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Research Article

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A Novel approach for formulating CO_2 Foam Based Fracturing Fluid by Synthesized Grafting Copolymerization to Enhance its Stability for HPHT Shale Reservoirs

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Abstract

Conventional Sources of energy are depleting at an alarming rate which give us unconventional resources as an only option for energy source. Unconventional sources of energy like Shale gas, tight gas, Coal bed methane are difficult to exploit as compared to the conventional sources of energy. Hydraulic Fracturing is the well stimulation technique used for exploitation and production of these unconventional resources. Foam fracturing is the most opted stimulation technique for low permeability shallow wells because of its reduced damage potential to reactive and sensitive formations. This research paper discusses about the evaluation of attempt made to develop an eco-friendly CO_2 foam based fracturing fluid which can be used at HPHT conditions for shale reservoirs by Grafting Copolymerization. The graft copolymer was developed by free radical polymerization of Gum Acacia (GA) and Lactic acid (LA) by using Potassium Persulphate (KPS) as an initiator and its characterization was done by FESEM and FTIR analysis. Then, the grafted copolymer (GA-g-LA) was processed with CO_2 foam based fracturing fluid as an additive. Lecithin is used to emulsify brine and liquid CO_2. The effect of graft copolymer was on rheology and stability of the formulated foam based fracturing fluid is evaluated as a function of surfactant concentration. The results are compared with the conventional foam based fracturing fluids. The results showed that grafted copolymer has increased the stability of the formulated fracturing fluid at high temperatures. Use of grafted copolymer results in higher viscosity and proppant carrying capacity which is beneficial for HPHT fracturing conditions. The results of the core flood studies were evaluated on a shale sample to determine its return permeability and it was comparable to non-foam based fracturing fluid.

Introduction

Fracturing is a stimulating technique use to increase the well conductivity. A fracture is a superimposed structure that remains undisturbed outside the fracture; therefore there is no change in the reservoir effective permeability. The increased wellbore radius increases the conductivity or near wellbore permeability which leads to high yielding of hydrocarbons, because a large contact surface between the well and the reservoir is created. Hydraulic fracturing is a modern technology, usually used in low permeability reservoirs like shale and other tight rocks formation. In this stimulation technique fluid that is used to generate fractures in the rock is known as fracturing fluid. During the hydro-fracturing process, the fracturing fluid is injected into the formations which increase the near wellbore permeability which leads to the increase in the conductivity of the reservoir those results in more flow of hydrocarbon. Fracturing fluid contains a propping agent commonly known as proppant which is usually permeable. Proppant is design in such way so that it can keep the induced hydraulic fractures open during or following a fracturing treatment therefore the fluid should have a certain amount of proppant holding capacity to keep the fractures open all around the wellbore.

Different types of Fracturing fluids are used in oil and gas industry which includes water-based, foam-based, acid-based, gas-based fracturing fluids. The basic composition of any fracturing fluid contains base fluid (90-94%), proppant (4-5%) and various additives (1-2%) like viscosifier, surfactant , scale inhibitor , gel stabilizer, cross-linker etc . The fracturing industry is in booming stage and use of conventational fracturing method requires millions of gallon of water and high amount of harmful chemicals in order to yield more hydrocarbons from the formation which gives rise to environmental concern, therefore the selection of fracking fluid is very vital and requires careful consideration while selecting the fracking fluid depending upon the type of formation.

A new fracturing fluid is developed by Canada based frac energy to minimize the damage simultaneously maximize the production. Canada based frac energy has developed foam based fracturing fluid for under pressured low permeability reservoirs to mitigate various problems such as clay swelling, formation damage, blockage in fractures etc. Foams based fracturing fluids are made with gases like CO_2 and N_2. Foams contain small amount of water as external phase and high amount of gas as internal phase thus helps in reducing the damage potential to the sensitive formations which include a stabilizing surfactant called foaming agent. Due to high productivity, the demand of foam based fracturing has been increased rapidly in recent years. The use of CO_2 foam based fracturing fluid started in 1965 where around 60 wells were fractured at a time and increased productivity was observed. Many mathematical models were prepared to compare the CO_2 foam based fracturing fluid with conventional Fracturing fluid and CO_2 Foam based fracturing fluid was found to be the best for low pressured and low permeable shallow reservoirs and due to physical and chemical properties it was unique tool in stimulation technique.

There are two limitations for Foam based fracturing fluids i.e; elevated temperatures and high pressurised condition where it's difficult to maintain its viscosity in deeper formations. Most of the fracturing fluid is designed for 200°F and below. Temperature and Pressure elevation lead to the degradation of base gel of fracturing fluid and causes to lose its viscosity abruptly and proppant carrying capacity. The most common gels used in all types if fracturing fluid are guar based or cellulose derivatives which is not stable at high temperature and high pressure conditions. The cleanup is also a challenge in guar based gels because it leaves residues after breakage which reduces fracture conductivity, for this reason cellulose derivatives come into play. Cellulose derivatives have linear chains of glucose which are non-toxic and water soluble. But still it's just reduces the clean-up problem and maintain the fracture conductivity. HTHP condition is still remaining un-encountered.

This paper shows the Development of a High temperature and High pressure stable CO_2 foam based fracturing fluid by Grafting Copolymerization. In this present study, Gum acacia-g-lactic acid (GA-g-LA) is synthesized using free radical polymerization by using Potassium per Sulphate (KPS) as initiator to formulate CO_2 foam based fracturing fluid. Various rheology tests against foam qualities, Foam Stability test, Shear rate test at various temperatures and return permeability test has been carried out for the analysis of grafted copolymer as an additive in the formulation.

Experimental Analysis

Materials

Gum Acacia and propylene glycol was purchased from Scientific Chemicals pvt. Ltd, New delhi, India. Lactic acid was purchased from Katyuri Chemicals Pvt Ltd, Dehradun, India. Other additive chemicals like KCL (Potassium Chloride), SLES (Sodium Laurly Ethyl Sulphate), Palmitic Acid, Borate salts, Ammonium per Sulphate were issued from the Department of Pharmacy, DIT University, Dehradun, India. Distilled water was used to prepare the brine solution.

Preparation and synthesis of Grafted Copolymer

Gum Acacia and Lactic has been grafted using KPS (potassium persulphate) to initiate the reaction. For this, inert atmosphere was provided during the process of the grafting. The procedure for the development of graft copolymer is:

100 ml Distilled water was used for dissolving 1gm of Gum acacia (GA) in a 250 ml round bottle flask at a constant stirring speed. For increasing the temperature the flask was kept in a oil bath and stirred by magnetic stirrer to maintain at a temperature of 150 ±1°F. When the temperature reaches at 150°F, 10 ml of lactic acid is injected at an instant by a syringe. The system is then allowed to mix at a constant temperature and speed for 2.5 hrs. After 2.5 hrs, 2.5 ml of potassium per sulphate is added to the solution and allowed to react with the homogeneous solution for another 1 hr. After the desired concentration is achieved the solution was cooled, by placing the flask in cool water bath. The temperature is reduced to 70 ± 1°F and the precipitates formed are separated out by filtration by using acetone. The filtered out precipitates are dried in a Hot Air Oven at 125°F for 12 hrs and then pulverized to obtain the desired graft copolymer (GA-g-LA). This graft copolymer was used as an additive for the formulation of CO_2 Foam Based Fracturing Fluid.

Development of CO_2 Foam Based Fracturing Fluid

A sample of 500 ml of base gel is prepared by using 70% of CO_2 liquid, 21% brine solution (water + 20% methanol) and 1.5% W/V Grafted copolymer (GA-g-LA). Lecithin is used to emulsify CO_2 liquid and brine solution. Grafted polymer and foaming agent is mixed with the base solution. Futhur various additives are added in fixed proportions as shown in Table1.

Table 1: Composition of the fluid

Additives	Concentration	Function
Sodium Lauryl Ethyl Sulphate (SLES) + Palmitic Acid	2% W/V	Foamer
Silica Sand	5% W/V	Proppant
Propylene Glycol	0.2% V/V	Thermal Stabilizer
Sodium Lauryl Sulphate (SLS)	0.1% W/V	Reduce surface tension (Surfactant)
Borate salts	0.15 % W/V	Cross liker
Potassium Chloride (KCL)	0.1 %W/V	Salt
Ammonium Per Sulphate	0.2 % W/V	Breaker

Testing Analysis and Methodology

Various test evaluation has been carried out including – Analysis of Grafted Copolymer, Rheology tests, Stability and Compatibility tests, Return permeability test and proppant carrying capacity test. Each test evaluation is discussed in detail.

Analysis of Grafted Copolymer

Gum Acacia is grafted with Lactic acid and the grafted result was characterized by using FESEM and FTIR Spectrum analysis. FTIR and FESEM describe the surface or morphological characteristics of polymer after grafting.

Rheology Tests

The Rheology properties of the developed fracturing fluid were determined by Anton Par Rheometer Model MCR 72. Viscosity is determined at different temperature ranges and varying foam quality.

Stability and Compatibility

The Stability and Compatibility of the base foam gel and emulsion stability with liquid CO_2 were evaluated at high temperature and pressure. The formulated fluid was kept at different temperature ranges to evaluate its half life.

Proppant Carrying Capacity Test

Proppant carrying capacity of the conventional foam based fracturing fluid and formulated fracturing fluid were carried out and compared with respect to the sedimentation time and sedimentation velocity.

Return permeability test

Return permeability test was carried by the core flooding apparatus. In the core flooding apparatus, the effect of the formulated fluid on the core sample was analysed. The test was conducted on the core sample collected from Cambay Basin, India. For permeability measurements, the constant pressure source used was Syringe Pump, Teledyne Isco; Model 500D (USA). The core was placed in the core holder and subjected to overburden pressure of 4000 psi .The initial permeability was establish by flooding brine solution at a pressure more than 4000 psi and 300 F. The liquid CO_2 and base gel were pumped separately to meet at a point where they mix properly and enter into the core. After flowing through the core, it was soaked for 2.5 hrs and then desired amount of breaker solution was added and the fluid was flowed back from the core. After flow back, the core was flushed with brine to evaluate the return permeability or final permeability.

Results and Discussion

Characterization of Synthesized graft copolymer (GA-g-PA)

The grafted copolymer was characterized by FESEM and FTIR analysis.

Field Emission Scanning Electron Microscopy (FESEM)

The morphological and surface characteristics were determined by FESEM analysis. The results of GA, LA and Grafted Copolymer were compared and shown in fig 1. It is observed that the surface morphology of GA and LA got changed after grafting as shown in fig c. ("Neelima Tripathi et.al 2017")

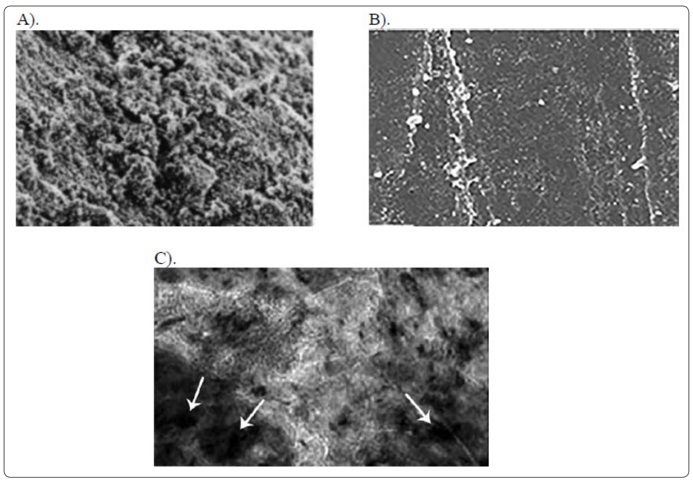

Figure 1: FESEM OF GA (A), LA (B), & GA-g-LA (C)

Fourier Transform Infrared Spectroscopy (FTIR)

In the FTIR spectrum of LA and GA-g-LA, the sharp and intense peaks at 1,750 cm^{21} and 1,454 cm^{21} are detected, which are assigned to carbonyl stretching (2C5O2) and $2CH_3$ bending respectively. The other characteristic peaks are also observed at 1,204 cm^{21}, 1,133 cm^{21}, and 1,094 cm^{21}, which attributes to 2C2O2 stretching in the structure of LA and GA-g-LA. However, the peak at 1,045 cm^{21} represents 2OH bending. The above mentioned peaks are not found in the IR spectra of neat GA, which proves that the chemical structure of GA is completely different from LA and GA-g-LA. A sharp peak is positioned at 1,600 cm^{21}, which represents 2C5O stretching as well as 2N2H bending. The other peak at 1,016 cm^{21} is attributed to 2C2O stretching of alcohols and carboxylic acids. A broad peak is also detected at 3,360 cm^{21}, which mainly attributes to –OH stretching. It is noteworthy to mention that no significant absorption band is detected for N2H stretching in FTIR spectra of GA due to presence of high molecular weight glyco- protein in trace amount of GA, LA and GA-g-LA. However, the grafting phenomena in GA-g-LA is explained with the help of peak shifting from 3,635 cm^{21} to 3,641 cm^{21} as well as by the reduction in peak intensity, which suggests that an appreciable quantity of –OH and N2H groups in GA are grafted with LA chains as shown in fig 2. ("Neelima Tripathi et.al 2017")

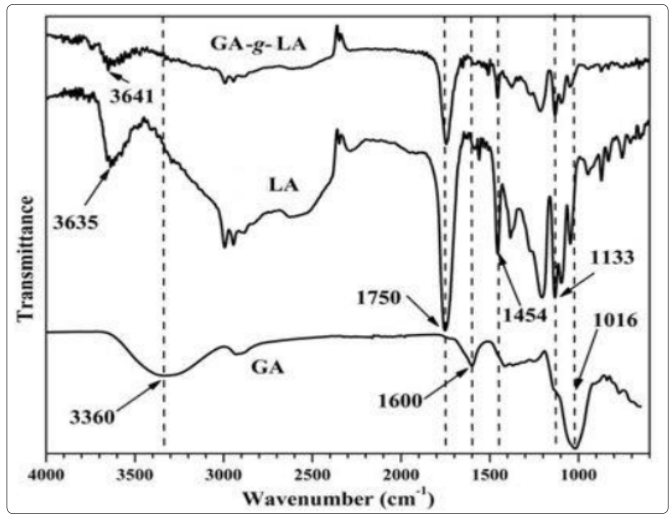

Figure 2: FTIR of GA-g-LA

Rheological Properties

The rheological properties were determined by Anton Par Rheometer Model MCR 72. The effect of Grafted copolymer on the developed foam based fracturing fluid is analysed as follows.

Foam quality (Q)

The viscosity and temperature variation at different foam quality of the grafted CO_2 foam based fracturing fluid is determined and shown in table 2. Foam quality depends upon the surfactant or foamer concentration as shown in the table. It can be mathematically be calculated as

$$Q= (Vf - Vt)/ Vf \%$$

Where Q = foam quality, Vf = volume of foam,
Vt = total volume of liquid in the foam.

Table 2: Foam quality with respect to surfactant concentration

Foam Quality (Q) %	Surfactant Concentration (w/v %)
20	0.25 %
40	0.34 %
60	0.55 %
80	0.78 %

With increase in the foam quality the increase in viscosity was observed. At 80 % foam quality the viscosity was found to be around 300 cp. The viscosity lowers with the increase in temperature. The reduction in viscosity with increase in the temperature was observed at different foam qualities i.e at 40 %, 60%, 80%. According to the results the best viscosity was observed at 80 % foam quality as shown in fig 3. Therefore the foam based fracturing fluid should have greater than 80 % of foam quality for attaining the desired viscosity.

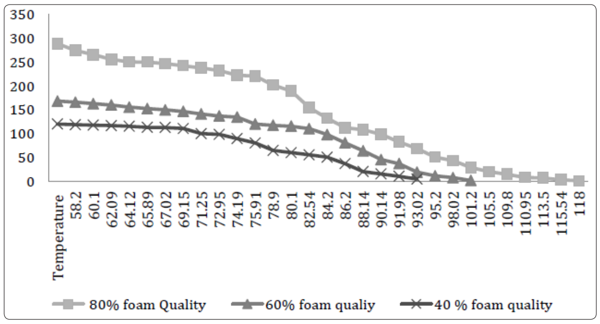

Figure 3: Viscosity v/s Temperature at different foam qualities

Viscosity

Significant effect of the graft copolymer was observed on the rheological properties of the formulated fracturing fluid at 90% foam quality. The results showed increased with viscosity with the increase in the concentration of the Graft Copolymer. The performance of graft copolymer at high temperatures is compared with the conventional foam based fracturing fluid which is shown in fig 4. The normal viscosity range was found to be around 75-120 cp at temperature from 150-200° F.

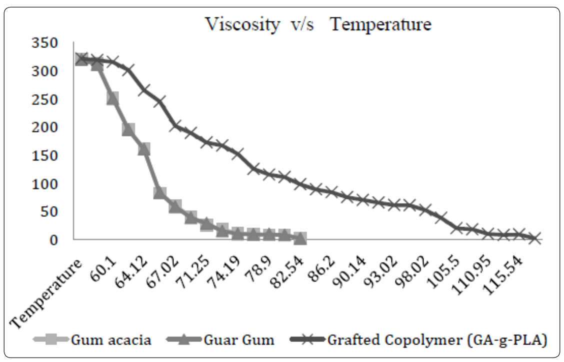

Figure 4

The results showed enhancement in the stability of viscosity as compared to Guar gum based foam fracturing fluid and Gum acacia based foam fracturing fluid. The guar gum and gum acacia has showed similar results to the formulated foam fracturing fluid. Grafted Copolymer imparted high viscosity due its long chain bonding with the formulation.

Shear rate and Shear stress

Shear rate and shear stress are used to determine the shear tolerance capacity of the foam. The shear rate and shear stress are carried out at different temperature ranges which are shown in fig 5 a), fig 5 b) and fig 5 c).

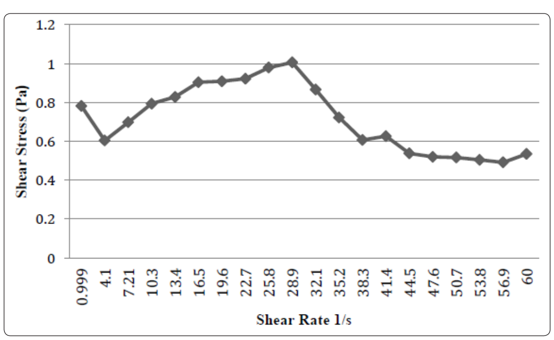

Figure 5 a): Shear Stress v/s Shear Rate at 140° F

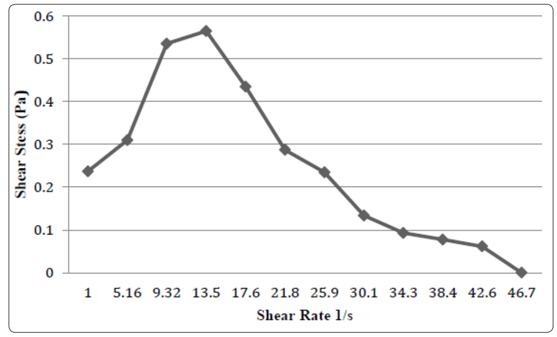

Figure 5 b): Shear Stress v/s Shear Rate at 176° F

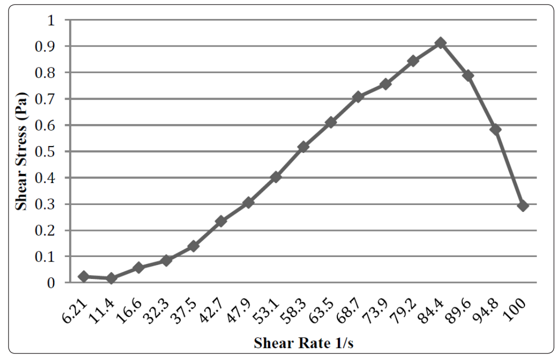

Figure 5 c): Shear Stress v/s Shear Rate at 220° F

Stability and Compatibility

The stability of the foam of the formulated fracturing fluid system was determined at 300° F and 8000-9000 psi. The High temperature test has been conducted in the Hot Air Oven and the High pressure has been done in Core flooding apparatus. The photo of the formulation before and after heating is shown in fig 6 a) and fig 6 b). After few minutes of heating at certain temperature the foam and the gel break down and at the end only small precipitates are left. The foam's breakdown time is called the half –life of the foam. It depends upon the foam quality and temperature. The variation in the half life with the increase in temperature is shown in fig. The results are compared with the conventional foam based fracturing fluid. The result were determined at a foam quality more than 90% and the result showed that the grafted copolymer based fluid has much more half-life time as compared to the conventional foam based fluid fig 7. The emulsion test was also carried out at 250° F and the test was continued for 24 hrs that without emulsion breakage.

Figure 6a: Before heating

Figure 6b: After heating

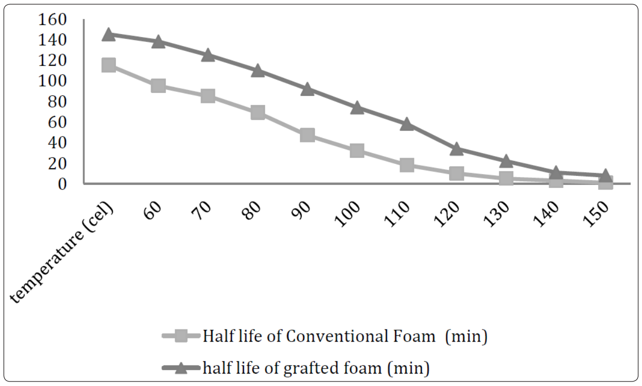

Figure 7: Half life v/s Temperature

Proppant carrying capacity

The proppant carrying capacity is on the main function for any fracturing fluid because the proppant are keep the fractures open to enhance the reservoir permeability which ultimately increases production from the unconventional reservoirs. Proppants generally increases the effectivesness of the well to increase its conductivity. However the effectiveness of hydraulic fracturing does not only depend upon the type of proppants used but also on the proppant carrying capacity of the fracturing fluid. The test was carried out in a conical flask to determine the proppant carrying capacity and with increase viscosity the proppant carrying capacity is found to be increased. So the foam based fracturing fluid has higher capacity to carry proppant than water based fracturing fluid. The results of the proppant carrying capacity are shown as the function of sedimentation time and velocity. The results of the grafted foam based fracturing fluid are compared with the water based and conventional foam based fracturing fluid and shown in Table 4. As per the results, as grafted foam has imparted more viscosity as compared to the conventional one so it showed slightly lower sedimentation time.

Table 4

Parameters	Water based fracturing fluid	Conventional Foam based fracturing fluid	Grafted CO_2 Foam based fracturing fluid
Height (cm)	12.7	15.5	15.5
Sedimentation Time (min)	18	210	340
Sedimentation Velocity (cm/s)	0.7055	0.07380	0.04558

Apart from the proppant carrying capacity the reservoir performance is also affected by proppant distribution. There are possibly three types of proppant distribution inside the fractures they are:

1. Distribution is uniform with high concentration of proppant.
2. Distribution is uniform with low concentration of proppant.
3. Distribution is uneven.

The Grafted Foam based fracturing fluids has higher viscosity than other water based and other non- foam based fracturing fluid which make it effective proppant carrying fracturing fluid.

Return Permeability

For testing the return permeability, Core flooding apparatus is used. The Core Flooding set up is shown in fig. In core flooding apparatus, the core is fixed in the core holder and kept in the core chamber where its temperature and overburden pressure is set. The core is kept at a temperature of 300°F and at 4000 psi overburden pressure so that HTHP reservoir condition can be achieved. The core is first flooded and saturated with brine (5wt % KCL) or formation water and the base permeability was established. The base permeability was found to be 50 mD. After the establishment of the base permeability, the Liquid CO_2 and the base gel foam was injected in the equal proportions and mixed in the tubes to achieve the desired emulsion. The formulation after mixing is injected in the core sample and at 3000 psi pressure the injection was stopped. After soaking for 2 hrs, the breaker solution was injected to the core to break the gels of the fracturing fluid and then the brine solution is injected again to displace the fluid. The differential pressure decreases as the fracturing fluid is started to displace. The final or return permeability is calculated and again the procedures are repeated to calculate the return permeability of the conventional water based fracturing fluid system. The results of the return permeability of Grafted CO_2 Foam based fracturing fluid and Conventional water based fracturing fluid system are compared and showed in Table 5.

Reduced permeability (Kr) = (Ki/Kf) x 100 %

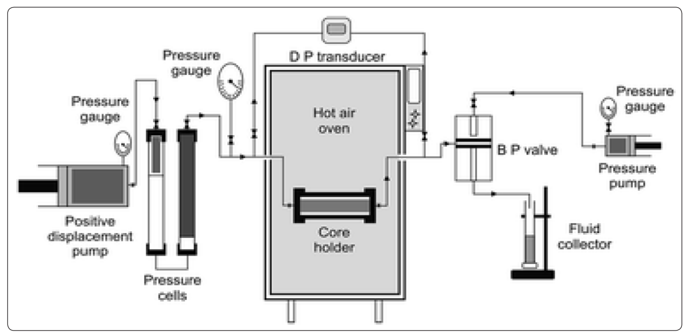

Figure 8

Table 5: Results of core flooding apparatus

Parameters	Water based Fracturing Fluid	Grafted CO_2 Foam based Fracturing fluid
Core Length	9.04 cm	9.04 cm
Core Diameter	3.07 cm	3.07 cm
Bulk Volume	13.37 cc	13.37cc
Porosity	0.13	0.13
Test Temperature	300° F	300° F
Intitial Permeability (Ki)	50 mD	50 mD
Final Permeability (Kf)	26 mD	41 mD
Reduced Permeability (Kr)	49 %	82 %

Conclusion

- The significant effect has been shown by the Grafted Copolymer on the rheological properties of the CO_2 foam based fracturing fluid due to the enhanced bonding of polymer with the formulation. The emulsion and viscosity was more stable at higher temperatures than conventional foam based fracturing fluid.
- The stability and compatibility of the grafted copolymer based foam is higher than conventional foam based fracturing fluid.

- The Proppant carrying capacity was increased with the increment of foam quality. The results showed that at foam quality of 80% & 70% proppant loading is 5.5% wt/v and 3%wt/v
- During the Core flood studies, it was found that the Grafted CO_2 Foam based fracturing fluid has shown reduced permeability value upto 82% which is comparable to other non-foam based fracturing fluids.
- The use of Graft Copolymer has enhanced the properties of foam based fracturing fluid. Ga-g-LA is a novel approach and has not been used in the well stimulation industry.
- Grafting has increased the stability of foam based fracturing fluid at higher temperature and pressure conditions which implies that it can be used in HTHP Unconventional Shale Reservoirs wells as a replacement of non-foam based fracturing fluid. This can be brought in practise in the coming time and can be used in the deep wells.

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