



Preparation of Cross Linker Liquid Frac Concentration (XLFC-1B) with Different Hydrocarbons like Petrol, Diesel, Kerosene compatibility & Breaker Test by using oxidiser, breakers

R.V.V.Ramana Murthy¹, Naresh Kumar Katari^{2*}, P. Satya Karuna² and M.R.P.Reddy³

1. BJ & BHI Services, Kakinada, AP, **INDIA**

2. Department of Sciences & Humanities, VIGNAN University, Vadlamudi, Guntur-522 213, AP, **INDIA**

3. C-MET, IDA Phase-II, Cherlapally, Hyderabad, AP, **INDIA**

Email: ramanam023@gmail.com

Received on 5th April and finalized on 20th April 2013.

ABSTRACT

We have been studied different hydrocarbons solvents like petrol, diesel and kerosene. The solute is a gumming agent, agro material while preparation of frac concentration need to mix suspending agents and the concentration should be in basic nature. Sodium bicarbonate is mixed in the concentration to maintain the pH. These frac concentrations are conformed with API standards. After the preparation of concentration we can prepare Gel with 7.5gpt (Gallon per thousand). The initial viscosity should be 26cp according API standards. The oxidative & breaker are used in this research project with the main objective to study on breaking pattern of fracturing fluid (i.e. guar gum polymer gel) as a function of time temperature and breaker concentration itself. Usually the gelling agents in fracturing fluids are guar gum derivatives such as hydroxyl propyl guar and carboxy methyl hydroxyl propyl guar (or) cellulose derivatives such as carboxyl methyl guar, hydroxyl ethyl cellulose, hydroxy propyl cellulose, xanthangum. So this study provides focuses on the way to mix the fracturing fluid, compositions of fracturing fluid and how to conduct Linear (gel) and breaker test the Linear gel that indicates the optimum linear gel concentration to produce good viscosity Linear gel and the break test gave the characteristics of the gel during degradation process and also the breaking time. Ammonium per sulphate (Ammonium peroxidisulphate) & J-134 used as oxidation purpose to break the gel gradually at particular static temperature. Degradation pattern observed from the break test showed that reduction in gel viscosity depends on time, temperature & breaker concentration. In this experiment used different types of hydrocarbon solvents. Observations from experiments revealed that small concentration of breaker provides rapid break compared to oxidative breakers.

Keywords: Degradation, Fracturing fluids, breaker powder, guarpolymergel, oxidative solid.

INTRODUCTION

The main functions of fracturing fluids are to open the fracture and to transport propping agents long for length of the fracture. They are four types of fracturing i.e. water fracturing, gelled fluids, linear gels, crosslink gels [3]. The chemistry of commonly used fracturing fluids and additives are guar. Guar is along chain, High molecular weight. Gymer composed of Mannose and galactose sugars. The guar polymer has a

high affinity for water. When the powder added to water, the guar particles swell and hydrate, which means the polymer molecules become associated with many Water molecules and unfold and extend out into the solution which tends to overlap and hinder motion, which elevates the viscosity of the solution. Hydroxy propyl substitution makes more stable at an elevated temperature than guar, therefore Hydroxyl propyl guar is better suited for use in high temperature greater than 150°C wells. Another guar derivative used in recent year is carboxy methyl hydroxyl propyl guar. This "double derivatized" guar contains the hydroxyl propyl functionality of HPG as well as a carboxylic acid substituent. It is used for low temperature wells. Cellulose derivatives have occasionally been used in fracturing fluids. Hydroxy ethyl cellulose (HEC) or hydroxyl propyl cellulose (HPC) is used when a very clean fluid is desired. Still another type of polymer is Xanthan Gum. Xanthan is a biopolymer, produced metabolically by the microorganism. Xanthan solutions behave as power law property enables Xanthan solutions to suspend sand better than HPG[6]. So, guar is the most popular polymer for preparing aqueous-based fracturing fluid. The guar polymer has a very high affinity for water. The guar polymer easily dissolves in water and readily establishes hydrogen bond with the water molecules and gets hydrated. This Linear gel is comes under Non-Newtonian fluids defined as materials that do not conform to a direct proportionality between shear stress and shear rate. Consequently non-Newtonian fluids do not exhibit a simple[5]. Viscosity and their shear stress changes as fluid flow rate changes i.e. the apparent viscosity of the fluid becomes less and less as it is pumped faster and faster down a pipe[4]. The importance of guar is the most efficient friction reducer for all aqueous systems; guar is the only friction reducer that reduces leak-off[2]. It is also the most economical agent for obtaining high apparent viscosity. So that's way it is most widely used as a friction reducer for aqueous base stimulation fluids in this research project.

Chemical breakers used to reduce viscosity of guar are generally grouped into three classes: oxidizers, enzymes and acids[1]. All of these materials reduce the viscosity of the gel by breaking connective linkages in the guar polymer chain. Once the connective bonds in the polymer are broken, the resulting pieces of the original polymer chain are the same regardless of the type of breaker used. A breaker should be selected based on its performance in the temperature, pH, time and desired viscosity profile for each specific treatment.

MATERIALS AND METHODS

Experimental Studies

The work is performed in fracturing & cementing laboratories in Kakinada. The basic composition to make a guar from Vasundara guar gum from Rajasthan. For preparation of XLFC (Linear Frac Concentration). The required chemicals given - Vasundara guar gum, Hydro Carbons solvents like petrol, diesel, kerosene, vegetable oils, Sodium bicarbonate, Polymer suspending agent in solid state, Polymer suspending agent in liquid state, Ammonium persulphate, Slb beaker (J-134), Gas flow (Methanol content water solution), Tap water as the base fluid, Sanchora guar, Antibacterial agent.

Synthesis of Frac Concentration (XLFC-1B) for 500 ml: -Take any Hydrocarbons solvents like petrol, diesel, kerosene, mustard oil, palm oil, soybean oil, bio diesel. For example take fossil diesel 309 ml into blender. (The blender should be maintain 1900-2000 Revolution Per Minute).

- . Take 4.5 g poly suspending agent added to fossil diesel together slowly mix continuously for 10 minutes in blender. Poly suspending agent must be allowed to disperse and yield.
- . Take 2 ml poly suspending agent which is in liquid state, added to the blender agitate for 5 minutes. (While taking this poly suspending agent should be use in 5ml syringe).
- . Add 60 g buffer (sodium bicarbonate) and mix until the material is dispersed and lump free for 5minutes. After mixing sodium bicarbonate it should be maintain the pH in basic nature.
- . Add 240 g guar gum and continue the mixing for 30 minutes (or) until the concentration slurry is smooth and lump free.
- . Measure the density of the slurry after mixing. If the density of the slurry varies more than 0.1 ppg, refer to "Cut back (or) weight-up" charts to correct the slurry density.
- . Measure the viscosity of the slurry. It should be keep 250 cp in order to pump the slurry.



500 ml kerosene XLFC Diesel XLFC Petrol XLFC Veg. oil XLFC

Liner frac concentration slurry physical properties: The Standard Specifications are - specific gravity 1.144, Slurry density - 9.550ppg, Free Diesel - <2% at 44.5°C (after 24 Hrs), Flash Point- 60°C Viscosity at 300 rpm - <250cp, % settled solids in 24 hrs- No settled solids.

Water Analysis: Usually for every linear gel testing. We should check water quality because water will affect more during formation of gel Hydration. If water has more hardness leads to gel early break. So always water should check with standard methods. The following parameters should check before testing. The water should be colour less, the turbidity of water should be low and the water pH should be 7. The chloride is determined by titration methods or chlorides strips. The chlorides should be in the range upto 600 ppm. Iron can check by using electronic instrument. Iron should be range up to 5 ppm. Hardness can check by titration method and it should be in the range upto 600 ppm. Specific Gravity of water can be determined by Hygrometer.

Test1 (Tap water) : It is colour less, pH: 7.1, Chlorides: 200 ppm, Iron: 0.7 ppm, Hardness: 110 ppm and Specific gravity: 1

Viscosity measurement: A direct viscosity reading in centipoises (cp) was obtained by taking the 300 rpm reading of VG meter with Rheometer (FI spring, BI bob and Rotor). The viscosity of few gel was measured when the gel exhibit stringly and pourable behaviour. So the apparent viscosity of gel was determined using the Fann 35 Rheometer.

RESULTS AND DISCUSSION

While Preparing the XLFC (Linear Frac Concentration) we should take hydro carbons solvent because it will store more days and not expired So the Diesel, Petrol, Kerosene, keeping XLFC long storage.

XLFC with Petrol: XLFC prepared with petrol as a solvent, we check the Physical properties and Breaks test with breaking agent (Diammonium per oxide sulphate and Breaks) or ammonium per sulphate acts as a oxidiser and it breaks the linear gel gradually, another Breaker (J-134) is also acts a Breaker, it will breaks for linear gel gradually at certain temperature in water bath. The Petrol XLFC Physical Properties are - Specific gravity is 1.128, Slurry Density is 9.32 ppg, Viscosity at 300 rpm is 220 cp and Free Diesel <2% (after 24 Hrs).

Procedure for preparation of 1000ml gel Hydration (1gpt is equal to 1 gallon per 1000 gallons): Take 7.5ml Linear Frac concentration (XLFC) should mix with 1000 ml tap water by using Chandler engineering (or) Fann company high speed mixer at 2000 rpm while mixing the gel. Mix upto 3 min and stop, then check for viscosity by using Fann 30 viscometer at 300rpm. First time we get the viscosity reading is 23 centipoises (cp). Again the same gel put it in blender and re-start the mixing up to 7 minutes, after 7 min stop the mixing then check the viscosity. Second time we get the Viscosity reading is 25 cp. The Same gel again put it in Blender and re-start the mixing up to 10 min, after 10 min stop mixing then check the viscosity. So we get the final viscosity 26 cp.

Breaker Test (7.5 gpt- Linear Gel):

1 ppt Breaker is equal to 1 pound/1000x1 gallon = $1 \times 453.2 / 1000 \times 1 \times 3.782 = 453.2 / 3782 = 0.12 \text{ gm/lit}$ where 453.2 grams is factor, 1 gallon = 3.782 lit. 1 ppt Breaker: 0.12 gms/lit, ammonium per sulphate (oxidiser), 0.12 grams/lit J134 (Breaker). Maintain Water bath at 60°C and another water bath at 45°C temperature.

Transfer that 26 cp Linear Gel into glass bottle. Put it in water bath at 60°C temperature and add 1 PPT oxidiser and breaker into glass bottle. Now check the Viscosity for every 10 min.

Table 1. Petrol XLFC Breaker test

S.No	Gel Breaking Time (minutes)	Linear Gel Viscosity (cp)	
		1 ppt breaker 60°C	45°C
1	0	26 cp	26
2	10	26	25
3	20	24	24
4	30	21	22
5	40	17	21
6	50	15	18
7	60	13	16
8	1 1/2 hrs	11	14
9	2 hrs	8	12
10	24 hrs	0	1

XLFC with Diesel: XLFC prepared with Diesel as a solvent, we check the Physical properties and Breaker test with breaking agent (Diammonium per oxide sulphate and Breaker) or ammonium persulphate acts as a oxidiser and it breaks the linear gel gradually, another Breaker (J-134) is also acts a Breaker, it will breaks the linear gel gradually at certain temperature in water bath.

Diesel XLFC Physical Properties: Specific gravity is 1.144, Slurry Density is 9.550 ppg, Viscosity at 300 rpm is 250 cp, Free Diesel is <2% (after 24 Hrs)

Breaker Test (7.5 gpt- 30ppt Linear Gel): In 1 PPT Breaker, J134, take ammonium per sulphate (oxidiser).

Maintain Water baths one at 60°C and another at 45°C temperature. Transfer that 26 cp Linear Gel into glass bottle. Put it in water bath at 60°C temperature and add 1 PPT oxidiser and breaker into glass bottle. Now check the Viscosity for every 10 min.



7.5 gpt Gel (Diesel XLFC used)

Table :-2 Diesel XLFC Breaker test

S.No	Gel Breaking Time (minutes)	Linear Gel viscosity	
		1ppt breaker 60°C	45°C
1	0	26 cp	26
2	10	26	25
3	20	23	24
4	30	20	23
5	40	17	21
6	50	15	18
7	60	12	16
8	1 1/2hrs	7	15
9	2 hrs	4	13
10	24 hrs	0	1

XLFC with Kerosene: XLFC prepared with Kerosene as a solvent, we check the physical properties and Breaker test with breaking agent (Diammonium per oxide sulphate and Breaker) or ammonium persulphate acts as a oxidiser and it breaks the linear gel gradually, another Breaker (J-134) is also acts a Breaker, it will breaks the linear gel gradually at certain temperature in water bath.

Kerosene XLFC Physical Properties: Specific gravity is 1.135, Slurry Density is 9.450 ppg, Viscosity at 300 rpm 240 cp, Free Diesel is <2% (after 24 Hrs).

Breaker Test (7.5 gpt- 30ppt Linear Gel): Take in 1 PPT Breaker, J134, 0.12g ammonium per sulphate (oxidiser). Maintain Water baths one at 60°C and another at 45°C temperature.

Table:-3 Kerosene XLFC Breaker test

S.No	Gel Breaking Time (minutes)	Linear Gel viscosity 1ppt breaker	
		60°C	45°C
1	0	26 cp	26
2	10	26	25
3	20	24	24
4	30	22	23
5	40	18	22
6	50	16	20
7	60	13	17
8	1 1/2hrs	11	15
9	2 hrs	8	13
10	24 hrs	0	1

Transfer that 26 cp Linear Gel into glass bottle put it in water bath at 60°C temperature and add 1 PPT oxidiser and breaker into glass bottle. Now check the Viscosity for every 10 minutes.

XLFC with Soybean (veg. oil): XLFC prepared with Soybeans oil as a solvent, we check the Physical properties and Breaker test with breaking agent (diammonium per oxide sulphate and Breaker) or ammonium persulphate acts as an oxidiser and it breaks the linear gel gradually, another Breaker (J-134) is also acts a Breaker, it will breaks the linear gel gradually at certain temperature in water bath.

Soya bean (veg. oil) XLFC Physical Properties: Specific gravity is 1.241, Surry Density is 9.635 ppg, Viscosity at 300 rpm is 300 cp and Free Diesel is <2% (after 24 Hrs)

Breaker Test (7.5 gpt- 30ppt Linear Gel): Take in 1 PPT Breaker, J134, 0.12g L⁻¹ ammonium per sulphate (oxidiser). Maintain Water baths one at 60°C and another at 45°C temperature.

Table:-4 Veg oil XLFC Breaker test

S.No	Gel Breaking Time (minutes)	Linear Gel 1ppt breaker	
		60°C	45°C
1	0	26 cp	26
2	10	26	26
3	20	26	26
4	30	25	25
5	40	23	24
6	50	21	23
7	60	19	22
8	1 1/2hrs	17	20
9	2 hrs	15	18
10	24 hrs	2	2

Transfer that 26 cp Linear Gel into glass bottle. Put it in water bath at 60°C Temperature and add 1 PPT oxidiser and breaker into glass bottle. Now check the Viscosity for every 10 minutes

XLFC with Mustered oil: XLFC prepared with Mustered oil as a solvent, we check the Physical properties and Breaker test with breaking agent (Diammonium per oxide sulphate and Breaker) or ammonium persulphate acts as a oxidiser and it breaks the linear gel gradually, another Breaker (J-134) is also acts a Breaker, it will Breaks the linear gel gradually at certain temperature in water bath.

Mustered oil XLFC physical Properties: Specific gravity is 1.211, Surry Density is 9.592 ppg, Viscosity at 300 rpm is 290 cp, Free Diesel is <2% (after 24 Hrs).

Breaker Test (7.5 gpt- 30ppt Linear Gel): Take in 1 PPT Breaker, J134, 0.12g L⁻¹ diammonium oxi sulphate (oxidiser). Maintain Water baths one at 60°C and another at 45°Ctemperature.

Table:-5 Mustered oil XLFC Breaker test

S.No	Gel Breaking Time (minutes)	Linear gel Viscosity (cp) 1ppt breaker	
		60°C	45°C
1	0	30 cp	30
2	10	30	30
3	20	28	28
4	30	26	28
5	40	22	26
6	50	18	22
7	60	17	20
8	1 1/2hrs	15	18
9	2 hrs	12	16
10	24 hrs	2	2

Transfer that 26 cp Linear Gel into glass bottle. Put it in water bath at 60°C Temperature and add 1 PPT oxidiser and breaker into glass bottle. Now check the Viscosity for every 10 minutes.

XLFC with Bio Diesel: XLFC prepared with Bio Diesel as a solvent, we check the Physical properties and Breaker test with breaking agent (Diammonium per oxide sulphate and Breaker) or ammonium per sulphate acts as a oxidiser and it breaks the linear gel gradually, another Breaker (J-134) is also acts a Breaker, it will breaks the linear gel gradually at certain temperature in water bath.

Bio Diesel XLFC Physical Properties: Specific gravity is 1.145, Slurry Density is 9.553 ppg, Viscosity at 300 rpm is 260 cp, Free Diesel is <2% (after 24 Hrs).

Breaker Test (7.5 gpt- 30ppt Linear Gel): Take in 1 PPT Breaker, J134, 0.12 g L⁻¹ diammonium oxi sulphate (oxidiser). Maintain Water baths one at 60°C and another at 45°C temperature.

Table:-6 Bio diesel XLFC Breaker test

S.No.	Gel Breaking Time (minutes)	Linear Gel 1ppt breaker 60°C	Viscosity (cp) 45°C
1	0	26 cp	26 cp
2	10	26	25
3	20	23	24
4	30	20	23
5	40	17	21

6	50	15	18
7	60	12	16
8	1 1/2hrs	7	15
9	2 hrs	4	13
10	24 hrs.	0	1

Transfer that 26 cp Linear Gel into glass bottle. Put it in water bath at 60°C Temperature and add 1 PPT oxidiser and breaker into glass bottle. Now check the Viscosity for every 10 minutes.

Blank Test: Without Breaker (Diesel XLFC used) water bath at 60°C & another water bath at 45°C Temperature.

Table: 7 Diesel XLFC Breaker test (without breaker)

S.No.	Gel Breaking Time (minutes)	Linear Gel 60°C	Viscosity (cp) 45°C
1	0	28 cp	28cp
2	10	28	28
3	20	28	28
4	30	28	28
5	40	27	27
6	50	26	27
7	60	25	26
8	1 1/2hrs	24	25
9	2 hrs	21	22
10	24 hrs	15	17

APPLICATIONS

When compared with fossil Diesel XLFC and few mustered oil XLFC, the results are good and economically reasonable price. Frac operation is applicable and is economical.

CONCLUSIONS

The first objective of this research was the preparation of linear frac concentrations with different Hydro carbon solvents and prepared Linear fracturing fluid (guar polymer gel). The second objective was to conduct a comprehensive study to evaluate free degradation pattern of fracturing fluid (using oxidisers, breakers) as a function of temperature, time and breaker concentration itself. The third objective was to make a comparison study on different solvents like petrol, diesel, kerosene, vegetable oil (soybean) XLFC applied at different temperatures, breaker test (Breakers using oxidiser J134) properties based on research and experiment results obtained. The compatibility of fossil diesel and Bio diesel used for preparation of XLFC almost similar physical properties obtained. During Breaker that under two different temperatures were used at 60°C and 45°C. The oxidative agent Ammonium Disulphate J134 Breaker with 1 ppt we got good results when compared to fossil diesel bio diesel is less expensive, more availability & friendly nature. So we can suggest to use in frac operations.

When compared with fossil Diesel XLFC and kerosene XLFC, kerosene XLFC is also five results obtained. During the preparation of XLFC, it mixes well, no settling observed after 24 Hrs. good viscosities, during Breaker test carried at 60°C & 45°C. The oxidative agent like Ammonium proxy

disulphate & J134 shows good degradation property. During few reaction process we got good results, so when compare to fossil diesel kerosene is cheap, un availability and not friendly nature.

ACKNOWLEDGMENT

The authors (s) wish to express their appreciation to BJ & BHI services frac & cementing Department, Essar oils, SLB for supporting their research project by providing the chemicals. We also express our thanks to Kakinada lab, Mumbai lab, Baroda lab and Barmer lab team members for providing assistance throughout this research.

REFERENCES

- [1] Reservoirs stimulation John Wiley and sons, New York, Geothermal chemistry Symposium
- [2] Phoenix, Arijona, USA, Oil field papers.
- [3] The Bakken oil field, Hydraulic fracturing Moratorium implications. Fort Peck fracturing fluids
- [4] J.F.R Jacob fracturing fluids. Prof.K.Ramesh Engineering fracture Mechanics
- [5] Elements of fracture of mechanics - Prashant kumar-MC graw Hill
- [6] Faraz Adil, Ajay Sharma & Sumit bhat, Hydraulic fracturing of CMB wells.