

# Novel Eco-friendly Linear Gel for Oil Well Recovery through Efficient Hydrofracturing

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## Abstract

A linear gel is prepared by treating bio-diesel with various water samples collected from different water bodies. The fresh biodiesel based linear gel was employed in the recovery of oil wells through hydrofracturing and pilot tests were conducted for the first time. The viscosity of gel was measured at various bottom hole-circulating temperatures and it was found to vary from 32 to zero dial reading in the range of 45°C to 60°C. The gel was observed to break at 45°C and 60°C in 120 min. So the final temperature was selected as 60°C for the application of gel for coal bed methane (CBM) wells. It was observed that higher levels of salinity in water helped in optimum utilization of gel in real-time application.

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**Keywords:** Bio-diesel, linear gel, slickwater, hydrofracturing, guar polymer, gel, breaker.

## 1. Introduction

Hydraulic fracturing deals with the pumping of gallons of fluid into oil or gas well at high pressure to induce fractures in the rock formation facilitating the liberation of oil or gas [1-4]. Until now, drinking water has always been the source of hydrofracturing operation. However, this strategy found to be different problems including water shortage and contamination [5-7]. Therefore, it is important to develop a hydrofracturing method with the not only recovery of water and decrease the water contamination but also capable to avoid microorganisms contamination.

Recently, polymers gel-based fracturing methods developed to avoid the above-mentioned problem. The polymers gel-based fracturing fluid undergoes enzymatic attack by the aerobic bacteria present in the base water [8-10]. Unless

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controlled, the growth of microorganism will make the polymer as non-functional. Therefore, biocides/bactericides are added to minimize bacterial contamination in the base water [11].

Currently, fossil diesel is used in the preparation of linear and cross-links gels, which are environmentally harmful and wasteful of natural resources [12-13]. Using fossil diesel for the preparation of frac concentration resulted in the release of harmful and contaminated carbon dioxide fumes that promotes the global warming condition which is a major drawback. Research reports that vegetable bio-diesel can be used as a substitute for fossil diesel [14-17]. The findings that were presented suggest that Biodiesel, an alternative eco-friendly fuel synthesized from “Jatropha seed” [18].

This research work explored to develop alternate methods for hydrofracturing process, which are feasible and eco-friendly. Pilot tests were also conducted for the first time by using the bio-diesel as the alternate fuel and are found to be more economical. Successful execution of pilot tests of the frac operations and the fruitful results are detailed. When compared with fossil diesel XLFC, the bio-diesel XLFC shows better and improved results for on-shore and off-shore fracturing operations.

## 2. Materials and methods

Various materials and reagents generally used in the preparation of linear gels, their purpose and characteristics are detailed as follows:

**Oil Based Fluid:** Bio-diesel, it is a continuous phase fluid. It is renewable and biodegradable fuel refined from vegetable oil consisting of long-chain alkyl esters. Bio-diesel prepared from chemically reacting lipids with vegetable oil [3].

**Dispersible agents:** Organophilic clay was prepared by reacting Smectite type clay with cation exchange capacity of at least 0.75 meq/g and methyl benzyl di-alkyl ammonium compound with 1.00 to 1.2 meq/g.

**Anti-sedimentation agent:** Iso tridecanoethoxylated is in liquid form. Buffering agents: Buffering agents is a base used to maintain the acidity of a fluid. It prevents a rapid change in pH when sodium acetate added to the fluid.

**Gelling agents:** The gelling agent used in the present study is guar gum, a polymeric substance derived from the seed of the plant. It is non-toxic in nature and is known to increase the viscosity of the medium.

**Breakers:** These fluids are used to reduce the fracturing fluid viscosity and normally mixed with the fluid while pumping.

**Gas Flow:** Following the completion of the hydrofracturing process, the fluid with composing of methanol 2-butoxyethanol, ethylene oxide, nonylphenol polymer alcohols, C12-16, ethoxylated tridecyl alcohol, nonylphenol ethoxylated nonionic surfactant will flow back.

**Biocide:** The polymeric gelling agents are mixed in water with biocides, bactericides to kill any existing microorganisms and to inhibit bacterial growth and deleterious enzyme production.

**Proppant:** 20/40 size proppant was used to open a hydraulic fracture with maximum permeability. This permeability depends upon proppant grain roundness, purity, and crush strength. Larger proppant volumes always help wider fractures to facilitate rapid flow back to the production well. In 30 min duration, 11000 pounds of fracturing fluid and of proppant were placed into the fracture.

## 3. Experimental studies

With an objective to investigate the suitability of water to prepare linear gel using biodiesel, water samples from different sources such as bore water, rainwater, seawater, produced water and river water were collected. The water samples from different sources were characterized by monitoring different physical and chemical quality parameters. Biocide was added to water samples to kill the bacteria before testing. Table 1 summarizes the results.

Table 1. Parameters of different water samples

Parameters	Produced water	Rainwater	River/canal water	Bore water	Seawater
Clarity, colour,	Clear	Clear	Not clear	Not clear	Not clear
Temp., °C	24	20	25	17	27
Sp. Gravity	1	1	1	1	1
Initial pH	7	5.4	7.67	7.44	8.1
Iron ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) ppm	1.1	NA	0.1	0.19	NA
Chloride, ppm	900	90	459	315	50000
Total Hardness, ppm	90	25	220	922	1000
Bicarbonate, ppm	820	120	150	119	900
Sulphates, ppm	160	40	70	400	120
TDS, ppm	700	300	150	1900	4100
Reducing Agent	Negative	Negative	Negative	Negative	Negative
Bacteria	500,000	400	30000	3000	100,000

NA- Not available

### 3.1. Synthesis of bio-biesel hydro frac solution

4.5 g of organophilic mud (anti-settling agent) was mixed with 309 ml of bio-diesel in a blender for 10 min at 1900-2000 rpm stirring. This solution was mixed with 2 ml of isotridecanoethoxylate (emulsifier), 5 ml of this additive and 60 g of sodium bicarbonate as a buffering agent. This mixture was thoroughly stirred for 15 min to make it lump-free. The addition of a buffering agent makes the slurry basic. 240 g of guar gum was added to the slurry with continuous mixing for 20 min so that it is free from any lumps. The density of the slurry was measured  $> 0.1$  ppg. The viscosity of the lump-free slurry was maintained at 250 (Supp. SF2).

### 3.2. Preparation of linear gel hydration

The preparation of the gel hydration process is illustrated in (Supp SF3 and SF4). Initially, 7.5 gpt bio-diesel frac was mixed in 1000 ml of the water in Chandler Engineering High-speed mixer at 2000 rpm. The resulting gel was agitated for 3 min and the viscosity was measured as 27 cp. The mixture was further agitated for 10 more minutes to obtain the viscosity as 32 cp. Table 2 summarizes the physical properties of bio-diesel frac concentration. High capacity water bath (PRECISDIG Company), Stop-watch (Fisher Scientific Company), Thermometer (Chandler Company) and pH meter (Chandler Company) were used for the studies. The viscosity of gel was measured using the Fann 35 Rheometer (Supp SF5) (Fann Company). The Funnel viscosity was measured by Marsh Funnel instrument, Fann company (Supp SF6) and found to be 110 s. After calibration, the viscosity of one quart of freshwater at  $70 \pm 5$  °F ( $21 \pm 3$ °C) was measured as  $26 \pm 0.5$ .

Table 2. Physical properties of bio-diesel frac concentration slurry

Specific Gravity	1.160
Slurry Density	9.750 ppg
Free Diesel	<2% (in 24 h)
Polymer Concentration	4.0 ppg
Flash Point	400°F (205°C)
Viscosity at 300 RPM	250 cp

## 4. Results and discussion

### 4.1. Breaker test

1ppt of Ammonium persulphate and 1gpt of Enzyme-G were mixed in a linear gel glass bottle and mixed well. The mixture was exposed to 60°C and 45°C separately and the viscosity was measured for 10 min interval. The gel breaking depends upon temperature (BHCT) and breaker concentration.

Guar gum and its derivatives like hydroxyl propyl guar (HPG), carboxymethylhydroxy propyl guar (CMHPG) are normally used as gelling agents in the fracturing fluids. Cellulose derivatives have also been tried as gelling agents in the form of like carboxy methylguar and hydroxyl ethyl cellulose.

### 4.2. Linear gel mechanism

This hydro fracturing operation initially starts with perforation with the help of coil tubing unit, it created fractures at zone-1, 2, and 3 like this entire well from top to bottom in production casing. In hydro fracturing operation, once linear gel was ready in hydration tank, the blender unit was collected the linear gel from hydration unit, 20-40 proppant moving slowly into blender from sand king unit, breakers (ammonium persulfate and Enzyme-G) flows into the blender, mix all together in the blender, the high-pressure pumps have displaced this fluid under pressure 3000 psi at the fluid rate was 3 to 4 barrel per minutes into well in 5 states within 40 min. While pumping this fluid, the linear gel viscosity was 30 cp checked by using a viscometer. So this linear gel has the ability to effectively transport proppant into well at fractures path filled with liner gel, proppant and breakers. The gel generates numerous small fissures in the shale thus liberating trapped gas which flows to the surface.

Ammonium persulphate (Oxidizer) and Enzyme-G reaction were taking place on the linear gel. One molecule of ammonium persulphate yields two free radicals per reaction. The free radicals released by persulphate reaction react upon susceptible and oxidizable bonds. The reactions involving free radicals are usually very rapid. It was observed that ammonium persulphate breakers are very reactive at temperatures 45°C and 60°C. During the reaction, the acetyl linkage bond gradually gets converted into monomers. So the linear gel ultimately becomes like water shown in figure 1. Enzyme-G was acting as to reduce the molecular weight of polymers to facilitate their removal from the formation without disturbing the proppant pack.

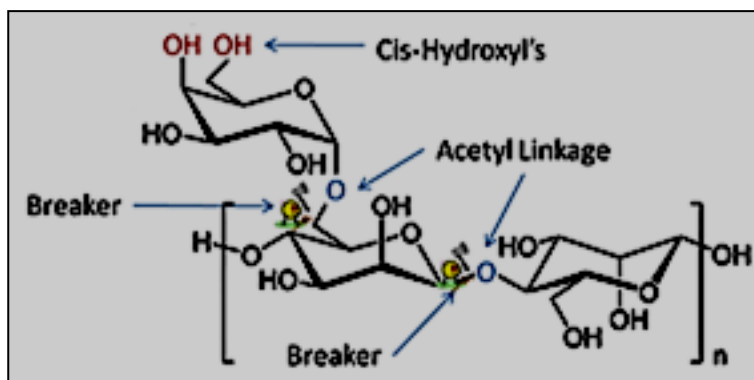


Fig. 1. Mechanism of linear gel with breakers

The structural dismantling of these polymers is effective by attacking the linkages among the mannose units and then the galactose and mannose units. The linkages in the polymer undergo cleavage and get converted to simple monosaccharide sugars on reduction as shown in fig. 1. After 2 hrs, the linear gel breaking and it became like water, it was flowing back to surface with help of gas flow solution.

### 4.3. Compatibility of linear gel with different water samples

7.5 gpt gel was taken in a rheometer and viscosity noted which was initially 32 cp. 1ppt oxidizer and 1gpt Enzyme-G were added to the breaker concentration, and pilot tests were conducted using different water samples (rainwater, river or canal water, bore water, produced water and seawater). The viscosity of gel measured at temperatures 45°C and 60°C, after 120 min period. Linear gel samples at different temperatures shown in Supp SF7 and SF8.

Pilot tests were conducted as follows: In pilot test 1, gel prepared with rainwater was used and it was broken very slowly. In the 120 min time, the viscosity was 23 cp at 60°C and 24 cp at 45°C. Details are provided in Tables format in the supplementary file (ST1). This was due to minimal ions in the rainwater. In test 2, the gel prepared with river water was employed. The viscosity was 15 cp at 60°C and 17 cp at 45°C, suggesting relatively faster degradation than gel with rainwater (ST2). In test 3, gel prepared with bore well water was examined. The gel viscosity values were 10 and 12 cp at 60°C and 45°C respectively, suggesting a faster degradation due to the presence of higher concentrations of anions and cations (ST3). In test 4, the gel was prepared with recycled water, which also known as “Produced Water”.

The contaminated water from the previous frac jobs was treated in the RO unit and was recycled back for utilization in various areas. This recycled water also referred to as flow backwater, which contains contaminants. The gel prepared with this water showed a significant drop in viscosity, because of contaminants. The recorded viscosity was 4 cp at 60°C and 6 cp at 45°C. The gel viscosity drop was sharp with produced water (ST4). Further, in test 5, the gel was prepared with seawater was assessed. The rate of the breaking of the fracturing fluid was found to be very fast and viscosity dropped to 1 cp at 60°C and 2 cp at 45°C. This was due to the presence of a high concentration of dissolved salts in seawater (ST5). There was no need to add any breakers to the linear gel when seawater was used in the gel preparation. In addition to the produced water, linear fluids were also successfully tried with seawater both in offshore and onshore operations.

The results of experiments with different water samples indicate that for the hydro frac operations, any water is workable, but with appropriate modifications (see fig. 2). Seawater is economically more cost-effective in offshore frac operations, as water is available on site and the use of breakers can be avoided.

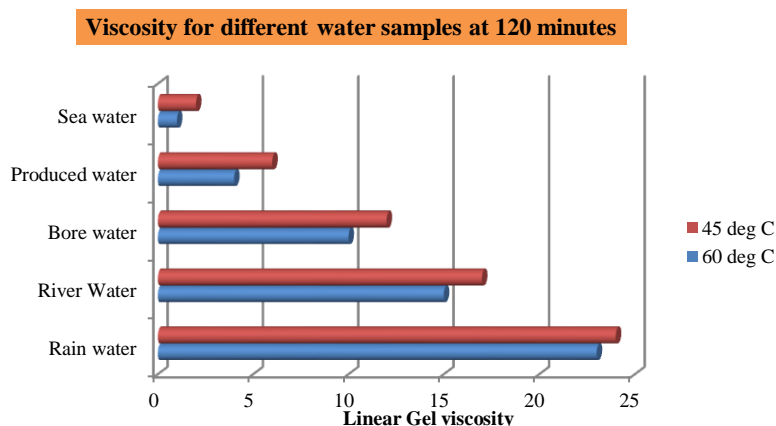


Fig. 2. Linear gel viscosity for different water samples at 120 min

A compatibility test of linear fracturing fluid system was successfully prepared with different kinds of water samples and implemented in oil field operations. Out of all the water samples, the sample collected from produced water source was found to be more economical. It is feasible to reuse that water, which could help to minimize water usage. Thus, it helps the environment by reducing produced water spills and contaminations [19]. The seawater-formulated fluids were found to be effective at different downhole temperatures and are compatible with a large variation in water TDS and hardness. The use of seawater significantly lower the operating cost and helped in produced water disposal.

#### 4.4. Hydrofracturing job

As the main objective of the study was to evaluate the degradation pattern of the fluid with gel breaking agents such as ammonium persulphate and enzyme-G, which act as oxidizers at the bottom hole circulating temperature. The frac concentration can be maintained for longer time periods and was less hazardous as its flashpoint was greater than 200°C.

The details of data related to the well are as follows:

Well name:	EDH-201 D1;
Zone-1:	Hydraulic Fracturing job;
Depth:	0 - 3000 meters;
Well head pressure:	0 - 7000 psi;
Fluid Rate (barrels per minute):	0 - 4 bpm;
Job duration time:	40 min;
Proppant loading (psa):	0 – 24;
Well temperature:	60°C and
Bottom hole sand ratio (psa):	0-0.8

The fracturing fluid starts to pumping with initial pressure was 1000 psi gradually the pumping rate increasing up to 3.5 barrel per min until the fluid-filled the fractures. After soaking, again the fluid was pumped for 20 min at 3.2 barrel per min. The calculated pressure is more than the actual pressure in this well and red and green colour lines indicate the respective profiles. Proppant ratio is the proppant concentration added to the fluid and BH sand ratio is the proppant concentration once it reached downhole as shown in fig. 3.

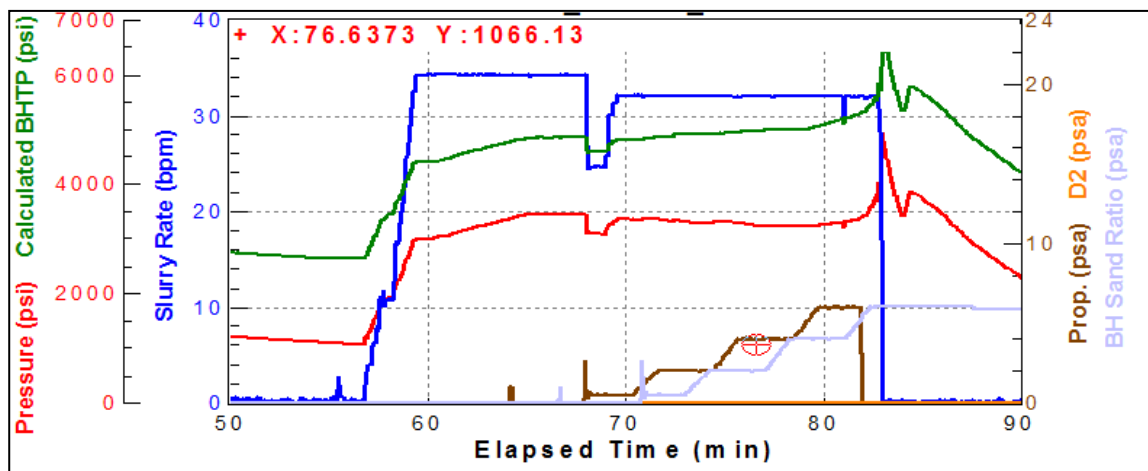


Fig.3. Hydraulic fracturing job graph in field

Fig. 4 illustrates and details the four steps involved in the well operations, which are drilling, cementing, fracturing by blasting and finally the fourth, which is the focus of the current study, the filling of cracks with frac fluid and sand. Fig. 5 further illustrates the details of the hydrofracturing job described in step 4 of fig. 4. The perusal of the illustration shows the successful pumping in of the linear gel and its settling at the target site through the hydrofracturing process, for the sand to keep the cracks open at the bottom of well.

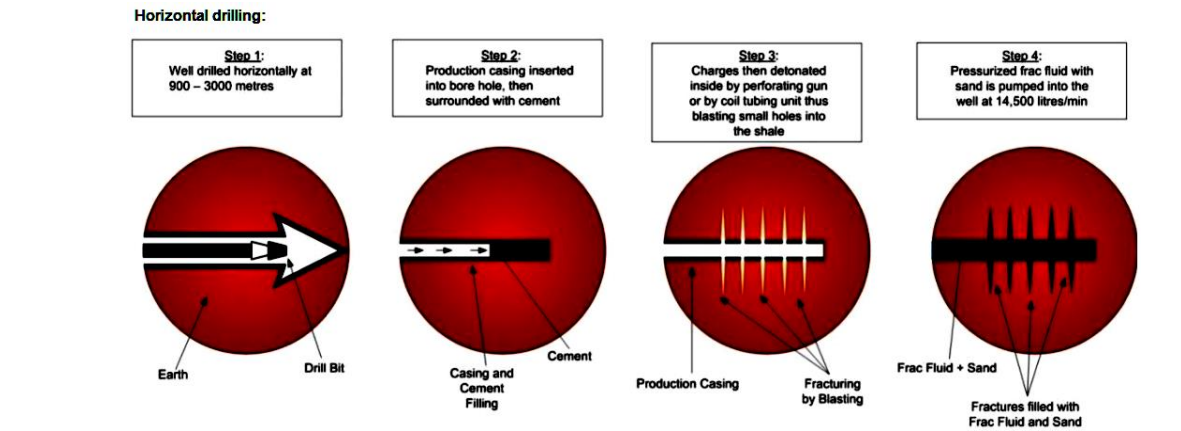


Fig. 4. Schematic diagram of sequential steps in horizontal drilling

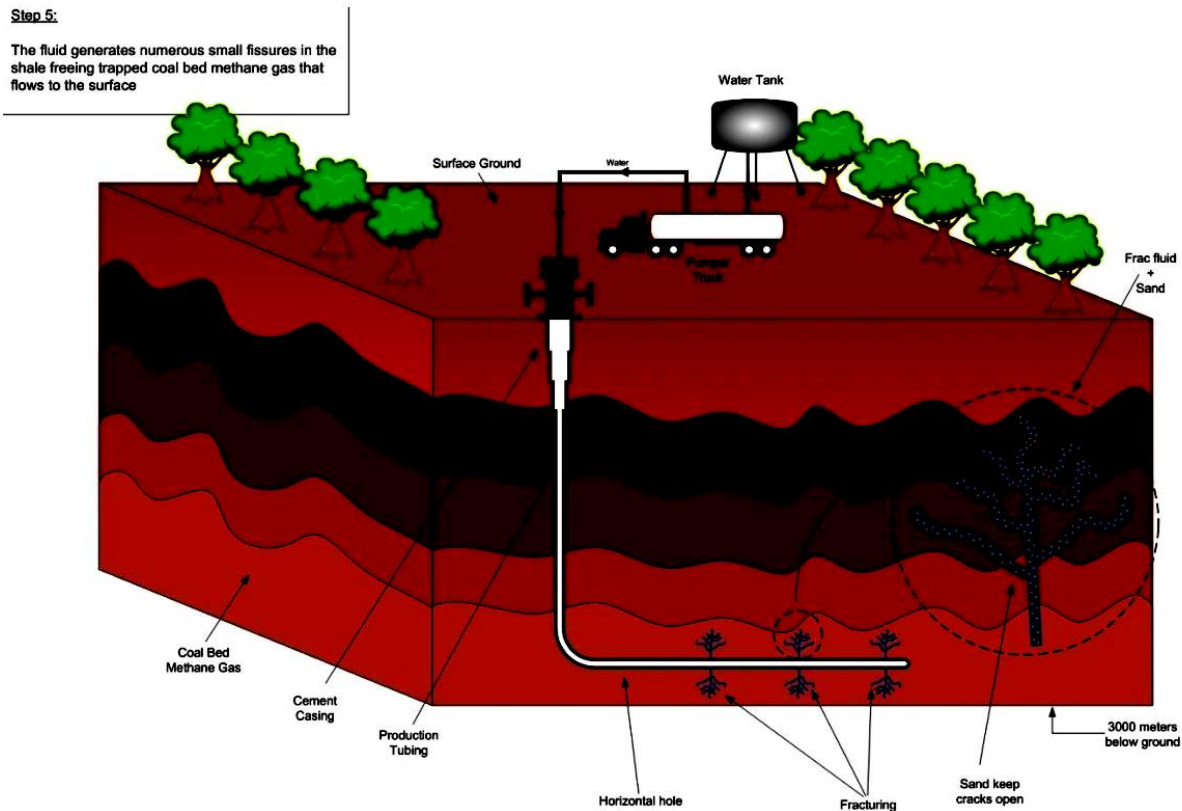


Fig. 5. Schematic diagram for process of hydraulic fracturing

## 5. Conclusion

We developed an efficient alternative method for hydrofracturing process by using novel linear gels, prepared with bio-diesel and water samples from different sources. Based on the improved results obtained in the pilot tests, several fluid systems were successfully implemented in various oil field operations. Using seawater with a gel made with biodiesel for hydrofracturing job is highly efficient and economical and gel needs no additional breakers. This method is a novel, eco-friendly, sustainable and advantageous as it saves freshwater usage.

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