to an upper limit selected from any one of 200, 220, 240 and 250 g/mol, where any lower limit may be paired with any upper limit. The fragmented polysaccharide may have a molecular weight of about 180 g/mol.

[0059] In one or more embodiments, the method includes purifying the fracturing fluid including a natural polysaccharide (step 110). The purification step 110 may include introducing the fracturing fluid extracted from the subterranean formation after oxidation

into a vessel, such as a purification tank, which includes a filter. Suspended solid components in the fracturing fluid is then separated from the fracturing fluid with the use of the filter. In one or more embodiments, the suspended solid components include clay, sand formation deposits, corrosion particles, drill cutting and combinations thereof. The suspended solid components may be removed from the vessel and discarded as a solid waste.

[0060] In one or more embodiments, the method includes treating the fracturing fluid including the fragmented natural polysaccharide (step 120). The fracturing fluid may be treated chemically, physically, enzymically, or combinations thereof. Chemical/enzymic treatment of the fracturing fluid may include introducing a modifier into the fracturing fluid. The modifier may be at least one selected from the group consisting of a biocide, a neutralizing agent, and a fragmentation agent.

[0061] In one or more embodiments, the biocide is included in the source fracturing fluid. Additional biocide may be introduced in the fracturing fluid in the treating step. A suitable biocide may be selected based on the target microorganisms such as methanogens and hydrogen-consuming bacteria. The biocide may be added to the fracturing fluid in an amount of from about 0.005 to about 0.01 wt%.

[0062] In one or more embodiments, a neutralizing agent is added to the fracturing fluid in the treatment step 120. The neutralizing agent is added to neutralize and inactivate the biocide such that the treated fracturing fluid would be suitable for the growth of the microbial biomass. The addition of the neutralizing agent may be conducted after the introduction of the biocide in order to neutralize the biocide after the undesired microorganisms are eliminated. In other words, the biocide and the neutralizing agent may be added in the sequential order. The neutralization and inactivation of the biocide is conducted such that the cell viability reduction of the microbial biomass in the subsequent biodegradation process is at most by a factor of 1000, such as in a range of by a factor of about 100 to by a factor of about 1000 in order to allow for normal microbial growth. Cell viability reduction by a factor of 1000 means that the number of viable cells as reduced is

1000 times fewer than before the reduction. For example, a viable cell culture having 10^8 CFU/mL reduced by a factor of 1000 would have a viable cell culture of 10^5 CFU/mL.

[0063] In one or more embodiments, the treating step 120 includes further degrading the fragmented natural polysaccharide. Additional fragmentation of the fragmented natural polysaccharide may be conducted by adding a fragmentation agent, which may be an enzyme, during the treating step 120. The enzyme used as the fragmentation agent may be a bacterial enzyme or fungi enzyme. The fragmentation agent included in the treating step 120 may degrade the fragmented natural polysaccharide, which may be oligomers, into monomers, such as simple sugars (monosaccharaides) including glucose, mannose, galactose and combinations thereof.

[0064] In one or more embodiments, the physical treatment of the fracturing fluid may include subjecting the fracturing fluid to a condition under which the undesired microorganisms in the fracturing fluid are eradicated. In one or more embodiments, the physical treatment includes exposing the fracturing fluid to an amount of ultraviolet (UV) radiation. The intensity of the UV radiation may be in a range of from about 20 to about 300 mJ/cm^2, such as in a range of from a lower limit selected from any one of 20, 30, 40 and 50 mJ/cm^2, to an upper limit selected from any one of 200, 250 and 300 mJ/cm^2, where any lower limit may be paired with any upper limit.

[0065] In one or more embodiments, the physical treatment includes subjecting the fracturing fluid to an elevated temperature, an elevated pressure, or a combination thereof. The elevated temperature may be at least 50 °C. The elevated temperature may be in a range of from about 50 °C to about 200 °C, such as in a range of from a lower limit selected from any one of 50, 60, 70 and 80 °C to an upper limit selected from any one of 90, 100, 121, 150, and 200 °C, where any lower limit may be paired with any upper limit. The elevated pressure may be in a range of from about 10 kPa gauge pressure to about 200 kPa gauge pressure, such as in a range of from a lower limit selected from any one of 10, 20, 30, 40, 50 and 100 kPa gauge pressure, to an upper limit selected from any one of 100, 150 or 200 kPa gauge pressure, where any lower limit may be paired with any mathematically compatible upper limit.

[0066] In one or more embodiments, the treating step 120 includes subjecting the fracturing fluid to a membrane purification treatment to remove undesired microorganism present in the fracturing fluid. A membrane used in the membrane purification treatment may be any membranes available in the art, provided that the membrane is capable of filtering the undesired microorganism out of the fracturing fluid while retaining the required components, such as the fragmented natural polysaccharides. In one or more embodiments, the membrane has an opening or pore size of about 0.2 microns.

[0067] In one or more embodiments, the method includes adjusting the fracturing fluid by adding at least one additive to provide suitable environment for microbial biomass (step 130). The additive added in the adjusting step may be one or more additives as described in the previous section, such as various nutrients, pH modifiers, salts and vitamins. Nutrients and a source of nitrogen may be added as a food source for the growth of the microbial biomass if the concentration of nutrients in the fracturing fluid is low and/or addition of supplements are required to maintain appropriate cell growth. Salts may be added as buffers to stabilize the osmotic pressure between the microbial biomass cells and surrounding fracturing fluid if the salt concentration in the fracturing fluid is low. Vitamins may be added to maintain appropriate cell growth of the microbial biomass.

[0068] In one or more embodiments, the adjusting step 130 includes adjusting the pH of the fracturing fluid by adding a pH modifier to provide an optimum pH level for the growth of the microbial biomass.

[0069] In one or more embodiments, the method includes introducing a microbial biomass to the fracturing fluid (step 140). The microbial biomass introduced to the fracturing fluid may be at least one of the microbial biomass as previously described, and may include at least one selected from the group consisting of one or more of a hydrogen-producing bacteria, and one or more of a degrader strain of natural polysaccharides. The microbial biomass is introduced to the adjusted fracturing fluid from step 130 in order to initiate the biodegradation step. In one or more embodiments, microbial biomass is additionally introduced to the fracturing fluid during the biodegradation process as the degradation of the natural polysaccharide is occurring. In case the microbial biomass is introduced during

the biodegradation process, the introduction of the biomass may be conducted continuously or intermittently. In case both the hydrogen-producing bacteria and the degrader strain of natural polysaccharides are introduced, they may be introduced to the fracturing fluid simultaneously, or separately. In one or more embodiments, the fluid produced as a result of introducing the microbial biomass into the fracturing fluid may be the fluid composition as described in the previous section.

[0070] As previously described, the microbial biomass may be immobilized onto a carrier. In one or more embodiments, the microbial biomass may be immobilized onto the carrier through various suitable processes such as chemical fixation, impregnation, and electrostatic immobilization.

[0071] In one or more embodiments, the carrier may be produced from a non-degraded product generated in the biodegradation process included in the presently disclosed method for generating hydrogen. A carrier from the non-degraded product may be produced by concentrating the non-degraded product, isolating the non-degraded product and thermally treated to produce the carrier, such as biochar. The concentration and isolation of the non-degraded product may be conducted via various processes available in the art, and suitable processes may be chosen based on the type and the composition of the non-degraded product. In one or more embodiments, the concentration and isolation are conducted by centrifugation, filtration, precipitation, crystallization, or evaporation, alone or in combination. The concentration and isolation steps may be conducted simultaneously or sequentially. The thermal treatment may be conducted via pyrolysis. The temperature at which the thermal treatment is conducted may depend on the composition of the non-degraded product. In one or more embodiments, the thermal treatment is conducted at a temperature in a range of from about 350 to 1000 °C, such as in a range of from a lower limit selected from any one of 350, 400, 450 and 500 °C and upper limit selected from any one of 850, 900, 950 and 1000 °C, where any lower limit may be paired with any upper limit. The thermal treatment may be conducted at a temperature of 700 °C.

[0072] In one or more embodiments, the method includes biodegrading the natural polysaccharide in the fracturing fluid with a microbial biomass to produce hydrogen and

reaction products. The biodegradation process may be an anaerobic microbial conversion process in which the degradation of the natural polysaccharide occurs in absence of oxygen.

[0073] In one or more embodiments, the biodegrading process includes biodegrading the natural polysaccharide with a hydrogen-producing bacteria. The biodegrading process may further include biodegrading the natural polysaccharide with a degrader strain of natural polysaccharides.

[0074] As previously described, the biodegrading process may include one or more strains of microbial biomass. In one or more embodiments, the microbial biomass in the biodegrading process includes one or more of the hydrogen-producing bacteria, and one or more of the degrader strain of natural polysaccharides. The microbial biomass may be any combinations of the previously-described hydrogen-producing bacteria and degrader strain of natural polysaccharides.

[0075] In one or more embodiments, the biodegrading process is conducted under a temperature in a range of about 20 °C to about 40 °C, such as in a range of from a lower limit selected from any one of 20, 25 and 30 °C to an upper limit selected from any one of 35 and 40 °C where any lower limit may be paired with any upper limit. However, the biodegrading process may be conducted outside of the aforementioned temperature range depending on various factors such as the composition of the medium, types of microbial biomass, the volume of the vessels, and the concentration of the microbial biomass.

[0076] In one or more embodiments, the biodegrading process is conducted under a pressure in a range of about 101 kPa (1 atm) to about 1013 kPa (10 atm), such as in a range of from a lower limit selected from any one of 101 (1 atm), 203 kPa (2 atm), to an upper limit selected from any one of 810 kPa (8 atm), 912 kPa (9 atm) and 1013 kPa (10 atm), where any lower limit may be paired with any upper limit.

[0077] In one or more embodiments, the biodegrading process includes a dark-fermentation process, a photo-fermentation process or a combination thereof. A dark-fermentation process refers to a degradation of the natural polysaccharides by a microbial

biomass in the absence of light. A photo-fermentation process refers to a degradation of the natural polysaccharides by a microbial biomass in the presence of light.

[0078] In one or more embodiments, the biodegrading process includes the dark-fermentation process as the first-stage biodegrading process, and the photo-fermentation process as the second-stage biodegrading process. The two-stage biodegradation process allows the removal of accumulated reaction products such as acetic acid, which may slow down the reaction process. As a result, such two-stage biodegradation process may allow a higher conversion of the natural polysaccharide into hydrogen and reaction products.

[0079] In one or more embodiments, the biodegrading process provides a percent conversion ratio of the natural polysaccharide into hydrogen and reaction products in a range of about 10 % to about 80%, such as a lower limit selected from any one of 10, 20 and 30 % to an upper limit selected from any one of 70 and 80 %, where any lower limit may be paired with any upper limit.

[0080] FIG. 2 is a schematic diagram illustrating the method for generating hydrogen from a natural polysaccharide which includes the two-stage biodegradation process. Steps 100 to 130 of FIG. 2 are the same as steps 100 to 130 of FIG. 1, which are described previously.

[0081] In step 140, the adjusted fracturing fluid from step 130 is introduced to a vessel 142 to undergo a first-stage biodegradation process, which is a dark-fermentation process. A microbial biomass 144 capable of dark-fermentation is introduced to the vessel 142 to biodegrade the natural polysaccharide 104 included in the fracturing fluid, which may be fragmented in the previous steps. The microbial biomass 144 may be immobilized on a carrier 146. The biodegradation of the natural polysaccharide 104 by the microbial biomass 144 results in generation of hydrogen 152 and rection products. Hydrogen 152 is separated from the fracturing fluid and collected from the vessel 142, while the produced reaction products remain in the fracturing fluid to be transported to the downstream process. The reaction products 256 produced during the first-stage biodegradation process 140 may be separated and removed from the fracturing fluid prior to the second-stage biodegradation step 200. Components in the adjusted fracturing fluid that are not degraded by the microbial biomass 144 are collected from the vessel 142 continuously or

intermittently as a non-degraded product 150. The non-degraded product 150 may be used as an input material to produce the carrier 146 to which the microbial biomass 144 is attached and immobilized.

[0082] In step 200, the fracturing fluid which has undergone the first-stage biodegradation process (step 140) is introduced to a vessel 202 for a second-stage biodegradation process, which is a photo-fermentation process. As noted previously, the reaction products 256 produced during the first-stage biodegradation process 140 may be separated and removed from the fracturing fluid prior to being introduced to vessel 202 in order to optimize the composition of the fracturing fluid. Additional additives may be added to the fracturing fluid, and/or the pH of the fracturing fluid may be adjusted in a similar manner as described in step 130 prior to introducing the fracturing fluid to the vessel 202. A microbial biomass 204 capable of photo-fermentation is introduced to the vessel 202 to further degrade the natural polysaccharide 104 included in the fracturing fluid. The microbial biomass 204 may be immobilized on a carrier 206. The biodegradation of the natural polysaccharide 104 by the microbial biomass 204 results in additional generation of hydrogen 252 and rection products 254, which are separated from the fracturing fluid and collected from the vessel 202. The separation and collection of hydrogen 252 and reaction products 254 may be conducted continuously or intermittently. The non-degraded product 250 may be used as an input material to produce the carrier 206. Either of the non-degraded product 150 from step 140 and the non-degraded product 250 from step 200 may be used to produce either of the carrier 146 in step 140 or the carrier 206 in step 200.

[0083] In one or more embodiments, the first-stage biodegradation process may be conducted for a duration of about 12 hours to about 48 hours, and the second-stage biodegradation process may be conducted for a duration of about 24 hours to about 96 hours. However, the duration of the first and second stage biodegradation processes may be shorter or longer than the aforementioned ranges depending on the types of microbial biomass used, volume of the vessel, and the amount and types of the additives such as nutrients.

[0084] In one or more embodiments, the method includes separating the produced hydrogen and reaction products, such as acetic acid, butyric acid and ethanol, from the fracturing fluid in order to maintain high metabolic activity of the microbial biomass in the fracturing fluid. The produced hydrogen may be separated from the fracturing fluid and purified via processes such as distillation and separation using membranes. The reaction products may also be separated by using ion exchange resins, and/or processes such as liquid-to-liquid extraction, and membrane separation/purification. The separated hydrogen and reaction products may be collected and transported, stored or consumed, based on the needs for such products. The reaction products may undergo additional separation processes to separate individual components included in the reaction products.

[0085] The separation of hydrogen from the fracturing fluid may be conducted under a low pressure of about 0 kPa to about 100 kPa absolute pressure, such as under a pressure in a range from a lower limit selected form any one of 0, 10, 20, 30 and 40 kPa absolute pressure to an upper limit selected from any one of 50, 60, 70, 80, 90 and 100 kPa absolute pressure, where any lower limit may be paired with any upper limit.

[0086] In one or more embodiments, the purifying, treating, adjusting and biodegrading steps may be conducted in separate vessels. In one or more embodiments, a portion or the entirety of the above steps may be conducted in the same vessel.

[0087] The vessels used in the present method may be vessels generally available in the art. The vessels may be capable of withstanding elevated temperature or elevated/reduced pressure. The vessels may include features such as an agitator/mixer, heating/cooling jacket/coil, ports, vacuum pumps, and fluid injection pumps.

[0088] Although only a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from this invention. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the following claims. It is the express intention of the applicant not to invoke means-plus-function for any limitations of any of the claims herein, except for those in which the claim expressly uses the words 'means for' together with an associated function.

CLAIMS

1. A method for generating hydrogen, comprising:
   oxidizing a natural polysaccharide comprised in a fracturing fluid in a subterranean formation;
   extracting the fracturing fluid from the subterranean formation;
   purifying the fracturing fluid;
   treating the fracturing fluid;
   introducing at least one additive into the fracturing fluid;
   introducing at least one microbial biomass into the fracturing fluid; and
   biodegrading the natural polysaccharide in the fracturing fluid with the at least one microbial biomass to produce hydrogen, reaction products and non-degrading products.

2. The method of claim 1, wherein the oxidizing is conducted by at least one selected from a group consisting of chemically and biologically.

3. The method of claim 1, wherein the oxidizing is conducted by:
   introducing an encapsulated oxidizer into the fracturing fluid; and
   activating the encapsulated oxidizer to oxidize the natural polysaccharide.

4. The method of claim 1 wherein the treating is conducted by at least one selected from a group consisting of chemically, physically, and enzymically.

5. The method of claim 1, wherein the treating comprises adding a biocide and a neutralizing agent sequentially.

6. The method of claim 1, wherein the at least one microbial biomass is immobilized on a carrier.

7. The method of claim 6, wherein the at least one microbial biomass is immobilized on the carrier by at least one process selected from the group consisting of chemical fixation, impregnation, and electrostatic immobilization.

8. The method of claim 7, further comprising producing the carrier from the non-degrading product produced in the biodegrading.

9. The method of claim 1, wherein the biodegrading is an anaerobic microbial conversion process.

10. The method of claim 1, wherein the biodegrading comprises a dark-fermentation process as a first-stage biodegradation process.

11. The method of claim 10, wherein the biodegrading further comprises a photo-fermentation process as a second-stage biodegradation process.

12. The method of claim 1, further comprising separating the hydrogen and the reaction products from the fracturing fluid.

13. A fluid composition, comprising:
    a natural polysaccharide;
    at least one microbial biomass;
    an oxidizing agent;
    at least one additive; and
    a fluid medium,
    wherein the at least one microbial biomass comprises a hydrogen-producing bacteria.

14. The fluid composition of claim 13, further comprising at least one modifier selected from the group consisting of a biocide, a neutralizing agent and a fragmentation agent.

15. The fluid composition of claim 13, wherein the at least one microbial biomass further comprises at least one selected from the group consisting of a bacterial degrader of the natural polysaccharide, a fungal degrader of the natural polysaccharide, a bacterial enzyme and a fungal enzyme.

16. The fluid composition of claim 13, wherein the at least one microbial biomass comprises at least one selected from the group consisting of a dark-fermentative strain and a photo-fermentative strain.

17. The fluid composition of claim 13, wherein the at least one microbial biomass is immobilized on a carrier.

18. The fluid composition of claim 17, wherein the carrier comprises a coal-based carrier.

19. A method for producing a fluid composition, comprising:

sequentially adding, to a source fracturing fluid:

an oxidizing agent;

an additive; and

a microbial biomass,

wherein the source fracturing fluid comprises:

a natural polysaccharide, and

a fluid medium.

20. The method of claim 19, further comprising adding a modifier prior to adding the additive, wherein the modifier is at least one selected from the group consisting of a biocide, a neutralizing agent and a fragmentation agent.

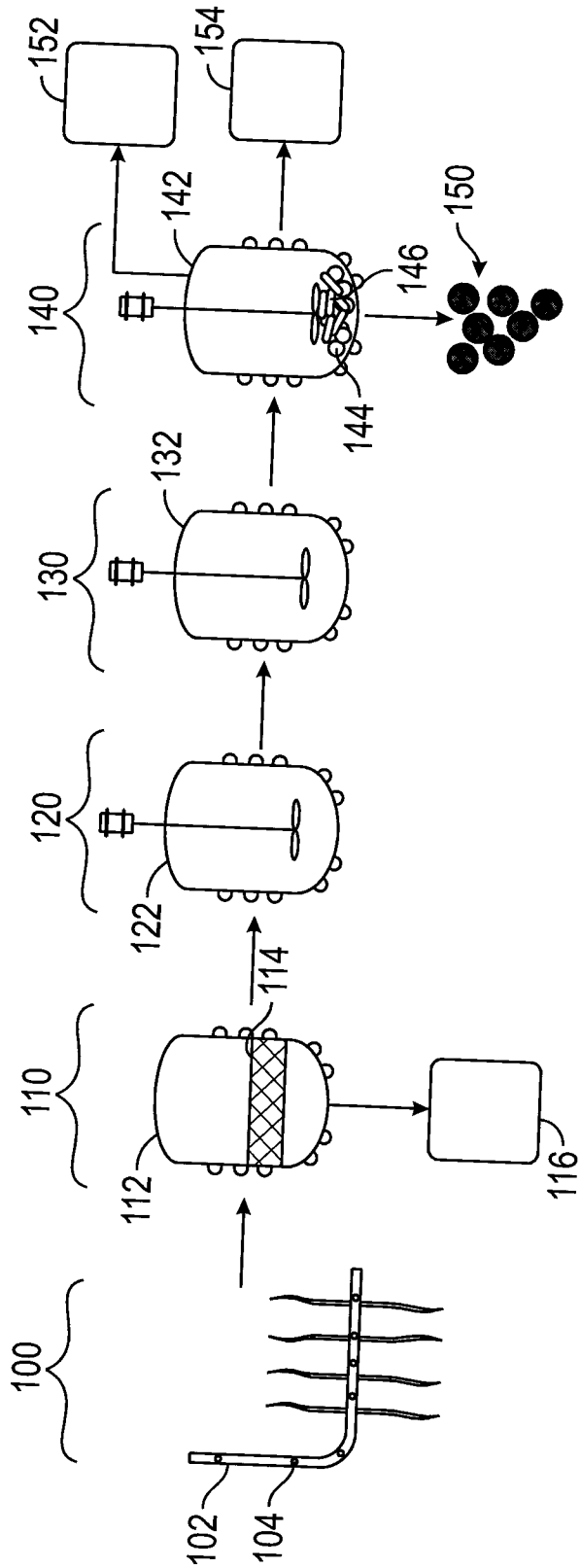

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FIG. 1

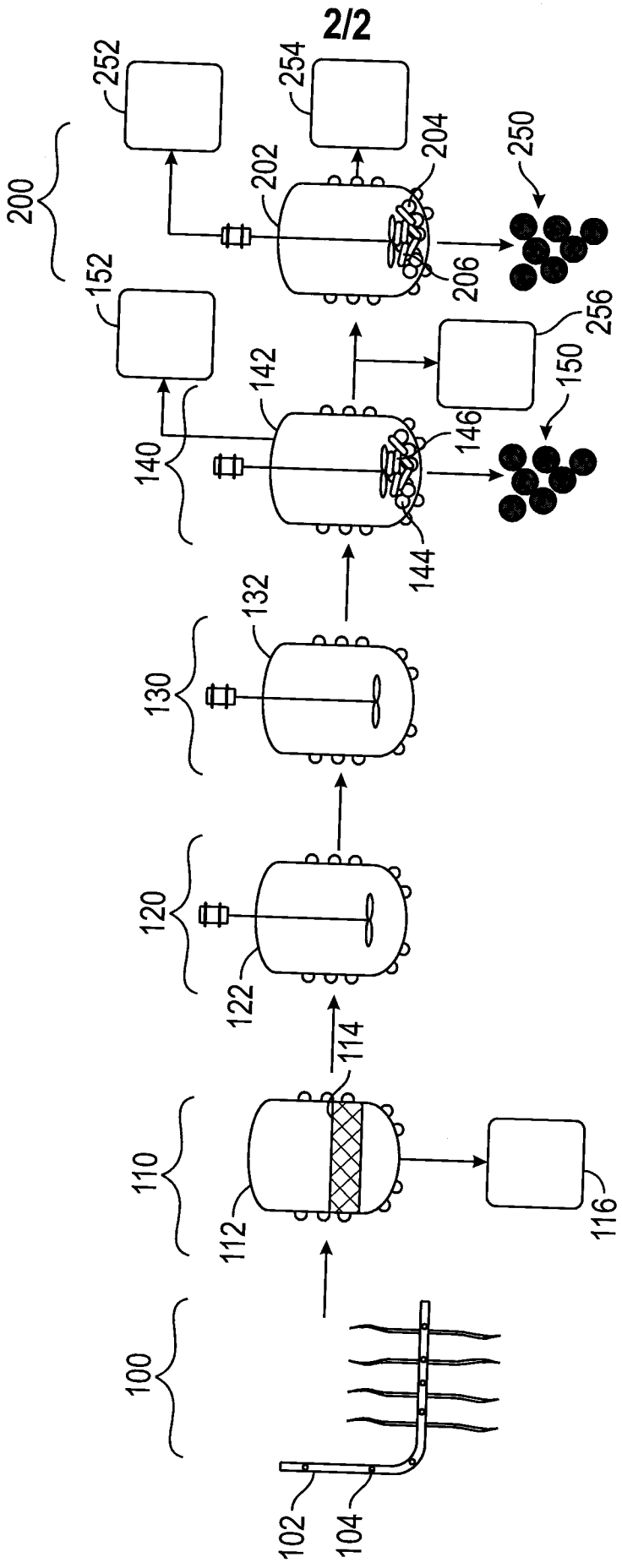

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FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/RU 2023/000366

A. CLASSIFICATION OF SUBJECT MATTER

C12P 3/00 (2006.01)
C08L 5/00 (2006.01)
C08J 3/205 (2006.01)
C09K 8/90 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C12P 3/00, C01B 3/22-3/48, C08L 1/00-1/32, 5/00-5/16, C08J 3/00-3/22, C09K 8/00-8/94, C22B 3/18

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)

Espacenet, PatSearch

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MA X. et al. Application of Guar Gum degrading bacteria in Microbial Remediation of Guar-based Fracturing Fluid Damage. Energy & Fuels, 2017, V. 31, N 8, pp. 7894-7903, abstract, 1. Introduction, 2.5.3 Experimental flow, fig. 1, 2.4.1 Insoluble residue collection, 2.4.2 Biodegradation experiment	19
Y		13-18, 20
A		1-12
Y	US 2008/0283242 A1 (CLEARWATER INTERNATIONAL, LLC et al.) 20.11.2008, abstract, example 1, paragraphs [0057], [0058]	14, 20

[X] 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

"D" document cited by the applicant in the international application

"E" earlier document 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	Date of mailing of the international search report
17 June 2024 (17.06.2024)	15 August 2024 (15.08.2024)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, 125993, Russian Federation Phone No: +7(499)240-60-15, Fax +7(495)531-63-18	Authorized officer E. Tuzhilkina Telephone No. 8 (495) 531-64-81

INTERNATIONAL SEARCH REPORT

International application No.

PCT/RU 2023/000366

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	US 2009/0298151 A1 (DR. ELMAR SCHMID AND JAMES GIBSON) 03.12.2009, claims 6, 8, 14, paragraphs [0010], [0016], [0021], [0056], [0062]	13-18 1-12
Y	US 2012/0077242 A1 (JAMES R. SWARTZ et al.) 29.03.2012, abstract, claims 1, 4	15
Y	MARKOV S.A. et al. Hydrogen Production By Microorganisms and Microbial Fuel Cells Using Wastewater And Waste Products. International Scientific Journal "Alternative Energy and Ecology", 2013, № 01/2 (118), pp. 108-116	16
Y	SU 899647 A1 (ODESSKY ORDENA TRUDOVOGO KRASNOGO ZNAMENI GOSUDARSTVENNY UNIVERSITET IM. I.I.MECHNIKOVA) 23.01.1982, claims	17, 18
A	JP 2019-47777 A (ESPEC CORP et al.) 28.03.2019, abstract	1-20