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NON-AQUEOUS FRACTURING TECHNOLOGIES FOR SHALE GAS RECOVERY

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Abstract: Fracturing technologies for shale gas production were developed mainly in the USA and are currently being adapted to geological conditions and environmental requirements in other countries. This paper presents literature on theoretical and practical aspects of gas production from shale with the emphasis placed on alternatives to hydraulic fracturing. Technical and environmental aspects of non-aqueous fracturing technologies are also considered.

Key words: *shale gas, hydraulic fracturing, unconventional gas resources, explosive fracturing*

Introduction

Hydraulic fracturing (HF) is a widely used method for fracturing rock during natural gas production. It is based on pumping fracturing fluid which contains proppant and other additives in order to stimulate oil and gas formations. Despite of HF advancement and its wide application in many world regions it is burdened with problems which need to be solved. Mentioned drawbacks consist of waste fluid management, investment costs, environmental costs, risk of surface and ground water contamination (USEPA, 2011), emission of methane and social disapproval/misunderstanding. All those shortcomings associated with HF resulted in developing new methods of shale gas production including fracturing with liquid carbon dioxide, carbon dioxide/nitrogen foams, and liquefied petroleum gas (LPG).

The all listed methods are designed to maintain compatibility of fracturing fluid and clay minerals consisting of expanding smectite [$Na_{0.3}Al_2(Si_{3.7}Al_{0.3})O_{10}(OH)_2$] and swelling illite [$K_{0.7}Al_2(Si_{3.3}Al_{0.7})O_{10}(OH)_2$] (Ahn and Peacor, 1986). This approach allows to eliminate potential fracture closing by smectite and illite, which decides about fracturing quality and gas productivity on perforations or created fractures.

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As can be seen in Table 1, smectite has much greater surface area and CEC (cation-exchange capacity) then illite, and for both of them those properties are more pronounced than for other clay minerals like kaolinite and chlorite. CEC shows ability of clays to bond water. Greater CEC means that much more water can be trapped in the clay's structure and clay's swell or expansion will be greater. Expanding smectite (much) and swelling illite (less) cause troubles in shales so, we have an additional argument to search for technologies that do not use water as a base fluid (Lal, 1999).

Table 1. Surface area and CEC of clay minerals
(Eslinger and Pevear, 1988, after Martin and Dacy, 2004)

Type of mineral	Surface area [m^2/g]			CEC [meq/100 g]
	Internal	External	Overall	
Smectite	750	50	800	80–150
Illite	5	15	30	10–40
Kaolinite	0	15	15	1–10
Chlorite	0	15	15	<10

Mentioned above methods are similar to HF since they use fracturing fluids, thus arising many technological problems and hazards, both technical and environmental. An alternative is explosive/propellant fracturing technology (Snider et al., 1997) not requiring any fracturing fluid. Such pre-completion method stimulates the rock formation using a series of cumulative charges detonations in order to perforate the rock, and creates fractures with gases generated by burning high energy fuel – so called propellant. The main disadvantage is low range of occurring fractures, limiting performance and permeability of the rock. Technology using explosives became a tool allowing low pressure hydraulic fracture opening instead of only perforator being used. This method of perforation is used with limited success in some shale in the USA and Canada.

Technologies using non wetting fluid

Liquid CO_2

Fracturing with carbon dioxide is a method patented in the early 80's (Bullen and Lillies, 1982). The method is well-established and has been repeatedly modified. Commonly used for dry fracturing in water-sensitive formations. It involves injecting sand with liquid carbon dioxide (CO_2) as the carrier fluid of proppant without the addition of water or other auxiliary compounds. Proppant, in addition to naturally occurring sand grains is a man-made or specially engineered material, such as resin-coated sand or high-strength ceramic materials. CO_2 on the surface is a liquid at a pressure of 1.4 MPa and a temperature of –34.5°C. It uses specialized equipment to enable proppant added directly to liquid CO_2 under these conditions on the surface. Liquid CO_2 viscosity is about 5 cP and therefore allows to increase viscosity to carry proppant in propagated fracture. After stabilization of temperature and pressure CO_2 partly dissolves in residual water and liquid hydrocarbon deposits

Biggest advantages of liquid CO_2 fracturing are: the elimination of potential formation damage normally associated with fracturing fluids, very rapid clean-up and evaluation of the well following the stimulation (Lillies and King, 1982). The technology has undergone many tests and improvements (Wright, 1998). By the end of the nineties of the twentieth century there were more than 1,200 successful CO_2 fracturings in Canada only. The technology was also used in the USA for Devonian shale in East Kentucky and West Pennsylvania, Texas and Colorado (Arnold, 1998). The results indicate, that the average gas production in some wells was as much as five-fold greater than the production from conventional HF treatments. If the wellhead pressure rapidly drops, CO_2 in such conditions may result in ice formation in a form of "X-mas tree" and tubing which eventually restricts the gas flow. Therefore, it was decided to optimize the process by adding nitrogen to the CO_2 gas which not only prevents ice build-up, but also reduces the cost of operating the well (Gupta et al, 1998).

The main problem associated with CO_2 or CO_2/N_2 gas mixture fracturing is their transport in the liquid state and storage in pressurized containers. In particular, the loss of CO_2 to the atmosphere should be avoided because of eventual impact on global warming. CO_2 fracturing keeps clays (smectite and illite) stabilized and prevents metal leaching and chemical interactions. Biggest successes in CO_2 fracturing were recorded in Canada and in the former Soviet Union in late eighties (Luk and Grisdale, 1994).

Nitrogen fracturing

Using nitrogen for oil and gas recovery from deposits of hydrocarbons dates back to year 1960 (Petty et al. 1967). At the beginning, nitrogen was commonly used as auxiliary fluid in first shale gas production process. Technologies using nitrogen as a fracturing fluid were developed in late seventies (Freeman et al. 1983). Previous attempts to employ nitrogen focused mainly on foam fracturing (see subpart Foams)). The initial successes associated with the elimination of large quantities of liquid and replacing them with gas did not eliminate all problems. The remaining amount of water and other additives were smaller, nevertheless, difficulties in the production process had occurred.

Solutions using nitrogen for the extraction of gas from Devonian shale in Washington County, OH, USA, dealt with the part of these problems (Gottschling et al., 1985). Applied technologies are based on trucks delivering liquid nitrogen, which after heating changes into the gaseous state. As a gas, nitrogen is pumped from numerous sources and injected under the pressure of 24 MPa (3500 psi) in shallow wells. Approximately 60% of the volume used for this operation is a pure nitrogen gas without proppant, designed to produce fractures in the stimulated formation. The remaining 40% is carrying 423–625 μm sand and is injected into the wellbore, where the sand particles mixed with nitrogen were propagated into the fracture. During field tests 270 m^3 of nitrogen per hole were used. Further tests followed to determine optimal conditions for fracturing various rock formations.

Another research on the application of nitrogen for rock fracturing using gas under high pressure was made by Lokhandwala and Jariwala (2005) who referred to many advantages both economical and ecological. Nitrogen as widely available and non expensive gas, reduces the cost of reservoir stimulation. It is an inert gas, therefore, it does not damage rock formation. Absence of water in the system excludes the possibility of rock swelling. In addition lack of water eliminates the formation W/O emulsion which otherwise requires the use of additional chemicals. Ease of removal of gas favors the clean-up processes, and thus prepares the well after fracturing into production. Gas can be removed easily and the clean-up process is fast.

All mentioned advantages would promote the gaseous nitrogen fracturing to be world's best solution for production of hydrocarbons. However, placing the proppant in high velocity gas stream is problematic, as well as resulting erosion. The size and geometry of fractures created during initial fracturing caused problems with proppant deposition from the carrying gas. This technology is limited to shallow wells as a result of reduction of hydrostatic pressure that affects bottom hole treating pressure (BHTP).

Foams

Shale reservoirs fracturing using foams exists for over 30 years (Harris et al., 1988). It is a modification of hydraulic fracturing which depends upon exchange of part of liquid with gas, usually nitrogen, rarely carbon dioxide (Chilingarian et al., 1989). The fracturing fluid consists of proppant, surfactants, and foam stabilizers. Chemicals are mixed with water and dispersed using gaseous nitrogen to create foam with various foam ratio (Gaydos and Harris, 1980). The advantage of using foams is less expanding smectite and swelling illite in comparison to HF. Unfortunately, it is not possible to totally eliminate clay swelling.

There are also other advantages of using foam fracturing (Phillips et al., 1987):

- foams have wide range of viscosities
- high efficiency of return fracturing foam to the surface
- less damage to the reservoir due to small volume of water remaining in the shales.

The disadvantages of this technology are:

- low proppant concentration in fluid
- very high costs of foam fluid systems
- less economical as compared to aqueous and oil-based fracturing fluids
- difficult rheological characterization of foams (Reidenbach, 1986),
- higher surface pumping pressure.

LPG fracturing

One of the most promising alternatives to HF is LPG fracturing (Loree and Mesher, 2007). LPG is applied as propane under high pressure in liquid form. LPG before the fracturing is gelled to allow the transport of proppant into the fracture. The main advantage of LPG for fracturing is to increase the productivity of the well. This is due to the different behavior of water and LPG in changed reservoir pressure. In the case of hydraulic fracturing, residual water in the narrow fracture is being held by closing fracture and capillary interactions. This causes a partial water block of the reservoir and reduces the gas flow. In the case of LPG, after pressure drop it changes the physical state from liquid to gas and freely flows through the fractures, without affecting smectite and illite (Taylor et al., 2005). Other advantages resulting from the use of LPG for fracturing include:

- lower viscosity, density and surface tension of the fluid, which results in lower energy consumption during fracturing
- full compatibility with reservoirs because LPG and hydrocarbons are mutually soluble,
- smaller volume of chemicals added to the fracturing fluid
- no fluid loss – possible 100% recover
- sustainable, recyclable and more environmentally friendly then HF. It is because there is no water use in fracturing operation, fracturing fluid is inert to reservoir minerals and can be recycled during operations
- numerous existing government and industry regulations and procedures about using LPG
- gaseous LPG is more dense than air, so there is no risk to air contamination and impact on global warming.

The use of LPG has its drawbacks:

- investment costs are higher than for HF, because LPG is pumped into well at a very high pressure, and after each fracturing it has to be liquefied again
- LPG must be stored in costly pressurize tanks (water in HF is stored in non-pressure tanks or in natural outdoor pools)
- LPG is explosive
- LPG is more dense than air and fills up the ground cavities.

These drawbacks cause LPG method has many opponents. especially in eco organizations. A letter to Commissioner of New York Department of Environmental Conservation was sent pertaining to LPG fracturing in New York to explore shale gas (Steven Russo et al., 2012). The views on the LPG fracturing negative impact on the environment were presented, followed by argument that it is against the law of New York. Unfortunately the sources refere to articles from newspapers and own speculations having no scientific base.

The greatest asset of LPG fracturing technology is its smaller environmental impact. This is due to the lack of use of frac water almost no chemicals, and thus lesser risk of environmental pollution due to flowbacks. So far, LPG fracturing has been used where it is prohibited to use water-based fracturing fluids, like in New Brunswick, Canada (Le Blanc et al., 2011). However, due to cost and geological conditions, this method is not widespread.

Explosive/propellant system – EPS

Perforation with cumulative explosives and shale's reservoir fracturing using explosion gas under high pressure has been known for several decades (Howard, 1971). The technology using both explosives and rocket fuel to stimulate shale exists for more than 30 years and constantly is being improved (Gilliat et al., 1999). Stimulation using high pressure gases received from burning propellant is known for couple of years (Page and Miskimins, 2009). In the USA work on developing the system is undergoing. Perforation, however, hardly exceeds 0.3–0.5 m (1.0–1.5 ft), reaching 0.7 m (2.3 ft) under some conditions. Such short range of perforation does not allow the above mentioned method to fully replace hydraulic fracturing in shale gas production. Today, the EPS is used for preliminary fracturing with effectiveness oscillating around 5–10% due to ineffective flow control of gases generated during perforation. Perforation technology using propellant (rocket fuel) simultaneously for generating high pressure gas is patent pending by one of the leading oil companies (Snider, 1997). It is used for low-range fracturing, mainly in sandstone formations in the vicinity of the reservoir water retention. It is commonly used for initiation of fracture in all perforation for HF.

Currently used in the field Trade Mark systems are Stimgun, StimTube, Gasgun, Pulsefrac etc. and combined perforation/propellant, and propellant only for specific applications. Propellant is an explosive used to propel a projectile or missile, or to do other work by the expansion of high pressure gas produced by burning, e.g. rocket fuel (Bailey and Murray, 1989). The EPS has basic features of Stimgun and Gasgun with dramatically improved performance such as:

- fracture length at given wellbore depth and bottom hole stimulation pressure
- energized dual cumulated detonation
- prolonging tip of perforation tunnel into the fracture
- classic cumulated propellant impact and all direction fracture development
- a new concept of shock reduction.

The approach is considered as environmentally friendly for shale gas and oil fracturing solution for contributing to return on investment (ROI) at a new level. Fracture geometry monitoring will have range to be visible in tomography pictures. The major gas flow mechanism is to be from fracture, fracturing slippage and desorption. The EPS has no impact on formation fluid compatibility, wetability, formation heavy and light metal leaching, smectite expansion, illite swelling, formation frac stress development (tilting) that locks up the perforation nor created fractures in HF. When full length is perforated with EPS with its limited frac entry compared to HF, the overall gas production is expected to be close to HF performance where induced formation stress affects perforation opening for fracture. The EPS is considered as a fraction of costs of HF.

Summary and final comments

The current fracturing technology is applicable to specific areas with fluid sensitive shale. Based on current hydraulic fracturing performances in Poland, shale has certain volume of low density smectite clay that has tendency to absorb frac water and to expand. It may also have impact on observed tilting effect caused by massive frac fluid and proppant injection and reorientation of existing formation stress by increasing dramatically its value. Increased formation stress and shale expansion in contact with water may cause both soft shale layers to move and plug perforation and close some

Table 2. Comparison of fracturing technologies (Krzysiek, 2012)

Consideration	Water Based	N_2 Foam	CO_2 Liquid	N_2 Gas	LPG Liquid	EPS
Environmentally friendly	N	N	N	Y	N	Y
Fluid availability	?	Y	Y	Y	N	-
Fluid recycling	Y	Y	?	N	Y	-
Chemicals used	Y	Y	?	?	?	N
Reservoir compatibility	?	?	Y	Y	Y	Y
Fracture creation	Y	Y	Y	Y	Y	Y
Proppant carrying	Y	Y	Y	Y	Y	?
Recovery to pipeline	N	N	N	N	Y	N
Heavy metals flowback	Y	Y	N	N	N	N
Frac cost	1	>1*	>>1*	>>1*	>>>1*	<<1*
Fluid left in formation	Y	Y	N	N	N	–
Well clean up	Y	Y	Y	N	N	Instant production
Frac geometry predictability	N	N	N	N	N	Y
Tilting stress development	Y	Y	Y	Y	Y	N
Zone water in flux risk	1	>1*	>1*	>1*	>1*	>>>1*
Fracture length	1	>1*	>1*	>1*	>1*	>>1*
Active flow frac perforation	?	?	?	?	?	Y
Fraced well performance	1	<1*	<<1*	<1*	<<1*	>1*
Local road damage risk	Y	Y	Y	Y	Y	N
Environmental risk	Y	Y	Y	Y	Y	Y
NOx and CO_2 in pumping	Y	Y	Y	Y	Y	N
Return on investment	1	<1*	<1*	<1*	<1*	<<<1*

Y – yes, N – no
*Average data from field applied technology by Jan Krzysiek

fracture. Frequently, most of the perforation is inactive with extremely high frac initiation pressure, sometimes beyond pump capacity. Production log time (PLT) may precisely define it, if it is run in hole.

In non-aqueous fracturing technologies application of the EPS provides most cost-effective and environmentally-friendly attention despite of lower production performance. EPS allows to expect that all perforations are productive and with sustained gas production level which may reach HF production performance at lower cost. It is preferred that EPS is being run on tubing conveyed perforator (TCP).

Unit operations and features associated with discussed featuring technologies are summarized in Table 2.

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References

AHN J.H., PEACOR D.R., 1986. *Transmission electron microscope data for rectiorite: Implications for the origin and structure of "fundamental particles"*. Clays and Clay Minerals, 34, 180–186.

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

BAILEY A., MURRAY S.G., 1989. *Explosives, Propellants and Pyrotechnics*, London: Brassey's (UK) April 1989, 180.

BULLEN R.S., LILLIES A.T., 1982. *Carbon dioxide fracturing process and apparatus*. US Patent No 4374545.

ESLINGER E., PEVEAR D, 1988. *Clay Minerals for Petroleum Geologists and Engineers*. SEPM Short Course Notes No. 22, Society of Economic Paleontologists and Mineralogists, Tulsa 1988.

FREEMAN E.R., ABEL J.C., KIM C.M., HEINRICH C., 1983. *A Stimulation Technique Using Only Nitrogen*. Society of Petroleum Engineers, 35, 12, 2165–2174.

GAYDOS J.S., HARRIS P.C., 1980. *Foam fracturing: Theories, Procedures and Results*. Society of Petroleum Engineers, DOI 10.2118/8961-MS, SPE Unconventional Gas Recovery Symposium, 18–21 May 1980, Pittsburgh, Pennsylvania.

GILLIAT J., SNIDER P.M., HANEY R., 1999. *Field Performance of New Perforating/Propellant Technologies*. 1999 SPE Annual Technical Conference and Exhibition, Houston, 3–6 October.

GOTTSCHLING J.C., ROYCE T.N., SHUCK L.Z., 1985. *Nitrogen Gas and Sand: A New Technique for Stimulation of Devonian Shale*. Journal of Petroleum Technology 37, 5, 901–907.

GUPTA D.V.S., BOBIER D.M., 1998, *The History and Success of Liquid CO_2 and CO_2/N_2 Fracturing System*. SPE, Canadian Fracmaster Ltd., SPE Gas Technology Symposium, 15–18 March 1998, Calgary, Alberta, Canada.

HARRIS P.C., KLEBENOW D.E., KUNDERT D.P., 1989. *Constant internal phase design improves stimulation results*. SPE Paper 17532.

HOWARD G.C., 1971. *Explosively fracturing formations in wells*. US Patent No 3587743.

KARGBO D.M., WILHELM R.G., CAMPBELL D.J., 2010. *Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities*. Environ. Sci. Technol. 2010, 44, 5679–5684.

KRZYSIEK J., 2012. *Is Polish Shale Gas posing challenge to players and researchers?* Workshop Abstract Proceedings, Interfacial Phenomena in Theory and Practice, VII Summer School, Sudomie June 24th-30th 2012.

LAL M., 1999. *Shale Stability: Drilling Fluid Interaction and Shale Strength*. SPE Paper 54356, SPE Latin American and Caribbean Petroleum Engineering Conference held in Caracas, Venezuela, 21–23 April 1999.

LEBLANC D., MARTEL T., GRAVES D., TUDOR E., LESTZ R., 2011. *Application of Propane (LPG) Based Hydraulic Fracturing in the McCully Gas Field*, New Brunswick, Canada. Society of Petroleum Engineers.10.2118/144093-MS.

LILLIES A.T., KING S.R., 1982, *Sand Fracturing With Liquid Carbon*. Publisher Society of Petroleum, DOI 10.2118/11341.

LOKHANDWALA K.A., JARIWALA A., 2005. *Natural gas treatment process for stimulated well*. US Patent No 7537641.

LOREE D.N., MESHER S.T., 2007, *Liquefied Petroleum Gas Fracturing System*. US Patent Application No 2007204991.

LUK S.W.M., GRISDOLE J.L., 1994. *High proppant concentration/high CO_2 ratio fracturing system*. US Patent No 5515920.

MADER D. et al., 1989. *Hydraulic proppant fracturing and gravel packing*. Elseviewer Science Publishers B.V., ISBN 0-444-87352-x (Volume 26), 0-444-41625-0 (series).

MARTIN P., DACY J., 2004. *Effective Qv by NMR core tests*. SPWLA 45th Annual Logging Symposium, June 6-9, 2004.

Office of Research and Development, U.S. Environmental Protection Agency. 2011. *Draft Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. Washington, D.C.

PAGE J.C., MISKIMINS J.L., 2009. *A Comparison of Hydraulic and Propellant Fracture Propagation in a Shale Gas Reservoir*. Journal of Canadian Petroleum Technology, 48(5), 26–30.

PETTY C.B., HENDRICKSON A.R., BROWN L.S., 1964. *Liquid Nitrogen In Well Operations*. US Patent No 3358763.

PHILLIPS A.M., COUCHMAN D.D., WILKE J.G., 1987. *Successful Field Application of High-Temperature Rheology of CO2 Foam Fracturing Fluids*. Society of Petroleum Engineers DOI 10.2118/16416-MS, Low Permeability Reservoirs Symposium, 18–19 May 1987, Denver, Colorado.

REIDENBACH V.G., HARRIS P.C., LEE Y.N., LORD D.L., 1986. *Rheological Study of Foam Fracturing Fluids Using Nitrogen and Carbon Dioxide*. Society of Petroleum Engineers DOI 10.2118/12026-PA.

SNIDER P.M. et al. 1997. *Apparatus and method for perforating and stimulating a subterranean formation*. United States Patent No. 5775426.

TAYLOR R.S., FUNKHOUSER P., DUSTERHOFT R.G., LESTZ R.S., BYRD A., 2005. *Compositions and methods for treating subterranean formations with liquefied petroleum gas*. US Patent No 7341103.

USEPA (United States Environmental Protection Agency), 2011. *Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*. U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C. [online], http://www.epa.gov/hfstudy/HF_Study__Plan_110211_ FINAL_508.pdf.

WRIGHT T.R., 1998. *Frac technique minimizes formation damages Dry Frac*. World Oil [online], http://findarticles.com/p/articles/mi_m3159/is_n1_v219/ai_20387355/.