Literature Review and Analysis of Waterless Fracturing Methods

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Preface

The U.S.–China Clean Energy Research Centers (CERC) are joint initiatives to accelerate research, development, and deployment of clean energy technologies in the U.S. and China. Advanced energy solutions can tap diverse energy sources, improve efficiency, and accelerate the transition to a low-carbon future. With these objectives in mind, CERC facilitates collaborative research and development, engaging scientists and engineers from world-class universities, top research institutions, and industry leaders.

One of the more recently established CERCs is the U.S./China Clean Energy Research Center for Water Energy Technologies (CERC-WET), led by the University of California together with Lawrence Berkeley National Laboratory for the U.S. side, and led by the Research Institute of Petroleum Exploration and Development (RIPED) on the Chinese side. The overall objective of CERC-WET is to build a foundation of knowledge, technologies, human capabilities, and relationships that position the U.S. and China to continue to thrive in a future with constrained energy and water resources.

One of the top water-energy priorities of research on the Chinese side is waterless fracturing using CO_2, which was not in the initial CERC-WET workscope on the U.S. side. Thus, while the Chinese CERC-WET team has a strong interest to establish joint R&D activities on using CO_2 as the alternative to replace water in hydraulic fracturing, the U.S. CERC-WET has had difficulty supporting a research team because the 2016-2020 funding had already been allocated to individual projects focusing on other objectives. Because non-water fracturing is a timely and high-impact topic for the U.S. as well and it aligns well with the overall CERC objective, the CERC director reached out to DOE/FE for seed funding support. The LBNL received such seed funding to initiate the first step towards designing and developing a productive long-term research collaboration with the Chinese team. The 2016 tasks specified by the DOE/FE are listed below, focusing on analyses of the state-of-the-technology, knowledge sharing with RIPED, and identifying a framework for collaboration.

Task 1: Conducting analyses of the current state-of-the-art and the application of non-water fluids in oil and gas fracture stimulation, and determining the characteristics of geologic formations amenable to the use of each fluid.

Task 2: Conducting analyses of CO_2-based stimulation techniques and mechanisms, and identifying the key future research questions for large-scale CO_2 usage in hydraulic fracturing.

Task 3: Visit RIPED for exploratory discussions, relationship-building, and knowledge sharing regarding current state-of-the-art using non-water stimulation techniques.

Task 4: Provide input to RIPED on designing and developing a long-term R&D collaboration to advance the most promising CO_2-based hydraulic fracturing techniques.

This report covers the literature review state-of-the-art analyses described in Task 1. Task 2, 3, and 4 results are described in a separate LBNL report (*Wan*, 2017).

Introduction

This report provides a brief literature review and analysis of several waterless fracturing methods. The methods included in this report are: Liquid CO_2/Sand Fracturing; Straight Nitrogen Based Fracturing; Liquefied Petroleum Gas (LPG) Fracturing; Liquefied Natural Gas (LNG) Fracturing; as well as Explosives and Propellant-Based Fracturing. Additional non-water carrier fluids are also identified. A discussion on CO_2-Foam Fracturing is given in the separate LBNL report mentioned above (*Wan*, 2017). The strengths and limitations of each non-water fracture stimulation carrier fluid are described below, and insights are provided on the characteristics of geologic formations amenable to the use of each fluid.

1. Liquid CO_2/Sand fracturing

1.1. Background/History

Fracturing with carbon dioxide is a method patented in the early 80's [*Bullen and Lillies*, 1982]. By the end of the 20th century, there had been more than 1,200 successful applications of the CO_2/sand fracturing technology in Canada alone. The method has not found wide acceptance in the U.S. for unknown reasons. In 1993, the U.S. Department of Energy (DOE) supported the demonstration of a single application of this liquid-free hydraulic stimulation technology (CO_2/sand) in a water-sensitive Devonian Shale reservoir in eastern Kentucky. Applications of the technology in the USA have been reported in Devonian shale reservoirs in West Pennsylvania, Texas and Colorado [*Arnold*, 1998].

The CO_2/sand stimulation process is unique in that no liquids remain in the formation following the treatment. Thus, the formation damage created by retained stimulation liquids, and the resulting adverse effects on the relative permeability (and, consequently, on gas production) are eliminated. The working fluid, carbon dioxide (CO_2), is pumped as a liquid and no chemicals, gels, or water are used. This method is most effective in reservoirs where the gas permeability can be significantly impaired by the introduction and/or the retention of stimulation liquids, provided that long fracture lengths are not required [*Mazza*, 2001].

1.2. Method Description and Features

As self-evident, this waterless stimulation method uses carbon dioxide (CO_2) as the working fluid. This is pumped as a liquid and requires a specially-designed pressurized blender. The blender mixes proppant with the liquid CO_2 under pressure. The high pressure required by the method is needed to keep CO_2 in its liquid state, to induce fractures in the the reservoir rock, and also to facilitate/enhance the transport proppant of proppants that are necessary to keep the fractures from closing when the pressure is released. The CO_2 blender is a closed pressurized vessel that is pre-loaded with proppant before the actual fracturing operation. The blender includes a manifold system that blends proppants into a liquid CO_2 stream prior to their introduction into the high-pressure fluid pumps. Liquid CO_2 is introduced into the enclosed blender at a temperature and pressure of 0°F and 300 psi, respectively. Nitrogen gas (N_2) is used as a positive displacement "blanket" that effectively forces the liquid CO_2 into the enclosed blender. The injection rates needed for fracturing operations with this technology may vary between 30-55 bpm, depending upon frictional effects and tubular constraints. The surface set-up for the application of this method is illustrated in **Figure 1** [*Campbell et al.*, 2000].

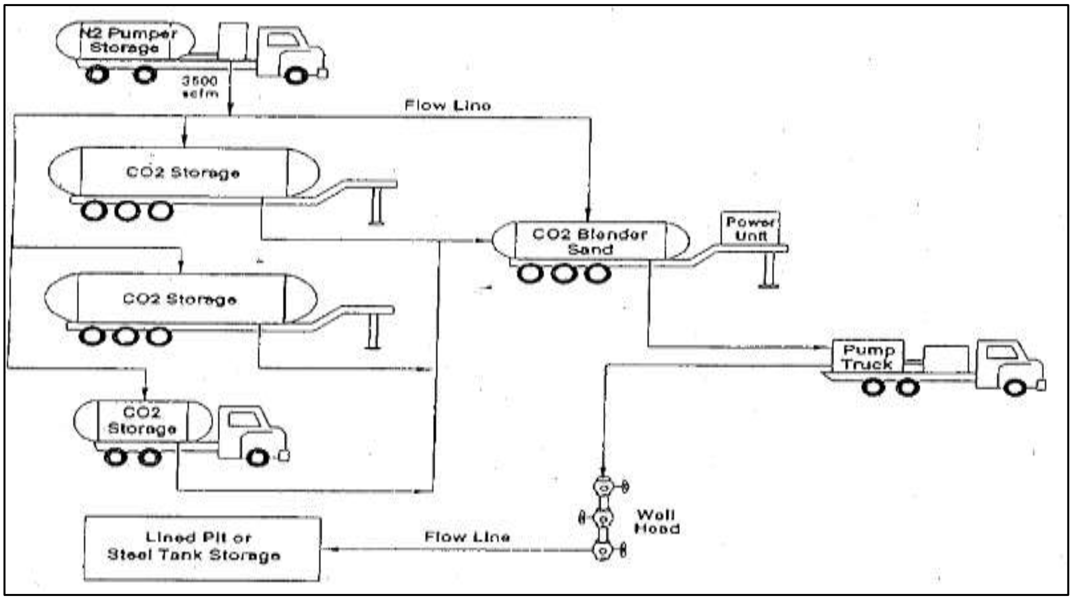

Figure 1. *Schematic of liquid CO_2 and sand stimulation equipment*

1.3. Unique Features of the CO_2/Sand technology

Compared to other hydraulic fracturing processes, CO_2/sand fracturing has some unique features that are considered to be advantageous in cases where the reservoir can retain a large fraction of the spent stimulation liquids (often water-based). This is almost invariably associated with substantially reduced relative permeabilities to gas and oil, resulting in correspondingly substantial reductions of production rates. The technology is considered an especially attractive alternative in low-pressure, dry-gas reservoirs, in which its application eliminates the potential for reservoir entrapment of stimulation liquids (phase trapping) while at the same providing the advantage of fracture aperture maintenance through the associated proppants. The inability to transport proppants is a significant weakness of several alternative waterless fracturing treatments.

An example of the application of this technology is at the Big Sandy gas field (a predominantly dry-gas reservoir with the greatest reserves of natural gas in eastern Kentucky), in which the majority of the natural gas resource occurs in (and is produced from) water-sensitive Devonian shales. The effectiveness of the technique is evidenced in Table 1, which lists the average 5-year cumulative production per fracturing stage in the Big Sandy field for several waterless fracturing technologies. The superiority of the CO_2/sand stimulations is evidenced by their significant improvement in gas production over those from competing waterless methods [*Mazza*, 2001].

Table 1. *Effect of Stimulation Method on Gas Production From the Big Sandy reservoir*

Stimulation Type	Average 5-Yr Cum (MMcf/Stage)
CO_2/Sand	68.3
N_2 gas	22.9
N_2 foam	10.5

Song [HGP1]*et al.* [2014] summarized the reasons why CO_2/sand fracturing may lead to an increase in the post-fracture production of strong water-locking reservoirs. Specifically:

(1) The fracturing fluid (liquid CO_2) has ultra-low interfacial tension, and can completely and rapidly flow back to the well (from the induced fractures and the interior of the reservoir it has reached) after vaporizing in response to the elevated natural temperature in the reservoir (usually well above the critical point of CO CO_2[HGP2]);

(2) The fracturing fluid is free of any potentially harmful residuum, leading to clean/open conductive beds of propped fractures, thus maintaining high fracture conductivity and large effective fracture length for high production;

(3) The high solubility of CO_2 can substantially decrease the viscosity of crude oil in the formation and thus improve oil mobility and recovery;

(4) Theoretically, the ultra-low interfacial tension of CO_2 in its supercritical state (after its vaporization by the reservoir heat) can accelerate the desorption of adsorbed gas in shale gas reservoirs.

1.4. Drawbacks of the CO_2/Sand Method

The method has several limitations. More specifically:

- The CO_2/sand fracturing method requires a specialized pressurized blender.
- The size/length/extent of the fractures is limited by volume of the pressurized blender.
- The transport of CO_2 or CO_2/N_2 in their liquid problem, and their storage in pressurized containers, may be challenging and potentially dangerous to operators.
- It is difficult to capture the vaporized CO_2 after the fracturing operation, and loss of CO_2 to the atmosphere is currently a difficult (if not unacceptable) proposition because of its eventual impact on global warming [*Rogala et al*., 2013].
- CO_2 has a low viscosity (0.1 mPa s in its liquid state and about 0.02 mPa s in its gaseous and supercritical states). These low viscosities can lead to significant losses through leak-off (flow into the low-permeability matrix), reduced/poor sand carrying capacity (proppant transport) and limited fracture-inducing potential (narrow apertures).
- During the fracturing operation, the CO_2/sand mixture is pumped at rates of 45 to 60 bpm to provide a sufficiently high velocity for proppant transport. For wells with small diameter casing, the corresponding friction pressure losses can be as large as 100 psi/100ft (**Figure 2.**), thus further limiting the fracture-inducing capacity of the method [*Campbell et al*., 2000]. Therefore, although CO_2/sand stimulation treatments have often

met significant success, the high rates they require and the associated frictional losses demand very powerful surface pumps [*Gupta*, 2009].

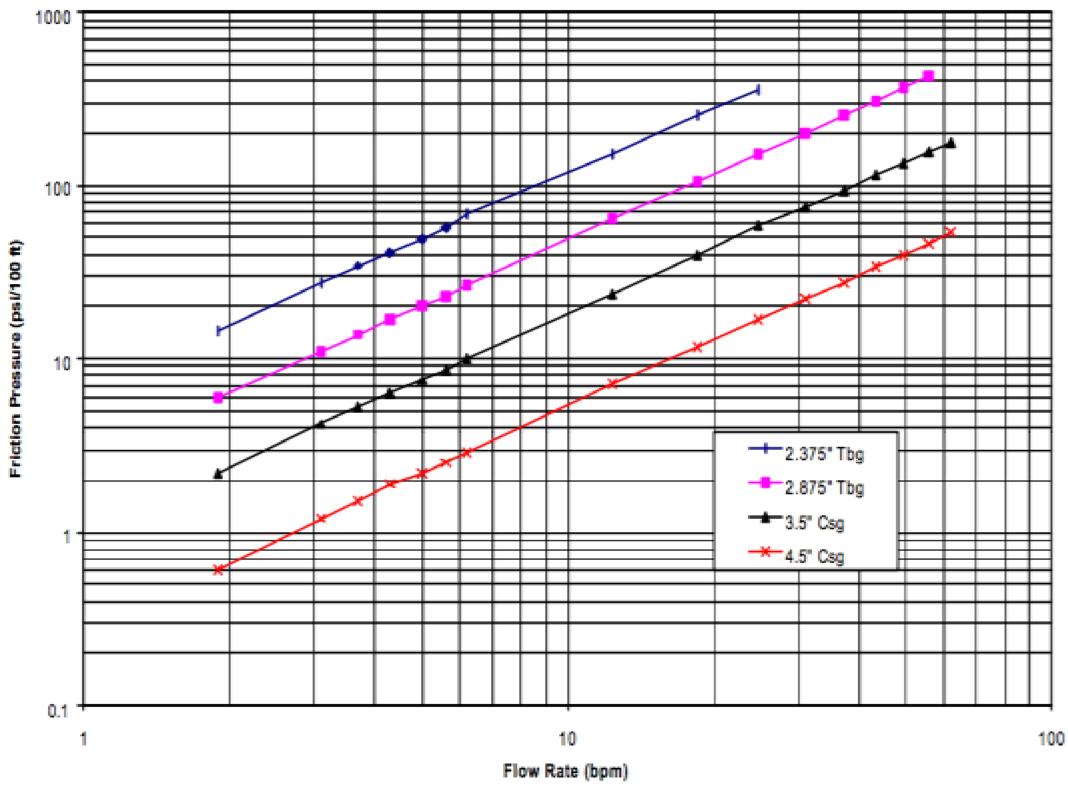

Figure 2. *Friction pressure loss of liquid CO_2 through various sizes of tubing*

1.5. Geologic Limitations of the CO_2/Sand Method

According to *Gupta and Bobier* [1998],

> "*Historical results demonstrate that liquid CO_2 and CO_2/N_2 system are very successful in some formations but not in others*" and "*The ideal candidate… is a dry gas well which has the following characteristics, dirty sandstone formation, damaged, under pressured, under saturated with fluid sensitivity*".

CO_2 by itself either does not react or reacts very slowly with reservoir minerals. In the presence of water and bivalent anions, (e.g., Ca^{2+}, Mg^{2+}, Fe^{2+}), CO_2 will precipitate as carbonate minerals and could quickly clog up existing pores, leading to significant reductions in porosity and permeability with a consequent reduction in the efficiency of the stimulation process and in production. However, the precipitation reaction will not proceed unless formation rock contains calcium plagioclase, i.e., feldspars $CaAl_2Si_2O$ [*Matter and Kellemen*[HGP3], 2009]. More specifically:

- Dissolved CO_2 dissociates into bicarbonate and carbonate ions

$$CO_2(aq) + H_2O = H_2CO_3 = HCO_3^- + H^+ = CO_3^{2-} + 2H^+ \quad (1)$$

- If bivalent cations are in solution, they will precipitate as carbonate minerals

$$(Ca,Mg,Fe)^{2+} + HCO_3^- = (Ca,Mg,Fe)CO_3 + H^+ \quad (2)$$

$$(Ca,Mg,Fe)^{2+} + CO_3^{2-} = (Ca,Mg,Fe)CO_3 \quad (3)$$

- Reactions (1) and (2) generate H^+ ions and will not proceed as written unless these ions are also consumed. Further water–rock reactions, such as calcium plagioclase dissolution (reaction (4)), consume H+ ions, driving reactions (1) and (2) to the right, and resulting in precipitation of carbonate minerals

$$CaAl_2Si_2O_8 + 2H^+ + H_2O = Ca^{2+} + Al_2Si_2O_5(OH)_4 \quad (4)$$

Existing CO_2 fracturing operations in Canada and U.S. have been designed for, and applied to, water sensitive formations involving no free formation water or injected water. Application of the method to a new formation with adverse geochemistry will need to account for formation water or the possibility of water injection.

1.6. References for the CO_2/Sand Method

Arnold D.L., Liquid CO_2-sand fracturing: the dry frac, *Fuel and Energy Abstracts*, **39**(3), 185–185(1), 1998.

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Campbell, S.M., N.R. Fairchild and D.L. Arnold, Liquid CO_2 and Sand Stimulations in the Lewis Shale, San Juan Basin, New Mexico: A Case Study. Society of Petroleum Engineers. doi:10.2118/60317-MS, January 2000.

Gupta D.V.S. and D.M. Bobier, The History and Success of Liquid CO_2 and CO_2/N_2 Fracturing System, Society of Petroleum Engineers paper SPE 40016, Gas Technology Symposium, 15–18 March 1998, Calgary, Alberta, Canada, 1998.

Gupta, D.V.S., Unconventional Fracturing Fluids for Tight Gas Reservoirs. Society of Petroleum Engineers. doi:10.2118/119424-MS, 2009.

Matter J. and P. Kelemen[HGP4], Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation, Nature Geoscience, Nov 2009.

Mazza, R.L., Liquid-Free CO_2/Sand Stimulations: An Overlooked Technology - Production Update. Society of Petroleum Engineers. doi:10.2118/72383-MS, 2001.

Rogala, A., M. Bernaciak, J. Krzysiek and J. Hupka, Non-aqueous fracturing technologies for shale gas recovery, *Physicochemical Problems of Mineral Processing*, **49**(1), 313–322, 2013.

2. Straight Nitrogen-Based Fracturing

2.1. Types of Nitrogen (N_2) Fracturing

The main types of nitrogen-based fracturing fluids are

- energized,
- foam,
- straight N_2 gas (mist), and
- cryogenic N_2 liquids.

Foam-based fracturing fluids typically consist of (a) a water-based system and (b) N_2 in a gaseous state with a composition in the range of 53% to 95% by volume. Below 53%, the fracturing fluid is considered energized. Because of the emphasis on waterless or near-waterless fracturing methods in the review, N_2-energized and N_2-foam systems and methods will not be further discussed here.

At a N_2 concentration of 95% (by volume) or higher, the fracturing fluid is considered a mist (straight nitrogen). Cryogenic N_2 liquids have also been used as fracturing fluids. However, they are rarely employed in commercial operations because of the need for special piping and equipment requirements [*Palmer* [HGP5]*et al*., 2013].

2.2. Straight Nitrogen

The technology of straight-N_2 (mist) fracturing was developed in the early 1980s. Pumped at sufficiently high rates and pressures, gaseous nitrogen alone was successfully used as a fracturing fluid in a field experiment in the Ohio Shale Formation of the Devonian shale trend [*Abel*, 1981]. Nitrogen was brought to the location of the well as a liquid, was heated to vaporize it, and was then injected into the discharge line as a warm gas. In that case, five shallow wells were stimulated using the straight nitrogen method, with perforation depths ranging from 2400 feet to 3500 feet. Another field application was conducted in 1985 in a Devonian shale reservoir in Washington County, OH. Approximately 60% of the injected volume used for this operation was a pure nitrogen gas without proppant, designed to pneumatically produce fractures in the stimulated formation. The remaining 40% carried sand 423–625 μm in diameter was injected into the wellbore, where the sand particles were mixed with nitrogen that carried them into the fractures [*Gottschling*[HGP6], 1985].

2.3. Method Applicability and Features

Nitrogen gas fracturing is used primarily for water-sensitive, brittle, and shallow unconventional oil and gas formations. The use of nitrogen prevents the swelling of clays (and their undesirable consequences on permeability and production) that evolves invariably following hydraulic fracturing with water-based fluids such as slickwater. Pure gaseous nitrogen produces best results in *brittle formations that have natural fractures and stay self-propped* after the cessation of injection and the end of fracturing. This is because nitrogen is an inert and highly-compressible gas with low viscosity, which makes it a poor proppant carrier.

Because of the low density of gaseous nitrogen, the main applications for nitrogen gas fracturing are shallow unconventional plays, such as coal beds (for coal-bed methane production), tight sands, and shale formations up to 5000 ft (1524 meters) in depth. Formations best suited for nitrogen gas fracturing also tend to have a permeability of 0.1 or less, and a porosity of 4% or less [*Air Products*, 2013].

The method has some additional advantages. Gaseous nitrogen is widely available and is relatively non-expensive. It is an inert gas and hence does not damage rock formation through chemical interactions that can change the physical properties of the rock. The gas can be removed easily after the treatment (i.e., the clean-up process is fast), and, unlike CO_2, it has no environmental impact.

2.4. Drawbacks of the N_2-Based Methods

Rogala et al. [2013] indicated that the many advantages offered by nitrogen-based fracturing would suggest that this technology would be a very good technical solution. However, they also conclude that placing the proppant in high velocity gas stream is problematic in terms of design and field application (especially given the uncertainties about the geometry of fractures in the heterogeneous subsurface), may result in erosion, and that the technology is limited to shallow formations in which evolving fractures are self-propped.

2.5. Geologic Limitations of the N_2-Based Methods

Nitrogen is an inert gas, and as such it is not sensitive to minerology of the formation rocks. As discussed earlier, it is limited to shallow wells [*Gupta and Bobier*, 1998] as a result of low fluid density that affects hydrostatic pressure and bottom hole treating pressure (BHTP) – see **Figure 3**. The method is applicable to cases where BHTP is larger than the formation minimum horizontal stress (otherwise, fracturing cannot occur). The formation minimum horizontal stress is controlled by the large-scale geomechanical regime at the site, and increases with the overburden stress, which is a function of depth. Given the density of N_2 (as a function of pressure and temperature), a reasonable estimate of the maximum depth of a formation targeted for fracturing is about 1600 m (**Figure 3**). Additionally, the limited proppant-carrying capacity of N_2 limits application of the method to formations in which stimulation that results in self-propping fractures (probably involving fragmentation at the surface of the fractures). This is the reason that the method is applicable to high brittleness index rock (e.g., quartz and dolomite), the fracturing of which leads to small fragments that can keep the fractures open. Softer more plastic materials like shales do not appear to be good candidates for N_2-based fracturing.

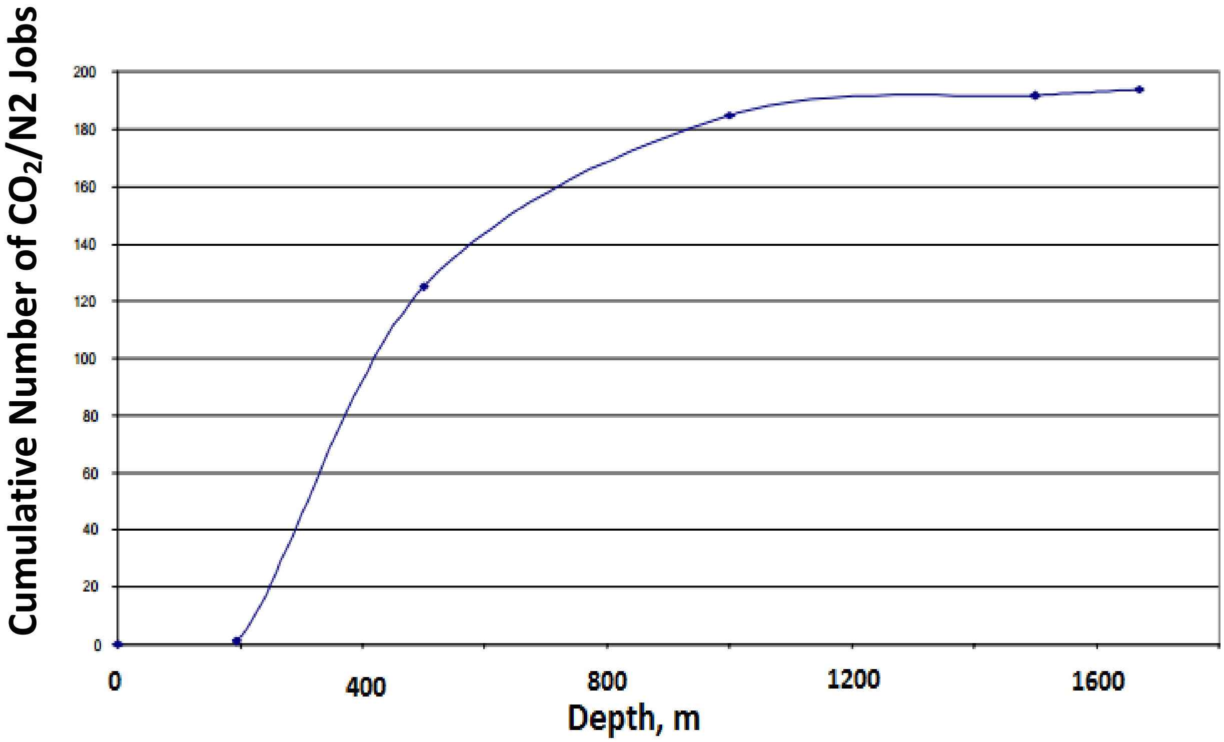

Figure 3. *Number of CO_2 and N_2 fracturing applications as a function of formation depth.*

2.6. References for the N_2-Based Methods

Abel, J.C., Application of Nitrogen Fracturing in the Ohio Shale. Society of Petroleum Engineers. doi:10.2118/10378-MS, 1981.

Air Products. *Enhanced Unconventional Oil and Gas Production with Nitrogen Fracturing*, from http://www.airproducts.com/industries/energy/oilgasproduction/oilfield-services/productlist/~/media/9546AD39B8FE4584B1F802F84D572D1B.pdf, 2013.

Gottschling, J.C. and T.N. Royce, Nitrogen Gas and Sand: A New Technique for Stimulation of Devonian Shale. Society of Petroleum Engineers. doi:10.2118/12313-PA, 1985.

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Palmer, C. and Z. Sito, Nitrogen and carbon dioxide fracturing fluids for the stimulation of unconventional shale plays, *Oil & Gas*, **30**(1), 191-198, 2013.

Rogala, A., M. Bernaciak, J. Krzysiek and J. Hupka, Non-aqueous fracturing technologies for shale gas recovery, *Physicochemical Problems of Mineral Processing*, **49**(1), 313–322, 2013.

3. LPG Fracturing

3.1. Background/ History

Liquefied Petroleum Gas (LPG) has been used as stimulation fluid for fifty years. The technology was developed for, and applied to, conventional reservoirs before being adapted to unconventional reservoirs. It has also been used to stimulate tight sands because of recovery improvements in reservoirs exhibiting high capillary pressures by eliminating the problem of phase trapping that often afflicts such systems. In 2007, a Canadian company (GasFrac, based in Calgary, Alberta), began using LPG gels to stimulate shale reservoirs. Since 2007, over 1500 applications of this technology have been reported in Canada and the United-States, using gellified propane as the fracturing fluid.

3.2. Description of the Method of Gelled LPG Fracturing

Propane under high pressure (i.e., in a liquid state) is the standard/main gas used in applications of the LPG technology. In most cases, LPG is gelled before fracturing because this approach enables/facilitates the transport of proppants into the fractures. However, there is a technology variant (developed and promoted by the EcopStim company in Houston, Texas) in which LPG is liquefied but not gelled. This variant uses buoyant proppants (such as fine sand and carbon fullerenes), but, this being a very new technology, the range of its applicability has yet to be fully studied, analyzed and proven. During fracturing the LPG remains liquid, but after completing the process it vaporizes and mixes with the reservoir gas and/or dissolved into the reservoir oil [*Gandossi*, 2013; *Rogala et al*., 2013].

Then gelled, LPG has a consistent and predictable viscosity, which tends to indicate an ability to evenly distribute proppants. Compared to the costly applications of CO_2- or N_2-based technologies (in terms of fracturing fluid and specialized equipment, see earlier discussions), the LPG fracturing method is relatively cost-effective and requires no special cooling or venting equipment. LPG is an abundant product of the natural gas industry, and is easily stored at ambient temperature. Using LPG also reduces the need to flare the initial production from the well in order to clean up the traditional fracturing fluids, thus reducing CO_2 emissions. Because the density of liquid propane is half that of water, the transportation cost of LPG to the application site is reduced. Finally, there is no need to remove the fracturing fluid from the site, thus eliminating the disposal costs (a significant issue in conventional hydraulic fracturing).

3.3. Features of LPG Fracturing Technology

The main advantage of the LPG fracturing technology is the rather consistent enhancement of the well productivity. This is due to the different behavior of water and LPG in the fractures and matrix of the targeted low-permeability reservoirs. In the case of hydraulic fracturing, residual water in the fractures (natural and induced) and in the matrix resist removal from the system because of entrapment (in closing fractures) and capillary interactions, leading to lower relative permeabilities to hydrocarbon flow (liquid and/or gaseous) and correspondingly lower production. An additional effect of water is the swelling of clays (smectite and illite) that can cause further reductions in porosity, permeability and production.

In the case of LPG, the pressure drop after the cessation of the injection in the fracturing process is coupled with the naturally higher temperature of the reservoir to effect a change of the physical state from liquid to gas. This does not affect adversely the relative permeability to gas through the fractures and the matrix, and it additionally enhances the advective flow of liquid hydrocarbons toward the production well through the reduction of their viscosity (a result of the large solubility of propane in oil).

Other **advantages** associated with the use of LPG for fracturing include:

- Lower viscosity, density and surface tension of the fluid, which jointly result in lower energy consumption during fracturing
- Full compatibility with the reservoirs because LPG and hydrocarbons are mutually soluble,
- Smaller amounts of (gelling) chemicals added to the fracturing fluid
- No fluid loss, possible 100% recovery of the LPG in the well production stream
- Sustainable, recyclable and more environmentally friendly then hydraulic fracturing. This is because there is no water used in the fracturing operation (and no need for disposal), the fracturing fluid is inert and does not interact with reservoir minerals, and can be recovered (and possibly recycled) during the early stages of production
- There is extensive experience and numerous existing government and industry regulations and procedures governing the use of LPG

3.4. Limitations of the LPG Fracturing Technology

The main drawback of this technology is that it involves the use and manipulation of large amounts (several hundred tons) of flammable propane (and the associated health and safety hazards). Therefore, it appears to be a more suitable solution in environments with low population density, provided of course that the workers safety can be safeguarded. Other drawbacks include:

- The investment costs of the technology are higher than those for hydraulic fracturing because LPG is pumped into well at a very high pressure, and after each fracturing it has to be liquefied again
- LPG must be stored in costly pressurized tanks (water in HF operations is stored in non-pressurized tanks or in outdoor pools)
- LPG is explosive
- LPG is denser than air and can accumulate and persist at ground low points, potentially posing a health hazard to humans and animals.

There is no obvious geological and/or geochemical limitation to the application of the technology, and no such evidence or discussion in the literature.

3.5. References for the LPG Fracturing Technology

Gandossi, L., An overview of hydraulic fracturing and other formation stimulation technologies for shale gas production, JRC Technical Reports EUR-26347-EN, 2013.

Rogala, A., M. Bernaciak, J. Krzysiek and J. Hupka, Non-aqueous fracturing technologies for shale gas recovery, *Physicochemical Problems of Mineral Processing*, **49**(1), 313–322, 2013.

4. LNG Fracturing

4.1. History/Background of LNG Fracturing

Liquefied Natural Gas (LNG) as a carrier fluid for fracturing is a new technology developed in 2011 by the *ENFRAC* company (subsequently acquired by the *Millennium* company in 2014). The initial motivation for its development was to find a non-aqueous and cost-effective fracturing fluid that would be readily available near well sites. LNG appears to have significant advantages over other waterless (gas-based, such as such as CO_2 and LPG-based) technologies used in the past. Thus, CO_2 is costly and not easily available in all locations, and additionally requires gas separation before hydrocarbon production can begin in earnest. LPG-based fracturing fluids have been operationally successful, but they are not as readily obtainable as LNG and carry inherent safety issues.

4.2. Description of the LNG Fracturing Method

Natural gas obtained from the nearest source (pipeline, gas well or plant) is cooled to -162 ^oC to create LNG. The LNG is stored in closed vessels and transported to the well site for use in the fracturing operation. The handling of LNG is similar to that of liquid nitrogen (-196 ^oC), which is a well-established practice in the oil and gas industry. *Note that LNG fracturing may not be a pure waterless method, but only a water-reducing fracturing method.*

During the fracturing operation, LNG is heated up to 15 ^oC and pressurized to 7000 psi. Because both the pressure and the temperature are increased, the LNG volume remains practically unchanged. At the wellhead the LNG is mixed/combined with the conventional fracturing fluid slurry (which may contain proppants), travels down the wellbore to the reservoir and serves to hydraulically fracture the formation. The friction pressure loss associated with this technology is close to the hydrostatic pressure change and, consequently, the bottom tubing pressure will slightly higher than the surface pressure (7000 psi).

The volume percentage of LNG varies, as it depends on the nature of additional fracturing liquid used in this technology. Thus, LNG can take up to 50% of the combined fracturing fluid volume if mixed with water, or 60-95% of the combined volume if mixed with water-based foam. For oil based fluids (e.g. diesel, crude oil and fracturing oils), LNG can take 10-70% volume [*ENFRAC*, 2016]. *Baker*[HGP7]-*Hughes* [2014] filed a patent claiming a new technology using gelled LNG for fracturing; however, no more details on the method have been released and no review, evaluation and publication on it is available.

4.3. Features of the LNG Fracturing Method

Unlike water, natural gas used as a fracturing fluid fully mixes with gaseous hydrocarbons and is readily soluble into liquid ones. Upon completion of fracturing, the natural gas used in the fracturing can be recovered with existing infrastructure as part of the hydrocarbon production (unlike water, the flow back of which has to be captured, processed and disposed of). As mentioned above, the LNG technology is not burdened with most transportation costs because natural gas is readily available near the well sites.

4.4. Limitations of the LNG Fracturing Method

As a new technology initiated by and patented by a service company, very limited technical details are available. No academic research data and review are available, which makes it difficult to evaluate the claims and the released data of company that developed and owns the technology.

There is no obvious geological and/or geochemical limitation to the application of the technology, and no such evidence or discussion in the literature.

4.5. References for the LNG Fracturing Method

US patent [HGP8]20140246199 A1, *Method of fracturing with liquefied natural gas*, 2014

ENFRAC[HGP9], Nature Gas Mixture Fracturing, www.ptac.org/attachments/1563/download

New LNG fracking process explained. http://www.pipelinenews.ca/features/production/new-lng-fracking-process-explained-1.2073234

5. Explosive- and Propellant-Based Methods

5.1. History/Background of Explosive- and Propellant-Based Methods

Using explosives to fracture rock formations and thus stimulate production is a very old technique. From the 1860s until the late 1940s, explosives were commonly used in wells to increase production ("well shooting"). Liquid nitroglycerin in a tin cylinder was lowered down the well and detonated. The technique was both effective and dangerous [*Hyne*, 2001]. Problems of wellbore damage, safety hazards, and unpredictable results reduced the relative number of wells stimulated by high-strength explosives [*Gandossi*, 2013]. However, more advanced methods of explosives-based stimulation of low-permeability formations are still used widely in the oil and gas industry.

More recently, studies appeared to indicate that propellants have advantages over explosives. Propellants are substances which deflagrate rather than detonate [*Schmidt et al*., 1980], and can release gases at controlled rates (unlike the volent, uncontrolled release of gases in explosives). The propellant techniques seem to offer a potential use for shale gas extraction. They are known by several generic names, such as Dynamic Gas Pulse Loading (Servo-Dynamics), High Energy

Gas Frac (Sandia National Laboratories), Controlled Pulse Fracturing (Mobil Research and Development Corporation), and others. Potential problems/limitations of propellant-based technologies are the insufficient energy that is available for fracturing (which leads to limited fracture length), in addition to the inability to transport propellants to ensure open fractures after the exhaustion of the propellant gases. A more recent technology proposed by Lawrence Berkeley National Laboratory (LBNL) and Lawrence Livermore National Laboratory (LLNL) aimed to address the shortcomings of both the older explosive-based technologies and of the propellant-based technologies.

5.2. Method Description

Solid propellants are deflagrated at appropriate locations in the well. These generate high pressure gases at a controlled rate that creates a fracturing behavior dramatically different from either hydraulic fracturing or explosives. The time to peak pressure is approximately 10,000 times slower than explosives and 10,000 times faster than hydraulic fracturing. Unlike explosives, the burn front in these materials travels slower than the speed of sound. The pressure-time behavior of propellants differs from that of explosives in that the peak pressures are lower, and the burn times are longer.

Solid propellants do not detonate, but deflagrate. Deflagration is a burning process that takes place without any outside source of oxygen. The gas pressures that result from the use of propellants are in the range of 20,000 psi and last approximately 10 milliseconds. No shock wave is produced, the rock is split rather than compacted (**Figure 4**), and multiple fractures are created [*GasGun*, 2013]. Depending on the tools used, the reservoir lithology and the depth, propellant fracture lengths are generally in the range from a few feet to a maximum, under the very best of conditions, of a few tens of feet [*Schatz*[HGP10], 2012].

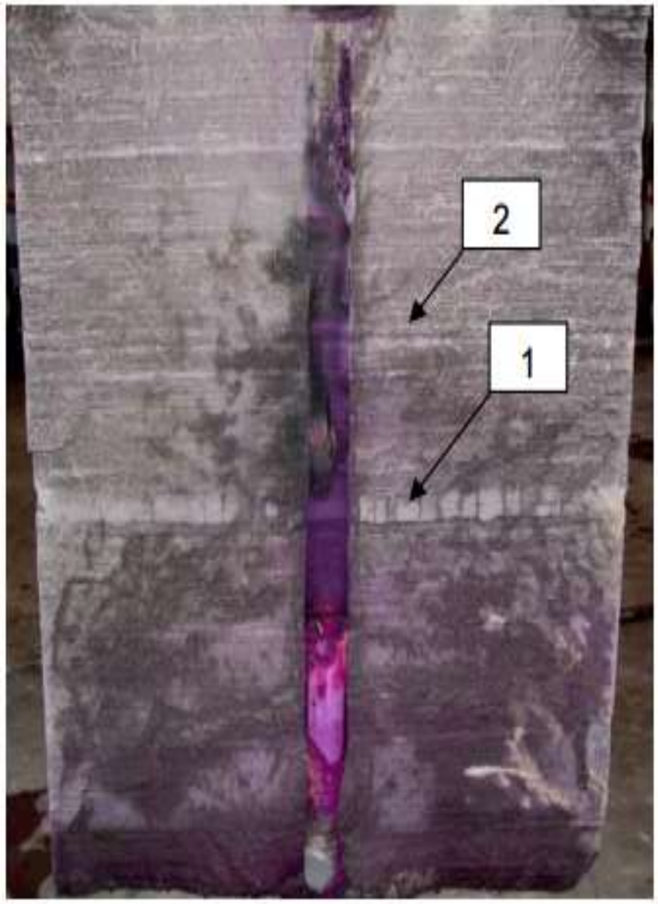

Figure 4. *Propellant-induced fracture in a block of Mancos shale [Page and Miskimins, 2008].*

A joint project of LBNL-LLNL proposed a new explosives-based technology that used a new generation of explosives and a designed approach that was based on experience stemming from the testing and analysis of subsurface defense systems. Using computer codes developed for the subsurface testing of explosive devices, the new technology involves appropriate siting of explosives, the use of shaped charges and carefully designed differential firing sequence of the charges to fragment (rather than fracture) the rock. The proposed method does not necessitate the use of proppants because it relies on minute displacement of the fragmented rock blocks to ensure persistently open fractures, and results in significantly higher surface areas for hydrocarbon flow from the matrix to the fractures and for production at the well. It is important to note that there has been no field testing of the proposed technology to-date.

5.3. Method Features

The use of propellants and other so-called tailored-pulse techniques depend on a controlled pressure-time behavior to minimize wellbore damage and maximize fracture growth by gas penetration. Both propellant- and explosive-based methods are applicable to water-sensitive reservoirs, and are free of the problems commonly associated with hydraulic fracturing (relative permeability issues, water availability restrictions and water-disposal environmental problems). The LBNL-LLNL technology is based on fragmentation, as opposed to fracturing, and is expected to result in a very large surface area for fluid release and production, in addition to affecting a much larger reservoir volume than propellants (because of significantly higher energy). Note that both methods are cost-effective compared to conventional fracturing methods.

5.4. Method Limitations and Drawbacks

Extensive research has shown that the pressure pulse created by high explosives enlarges the wellbore by crushing and compacting the rock. The enlarged wellbore is left with a zone of residual compressive stress. These residual stresses and compacted rock can actually reduce permeability near the wellbore. Extensive caving often fills the wellbore with debris that require days, even weeks, to clean up [*GasGun*, 2013]. Additionally, propellant-based methods result in a fracture zone of limited extent.

The LBNL-LLNL proposed technology involves high-energy explosives, with associated hazards and legal/liability issues. Additionally, the method results in a complete destruction of the original (unlined) wellbore and requires the drilling of a second wellbore (often coinciding with the original collapsed one).

There is no obvious geological and/or geochemical limitation to the application of proppant- and explosive-based technologies, and no such evidence or discussion in the literature.

5.5. References for Explosive- and Propellant-Based Methods

Gandossi, L., An overview of hydraulic fracturing and other formation stimulation technologies for shale gas production, JRC Technical Report EUR-26347-EN, 2013.

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6. Additional Waterless Fracturing Methods

6.1. Liquid Helium-Based and Other Stimulation Methods

The use of liquid helium as fracturing fluid is mentioned in very few sources [*Gandossi*, 2013], notably in a study prepared for the Parliamentary Office for the Evaluation of Scientific and Technological Choices of the French republic [*Lenoir and Bataille*, 2013].

6.2. Method Description

According to Chimera Energy Corp. (reported in *BusinessWire* [2012]), the helium-based fracturing technique "*does not use steam, LPG gel, natural gas or the pumping of anything hot into the well being used. The central operation in the process uses only inert elements. These elements are non-toxic or caustic in any way. First, the horizontal well casing is perforated pneumatically. This allows the extraction process to reach the target area surrounding the casing. Depending on the size of the casing in the well, moveable pressure plugs are placed at optimum distances to segment the horizontal section and allow for engineered pressures. Then helium, beginning in its liquid state, is used to create the pressures needed to open up existing fractures and form new ones. Under exothermic control, Helium will increase in volume 757 times in transitioning from a liquid to gaseous form. With plentiful pressure available, engineering the segmenting distances multiply the effect*." This is the extent of the information on the subject, which, given some of the known properties and behavior of helium in porous media, raises a wide range of questions and uncertainties.

6.3. Method Features

The diffusion rate of helium through solids is extremely high (by virtue of its molecular size, the smallest of all molecules), negating the need for solvents in the process. Neither water nor other chemical additives would be required. Although helium is the second most abundant element in the known universe after hydrogen, in the atmosphere is present only at 5.25 parts per million at sea level and is only the 71st most abundant element in the Earth's crust (8 parts per billion). At current prices, the cost of a helium-based fracturing technology is expected to be very high. An environmental benefit of helium is that at standard conditions it is nontoxic and plays no biological role.

6.4. References Additional Waterless Fracturing Methods

BusinessWire, Chemical Engineer Announces Details of Chimera Energy Corp's Revolutionary Non-Hydraulic Shale Oil Extraction, from http://www.businesswire.com/news/home/20120822005366/en/Chemical-Engineer-Announces-Details-Chimera-Energy-Corp%E2%80%99s, 2012.

Gandossi, L., An overview of hydraulic fracturing and other formation stimulation technologies for shale gas production, JRC Technical Report EUR-26347-EN, 2013.

Lenoir, J.-C. and C. Bataille, Les techniques alternatives à la fracturation hydraulique pour l'exploration et l'exploitation des hydrocarbures non conventionnels, 2013.