An overview of hydraulic fracturing and other formation stimulation technologies for shale gas production

Update 2015

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Abstract

An overview of hydraulic fracturing and other formation stimulation technologies for shale gas production – Updated 2015

This report presents an update of the original study carried out in 2013 (EUR 26347). It reviews the latest trends in hydraulic fracturing and alternative fracturing technologies. For each identified technique, an overview is given along with its rationale. Potential advantages and disadvantages are identified and the technological readiness status is identified for its application to shale gas production.
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**Executive summary**

The technology of hydraulic fracturing for hydrocarbon well stimulation is not new, but only fairly recently has 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 (tight sands, coal beds and 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 worries and high expectations: worries 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 considerations.

As for any other industrial activity, the deployment of high-volume hydraulic fracturing could potentially entail some risks to the environment. Among the concerns raised are high usage of water, methane infiltration in aquifers, aquifer contamination, extended surface footprint, induced local seismicity, etc. New technologies could help addressing these concerns (for instance by using non-toxic chemicals, by reducing or eliminating altogether the usage of water, by considerably reducing the surface footprint of a well, etc.).

This report is an update of the original study carried out in 2013 (2013). It reviews the latest trends in hydraulic fracturing and alternative fracturing technologies, by searching the open literature, patent databases and commercial websites (mainly in the English language). For each identified technique, an overview is given. The technique is then briefly explained, and its rationale (reasons for use) is identified. Potential advantages and disadvantages are identified, and some considerations on costs are given. Finally, the status of the technique (for instance, commercially applied, being developed, concept, etc.) is given for its application to shale gas production.
1. Introduction

1.1. Background

This report is an updated of the original JRC report published in 2013 (Gandossi 2013), compiled taking into account new relevant information that has been published in the course of 2014 and 2015.

The technology of hydraulic fracturing for hydrocarbon well stimulation is not new, with the first experiments done in 1947, and the first industrial use in 1949. It has been used since then for reservoir stimulation (in Europe as well) and enhanced hydrocarbon recovery.

Hydraulic fracturing has 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 (tight sands, coal beds and shale formations). The so-called high volume hydraulic fracturing (with treatments typically an order of magnitude larger than the conventional fracturing procedures) began in 1968. This was complemented by horizontal drilling since the late 1980s, and the use of chemicals (known as "slickwater fracturing") since 1997.

The conjunction of these techniques (directional drilling, high volume fracturing, fracture divergence systems, slickwater) with the development of multi-well pads has been especially successful in North America in the last years in their application to shales, making gas production from shales technically and economically feasible. Shale gas development is considered “unconventional” when contrasted with “conventional” subterranean natural gas reservoirs.

In Europe, experience to date has been focused on low volume hydraulic fracturing in some conventional and tight gas reservoirs, mostly in vertical wells, and constituted only a small part of past EU oil and gas operations. The scale, frequency and complexity of the fracturing technique necessary for shale gas extraction differ from past EU experiences, and the potential application of this technology has therefore led to both great worries and high expectations: worries regarding the alleged magnitude of the environmental impact, and expectations about production of indigenous hydrocarbons.

Other methods for fracturing (or, more broadly, 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 not extensively applied due to performance considerations.

Foam technologies, thus more expensive than water based stimulations do offer an alternative to reduce the amount of water used in shale gas stimulation. These are available across the industry.

The deployment of high-volume hydraulic fracturing could entail some risks to the environment. Among the concerns raised the following can be mentioned: high usage of water, methane infiltration in aquifers, aquifer contamination, extended surface footprint, induced local seismicity, etc.

New technologies could help addressing these concerns (for instance by using non-toxic chemicals, by reducing or eliminating altogether the usage of water, by considerably reducing the surface footprint of a well, etc.), but it is noted that hydraulic fracturing is still the preferred method by the industry (OGP 2013).

1.2. Scope and objective

This paper reviews hydraulic fracturing and alternative fracturing technologies, by searching the open literature, patent databases and commercial websites (mainly in the English language).
For each identified technique, an overview is given. The technique is then briefly explained, and its rationale (reasons for use) is identified. Potential advantages and disadvantages are identified, and some considerations on costs are given. Finally, the status of the technique (for instance, commercially applied, being developed, concept, etc.) is given for its application to shale gas production.

1.3. Method and limitations
This report was compiled by and large by accessing available literature (relevant journal and conference papers, patent databases and commercial websites), sometimes authored by individuals or organisations wishing to promote a certain technology.

The report does not include full life cycle analysis of cost or environmental impacts, nor any other measure of quantification of advantages or disadvantages of the specific technologies at hand. Thus, the inclusion of positive or negative aspects of a certain technology (economic, environmental, or otherwise) does not constitute an endorsement of the net benefits and/or costs and disadvantages of that stimulation method in comparison with other methods.

Advantages and disadvantages of any applied technology are in most cases dependent on the specific situation under which formation stimulation is performed (location, formation characteristics, etc.). In this report, no objective criteria were developed and applied to identify potential advantages and disadvantages of each technique. As an example, when it is noted that a certain technology leads to “reduced water usage”, this is not a judgment to whether there is an environmental, economic or otherwise need to reduce water consumption, and whether the alternative is overall a better choice. Such a choice would typically depend on the specific condition for a given situation.

1.4. Report structure
The paper is structured as follows. The technologies are divided in four main chapters:

- **Hydraulic Fracturing**
- **Pneumatic Fracturing**
- **Fracturing with Dynamic Loading**
- **Other Methods**

**Hydraulic Fracturing** is herein defined as the technique that makes use of a liquid fluid to fracture the reservoir rocks. The following techniques are identified and discussed:

- Water-based fluids
- Foam-based fluids
- Oil-based fluids
- Acid-based fluids
- Alcohol-based fluids
- Emulsion-based fluids
- Cryogenic fluids (CO\textsubscript{2}, N\textsubscript{2}, etc.)
- Fluids based on produced water

**Pneumatic Fracturing** is the technique that makes use of a gas (typically air or nitrogen) to fracture the reservoir rock. It is a technique normally used in shallow formations.
In *Fracturing with Dynamic Loading* fluids are not used. The following techniques are identified and discussed:

- Explosive fracturing section 4.1
- Electric fracturing section 4.2

Under **Other Methods** we review all remaining fracturing techniques that do not readily fall in one of the previous categories. The following techniques are identified and discussed:

- Cryogenic fracturing section 5.1
- Mechanical cutting of the shale formation section 5.2
- Enhanced bacterial methanogenesis section 5.3
- Heating of the rock mass section 5.4
- In-situ combustion section 5.5
- Enhanced oil recovery in shale reservoirs section 5.6

Summary and conclusions are given in Chapter 6.
2. 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. In general terms, hydraulics is a topic in applied science and engineering dealing with the mechanical properties of liquids (not just water). Though a matter of definitions, in this note we choose to categorize under “hydraulic fracturing” all techniques that make use of liquids (including foams and emulsions) as the fracturing agent.

Indeed, using water as base fluid for hydraulic fracturing is a more recent development. (Montgomery and Smith 2010) give a good account of the history of hydraulic fracturing. The first fracture treatments were initially performed with gelled crude and later with gelled kerosene. By the end of 1952, many fracturing treatments were performed with refined and crude oils. These fluids were inexpensive, permitting greater volumes at lower cost. In 1953 water started to be used as a fracturing fluid, and a number of gelling agents was developed. 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.

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. 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.

As more and more fracturing treatments have involved high-temperature wells, gel stabilizers have been developed, the first of which was the use of approximately 5% methanol. Later, chemical stabilizers were developed that could be used alone or with the methanol. Improvements in crosslinkers and gelling agents have resulted in systems that permit the fluid to reach the bottom of the hole in high-temperature wells prior to crosslinking, thus minimizing the effects of high shear (Montgomery and Smith 2010).

The fracturing fluid used is a crucial component of hydraulic fracturing, not only concerning the technical characteristics (rheology\(^1\), 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.

2.1. Hydraulic fracturing of shales

Shale formations present a great variability, and for this reason no single technique for hydraulic fracturing has universally worked. Each shale play has unique properties that need to be addressed through fracture treatment and fluid design. For example, numerous fracture technologies have been applied in the Appalachian basin alone, including the use of CO\(_2\), N\(_2\) and CO\(_2\) foam, and slickwater fracturing. The composition of fracturing fluids must be altered to meet specific reservoir and operational conditions. 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.

\(^1\) Rheology is the branch of physics concerned with the study of the deformation and flow of matter.
Ductile reservoirs require more effective proppant placement to achieve the desired permeability. Other fracture techniques, including CO\textsubscript{2} polymer and N\textsubscript{2} foams, are occasionally used in ductile rock (for instance, in the Montney Shale in Canada). As discussed below in Sections 2.4 and 2.9.1, CO\textsubscript{2} fluids eliminate the need of water while providing extra energy from the gas expansion to shorten the flowback time.

In general, a fracturing fluid can be thought as the sum of three main components:

\begin{center}
Fracturing Fluid = Base Fluid + Additives + Proppant
\end{center}

A fracturing fluid can be “energized” with the addition of compressed gas (usually either CO\textsubscript{2} or N\textsubscript{2}). This practice provides a substantial portion of the energy required to recover the fluid and places much less water on water-sensitive formations, but has the disadvantage that it reduces the amount of proppant that is possible to deposit in the fracture. Table 1 summarises a useful classification system developed to characterise different types of hydraulic fracturing fluid systems (Patel, Robart et al. 2014).

<table>
<thead>
<tr>
<th>Fracturing type</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>Treatment type that uses a gelling agent and one or more crosslinkers in order to transport proppant into a hydraulic fracture.</td>
</tr>
<tr>
<td>Water Frac</td>
<td>Treatment type that uses a friction reducer, a gelling agent or a viscoelastic surfactant in order to transport proppant into a hydraulic fracture.</td>
</tr>
<tr>
<td>Hybrid</td>
<td>Treatment type that uses a combination of a friction reducer, gelling agent, acid gelling agent, or one or more crosslinkers in order to transport proppant into a hydraulic fracture.</td>
</tr>
<tr>
<td>Energized</td>
<td>Treatment type that incorporates an energizer, normally nitrogen or carbon dioxide, into the base fluid in order to generate foam that transport proppant into a hydraulic fracture.</td>
</tr>
<tr>
<td>Other/Unknown</td>
<td>Treatment type category that includes the following less common types: acid frac, gas frac, matrix acidizing.</td>
</tr>
</tbody>
</table>

Typically, water-based fluids are the simplest and most cost-effective solution to fracture a rock formation. However, alternatives to water-based fluids have significantly outperformed water treatments in many reservoirs. For instance, foams have been extensively used in the seventies in depleted conventional reservoirs in which water fractures were not effective. More recently, the development of some unconventional reservoirs (tight gas, shale gas, coal bed methane) has prompted the industry to reconsider "waterless" fracturing treatments as viable alternatives to water-based fracturing fluids. In these reservoirs, the interactions between the rock formation and the fracturing fluids may be detrimental to hydrocarbon production. (Ribeiro and Sharma 2013). There are several reasons to consider fluids that contain little or no water, namely:

1. **Water sensitivity of the formation.** The base mineral composition of a given rock formation impacts the recovery process of water, gas, and oil. For example, oil-based fluids, LPG, CO\textsubscript{2} and high-quality foams are recommended in water-sensitive formations to prevent excessive fines migration and clay swelling. In many shales, proppant conductivity drops considerably in the presence of water because the rock-fluid interactions soften the rock leading to proppant embedment.
2. **Water blocking.** In under-saturated gas formations, the invasion of water from the fracturing fluid can be very detrimental to gas productivity as any additional water remains trapped because of capillary retention. The increase in water saturation (referred to as water blocking or water trapping) significantly reduces the relative permeability to gas, sometimes by orders of magnitude (Parekh and Sharma 2004).

3. **Proppant placement.** Foams and other gelled non-aqueous fluids can transport proppant much more effectively than slickwater fluids. At high foam qualities (gas volume fraction typically higher than 0.5), the interactions between gas bubbles cause a large energy dissipation that results in a high effective viscosity. At low foam qualities (less than 0.5) the interactions between bubbles are minimal so the fluid viscosity resembles that of the base fluid (which is typically gelled).

4. **Water availability and cost.** Operators are limited by the equipment and the fluids readily available on site. In areas prone to drought fresh water can become difficult to obtain. In some regions, the local legislation even limits water usage, which has prompted some operators to use waterless fracturing treatments. Alternatively, the supply and the cost of Liquefied Petroleum Gas (LPG), CO₂ and N₂ are strongly site-specific. Much of the cost savings depend on the availability of the fluid. The use of large quantities of gases requires the deployment of many trucks, pressurized storage units, and specific pumping equipment. In addition, handling of LPG will require additional safety measures

Table 2 broadly summarizes the different fluids that are used for hydraulic fracturing (EPA 2004; PetroWiki - Society of Petroleum Engineers 2013). In Section 2.3, recent analyses of trends in hydraulic fracturing fluids, additives and proppants are summarised. It is also worth to mention that (Barati and Liang 2014) very recently presented a review of fracturing fluid systems used for hydraulic fracturing.

<table>
<thead>
<tr>
<th>Base Fluid</th>
<th>Fluid type</th>
<th>Main Composition</th>
<th>Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-based</td>
<td>Slickwater</td>
<td>Water + sand (+ chemical additives)</td>
<td>2.2</td>
</tr>
<tr>
<td>Linear fluids</td>
<td></td>
<td>Gelled water, GUAR&lt;HPG, HEC, CMHPG</td>
<td></td>
</tr>
<tr>
<td>Cross-linked fluids</td>
<td>Crosslinker + GUAR, HPG, CMHPG, CMHEC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscoelastic surfactant gel fluids</td>
<td>Electrolite+surfactant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foam-based</td>
<td>Water based foam</td>
<td>Water and Foamer + N₂ or CO₂</td>
<td>2.4</td>
</tr>
<tr>
<td>Acid based foam</td>
<td>Acid and Foamer + N₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohol based foam</td>
<td>Methanol and Foamer + N₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil-based</td>
<td>Linear fluids</td>
<td>Oil, Gelled Oil</td>
<td></td>
</tr>
<tr>
<td>Cross-linked fluid</td>
<td>Phosphate Ester Gels</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water Emulsion</td>
<td>Water + Oil + Emulsifiers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid-based</td>
<td>Linear</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Cross-linked</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil Emulsion</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohol-based</td>
<td>Methanol/water mixes or 100% methanol</td>
<td>Methanol + water</td>
<td></td>
</tr>
<tr>
<td>Emulsion-based</td>
<td>Water-oil emulsions</td>
<td>Water + Oil</td>
<td></td>
</tr>
<tr>
<td>CO₂-methanol</td>
<td>CO₂ + water + methanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other fluids</td>
<td>Liquid CO₂</td>
<td>CO₂</td>
<td></td>
</tr>
<tr>
<td>Liquid nitrogen</td>
<td>N₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid helium</td>
<td>He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid natural gas</td>
<td>LPG (butane and/or propane)</td>
<td>2.9.4</td>
<td></td>
</tr>
</tbody>
</table>
2.2. Water-based hydraulic fracturing

Table 2, adapted from (King 2012), demonstrates how unconventional gas production is driven by the development and application of technologies, by showing the increased recovery of gas and oil from the shales. An essential element, not only from a technological point of view but also from an environmental one, is the type of fluid used to perform the fracturing of the formation. This will dictate the type of required chemical additives, the need for flowback treatment, etc.

The predominant fluids currently being used for fracture treatments in the gas shale plays are water-based fracturing fluids mixed with friction-reducing additives (called slickwater). Many other water-based fluids are used, broadly speaking: linear fluids, cross-linked fluids, and viscoelastic surfactant fluids. These are discussed in the following.

Slickwater fracturing is probably the most basic and most common form of well stimulation in unconventional gas. The fracturing fluid is composed primarily of water and sand (> 98%). Additional chemicals are added to reduce friction, corrosion, bacterial-growth, and provide other benefits during the stimulation process. Low viscosity slick-water fluids generate fractures of lesser width and therefore greater fracture length, theoretically increasing the complexity of the created fracture network for better reservoir-to-wellbore connectivity.

Unfortunately, slickwater fluid is an inherently poor proppant carrier, necessitating high pump rates to achieve flow velocities sufficient to overcome the tendency of the proppants to settle. Proppant settling within surface equipment or long horizontal laterals can result in premature treatment termination and poor productivity. Linear gel and crosslinked systems have been used to mitigate the proppant settling and placement concerns, but the high viscosity that accomplishes this objective may significantly reduce the desired fracture complexity. Also, the long fracture closure times and the lack of efficient gel delayed breakers makes the proppant placement advantage of gel systems very limited as proppant settles while gel is breaking up and fracture has not yet closed.

More than 30% of stimulation treatments in 2004 in North America have been slickwater fracturing (Schein, 2005). The most important benefits of slickwater fracturing are reduced gel damage, cost containment, higher stimulated reservoir volume, and better fracture containment. But there are concerns such as poor proppant transport, excessive usage of water, and narrower fracture widths (Kishore K. Mohanty 2012).

Some fracturing treatments require a higher viscosity fluid, such as linear fracturing fluids. These are formulated by adding a wide array of different polymers to water. Such polymers are dry powders that swell when mixed with an aqueous solution and form a viscous gel. The gel-like fluid is then more able to transport the proppant than would a normal low-viscous (slickwater) fluid. Common polymer sources used with the linear gels are guar, Hydroxypropyl Guar (HPG), Hydroxyethyl Cellulose (HEC), Carboxymethyl hydroxypropyl gua r (CMHPG), and Carboxymethyl Hydroxyethyl cellulose (CMHEC) (EPA 2004). In low-permeability formations, linear gels control fluid loss very well, whereas in higher-permeability formations fluid loss can be excessive. Linear gels tend to form thick filter cakes on the face of lower-permeability formations, which can adversely affect fracture conductivity. The performance of linear gels in higher-permeability formations is just the opposite, since it forms no filter cake on the formation wall. Much higher volumes of fluid are lost due to viscous invasion of the gel into the formation.

Crosslinked fluids were developed in order to improve the performance of gelling polymers without increasing their concentration. Borate crosslinked gel fracturing fluids utilize borate ions to crosslink the hydrated polymers and provide increased viscosity. The polymers most often used in these fluids are guar and HPG. The crosslink obtained by using borate is reversible and is triggered by altering the pH of the fluid system. The reversible characteristic of the crosslink in borate fluids helps them clean up more effectively, resulting in good regained permeability and conductivity.
Table 3. Increased recovery of gas and oil from shales driven by the development and application of technologies (adapted from (King 2012))

<table>
<thead>
<tr>
<th>Year</th>
<th>Technologies Applied</th>
<th>% Recovery of Original Gas in Place</th>
<th>Shale Play</th>
</tr>
</thead>
<tbody>
<tr>
<td>1980’s</td>
<td>Vertical wells, low rate gel in fracs</td>
<td>1%</td>
<td>Devonian</td>
</tr>
<tr>
<td>1990’s</td>
<td>Foam fracs 1st slickwater in shale</td>
<td>1.5 to 2%</td>
<td>Devonian</td>
</tr>
<tr>
<td>2001</td>
<td>High rate slickwater fracs</td>
<td>2 to 4%</td>
<td>Barnett</td>
</tr>
<tr>
<td>2004</td>
<td>Horizontal well dominant, 2 to 4 fracs</td>
<td>5 to 8%</td>
<td>Barnett</td>
</tr>
<tr>
<td>2006</td>
<td>Horiz, 6 to 8 fracs, stimul fracs, water recycle trial</td>
<td>8 to 12%</td>
<td>Barnett</td>
</tr>
<tr>
<td>2008</td>
<td>16+ fracs per well, Petrophysics increases</td>
<td>12 to 30%</td>
<td>Barnett</td>
</tr>
<tr>
<td>2010</td>
<td>Technology to flatten decline curve, feeling pinch for frac water</td>
<td>30 to 40%</td>
<td>Haynesville</td>
</tr>
<tr>
<td>2011</td>
<td>Pad development drains 5000 acres, salt water displacing fresh for fracs</td>
<td>45%+</td>
<td>Horn River</td>
</tr>
<tr>
<td>Future developments</td>
<td>Green chemicals, salt water fracs, low disposal volume, reduced truck traffic, pad drilling, electric rigs and pumps</td>
<td>45 - 55%</td>
<td>Numerous</td>
</tr>
</tbody>
</table>

Borate crosslinked fluids have proved to be highly effective in both low and high permeability formations. They offer good proppant transport, a stable fluid rheology at temperatures as high as 300°F, low fluid loss and good cleanup properties (Haliburton 2011). Organometallic crosslinked fluids are also a very popular class of fracturing fluids. Primary fluids that are widely used are zirconate and titanate complexes of Guar, Hydroxypropyl Guar (HPG) and Carboxymethyl-Hydroxypropyl Guar (CMHPG). Organometallic crosslinked fluids are routinely used to transport the proppant for treatments in tight gas sand formations that require extended fracture lengths. They provides advantages in terms of stability at high temperatures and proppant transport capabilities. According to Halliburton, they provides excellent stability at high temperatures and proppant transport capabilities and offer more predictable rheological properties (Halliburton 2011a).

**Viscoelastic surfactant gel fluids** (VES) have been described in the patent literature for friction reduction and as well treatment fluids since the early 80s, but their use as fracturing fluids is relatively a new phenomenon. Principally, these fluids use surfactants in combination with inorganic salts to create ordered structures, which result in increased viscosity and elasticity. These fluids have very high zero-shear viscosity and can transport proppant with lower loading and without the comparable viscosity requirements of conventional fluids (Satya Gupta in (EPA 2011)).

The technology of VES systems can be broken down into several categories based on the structure the system creates: worm-like micelles, lamellar structures or vesicles. As the concentration of surfactant increases in water, micelles start to form and start interacting with each other. These interactions are based on ionic forces and can be amplified by adding electrolytes (salts) or other ionic surfactants. These fluids are operationally simple: only one or two additives are added without any need to hydrate polymers. They do not require any biocides because they do not contain any biopolymers. They do not require additional flowback surfactants because they have inherently low surface and interfacial tension. No additional clay control additives are needed.
(Stringfellow, Domen et al. 2014) is a recent, thorough analysis of the characteristics of the chemicals found in hydraulic fracturing fluids with the aim to evaluate potential environmental fate and human health impacts. In this study, eighty-one common chemical additives were identified and categorized according to their functions. Physical and chemical characteristics of these additives were determined using publicly available chemical information databases. Most of the hydraulic fracturing chemicals evaluated were identified as non-toxic or of low toxicity and only three were classified as Category 2 oral toxins according to standards in the Globally Harmonized System of Classification and Labeling of Chemicals. Toxicity information was not located for thirty of the hydraulic fracturing chemicals evaluated, suggesting a certain deficiency in the current state of knowledge.

Several interesting technologies have been recently developed. These are reviewed in the following.

2.2.1. Zipper fracturing

Zipper fracturing involves simultaneous stimulation of two parallel horizontal wells. In this technique, created fractures in each cluster propagate toward each other so that the induced stresses near the tips force fracture propagation to a direction perpendicular to the main fracture (Rafiee, Soliman et al. 2012). This technique typically makes use of slick-water as fracturing fluid, and it is applied to shale formations (Yu and Sepehrnoori 2013).

2.2.2. Cavitation Hydrovibration fracturing

Cavitation Hydrovibration is a proprietary technique developed at the Institute of Technical Mechanics in Dnipropetrovsk, Ukraine, and it is designed to fracture rock using a pressurized water pulse action. No literature sources or patent applications were found to confirm the technical details of the status of application of the system, except for an online article authored by blogger Walter Derzko (Derzko 2008).

The technique is described as a green technology that operates using pure water, without the use of any chemical. The cavitation hydrovibrator is mounted in a drilling line and inserted into a vertical or horizontal borehole at the appropriate stratum level. Pressured water is fed to the cavitation hydrovibrator inlet through the drilling line using a drill pump. Then the water passes through the hydrovibrator flow passage and enters the borehole where the gas-saturated stratum is located. Due to the pressure differential across the hydrovibrator, the regime of periodically detached cavitation is set up in its flow passage. In this regime, the steady water flow is transformed into a high-frequency pulsating flow. The pulse-repetition frequency can be varied from 100 to several thousand Hertz. The water pressure pulse acts on the gas-bearing formation and it increases its degree of fracturing.

(Derzko 2008) reports that this method has been tested and used in the Novojarovskoje sulfur deposit (in the Lviv Region of Ukraine) and that the method performed well in the recovery of old water wells in the Moscow region and in the Pskov region (Russian Federation). It appears that the technology has not been tested yet to enhance gas recovery in conventional reservoirs, nor for shale gas production.

2.2.3. Hydra-jet fracturing

Hydrajet fracturing combines hydrajetting with hydraulic fracturing. This process involves running a specialized jetting tool on conventional or coiled tubing. To initiate the hydraulic fracture, dynamic fluid energy jets form tunnels in the reservoir rock at precise locations. The hydraulic fracture is then extended from that point outward. By repeating the process, one can create multiple hydraulic fractures along the horizontal wellbore (Loyd E. East, Grieser et al. 2004; McDaniel and Surjaatmadja 2009; Gokdemir, Liu et al. 2013).
This technique is applied on unconventional reservoirs, including shales (McKeon 2011). It appears to offer improvements on how the fractures are initiated, but it does not offer substantial advantages regarding the usage of water and chemical additives in the fracturing fluid.

(McDaniel 2014) offers a recent and pretty comprehensive review of the use of hydrajetting deployed in conjunction with coiled tubing technology. According to this author, hydrajet perforating has been used in many new oilfield applications since the mid-1990's, and many promising variations (improved jetting nozzles, tool compositions, etc.) are being developed.

2.2.4. Exothermic hydraulic fracturing

(Al-ajwad, Abass et al. 2013) describe the idea of injecting chemicals during the hydraulic fracturing treatment that – upon reaction – generate heat and gas. The temperature and gas increase then create localized pressure that results in thermal and mechanical fracturing.

This idea was tested in laboratory specimen (cores) collected from tight reservoirs in Saudi Arabia. The permeability of tested cores showed significant increase after applying the new treatment technique. Enhanced communication between micro and macro pores was also found.

A likely shortcoming of this technique is the localized effect. Unconventional gas reservoirs, being so tight, require stimulation that reaches far into the reservoir. As shown in thermal heavy oil recovery projects, it takes substantial energy (or well count) to cover a large extension of the reservoir with relevant temperature changes.

2.2.5. Hydraulic fracturing enhanced by water pressure blasting.

(Huang, Liu et al. 2011) describe the idea of enhancing the effectiveness of hydraulic fracturing by using water blasting for fracturing coal seams.

Water pressure blasting is a method that combines the use of water with that of explosives (note that explosive fracturing is discussed in details in section 4.1). In this technology, water is used as a coupling medium to transfer the generated explosion pressure and energy as to break the rock.

According to (Huang, Liu et al. 2011), traditional hydraulic fracturing techniques generally form main hydraulic cracks and airfoil branch fissures, with the former relatively fewer in number. These authors state that experimental tests prove that the method is an effective way to increase the number and range of hydraulic cracks, as well as for improving the permeability of coal seams.

The working principles of the method are described in the following. A hole is drilled in the coal seam and is injected with a gel explosive. Water is injected into the hole to seal it (at low enough pressure to prevent cracks from forming). Water pressure blasting is carried out by detonating the explosive. The water shock waves and bubble pulsations produced by the explosion cause a high strain rate in the rock wall surrounding the hole. The rock breaks and numerous circumferential and radial fractures propagate outward. Finally, conventional hydraulic fracturing is performed. The fissures open by the detonation are further expand.

This technique has been proposed very recently (2011) and it appears an experimental idea. It has been suggested for low-permeability coal-seam gas extraction, but it is judged that it could potentially be applied to shale formations. It appears to offer improvements on how the fractures are initiated, and could potentially reduce the quantity of water required for the hydraulic fracturing stage. Without any reports on depth of stimulation away from the well, this technique does not appear to be economical.
2.3. Trends in hydraulic fracturing fluids, additives and proppants

Some excellent studies were published in 2014 and 2015, analysing trends in the deployment of hydraulic fracturing, mainly in North America where the overwhelming majority of activities has taken place: distributions, treatment fluids, additives, proppants, water volumes, etc.

(Gallegos and Varela 2015) is a report of the US Geological Survey. They noted that comprehensive and publicly available information regarding the extent, location, and character of hydraulic fracturing in the United States is scarce. They nonetheless analysed data related to nearly 1 million hydraulically fractured wells and 1.8 million fracturing treatment records from 1947 through 2010 and used such information to identify hydraulic fracturing trends in drilling methods and use of proppants, treatment fluids, additives, and water. These trends were then compared to the literature to establish a common understanding of the differences in drilling methods, treatment fluids, and chemical additives and of how the newer technology has affected the water use volumes and areal distribution of hydraulic fracturing. The analysis showed that directional drilling increased from 6 percent of new hydraulically fractured wells drilled in the United States in 2000 to 42 percent of new wells drilled in 2010. This also coincided with the emergence of water-based fracturing fluids.

(Patel, Robart et al. 2014) provided a comprehensive analysis of hydraulic fracturing fluid systems and proppant trends across major shale plays in the United States between 2011 and the first half of 2013, by categorizing and analyzing over 55000 hydraulic fracturing treatments collected from FracFocus.org, a web-based initiative established in early 2011 with a centralized database to provide hydraulic fracturing chemical disclosures across the United States. The analysis identified changes over time in fracturing type, using the broad categories reported in Table 1. It also included a study on proppant trends, including usage rates for key proppant types (sand, resin-coated sand, and ceramics) and proppant loading trends. The full results cannot be summarized here for reasons of space, and the interested reader is referred to the original source.

(Al-Muntasheri 2014) presented a review of the available water-based fracturing fluids over the last ten years for fracturing reservoirs with low permeability. The review revealed the evolution of several interesting developments, including the use of cleaner guar-based polymers, of synthetic polymers and of larger-sized crosslinker molecules. The study also concluded that nanotechnology can be a promising tool to develop better performing fluids. According to the author, guar-based polymers are still being used for fracturing oil and gas wells, mainly because of their high shear stability and better cleanup compared with other systems. When fracturing hot reservoirs, synthetic polyacrylamide-based polymers can be used. The use of larger-sized boronic-based crosslinkers is helping reducing the concentration of polymers used in preparing fracturing fluids, even if no field application data have been reported yet for this system. Nanoparticles are being used to improve leak-off of viscoelastic-surfactant-based fluids, but an optimal employment of such materials still requires further research. Produced water can present an opportunity to address environmental concerns about water preservation. However, not all produced waters are compatible with fracturing fluids.

A review of fracturing fluid systems used for hydraulic fracturing was also very recently presented by (Barati and Liang 2014).

We conclude this brief section by mentioning an investigation by (Lee and Sohn 2014), who studied the current development status of shale gas technology in China as compared to that in the US by analysing patents registered in the two countries.
### 2.4. Foam-based fluids

**Overview**

For water-sensitive formations and environments where water is scarce, foams have long been considered as one of the best fracturing fluids (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 being used in a number of petroleum industry applications that exploit their high viscosity and low liquid content. Some of the earliest applications for foam dealt with its use as a displacing agent in porous media and as a drilling fluid. In the mid-1970's, N₂-based foams became popular for both hydraulic fracturing and fracture acidizing stimulation treatments.

Most recently, CO₂ foams have been found to exhibit their usefulness in hydraulic fracturing stimulation. Different foam-based fluids can be used, as summarized in the table below (adapted from (EPA 2004)). The liquid CO₂-based fluid consists of a foam of N₂ gas in liquid CO₂ as the external phase stabilized by a special foamer soluble in liquid or supercritical CO₂ (Gupta 2003). The main advantage of this fluid is the additional viscosity gained by the foam over liquid CO₂. The use of 75% volume of N₂ 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 (EPA 2004)). Table 4 gives a broad summary of the types of foams used as fracturing fluids.

<table>
<thead>
<tr>
<th>Type of foam</th>
<th>Main composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-based foams</td>
<td>Water and Foamer + N₂ or CO₂</td>
</tr>
<tr>
<td>Acid-based foams</td>
<td>Acid and Foamer + N₂</td>
</tr>
<tr>
<td>Alcohol-based foams</td>
<td>Methanol and Foamer + N₂</td>
</tr>
<tr>
<td>CO₂-based foams</td>
<td>Liquid CO₂ + N₂</td>
</tr>
</tbody>
</table>

The influence of foam quality on effectiveness of hydraulic fracturing in shales was recently studied by (Gu and Mohanty 2014)

**Description**

A foam is used as the fracturing fluid. 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).

Foams are very unique and versatile because of low-density and high-viscosity characteristics. Previous studies show that foam viscosity strongly depends on foam quality (the gas fraction in the total gas and liquid mixture) and foam texture (the number of bubbles in unit mixture volume) (Edrisi and Kam 2012).
Rationale

It is claimed (Edrisi and Kam 2012) that for shale gas development in environmentally sensitive regions, 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. Expansion of the gas phase after the treatment also helps recover the liquid phase introduced into the formation with foams.

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 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.

Potential advantages and disadvantages

Potential advantages
- Water usage reduced (or completely eliminated in case of CO₂-based foams).
- Reduced amount of chemical additives.
- Reduction of formation damage.
- Better cleanup of the residual fluid.

Potential disadvantages
- Low proppant concentration in fluid, hence decreased fracture conductivity.
- Higher costs.
- Difficult rheological characterization of foams, i.e. flow behaviour difficult to predict.
- Higher surface pumping pressure required.

Status of technique application for unconventional reservoirs

Foams are commercially used to fracture shale formations. For instance, (Rowan 2009) reports the use of foams to stimulate gas wells in the Lower Huron Shale in the Appalachian Basin. (Brannon, Kendrick et al. 2009) discuss the application of foams in the Big Sandy (a productive field of more than 25,000 wells, located in the eastern USA), characterized by ultra-low permeability, the Berea tight gas sands and Devonian Ohio shales such as the Huron formation.

NETL has an ongoing project² (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 (< 25 vol. %) yet exhibit high apparent viscosity, so that they can be used as nearly water-less fracturing fluids. The latest quarterly report available (Bryant and Huh 2014) reports on the examination of the effects of polymer addition upon increasing the foam quality (reducing water content) without breaking the foam and on the development of a mechanistic foam dynamics model.

2.5. Oil-based fluids

Oil-based fracturing fluids were the first high-viscosity fluids used in hydraulic fracturing operations. A major advantage to this type of fluid is its compatibility with almost any formation type. 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

² http://www.netl.doe.gov/research/oil-and-gas/project-summaries/enhanced-oil-recovery/fe0013723-UTA
promising technique, which has been developed especially for shale gas production, makes use of liquefied petroleum gas (LPG\(^3\)). This is analysed in details in the following section.

### 2.5.1. LPG

**Overview**

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 (C\(_3\)H\(_8\)) (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).

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.

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.

**Description of the technique**

LPG is used as the fracturing fluid (Taylor, Lestz et al. 2006; Lestz, Wilson et al. 2007). In the GasFrac system, LPG is gelled before the fracturing to allow better transport of

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\(^3\) Liquefied petroleum gas (LPG) is a flammable mixture of hydrocarbon gases normally used as a fuel in heating appliances and vehicles. Varieties of commercial LPG include mixes that are primarily propane (C\(_3\)H\(_8\)), primarily butane (C\(_4\)H\(_{10}\)) or mixtures including both propane and butane.
proppant into the fracture. In the ecorpStim system, LPG is not gelled. Buoyant proppants such as fine sand and carbon fullerenes are used, but it still needs to be proven that they are strong enough for widespread application.

When fracturing, the LPG remains liquid, but after completing the process it goes into solution with the reservoir gas.

**Rationale**

Liquid propane is particularly suitable for use as fracturing fluid because it is less viscous than water. Many shale formations are water-sensitive, and using LPG would avoid this problem.

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 CO₂ or N₂, 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 CO₂ emissions. Because propane liquid is half the specific gravity of water, there is reduced trucking to the site and no trucking to transport post stimulation - which can reduce truck traffic by up to 90%.

The main drawback of this technology is that it involves the manipulation of large amounts (several hundred tons) of flammable propane (and the associated risks/safety hazards). It is therefore a more suitable solution in environments with low population density, provided of course that the workers safety can be strictly guaranteed.

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.

Potential advantages and disadvantages

Potential advantages
- Water usage much reduced or completely eliminated.
- Fewer (or no) chemical additives are required.
- Flaring reduced.
- Truck traffic reduced.
- Abundant by-product of the natural gas industry.
- Increased the productivity of the well.
- Lower viscosity, density and surface tension of the fluid, which results in lower energy consumption during fracturing.
- Full fluid compatibility with shale reservoirs (phase trapping virtually eliminated).
- No fluid loss. Recovery rates (up to 100%) possible.
- Very rapid clean up (often within 24 hours).

Potential disadvantages
- Involves the manipulation of large amounts of flammable propane, hence potentially riskier than other fluids and more suitable in environments with low population density. This disadvantage completely disappears if using heptafluoropropane.
- Higher investment costs.
- Success relies on the formation ability to return most of the propane back to surface to reduce the overall cost.
- Heptafluoropropane is a very stable hydrocarbon, and as such presents a global warming potential.

Costs

Investment costs are estimated to be higher than for hydraulic fracturing, because LPG is pumped into well at a very high pressure, and after each fracturing it has to be liquefied again (Rogala, Krzyszek et al. 2013). In addition, propane costs more than water both initially and as an ongoing cost, to make up for the portion that is not returned to the surface after each operation.

Status of technique application

The LPG-based fracturing techniques reviewed (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 at the time of writing (November 2015).

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 during the course of 2015.
2.6. Acid-based fluids

Overview
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 CO₂ 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 CO₂ 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 CO₂ conducted on a tight gas well reservoir in Saudi Arabia, and concluded that CO₂ used to energized fracturing fluids can increase the productivity of the well while using less water and less acid than conventional acid fracturing.

(Gensheng, Mao et al. 2012) presents an acid fracturing methodology, called "hydraulic jet acid fracturing technique", for deep carbonate reservoirs, where high temperature, high fracture pressure (>2.0 MPa/m), high flow friction, and strong reservoir heterogeneity present severe challenges.

Status of technique application
For the reasons highlighted above, the application of acid fracturing is confined to carbonate reservoirs and is never used to stimulate sandstone, shale, or coal-seam reservoirs.

2.7. Alcohol-based fluids

Overview
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 report prepared for Methanol Institute in 2012 (“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.

Noneetheless, 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.

**Description of the technique**

A methanol-based fluid is used as the fracturing fluid.

Several methods to increasing 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. The most recent development (Gupta, Pierce et al. 1997) describes a modified guar dissolved in anhydrous methanol crosslinked and has been successfully used in the field. 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.

These fluids should be selectively used with special safety considerations due to the flammability of methanol. The flash point (i.e. the lowest temperature at which it can vaporize to form an ignitable mixture in air.) of methanol is 53°F (11.6°C) and its density is greater than that of air, which presents a safety hazard to field personnel. Oxygen contact must be avoided and therefore a “blanket” of $CO_2$ vapor is used to separate methanol vapor from any oxygen source. Personnel must wear fire-resistant coveralls.

**Rationale**

For formations with severe liquid trapping problems or irreducible water and/or hydrocarbon saturation, non-aqueous methanol fracturing fluids may be the best (or the only viable) 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).

**Potential advantages and disadvantages**

**Potential advantages**

- Water usage much reduced or completely eliminated.
- Methanol is not persistent in the environment (biodegrades readily and quickly under both anaerobic and aerobic conditions and photo-degrades relatively quickly).
- Excellent fluid properties: high solubility in water, low surface tension and high vapor pressure.
- Very good fluid for water-sensitive formations.
Potential disadvantages
- Methanol is a dangerous substance to handle:
  a. Low flash point, hence easier to ignite.
  b. Large range of explosive limits.
  c. High vapor density.
  d. Invisibility of the flame.

Costs
(Saba, Mohsen et al. 2012) indicate that, because of its low viscosity compared to water, methanol reduces the pumping pressure required to deliver the fracturing fluids to the formation. Because lower piping friction requires less hydraulic power, this can have a significant impact on reducing costs.

(Antoci, Briggiler et al. 2001) describe a study where more than 200 hydraulic fracturing jobs using crosslinked anhydrous methanol as fracture fluid were performed in Argentina. These treatments were carried out in conventional (sandstone) reservoirs. The introduction of crosslinked methanol was aimed at reducing treatment cost while maintaining better stimulation results associated with CO$_2$ foam. This was accomplished: crosslinked methanol cost was less than 50% compared to using CO$_2$ foam. Other cost-reducing advantages were given by the nature of the completion procedure, for instance by allowing fracturing in as many intervals as considered necessary without killing the well or without having to invade the zones with water base completion fluids.

Status of technique application
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).

2.8. Emulsion-based fluids

Overview
There are many 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 (section 2.5). A comprehensive review of these fluids is beyond the scope of this review. Broadly speaking, emulsion-based fluids reduce or completely eliminate the use of water.

A high-quality emulsion of CO$_2$ 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 CO$_2$ foams, with the added advantage of minimizing the amount of water introduced into the well (Gupta, Hlidek 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.
Description of the technique

An emulsion, i.e. a mixture of two or more liquids that are normally immiscible (i.e. non-mixable), is used as the fracturing fluid.

Rationale

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 CO₂ 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).

Potential advantages and disadvantages

Potential advantages
- Depending on the type of components used to formulate the emulsion, these fluids can have potential advantages such as:
  a. Water usage much reduced or completely eliminated.
  b. Fewer (or no) chemical additives are required.
- Increased the productivity of the well.
- Better rheological properties.
- Fluid compatibility with shale reservoirs.

Potential disadvantages
- Potentially higher costs.

Costs

Costs could potentially be higher when compared to water-based hydraulic fracturing, depending on the type of emulsion formulation.

Status of technique application

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 study.

2.9. Cryogenic fluids

2.9.1. Liquid CO₂

Overview

It appears that CO₂ is (or can be) used in different ways:
- Liquid CO₂ for hydraulically fracturing the reservoir (commercially used).
- Super-critical CO₂ for hydraulically fracturing the reservoir (concept stage).
- CO₂ foams. These are described more in detail in section 2.4.
- CO₂ thermal hydraulic fracturing, a method that combines conventional hydraulic fracturing with fractures caused by the thermal stresses that are generated when the cold fluid enters the hotter reservoir). This method is described more in detail in section 2.9 (concept stage).
- Hybrid systems: CO₂ in conjunction with other fluids.
**Description of the technique**

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 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).

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 CO$_2$ 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.

**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.

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. 2015)

**Hybrid systems** making use of CO$_2$ in conjunctions with other fluids have been recently proposed (Ribeiro, Li et al. 2015).

**Rationale**

According to D.V. Satya Gupta (quoted in (EPA 2011), fluids based on liquid CO$_2$ are at the technological cutting edge. These fluids have been very successfully used in tight gas applications in Canada and several US formations.

During hydraulic stimulation using conventional fracturing fluid, water-based fracturing 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. Another problem could be the swelling of clays which reduce the permeability as well. The injected fluid during hydraulic fracturing should 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 (CH4). Thus, it can replace CH4 in the shale formation, enhancing gas production and at the same time remaining locked underground. At reservoir
conditions, CO₂ adsorption exceeded CH₄ adsorption by a factor of five, suggesting that CO₂ enhanced gas recovery from shale could serve as a promising mean to reduce life cycle CO₂ emission for shale gas. On a strictly volumetric basis, gas shales have the potential to sequester large amounts of CO₂, provided that CO₂ can diffuse deep into the matrix (Nuttall, Eble et al. 2005).

When taken into fracturing, it can cause much more complicated fractures for its lower viscosity property, which has a benefit to shale gas exploitation (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 CO₂ results in the elimination of all residual liquid left in the formation from the fracturing fluid. The gaseous CO₂ also aids in lifting formation fluids that are produced back during the clean-up operation.

The biggest advantage is that the CO₂ adds no pollution to the environment, and it can have a positive net effect when considering the greenhouse gas emissions issue. An article in New Scientist has recently discussed the possibility that fracturing with CO₂ could spur the development of large-scale carbon sequestration (McKenna 2012).

(He, Feng et al. 2014) conclude that liquid CO₂ fracturing offers unique advantages but their analysis also shows that there are still existing disadvantages. These authors identify the high friction of liquid CO₂; the lack of suitable drag reducer; the very low viscosity of the fluid and its poor proppant carrying capacity; and the high fluid loss in fracturing. They also conclude that the CO₂ phase behaviour change is very complicated, and precise prediction methods are lacking. Finally, they identify supercritical CO₂ fracturing, because of better stimulation capability, reduced fracturing pressure and hence lesser requirements on equipment, as representing the development trend within the field of CO₂ fracturing.

Some researchers are proposing the use of supercritical CO₂ as a fracturing fluid for shale gas production in conjunction with gas turbines using the same fluid (Contri 2015; Giacomazzi and Messina 2015).

(Ribeiro, Li et al. 2015) have very recently introduced a new CO₂-hybrid fracturing design, consisting of (1) injecting pure CO₂ 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.

**Potential advantages and disadvantages**

**Potential advantages**
- Potential environmental advantages:
  a. Water usage much reduced or completely eliminated.
  b. Few or no chemical additives are required.
  c. Some level of CO₂ sequestration achieved.
- Reduction of formation damage (reduction of permeability and capillary pressure damage by reverting to a gaseous phase; no swelling induced).
- Form more complex micro-fractures, which can connect many more natural fractures greatly, increasing maximally the fractures conductivity. (Wang, Li et al. 2012 ).
- Enhance gas recovery by displacing the methane adsorbed in the shale formations (Wang, Li et al. 2012).
- Evaluation of a fracture zone is almost immediate 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.
- Better cleanup of the residual fluid, so smaller mesh proppant can be used and supply adequate fracture conductivity in low permeability formations.
- The use of low viscosity fluid results in more controlled proppant placement and higher proppant placement within the created fracture width.

**Potential disadvantages**
- The main disadvantages follow from the fluids’ low viscosity. Proppant concentration must necessarily be lower and proppant sizes smaller, hence decreased fracture conductivity.
- CO\(_2\) must be transported and stored under pressure (typically 2 MPa, -30°C).
- Corrosive nature of CO\(_2\) in presence of H\(_2\)O.
- Unclear (potentially high) treatment costs.

**Costs**
Some sources indicate that one of the major limitations of this technology has been their high treatment cost. Although stimulation treatments using the low-viscosity liquid CO\(_2\) system have been successful, the high pumping rates required to place these jobs and the associated frictional losses raised horsepower requirements. [D.V. Satya Gupta, quoted in (EPA 2011)]

Other authors state that fracturing with CO\(_2\) can be economical. For instance, Sinal and Lancaster 1987) state that the costs for fracturing fluid clean-up and associated rig time are considerably less than with conventional fracturing fluids. These advantages are reported: swabbing of the well is completely eliminated as a post-fracturing treatment; no disposal of recovered fracturing fluid is required; and evaluation of the well takes less time.

(Wang, Li et al. 2012) state that fracturing with supercritical CO\(_2\) can offer a reduction of costs, mainly because of an enhancement of gas.

**Status of technique application**
Liquid CO\(_2\) as fracturing fluid is already commercially used in many unconventional applications (most notably, tight gas) in Canada and the 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 study (2015) is (Fang, Chen et al. 2014).

**2.9.2. Liquid Nitrogen (N\(_2\))**

**Overview**
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).
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.

**Description of the technique**

Liquid nitrogen is used as the fracturing fluid.

For nitrogen to be pumped safely into a well, the entire surface manifold and wellhead must be made of stainless steel. In some cases, operators may use special fiberglass tubing to protect the casing from the extremely low temperatures.

**Rationale**

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.

**Potential advantages and disadvantages**

**Potential advantages**

- Potential environmental advantages:
  a. Water usage completely eliminated.
  b. No chemical additives are required.
- Reduction of formation damage.
- Self-propping fractures can be created by the thermal shock, hence need for proppant reduced or eliminated.

**Potential disadvantages**

- Special equipment required to safely handle liquid N2, due to the very low temperature of the fluid.
- Higher costs.
- Difficult to implement as liquid nitrogen travelling down the well will heat up and become a gas thus not able to transport proppant. Even if well temperature insulation is applied successfully, the nitrogen will become a gas very soon after entering the formation thus losing all ability to place proppant.

**Costs**

Nitrogen is a very common component of the atmosphere (~78% in volume) so it is assessed that liquid nitrogen can be manufactured anywhere and will still be relatively cheap. The need to use special pumping and handling equipment will increase costs.

**Status of technique application**

Using nitrogen as a component (in mists, foams or other energised fluids) of the fracturing medium is very common in the petroleum industry. The use of gaseous nitrogen in pneumatic fracturing is discussed in Chapter 3. 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 (Grundmann, Rodvelt et al. 1998), but its usage appears to be limited. This is probably due to its higher costs.

2.9.3. Liquid Helium

The use of liquid helium as fracturing fluid is mentioned in very few sources, notably in a study prepared for the Parliamentary Office for the Evaluation of Scientific and Technological Choices of the French Republic⁴ (Lenoir and Bataille 2013). No further details or references were given therein, except for a passing mention.

Chimera Energy Corp announced in 2012 the development of a fracturing technique that makes use of liquid helium. No literature sources or patent applications were found to confirm the technical details of the status of application of the system at the time of publication of (Gandossi 2013).

On 25 October 2012, Chimera Energy Corporation was suspended from trading by the US Securities and Exchange Commission because of questions regarding the accuracy of its statements in press releases to investors concerning, among other things, the company’s business prospects and agreements. Its website (http://www.chimeraenergyusa.com/) did not appear to be working.

It now appears that the company run a fraudulent scheme in which media hype was created by issuing news releases about a fracturing technology touted as an environmentally friendly alternative to hydraulic fracturing, with the aim of increasing the company’s stock price. After an investigation whose results were published in 2014, the Securities and Exchange Commission (a US Federal regulatory agency) concluded that Chimera never had any significant assets and that the technology was fictitious. The owners of the company were charged with securities fraud (http://fuelfix.com/blog/2014/08/15/sec-charges-houston-energy-firm-in-stock-pump-and-dump-scheme/).

2.9.4. Other cryogenic fluids

Overview

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.

⁴ Office parlementaire d'évaluation des choix scientifiques et technologiques (OPE CST).
Status of technique application

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

2.10. Potential new developments

Gupta (in EPA 2011) suggests the following potential new developments in the area of unconventional fluids:

- High-temperature viscoelastic fluids;
- Polymers that associate with surfactants that can be used as straight fluid or foams (Gupta and Carman 2011);
- Fluids based on produced water (also based on associative polymers). These fluids are described more in detail in the following sub-section.

2.10.1. Fluids based on produced water

With the increasing demands and rising cost of fresh water for oilfield operations, there is a drive to use produced water in place of fresh water in stimulation operations (Li, Sun et al. 2014). Produced water in the oil industry usually refers to water that is produced along with oil and/or gas from hydrocarbon wells, whereas flowback water usually refers to the fraction of the original fracturing fluid that flows back through the well after the treatment is performed. Flowback water can be considered as a subcategory of produced water.

Produced water often contains high levels of salinity. For instance, produced water from shale formations such as the Marcellus and Bakken basins has high total dissolved solids (TDS) content and high hardness. TDS are the total amount of mobile charged ions, including minerals, salts or metals dissolved in a given volume of water, whereas hardness is defined as the amount of dissolved calcium and magnesium in the water. High levels of TDS and hardness in produced water can pose challenges for a wide spectrum of fracturing fluids that are commonly formulated with clean water. Many fracturing fluids that are originally prepared with clean water may show significantly lower performance or even completely fail if salty produced water is used instead.

Some companies treat produced water to obtain a water quality suitable for formulating a suitable fracturing fluid. However, it is often cost-prohibitive to treat high-TDS produced water enough that it can be stably used to formulate fracturing fluids. At the same time, it can also be expensive to dispose of produced water by underground deep well injection or to transport it to a suitable disposal facility. Fluid systems that can be formulated directly with salty produced water without compromising the performance are therefore very desirable.

To be considered practical and successful, a fracturing fluid prepared with treated high-TDS and hard produced water should deliver a comparable performance as the fluid formulated with fresh water. For example, the fluid should possess sufficient viscosity to transmit the high pumping pressure exceeding the rock strength to create fractures in the formation and to transport proppant into the created fractures.

Untreated produced water has been used directly to formulate a number of fracturing fluid systems. For example, zirconium-crosslinked CMHPG fluids have been reported to work with produced water with some water having TDS above 300k mg/L (Kakadjian, Hamlat et al. 2013). Borate-crosslinked guar fluids were successfully made with produced water for bottom hole temperature up to about 212°F (Fedorov, Carrasquilla et al. 2014). Several other examples are available (Li, Sun et al. 2014).
3. Pneumatic fracturing

Overview

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.

Nitrogen gas fracturing is used primarily for water-sensitive, brittle, and shallow unconventional oil and gas formations. 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. This is because nitrogen is an inert and compressible gas with low viscosity, which makes it a poor proppant carrier. In addition, due to the low density of gaseous nitrogen, the main applications for nitrogen gas fracturing are shallow unconventional plays, namely coal bed methane, tight sands, and shale formations up to 5000 ft (1524 meters) in depth. Formations best suited for nitrogen gas fracturing also tend to have low permeability (less than 0.1 md) and low porosity (less than 4%) (Air Products 2013).

Description of the technique

In pneumatic fracturing, a gas (air, nitrogen, etc.) is injected into the subsurface at pressures exceeding the natural in-situ pressures present in the formation interface and at flow volumes exceeding the natural permeability of the rock.

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.

There is no theoretical maximum depth limit for initiating a fracture in a geologic formation as long as sufficient pressure and flow can be delivered to the fracture zone. In pneumatic fracturing the injection pressure required to lift the formation is typically two to three times higher than for hydraulic fracturing on account of gas compressibility effects in the system.

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, it may be advisable to use proppants since elevated overburden pressures can inhibit self-propping.

Rationale

Without the carrier fluids used in hydraulic fracturing, there are no concerns with fluid breakdown characteristics for pneumatic fracturing. There is also the 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. Pneumatic fractures, in particular, may propagate along existing fracture patterns. Hydraulic fractures have been found to be less influenced by existing fractures.

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 (Rogala, Krzysiek et al. 2013).
(Rogala, Krzysiek et al. 2013) conclude 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.

**Potential advantages and disadvantages**

**Potential advantages**
- Potential environmental advantages:
  a. Water usage completely eliminated.
  b. No chemical additives are required.
- Potential for higher permeabilities due to open, self-propped fractures that are capable of transmitting significant amounts of fluid flow.

**Potential disadvantages**
- Limited possibility to operate at depth.
- Limited capability to transport proppants.

**Status of technique application**

Shallow shale formations have been fractured with pneumatic fracturing (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) report 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™. This uses 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 (i.e. a proppant pack that is literally “one particle thick”). 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. Their proprietary proppant is being tested for deeper applications, specifically in the Montney and Cardium plays (Canyon 2013).
4. Fracturing with dynamic loading

In this section we review fracturing techniques that do not make use of fluids, but rather by inducing a dynamic loading by detonating explosives placed at the bottom of the well or by applying electrical impulses.

4.1. Explosive fracturing

Overview

Using explosives to fracture rock formations and hence 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).

In the late 1960s nuclear devices were tested as a mean to fracture rock formations in order to enhance the recovery of natural gas. In the United States, Project Gasbuggy (Lemon and Patel 1972; American Oil & Gas Historical Society 2012) tested a 29-kiloton nuclear device lowered at a depth of 1288 meters underground. The detonation created a molten glass-lined cavern about 160 feet in diameter and 333 feet tall, which collapsed within seconds. Subsequent measurements indicated that fractures extended more than 200 feet in all directions – and significantly increased natural gas production. Two further nuclear explosions (Project Rulison and Project Rio Blanco) were also carried out in Colorado. The natural gas proved to be too radioactive to be commercially viable. It is also reported that similar test where conducted in Russia to fracture oil and gas wells. The Soviet Union had a similar program: "Peaceful Nuclear Explosions for the National Economy", also referred to as "Program 7," involved testing of industrial nuclear charges for use in peaceful activities. (Nordyke 2000) reports that nuclear detonations were conducted with the stated purpose of searching for useful mineral resources with reflection seismology, breaking up ore bodies, stimulating the production of oil and gas, and forming underground cavities for storing the recovered oil and gas. All together, the Program 7 conducted 115 nuclear explosions, among them 12 explosions for oil stimulation and 9 explosions for gas stimulation (Nordyke 2000).

In the 1970s many different explosive-based fracturing techniques were studied, for instance: (1) displacing and detonating nitro-glycerine in natural or hydraulically induced fracture systems, (2) displacing and detonating nitro-glycerine in induced fractures followed by wellbore shots using pelletized TNT, and (3) detonating wellbore charges using pelletized TNT. These techniques were 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 have strong advantages over explosives. Propellants are substances which deflagrate rather than detonate. (Schmidt, Warpinski et al. 1980). The propellant techniques seem to offer a potential use for shale gas extraction and are reviewed more in details in the following. 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.

(Boyun Guo 2014) presents an analysis of well productivity of different types of well architectures to be completed with the explosive fracturing in liquid-rich shale gas formations. The analysis is based on numerical modelling but case studies indicate a good agreement between the result given by the models and field observation. Sensitivity analyses indicate that the initial productivity of fractured wells increases non-linearly with the number of radial fractures and fracture penetration, but the benefits of increasing fracture depth reaches a plateau as the amount of explosives increases.
**Description of the technique**

Substances (solid propellants) are deflagrated at appropriate locations in the rock formation. These generate high pressure gases at a rate that creates a fracturing behaviour 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 behaviour of propellants differs from explosives in that peak pressures are lower, and burn times are longer.

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 (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 2012).

Different commercial techniques have been identified. Some may simply be the same technique with a different company name.

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)

**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).

**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).

**Dynamic Gas Pulse Loading**

Dynamic Gas Pulse Loading (DGPL) is a the commercial name of a technique for inducing multiple, radial fractures in a wellbore, using rapid gas-pressure loading of the rock during the deflagration (burning) of downhole gas generators (Servo-Dynamics 1998). By controlling the energy release during this process, the in situ stresses can be exceeded by a substantial amount while pressures remain significantly below the level which deforms and crushes the rock.
**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).

**Dry Fracturing EPS**

This technique is at the concept stage, and is being developed by Prof. J. Krzysiek of Gdansk University of Technology to target the fracturing of shale formations. It is designed to combine feature from StimGun and GasGun. StimGun is classic perforator with external sleeve as elastic propellant in combined perforation and stimulation. GasGun has two type propellant loaded with staged ignition system used for stimulation of already perforated intervals. Dry Fracturing EPS intends to extend the traditionally limited perforation range of propellant fracturing systems and to offer controllable fracturing geometry, regardless of formation stress direction and shale water sensitivity. Both the energy of perforation and stimulation are concentrated in perforation tunnels for optimal fracture propagation (Krzysiek 2013; Rogala, Krzysiek et al. 2013).

**Rationale**

The use of propellants and other so-called tailored-pulse techniques depend on a controlled pressure-time behaviour to minimize wellbore damage and maximize fracture growth by gas penetration.

High explosives, such as nitroglycerine or gelatin, detonate and create a shock wave. Pressures created are extremely high but last only a few microseconds. 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 cavings often fill the wellbore with debris that require days, even weeks, to clean up (GasGun 2013).

The problems commonly associated with hydraulic fracturing are avoided. No water is used (and hence no chemical additives). The energy released underground, albeit relatively low, could potentially induce seismic events.

**Potential advantages and disadvantages**

**Potential advantages**

- Potential environmental advantages:
  - a. Water usage completely eliminated.
  - b. No chemical additives are required.
- Minimal vertical growth outside the producing formation.
- Multiple fractures.
- Selected zones stimulated without the need to activate packers\(^5\).
- Minimal formation damage from incompatible fluids.
- Homogeneous permeability for injection wells.
- Minimal on-site equipment needed.
- Lower cost when compared to hydraulic fracturing.

---

\(^5\) Packers are special equipment used to isolate zones of the well where hydraulic fracturing is carried out.
- Can be used as a pre-fracturing treatment (to reduce pressure losses by friction in the near wellbore).

**Potential disadvantages**
- Can replace hydraulic fracturing only for small to medium treatments, i.e. the fracture penetration is somewhat limited.
- Proppant is not carried into the fracture. Instead, propellant fracturing relies upon shear slippage to prevent the fracture from fully closing back on itself.
- The GasGun website explicitly admits that "the GasGun will never replace hydraulic fracturing. Large hydraulic fracture treatments can create a fracture hundreds, if not thousands, of feet in length. But many small pay zones in marginal wells cannot justify the expense of these treatments". (GasGun 2013)
- The energy released underground, albeit relatively low, could potentially induce seismic events.

**Costs**
Costs are impossible to assess given the scarce experience.

**Status of technique application**
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). This study concluded that both propellant and hydraulic fracturing can provide stimulation benefits, but only when applied in appropriate situations.

Dry Fracturing EPS is at the concept stage, but it is reported that a pilot study will be conducted in the near future on wells operated by PGNiG in Poland (Krzysiek 2013).

4.2. Electric fracturing

**Overview**
In electric fracturing, electricity is used to induce mechanical loads into the rock. If high enough, this loading will fracture the rock.

Laboratory studies to evaluate the use of electricity for fracturing various grades of Colorado oil shale were started 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\(^6\) process (Melton and Cross 1968).

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).

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.

\(^6\) Retorting is the oldest and the most common extraction method for oil shale. In this process oil shale is heated in the absence of oxygen (pyrolysis) until its kerogen decomposes into condensable shale oil vapours and non-condensable combustible oil shale gas. Oil vapours and oil shale gas are then collected and cooled, causing the shale oil to condense.
This makes use of pulsed arc electrohydraulic discharges, and it is described in Section 4.3.1.

Another experimental technique has been identified, called Plasma Stimulation & Fracturing (Awal 2013). This is described in Section 4.3.2.

**4.3.1. Pulsed Arc Electrohydraulic Discharges (PAED)**

*Description of the technique*

The method proposed by the researchers at the University of Pau and Pays de l'Adour 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).

*Rationale*

This technique would allow fracturing of the rock without any use of fracturing fluids (and hence no chemical additives).

(Kalaydjian and Goffé 2012) report that in 2011 Total commissioned research on this technique, and 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. The authors also conclude that the technique would require management of electrical installations on the surface and that the environmental consequences of this remain to be studied.

**Potential advantages and disadvantages**

**Potential advantages**

- Potential environmental advantages:
  a. Water usage much reduced or completely eliminated.
  b. Few or no chemical additives are required.

**Potential disadvantages**

- Limited capability of increase rock permeability away from the wellbore.
- Proppant not carried into the fracture.
- Can only replace hydraulic fracturing only for small to medium treatments, i.e.
  the fracture penetration is somewhat limited.

**Costs**

Costs are impossible to assess given the current knowledge.

**Status of technique application**

The technique 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).
4.3.2. Plasma Stimulation & Fracturing Technology (PSF)

Description of the technique

The method has been recently proposed by Dr. M. R. Awal at the Texas Tech University (Department of Petroleum Engineering). Development was started in February 2010 (Awal 2013).

According to the inventor, PSF creates multiple radial fractures of self-propped type fractures by fast-expanding plasma generated using a proprietary, high-energy pulsed-power electrical discharge technique. While the plasma tool alone can create 5-20 ft (1.5-6 meters) long multiple radial fractures of self-propped type, the implementation of the pulse stepping algorithm can extend these fractures over 50 ft (15.2 meters).

PSF employs multiple cycles of extremely fast (in the micro-second range) dynamic pressurization in the wellbore. The multiple radial fractures created by PSF are self-propped because of shear displacement. This phenomenon occurs by virtue of emergence of shear stresses along the newly created fracture planes aligned in the directions of non-principal in-situ stresses. Hydraulic fracturing never generates such shear stresses along the bi-wing fractures, which are aligned in the direction of principal stress.

Rationale

This technique would allow fracturing of the rock without any use of fracturing fluids (and hence no chemical additives).

According to the inventor, “PAED employs a 1st generation, very low efficiency (~10%) electric-to-shockwave conversion (ESC) process, compared to Texas Tech’s 3rd generation highly energy efficient (70-80%) process. Besides, PFS continues its lead by growing into a full scale prototype for field demonstration” (Awal 2013).

Potential advantages and disadvantages

Potential advantages
- Potentially more environmentally friendly than high-volume water fracturing:
  a. Water usage much reduced or completely eliminated.
  b. Few or no chemical additives are required.
  c. Technique deployable with a very limited number of trucks, hence much reduced traffic.

Potential disadvantages
- Limited capability of increase rock permeability away from the wellbore.
- Proppant is not carried into the fracture.

Costs

Costs are impossible to assess given the current knowledge. The inventor claims that “the estimated revenue from PSF job is approx. $1,000 per foot of depth” (Awal 2013).

Status of technique application

According to the inventor, PSF can be custom-designed for use in both conventional and unconventional oil and gas reservoirs (Awal 2013).

The technique appears to be at the concept stage, but the inventor reports that the design parameters for an up-scaled field prototype have been established, and hence that a pilot project can be undertaken. The pilot would entail fabricating the PSF hardware for demonstration in a 10,000 ft vertical or horizontal well.
5. Other methods

In this section we review some other formation stimulation techniques that do not fall directly under the previous categories

5.1. Cryogenic fracturing

Overview

Fracturing can be achieved by using a fluid colder than the reservoir. This will create thermal stresses that could fracture the rock. Even if a fluid is used this is not strictly speaking hydraulic fracturing in the traditional sense, because it is not the elevated pressure of the fluid and high injection rates that breaks the rock.

Several authors (Svendson, Wright et al. 1991; Charlez, Lemonnier et al. 1996) have shown that thermally induced fractures may take place in oil and gas reservoir stimulation applications. They investigated different cases where cold water was injected into deep hot reservoirs with a constant injection rate (below the formation collapse pressure). After a certain time a sharp increase in injectivity was observed, as if the formation were fractured.

Recently an interesting fracturing technique has been proposed, based on the injection of large quantities of cold CO2 to create thermal stresses that lead to fractures in significant magnitude. (Mueller, Amro et al. 2012). This technique, discussed more in details below, is at the concept stage and it has been proposed for tight reservoirs. (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).

Description of the technique

(Mueller, Amro et al. 2012) have proposed a technique called “CO2 thermal hydraulic fracturing”. It combines conventional hydraulic fracturing and fractures which are caused by thermal stresses, due to the injection of cold CO2.

To create thermal stresses that lead to fractures in significant magnitude, a large quantity of liquid CO2 is needed to be injected. During high pressure injection the CO2 will stay in liquid state. Due to its low temperature and the high quantity of CO2 a large area around the wellbore will cool down. Depending on the injection rate a temperature reduction of 50-100°C might be achieved in this way. 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 (Mueller, Amro et al. 2012), 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. CO2 injection would continue for several years, and gas production would only start after two years from the beginning of the treatment. Through the continuous injection, the temperature front propagates, inducing an ongoing fracturing process in reservoir regions farther away from the well. The cap
rock above the formation should guarantee the sealing of the reservoir and prevent seismic impact on the overburden layers.

*Rationale*

As discussed in Section 2.9.1, using CO₂ as fracturing fluid offers many advantages. Large quantities of liquid CO₂ would be needed for injection. One promising source could be power plants which have a CO₂ emission up to 1 million tons/ year. Transport could be realized by pipelines from the plant site to the injection site.

*Potential advantages and disadvantages*

**Potential advantages**
- Potentially more environmentally friendly than high-volume water fracturing:
  a. Water usage much reduced or completely eliminated.
  b. No chemical additives are required.
- Could be used in conjunction with CO₂ sequestration schemes.
- Reduction of formation damage (reduction of permeability and capillary pressure damage by reverting to a gaseous phase; no swelling induced).
- Enhance gas recovery by displacing the methane adsorbed in the shale formations (Wang, Li et al. 2012).

**Potential disadvantages**
- Large quantities of liquid CO₂ would be needed.
- Long times required: CO₂ injection would need to occur for several years, and gas production would only start after 2 years from the beginning of the treatment.

**Costs**

Costs associated with this technique are impossible to evaluate with the current status of knowledge.

**Status of technique application**

The concept idea has been proposed for tight formations (Mueller, Amro et al. 2012). No specific information relating to its application to shales could be found.

**5.2. Mechanical cutting of the shale formation**

**Overview**

A patent from 2010 (Coleman and Hester 2010) presented a method to remove mass from a formation between two connected wellbores using a flexible cutting cable. According to this idea, two wellbores are drilled and connected; a cutting cable is inserted into the first well and fished out from the second; finally, the cable is repeatedly pulled back and forth. This sawing action removes formation material between the wellbores to form an opening in the shape of a plane. Earlier patents were filed proposing methods to remove minerals such as coal from seams using a chain cutter that is pulled through the seam, for instance from a tunnel drilled in a U shape (Hurd 1980; Farrar, Mayercheck et al. 1991). Other patents presenting similar ideas can be found, for instance (Carter 2009).

Drawing on these ideas, an interesting project (“Novel Concepts for Unconventional Gas Development in Shales, Tight Sands and Coalbeds”) was launched and funded by the
National Energy Technology Laboratory (NETL)\textsuperscript{7} and performed by Carter Technologies between 2008 and 2009 (Carter 2009).

The project objective was to develop an alternative method of stimulation to increase the net production of gas from shale while reducing the amount of water required. Over a dozen new concepts (from rotating mills to high-pressure water jets) were evaluated including one promising method (called Slot Drill) that appears to be able to cut 100 foot deep slots all along a 2500 foot long horizontal well. According to the project’s final report (Carter 2009), the method appears to have a low capital cost and be sufficiently robust to withstand the rigors of the down hole drilling environment.

\textbf{Description of the technique}

The Slot-Drill is an advanced cable saw method that operates like a down-hole hacksaw, and it is hence mechanically simple. A well is drilled to depth in the target formation and a casing cemented. The hole is then directionally drilled to curve back upward in the shape of a “J” within the producing formation. The drill string is retrieved back to the surface and an abrasive cable is attached to the tip of the drill pipe. A winch on the rig holds a specific tension on the cable as the pipe is lowered back into the hole under its own weight. Such tension causes the cable to hug the inside radius of the curved hole. The cable is moved back and forth, and this motion cuts a pathway upward from the hole on each downward stroke. The cutting force at any point is a function of local cable tension and radius of curvature so the shape of the cut may be tailored to some extent. The cut is nominally upward along a vertical path but can also be made to turn horizontally.

An operation may last for 2 to 5 days, depending on the desired depth of cut and the hardness of the rock. Drilling fluid is circulated through the drill pipe to flush the cuttings back to the surface. The abraded cuttings are very small particles and circulate out easily. A special tool is also used to allow a standard blow out preventer to seal on the cable and drill pipe.

The system should be able to cut a 100 foot deep vertical slot upward from the horizontal lateral in a shale formation, and the cut length could exceed 2500 feet. This system would operate in a blind hole from a conventional drilling rig and is powered by the drilling rig. The only special equipment required is a constant tension winch and a downhole tool that connect the abrasive cable to the drill pipe.

\textbf{Rationale}

Successful development of the proposed Slot Drill concept could provide an alternative stimulation method comparable to high-volume hydraulic fracturing but at a lower cost and without the very high water resource requirements.

Fully developed Slot-Drilled wells could result in much greater total recovery from a given lease acreage, thus increasing the total proven reserves. These slots may also reduce production decline, reduce the effects of formation damage, and allow a larger percentage of the in-place gas to be recovered.

According to the project results, reservoir simulations indicated that the slot alone may increase well flow rates significantly compared to current state of the art fracturing treatments. Unlike hydraulic fracturing, the location of a slot can be selected and precisely placed, is much thicker, and has near unlimited conductivity (Carter 2009).

\textsuperscript{7} NETL is part of the U.S. Department of Energy (DOE) national laboratory system. NETL supports DOE’s mission is to advance the national, economic, and energy security of the United States.
Potential advantages and disadvantages

Potential advantages
- Potentially more environmentally friendly than high-volume water fracturing:
  a. Water usage much reduced or completely eliminated.
  b. No chemical additives are required.
- Possibly enhanced recovery of total gas in place, accelerated rates of unconventional gas production, and development of reserves in fields that would not otherwise be produced.

Potential disadvantages
- None identified.

Costs
The primary costs of the method are the rig time, the winch, and the consumable abrasive cable materials. The total cost for comparable stimulation benefit is estimated to be less than half the cost of current fracturing technology.

Status of technique application
This is a technique specifically developed for shale formations. The technique is at the concept stage, and the project was currently awaiting funding to perform a demonstration in a test well in 2009 (Carter 2009).

5.3. Enhanced bacterial methanogenesis

Overview
A 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.

Microbiologically assisted methanization of the organic matter is a promising technologies being considered. 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 (Michigan) and the Forest City Basin (Kansas) 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. According to the authors, this is a significant percentage of the total gas production and hence there is great potential to enhance methanogenesis within these reservoirs.

**Description of the technique**

Naturally-occurring microorganisms (methanogens) are stimulated within the shale formations to enhance the production of methane as by-product of their normal metabolic processes.

**Rationale**

It is reported that shallow biogenic shale gas reservoirs generate gas by microbial activity, implying that current production to the surface consists of ancient adsorbed gas as well as recent biogenerated gas. Approximately 20% of all of the methane generated is generally thought to be of microbial origin. Most shallow shale gas reservoirs are at temperatures of less than 80 °C, and given the supply of carbon, water, and minerals, they can be thought of as multi-kilometer-scale bioreactors. (Cokar, Ford et al. 2013)

Enhanced bacterial methanogenesis may have a large impact, especially in shallow reservoirs. Methanogens can produce a significant amount of methane without any stimulation. As shown in preliminary modelling by (Cokar, Ford et al. 2013), microbial methane generation can account for 12% of the total gas production.

**Potential advantages and disadvantages**

**Potential advantages**
- Potential to tap into hydrocarbon resources of immature source rock (which would otherwise be unusable).
- Potential environmental advantages: no usage of water nor chemical additives, etc.

**Potential disadvantages**
- None identified.

**Costs**

Costs are impossible to assess given the current knowledge.

**Status of technique application**

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. Further work is required to determine how to stimulate the microorganisms within the reservoir to consume more of the organic carbon and thus increase gas production rates.

**5.4. Heating of the rock mass**

**Overview**

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.

A very interesting discussion on the possibilities of this technology and its application to unconventional hydrocarbon production is given in (Kalaydjian and Goffé 2012).
A conceptual study of thermal stimulation in shale gas formations was more recently published by (Han Yi Wang 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.

**Description of the technique**

The rock is heated, for instance by injecting steam or by other suitable methods. This enhances the permeability of the reservoir and/or increase the thermal maturity of the organic matter (kerogen) in the formation, as discussed in the next section.

**Rationale**

(Kalaydjian and Goffé 2012) identify three principal mechanisms by which the effects of heating the rock mass could have beneficial effects:

- Mineralogical changes;
- Changes in the chemical decomposition of kerogen;
- Evolution of the carbon structure of kerogen.

The first possible beneficial effect of heat is to induce mineralogical changes. A relevant effect when considering rock types containing clay (such as shales) is dehydration. (Vidal and Dubacq 2009) demonstrated that dehydration may indeed produce up to 150 liters of water per cubic meter of clay in place. The space vacated by removing water increases the porosity and therefore the permeability. Also, the thermal expansion of the rock can result in beneficial changes in permeability.

The 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. These techniques are especially applicable in the case of oil shales. Fluids and gases increase local pressures and either allow the use of existing microcracks or create new ones (Kobchenko, Panahi et al. 2011). The increase in permeability is achieved by induced microcracks in the rock.

The third effect is the possible evolution of the carbon structure of kerogen. The increased temperature may have the effect to open up porosity of micro-scale and nano-scale carbon structures in the kerogen.

These effects, combined, could have the effect to significantly enhancing the permeability of the shale formations, without the need to perform any hydraulic fracturing.

**Potential advantages and disadvantages**

**Potential advantages**

- Water usage much reduced.
- No chemical additives are required.

**Potential disadvantages**

- None identified.

**Costs**

(Kalaydjian and Goffé 2012) argue that one of the main challenges of this technology (if using electrical heating) would be its economic profitability, which in turn would be strongly dependent on the cost of electricity consumed and the efficiency of the gas production.
**Status of technique application**

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.

5.5. **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.

5.6. **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.
6. Summary and conclusions

In this report we reviewed hydraulic fracturing and other formation stimulation technologies, by searching the open literature, patent databases and commercial websites (mainly in the English language). This is an updated version of the original JRC report published in 2013 (Gandossi 2013), compiled taking into account new relevant information that became available during 2014 and 2015.

Several techniques were identified and described, at various level of technological readiness: some are commercially available, whilst many others are currently being developed or are at the concept stage.

Table 5, below, present an overall summary of the information gathered, showing in particular some of the potential advantages and disadvantages that each technique could offer.
<table>
<thead>
<tr>
<th>Technique</th>
<th>Potential advantages</th>
<th>Potential disadvantages</th>
<th>Status of application for shale gas production</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Foam-based fracturing fluids</strong></td>
<td>- Water usage much reduced or completely eliminated</td>
<td>- Higher costs.</td>
<td>Commercially applied to fracture shale formations.</td>
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<tr>
<td></td>
<td>- Reduced amount of chemical additives.</td>
<td>- Difficult rheological characterization of foams.</td>
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<td></td>
<td>- Better clean-up of the residual fluid.</td>
<td>- Difficult flow behavior difficult to predict.</td>
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<tr>
<td><strong>Oil-based fracturing fluids (LPG)</strong></td>
<td>- Water usage much reduced or completely eliminated</td>
<td>- Higher surface pumping pressure required.</td>
<td>Commercially applied to fracture unconventional reservoirs (not clear if this include shales).</td>
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<tr>
<td></td>
<td>- Fewer (or no) chemical additives are required.</td>
<td>- Higher investment costs.</td>
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<td></td>
<td>- Flaring reduced.</td>
<td>- Success relies on the formation ability to return most of the propane back to surface</td>
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<td></td>
<td>- Increased productivity of the well.</td>
<td>- Lower viscosity, density and surface tension of the fluid.</td>
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<tr>
<td></td>
<td>- Lowering viscosity, density and surface tension of the fluid results in lower</td>
<td>- Full fluid compatibility with shale reservoirs (phase trapping virtually eliminated).</td>
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<td></td>
<td>- Energy consumption during fracturing.</td>
<td>- No fluid loss.</td>
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<td></td>
<td>- Fast clean up (often within 24 hours).</td>
<td>- Recovery rates (up to 100%) possible.</td>
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<tr>
<td><strong>Acid-based fracturing fluids</strong></td>
<td>- The application of acid fracturing seems to be confined to carbonate reservoirs.</td>
<td>- Methanol is a dangerous substance to handle:</td>
<td></td>
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<tr>
<td></td>
<td>- Very fast clean up (often within 24 hours).</td>
<td>a. Low flash point, hence easier to ignite.</td>
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<tr>
<td></td>
<td>- Water usage much reduced or completely eliminated</td>
<td>b. Large range of explosive limits.</td>
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<td></td>
<td>- Methanol is not persistent in the environment.</td>
<td>c. High vapour density.</td>
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<td></td>
<td>- Excellent fluid properties: high solubility in water, low surface tension and high</td>
<td>d. Invisibility of the flame.</td>
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<td></td>
<td>- Very good fluid for water-sensitive formations.</td>
<td>- Methanol-based fluids have been used on low permeability reservoirs, but it is not</td>
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<td></td>
<td>- Methanol is a very stable hydrocarbon, and as such presents a global warming</td>
<td>clear if their application has been extended to shales.</td>
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<tr>
<td></td>
<td>- No fluid loss.</td>
<td>- Heptane is a very stable hydrocarbon, and as such presents a global warming potential.</td>
<td></td>
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<tr>
<td><strong>Alcohol-based fracturing fluids (Methanol)</strong></td>
<td>- Methanol is a dangerous substance to handle:</td>
<td>- Methanol is a very stable hydrocarbon, and as such presents a global warming potential.</td>
<td></td>
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<tr>
<td></td>
<td>a. Low flash point, hence easier to ignite.</td>
<td>- Methanol is a very stable hydrocarbon, and as such presents a global warming potential.</td>
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<tr>
<td>Technique</td>
<td>Potential advantages</td>
<td>Potential disadvantages</td>
<td>Status of application for shale gas production</td>
</tr>
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</tr>
</tbody>
</table>
| Emulsion-based fluids | - Depending on the type of components used to formulate the emulsion, these fluids can have potential advantages such as:  
  a. Water usage much reduced or completely eliminated.  
  b. Fewer (or no) chemical additives are required.  
  c. Increased the productivity of the well; better rheological properties (i.e. better flow behaviour); fluid compatibility with shale reservoirs. | - Potentially higher costs.               | Emulsion-based fluids have been used on unconventional (low permeability) formations, but no direct usage for shale gas stimulation could be found as a part of the present study. |
| Liquid CO₂        | - Potential environmental advantages:  
  a. Water usage much reduced or completely eliminated.  
  b. Fewer (or no) chemical additives are required.  
  c. Some level of CO₂ sequestration achieved.  
  - Reduction of formation damage.  
  - Form more complex micro-fractures.  
  - Enhance gas recovery by displacing the methane adsorbed in the shale formations.  
  - Evaluation of a fracture zone is almost immediate because of rapid clean-up. Better clean-up of the residual fluid, so smaller mesh proppant can be used. More controlled proppant placement and higher proppant placement within the created fracture width. | - Proppant concentration must necessarily be lower and proppant sizes smaller, hence decreased fracture conductivity.  
  - CO₂ must be transported and stored under pressure (typically 2 MPa, -30°C).  
  - Corrosive nature of CO₂ in presence of H₂O.  
  - Unclear (potentially high) treatment costs. | Liquid CO₂ as fracturing fluid is commercially used in unconventional applications (most notably, tight gas) in Canada and the US. Devonian shale formations in Kentucky (USA) have been stimulated with liquid CO₂ as early as 1993.  
  Super-critical CO₂ usage appears to be at the concept stage. |
| Liquid N₂         | - Potential environmental advantages:  
  a. Water usage much reduced or completely eliminated.  
  b. Fewer (or no) chemical additives are required.  
  - Reduction of formation damage.  
  - Self-propping fractures can be created by the thermal shock, hence need for proppant reduced or eliminated. | - Special equipment required to safely handle liquid N₂ due to the very low temperature of the fluid.  
  - Higher costs. | Nitrogen as a component (in mists, foams or other energised fluids) of the fracturing medium is common. The use of liquid nitrogen is less typical. The technique is commercially available and has been applied for fracturing shale formations but its usage appears limited. |
<table>
<thead>
<tr>
<th>Technique</th>
<th>Potential advantages</th>
<th>Potential disadvantages</th>
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</thead>
<tbody>
<tr>
<td><strong>Hydraulic Fracturing</strong></td>
<td></td>
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<tr>
<td>Cryogenic fluids</td>
<td></td>
<td></td>
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<tr>
<td>Liquid He</td>
<td>N/A</td>
<td>N/A</td>
<td>See Section 2.9.3</td>
</tr>
<tr>
<td>Liquid LPG</td>
<td>N/A</td>
<td>N/A</td>
<td>Very little information available. See section 2.9.4</td>
</tr>
<tr>
<td><strong>Pneumatic Fracturing</strong></td>
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</tbody>
</table>
| (Air) (N₂)                      | - Potential environmental advantages:  
- Water usage completely eliminated.  
- No chemical additives are required.  
- Potential for higher permeabilities due to open, self-propped fractures that are capable of transmitting significant amounts of fluid flow. | - Limited possibility to operate at depth.  
- Limited capability to transport proppants. | Shallow shale formations have been fractured with pneumatic fracturing (EPA 1993) with the purpose of facilitating the removal of volatile organic contaminants. Pneumatic fracturing with gaseous nitrogen is applied to shale gas production, but limited information on the scale is available. |
| **Explosive**                   |                       |                         |                                               |
| **Dynamic loading**             |                       |                         |                                               |
| Explosive fracturing (solid propellants) | - Potential environmental advantages:  
- Water usage completely eliminated.  
- No chemical additives are required.  
- Minimal vertical growth outside the producing formation.  
- Multiple fractures.  
- Selected zones stimulated without the need to activate packers.  
- Minimal formation damage from incompatible fluids.  
- Homogeneous permeability for injection wells.  
- Minimal on-site equipment needed.  
- Lower cost when compared to hydraulic fracturing.  
- Can be used as a pre-fracturing treatment (to reduce pressure losses by friction in the near wellbore). | - Can replace hydraulic fracturing only for small to medium treatments, i.e. the fracture penetration is somewhat limited.  
- Proppant is not carried into the fracture. Instead, propellant fracturing relies upon shear slippage to prevent the fracture from fully closing back on itself.  
- The energy released underground, albeit relatively low, could potentially induce seismic events. | Techniques based on explosive fracturing seem to have been largely superseded. On the other hand, techniques based on propellant fracturing are commercially available and have been used on shale formations, but very limited information on the scale is available. New techniques are currently being developed (for instance, Dry Fracturing EPS). |

Table 5 (cont.) Summary of potential advantages and disadvantages for identified fracturing techniques.
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<table>
<thead>
<tr>
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<th>Potential disadvantages</th>
<th>Status of application for shale gas production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynamic</td>
<td>- Limited capability of increase rock permeability inside the wellbore.</td>
<td>- Propellant not carried into the fracture. Can only replace hydraulic fracturing only for small to medium treatments, i.e. the fracture penetration is somewhat limited.</td>
<td>The concept idea has been proposed for light formations.</td>
</tr>
<tr>
<td>Electric Fracturing</td>
<td>- Potential environmental advantages:</td>
<td>- Large quantities of propellant would be needed.</td>
<td>Both identified technologies (see section 4.2.1 and 4.2.2) are at the concept stage. Plasma stimulation (4.2.2) is reported as ready for being tested in the field.</td>
</tr>
<tr>
<td>Thermal (cryogenic) Fracturing</td>
<td>- Potential environmental advantages:</td>
<td>- Propellant not carried into the fracture. Can only replace hydraulic fracturing only for small to medium treatments, i.e. the fracture penetration is somewhat limited.</td>
<td>The concept idea has been proposed for light formations.</td>
</tr>
<tr>
<td>Mechanical Cutting of the shale formation</td>
<td>- Potential environmental advantages:</td>
<td>- Large quantities of propellant would be needed.</td>
<td>Both identified technologies (see section 4.2.1 and 4.2.2) are at the concept stage. Plasma stimulation (4.2.2) is reported as ready for being tested in the field.</td>
</tr>
<tr>
<td>Enhanced Bacterial Methanogenesis</td>
<td>- Potential to tap into vast hydrocarbon resources of immature source rock.</td>
<td>- None identified.</td>
<td>The technique is at the concept stage. Enhanced bacterial methanogenesis appears to be at the concept stage. The technique has been successfully applied in laboratory specimen.</td>
</tr>
<tr>
<td>Heating of the rock mass</td>
<td>- Potential environmental advantages:</td>
<td>- None identified.</td>
<td>The technique is at the concept stage. Enhanced bacterial methanogenesis appears to be at the concept stage. The technique has been successfully applied in laboratory specimen.</td>
</tr>
</tbody>
</table>

Other methods: None identified.
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