Pyrolase® Cellulase Enzyme Breaker as Biodegradable Replacement for Corrosive Acids and Oxidizers in Hydraulic Fracturing Operations

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Short description:

To provide the energy industry with a way to reduce source pollution in oil and gas extraction through hydraulic fracturing, Verenium Corporation last year launched a new U.S. campaign to commercialize the high-performance, 100% biodegradable Pyrolase® cellulase enzyme as a replacement for toxic chemical breakers. Developed using Verenium's proprietary enzyme discovery and development technology, Pyrolase® fits all three of the EPA award focus areas: 1. The use of greener synthetic pathways; 2. The use of greener reaction conditions; and 3. The design of greener chemicals. With $52 million in 2010 revenue, the company does not qualify for the small business award. California-based Verenium Corporation researched and developed Pyrolase® in its San Diego laboratory and is marketing this greener alternative in the United States.

Abstract:

Hydraulic fracturing is an advanced drilling technique to unlock vast stores of oil and shale gas across the country. It involves pumping pressurized water, sand and chemicals underground to open fissures in oil and gas containing formations, such as shale, to improve the flow to the surface. While there is no doubt that America needs to take advantage of all domestic energy resources, the fracturing process has drawn harsh, organized criticism from environmentalists who say it poses a risk to public health. They claim that the potential for deep underground water contamination in the fracking process poses a significant environmental risk. Most recently, in early December 2011, the U.S. Environmental Protection Agency for the first time publicly stated that fracking might be to blame for causing groundwater pollution in Wyoming. Among the toxic chemicals used in fracturing are a host of corrosive acids and oxidizers used to degrade and remove fracturing fluid residues from formation pores. In response to the need to reduce such source pollution, Verenium launched a new campaign in 2011 to commercialize the Pyrolase® product to the oil and gas services industry. Pyrolase®, developed using Verenium's proprietary discovery and development technology, is a broad-spectrum β-glycosidase enzyme that provides a complete viscosity break on fracturing fluids across a broader range of temperatures, wider pH ranges and higher salinity than other commercial enzymes, and can be used in a wider variety of down-hole conditions. It excels in the hydrolysis of linear and cross-linked fluids, such as guar gum, derivatized guar and carboxymethyl cellulose, with break time easily controlled by varying the enzyme loading. Pyrolase® is an easy-to-use liquid and replaces the corrosive acids and hazardous oxidizers used in fracturing. It offers superior performance with zero environmental impact. One pound of biodegradable Pyrolase® can replace more than 20 pounds of hazardous chemicals, some of which are implicated in concerns over soil and water contamination. Pyrolase® is a significant step forward in addressing the environmental and health concerns over hydraulic fracturing both for workers and for those living in communities near fracturing operations. Effectively addressing such concerns removes a key obstacle in allowing America to fully exploit available energy reserves.

Nomination:

Shale is an unconventional source of natural gas. It has low permeability and can only be tapped through hydraulic fracturing that creates new fissures and fractures that facilitate gas flow into the wellbore. In the United States, gas shale can be found from Pennsylvania to Wyoming, and from Michigan and New York south to Texas, Louisiana and Oklahoma. Access to shale gas often requires horizontal drilling with lateral sections extending 3,000-5,000 meters from the wellbore followed by fracking of the shale zone to facilitate gas flow. U.S. shale production rose by 71% between 2007 and 2008, and grew another 54% in 2009 to 3.11 trillion cubic feet (88 billion cubic meters). The U.S. Energy Information Administration (EIA) in its 2011 Annual Energy Outlook more than doubled its estimate of technically recoverable shale gas reserves in the United States. Shale production is projected to increase from 14% of total domestic gas production in 2009 to 45% by 2035.

But this unprecedented and wide-spread use of hydraulic fracturing has generated public concerns over health, safety and environmental impact. Given these concerns, there is a need for environmentally benign and safe alternatives to toxic chemicals that minimize or even eliminate risks.

The chemical technology presented here, Pyrolase® cellulase, is a high-performance, thermo-tolerant, thermo-active enzymatic viscosity breaker used in the hydraulic fracturing of oil and gas wells. This enzyme hydrolyzes the gel-forming carbohydrates, such as guar gum and its derivatives, under taxing oil and gas reservoir conditions that include high temperatures, wide pH range and the presence of various chemicals. A small amount of Pyrolase® replaces much larger quantities of conventional viscosity breakers that include ammonium persulfate and hypochlorite salts, as well as peroxygen compounds, such as dichromates, permanganates, peroxydisulfates, sodium perborate, sodium carbonate peroxide, hydrogen peroxide, magnesium peroxide, tertiarybutylhydroperoxide, potassium diperphosphate, and ammonium and alkali metal salts of dipersulfuric acid. One pound of biodegradable Pyrolase® can replace more than 20 pounds of these hazardous chemicals, some of which are implicated in concerns over soil and water contamination.[1]

Pyrolase® is a liquid product that generates no fumes or dust during storage on-site or once the containers are opened and used in operations. The major, non-active ingredient of this product is glycerol that poses no immediate health or environmental risk if spilled in transport or storage. The elimination of toxic fumes and dust that impact air quality is especially important to workers at drilling sites and people living in adjacent communities.

Pyrolase® replaces highly corrosive chemicals that come in powdered form and are considered hazardous to the health and safety of oilfield workers, chemical suppliers and transportation agents who must be highly trained in their use. Improper handling or inhalation of these chemicals during mixing in a mixing hopper can cause

[1] Pyrolase® is formulated as a concentrated product based on extensive laboratory testing and field trials conducted by one of the country's three largest oilfield service companies. Such formulation minimizes packaging and transportation costs and enhances ease of use in the field.

burning and irritation to the skin, eyes, nose, and throat. Further, the free radicals generated by the decomposition of chemical breakers attack well metallurgy and corrode equipment, creating additional costs for industry.

Hydraulic fracturing is an intense industrial operation during which very large volumes of a viscous fluid (several hundred thousands of gallons) are pumped into a wellbore under high hydrostatic pressure (Fig. 1). The fluid contains a gelling agent, such as guar and its derivatives, sand particles, and other chemicals. Under pressure, the fluid fractures the formation and creates new fissures and channels that allow oil and gas to flow into the wellbore. The gelatinous nature of the fracturing fluid, frac gel, suspends sand particles and carries them deep into new fissures. Once the sand is inserted, the gel is degraded to flow back out of the well by 'breaking' the long chain of carbohydrates contained in guar and other viscosifying material. Conventional chemical 'breakers' do this by generating free radicals that attack the backbone of the viscosifying polymers, reducing fluid viscosity and facilitating the flow of the material out of the wellbore. On the surface, toxic flowback is stored in holding ponds. When dry, wind-borne toxic dust can blow into the atmosphere or over surrounding populated areas.

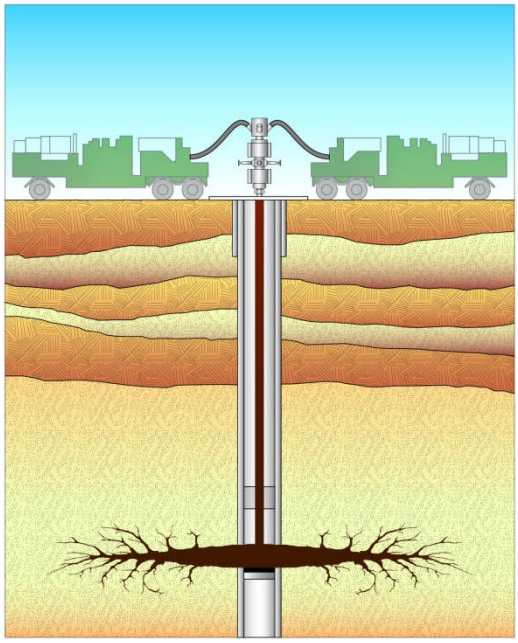

Fig.1. Hydraulic Fracturing: Injection of a highly pressurized fluid, containing viscosifying polymers and sand particles, fractures the formation and increases gas and oil flow to the wellbore.

For more than a decade, Verenium Corporation, based in San Diego, California, has been discovering, developing and commercializing a portfolio of enzyme products for various industrial applications. Using its proprietary, patented technology platform, Verenium discovered and isolated the specific gene for the thermostable enzyme, Pyrolase®, from the eubacterium *Thermotoga maritima* found in geothermically heated marine sediment on the ocean floor. It is a strictly anaerobic, rod-shaped and fermentative thermophilic bacterium that grows between 55°-90°C (optimally at 80°C). The Pyrolase® enzyme produced from this organism withstands similarly high temperatures and shows exceptional activity under taxing conditions on industrially relevant substrates, including cross-linked guar. A boron-based cross-linking agent is

used to increase and retain viscosity under high-shear, high-temperature pumping operations.[2]

Pyrolase® is covered by five patents issued between 1999 and 2008 on aspects of development such as its polynucleotide sequence and gene structure (Patent Numbers: US5925749, US5962258, US6008032, US6245547 US7422876).[3] The enzyme has a molecular weight of about 35 kD. It has exceptional cellulolytic activity, as well as activity on a variety of other carbohydrate type substrates, such as galactomannans found in guar gum and carob beans, barley β-glucan, and carboxymethyl cellulose (CMC). Owing to its thermoactive nature, Pyrolase® enzyme exhibits a fast and highly efficacious hydrolytic impact on these substrates at high temperatures (80°-110°C) and under a wide range of pH conditions (pH 5-10). The combination of this thermal activity and pH tolerance makes Pyrolase® highly effective in degrading guar and its derivatives, as well as carboxymethyl cellulose used for fracturing hydrocarbon reservoirs. Oil and gas wells, especially deeper wells, often are places of high temperatures and widely varied pH levels.

Pyrolase® is a unique enzyme in possessing both endo- and exo-glucanase activities. It is well established that the enzymatic hydrolysis of cellulose and similar polysaccharides, such as derivatized mannan in guar gum, requires the synergistic action of both endoglucanases and exoglucanases (cellobiohydrolases). These two activities cleave respectively the internal and the external near chain-end β-1,4 glycosidic bonds on the polysaccharide backbone (Fig. 2). Effective degradation of polysaccharide requires both activities to break the backbone and then shorten the chain size to small oligomers that can be further hydrolyzed by a β-glucosidase.

[2] Pyrolase® has been tested and characterized extensively using both biochemical assays (at Verenium) and industry approved rheology based application tests at several specialized laboratories, including C&A Labs and those run by three of the largest oilfield service companies, Baker-Hughes, Halliburton Energy Services and Schlumberger. The use of Pyrolase® in field trials and ongoing hydraulic fracturing operations in Argentina, Canada, the United States and elsewhere has been highly successful.

[3] These patents cover the DNA sequence, amino acid sequence, cDNA description, polynucleotide sequence and methods of generating a nucleic acid that encodes the enzyme Pyrolase® cellulase.

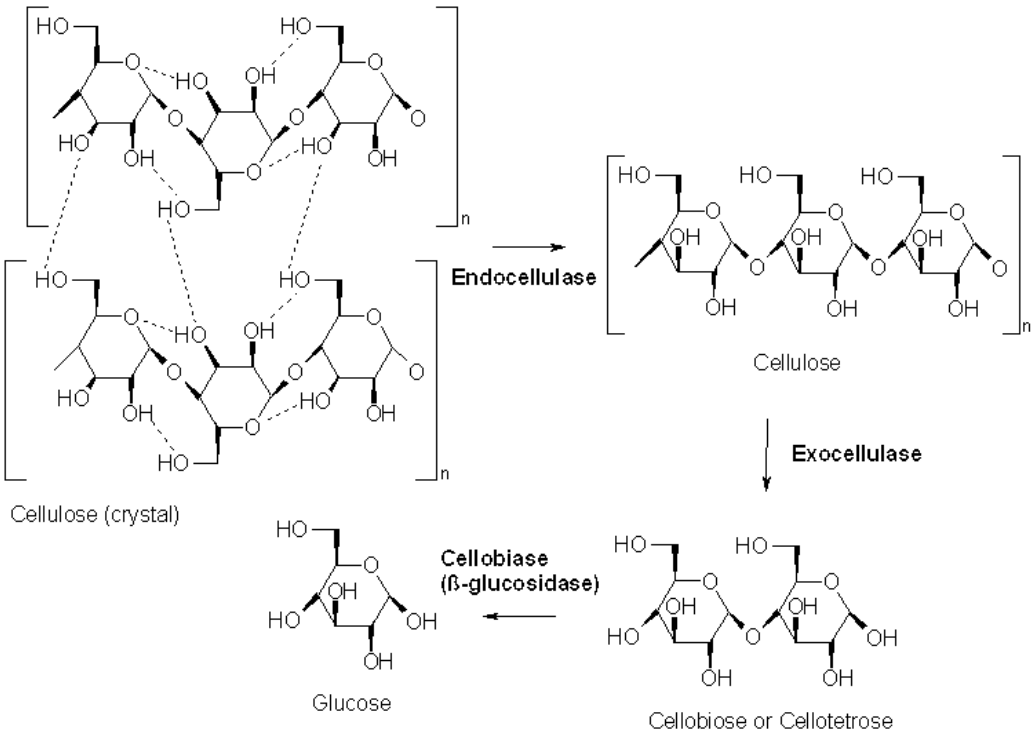

Fig.2. Cellulose hydrolysis requires both endocellulase and exocellulase activities to effectively degrade the polymer.

Guar gum consists of a β-mannan backbone on which every other mannose residue is substituted with a galactose molecule. In both regular guar and derivatized guar, where the galactose side units contain additional groups such as hydroxypropyl in HP guar, carboxymethyl in CM guar and hydroxypropyl carboxymethyl in CMHP guar, the steric hindrance on the heavily substituted polymer does not hinder action of Pyrolase®. The enzyme accesses the backbone, creating cleavages manifested as a rapid decline in gel viscosity (Fig. 3).

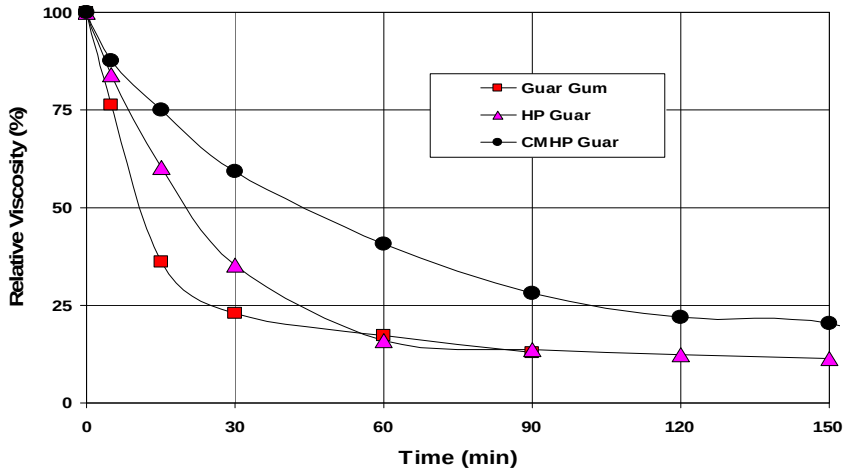

Fig.3. Pyrolase®: Active on linear and derivatized guar. HP guar and CMHP guar are often used to produce higher strength gels for hydraulic fracturing of gas shales.

The endo- and exo-acting properties of Pyrolase® effectively degrade guar and CMC polymers, without auxiliary enzymes, to very small chain size that can no longer form a gelatinous fluid (Fig.4). This is an important property for users, as the breakers are required to reduce gel viscosity to less than 10 centiPoise (cP) and generate a so-called water-thin liquid that can be readily flowed out of the well to enhance formation conductivity and increase well productivity.

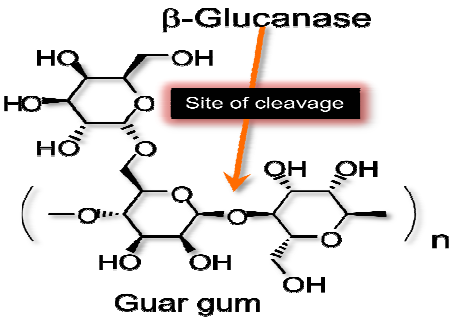

Fig.4. Pyrolase® cleaves the β-1,4 glycosidic linkage on the polymer backbone and generates shorter chains to reduce gel viscosity, improving formation conductivity and well productivity.

The most commonly used oxidative chemical breakers are peroxydisulfates, which generate highly reactive sulfate radical anions upon decomposition at higher temperatures. While the rate of decomposition is slow below 50°C, it is accelerated by adding additional chemicals (amines). At temperatures above 50°C, peroxydisulfates decompose rapidly. This means that extremely precise dosing regimens of the breaker are required to avoid premature breaking of the fluid.

By comparison, Pyrolase® offers enormous flexibility and numerous opportunities for innovative applications. Rather than slowly breaking down, Pyrolase® remains dormant at temperatures below 25°C but gains activity as it is heated. Thus, as it goes down the wellbore and the well temperature increases, it becomes active and ready to function precisely when and where it is needed to break down viscosity. As a result, there is no longer any issue of premature breaking while pumping the gel down-hole, as there is with conventional chemicals. In addition, Pyrolase® is highly active within the pH range of 5 to 10. Therefore, it can be included in high-pH fluids (pH>10) where it will remain dormant until the fluid pH is reduced to below 10 down-hole and the enzyme is activated. At that point, Pyrolase® begins degrading the frac fluid.

In fact, Pyrolase® allows operators to use temperature and pH as control parameters to trigger the enzyme action. The application rate (0.05-1 lb. enzyme/1,000 gallons fluid) serves as another control measure to attain desired reaction speed and optimal break profile for the conditions of the well.[4] In other words, Pyrolase® helps the operator create a smooth viscosity profile by modifying the amount of Pyrolase used in the mix. Pyrolase® is not as aggressive as chemical breakers and has a wider and more forgiving range of activity.

[4] The required amount of enzyme depends on the desired break time as well as the well conditions. In faster operations, under similar conditions, higher doses of enzyme may be required to facilitate shorter break times.

Pyrolase® is formulated and delivered as a concentrated, high-efficacy liquid that can be safely and conveniently added during the fluid preparation. Typical required loadings for the Pyrolase® breaker (0.05-1 lb./1,000 gallons fluid) are much smaller than those required for chemical breakers (2-10 lbs./1,000 gallons of fracturing fluid). Because of the small volumes and safe packaging, as well as ease of use, Pyrolase® technology provides improvements in housekeeping of on-site chemical inventories. Workers also require less training in the handling of the product compared to those highly toxic chemicals used as viscosity breakers.

The cellulase enzyme that is the active ingredient in Pyrolase® is entirely biodegradable and will not persist in the environment after the fracturing fluid is flowed back and processed on site.

During manufacture, Pyrolase® is produced from non-pathogenic microorganisms in large-scale fermentation operations using safe ingredients for easy delivery and application. Pyrolase® receives special treatment after the fermentation stage to eliminate all live production organisms from which the enzyme was produced. The result is that no live organisms are introduced into the environment from using Pyrolase®. Beyond the active cellulase enzyme itself, the non-active ingredient in the product is glycerol, but no other ingredients are contained within the product at significant concentrations to be hazardous, to our knowledge.

Pyrolase® was developed through extensive R&D at Verenium Corporation (formerly Diversa) and approved by the Environmental Protection Agency in 2001. Since then, it has been tested further in multiple specialized testing labs including many of the world's major oilfield service companies. It has been used in field trials and operations in South America by one of the major international oilfield service companies and sold in Canada to multiple smaller companies, where it worked at or beyond the promised performance. Verenium initiated the campaign to market Pyrolase® in the United States in 2011.

Pyrolase® was developed in the belief that it is better to prevent waste than to treat it or clean it afterward. It was designed to perform better than conventional chemicals and without toxicity. It is derived from a renewable bacteria found in nature as its starting point. It performs at a wide variety of temperatures and conditions, minimizes energy use and is biodegradable and fades back into the environment after it has performed its function. All of these align Pyrolase® with the principles of green chemistry.

Pyrolase® is a green alternative to a range of chemical breakers that are considered hazardous, corrosive and/or aggressive in their mechanism of action. It uses greener synthetic pathways to address the problem of breaking down fracturing fluids, and it operates under greener reaction conditions. It is, in every way, an improvement on the environmental profile of hydraulic fracturing and a step forward in making this form of oil and gas recovery safe and clean.