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State of the art report on waterless stimulation techniques for shale formations

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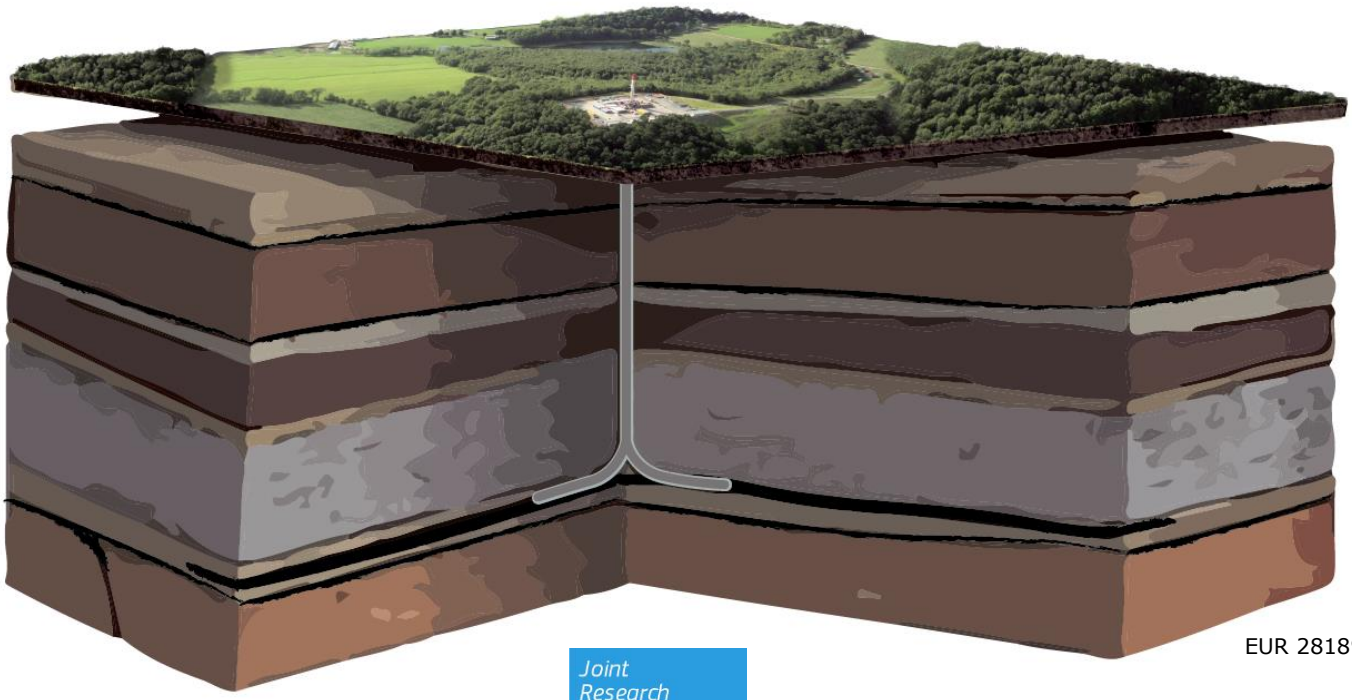

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Executive summary

The technology of hydraulic fracturing for hydrocarbon well stimulation is has recently become a very common and widespread technique, especially in North America, due to technological advances that have allowed extracting natural gas from so-called unconventional reservoirs (in particular shale formations). The conjunction of techniques such as directional drilling, high volume fracturing, micro-seismic monitoring, etc. with the development of multi-well pads has been especially successful in the last years in their application to shales, making gas production from shales technically and economically feasible.

In Europe, the potential application of this technology has led to both great concerns and high expectations: concerns regarding the alleged magnitude of the environmental impact, and expectations about production of indigenous hydrocarbons. Other types of formation stimulation exist that do not make use of water-based fluids (for instance, explosive fracturing, dynamic loading, etc.), or that make use of fluids other than water. These are currently not extensively applied due to performance and economic considerations.

As for any other industrial activity, the deployment of high-volume hydraulic fracturing could potentially entail risks to the environment and the safety of workers and neighbouring areas. Among the questions raised, several are related to water: a high water usage, chemical contamination methane infiltration in aquifers, contamination of surface water sources, etc. New technologies could help addressing these concerns by reducing or eliminating altogether the usage of water.

This report builds on previous JRC studies, in particular the 2015 report "An overview of hydraulic fracturing and other stimulation technologies - Update 2015" but focus on the identification of the most recent technological trends in the area of waterless well stimulation for shale gas production.

By searching the open literature, patent databases and commercial websites, many techniques are identified and explained, and their deployment status (for instance, whether the method is commercially applied, being developed, at the concept stage, etc.) is discussed.

1 Introduction

The technology of hydraulic fracturing for hydrocarbon well stimulation is has recently become a very common and widespread technique, especially in North America, due to technological advances that have allowed extracting natural gas from so-called unconventional reservoirs (in particular shale formations). The conjunction of techniques such as directional drilling, high volume fracturing, micro-seismic monitoring, etc. with the development of multi-well pads has been especially successful in the last years in their application to shales, making gas production from shales technically and economically feasible.

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This study is focused on the identification of the most recent technological trends in the area of waterless fracturing, with a particular focus on shale gas production. By building on previous JRC studies, in particular the 2015 report "An overview of hydraulic fracturing and other stimulation technologies - Update 2015" (Gandossi and Estorff 2015), all relevant technologies are identified and explained, and their deployment status (for instance, whether the method is commercially applied, being developed, at the concept stage, etc.) is discussed. The reader should bear in mind that the report has been compiled by and large by accessing publicly available literature (peer-reviewed journal papers and conference papers, but also patent databases, commercial websites, etc.), sometimes authored by individuals or organisations wishing to promote a certain technology.

2 Waterless Hydraulic Fracturing

The technique of hydraulic fracturing makes use of a liquid to fracture the reservoir rocks. A hydraulic fracture is formed by pumping the fracturing fluid into the wellbore at a rate sufficient to increase pressure downhole to exceed the strength of the rock.

The term "hydraulic fracturing" is nowadays widely used to mean the process of fracturing rock formations with water-based fluids but in applied science and engineering hydraulics is a topic dealing with the mechanical properties of liquids (not just water). Indeed, using water as base fluid for hydraulic fracturing is a fairly recent development (Montgomery and Smith 2010). The first fracture treatments were initially performed with gelled crude and later with gelled kerosene. In the early 1950s', many fracturing treatments were performed with refined and crude oils. Water started to be used as a fracturing fluid in 1953, with the concomitant development of a number of gelling agents. Surfactants were added to minimize emulsions with the formation fluid. Later, other clay-stabilizing agents were developed, permitting the use of water in a greater number of formations. In the early 1970s, a major innovation in fracturing fluids was the use of metal-based crosslinking agents to enhance the viscosity of gelled water-based fracturing fluids for higher-temperature wells. Other innovations, such as foams and the addition of alcohol, have also enhanced the use of water in more formations. Aqueous fluids such as acid, water, and brines are used now as the base fluid in approximately 96% of all fracturing treatments employing a propping agent.

The fracturing fluid used is a crucial component of hydraulic fracturing, not only concerning the technical characteristics (rheology, formation compatibility, etc.) but its environmental impact. Indeed, several among the main environmental concerns associated with shale gas fracturing today are due to the usage of water: the high volumes of water used and lost underground, the need to process flowbacks, the potential contamination of aquifers by leaks of chemicals employed in the fracturing fluids, etc.

Shale formations present a great variability, and for this reason no single technique for hydraulic fracturing has universally worked. Slickwater hydraulic fracturing, which is used extensively in Canadian and U.S. shale basins, is suited for complex reservoirs that are brittle and naturally fractured and are tolerant of large volumes of water. Ductile reservoirs require more effective proppant placement to achieve the desired permeability. Numerous other fracture technologies have been applied, including the use of CO_2, N_2 and CO_2 foams.

2.1 Foam-based fluids

In this particular technology, a foam is used as the fracturing fluid. Foams have long been considered as one of the best fracturing fluids for water-sensitive formations and environments where water is scarce (Neill, Dobbs et al. 1964; Komar, Yost II et al. 1979; Gupta 2009). In particular, foams are believed to be an appropriate means for fracturing shale gas reservoirs. They require lower (or no) water consumption, cause less damage in water sensitive formations and there is less liquid to recover and handle after the fracturing process. Expansion of the gas phase after the treatment also helps recover the liquid phase introduced into the formation with foams (Edrisi and Kam 2012).

Foams are structured, two-phase fluids that are formed when a large internal phase volume (typically 55 to 95%) is dispersed as small discrete entities through a continuous liquid phase (Reidenbach, Harris et al. 1986). These fluids are very versatile because of low-density and high-viscosity characteristics. Some authors claim that foam fracturing appears to be advantageous over the conventional water-based hydraulic fracturing because less amount of water usage can be translated into fewer amounts of health-hazardous chemical additives in fracturing liquid (Edrisi and Kam 2012).

The most common application for high-quality foams is in water-sensitive gas-bearing formations, typically an under-saturated gas reservoir where water blockage is a major concern. Foams are also beneficial when used for liquids-rich gas wells, such as in the Alberta Deep Basin and work in certain oil-bearing formations, such as the Cardium. Lastly, in areas where water is in short supply or hard to source, foams can present a very obvious advantage.

N_2-based foams became popular in the mid-1970's for both hydraulic fracturing and fracture acidizing stimulation treatments. Most recently, CO_2 foams have been found to exhibit their usefulness in hydraulic fracturing stimulation. Different foam-based fluids can be used. The liquid CO_2-based fluid consists of a foam of N_2 gas in liquid CO_2 as the external phase stabilized by a special foamer soluble in liquid or supercritical CO_2 (Gupta 2003). The main advantage of this fluid is the additional viscosity gained by the foam over liquid CO_2. The use of 75% volume of N_2 makes the fluid very cost-effective. The fluid has also found niche application in coalbed fracturing in Canada on dry coalbeds where any water introduced into the formation damages the cleats (Gupta in (US EPA 2004)). The influence of foam quality on effectiveness of hydraulic fracturing in shales was recently studied by (Gu and Mohanty 2014) and more recently by (Gu and Mohanty 2015).

Four main categories of foams can be identified:

- Water-based foams: Water and Foamer + N_2 or CO_2
- Acid-based foams: Acid and Foamer + N_2
- Alcohol-based foams: Methanol and Foamer + N_2
- CO_2-based foams: Liquid CO_2 + N_2

Foams are commercially used to fracture shale formations. A study from 2009 reports the use of foams to stimulate gas wells in the Lower Huron Shale in the Appalachian Basin(Rowan 2009). (Brannon, Kendrick et al. 2009) discuss the application of foams in the Big Sandy, a gas field in Kentucky characterized by ultra-low permeability, the Berea tight gas sands and Devonian Ohio shales such as the Huron formation.

NETL has an ongoing project (2013 to 2016) on the development of nanoparticle-stabilized foams to improve performance of water-less hydraulic fracturing. One of the objectives of the project is to develop nanoparticle-stabilized foams that have a very low water content yet exhibit high apparent viscosity, so that they can be used as nearly water-less fracturing fluids.

A recent study modelling fracture propagation and clean-up for dry nanoparticle stabilized-foam fracturing fluids is presented by (Qajar, Xue et al. 2016). An experimental study on the application of nanoparticles in unconventional gas reservoirs with CO_2 fracturing is reported by (Li, DiCarlo et al. 2015).

2.2 Oil-based fluids

A major advantage to this type of fluid, which was first type of high-viscosity fluid used in hydraulic fracturing, is its compatibility with almost any type of shale formation. Disadvantages are associated with potential high costs and greater concerns regarding personnel safety and environmental impact as compared to most water-based fluids. There are several oil-based fluids, for instance based on diesel, but a promising technique, which has been developed especially for shale gas production, makes use of liquefied petroleum gas (LPG). This is analysed in details in the following section.

2.2.1 LPG

Liquefied petroleum gas has been used as stimulation fluid for fifty years. It was developed for conventional reservoirs before being adapted to unconventional reservoirs. For instance, it was used to stimulate (or re-stimulate) oil wells. It has also been used to stimulate tight sands because of recovery improvements in reservoirs exhibiting high capillary pressures by eliminating phase trapping.

In 2007, the Canadian company GasFrac, based in Calgary (Alberta), started to use LPG gel to stimulate shale rocks. Since then, over 1500 operations of stimulation have been performed using this gellified propane technique both in Canada and United-States. The LPG used in the GASFRAC system is primarily propane (C3H8) (GasFrac 2013).

The technology is also developed by ecorpStim, based in Houston (Texas). In 2012, ecorpStim was at the origin of several technological developments: (1) removal of chemicals, by developing a new formula for the stimulation fluid (now composed exclusively of pure propane and sand, with no chemicals additives) and (2) reduced volumes of propane to meet stricter safety requirements. Pure propane is used (with the possibility of using butane and/or pentane for some rock types) (ecorpStim 2013a).

According to a report commissioned by Arnaud Montebourg, French Minister of the Economy, Industrial Recovery and Digital Development (Montebourg 2015), the Ministry identified the LPG technology implemented by eCorp as very promising to address the environmental concerns raised by water-based hydraulic fracturing. The Ministry was concerned about the high flammability of LPG, and toward the end of 2012 asked eCorp to perfect a technology that would eliminate such risk. eCorp is thus developing a fracturing technology based on non-flammable propane (NFP), i.e. heptafluoropropane, combined with and a proppant (mesoporous silica), described more in detail below (ecorpStim 2013b). In 2015 ecorpStim has announced a non-flammable, non-toxic shale stimulation fluid based on light alkanes (ecorpStim 2015). This technology makes use of naturally occurring components in conventional and shale hydrocarbon production , i.e. a selection of low molecular weight alkanes ("light alkanes"). These alkanes are non-flammable are approved by the U.S. Food and Drug Administration for human ingestion and exposure. They also have no adverse impacts on the environment: they are non-ozone depleting and have zero global warming potential.

A recent analysis of effective fracture lengths and clean-up behaviour is presented by (Soni 2014). This paper also discusses major advantages and disadvantages of this technique along with some considerations on economics.

A fracturing fluid based on LPG as base fluid is proposed by (Xiangqian, Yongjun et al. 2013). The developed fracturing fluid system uses dialkyl phosphate ester as the gelling agent and a ferric complex as the cross-linking agent, and it is shown to have a very good crosslinking performance which makes it suitable for unconventional reservoirs.

The GasFrac LPG gel properties include: low surface tension, low viscosity, low density, and solubility within naturally occurring reservoir hydrocarbons. These properties are suggested to lead to more effective fracture lengths are created and thus enable higher production of the well. Another reported advantage is the ability to evenly distribute proppant. The fracturing fluids are totally recovered within days of stimulation, creating economic and environmental advantages by reducing clean-up, waste disposal and post-job truck traffic (GasFrac 2013).

The ecorpStim system completely avoids the use of chemical additives. The company reports that, while in hydraulic fracturing 30-80% of water is recovered, propane stimulation allows a recovery of 95-100% of injected gas. The recovered propane can be sold as such (i.e. directly inserted in the pipelines) or used for another stimulation operation. The seismic risk related to the injection of waste water in the subsoil is suppressed as well (ecorpStim 2013a).

When gelled, LPG provides a consistent viscosity, does not require the costly use of CO_2 or N_2, nor does it require any special cool down or venting of equipment. LPG is an abundant by-product of the natural gas industry and is stored at ambient temperature. Using LPG also reduces the need to flare production to clean up the traditional fracturing fluids, reducing CO_2 emissions. The main drawback of this technology is that it involves the manipulation of large amounts of flammable propane, with the ensuing safety hazards).

As described above, to mitigate the risk of flammability, ecorpStim is currently developing and testing a technology that makes using of non-flammable propane (NFP), i.e. heptafluoropropane. Non-flammable propane is a well-known gas, used in products including fire extinguishers and medical inhalers. NFP stimulation is reported to have all the advantage of pure propane stimulation (no water, no chemical additives), and to eliminate the risks of flammability associated with propane (Montebourg 2015). Other advantages are associated with non-flammable propane, as replacing water with propane leads to a reduction of the footprint on the surface, the equipment needed, the number of heavy vehicles and the volumes of fluids required. The time needed to stimulate the rock is also reported to be between one third and one tenth shorter. The reduction of the volume of fluid necessary to carry out a stimulation operation (estimated at between 1/10th to 1/30th when compared to water) means that an extra layer of tubing can be added to the well, reinforcing the protection of the well and thus reducing the risk of breaching the well integrity during the stimulation phase.

Light alkanes stimulation is based on the idea that – just like in pure propane stimulation – these alkanes are a component of natural hydrocarbon production from shales and conventional reservoirs. Thus, their use as the stimulation fluid does not damage the reservoir rock and therefore should allow increased production from the well compared with traditional hydraulic fracturing. Likewise, light alkanes can also be self-supplied from the reservoir being stimulated. Finally, they can be recycled through the reservoir and recovered for further use, in the same way as for propane and heptafluoropropane (ecorpStim 2015). According to the developers, light alkanes stimulation provides a greater flexibility (broad range of viscosity / density) which enables this new method to be used in different shale formations and under varied operating conditions.

The LPG-based fracturing techniques discussed herein (GasFrac and ecorpStim) are both commercially applied in unconventional reservoirs in North America. (Lenoir and Bataille 2013) report that between 2008 and 2013, 2000 fracturing operations were carried out by the GasFrac company in North America (primarily in Canada and, since 2010, in Texas). In 2013 ecorpStim announced the successful field application of the technique employing pure liquid propane, by stimulating the Eagle Ford Shale at a depth of 5950 feet. The test took place in Frio County, Texas, and was completed in late December 2012. No chemical additives of any kind were used. Heptafluoropropane stimulation is being tested in field experiments by ecorpStim. Light Alkanes Stimulation is being patented by ecorpStim and the company was conducting further testing and experimentation of this technology in several basins in the United States at the beginning of 2015.

A low carbon hydrocarbon-based set of fluids was recently proposed by (Mao, Wang et al. 2016), mainly composed of phosphate anhydrous gelling agents, cross-linking agents and base fluid of light alkanes such as LNG, LPG, n-pentane and n-hexane. The gelling agent was generally synthesized from the polymerization reaction of triethylphosphate and phosphorus pentoxide and then mixed with alcohol by condensation reaction in the system. It found that these various components including iron crosslinking agent, phosphate ester together with base fluid can greatly influence the performance of the gelling. This novel system was found to exhibit excellent heat and shear resistance, while maintaining high viscosity at high temperature (up to 150 °C).

2.3 Acid-based fluids

The main difference between acid fracturing and proppant fracturing is the way fracture conductivity is created. In proppant fracturing, a propping agent is used to prop open the fracture after the treatment is completed. In acid fracturing, acid is used to "etch" channels in the rock that comprise the walls of the fracture. Thus, the rock must be partially soluble in acid so that channels can be etched in the fracture walls.

In shale formations, although many have a significant amount of dissolvable carbonate and limestone, the content in the rock is not a continuous phase. Hence, it is difficult to

use acid-based fluids even in the few high carbonate reservoirs such as the Eagle Ford in the USA. Without a continuous carbonate/limestone phase it is very difficult to etch the required "continuous" channel. Also, flow-back needs to manage the disposal of significant calcium carbonate/limestone volumes that come dissolved in the spent acid. Long etched fractures are difficult to obtain, because of high leakoff and rapid acid reaction with the formation (PetroWiki - Society of Petroleum Engineers 2012). However, (Burgos, Buijse et al. 2005) have recently reported on how better acid fracturing mixtures have improved penetration even at higher temperatures.

More recently (Sanchez Bernal, Tate et al. 2015) have discussed acid fracturing in tight gas carbonates reservoirs using CO_2 to assist stimulation fluids. This paper outlines the fact that there are very limited applications for low permeable tight carbonate reservoirs due to complexities associated with the physical and mechanical properties of carbonate rocks and its interaction with fracturing fluid. Nevertheless the advantages of using assisted CO_2 stimulation fluids are noteworthy, because of the elimination of potential formation damage normally associated with fracturing fluids and the very rapid clean-up. The study presents one of the first acid fracturing jobs assisted with CO_2 conducted on a tight gas well reservoir in Saudi Arabia, and concluded that CO_2 used to energized fracturing fluids can increase the productivity of the well while using less water and less acid than conventional acid fracturing.

A summary of acid treatment stimulation methods in shale oil and gas is presented in (Li, Dai et al. 2016). These authors report that the common technique in acid treatments, at least in Chine, includes the following steps: acid wash, matrix acidizing, prop fracturing with acid pre-flush, and multi-stage alternate-inject acid fracturing. They also describe the main stimulation mechanisms of acid treatment, falling into three categories: (1) the acid-induced increase of porosity and permeability in the shale matrix; (2) the influence on rock mechanical properties (shale brittleness, toughness and Young modulus); (3) the influence on fracture conductivity, caused by the acid dissolving calcite-rich areas in the shale and increasing fracture surface roughness (Li, Dai et al. 2016).

An acid fracturing methodology, called "hydraulic jet acid fracturing technique", was suggested in 2012 for deep carbonate reservoirs, where high temperature, high fracture pressure, high flow friction, and strong reservoir heterogeneity present severe challenges (Gensheng, Mao et al. 2012).

2.4 Alcohol-based fluids

In this type of fracturing, a methanol-based fluid is used. Several methods to enhance the viscosity of methanol have been described in the literature, ranging from foaming methanol to gelling it with synthetic polymers and guar. Attempts have also been made to crosslink gelled methanol with metal crosslinkers. In underpressured wells, it has been energized with N_2. Methanol-based fluids can also be energized with CO_2 for formations with severely under-pressured wells.

The flammability of methanol presents safety concerns. Its flash point (i.e. the lowest temperature at which it can vaporize to form an ignitable mixture in air.) is 11.6°C and its density is greater than that of air. Oxygen contact must be avoided and therefore a "blanket" of CO_2 vapor is normally used to separate methanol vapor from any oxygen source. Personnel must wear fire-resistant coveralls.

For formations with severe liquid trapping problems or irreducible water and/or hydrocarbon saturation, non-aqueous methanol fracturing fluids may be the best a solution. Methanol has excellent properties such as high solubility in water, low surface tension and high vapor pressure. These are favorable for the recovery of the fracture and formation fluids, hence increasing the permeability of the gas in the treated zone (Hernandez, Fernandez et al. 1994).

In the 1990s and up until 2001, some companies (for instance BJ Services, now part of Barker Hughes) used methanol as a base fluid in fracturing applications in Canada and Argentina (Antoci, Briggiler et al. 2001). In those cases, the fractured formations either had low permeability with high clay content, low bottom-hole pressure, and/or minimal load fluid recovery.

However, a recent study carried out on behalf of the Methanol Institute ("White Paper - Methanol Use in Hydraulic Fracturing Fluids") reviewed the literature and concluded that methanol was used infrequently as a base fluid (Saba, Mohsen et al. 2012). The main reason given was the problem of safe handling issues and additional expenses to ensure that all personnel involved with methanol treatments are thoroughly trained in the proper procedures for handling flammable materials. This study also concluded that, compared to water-based fracture fluids, methanol-based fluids are 3 to 4 times as expensive. In summary, concerns about safety and associated costs to use methanol has led to shifting away from methanol as a base fluid and limiting its use to being only an additive.

Nonetheless, in formations with severe liquid (aqueous and hydrocarbon) trapping problems, non-aqueous methanol fluids may be a solution (Gupta 2010). Over the years, several authors have identified the advantages of alcohol-based fluids, including low freezing point, low surface tension, high water solubility, high vapor pressure and formation compatibility. Methanol is also the fluid of choice for formations with irreducible water and/or hydrocarbon saturation (Bennion, Thomas et al. 1996; Bennion, Thomas et al. 2000).

Methanol-based fluids have been used on low permeability reservoirs, but it is not clear if their application has been extended to shales. Methanol as an additive is widely used in hydraulic fracturing, for instance as a corrosion or scale inhibitor, friction reducer, formation water flowback enhancer and fracturing fluid flowback enhancer (Saba, Mohsen et al. 2012).

2.5 Emulsion-based fluids

In this type of fracturing, an emulsion (i.e. a mixture of two or more liquids that are normally immiscible) is used as the fracturing fluid. There are several different emulsion-based fluids that have been developed and used as fracturing fluids. Many of such fluids use emulsions of oil and water, and could therefore be classified under the oil-based fluids. Broadly speaking, emulsion-based fluids reduce or completely eliminate the use of water.

Certain formations have potential to retain even the small amounts of water contained in foams. These fluids may damage these sensitive formations because of irreducible water saturation and liquid trapping. In these formations, replacing 40% of the water phase used in conventional CO_2 foams with methanol can minimize the amount of water. (Gupta, Hlidek et al. 2007) showed that a 40% methanol aqueous system yielded gave very good production results in several Canadian gas formations (Gupta et al., 2007).

(Liu, Fan et al. 2010) describe a new fracturing fluid (called SPME-Gel) obtained with the combination of a single phase micro-emulsion and a gellable polymer system. A microemulsion is defined as a dispersion consisting of oil, surfactant and aqueous phase, which is a single optically isotropic liquid solution with a droplet diameter usually within the range of 10–100 nm. This formulation was prepared by adding a microemulsion into a gelable polymer system at various concentrations obtaining the characteristics of high viscosity, low fluid loss and low friction. It was also shown that the broken SPME-Gel systems have low residues remaining in formation, low surface tension, low pressure to initiate cleanup and high core permeability maintaining, thus offering promising characteristics.

A high-quality emulsion of $C0_2$ in aqueous alcohol-based gel was used in the western Canadian sedimentary basin as a fracturing fluid in 1981. Since then, the use of such

fluid has been very successful, particularly in low-pressure, tight gas applications. The fluid has the same advantages as conventional high-quality $C0_2$ foams, with the added advantage of minimizing the amount of water introduced into the well (Gupta, Hlidek et al. 2007).

Emulsion-based fluids have been used on several unconventional (low permeability) formations, but no direct usage for shale gas stimulation could be found as a part of the present review.

2.6 Cryogenic fluids

2.6.1 Liquid CO_2

During a conventional hydraulic fracturing stimulation, water-based fluids can get trapped as liquid phase in rock pores next to the fractures due to very low permeability in tight gas and shale formations. This phenomenon is called water-phase trapping and can significantly damage the region near the wellbore. Water blocking may plague the success of hydraulic fracturing in low permeability gas reservoirs, and resulted significant loss of relative permeability due to the capillary effects between the treatment fluid and reservoir fluids. The injected fluid during hydraulic fracturing should then be compatible with the formations to avoid swelling. CO_2 has the necessary properties that may support such requirements (Mueller, Amro et al. 2012). An important feature is the fact that the CO_2 adsorption capacity with shale is stronger than that of methane (CH_4). Thus, it can replace CH_4 in the shale formation, enhancing gas production and at the same time remaining locked underground. At reservoir conditions, CO_2 adsorption exceeded CH_4 adsorption by a factor of five, suggesting that CO_2 enhanced gas recovery from shale could serve as a promising mean to reduce life cycle CO_2 emission for shale gas. On a strictly volumetric basis, gas shales have the potential to sequester large amounts of CO_2, provided that CO_2 can diffuse deep into the matrix (Nuttall, Eble et al. 2005).

A CO_2 fracturing fluid cause more complex fracture networks due to its lower viscosity property (Al-Adwani et al., 2008; Wang, 2008; Gupta et al., 2005). After the treatment, the evaluation of a fractured zone can take place almost immediately because of rapid clean-up. The energy provided by CO_2 results in the elimination of all residual liquid left in the formation from the fracturing fluid. The gaseous CO_2 also aids in lifting formation fluids that are produced back during the clean-up operation. Finally, a big advantage offered by CO_2 would be its positive net effect when considering the issue of greenhouse gas emissions. An article in New Scientist recently discussed the possibility that fracturing with CO_2 could spur the development of large-scale carbon sequestration (McKenna 2012).

The use of liquid CO_2 as fracturing fluid has been proposed in different forms, mainly as:

- Liquid CO_2 for hydraulically fracturing the reservoir.
- Super-critical CO_2 for hydraulically fracturing the reservoir.
- CO_2 foams. These are described in Section 2.1.
- Hybrid systems: CO_2 in conjunction with other fluids.

Liquid (or super-critical) CO_2 is used instead of water as the fracturing fluid. The family of these fluids consists of pure liquid CO_2 and a binary fluid consisting of a mixture of liquid CO_2 and N_2 to reduce costs. In these systems, the proppant is placed in the formation without causing damage of any kind, and without adding any other carrier fluid, viscosifier or other chemicals.

Liquid CO_2 has been used in fracture operation since the early 1960's. In the beginning it was used as an additive to hydraulic fracturing and acid treatments to improve recovery of treating fluid. (Mueller, Amro et al. 2012). The concept of fracturing with 100% CO_2 as the sole carrying fluid was first introduced in 1981.(Sinal and Lancaster 1987). The physical properties of liquid CO_2 make it a unique fluid. CO_2 is relatively inert compound

that, depending on the temperature and pressure, exists as a solid, liquid, gas or super critical fluid. Above the critical point, it is considered to be a super critical fluid. In field operations, liquid C02 is at 2.0 MPa and -35°C in the storage vessel. After the addition of proppants, high pressure pumps increase the pressure (example 35 to 40 MPa). As the fluid enters the formation, the temperature increases toward bottom-hole temperature. During flow back, the pressure decreases and CO_2 comes to the surface as a gas.

The use of supercritical CO_2 for fracturing has been recently suggested ((Gupta, Gupta et al. 2005; Gupta 2006), (Al-Adwani, Langlinais et al. 2008)). Two recent papers discussing opportunity and challenges for supercritical CO_2 fracturing are (Middleton, Viswanathan et al. 2014) and (Middleton, Carey et al. 2015). Supercritical CO_2 is a fluid state where CO_2 is held at or above its critical temperature (31.1°C) and critical pressure (72.9 atm or 7.39 MPa). Owing to its unique physical and chemical properties, supercritical CO_2 can obtain a higher penetration rate in shale formation and adds no damage to the reservoir. Some researchers have proposed the use of supercritical CO_2 as a fracturing fluid for shale gas production in conjunction with gas turbines using the same fluid (Coltri 2015; Giacomazzi and Messina 2015). (Yin, Zhou et al. 2016) have recently investigated the physical and structural changes of shale rock matrix after exposure to supercritical CO_2.

A 2014 review of application status and development trends of CO_2 fracturing is offered in (He, Feng et al. 2014). (Godec, Koperna et al. 2014) reports on research sponsored by the U.S. Department of Energy to assess factors influencing enhanced gas recovery and CO_2 storage in selected shale basins in the Eastern USA. Other very recent studies are given by (Song, Su et al. 2014). (Pei, Ling et al. 2015) have investigated the feasibility of a new CO_2-based reservoir treatment technology. In their study, the authors discussed the theoretical principles and feasibility of using CO2 in both the stimulation stage and the secondary gas recovery stage, further discussing the outcome of a case study performed to simulate applying the CO_2 process in the Barnett, Eagle Ford, and Marcellus shale plays. (Luo, Wang et al. 2015) carry out an experimental investigation on the rheological properties and friction performance of a thickened CO_2 fracturing fluid.

A recent study was conducted to document and assess the effects of fluid–rock interactions when CO2 is used, with primary objectives to identify and understand the geochemical reactions of CO2-based fracturing, and to assess potential changes in porosity and permeability of formation rock (Lu, Nicot et al. 2016).

Hybrid systems making use of CO_2 in conjunctions with other fluids have been recently proposed. For instance, (Ribeiro, Li et al. 2015) have very recently introduced a new CO_2-hybrid fracturing design, consisting of (1) injecting pure CO_2 to generate a complex fracture network and (2) injecting a gelled slurry to generate near-wellbore conductivity. According to the authors, the motivation behind this concept is that while current aqueous fluids provide sufficient primary hydraulic fracture conductivity back to the wellbore, they under-stimulate the reservoir and/or leave behind damaged stimulated regions deeper in the fracture network. The proposed design is indicated as particularly attractive for brittle reservoirs, capable of sustaining substantial production from unpropped fractures. The concept is based on experimental and numerical studies and has not been applied as yet in the field.

Liquid CO_2 as fracturing fluid is already commercially used in many unconventional applications (most notably, tight gas) in Canada and the US (US EPA 2011). (Yost II, Mazza et al. 1993) reports that wells in Devonian shale formations (Kentucky, USA) were stimulated with liquid CO_2 and sand as early as 1993.

Super-critical CO_2 use appears to be at the concept stage. Studies have analysed its potential use to fracturing shale formation, with positive conclusions. (Ishida, Niwa et al. 2012; Wang, Li et al. 2012). According to (Ishida, Niwa et al. 2012), "*combining the characteristics of SC-CO_2 fluid and shale gas reservoir exploitation, the feasibility of*

shale gas exploitation with SC-CO_2 is demonstrated in detail". Another recent study is (Fang, Chen et al. 2014).

2.6.2 Liquid Nitrogen (N_2)

Generally, fracturing using nitrogen tend to use the gas mixed with other fluids: mists (mixtures composed of over 95% nitrogen carrying a liquid phase), foams (mixture composed of approximately 50% to 95% of nitrogen formed within a continuous liquid phase), or energized fluids (mixtures composed of approximately 5% to 50% nitrogen).

The two main reasons for using pure nitrogen as fracturing fluid in shale formations are (1) when the formation is under pressured and (2) because shale can be sensitive to fluids. The nitrogen helps fluid recovery by adding energy to help push any fluid from the fracturing process or the reservoir out of the wellbore. These fluids can accumulate and create enough hydrostatic pressure that the reservoir cannot overcome.

Liquid nitrogen used as a hydraulic fracturing fluid is a technology that is still fairly new, but it has been applied for fracturing shale formations (Grundmann, Rodvelt et al. 1998; Rowan 2009).

The extremely low temperature of the fluid (-184°C to -195°C) will induce thermal tensile stresses in the fracture face. These stresses exceed the tensile strength of the rock, causing the fracture face to fragment. Theoretically, self-propping fractures can be created by the thermal shock of an extremely cold liquid contacting a warm formation. As the fluid warms to reservoir temperature, its expansion from a liquid to a gas results in an approximate eightfold flow-rate increase (Grundmann, Rodvelt et al. 1998). Recently, (Cai, Li et al. 2014) have carried out an experimental study on the effect of liquid nitrogen cooling on rock pore structure. A recent review and discussion on the usage of liquid nitrogen is given by (Wang, Yao et al. 2016).

An idea has been proposed to achieve fracturing with a liquid nitrogen jet (Cai, Li et al. 2014; Cai, Huang et al. 2016). To analyse the feasibility of this treatment, the flow field of the liquid nitrogen jet was simulated using computational fluid dynamics method and the cracking effect of liquid nitrogen was tested in the laboratory on rock samples.

Other authors have proposed a technology called "liquid nitrogen gasification fracturing" (Li, Xu et al. 2016). In this approach fracturing is brought about by different mechanisms: liquid nitrogen pressure, rock contraction, rock embrittlement and nitrogen expansion. The idea seems to be at the concept stage.

Using nitrogen as a component (in mists, foams or other energised fluids) of the fracturing medium is very common in the petroleum industry (section 2.1). The use of gaseous nitrogen in pneumatic fracturing is discussed in section 3.2. On the other hand, the use of liquid nitrogen is less typical. The technique is commercially available, and it has been applied for fracturing shale formations as early as 1998 (Grundmann, Rodvelt et al. 1998), but its usage appears to be limited. A recent review and discussion on the usage of liquid nitrogen is given by (Wang, Yao et al. 2016).

2.6.3 Other cryogenic fluids

Other cryogenic fluids can be used. For instance, Expansion Energy has patented a technique that makes use of cryogenically processed natural gas extracted from nearby wells or from the targeted hydrocarbon formation itself (Vandor 2012; Expansion Energy 2013). According to the developers, this technique has been developed especially to target shale formations. The invention is called VRGETM (also called "dry fracturing", US Patent N. 8342246).

VRGETM creates cold compressed natural gas (CCNG) at the well site. This fluid is then pumped to high pressure before expanding it and blending it with a proprietary, foam-based proppant delivery system. This "gas-energized" fluid is then sent down-hole where it fractures the formation and holds open the fissures in the formation with proppant delivered by the foam system. Expansion Energy claims that VRGE virtually eliminates

the use of chemical additives because VRGE uses little or no water. Further, natural gas used by VRGE for fracturing eventually resurfaces and can be sold to the market or used for additional VRGE fracturing. As a result, there is no economic loss from using natural gas as the fracturing medium. After fracturing is complete, the CCNG plant can either be moved to the next well site for fracturing or it can remain at the original well site to produce LNG for the market.

According to the developers, VRGE is "available for license". It is not clear if it has been already commercially deployed.

3 Other Waterless Methods

3.1 Fracturing with dynamic loading

In this section we review fracturing techniques that do not make use of fluids, but rather aim to fracture the reservoir rock by inducing a dynamic loading, either by detonating explosives or by creating electrical impulses.

3.1.1 Explosive fracturing

Using explosives to fracture rock formations and hence stimulate production is a very old technique (Hyne 2001). In the late 1960s, both in the USA and in the Soviet Union, even nuclear devices were tested as a mean to fracture rock formations to enhance the recovery of natural gas (Nordyke 2000; American Oil & Gas Historical Society 2012). In the 1970s many different explosive-based fracturing techniques were studied and for instance applied to oil shale formations. (Miller and Johansen 1976).Problems of wellbore damage, safety hazards, and unpredictable results reduced the relative number of wells stimulated by high-strength explosives.

More recently, studies have shown that propellants - substances which deflagrate rather than detonate - have strong advantages over explosives (Schmidt, Warpinski et al. 1980). The solid propellant does not detonate, but deflagrates. Deflagration is a burning process that takes place without any outside source of oxygen. Gas pressures in the range of 20,000 psi are produced that last approximately 10 milliseconds. No shock wave is produced, the rock is split rather than compacted, and multiple fractures are created. The time to peak pressure is approximately four orders of magnitude slower than explosives. Unlike explosives, the burn front in these materials travels slower than the speed of sound. 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 2012).

A significant disadvantage to propellant fracturing is that it does not carry proppant into the fracture. Instead, propellant fracturing relies upon shear slippage to prevent the fracture from fully closing back on itself, leaving a conductive path back to the wellbore. (Page and Miskimins 2009). A fairly recent analysis of well productivity of different types of well architectures to be completed with the explosive fracturing in liquid-rich shale gas formations was carried out by (Boyun Guo 2014).

Commercial techniques based on the use of propellants are known by several generic names, such as GasGun, High Energy Gas Fracturing, StimGun, etc.

GasGun

The Gas Gun uses solid propellant to generate high pressure gas at a rapid rate. The rate is tailored to the formation characteristics to be rapid enough to create multiple fractures radiating 10 to 50 feet from the wellbore, but not so rapid as to pulverize and compact the rock as is experienced with classic high explosives such as nitroglycerine. The star-shaped pattern of multiple fractures removes wellbore damage or blockage and increases the formation permeability near the wellbore (GasGun 2013; GasGun 2015).

High Energy Gas Fracturing

This technology (Servo-Dynamics 2013) consists of a perforating with propellants, which are transported to the area of interest by wireline, coiled tubing or tubing. The propellant is an oxidizing agent consisting of potassium perchlorate particles and epoxy resin. Once ignited the propellant deflagrates, releasing gas (contained in a column of fluid in the face of the well), which in tum produces the pressure pulse and by the expansion is responsible for generating multiple fractures of short length (up to 50 feet in shale), in all radial directions in the well where the perforating was oriented. Successful

stimulations are reported to have been achieved in many lithologies, including shale (Plata, Castillo et al. 2012).

StimGun

StimGun is a propellant-assisted perforating system, developed by a group of industries that includes among others Marathon Oil Company and Weatherford. The propellant releases a controlled-dynamic pulse of high-pressure gas at the time of perforating. The tool simultaneously perforates and stimulates the well. A cylindrical sleeve of propellant is placed over a specially configured perforating carrier. The pressure wave generated by the perforating charge ignites the propellant. Gas from the propellant enters the newly created perforations, breaking them down and stimulating the formation (StimGun 2012).

Techniques based on explosive fracturing seem to have been largely superseded. On the other hand, techniques based on propellant fracturing are commercially available, have been used on shale formations and they appear to be a potential alternative to high-volume hydraulic fracturing in some situations. Laboratory and field experiments were conducted to compare hydraulic and propellant fracturing techniques in the Mancos Shale in Colorado (a Cretaceous shale approximately 2,000 feet thick) (Page and Miskimins 2009).

3.1.2 Electric fracturing

The idea behind electric fracturing is to apply electricity to induce mechanical loads into the rock. Laboratory studies to evaluate the use of electricity for fracturing various grades of Colorado oil shale were started as early as in 1964, the rationale being that it was necessary to develop techniques to increase the permeability of the oil shale formation in order to carry out an in-situ retorting process (Melton and Cross 1968).

A technique that could be especially applied for shale gas stimulation is being developed and tested at the University of Pau and Pays de l'Adour (Chen 2012; Martin, Reess et al. 2012a; Martin, Reess et al. 2012b). This method is based on generating a pressure wave by an electrical discharge between two electrodes placed in a wellbore filled with water. The amplitude of this wave of pressure can reach up to 200 MPa (2000 times the atmospheric pressure) while its duration is around one hundredth of microsecond. This pressure wave is transmitted to the rock by the fluid inside the wellbore, and will create micro-cracks of decreasing density, according to the distance from the well (Chen 2012; Martin, Reess et al. 2012a; Martin, Reess et al. 2012b).

This technique would allow fracturing of the rock without any use of fracturing fluids (and hence no chemical additives). (Kalaydjian and Goffé 2012) reported that in 2011 Total commissioned research on this technique but concluded that the technology is not a currently viable alternative to hydraulic fracturing. One major problem seems to be that rock permeability is increased only up to several meters from the wellbore, but no further.

Pulsed Arc Electrohydraulic Discharges is at the concept stage, and it is being developed as a potential alternative to hydraulic fracturing. One journal article (Chen, Maurel et al. 2012), two patents applications (Martin, Reess et al. 2012a; Martin, Reess et al. 2012b) and two doctoral theses (Chen 2012; Martin 2013) documenting the ongoing research at the University of Pau and Pays de l'Adour were found. The authors have announced that the main results of their research will be published in the near future in different international journals (Reess 2013).

NOVAS Energy, a US company based in Houston, currently offers a technology that makes uses plasma pulses to enhanced oil recovery in conventional reservoirs (NOVAS Energy 2014).

3.2 Pneumatic fracturing

Pneumatic fractures can be generated in geologic formations when air or any other gas is injected at a pressure that exceeds the natural strength as well as the in situ stresses present in the formation (Suthersan 1999). It is a technique normally used in shallow formations, and it has emerged as one of the most cost effective methods for enhanced remediation of contaminated soil and groundwater.

The pneumatic fracturing procedure typically does not include the intentional deposition of foreign propping agents to maintain fracture stability. The created fractures are thought to be self-propping, a circumstance which is attributed to both the asperities present along the fracture plane as well as the block shifting which takes place during injection. In theory there is a potential for higher permeabilities within the fractures formed pneumatically, in comparison to hydraulic fractures, as these are essentially air space and are devoid of propping agents. The open, self-propped fractures resulting from pneumatic fracturing are capable of transmitting significant amounts of fluid flow. Such fractures, in particular, may propagate along existing fracture patterns.

Nitrogen gas fracturing is used primarily for water-sensitive, brittle, and shallow unconventional oil and gas formations. Gaseous nitrogen is widely available and non-expensive. It is an inert gas and hence does not damage rock formation. The gas can be removed easily after the treatment and hence the clean-up process is fast. The use of nitrogen prevents clay swelling that would otherwise be caused by slickwater. Pure gaseous nitrogen produces best results in brittle formations that have natural fractures and stay self-propped once pressure pumping is completed. (Rogala, Krzysiek et al. 2013) observed that the many advantages offered by nitrogen would suggest nitrogen fracturing as a very good technical solution. However, they also conclude that placing the proppant in high velocity gas stream is problematic, as well as resulting in erosion, and that the technology is limited to shallow wells or geologies that can fail the rock in a self-propping manner. It is nonetheless questionable if such geologies are widespread.

To date, the target depths of most pneumatic fracturing projects have ranged from 3 to 15 meters. The deepest applications of pneumatic fracturing for site remediation purposes have been 60 meters. For fracturing applications below a depth of around 25 to 30 meters, the usage of proppants may become unavoidable. Shallow shale formations have been fractured with pneumatic fracturing (US EPA 1993) with the purpose of facilitating the removal of volatile organic contaminants.

Pneumatic fracturing with gaseous nitrogen is applied to shale gas production (Rogala, Krzysiek et al. 2013). (Gottschling and Royce 1985) reported that as early as 1985 a technology was developed, using nitrogen for the extraction of gas from Devonian shale formations in Ohio (USA). In this system, gaseous nitrogen was injected at a pressure of 24 MPa in shallow wells. Approximately 60% of the volume used was a pure nitrogen gas without proppant, designed to produce fractures in the stimulated formation. The remaining 40% carried sand.

The Canadian company Canyon has patented a process called Grand Canyon™, making use of a high-pressure pumping unit that accurately meters a proprietary light-weight proppant into a stream of pure nitrogen. This allows creating a very thin fracture held open by a partial monolayer. Canyon reports that the technique has been used to perform thousands of fracturing jobs (delivering hundreds of successful wells) in water-sensitive Cretaceous shales and silts. A proprietary proppant is being tested for deeper applications, specifically in the Montney and Cardium plays (Canyon 2013).

3.3 Cryogenic fracturing

According to this concept, fracturing can be achieved by using a fluid colder than the reservoir to create thermal stresses that will fracture the rock. Unconventional gas reservoirs (shale gas, tight gas and coal bed methane) constitute a large percentage of natural gas supply. Hydraulic fracturing is commonly used to break-up rock matrix and

connect natural fractures and cleats to create gas flow pathways. Application of hydraulic fracturing, however, poses several problems including extremely low matrix permeability and poor connectivity between matrix and fractures. Several studies have been made in field and in laboratory to open and interconnect these natural fractures and cleat system with cold fluid, results of which are found to be promising. In this paper we present a parametric design analysis as to the application of thermal stress (due to cold fluid injection) induced hydraulic fracture treatment.

Different studies have shown that thermally induced fractures may take place in oil and gas reservoirs. For instance, different cases were investigated where cold water was injected into deep hot reservoirs with a constant injection rate and a pressure that was below the formation mechanical strength. After a certain time a sharp increase in injectivity was observed, indicating that the formation had been fractured (Svendson, Wright et al. 1991; Charlez, Lemonnier et al. 1996).

More recently an interesting fracturing technique has been proposed, based on the injection of large quantities of cold CO_2 to create thermal stresses that lead to fractures in significant magnitude (Mueller, Amro et al. 2012). This technique, which is at the concept stage and it has been proposed for tight reservoirs, combines conventional hydraulic fracturing and fractures which are caused by thermal stresses, due to the injection of cold $C0_2$. To create thermal stresses that lead to fractures in significant magnitude, a large quantity of liquid CO_2 is needed to be injected. During high pressure injection the CO_2 will stay in liquid state. Due to its low temperature and the high quantity of CO_2 a large area around the wellbore will cool down. This effect should lead to large thermal stresses in the ground which cause fracturing along with the hydraulic pressure of the injection pump. According to proponents, the temperature reduction would not be high enough to achieve the necessary thermal stresses to induce fractures in the first months of the process. During this initial period, the injection would take place in the so-called "frac" regime, i.e. injection at high pressure. CO_2 injection would then continue for several years, with gas production only starting after two years from the beginning of the treatment. Through the continuous injection, the temperature front would propagate, inducing an ongoing fracturing process in reservoir regions farther away from the well.

(Cha, Yin et al. 2014) report a very recent laboratory study of cryogenic fracturing. It was shown that the injection of liquid nitrogen in laboratory specimen created cracks and altered rock properties. Fractures were created by generating a strong thermal gradient. Several topics requiring further investigation were identified, for instance the poorly understood effect of borehole pressurization, the effects of stress level and stress anisotropy the characteristics of material properties.

An ongoing study funded by RPSEA is concerned with the study, testing and development of a cryogenic fracturing technology to obtain a significant reduction of flow resistance near the well and to increase mobile gas volume in unconventional gas reservoirs (http://www.rpsea.org/projects/10122-20/). The study is expected for completion in July 2016. The first year report is available (Yu-Shu Wu 2013).

Fractured shale reservoirs can be used as CO_2 storage. The US Department of Energy National Energy Technology Laboratory (NETL) has recently presented a methodology for screening-level assessment of prospective CO_2 storage. Prospective shale formations require prior hydrocarbon production using horizontal drilling and fracturing; and depths sufficient to maintain CO_2 in a supercritical state (generally around 800 m) (Levine, Fukai et al. 2016).

The concept idea has been proposed for tight formations (Mueller, Amro et al. 2012). (Song, Liang et al. 2016) very recently present a quantitative analysis of the effect of thermal stress on fracture propagation behaviour in unconventional reservoirs.

3.4 Enhanced bacterial methanogenesis

Microbiologically assisted methanization of the organic matter is a promising technology being considered. A very significant part of organic-rich shales have not undergone a sufficient burial to generate the pressure and temperature conditions necessary for the complete transformation of the organic matter into oil or coal. These immature source rocks may represent a huge fossil carbon resource. Naturally-occurring microorganisms (methanogens) are stimulated within the shale formations to enhance the production of methane as by-product of their normal metabolic processes. Methanization is known to occur in shales from field data showing the natural accumulation of biogenic methane in several sedimentary basins (Meslé, Charlotte Périot et al. 2012).

Research projects have been carried out very recently, in both the Antrim shale formation in the Michigan Basin and in the western Canadian sedimentary basin. RPSEA conducted a seed study on Antrim Shale and the Forest City Basin formations (Martini, Nüsslein et al. 2004). The results of this project indicated that microbial methane generation in sedimentary basins is an active process, with a high potential for stimulation. The project's final report concluded that the research may contribute towards development of technologies to enhance methane production in shale gas plays, and thus to help secure natural gas resources from the extensive occurrence of fractured black shales and coal beds found throughout the USA (Salehi and RPSEA 2012).

Schlumberger-Doll Research funded a project ("Toward microbially-enhanced shale gas production.") to genetically profile the bacterial communities present in formation water of three gas-producing Antrim shale wells. Incubation experiments were established by adding different substrates to aliquots of these waters in an effort to stimulate the microbial methane generation. Increases in direct methane production were obtained. (Coolen 2013; Wuchter, Banning et al. 2013).

(Cokar, Ford et al. 2013) reported a study conducted on shales from the Abbey Field in Western Canada, in which the reaction rate kinetics for methane production were determined from experimental data using produced water and core samples from a shallow shale gas reservoir. The results showed that biogenic shale gas generation accounted for about 12% of the total gas produced. Enhanced bacterial methanogenesis may have a large impact, especially in shallow reservoirs. Methanogens can produce a significant amount of methane without any stimulation.

Several recent studies review the current scientific activities and knowledge gaps in the area of enhanced microbial coalbed methane generation. The biological conversion of coal to methane could be an efficient and environmentally friendly way to employ current coal reserves. (Park and Liang 2016) review various approaches, such as bioaugmentation, biostimulation and physical, chemical and biological pre-treatment aimed at of enhancing methane yield. Another recent review of current research and commercial activities is given by (Ritter, Vinson et al. 2015). (Colosimo, Thomas et al. 2016) discuss biogenic methane production in coalbeds but cover shale gas formation as well. Other relevant studies are the following: (Hamilton, Golding et al. 2015; Bao, Huang et al. 2016; Shelton, McIntosh et al. 2016; Wang, Lin et al. 2016).

Enhanced bacterial methanogenesis appears to be at the concept stage for what it concerns in-situ application. The technique has been successfully applied in laboratory.

3.5 Heating of the rock mass

Technologies based on heating the underground formations exist and have been used by the oil industry for many applications, in particular to increase the recovery of oil or to increase the thermal maturity of organic material. These processes can for instance use steam (without fracturing) in porous rocks or electric heaters. The rock is heated, for instance by injecting steam or by other suitable methods, enhancing the permeability of the reservoir and/or increasing the thermal maturity of the kerogen in the formation.

A recent discussion on the possibilities of this technology and its application to unconventional hydrocarbon production is given in (Kalaydjian and Goffé 2012). These authors identify three principal mechanisms by which the effects of heating the rock mass could have beneficial effects: (a) mineralogical changes; (b) changes in the chemical decomposition of kerogen; and (c) evolution of the carbon structure of kerogen.

Mineralogical changes occur for instance following dehydration. (Vidal and Dubacq 2009) demonstrated that clay dehydration in shales may produce up to 150 litres of water per cubic meter of clay in place. The space vacated by removing water increases the porosity and therefore the permeability. A second desired effect of heating is the chemical decomposition of kerogen heavy hydrocarbons to light hydrocarbons. The increase in temperature makes it possible to degrade certain kerogen molecules (in the case of incomplete maturation), and to promote the conversion of heavier hydrocarbons to lighter compounds. The third effect is the possible evolution of the carbon structure of kerogen, with increased temperature contributing to the opening of porosity at micro- and nano-scale. In combination, these three effects could significantly enhance the permeability of the shale formations without the need to perform any hydraulic fracturing.

A conceptual study of thermal stimulation in shale gas formations was published by (Wang, Ajao et al. 2014) to understand the effects of fracture heating on the shale gas adsorption and desorption characteristics, and how these can be exploited to enhance shale gas recovery from hydraulically fractured reservoirs.

A very recent study on the concept was carried out by (Zhu, Yao et al. 2016), concluding that this method can enhance shale gas recovery by altering gas desorption behaviour and that is suitable for long-term production. The study showed that more adsorbed gas could be recovered with increasing simulation temperature, whereas the thermal properties of the shale formation only had a limited impact on the long-term production.

(Kang, Chen et al. 2016) investigated experimentally the changes in the multiscale gas transport ability after a high temperature treatment in core samples from the Longmaxi shale basin in China. Results indicated that the quality of the shale matrix was very much improved after a high temperature treatment. The study also presented ideas for practical field applications, employing for instance a combination of electrical heating and microwave heating.

The technique is applied for producing oil shale. It is at the concept stage concerning application for other unconventional hydrocarbons such as shale gas. (Kalaydjian and Goffé 2012) present a very good discussion on the possibilities and challenges offered by the technique.

3.6 In-situ combustion

(Chapiro and Bruining 2015) have recently presented a conceptual study on the possibility of using in-situ combustion to stimulate production in shale gas formations. The main goal of this paper was to understand under which conditions this is feasible. Two possibilities for the in-situ fuel source were considered: methane or kerogen.

The authors concluded that possibility of using this method for recovery of shale gas needs to consider a number of mechanisms such as gas production from kerogen, initial permeability of the reservoir, compression costs and the coupling of the method to existing fracturing techniques. In summary, more research is needed.

3.7 Enhanced oil recovery in shale reservoirs

(Sheng 2015) recently provided a review of the current status of enhanced oil recovery (EOR) methods in shale oil and gas condensate reservoirs that have already a network of

fractures (for instance created by one of the fracturing methods described elsewhere in this report. The focus of the study is on gas injection, but other possible methods are also considered, such as thermal recovery, chemical methods (by water injection) and microbial methods. The data presented show that gas injection is more feasible in shale reservoirs than water flooding and any other EOR methods, but the study also concludes that enhanced oil recovery in shale reservoirs is a new topic and more research is needed.

4 Summary and Conclusions

This study is focused on the identification of the most recent technological trends in the area of waterless fracturing, with a particular focus on shale gas production. By building on previous JRC studies, in particular the 2015 report "An overview of hydraulic fracturing and other stimulation technologies - Update 2015" (Gandossi and Estorff 2015), all relevant technologies are identified and explained, and their deployment status (for instance, whether the method is commercially applied, being developed, at the concept stage, etc.) is discussed. The report has been compiled by accessing publicly available literature (peer-reviewed journal papers, conference papers, patent databases, commercial websites, etc.).

While the industry has often used nitrogen and CO_2 in foamed fracturing fluids to reduce water usage, recent research has focused on the use of oil-based or $C0_2$–based fluids to completely eliminate water used in fracking.

CO_2 could be used in its super-critical state, where it behaves neither as a solid nor as a liquid. In this case, a major technological challenge is determining the right viscosity for the CO_2 in order to properly carry and deposit proppant in the fissures created in the shale rock. Another technical issue is how to transport CO_2 in large enough quantities for use in wells that are located far from pipelines.

Waterless fracking has been tried before but so far has not been adopted in a meaningful way by the industry. Many companies are experimenting with various techniques, but these efforts either seem to have met limited success, or are at an early development stage.

In a recent analysis, (Topf 2014) concludes that if waterless fracking can indeed improve productivity, there is a good chance the industry will move faster to adopt it. In conventional fracturing, the water pumped in may remain in the formation and thus block the flow of natural gas, therefore slowing down production and decreasing the amount it can produce over its lifetime. In contrast, using CO_2 allows the gas to flow more freely and results in a better network of fractures. While an industry-wide shift to waterless fracking is likely years away, companies that show promise in developing alternative and environmentally-friendly methods of fracturing are likely to be rewarded by the market and may even receive support from the public and governments.

References

Al-Adwani, F. A., J. Langlinais, et al. (2008). Modeling of an Underbalanced Drilling Operation Utilizing Supercritical Carbon Dioxide. SPE/IADC Managed Pressure Drilling and Underbalanced Operations Conference and Exhibition. Abu Dhabi, UAE, SPE/IADC Managed Pressure Drilling and Underbalanced Operations Conference and Exhibition.

American Oil & Gas Historical Society. (2012). "Project Gasbuggy tests Nuclear Fracking." from http://aoghs.org/technology/project-gasbuggy/.

Antoci, J. C., N. J. Briggiler, et al. (2001). Crosslinked Methanol: Analysis of a Successful Experience in Fracturing Gas Wells. SPE Latin American and Caribbean Petroleum Engineering Conference. Buenos Aires, Argentina, Copyright 2001, Society of Petroleum Engineers Inc.

Bao, Y., H. Huang, et al. (2016). "Microbial enhancing coal-bed methane generation potential, constraints and mechanism – A mini-review." Journal of Natural Gas Science and Engineering **35, Part A**: 68-78.

Bennion, D. B., F. B. Thomas, et al. (1996). Low Permeability Gas Reservoirs: Problems, Opportunities and Solutions for Drilling, Completion, Stimulation and Production. SPE Gas Technology Symposium. Calgary, Alberta, Canada, 1996 Copyright 1996, Society of Petroleum Engineers, Inc.

Bennion, D. B., F. B. Thomas, et al. (2000). Low Permeability Gas Reservoirs and Formation Damage -Tricks and Traps. SPE/CERI Gas Technology Symposium. Calgary, Alberta, Canada, Copyright 2000, Society of Petroleum Engineers Inc.

Boyun Guo, J. S., Yin Feng (2014). "Productivity of blast-fractured wells in liquid-rich shale gas formations." Journal of Natural Gas Science and Engineering **18** 360-367.

Brannon, H. D., D. E. Kendrick, et al. (2009). Multi-Stage Fracturing of Horizontal Wells Using Ninety-Five Quality Foam Provides Improved Shale Gas Production. SPE Eastern Regional Meeting. Charleston, West Virginia, USA, Society of Petroleum Engineers.

Burgos, G. A., M. A. Buijse, et al. (2005). Acid Fracturing in Lake Maracaibo: How Continuous Improvements Kept on Raising the Expectation Bar. SPE Annual Technical Conference and Exhibition. Dallas, Texas, Society of Petroleum Engineers.

Cai, C., Z. Huang, et al. (2016). "Feasibility of reservoir fracturing stimulation with liquid nitrogen jet." Journal of Petroleum Science and Engineering **144**: 59-65.

Cai, C., G. Li, et al. (2014). "Experimental study of the effect of liquid nitrogen cooling on rock pore structure." Journal of Natural Gas Science and Engineering **21**: 507-517.

Canyon. (2013). "Grand Canyon™ Process." from http://www.canyontech.ca/Products-and-Services/Service-Lines/Grand-Canyon-Process/default.aspx.

Cha, M., X. Yin, et al. (2014). "Cryogenic fracturing for reservoir stimulation – Laboratory studies." Journal of Petroleum Science and Engineering **124**: 436-450.

Chapiro, G. and J. Bruining (2015). "Combustion enhance recovery of shale gas." Journal of Petroleum Science and Engineering **127**: 179–189.

Charlez, P., P. Lemonnier, et al. (1996). Thermally Induced Fracturing: Analysis of a Field Case in North Sea. European Petroleum Conference. Milan, Italy, 1996 Copyright 1996, Society of Petroleum Engineers, Inc.

Chen, W. (2012). Fracturation électrique des géomatériaux - Etude de l'endommagement et de la perméabilité, L'UNIVERSITE de PAU et des PAYS de l'ADOUR.

Chen, W., O. Maurel, et al. (2012). "Experimental study on an alternative oil stimulation technique for tight gas reservoirs based on dynamic shock waves generated by Pulsed Arc Electrohydraulic Discharges." Journal of Petroleum Science and Engineering **88–89**(0): 67-74.

Cokar, M., B. Ford, et al. (2013). "Reactive Reservoir Simulation of Biogenic Shallow Shale Gas Systems Enabled by Experimentally Determined Methane Generation Rates." Energy Fuels **27**(5): 2413–2421.

Colosimo, F., R. Thomas, et al. (2016). "Biogenic methane in shale gas and coal bed methane: A review of current knowledge and gaps." International Journal of Coal Geology **165**: 106-120.

Coltri, C. (2015). "Extracting shale gas with supercritical CO2." La termotecnica **Settembre 2015**.

Coolen, M. (2013). "Toward microbially-enhanced shale gas production." from http://www.whoi.edu/page.do?pid=115657&tid=3622&cid=158790.

ecorpStim. (2013a). "Propane Stimulation." from http://www.ecorpstim.com/propane-stimulation/.

ecorpStim. (2013b). "Non-Flammable Propane : Key facts." from http://www.ecorpstim.com/propane-stimulation/nfp-stimulation/.

ecorpStim. (2015). "ecorpStim announces Light Alkanes Stimulation." from http://www.ecorpstim.com/blog/2015/07/23/ecorpstim-announces-light-alkanes-stimulation/.

Edrisi, A. R. and S. I. Kam (2012). A New Foam Rheology Model for Shale-Gas Foam Fracturing Applications. SPE Canadian Unconventional Resources Conference. Calgary, Alberta, Canada, Society of Petroleum Engineers.

Expansion Energy (2013). "VRGE(TM)" Overview - Patented Non-Hydraulic Fracturing Technology for Unconventional Oil & Gas Production.

Fang, C., W. Chen, et al. (2014). Simulation Study of Hydraulic Fracturing Using Super Critical CO2 in Shale, Society of Petroleum Engineers.

Gandossi, L. and U. V. Estorff (2015). An overview of hydraulic fracturing and other formation stimulation technologies for shale gas production - Update 2015, European Commission.

GasFrac. (2013). "A completely closed system with automated remote operations." from http://www.gasfrac.com/safer-energy-solutions.html.

GasGun. (2013). "Propellant Stimulations of Oil & Gas Wells." from http://www.thegasgun.com/.

GasGun. (2015). "GasGun Propellant Stimulations." from http://www.thegasgun.com/.

Gensheng, L., S. Mao, et al. (2012). "Multistage hydraulic jet acid fracturing technique for horizontal wells." Petroleum Exploration and Development **39**(1).

Giacomazzi, E. and G. Messina (2015). "Exploitation of Supercritical CO2 Properties - A Holistic Solution for the 21st century power generation." Impiantistica Italiana **Settembre-Ottobre 2015**.

Godec, M., G. Koperna, et al. (2014). "Enhanced Gas Recovery and CO2 Storage in Gas Shales: A Summary Review of its Status and Potential." Energy Procedia **63**: 5849 – 5857.

Gottschling, J. C. and T. N. Royce (1985). "Nitrogen Gas and Sand: A New Technique for Stimulation of Devonian Shale." Journal of Petroleum Technology **37**(5): 901-907.

Grundmann, S. R., G. D. Rodvelt, et al. (1998). Cryogenic Nitrogen as a Hydraulic Fracturing Fluid in the Devonian Shale. SPE Eastern Regional Meeting. Pittsburgh, Pennsylvania, Society of Petroleum Engineers.

Gu, M. and K. K. Mohanty (2014). "Effect of foam quality on effectiveness of hydraulic fracturing in shales." International Journal of Rock Mechanics and Mining Sciences **70**: 273–285.

Gu, M. and K. K. Mohanty (2015). "Rheology of polymer-free foam fracturing fluids." Journal of Petroleum Science and Engineering **134**: 87-96.

Gupta, A. (2006). Feasibility of supercritical carbon dioxide as a drilling fluid for deep underbalanced drilling operations. Master of Science in Petroleum Engineering, Louisiana State University and Agricultural and Mechanical College.

Gupta, A. P., A. Gupta, et al. (2005). Feasibility of Supercritical Carbon Dioxide as a Drilling Fluid for Deep Underbalanced Drilling Operation. SPE Annual Technical Conference and Exhibition. Dallas, Texas, Society of Petroleum Engineers.

Gupta, S. (2003). Field Application of Unconventional Foam Technology: Extension of Liquid CO2 Technology. SPE Annual Technical Conference and Exhibition. Denver, Colorado, Society of Petroleum Engineers.

Gupta, S. (2009). Unconventional Fracturing Fluids for Tight Gas Reservoirs. SPE Hydraulic Fracturing Technology Conference. The Woodlands, Texas, Society of Petroleum Engineers.

Gupta, S. (2010). Unconventional Fracturing Fluids : What, Where and Why.

Gupta, S., B. T. Hlidek, et al. (2007). Fracturing Fluid for Low-Permeability Gas Reservoirs: Emulsion of Carbon Dioxide With Aqueous Methanol Base Fluid: Chemistry and Applications. SPE Hydraulic Fracturing Technology Conference. College Station, Texas, U.S.A., Society of Petroleum Engineers.

Hamilton, S. K., S. D. Golding, et al. (2015). "Conceptual exploration targeting for microbially enhanced coal bed methane (MECoM) in the Walloon Subgroup, eastern Surat Basin, Australia." International Journal of Coal Geology **138**: 68-82.

He, L., W. Feng, et al. (2014). "Fracturing with carbon dioxide: Application status and development trend." Petroleum Exploration and Development **41**(4): 513–519.

Hernandez, J. M., C. T. Fernandez, et al. (1994). Methanol as Fracture Fluid in Gas Wells. SPE Latin America/Caribbean Petroleum Engineering Conference. Buenos Aires, Argentina, 1994 Copyright 1994, Society of Petroleum Engineers, Inc.

Hyne, N. J. (2001). Nontechnical Guide to Petroleum Geology, Exploration, Drilling and Production (2nd Edition), Pennwell Books; 2 edition (December 15, 2001)

Ishida, T., T. Niwa, et al. (2012). AE Monitoring of Hydraulic Fracturing Laboratory Experiment With Supercritical And Liquid State CO2, BeFo and International Society for Rock Mechanics.

Kalaydjian, F. and B. Goffé (2012). Programme de recherche sur l'exploitation des hydrocarbures de roches mères – Rapport ANCRE

Kang, Y., M. Chen, et al. (2016). "Investigation of formation heat treatment to enhance the multiscale gas transport ability of shale." Journal of Natural Gas Science and Engineering **35, Part A**: 265-275.

Komar, C. A., A. B. Yost II, et al. (1979). Practical Aspects of Foam Fracturing in the Devonian Shale. SPE Annual Technical Conference and Exhibition. Las Vegas,

Nevada, Not subject to copyright. This document was prepared by government employees or with government funding that places it in the public domain.

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

Levine, J. S., I. Fukai, et al. (2016). "U.S. DOE NETL methodology for estimating the prospective CO2 storage resource of shales at the national and regional scale." International Journal of Greenhouse Gas Control **51**: 81-94.

Li, N., J. Dai, et al. (2016). "Application status and research progress of shale reservoirs acid treatment technology." Natural Gas Industry B **3**(2): 165-172.

Li, Y., D. DiCarlo, et al. (2015). "An experimental study on application of nanoparticles in unconventional gas reservoir CO2 fracturing." Journal of Petroleum Science and Engineering **133**: 238-244.

Li, Z., H. Xu, et al. (2016). "Liquid nitrogen gasification fracturing technology for shale gas development." Journal of Petroleum Science and Engineering **138**: 253-256.

Liu, D., M. Fan, et al. (2010). "A new fracturing fluid with combination of single phase microemulsion and gelable polymer system." Journal of Petroleum Science and Engineering **73**: 267–271.

Lu, J., J.-P. Nicot, et al. (2016). "Alteration of Bakken reservoir rock during CO2-based fracturing—An autoclave reaction experiment." Journal of Unconventional Oil and Gas Resources **14**: 72-85.

Luo, X., S. Wang, et al. (2015). "Experimental investigation on rheological properties and friction performance of thickened CO2 fracturing fluid." Journal of Petroleum Science and Engineering **133**: 410-420.

Mao, J., D. Wang, et al. (2016). "Application and optimization: Non-aqueous fracturing fluid from phosphate ester synthesized with single alcohol." Journal of Petroleum Science and Engineering **147**: 356-360.

Martin, J. (2013). "THESIS - Etude et caractérisation d'onde de pression générée par une décharge électrique dans l'eau: application à la fracturation électrique de roches.".

Martin, J., T. Reess, et al. (2012a). PATENT: Electrical and Static fracturing of a reservoir. **WO/2012/123458**

Martin, J., T. Reess, et al. (2012b). PATENT: Electrical Reservoir Fracturing. **WO/2012/123458**

Martini, A. M., K. Nüsslein, et al. (2004). "Enhancing Microbial Gas From Unconventional Reservoirs: Geochemical And Microbiological Characterization Of Methane-Rich Fractured Black Shales."

McKenna, P. (2012). Fracking could be combined with carbon capture plans New Scientist.

Melton, N. M. and T. S. Cross (1968). Fracturing Oil Shale With Electricity.

Meslé, M., Charlotte Périot, et al. (2012). "Biostimulation to identify microbial communities involved in methane generation in shallow, kerogen-rich shales." Journal of Applied Microbiology **114**(55--70).

Middleton, R., H. Viswanathan, et al. (2014). "CO2 as a fracturing fluid: Potential for commercial-scale shale gas production and CO2 sequestration." Energy Procedia **63**: 7780 – 7784.

Middleton, R. S., J. W. Carey, et al. (2015). "Shale gas and non-aqueous fracturing fluids: Opportunities and challenges for supercritical CO2." Applied Energy **147** 500-509.

Miller, J. S. and R. T. Johansen (1976). Fracturing oil shale with explosives for in situ recovery.

Montebourg, A. (2015). Unconventional Hydrocarbons in France: Perspectives Opened by New Technologies for Exploration and Exploitation.

Montgomery, C. T. and M. B. Smith (2010). "Hydraulic fracturing: history of an enduring technology."

Mueller, M., M. Amro, et al. (2012). Stimulation of Tight Gas Reservoir using coupled Hydraulic and CO2 Cold-frac Technology. SPE Asia Pacific Oil and Gas Conference and Exhibition. Perth, Australia, Society of Petroleum Engineers.

Neill, G. H., J. B. Dobbs, et al. (1964). Field and Laboratory Results of Carbon Dioxide and Nitrogen in Well Stimulation.

Nordyke, M. D. (2000). The Soviet Program for Peaceful Uses of Nuclear Explosions.

NOVAS Energy (2014). Plasma Pulse Enhanced Oil Recovery Technology.

Nuttall, B. C., C. F. Eble, et al. (2005). Analysis of Devonian black shales in Kentucky for potential carbon dioxide sequestration and enhanced natural gas production.

Page, J. C. and J. L. Miskimins (2009). "A Comparison of Hydraulic and Propellant Fracture Propagation in a Shale Gas Reservoir." Journal of Canadian Petroleum Technology **48**(5): 26-30.

Park, S. Y. and Y. Liang (2016). "Biogenic methane production from coal: A review on recent research and development on microbially enhanced coalbed methane (MECBM)." Fuel **166**: 258-267.

Pei, P., K. Ling, et al. (2015). "Shale gas reservoir treatment by a CO2-based technology." Journal of Natural Gas Science and Engineering **26**: 1595-1606.

PetroWiki - Society of Petroleum Engineers. (2012). "Acid fracturing." from http://petrowiki.org/Acid_fracturing.

Plata, M. J., R. D. Castillo, et al. (2012). High Energy Gas Fracturing: A Technique of Hydraulic Prefracturing To Reduce the Pressure Losses by Friction in the Near Wellbore - A Colombian Field Application. SPE Latin America and Caribbean Petroleum Engineering Conference. Mexico City, Mexico, Society of Petroleum Engineers.

Qajar, A., Z. Xue, et al. (2016). "Modeling fracture propagation and cleanup for dry nanoparticle-stabilized-foam fracturing fluids." Journal of Petroleum Science and Engineering **146**: 210-221.

Reess, T. (2013). Personal communication.

Reidenbach, V. G., P. C. Harris, et al. (1986). "Rheological Study of Foam Fracturing Fluids Using Nitrogen and Carbon Dioxide." SPE Production Engineering **1**(1): 31-41.

Ribeiro, L. H., H. Li, et al. (2015). Use of a CO2-Hybrid Fracturing Design to Enhance Production from Unpropped Fracture Networks, Society of Petroleum Engineers.

Ritter, D., D. Vinson, et al. (2015). "Enhanced microbial coalbed methane generation: A review of research, commercial activity, and remaining challenges." International Journal of Coal Geology **146**: 28-41.

Rogala, A., J. Krzysiek, et al. (2013). "Non-Aqueous Fracturing Technologies For Shale Gas Recovery." Physicochemical Problems of Mineral Processing **49**(1): 313−322.

Rowan, T. (2009). Spurring the Devonian: Methods of Fracturing the Lower Huron in Southern West Virginia and Eastern Kentucky. SPE Eastern Regional Meeting. Charleston, West Virginia, USA, Society of Petroleum Engineers.

Saba, T., F. Mohsen, et al. (2012). White Paper: Methanol Use in Hydraulic Fracturing Fluids.

Salehi, I. and RPSEA (2012). New Albany Shale Gas Project.

Sanchez Bernal, M., J. Tate, et al. (2015). Acid Fracturing Tight Gas Carbonates Reservoirs Using CO2 to Assist Stimulation Fluids: An Alternative to Less Water Consumption while Maintaining Productivity, Society of Petroleum Engineers.

Schatz, J. (2012). Myths and misconceptions. I. John F. Schatz Research & Consulting.

Schmidt, R. A., N. R. Warpinski, et al. (1980). In situ evaluation of several tailored-pulse well-shooting concepts. SPE Unconventional Gas Recovery Symposium. Pittsburgh, Pennsylvania, 1980 Copyright 1980, Society of Petroleum Engineers.

Servo-Dynamics. (2013). "High Energy Gas Fracturing (HEGF) technology." from http://www.west.net/~servodyn/index.html.

Shelton, J. L., J. C. McIntosh, et al. (2016). "Impact of formation water geochemistry and crude oil biodegradation on microbial methanogenesis." Organic Geochemistry **98**: 105-117.

Sheng, J. J. (2015). "Enhanced oil recovery in shale reservoirs by gas injection." Journal of Natural Gas Science and Engineering **22**: 252-259.

Sinal, M. L. and G. Lancaster (1987). "Liquid CO2 Fracturing: Advantages And Limitations." Journal of Canadian Petroleum Technology **26**(5).

Song, H., Z. Liang, et al. (2016). Thermal-Stress Induced Fracture Propagation by Cold Fluid - An Improved Hydraulic Fracturing Treatment for Unconventional Gas Reservoirs. SPE Asia Pacific Hydraulic Fracturing Conference. Society of Petroleum Engineers. Beijing, China

Song, Z., W. Su, et al. (2014). "An experimental study on the CO2/sand dry-frac process." Natural Gas Industry B **1**(2): 192–196.

Soni, T. M. (2014). LPG-Based Fracturing: An Alternate Fracturing Technique in Shale Reservoirs, Society of Petroleum Engineers.

StimGun (2012). "StimGun® Assembly."

Suthersan, S. S. (1999). Hydraulic and Pneumatic Fracturing. Remediation Engineering: Design Concepts. B. R. CRC Press LLC, FL.**:** 237-254.

Svendson, A. P., M. S. Wright, et al. (1991). "Thermally Induced Fracturing of Ula Water Injectors." SPE Production Engineering **6**(4): 384-390.

Topf, A. (2014). "Water-less Fracking Could Be Industry Game Changer." from http://oilprice.com/Energy/Energy-General/Water-less-Fracking-Could-Be-Industry-Game-Changer.html.

US EPA (1993). Accutech Pneumatic Fracturing Extraction™ and Hot Gas Injection, Phase I Applications Analysis Report

US EPA (2004). Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed Methane Reservoirs.

US EPA (2011). Proceedings of the Technical Workshops for the Hydraulic Fracturing Study: Chemical & Analytical Methods.

Vandor, D. (2012). PATENT: Fracturing systems and methods utilyzing metacritical phase natural gas. USA. **US Patent # 8342246**.

Vidal, O. and B. Dubacq (2009). "Thermodynamic modelling of clay dehydration, stability and compositional evolution with temperature, pressure and H2O activity." Geochimica et Cosmochimica Acta **73**(21): 6544-6564.

Wang, H., G. Li, et al. (2012). "A Feasibility Analysis on Shale Gas Exploitation with Supercritical Carbon Dioxide." Energy Sources, Part A: Recovery, Utilization, and Environmental Effects **Volume 34**(Issue 15).

Wang, H., H. Lin, et al. (2016). "Enhancing biogenic methane generation from a brown coal by combining different microbial communities." International Journal of Coal Geology **154–155**: 107-110.

Wang, H. Y., O. Ajao, et al. (2014). "Conceptual study of thermal stimulation in shale gas formations." **21**: 874-885.

Wang, L., B. Yao, et al. (2016). "Waterless fracturing technologies for unconventional reservoirs-opportunities for liquid nitrogen." Journal of Natural Gas Science and Engineering **35, Part A**: 160-174.

Wuchter, C., E. Banning, et al. (2013). "Diversity and methanogenic capabilities of Antrim Shale formation water microbial communities." Environmental Microbiology(submitted).

Xiangqian, H., L. Yongjun, et al. (2013). "Waterless fracturing fluid with low carbon hydrocarbon as base fluid for unconventional reservoirs." Petroleum Exploration and Development **40**(5).

Yin, H., J. Zhou, et al. (2016). "Physical and structural changes in shale associated with supercritical CO2 exposure." Fuel **184**: 289-303.

Yost II, A. B., R. L. Mazza, et al. (1993). CO2/Sand Fracturing in Devonian Shales. SPE Eastern Regional Meeting. Pittsburgh, Pennsylvania, Not subject to copyright. This document was prepared by government employees or with government funding that places it in the public domain.

Yu-Shu Wu, X. Y., Timothy Kneafsey, Jennifer Miskimins, Minsu Cha, Taylor Patterson, Bowen Yao, Naif Bandar Alqahtani. (2013). "Development of Non-Contaminating Cryogenic Fracturing Technology for Shale and Tight Gas Reservoirs." from http://www.rpsea.org/projects/10122-20/.

Zhu, G.-p., J. Yao, et al. (2016). "The numerical simulation of thermal recovery based on hydraulic fracture heating technology in shale gas reservoir." Journal of Natural Gas Science and Engineering **28**: 305-316.

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