

Applications of Surfactants as Fracturing Fluids: Chemical Design, Practice, and Future Prospects in Oilfield Stimulation Operations



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Abstract Oil and gas recovery from subsurface reservoir formations requires the application of appropriate stimulation and production techniques, aimed at restoring sufficient pressure difference within drilled formations. Proper implementation of surfactants aids in enhanced fluid connectivity of the reservoir at initial stages of well stimulation, as well as maintain long-term hydrocarbon production. Nowadays, it is being considered as an effective alternative to conventional fracturing fluids such as polymers, gels, etc. due to low cost of application, alteration of inter-molecular interactions, and prevention of insoluble residues' formation. It is evident that the physicochemical attributes of surfactant-based fracturing fluids can be suitably modified through the use of combination of additives such as friction reducers, clay stabilizers, acids, iron-control agents, cross-linking agents, non-emulsifiers, buffers, inhibition agents, gels, and associated gel breakers. The primary objective of this method lies in minimizing the extent of oil-water block near the wellbore matrix and develop pore-connectivity in hydrocarbon pay-zones to attain good recovery characteristics. Surfactant fracturing fluids, if injected properly, are capable of reducing flowback, improving fluid stability and effective clean-up. Therefore, it is a possible route for petroleum engineers and fracture design professionals to produce oil and gas from low permeability reservoir zones via hydraulic fracturing technique, whilst attaining maximum recovery efficacy, production rate and economical operation. This chapter provides a detailed description of design and methodology of surfactants as fracturing fluids in the petroleum industry.

Keywords Surfactants · Fracturing fluid · Geotechnical & Process considerations · Chemical design · Functional evaluation · Fracture pore connectivity

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1 Introduction

Oil and gas recovery from subsurface reservoir formations requires the application of appropriate stimulation and production techniques, aimed at restoring sufficient pressure difference within drilled formations. These permit the lifting of in-situ hydrocarbon reserves trapped due to capillary forces previously existing within rock pore-spaces [63, 62]. All resources are not conveniently located in accessible regions and may be present in heterogeneous formation layers with complex, impermeable oil windows (pay zones). Therefore, the use of favorable well stimulation techniques such as fracturing, acidization etc. are essential to access a larger area of the reservoir [21, 27]. In the past few years, hydraulic fracturing technologies have been increasingly used on a commercial scale that eventually became crucial to production operations in the mature oilfields. Proper planning and accountability of hydraulic fracturing projects are useful to devise facilities, implement the solution and attain cost-profitability for the industry.

Hydraulically fracturing is a widely employed field of hydrocarbon production in the petroleum industry with significant potential in terms of technical as well as beneficial economic ties. It involves the introduction of a proppant-laden fluid, which effectively perforates the otherwise hydrocarbon-containing tight formations. The fractures, so formed, retain their connectivity due to the presence of proppant. After that, the fracturing fluids allowed to flow-back completely, and thereafter, the oil zones are produced via pressure drive and subsequent methods [5]. The associated loss of hydrocarbon conductivity is one of the major problems affecting fracturing results to achieve an efficient stimulation plan [18, 59]. To maximize recovery from the porous network, the fracturing process creates an open pathway for hydrocarbon flow.

Fracturing fluid normally consist of high viscosity components, which can not only create an effective fracture but also transport the proppant (sand) to the fracture zones. The fracturing fluid must contain sufficient gelation property to support the proppant under dynamic shear conditions. It must be designed, whilst keeping in mind, the reservoir characteristics, in-situ fluid properties and geotechnological conditions.

The use of conventional polymers is facing operational difficulties owing to the formation of insoluble residues, high cost and improper planning on the part of oilfield professionals [77]. Insoluble polymer fragments form large flocs with inter-molecular interactions, which plug the fractured regions within reservoir formations and reduce the conducive property of proppant-packed network of interconnected (fracture) zones. However, these drawbacks can be controlled by addition or replacement of different types of “surface-active agents” or surfactants in fracturing fluid compositions [34, 38, 49]. Surfactants function by altering the extent of inter-molecular polymer interactions to inhibit the build-up of oligomeric aggregates. Burman and Hall [13] showed that better fluid loss control and flow-back efficiency could be achieved with surfactant-based fracturing fluids. Other works by Paterniti [48], Xu and Fu [83] and Xu [82] further corroborate this observation, and stress on the employment of appropriate surfactant type/dosage in hydraulic fracturing

applications. In this chapter, the implications of surfactant-assisted hydraulic fracturing processes have been studied in detail. The geological considerations, formation evaluation, fluid characterization, and optimization have been presented herein to assess the functionality of surfactants in well stimulation operations. This constitutes an essential application of surfactant-based fluid systems in the area of enhanced hydrocarbon production within the purview of the petroleum sector.

2 Reservoir Evaluation and Geotechnical Considerations

Before the design and approval of any fracturing project, it is pivotal to consider reservoir characteristics, as well as that of present fluid phases and surrounding formations [53, 61, 71]. Permeability zones within conventional reservoirs exhibit values of the order of Darcys, whereas that of tight formations have permeability levels in terms of milliDarcies. However, significant variations may exist among different oil pay sections in a reservoir, which may further complicate the planning process. Therefore, no true relationship exists between porosity and permeability, especially when developing strategies to enhanced oil flow through the production wells. Evaluation of fracture length is also an intricate factor in understanding fracture pattern/geometry and determining well spacing from a development standpoint [32]. During selection, the reservoir parameters/variables that need considerations with critical information as follows:

- (a) Formation permeability;
- (b) In-situ stress distribution;
- (c) In-situ fluid saturation and viscosity properties;
- (d) Vertical depth of the reservoir;
- (e) Reservoir pressure and temperature;
- (f) Skin factor effect, which identifies if the reservoir is stimulated or damaged;
- (g) Well-bore condition and extent of completion.

The typical skin factor values range from 100 for poorly consolidated gravel pack, to -6 for an extensive hydraulic fracture with infinite-conductivity. These values differ with nature of the reservoir, type of drilling and completion operations performed, reservoir fluid properties and location of oil pay zones. As a result, no single technique of hydraulic fracturing has ever worked universally. Each method has unique methodologies and benefits that cater to reservoir requirements through specified fracture treatment and fluid design. For example, ductile formations require greater proppant placement ability of fracking fluids as compared to that of brittle formations. This variation in porosity and consequently permeability is because of two reasons; gas desorption from shale surface (unlike conventional reservoirs) and increasing significant stresses by pressure depletion. The critical life-time of a reservoir is influenced by compaction and available pore volume. Reservoir porosity may decrease with the domination of the compaction effect over porosity change against

desorption, and vice-versa. Seismic technologies serve as a useful tool to map conventional as well as unconventional formations, to plan a beneficial fracturing treatment operation. In onshore formations, these include exploding dynamite and vibroseis, or measuring vibrations produced by purpose-built trucks. Since marine seismic survey technologies are much better as compared to land seismic tools, they are now being customized for use in onshore reservoirs around the world. Vertical wells are not very conducive in case of tight gas formations, which results in the need to establish directional drilling procedures with an effective hydraulic fracturing plan for the greatest possible amount of hydrocarbon extraction. This also lessens the drilling footprint and lowers the cost of drilling as compared to multiple well developments.

Reservoir evaluation before, during and after the fracturing treatment is necessary to interpret rock-fluid characteristics, develop a combination of datasets measured inside the wellbore to detect the amount of oil/gas reserves and alter stimulation strategies, if necessary. Formation evaluation not only provides information about the properties such as thickness, permeability, fluid saturation, porosity, in-situ stress and conductivity; but also assesses the ability of a wellbore to produce hydrocarbons [33]. The feasibility of a fracturing process is dependent on the knowledge of geological properties of the reservoir, rock-fluid interactions, porosity–permeability analyses in different crude oil-containing sections, contaminants present if any, location of aquifers and groundwater sources, and depth of the formation. Hence, the geotechnical considerations for a reservoir for predicting its suitability in the hydraulic fracturing process can be summarized by determination of the lower limits for porosity, permeability, and upper limits for water saturation. A baseline estimate of permeability range, rock nature, the volume of oil/gas reserves, and process cost must be available for analyses by oilfield managers, engineers and project analysts prior to application of a proposed hydraulic fracturing process. Techniques which favour improvement of fluid conductivity and permeability characteristics of reservoir formations at the minimum cost and longer efficacy is amenable and likely to be more successful for the industry.

3 Fluid Design and Characterization

The composition and properties of the fracking fluid candidate directly control the economic productivity of the hydraulic fracturing treatment process. Fracturing involves pumping high viscosity fluids under high pressure to segregate the rocks in reservoir formation. Sometimes, acidization is performed in conjunction with fracturing technologies to re-develop natural fissures, which were present in the reservoir formation before compaction and cementation. A fracturing fluid must possess sufficient stability, viscosity, proppant carrying capacity and fluid loss control ability. The introduction of suitable proppants, attainment of fluid characteristics, and ideal pumpability rates are vital from the technical viewpoint. While fracking fluids are being pumped into the system, the formed fractures are held open by fluid pressure. However, once this process is stopped, and the injection pressure disrupts, the

minimum principal stress will act to close the created fracture pores. However, sufficient optimization and design will lead to retention of proppant materials within fracture zones, even after the removal of fracturing fluids. This results in the establishment of an open, conductive fracture zone within hydrocarbon-bearing reservoirs.

Fluid viscosity and pump rate are essential parameters that simultaneously control the net pressure differential required to attain the favorable fracture depth/width. This must ensure sufficient conductivity to allow displacing fluid to transport deep into the formation and proppant (such as sand) to enter the fracture. Adequate viscosity is helpful in decreasing frictional pressure losses during pumping. Stability of fracking fluids in high-temperature conditions is necessary to attain the desired flowability, minimize adsorption losses and decrease the formation of in-situ insoluble aggregates, which lessen the efficacy of fractures. A combination of additives such as acids, friction reducers, clay stabilizers, biocides, scale inhibitors, gels, buffers, gel breakers, scale inhibition agents, cross-linkers, non-emulsifiers, and iron control agents in surfactant-based fracturing fluids is incorporated in order to achieve optimal formulation for use in fracturing.

4 Physicochemical Attributes of Surfactant-Based Fracturing Fluids

4.1 Friction Reduction (FR) Capacity

Friction reduction is an important property of hydraulic fracturing fluids. Generally, conventional polymers and novel surfactants are employed to reduce pipe friction and allow the job to occur successfully under desired pressure [7]. In the absence of friction reducers (FR), frictional pressure inside the pipe reaches very high values in the presence of high flow rates. The concentration of FR varies in the range 0.5–1.0 gpt (gallons per thousand gallons of water), depending on the quality of concentrate and solvent fluids. The type of source water (freshwater/reused water), salinity and quality of FR affects the cost and efficacy of fracturing operation. Common FR materials are used in dry powder as well as liquid (with mineral oil base). At the end of fracturing, oxidizer or enzymatic compounds are added as FR breakers to degrade filter cakes/fluids and prevent damage to fracture conductivity. Polymer/surfactant in low concentrations serve primarily in reducing friction loss along the flow-lines, whilst employing slickwater and hybrid fracturing jobs.

4.2 Low Pipe Frictional Pressure

Low frictional pressures are considered beneficial during fracturing operations. During fluid injection, the friction pressure is a function of fluid viscosity, fluid

density, flow rate, and diameter of pipe/pore spaces within the formation. For example, usage of a smaller diameter pipe generally causes friction pressure to increase. In addition, proper selection and composition of fracturing fluid is necessary to derive improved flow conductivity and decreased friction pressure. As the rate of fluid pumping rate increases, the frictional pressure increases as well. However, insignificant flow rates reduce the operational capacity of the fracturing process, thereby creating a need to formulate an optimal fluid flow-rate. Rabaa [50] found that the stress field altered after the creation of fracture; the subsequent created fracture would be affected by the new stress field and would not be parallel to the first fracture. In another work, Zhou et al. [86] reported that hydraulic fracture was a dominating fracture with multiple random branches within high horizontal stress difference, while the hydraulic fracture was partly vertical (planar fracture with branches) within the scope of low horizontal stress difference. Weijers and co-workers [78] observed that the formation of transverse fractures with low flow-rate, low viscosity and high-stress contrast, whilst axial fractures were initiated during fracturing application for horizontal well-bores. Numerical simulation tools are effective for elucidating the mechanisms responsible for friction pressure reduction and scale inhibition during hydraulic fracturing.

4.3 Tortuosity

Tortuosity is defined as a measure of the restricted, convoluted pathways between the perforations and fracture zones. This phenomenon is severe in horizontal wells, moderate-to-high inclined wells, hard rock reservoirs, perforated wells; not a problem in vertical wells. The addition of surfactant-polymer based fluids with viscoelastic properties can solve the tortuosity issue, and successfully carry the proppant sand particles in-between the formations [10]. This leads to a decline in surface-treating pressures as soon as the fracking fluid reaches the perforations. However, if the sand slug causes an increase in pressure with a considerably sharp or smooth break-in pressure, it indicates the absence of tortuosity problem. Finally, if sand hits the perforations and no impact is obtained, problems with tortuosity are very unlikely to exist. Furthermore, the differential (>400 psi) between the closure pressure and instantaneous shut-in pressure (ISIP) also suggests the possibility of tortuosity. It can be mitigated by pumping low-concentration proppant slugs, loading of strong gelling agents (>15 lb system), and flow-rate increase. Tortuosity is dependent on the formation factor; as well as the ratio of a fluid's diffusion coefficient (when not confined) to effective diffusion coefficient (confined in porous medium).

4.4 Stability

Formulation of optimal fracturing fluids is a complex matter due to stabilization and compatibility requirements on the part of different compositions within a single system. A fracturing fluid must exhibit stability at elevated temperatures, high pumping rates, and dynamic shear conditions. Failure to comply with these parameters may cause the fluids to degrade, and settle out of the dispersed proppant(s) prematurely. Commercially, fracturing fluids are aqueous-based liquids with the ability to be either gelled or foamed. Addition of surfactants aid in retaining the proppant carrying ability of fluids, creating a conductive flow path from the formation to the wellbore, and reduce the quantity of insoluble aggregates formed within the formation during operation [58]. An important measure of stability for fracking fluids is viscosity enhancement. Fracturing fluids, when designed for a certain reservoir, are specifically tested to confirm suitable rheological attributes under dynamic flow conditions. Gelled based fracking fluids are favourable for high-temperature applications, whereas foam fluids are employed in sensitive operations with environmental concerns [64]. With respect to time, stability to a few hours or days is generally preferred. Despite the presence of dissolved solids and contaminants, it is necessary to achieve desired viscosity without flocculation/coagulation tendencies. Reusability, viscosity and temperature resistivity of fluids translate to the ability of a relatively low volume of stable fracturing fluids to displace and propagate a large quantity of proppant [12, 79].

4.5 Flow Pumpability and Flow Loop Testing

Significantly high pumping rates establish beneficial oil and gas production rates during fracturing stimulation into conventional/unconventional reservoir formations. However, many technical and environmental constraints associated with this approach need to be resolved. The main factor whilst increasing flow pumpability is the tubular friction pressure. The frictional pressure limit must be exceeded by injection pressure, to reduce the hydraulic power demand by 80% of the initial pumping energy requirement [10, 75]. Addition of appropriate surfactant fluids to fracturing fluid compositions improves the pumpability of fluids, as well as the flowback post-fracturing. Flow loop experiments identify the optimal flowability of different fracturing fluids and constitute a significant element of hydraulic fracturing fluid design. Herein, the pressure is allowed to drop while maintaining a constant rate of flow rate, as friction reducer and other components are added to the frac fluid system. It is pivotal to evaluate the relationship between different fracturing constraints such as FR such as polymer/surfactant, proppant, and additional components; and assess the specific function and influence of each chemical on hydraulic fracturing process.

5 Surfactant as Fracturing Fluid

Hydraulic fracturing, informally known as “fracking,” is a reservoir development technique, which involves the injection of water, sand, and chemicals under high pressure. This process is primarily intended to create and establish new fracture zones within the rock and increase the fluid connectivity of existing fractures. Though it is generally used in low-permeability formations such as tight oil, shale, and some coal beds, it can also be effectively employed to improve the producing life of a mature conventional well. The first field application of hydraulic fracturing comprised “slickwater multistage horizontal stimulation” or “slickwater frac” in the year 1947. However, modern fracturing practices have been continuously developed since then, keeping in mind the efficacy and cost-effectiveness of the project. For example, an advanced form of multistage fracturing was employed in 1998 in the Barnett Shale reserve, Texas, the United States, with the injection of more water and higher pump rate. A stage in the well life-cycle occurs when no additional oil can be produced, despite large reserves due to high capillary forces, reservoir heterogeneities and gravity drainage. Hydraulic fracturing is a promising way to alleviate this problem. In contrast, unconventional formations would be economically feasible in the presence of hydraulic fracturing techniques.

Surfactant injection decreases the oil-aqueous interfacial tension and ‘wets’ oil-saturated rock surfaces. This is useful in effectively removing oil–water blocks during hydraulic fracturing processes in and near the wellbore matrix [6, 85]. It is undeniable that surfactant fracturing is necessary to develop hydrocarbon pay-zones with good recovery results [65]. The various functional advantages of surfactant-induced hydraulic fracturing include:

- Connect fracture zones with existing natural fractures
- Reduce the formation of insoluble residues within the reservoir formation
- Increase the oil window or the degree of formation contact with the wellbore
- Reduce the drilling of infill wells with horizontal fracturing strategy
- Enhance the oil displacement ability of polymer-based fracturing fluids
- Suppress the formation of detrimental in-situ emulsion droplets
- Reduce sand production by reducing the pressure drop around the well
- Increase flow connectivity within low-permeability reservoirs with geological complexities
- Increase flow-rates from damaged wells (and reduce skin damage).

Surfactant addition, in proper formulations, can suppress the formation of in-situ emulsion phases and mobilize a greater amount of oil. Emulsion fluids stabilized by surfactant are characterized by smaller oil dispersions, which could effectively squeeze through tiny fractures [17]; and additional benefits are attained through improved mobility ratio and oil sweep efficiencies. In unconventional and impermeable formations, the formation of large-sized emulsion droplets and polymeric chains/aggregates must be avoided to prevent effective plugging of tiny pores [55]. Hydraulic fracture fluid systems are unique for each reservoir, and depends on the

geology, reservoir fluid characteristics and degree of pacing/heterogeneity of the reservoir. Table 1 shows some recent research works for the utilization of various surfactants for the hydraulic fracturing application.

6 Components of Surfactant-Based Hydraulic Fracturing Fluids

For hydraulic fracturing, different components/additives are selected by the industry, depending on the properties of the reservoir and fluids. Surfactants are gaining rapid interest as the primary constituents of conventional as well as novel fracking fluids. Table 2 shows a list of additives employed to avoid problems associated with oil production, rock permeabilities and environmental contamination, respectively.

7 Different Kinds of Fracturing Fluids

The base fluid can be categorized mainly into the water-based and oil-based fracturing fluid. Water-based fluids have been the primary fluids over the oil-based fluids since the introduction of thick water base gels, and the research and developments in the last 50 years are mainly devoted to water-base fluids. However, there has also been a need for oil-based fluids to treat the water-sensitive formations, [3, 26, 36, 60]. The other categories include acid-base, foam-base, emulsion-based, and alcohol-based fracturing fluids.

7.1 Water-Based Fracturing Fluids

Water fracturing fluids, for example, slick-water, linear & cross-linked polymer-based and viscoelastic based fluids have been used in many reservoirs fields as the conventional fracturing fluids. The slick-water type of fracturing fluids are widespread and frequently used for most of the oil and gas fields. The slick-water fracturing fluids mainly consist of a high percentage of water (greater than 90%) and supported with a minimum concentration of polymers (guar gum, xanthan gum, etc.) so that the viscosity of the water-based fluids is enhanced which consequently helps in proppant carrying capacity and transportation into the fractures points [43]. Slick-water can improve fracture length by creating very long skinny fracture, whereas the fracture width is mainly increased by gelled fluids [11, 40, 35]. Slick-water type of the fracturing fluids approach is simple to tackle and has been observed to generate small fractures [24, 23, 70].

Table 1 Earlier literature showing research works in the field of surfactant-assisted fracturing applications in the pilot and field operations

References	Surfactant used for the fracturing fluid characterization	Investigation parameters and results/outcomes
[39]	A novel anionic VES fracturing fluid "D3F-AS05"	D3F-AS05 fracturing fluid controls fracture geometry without compromising proppant transport. Real-time application of the devolved fracturing fluids in various oilfields in China
[28]	Bioterger AS-40; Viscoelastic surfactant (VES)	The temperature has an indirect effect on the foam rheology, viscosity of foam decreases with increase in temperature. Pressure effect on the foam viscosity is insignificant
[56]	Cocamidopropyl betaine (CAPB) ($C_{19}H_{38}N_2O_3$), sodium dodecylbenzene sulfonate (SDBS) ($C_{18}H_{29}NaO_3S$)	VES gels are stable in the temperature range (10–35 °C). The wormlike micellar network characterizes it. The improved rheological behaviour enhanced the fracturing application
[9]	Zwitterionic surfactant Cocamidopropyl betaine (CAPB), anionic sodium dodecyl Sulphate (SDS), sodium oleate (NaOA)	Pseudo-plastic and shear thinning nature of the VES fluids results in low frictional losses during pumping of the fluids downhole in an oil well. Enhanced viscoelasticity, good miscibility and better static proppant suspension capacity are obtained
[84]	0.5% VES (BET/SLP) fluid mixed with 0.25% HMP	The dynamic rheological properties of the VES fluid shows high viscoelasticity, in which the elastic moduli are higher than the loss moduli. The fluid has 50% lower formation damage than conventional guar
[24, 23]	Sodium Dodecyl Sulfonate (SDS), Sodium dodecylbenzene sulfonate (SDBS), Cocamidopropyl betaine (CAPB)	Proppant settling and foam stability were significantly affected by variation in the time of fracture closure. Proppant settling was enhanced with an increase in the fracture closure time
[2]	Alfa olefin sulfonate (AOS), Sodium chloride salt	Pressurized foam rheometer model 8500. Power-law model was modified, and the effect of shear rate and surfactant concentration was incorporated. Power-law model indexes (n, K) were depended on the surfactant and salinity effect

(continued)

Table 1 (continued)

References	Surfactant used for the fracturing fluid characterization	Investigation parameters and results/outcomes
[15]	Sodium dodecyl sulfate (SDS), ammonium lauryl sulfate, Isoamyl alcohol (3-methylbutan-1-ol), used as co-surfactant	Rheology of the gels shows shear thinning behaviour with good viscoelasticity. Elasticity is dominant over the viscous nature of the gel fluid, which helps to suspend and transport the proppant carrying capacity. The mixture of ALS and SLS shows a better gel system with higher viscosity compared to individual surfactants
[69]	Alfa Olefin Sulfonate (AOS) at 0.5 wt. % HPAM at 100 ppm and NaCl at 1.0 wt. %	80% of foam quality fluids carry and transport the proppant very efficiently within the lamellas with the significantly less vertical setting. 70% of foam quality fluid was not so efficient due to liquid drainage and less viscosity. Proppant bed forms near the injection well
[81]	Viscoelastic surfactant (0.4% VES + 0.15% SSN)	Core displacement analysis reveals that the high compatibility between the gel, core and formation water. The field application in Qinshui Basin of Shanxi Province shows that the production of the well, which is fractured by the developed VES clean fluid. It has a vital application in the coalbed gas
[45]	VES containing both unsaturated carbon-carbon double bond and amide group	Novel Gemini VES fracturing fluid has good heat resistance Gemini VES was improvised VES fracturing fluid, whose viscosity could be maintained about 40 mPa·s at 160 °C
[1]	Alfa olefin sulfonate (AOS), betaine Sodium chloride salt	The modified power-law models for polymer-free supercritical CO ₂ foam (AOS and betaine) is a function of temperature, pressure, and shear rate. Empirical correlations were found to be significant for the all tested temperature and pressure
[74]	Alfa olefin sulfonate, sodium dodecylbenzene sulfonate, Cocamido- propyl betaine	Thermally stable foam enhanced the viscosity and elastic properties of the fluids, and capable of carrying proppants by reducing formation damage

(continued)

Table 1 (continued)

References	Surfactant used for the fracturing fluid characterization	Investigation parameters and results/outcomes
Chaudhary et al. [14]	Sodium Lauryl Ethyl Sulphate (SLES) + Palmitic Acid, Silica Sand, Propylene Glycol Potassium Chloride	Stability of the grafted copolymer foam is higher than conventional foam fluid system. Improvement in the Proppant carrying capacity was reported with an increase in the foam quality. The reduced permeability value of up to 82% was reported
[16]	CTAB, citric acid (CA), and maleic acid (MA)	VES fluids were showed the shear thickening behaviour through the formulation of mixing long chain cationic surfactant with organic acids

Polymer-based fluid systems, consisting of high-molecular-weight components, are conventionally employed for well stimulation and other production operations. For example, linear polymer fluids are thermally unstable under high-pressure, high temperature (HPHT) conditions. However, in the presence of nanoparticles, these fluids were cross-linked to attain thermal stability. A detrimental effect of polymer fracturing fluids is related to formation damage issues due to pore-plugging, and the existence of insoluble residues. Polymer fluids are unfavourable to control the growth of fracture height, fracture length, and to improve fluid permeability. However, such fluids show good proppant carrying ability to producing zones of interest. Therefore, the use of surfactants can help mitigate these problems. Viscoelastic surfactant (VES) based fracturing fluid has been used since 1997, which is an alternative to conventional polymer and can develop sufficient viscosity to create fractures and transport proppants. VES fluids are effective agents to fracture low and high permeability regions within the reservoir. These fluids exhibit excellent stabilization, rheological attributes and low formation damage characteristics as compared to cross-linked polymers. Surfactant based fracturing fluids are associated with easy preparation technique, low cost/complexities, and a lesser number of chemicals required. Conventional polymer fluids, on the other hand, are much more complex in the presence of other phenomena (such as polymer hydration, cross-linkers, beakers etc). Surfactant-stabilized fracturing systems achieve high fracture conductivity, stability and proppant suspension ability [39].

Table 2 Different components of the hydraulic fracturing fluid(s)

The aqueous phase and enhancers/proppants (approximately 98% v/v composition)			
Composition	Examples	Behaviour	Functional application
Water	Seawater, formation water, deionized/treated water	A part of water/aqueous returns with formation water phase as produced water, whilst the remaining stays within the reservoir. This depends on the type of reservoir and chemical fluid used	Expands the fracture and delivers proppant (sand) deep into the formation
Proppant	Sand, ceramics, resin-coated sand	Remains within the formation zones to hold the fractures in-place, post-stimulation operation	Improves oil and gas productivity by establishing fracture zones in low-permeability reservoirs
Polymer/gels	Polyacrylamides, copolymers and gelation agents	Enter into the formations, and improve the rheological characteristics of fracturing fluid	Improve viscosity, thermal stability and prevents emulsion formation
Surfactant	Ionic, Nonionic, Zwitterionic species	Forms stabilized aggregates/micelles in bulk solution phase and improve network structure in polymer-based fluid systems to attain favourable interfacial, stabilization and rheological characteristics	Reduce IFT, alter wettability, reduce/prevent the formation of insoluble residues with “clean-up” after fracturing
<i>Other additives (approximately 2% v/v composition)</i>			
Friction reducers (FR)	Surfactant, foam, polymer, gel, nanoparticles	Remains in the formation to allow effective propagation/transport of fracturing fluids	Reduces frictional pressure during a fracking operation
FR breakers	Hydrogen peroxide, oxalate	Reacts with FR to contribute to their breakdown and degradation; consumed by natural microbes	Permits breakdown of friction reducer (FR) in fluid; to cause easier fluid flow back to the wellbore

(continued)

Table 2 (continued)

The aqueous phase and enhancers/proppants (approximately 98% v/v composition)			
Composition	Examples	Behaviour	Functional application
Crosslinkers	Borate (high pH & low-to-moderate temperatures); zirconate (low pH & elevated temperatures)	Interacts with frac components to form ions/salts information, which is returned with produced water	Helps in maintaining fluid viscosity at varying shear and temperature conditions
Acids	Hydrochloric acid	Reacts with the formation minerals to result in the creation of salts, water and neutralized carbon dioxide	Dissolves minerals to initiate fractures/cracks within the rock
Clay stabilizers	Potassium chloride, sodium chloride, calcium chloride	Interacts with clays through sodium–potassium ion exchange	Restricts swelling behaviour of clays within the formation
Gelling agents	Guar, polyacrylamide, hydroxyethylcellulose, other polymers	Enhances fluid viscosity and thermal stability	Improves proppant suspension and propagation ability of fluid
Gel breakers	Acids, bleach, hydrogen peroxide, oxalate	Reacts with cross-linker and gel information; decrease fluid viscosity to improve flow back	Allows delayed breakdown of the gel
Corrosion/scale inhibitors	Ethylene glycol	Forms bonds with metal surfaces such as fluid pipe; designed to be bio-degradable by microbes	Prevents scaling and corrosion of the pipe
Anti-bacterial agents & other biocides	Oxidizing biocide: chlorine, bromine, ozone, chlorine dioxide Non-oxidizing biocide: aldehydes, bronopol, DPNPA, acrolein	Reacts with bacteria and other micro-organisms existing in the treatment fluid and formation	Kill bacteria to control fluid rheology
Non-emulsifiers	Polymer; NE-1225, NE-43R, NE-43X (ChemEOR) NE-200, NE-300, NE-400 (Tetra Co.)	Influences molecular arrangement to prevent the formation of agglomerates; returns to the surface with produced water/produced oil and natural gas streams	Prevents the formation of undesirable emulsions with the formation during operation by separating in-situ oil/water mixtures

(continued)

Table 2 (continued)

The aqueous phase and enhancers/proppants (approximately 98% v/v composition)			
Composition	Examples	Behaviour	Functional application
pH adjusters/Buffers	Acidic/basic types: Potassium carbonate, acetic acid	Reacts with in-situ or existent acidic. Basic agents in stimulation fluid to attain close-to-neutral pH	Retains efficacy of FR, breakers, gelling agents and cross-linkers
Iron control agents	Ammonium chloride, Ethylene, Citric and other weak acids, Glycol	Reacts with minerals in formation to generate salts, water and carbon dioxide, while reducing the percentage of dissolved iron	Prevents precipitation of metal, minimise the formation of insoluble residues and prevent plugging-off of formations

7.2 Oil-Based Fracturing Fluids

Oil-based fracturing fluids were implemented in fracturing treatments at the beginning stage, and the reason was their compatibility with almost all kinds of formation. However, the higher cost, safety, and environment concerns limited their usage and led to the initiation of a water-based fracturing fluid system. Gelled crude oil, diesel, and kerosene had found its application in the past as an oil-based fracturing fluid. Though LPG has been used for stimulating conventional reservoirs for the last 50 years, now it is being adapted for unconventional reservoirs like shale gas and tight sands as they eliminate phase trapping by exhibiting high capillary pressure thus improving the recovery. They demonstrate various advantages like reduced water usage, fewer chemical additives, increased productivity, no fluid loss, rapid clean up, and full fluid compatibility with shale reservoirs, which are sometimes water-sensitive [26]. However, its massive application has been limited due to the higher investment cost, and it requires manipulation of large amounts of flammable proppant, [3, 26, 36, 60].

7.3 Alcohol-Based Fracturing Fluids

Methanol has been infrequently used as an alcohol-based fracturing fluid in Argentina and Canada (from the 1990s to 2001) for the reservoir with irreducible high water or hydrocarbon saturation (minimal fluid recovery), high clay content-low permeability reservoirs, and low bottom hole pressures due to its properties like a low freezing point, high water solubility, low surface tension and high compatibility with the formation. Methanol (less viscous than water) has been gelled using foaming with

guar or synthetic polymer and CO₂ and has also been metal crosslinked. However, the three to four times higher cost than water-based fluid and issues related to safe handling (low flash point makes it highly ignitable) have made a shift from using methanol as a base fluid to methanol as just an additive [3, 26], 36, 60].

7.4 Acid-Based Fracturing Fluids

Acid fracturing is generally used in carbonate/limestone reservoirs to “etch” the channels in the rock. For these types of fluids, the formation should be slightly soluble in acid to etch ‘artificial’ channels within the fractured wells. Its usage is limited to only carbonate reservoirs and cannot be applicable to fracture the coal bed methane, sandstone, and shales reservoirs [26].

7.5 Emulsion-Based Fracturing Fluids

An emulsion-based fluid is a mixture of two or more immiscible liquids mainly developed to reduce or eliminate the usage of water in water-sensitive reservoirs. One such fluid is an emulsion of CO₂ in the aqueous alcohol-based gel applied in the western Canadian sedimentary basin in 1981, and such fluids have been significantly used in tight gas and low-pressure applications. The fluid provides advantages similar to the conventional high-quality CO₂ foam but with higher water loading [26].

7.6 Foam Fracturing System

Foam based fracturing fluids have been used in the petroleum industry mainly for the unconventional low permeable reservoirs, water-sensitive formation generally for undersaturated gas reservoirs, and areas having water scarcity. Foam based fracturing fluid are considered the best for unconventional reservoirs since it causes less damaging in water-sensitive formations with easy cleanup and less water to recover post-fracturing [52, 72]. Foams are produced on-site by a mixture of two phases, i.e. liquid and gas. Moreover, surfactants are used to reduce the interfacial tension between the two phases, which consequently enhance foaming capacity and the stability of foam [47, 73].

The foam quality is an important property for effective fracturing. In preparation of foam-based fluid, it is required to maintain the desired quality (percentage of gas volume) of the generated foam as given by Eq. (1) [25, 74]. During foam production, the internal phase- gas and external phase, the mixture of surfactant and water are mixed. Initially, the surfactant is combined with an external phase (mainly water) [25]. Then after, the prepared mixture of surfactant solution and gas (mainly N₂/CO₂)

are together pumped into the formation through the wellbore [22, 67]. Proppants are combined with the foam fluid before pumped into the wellbore so that clogging inside pipeline and foam generator can be avoided.

$$Q = \frac{V_{\text{gas}}}{V_{\text{gas}} + V_{\text{liquid}}} \quad (1)$$

where Q is the foam quality, V_{gas} is the total volume in the foam, and V_{liquid} is the volume of liquid in the foam.

Foam fracturing fluid can be classified based on gas usage during foam preparation [26, 54] as given below:

1. Water-Based Foam (a combination of water, foaming agent and CO_2/N_2 gas)
2. Acid-Based Foam (the combination of acid, foaming agent and N_2 gas)
3. Alcohol-Based Foam (the combination of methanol, foaming agent and N_2 gas)
4. CO_2 -Based Foam (the combination of liquid CO_2 and N_2 gas).

Carbon dioxide (CO_2) and nitrogen (N_2) are the most used gases for the generation of the foam fracking fluids. CO_2 based foams have wider application, and it has a higher hydrostatic pressure as compared to N_2 , and more suitable for reservoirs having higher breakdown pressure. N_2 foam injected at low hydrostatic pressure requires high surface treating pressures in contrast to the CO_2 foam fluids [44]. Therefore, N_2 foam fracturing fluid is mostly affected by high surface injecting requirements [24, 23, 76]. The comparison of the various fracturing fluids in terms of advantages and disadvantages as mentioned in Table 3, and followed with the brief discussion are presented.

8 Hydraulic Fracturing Process Considerations

The selection of fracturing fluid is a critical decision. It encompasses a number of factors such as reservoir temperature, reservoir pressure, the expected value of fracture half-length, and any water sensitivity. The following list shows the industrial and professional standards to be maintained whilst designing a fracture process:

- Fluid must create a fracture wide enough, and pump proppants at concentrations high enough, to achieve the flow conductivity.
- The model should account for compromise fracture length, and conductivity in situations, wherein substantial damage to the formation may occur around the fracture.
- Transverse fractures are tough to achieve and require a greater degree of planning as compared to longitudinal fractures, but more favourable for production viewpoint.
- Fracture size must be controlled during the process.

Table 3 Different types of fracturing fluids employed in the petroleum sector

Fluid type	Properties of fluids (ambient conditions)	Advantages	Limitations	Remark	References
Water-based fluid	Density = 1 g/cm ³ Apparent viscosity = 2 cP	Formation damage reduced Economical reservoir volume is higher during fracturing Better fracture confining	Proppant suspension capacity is poor Freshwater consumption is high Environmental problems	Water usage is 99.5%, and other chemicals are 0.5%, i.e., friction reducers, pH-adjusting agents, etc Not suggested for water-sensitive reservoirs	[67]
Oil-based fluid	Density = 0.85 g/cm ³ Apparent viscosity = 100 cP	Water requirement is less Logistic cost reduced Rate of recovery is high Fast clean-up of well	Not Economical Initial set up cost is high flammability issues are very high	Usage of Crude oil, kerosene, and diesel oil Recommended for water-sensitive reservoir	[26, 47]
Acid-Based Fluid	Density = 1.2 g/cm ³ Apparent viscosity = 2 cP	Proppant usage is a decline Water requirement is reduced	Not economical Never recommended for carbonate formations Very fast and frequent acid interaction with the reservoir	Usage of Hydrochloric acid, acetic and formic acids Recommended for limestone reservoir	[20, 26]
Alcohol-based fluid	Density = 0.8 g/cm ³ Apparent viscosity = 0.5 cP	Fast clean up of well Corrosion or scale inhibition Friction reduces	Flammability creates the problem of safety Proppant suspension capacity is not good	Methyl and isopropyl alcohol are used Recommended for low-permeable and dry gas reservoir	[19, 57]

(continued)

Table 3 (continued)

Fluid type	Properties of fluids (ambient conditions)	Advantages	Limitations	Remark	References
Emulsion-based fluid	Density = 0.75 g/cm ³ Apparent viscosity = 750 cP	Water requirement is a decline The additive is very less required Enhanced productivity	Not Economical Logistic needs are high	Non-mixable fluid are used such as oil Recommended for low-pressure reservoir	[37, 42]
Foam-based fluid	Density = 0.25 g/cm ³ Apparent viscosity = 150 cP	Water requirement is very less (only 5–30%) Formation damage is less Proppant suspension capacity improved	Initial running cost is very high Logistic usage is high High temperature is highly unstable	Foam is a combination of liquid and gas (nitrogen or carbon dioxide) Recommended for water-sensitive and unconventional reservoirs	[30], [31, 75–74]

- Parameters such as geometry, fluid characteristics, reservoir heterogeneities, permeability, and formation thickness play an essential role in project feasibility.
- Information regarding in-situ stresses is necessary to predict fracture half-length, width, height and complexities prior to production testing.
- Rock properties such as ductility and depth also provide an impetus to the formation of an appropriate fracture.

The extent of a created fracture and its resulting propagation is controlled by the in-situ fluid characteristics, upper confining zone, injected fluid parameters and reservoir heterogeneities. Previous studies have proved the influence of fractures on reservoir characteristics. The significant phenomena affecting rock behaviour are porosity, rock-volume shrinkage due to dolomitization, porosity increase due to solution, and other geological factors. Fracturing plan should also involve effective flowback model after the completion of fracture treatment during diagnostics and monitoring.

9 Applications of Surfactants as Fracturing Fluids

The different surfactant based fracturing fluids have been developed with time. Mathis et al. [46] presented that the proppant suspension capacities of viscoelastic surfactant

fracturing fluids were not due to the drastic enhancement in the viscosity. They concluded that the proppant carrying capacity of viscoelastic surfactant is mainly because of the elastic nature and structure of fluid rather than viscosity [66] reported the rheology and phase behaviour of sodium oleate surfactant. The increase in the concentration of sodium oleate surfactant (above CMC) leads to self assembles into worm-like micelles either in the presence of inorganic or binding salt that screens the inter-micellar electrostatic interactions and reduces the micellar surface charge. In 2006, Sullivan et al. were utilized the zwitterionic surfactant fluid in high permeability reservoir that leads to low friction pressure, effective proppant transport and high proppant pack conductivity. Welton et al. [80] developed an anionic surfactant based fracturing fluid with improved fluid loss and de-emulsification characteristics, which do not adversely change rock-wettability. Nonionic Tween and Brij surfactants form worm-like micelles in solution phase, which can be employed a fracturing fluid.

Similarly, an anionic surfactant with an easy method of synthesis, favourable viscosity, low frictional resistance, and enhanced stability at 30–100 °C was reported as a potential fracking agent by Khair and others [39]. The fluid exhibited good suspension and proppant transportation attributes at lower viscosities than conventional systems. Thampi and co-workers [68] compared the effect of co-solvents and branched alcohols on phase behaviour and physicochemical properties of viscoelastic surfactant-based gel fracturing fluids. Gel-stabilized systems have viscoelasticity much greater than the minimum requirement for the fracturing application [68]. Rao et al. [51] discussed ionic liquid-based microemulsions as fracturing fluids over a wide range of temperature, i.e. 278–423 K. Viscoelastic surfactant-stabilized fluids characterized by wormlike micellar structures are considered as potent, functional alternatives to hydraulic fracturing applications [4, 41].

Surfactant molecules form micelles in the bulk phase, with the polar head pointing towards aqueous phase and non-polar tail oriented toward oil (hydrocarbon) phase. Baruah et al. [7] worked on the effect of concentration on the micellar arrangement and physicochemical properties of sodium oleate (NaOA) based fracturing fluids, and identified the existence of a liquid crystal phase from loosely packed surfactant molecule patterns to form lamellar hexagonal structures. These properties contribute to extraordinary proppant suspension characteristics at low viscosities than polymer-containing fluids. Another work on mixed ionic-ionic surfactant confirmed the sensitivity of formulation characteristics to the quantity of surfactant, cosurfactant, hydrocarbon and aqueous phases involved [8]. The developed lamellar crystals are characterized by pseudoplastic attributes, which is desirable for pumping under high shear conditions and transporting proppant (sand) effectively to the fracture zone. Additionally, the rheology of polymer fluids is completely reversible with no permanent degradation properties, even under high shear. VES fluids easily segregate into low viscosity components via wormlike-to-spherical micelle transition at the end of fracturing jobs, which allows them to recover from sub-surface formations.

10 Summary and Outlook

The impact of hydraulic fracturing on the petroleum production industry is becoming an increasingly sought topic of interest globally. This method is a promising area with the capability to create a large fracture network in low permeability formations and achieve economical production results. However, groundwater can enter into the oil-producing zones during this process, which can have adverse repercussions on both production and environmental aspects. Conventional polymer-induced fracturing routes are associated with drawbacks in the current industry owing to issues of less fluid loss control, the formation of insoluble residues, and flow back. The field of surfactant has generated a marked improvement in optimizing and attaining beneficial hydraulic fracturing solutions. Systems consisting of a single surfactant, mixed surfactant, hybrid formulations with polymer/nanoparticles, have proved to be effective fracturing fluids based on a documented history of experimental and numerical simulation investigations. Surfactant based fluids help in mitigating stability, flow back and water-blockage issues faced by the oilfield managers during operation. Surfactants are effective clean-up additives, which reduce the amount of residues or precipitates remaining within the reservoir formation post-application.

Furthermore, surfactant-based fluids reduce interfacial tension, alter wettability to a water-wet state, reduce flow friction and provide good proppant suspension for fracturing jobs in difficult, complicated formations. Polymer-surfactant aggregate structures show better rheological attributes in comparison to (only) polymer systems. Earlier reports by researchers and academicians have corroborated to the favorability of surfactant-assisted hydraulic fracturing in the petroleum industry. Hence, the introduction of surfactants in fracturing operations provides a sustainable fracturing technique to meet the needs of on-site fracturing considerations from the industry viewpoint. This chapter provides a detailed, systematic description of the concepts, function and prospects of surfactant-based hydraulic fracturing in the oil & gas sector.

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