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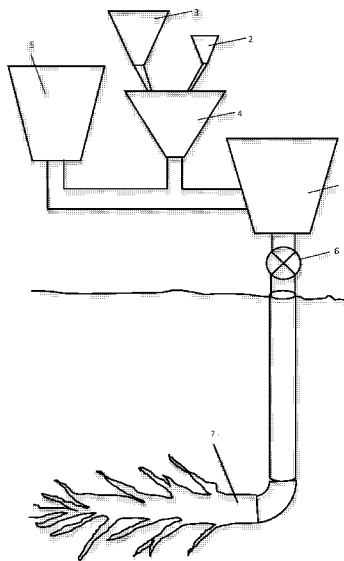
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Figure 1:



(57) Abstract: Provided is an enzyme immobilized on a proppant. Also provided is a viscified fracture fluid 1 formed by combining a solid proppant, a binding agent and an enzyme to form a proppant-immobilized enzyme 2, mixing the proppant-immobilized enzyme 2 with a second proppant 3 to form a heterogeneous proppant pack 4 and mixing said heterogeneous proppant pack 4 with a gelled liquid fracturing fluid 5 to form the viscified fracture fluid 1 containing the heterogeneous proppant pack 4. The viscified fracture fluid 1 containing the heterogeneous proppant pack 4 is pumped 6 into a subterranean zone 7 to form one or more fractures therein. The proppant-immobilized enzyme 2 that is part of the heterogeneous proppant pack 4 has the dual purpose of propping open the subterranean fractures and reducing the viscosity of the viscified fracture fluid.



A PROPPANT IMMOBILIZED ENZYME AND A VISCOFIED FRACTURE FLUID

This application claims priority to U.S. provisional patent application serial Nos. 61/816,215, filed 26 April 2013 and 61/844,050, filed 9 July 2013, the complete disclosures of which are incorporated herein by reference.

FIELD OF THE INVENTION

The invention relates to a proppant having an immobilized enzyme, a viscofied fracture fluid suitable for use in improving flow of liquids and gases from a subterranean hydraulic fracture, and a method for improving the extraction of oil and gas from subterranean fractures.

BACKGROUND OF THE INVENTION

Liquid enzyme solutions are now being used as breakers in hydraulic fracturing and horizontal drilling applications in the oil and gas industry. One of the requirements of an enzyme used as a breaker in a subterranean formation is that it retains its activity at high pressure, such as at temperatures reaching up to 150 degrees Celsius and at a pH ranging from 4 to 12.

Fracturing fluids are mixtures that contain various components, each with a purpose in the fracturing method. Fracturing fluids include drilling fluids, diverting fluids and gravel-packing fluids. Fracturing fluid components include proppants, such as sand, silica, glass beads, metal particulate matter, sintered bauxite and other ceramic proppants, ultra-light weight (ULW) and other matter, to 'prop' open subterranean fractures from which oil and gas flow into a wellbore and are recovered; viscosifying agents or gelling agents such as guar gum, xanthan gum and others, are added to increase the specific gravity of the fracturing fluid to carry proppants to the subterranean fractures; and breakers which reduce the viscosity of the viscosifying agents so that the oil and gas can flow into the wellbore. The breakers are important in maximizing the recovery of oil and gas from the well. The viscosifying agents are typically selected from galactomannan gums, guar, derivatized guar, cellulose, cellulose derivatives,

starch, starch derivatives, xanthan, xanthan derivatives and mixtures thereof. While these viscosifying agents are effective at carrying sand or other proppants into the subterranean formations, they often form a rubbery solid with elastic properties called "filter cake" that reduces the flow of gas and/or oil from the subterranean formation. It is therefore useful to prevent formation of filter cake, or to dissolve the filter cake once it is formed. Breakers are a class of chemical that reduce the viscosity of fracturing fluid and prevent filter cake build-up.

Breakers are typically selected from three different classes of chemicals: oxidizers, enzymes and acids. Enzymes are useful as breakers because they are naturally occurring proteins that are specific to the viscosifying polymers listed above. Enzymes such as alpha-amylases, glucoamylases, xanthanases, xylanases, cellulases, hemicellulases, cellobiohydrolases, beta-glucanases, and others, hydrolyze the bonds that characterize viscosifying polymers. Enzymes are generally preferable from an environmental perspective, to oxidizers such as sodium persulfate, ammonium persulfate, chlorates, bromates, periodates and acids such as citric acid and fumaric acid among others.

Typically, viscosifying agents and proppants are pumped into a wellbore under sufficient pressure to cause the subterranean formation to fissure. The viscosifying agent ensures the proppant is carried into the fissure. Subsequently, the breaker is pumped into the wellbore. Breaker and viscosifying agents come into contact and the breaker reduces the viscosity of the fracturing fluid. It is difficult to ensure the breaker reaches the viscosifying agent and filter cake located in the fissures. In addition, since breakers are typically water soluble and there is significant fluid loss, in the subterranean formation, much of the breaker is lost with the fluid. The increased viscosity of the fracturing fluid also reduces the diffusion of the breaker in the formation. In order to overcome the loss and reduced diffusion, increased volumes of breaker are required which increases cost.

U.S. Patent No. 8,343,747, and published U.S. Patent Application No. 20100011456 assigned to Verenum Corporation, disclose a series of genetic sequences that code for enzymes that can be used in hydraulic fracturing to

reduce the viscosity of drilling mud and other viscofied treatment fluids used in subterranean formations. These documents do not teach or suggest that such enzymes can be immobilized on the proppant such as sand or silica as a delivery mechanism to co-locate the enzyme breaker with the viscosifying agent that the enzyme is designed to hydrolyze.

Cochet et al., U.S. Patent No. 8,393,395, describes encapsulation of breakers, including enzymes in a water-insoluble matrix and pumping these into a subterranean formation for the purpose of delayed release of breaker to reduce viscosity of a viscofied fracturing fluid. While Cochet's method provides benefits in terms of delaying the viscosity reduction until proppant has entered the fracture, Cochet requires the addition of both the water-insoluble matrix and the proppant.

Abad et al., U.S. Patent No. 7,677,311, describes a composition and method for breaking viscous fluids by providing a solid particle that can be located in a subterranean fracture then subsequently decomposing into a breaker for the viscosifying fluid. Abad's method also ensures that breaker is localized in the fracture where needed, at least initially. Sullivan et al., U.S. Patent No. 7,287,590, describes a delayed breaker. However, a limitation of both the Abad and Sullivan methods is that once solubilized, the breaker could be carried back up to the well surface, thereby nullifying its ability to reduce viscosity in the formation. The solubilized breaker may also be lost within the porous formation itself.

U.S. Patent Application No. 20130112413 (Muthusamy et al.), discloses a method of controlled release of enzyme breakers for oil field applications. Muthusamy discloses a viscofied treatment fluid consisting of a gelling agent, a crosslinking agent, a proppant, an aqueous-base fluid and a poly(meth)acrylate encapsulant that encapsulates at least one of an enzyme, an oxidizer, a chelator and an acid. Muthusamy's encapsulation method suffers from the same problems as the Abad and Sullivan methods.

Powell, U.S. Patent No. 7,195,071, discloses that a succinoglycan hydrolysis enzyme can be impregnated on a carrier for delayed release. This method is suitable when delayed release of enzyme is desired however the enzymes eventually become soluble and may be lost to the formation with other fluids, or inactivated over time as is often the case with soluble enzymes. In addition, any improved stability of the enzyme conferred by impregnating the enzyme on a carrier is likely reversed when the enzyme is released.

Both, U.S. Patent No. 5,437,331 (Gupta et al.) and U.S. Patent No. 7,000,701 (Todd) disclose a method of fracturing a subterranean formation by, *inter alia*, encapsulating an enzyme breaker. In the case of U.S. Patent No. 5,437,331, the enzyme breaker uses open cellular encapsulation to protect and delay the action of the enzyme. Todd uses a partially hydrolyzed acrylic material as polymer for encapsulation.

Gupta, Todd, Powell, Muthusamy, Cochet and Abad do not teach or even suggest a method for retaining the breaker on the solid particle so that the breaker is not lost in the formation or when the petroleum fluids flow back to the surface of the earth. Moreover, these patents do not teach that the proppant can be used as an immobilization media and that in doing so, the fracturing method can be improved and simplified and, in certain cases, the enzyme breaker can be recovered and reused.

U.S. Patent No. 7,021,379 (Nguyen) describes a method of forming subterranean fractures penetrated by a well bore and consolidating proppant particles therein where the particles are coated with a hardenable organic resin, a silane coupling agent and a gel breaker. Nguyen discloses the use of enzymes as gel breakers, among other chemicals such as oxidizers and acids. Nguyen's proppant requires three separate chemicals as part of the coating composition; a hardenable resin, a silane coupling agent and a gel breaker. Nguyen's method employs breakers that facilitate removal of gelled carrier fluid from the surface of hardenable resin-coated proppant particles allowing for resin coated particle-to-particle contact.

U.S. Patent No. 6,186,235 (Tjon-Joe-Pin) discloses a method of forming a

breaker-crosslinker-polymer complex where the breaker is in an inactive form prior to a change in subterranean conditions at which point the breaker is activated. Once the breaker begins to breakdown the gelled polymer complex, the soluble breaker can be lost through the formation. Tjon-Joe-Pin does not disclose the use of proppant as a solid phase upon which the breaker can be immobilized.

U.S. Patent No. 5,998,183 (LeFevre et al.) and U.S. Patent No. 7,312,056 (Saville and Khavkine) disclose methods of immobilizing enzymes on a support matrix for use in commercial chemical production methods, such as pharmaceuticals and syrups. Both of these immobilization methods do not disclose forming a proppant having an immobilized enzyme. The methods in these patents can be modified using the present invention to provide the formation of an improved proppant-immobilized enzyme described herein. The complete disclosures of U.S. Patent Nos. 5,998,183 and 7,312,056 are incorporated herein by reference.

SUMMARY OF THE INVENTION

The present invention relates to a novel proppant and a novel viscofied fracture fluid comprising the proppant that is suitable for use in improving flow of liquids and gases from a subterranean hydraulic fracture. The proppant has both proppant functionality and gel-breaking functionality. This dual function proppant can reduce the cost of hydraulic fracturing and improve the recovery of hydrocarbon-rich gases and fluids from a subterranean formation.

The present invention provides an improvement over U.S. Patent No. 7,021,379 (Nguyen) since the novel method by which a breaker is immobilized on a proppant is less costly and less time-consuming. More importantly the effectiveness of the immobilized breaker according to the present invention is unexpectedly greater than that disclosed in U.S. Patent No. 7,021,379 as measured by the slope of the curve of viscosity vs. time. The unexpected results shown in the Examples illustrate the advantages of the present invention over Nguyen.

The present invention further relates to a method of hydraulic fracturing using the novel proppant that acts to prop open subterranean fractures and also acts as a gel breaker to reduce the viscosity of the gelled fracturing fluid. By immobilizing an enzyme capable of reducing the viscosity of the viscosifying and gelling agents, and locating the enzyme on the proppant itself, localization of the gel breaker to the subterranean fractures through which oil and gas flow into the wellbore is assured. Moreover, loss of soluble breaker by absorption into the subterranean formation is prevented.

A novel way to ensure breakers diffuse into the subterranean fractures to reduce filter cake and maximize oil and gas recovery, is to immobilize breakers on the proppant itself. This procedure eliminates the need for complex encapsulation reactions, increases the stability of the enzyme breaker and ensures the enzyme breaker is localized in the subterranean fracture so that viscosity reduction in these small fracture channels is maximized. The present invention provides unexpected stability enhancements under the high temperatures varied pH ranges and high pressures found in subterranean fractures.

The present invention also relates to the recovery and reuse of the novel proppant by methods such as those published in U.S. Patent No. 7,659,099, the complete disclosure of which is incorporated herein by reference.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates a method of fracturing.

Fig. 2 illustrates the proppant remaining in a fracture.

DETAILED DESCRIPTION

The present invention relates to a novel proppant, a novel viscofied fracture fluid comprising the proppant, and a method of using the proppant or viscofied fracture fluid for improving flow of liquids and gases from a subterranean hydraulic fracture. The proppant also acts to reduce the viscosity of the fluid used to deliver the proppant to the subterranean fractures thereby acting as a gel

breaker. By immobilizing an enzyme capable of reducing the viscosity of the viscosifying and gelling agents, and locating the enzyme on the proppant itself, diffusion of the gel breaker to the subterranean fractures through which oil and gas flow into the wellbore is assured. The invention will be explained with reference to the attached non-limiting drawings.

As shown in Figs. 1 and 2, the viscofied fracture fluid 1 can be formed by combining a solid proppant, a binding agent, and an enzyme to form a proppant-immobilized enzyme 2; mixing said proppant-immobilized enzyme 2 with a second proppant 3 to form a heterogeneous proppant pack 4; and mixing said heterogeneous proppant pack 4 with a gelled liquid fracturing fluid 5 to form a viscofied fracture fluid 1 containing the heterogeneous proppant pack 4. The viscofied fracture fluid 1 containing the heterogeneous proppant pack 4 can then be pumped 6 or delivered into a subterranean zone 7 to form one or more fractures 8 therein. The proppant-immobilized enzyme 2 that is part of the heterogeneous proppant pack 4 has the dual purpose of propping open the subterranean fractures 8 and reducing the viscosity of the viscofied fracture fluid 1. As the viscosity of the viscofied fracture fluid 1 is reduced, it is removed from the subterranean zone 7. Subsequently, the flow of liquids and gases into the subterranean fractures 8 that are propped open by the heterogeneous proppant pack 4 containing proppant-immobilized enzyme 2 is improved.

Enzymes useful in the present invention include any enzyme that acts on a substrate that is used as a gelling or viscosifying agent such as, but not limited to guar gum, xanthan gum, starchy polysaccharides, cellulose and cellulose-based gelling agents. Many commercially available enzymes are available to hydrolyze these viscosifying agents. An example of suitable enzymes include, but are not limited to, the group 3 hydrolases. Specific examples of suitable enzymes include, but are not limited to, mannanase, alpha-amylase, glucoamylase, cellulase, hemicellulase, xylanase, beta-glucanase, cellobiohydrolase, xanthanase or asparaginase.

Proppants are now well known. Non-limiting examples of suitable proppants are sand, fracking sand, silica, aluminum silicate, zeolite, sintered bauxite, ceramic

beads, glass beads, glycoxy-agarose, curable or non-curable resin and metal particulate matter. A preferred proppant is fracking sand granules.

Enzyme immobilization methods using binding agents to immobilize an enzyme to a substrate are now well-known, a few of which are described in the background section above. However, prior to the present invention, such methods have not been used to bind an enzyme to a proppant. The prior art methods utilize a support matrix to bind the enzyme for use in chemical processes, such as for forming pharmaceuticals or syrups. The prior art support matrix is different from a proppant. Proppants have specific properties not required from the prior art support matrix. The prior art immobilization methods can be modified by replacing the support matrix with a proppant. Any suitable immobilization method can be used to bind the enzyme to the proppant.

Immobilization of an enzyme to the proppant, such as fracking sand, can be accomplished using any suitable binding agent. An example of a suitable binding agent includes, but is not limited to, crosslinkers. Preferred binding agents are dialdehydes. A most preferred binding agent is glutaraldehyde. Commercially available glutaraldehyde solutions are commonly used in fracking fluid as a biocide. Therefore, the present invention can use existing fracking fluid components to create a simplified and enhanced fracking fluid wherein the biocide can now be used as an immobilized enzyme cross-linker in addition to a biocide.

There are numerous advantages of creating a proppant-immobilized enzyme and using the same as a breaker:

- 1) the proppant-immobilized enzyme can be recovered and reused in subsequent fractures,
- 2) proppant and immobilized breaker can be localized in the subterranean fractures to ensure that viscous fluid and hardened thickening agents can be hydrolyzed to improve flow of hydrocarbon-rich liquids and gases,
- 3) immobilized enzymes often display enhanced thermal stability and pH stability, allowing breakers to continue to function over long periods of time under harsh conditions, and

4) dialdehyde cross-linkers can be used as biocides, reducing the requirements to add exogenous biocides.

The proppant-immobilized enzyme has unexpected, increased enzyme stability at high temperatures and pressures. In a preferred embodiment, the enzyme is more stable immobilized on the proppant than it would be as an enzyme breaker that is soluble in the fracking fluid. The proppant-immobilized enzyme is surprisingly active at temperatures up to 80 Celsius degrees.

The enzyme immobilized to the proppant is also more stable to chemical denaturation as a function of its immobilization. This characteristic allows for new fracking fluid components that otherwise could not be used due to their deleterious effects on the soluble enzyme breakers. For example, a fracturing fluid with a pH outside of the soluble enzymes active range may not be feasible for use with a soluble enzyme breaker. However, the novel proppant-immobilized enzyme disclosed herein can now be used in a broadened pH range, allowing for a wider selection of fracturing fluid components, and lower costs and better performance.

A viscofied fracture fluid can be formed by mixing the proppant with a suitable liquid fracturing fluid. Fracturing fluids are now well known. Any suitable fracturing fluid can be used. The viscofied fracture fluid can also contain at least one more additional proppant. The additional proppant can be any conventional proppant not having an immobilized enzyme thereon.

A preferred viscofied fracture fluid can be formed by combining the solid proppant, the binding agent and the enzyme to form a proppant-immobilized enzyme; mixing the proppant-immobilized enzyme with a second proppant to form a heterogeneous proppant pack; and mixing said heterogeneous proppant pack with a gelled liquid fracturing fluid to form a viscofied fracture fluid containing the heterogeneous proppant pack.

The viscofied fracture fluid can be used to improve a flow of liquids and gases from a subterranean hydraulic fracture comprising the steps of pumping the

viscosified fracture fluid into a subterranean zone to form one or more fractures therein; and removing the fracture fluid from the subterranean zone leaving the proppant in the formation. The proppant-immobilized enzyme reduces viscosity of the viscosified fracture fluid in the subterranean zone. The proppant-immobilized enzyme can be recycled from the subterranean fracture and the proppant-immobilized enzyme reused as a proppant in a second subterranean fracture.

The rate of hydrolysis of the viscosified fracture fluid by the proppant-immobilized enzyme can be between 10% and 25% of that of the soluble enzyme from which the proppant-immobilized enzyme is derived. More preferably the rate of hydrolysis of the viscosified fracture fluid by the proppant-immobilized enzyme is between 26% and 50% of that of the soluble enzyme from which the proppant-immobilized enzyme is derived. Even more preferably the rate of hydrolysis of the viscosified fracture fluid by the proppant-immobilized enzyme is between 51 - 100% of that of the soluble enzyme from which the proppant-immobilized enzyme is derived. Most preferably the rate of hydrolysis of the viscosified fracture fluid by the proppant-immobilized enzyme is over 100% of that of the soluble enzyme from which the proppant-immobilized enzyme is derived.

The half-life of the proppant-immobilized enzyme is preferably equivalent to the half-life of the soluble enzyme from which the proppant-immobilized enzyme is derived. More preferably the half-life of the proppant-immobilized enzyme is 1.1-fold to 2-fold greater than the half-life of the soluble enzyme from which the proppant-immobilized enzyme is derived. Even more preferably the half-life of the proppant-immobilized enzyme is greater than 2-fold the half-life of the soluble enzyme from which the proppant-immobilized enzyme is derived. Most preferably, the half-life of the proppant-immobilized enzyme is between 1.5 times and 5 times the half-life of the soluble enzyme.

Example 1

An enzyme was immobilized on a proppant using a binding method similar to that disclosed in Le Fevre in U.S. Patent 5,998,183. Briefly, 200 mL of water was

mixed manually with 32 mL of 25% glutaraldehyde. To the water/glutaraldehyde solution, 32 grams of proppant (hydraulic fracturing sand), with a mesh size of 20 x 40, was added. The mixture was mixed in a blender at low speed for three hours and fifty minutes to modify the proppant to produce a glutaraldehyde-bound proppant. The glutaraldehyde-bound proppant was separated from the water/glutaraldehyde mixture by vacuum filtration through a 1 μ m filter and dried. An enzyme solution comprising mannanase, cellulase, hemicellulase and other hydrolase activities was mixed in a pH 6.0, 0.01M phosphate buffer in a ratio of 1 part enzyme to 9 parts phosphate buffer to form a dilute enzyme solution.

Glutaraldehyde-bound proppant was gently mixed with the dilute enzyme solution on a magnetic stir plate for 4 hours to form a proppant-immobilized enzyme where enzyme was immobilized via glutaraldehyde cross-linkages.

Subsequently, the filtrate was removed by vacuum filtration through a 2.5 μ m filter. The proppant-immobilized enzyme was dried.

Proppant-immobilized enzyme was assayed for its ability to reduce the viscosity of a viscous guar solution over time. The following table shows the results of the assay using no enzyme (blank), the usual soluble enzyme dose (1 Litre/m³) and the proppant-immobilized enzyme. Results are measured in units of Apparent Viscosity (cP).

Table 1

Time (min)	Blank	Standard soluble enzyme dose (1 Litre/m ³)	Proppant Immobilized Enzyme (1 gram/L)
	(cP)	(cP)	(cP)
0	58	58	58
15	50	42	40
30	48	33	32
60	44	25	20
90	42	20	13
210	37	13	7
270	33	12	6
330	28	10	5
1470	7.5	5	-

The enzyme immobilized on modified hydraulic fracturing sand clearly reduced the viscosity of the guar solution over 1470 minutes. By immobilizing enzyme breaker on proppant to create an enhanced hydraulic fracturing proppant and using the present invention to localize the enhanced hydraulic fracturing proppant in the subterranean fractures, the viscosity of the solution in the fractures can be reduced allowing increased volumes of oil and gas to flow into the well for recovery.

Example 2

Immobilized enzyme was prepared by incubating 2% N-2-(aminoethyl)-3-aminopropyltrimethoxysilane (APTS) in acetone with 16 grams of proppant. The APTS/proppant was then incubated with 40 mL of 2% glutaraldehyde in sodium phosphate buffer, pH 7.0 for 3 hours. The resulting proppant was incubated overnight with 100 mL of a 10% enzyme breaker and borate buffer solution (pH 9.0). The enzyme solution was decanted and the proppant was then washed with distilled water, vacuum filtered and left to dry overnight. The proppant was then baked at 60 degrees Celsius for 1 hour. Enzyme immobilized using the APTS method was assayed as explained in Example 1.

Similarly, immobilization with 3-glycidoxypyltrimethoxysilane (GPTMS) was carried out by incubating 2.5 mL GPTMS in 47.5 mL of 0.01M pH 9 borate buffer with 16 grams of proppant for 2 hours at 60 degrees Celsius. The GPTMS-treated proppant was then washed and dried followed by incubation in 20 – 50 mL of 0.1M sulfuric acid for 2 hours. The sulfuric acid was decanted, the GPTMS-treated proppant was washed with distilled water and left to dry overnight. The resulting proppant was incubated overnight with 100 mL of a 10% enzyme breaker and borate/carbonate buffer solution (pH 10.0). The enzyme solution was decanted and the proppant was then washed with distilled water, vacuum filtered and left to dry overnight. The proppant was then baked at 60 degrees Celsius for 1 hour. Enzyme immobilized using the GPTMS method was assayed as explained in Example 1.

The Table 2 below shows a comparison of viscosity reduction of various enzyme breakers in a 40 degree C, pH 9.5 viscofied fracturing fluid where the gelling

agent was guar. Relative viscosity, measured in centipoises (cP) was tracked over time. The immobilized breaker used in the present invention reduced viscosity more than both the soluble enzyme and the coated resin particle described by U.S. Patent No. 7,021,379 (Nguyen).

Table 2

	Negative Control (no breaker)	Soluble Enzyme	APTS Proppant breaker	GPTMS Proppant breaker	Immobilized Breaker (present invention)
0	58	58	55	55	58
15 min	50	42	53	54	40
30 min	48	33	53	52	32
60 min	44	25	50	52	20
90 min	42	20	48	52	13
210 min	37	13	41	50.5	7
270 min	33	12	39	50	6
330 min	28	10	33	48	5
1470 min	7.5	5	12	34	2.5

While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

CLAIMS

1. A proppant suitable for use in improving flow of liquids and gases from a subterranean hydraulic fracture comprising: a proppant, a hydrolytic, viscosity-reducing enzyme, and a binding agent binding the enzyme to the proppant so that the enzyme is immobilized on the proppant.
2. The proppant of claim 1, wherein the enzyme is a group 3 hydrolase.
3. The proppant claim 1, wherein the enzyme comprises at least one enzyme selected from the group consisting of mannanase, alpha-amylase, glucoamylase, cellulase, hemicellulase, xylanase, beta-glucanase, cellobiohydrolase, xanthanase or asparaginase.
4. The proppant of any of claims 1-3, wherein the proppant comprises at least one proppant selected from the group consisting of sand, fracking sand, silica, aluminum silicate, zeolite, sintered bauxite, ceramic beads, glass beads, glycoxyl-agarose, curable or non-curable resin and metal particulate matter.
5. The proppant of any of claims, 1-4, wherein the binding agent comprises a dialdehyde.
6. The proppant of any of claims, 1-4, wherein the binding agent comprises a glutaraldehyde cross-linker.
7. A viscofied fracture fluid comprising a proppant according to any of claims 1-6 and a liquid fracturing fluid.
8. The viscofied fracture fluid according to claim 7, further comprising a second proppant.
9. The viscofied fracture fluid according to claim 7, formed by combining the solid proppant, the binding agent and the enzyme to form a proppant-immobilized enzyme; mixing said proppant-immobilized enzyme with a second proppant to form a heterogeneous proppant pack; and mixing said

heterogeneous proppant pack with a gelled liquid fracturing fluid to form a viscofied fracture fluid containing the heterogeneous proppant pack.

10. Use of the proppant of any of claims 1-6 for improving a flow of liquids and gases from a subterranean hydraulic fracture.
11. Use of the viscofied fracture fluid according to any of claim 7-9 for improving a flow of liquids and gases from a subterranean hydraulic fracture.
12. A method of improving a flow of liquids and gases from a subterranean hydraulic fracture comprising the steps of pumping the viscofied fracture fluid according to any of claims 7-9 into a subterranean zone to form one or more fractures therein; and removing the fracture fluid from the subterranean zone leaving the proppant in the formation.
13. The method of claim 12, wherein the proppant-immobilized enzyme reduces viscosity of the viscofied fracture fluid in the subterranean zone.
14. The method of claim 12, wherein the proppant-immobilized enzyme is recycled from the subterranean fracture and said proppant-immobilized enzyme is reused as proppant in a second subterranean fracture.
15. The method of claim 12, wherein the rate of hydrolysis of the viscofied fracture fluid by the proppant-immobilized enzyme is between 10% and 25% of that of the soluble enzyme from which the proppant-immobilized enzyme is derived, more preferably the rate of hydrolysis of the viscofied fracture fluid by the proppant-immobilized enzyme is between 26% and 50% of that of the soluble enzyme from which the proppant-immobilized enzyme is derived, more preferably the rate of hydrolysis of the viscofied fracture fluid by the proppant-immobilized enzyme is between 51 - 100% of that of the soluble enzyme from which the proppant-immobilized enzyme is derived, and more preferably the rate of hydrolysis of the viscofied fracture fluid by the proppant-immobilized enzyme is over 100%

of that of the soluble enzyme from which the proppant-immobilized enzyme is derived.

16. The method of claim 12, wherein the half-life of the proppant-immobilized enzyme is equivalent to the half life of the soluble enzyme from which the proppant-immobilized enzyme is derived, more preferably the half-life of the proppant-immobilized enzyme is 1.1-fold to 2-fold greater than the half life of the soluble enzyme from which the proppant-immobilized enzyme is derived, more preferably the half-life of the proppant-immobilized enzyme is greater than 2-fold the half life of the soluble enzyme from which the proppant-immobilized enzyme is derived, and more preferably the half-life of the proppant-immobilized enzyme is between 1.5 times and 5 times the half-life of the soluble enzyme .

1/2

Figure 1:

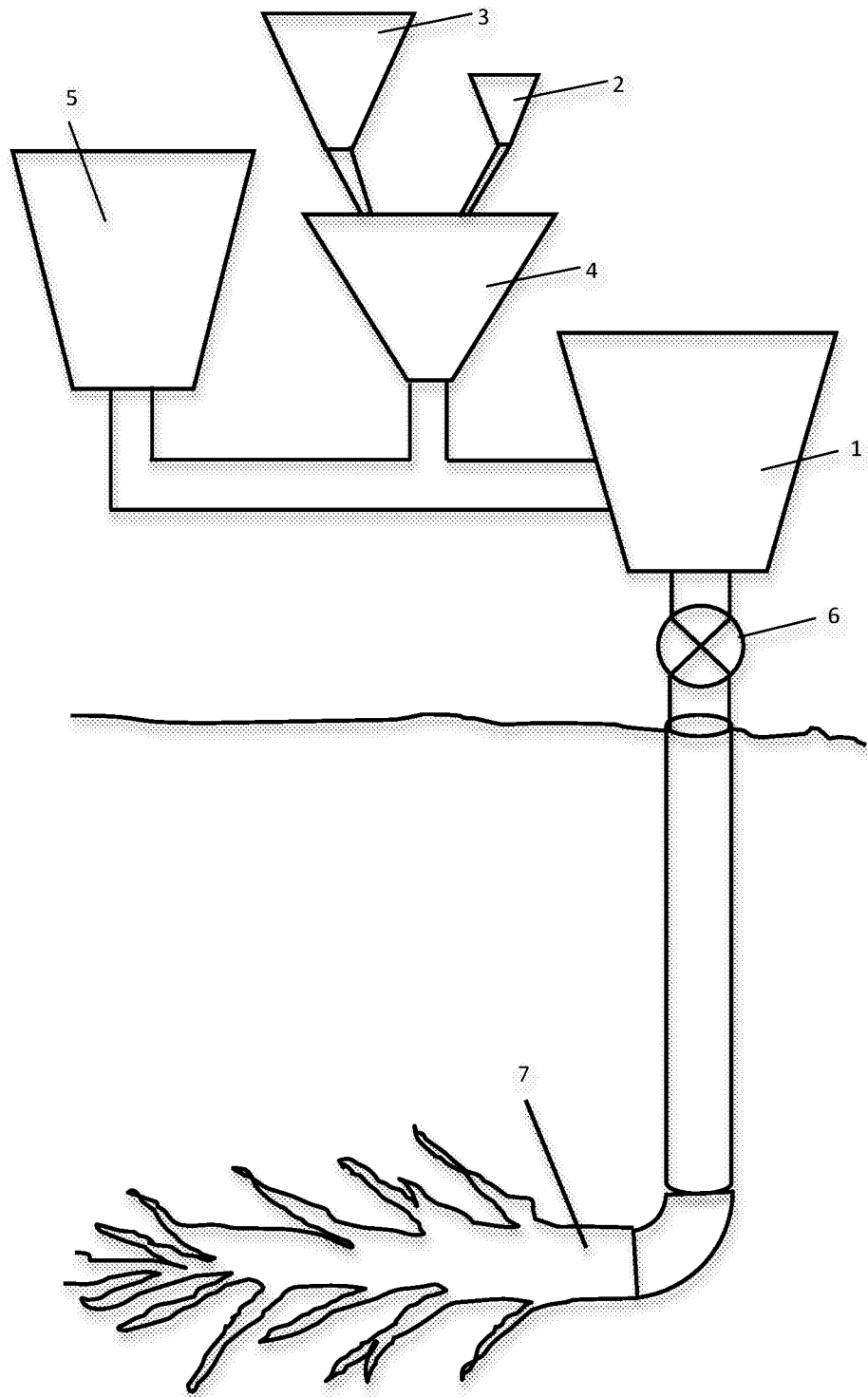
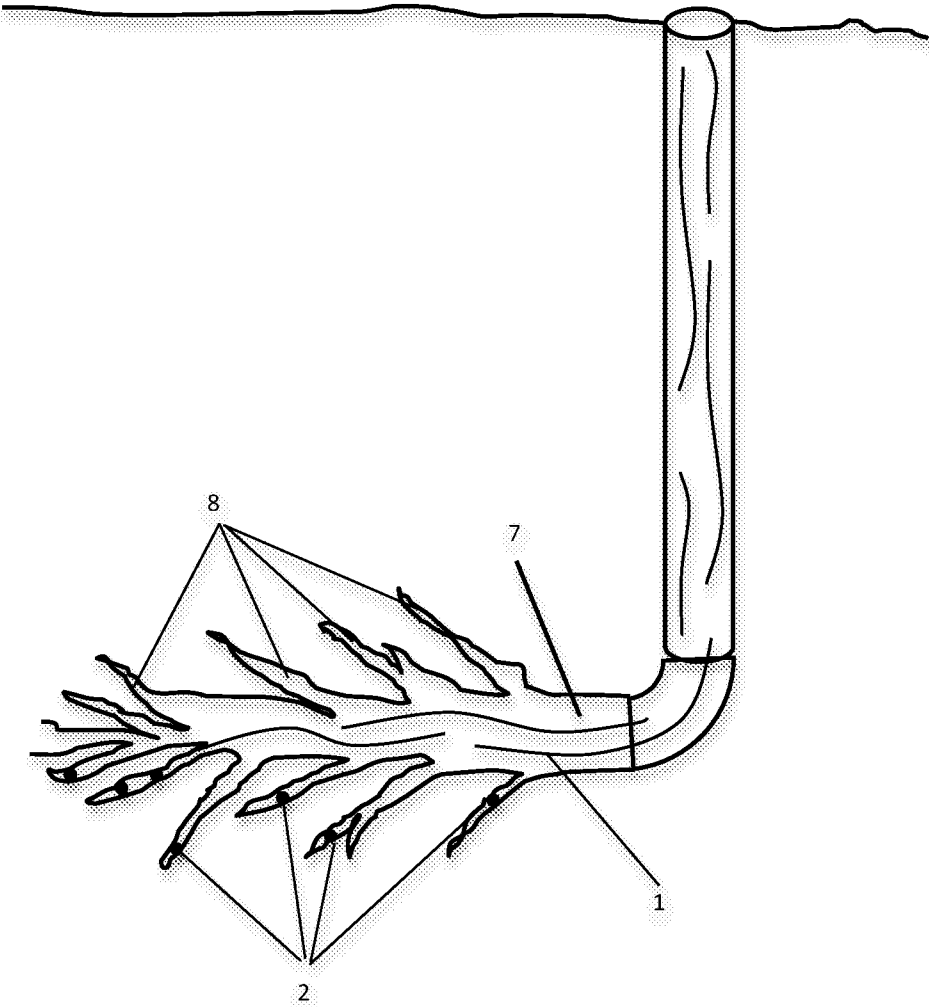


Figure 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2014/060980

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C09K 8/80** (2006.01), **C09K 8/58** (2006.01), **E21B 43/267** (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)
IPC: **C09K 8/80** (2006.01), **C09K 8/58** (2006.01), **E21B 43/267** (2006.01)

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Canadian patent database, Questel orbit (Fampat), Scopus (sample search terms: proppant, enzyme, binding agent, binder, subterranean, sand, silica, bauxite, glass beads, mannanase, amylase, cellulase, xylanase, xanthanase, cellobiohydrolase, glutaraldehyde and related terms)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 2,337,122 A1 [NGUYEN, P. D. et al] 06 September 2001 (06-09-2001) (see page 7, line 5 – page 9, line 5; page 15, line 3- page 17, line 24; Example 3 and Table 3, Sample #2)	1-16
X	US 5,998,183 A [LE FÈVRE, G. N. et al.] 07 December 1999 (07-12-1999) (see entire document)	1-6
X	US 7,312,056 B2 [SAVILLE, B. A. et al.] 25 December 2007 (25-12-2007) (see entire document)	1-6
X	CA 2,277,371 A1 [LE FEVRE, G. N. et al.] 08 January 2001 (08-01-2001) (see page 4, lines 6-29; page 6, line 10- page 7, line 27 and Examples)	1-6

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

* “A” “E” “L” “O” “P”	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier application or patent but published on or after the international filing date 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) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	“T” “X” “Y” “&”	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 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 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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Date of the actual completion of the international search
11 July 2014 (11-07-2014)Date of mailing of the international search report
20 August 2014 (20-08-2014)Name and mailing address of the ISA/CA
Canadian Intellectual Property Office
Place du Portage I, C114 - 1st Floor, Box PCT
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2014/060980

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005/0006093A1 [NGUYEN, P. D. et al.] 13 January 2005 (13-01-2005) (see entire document)	1-16

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/IB2014/060980

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US5998183A	07 December 1999 (07-12-1999)	None	
US7312056B2	25 December 2007 (25-12-2007)	CA2421829A1 WO2004081208A1	13 September 2004 (13-09-2004) 23 September 2004 (23-09-2004)
CA2277371A1	08 January 2001 (08-01-2001)	CA2277371C	10 May 2005 (10-05-2005)
US2005006093A1	13 January 2005 (13-01-2005)	CA2531216A1 RU2006103366A WO2005005775A1	20 January 2005 (20-01-2005) 27 July 2006 (27-07-2006) 20 January 2005 (20-01-2005)