

Fracturing Fluid (Guar Polymer Gel) Degradation Study by using Oxidative and Enzyme Breaker

Aung Kyaw, Bibi Syabila Binti Nor Azahar and Saleem Qadir Tunio

Faculty of Geoscience and Petroleum Engineering, Universiti Teknologi PETRONAS, Malaysia

Abstract: Oxidative and enzyme breakers are used in this research project with the main objective to study on the degradation pattern of fracturing fluid (i.e., guar polymer gel) as a function of time, temperature and breaker concentration itself. The fracturing fluid used in hydraulic fracturing or frac pack contain a chemical breakers to reduce the viscosity of the fluid intermingled with the proppant. Chemical breakers reduce viscosity of the guar polymer by cleaving the polymer into small-molecular-weight fragments. The reduction of viscosity will facilitate the flow-back of residual polymer providing rapid recovery of polymer from proppant pack. Ineffective breakers or misapplication of breakers can result in screen-outs or flow-back of viscous fluids both of which can significantly decrease the well productivity. Breaker activity of low to medium temperature range oxidative and enzyme breaker systems was evaluated. ViCon NF an oxidative breaker (Halliburton product) and GBW 12- CD an enzyme breaker (BJ Services product) were used in this research project with the main objective to study on the degradation pattern of fracturing fluid (guar polymer gel) as a function of (time, temperature and breaker concentration itself). This study provides focuses on the way to mix the fracturing fluid, compositions of the fracturing fluid and how to conduct the crosslink and break test. Crosslink test indicate the optimum cross-linker concentration to produce good crosslink gel and the break test gave the characteristic of the gel during degradation process and also the break time. Besides relying on the laboratory experiment, information obtained from research on SPE and US Pattern papers were used to make a comparison study on oxidative and enzyme breakers properties. Degradation pattern observed from the break test showed that reduction in gel viscosity depends on time, temperature and breaker concentration. Observations from experiment also revealed that small concentration of enzyme breakers provides rapid break compared to oxidative breakers.

Key words: Degradation, enzyme breaker, fracturing fluid, guar polymer gel, oxidative

INTRODUCTION

Hydraulic fracturing commonly referred to as fracking is a proven technology to enhance productivity and maximize recovery in oil and gas wells. Hydraulic fracturing method is almost the same as frac pack but differ in term of treatment purpose. Frac pack is aimed for sand control while hydraulic fracturing is to stimulate the well. 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.

The hydration of the polymer particles causes it to swell, exposing more sites on the guar to establish more hydrogen bonds with the water molecule. The hydration of the polymer continues until each guar molecule is well bonded with water molecule.

The fracturing fluid has a sufficiently high viscosity to penetrate into the formation to realize the fracturing and to retain the proppant in suspension or at least to reduce the tendency of the proppant to settle out of the

fracturing fluid. After the high viscosity fracturing fluid has been pumped into the formation and the fracturing of the formation has been obtained, it is desirable to remove the fluid from the formation to allow hydrocarbons production through the new fractures. Generally, the removal of the highly viscous fracturing fluid is realized by “breaking” the gel or emulsion or, in other words, by converting the fracturing fluid into a low viscosity fluid. Breaking the gelled or emulsified fracturing fluid has commonly been obtained by adding a “breaker,” that is, a viscosity-reducing agent, to the fracturing fluid.

Chemical breakers used to reduce viscosity of guar are generally grouped into three classes: oxidizers, enzymes and acids. 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. (Halliburton Energy Services, 2005).

However, improper selection of breaker can be unreliable and at times result in incomplete breaking of the fluid and/or premature breaking of the fluid before the fracturing process is complete. Premature breaking can cause a decrease in the number of fractures obtained and thus, the amount of hydrocarbon recovery.

Size exclusion chromatography method was used by (Gall and Raible, 1985) to determine the decrease in molecular size of the broken polymers. The study revealed that partially broken or unbroken polymer can cause significant reduction of flow through a porous medium and the insoluble residue that was generated during the degradation of guar polymers can affect the pore size of the medium. This is something interesting to note that polymers containing naturally occurring residue require greater reduction in molecular weight than the ones without residue. (Gall and Raible, 1985) also states that viscosity reduction does not necessarily mean that proppant pack damage will not occur because the amount of breakers used typically are insufficient to break the polymer completely.

This study focuses on two types of test. First is the crosslink test to determine the optimum crosslinker accelerator concentration to give good crosslink gel. Second is break time test for each type of breakers at 140°F and 200°F temperature.

MATERIALS AND METHODS

Experimental studies: This research is performed in Universiti Teknologi PETRONAS (UTP) Laboratories in 2011. All materials used for this research project except enzyme breaker were provided by Halliburton Energy Services. Enzyme breaker was provided by BJ Services. The basic composition to make a guar polymer gel include:

- Tap water as the base fluid
- Guar polymer : LGC-16
- pH buffer : MO-67 and BA-20
- Crosslinker : CL-28M
- Crosslinker accelerator : CL-28M
- Oxidative breaker : ViCon NF
- Enzymatic breaker : GBW 12-CD

Crosslink test:

- Proper amount of gel was measured and mixed into 6% NaCl brine.
- Acidic buffer was added to bring down the pH to about 5-6.
- The gel was circulated at low speed for about 30 mins to allow complete hydration of the gel.
- The required amount of alkaline buffer was added to raise the pH up to about 10-11.

- Crosslinker concentration was fixed to 3.0 gal/Mgal and crosslinker accelerator concentration was varied to get the optimum crosslinker accelerator concentration to give good crosslinked gel.

Break time test:

- Liner gel was prepared by following the crosslink procedure stated from step i to iv.
- Breaker was added first before crosslinker and crosslinker accelerator.

If breaker is added after the crosslinker, the breaker could not dissolve properly since the molecular chains in the gel have been crosslinked to each other:

- The gel was mixed in the blender until vortex has closed.
- Lip test was performed in glass sample jar until the gel shown strong crosslink by the gel hanging at least one inch over the mouth of the jar and returned easily.
- The mixture was poured into bottles and placed in a preheated water bath to observe the degradation pattern and determine the break time.

pH determination: pH adjusters usually implored to adjust the pH of fracturing fluids. pH strips or pH meter were used for a quick pH check.

Viscosity measurement: The viscosity of the gel was measured when the gel exhibit stringy and pourable behavior. Stringy and pourable was characterized when the gel was almost like water but it still stick together like slime with apparent viscosity >10cp. The apparent viscosity of gel was determined using the Fann 35 Viscometer. A direct viscosity reading in centipoises (cp) was obtained by taking the 300rpm reading of VG meters with F1 spring, B1 bob and R1 rotor.

RESULTS AND DISCUSSION

Crosslink test: The initial crosslink concentration of 0.4gal/Mgal CL-31 could not achieve a clean jar crosslink, hence the concentration were slightly increased to achieve a clean jar crosslink gel. A clean jar crosslink was finally achieved using 0.8 gal/Mgal CL-31 and 3 gal/Mgal of CL-28TM. Thus, CL-31 concentration of 0.8 gal/Mgal will be fixed to be used in preparing all samples required for break test. Result for crosslink test was tabulated in Table 1.

Break time test: Break time test was conducted using two types of breakers. ViCon NF an oxidative breaker and GBW 12-CD a hemicelluloses enzyme were tested with

Table 1: Crosslink test

CL-31 conc	Gel crosslink	Vortex closure	Clean test time	Lip jar test
0.4	Crosslink but not	-	-	-
0.5	Crosslink but not	-	-	-
0.8	Good crosslink	4 s	25 s	1.35 min
1.50	ver crosslink	-	-	-

Table 2: Pilot test 1 at 200°F using ViCon NF (oxidative breaker)

Breakers conc. Gel description @ 200°F, (min)											
No	ViCon NF (gal/Mgal)	0	30	60	90	120	150	180	210	240	
Control	0	C	C	C	C	C	C	C	C	C	
A	1	C	C	C	C	C	WC	WC	WC	WC	
B	5	C	C	C	C	WC	S	S	S	S	
C	10	C	C	C	WC	WC	S	S	S	S	

Table 3: Pilot test 2 at 200°F using combination of ViCon NF (oxidative breaker) and CAT-3(breaker activator)

Breakers conc. Gel description @ 200°F, (min)											
No	ViCon NF (gal/Mgal)	CAT-3 (gal/Mgal)	0	30	60	90	120	150	180	210	240
Control	0	0	C	C	C	C	C	C	C	C	C
G	10	0.2	C	C	C	WC	S	S	SP	SP	B(5cp)

Table 4: Pilot test 3 at 140°F using ViCon NF (oxidative breaker)

Breakers conc. Gel description @ 200°F, (min)											
No	ViCon NF (gal/Mgal)	0	30	60	90	120	150	180	210	240	
Control	0	C	C	C	C	C	C	C	C	C	
A	1	C	C	C	C	C	C	C	C	C	
B	5	C	C	C	C	C	C	C	C	WC	
C	10	C	C	C	C	C	C	WC	WC	WC	

40gal/Mgal gels at two different working temperatures, i.e., 140°F and 200°F. However, during experiment enzyme breaker was found to degrade upon the addition of breaker at ambient temperature. Thus, another test for enzyme was conducted at ambient temperature and brought for heated at 200°F. These results are shown in Table 2 to 7.

Pilot test 1 (Table 2): ViCon NF (oxidative breaker) at 200°F.

Result showed that a break-time of 4 h cannot be achieved by using the oxidative breaker (ViCon NF) alone. Thus, another test was conducted to see the break behavior of the gel when 10 gal/Mgal of oxidative breaker was used together with breaker activator (CAT-3). Also interesting to note was breaker concentration influenced the break time test. The higher the concentration of the breaker, the more rapid the fluid system (fracturing fluid) degrade.

Pilot test 2 (Table 3): Combination of ViCon NF (oxidative breaker) and CAT-3 (breaker activator) at 200°F.

The result revealed that ViCon NF (breaker) concentration at 10 and 0.2 gal/Mgal of CAT-3 (breaker activator) resulted in a comparatively break profile in four hours. While the control test without any breaker or

activator showed that the fluid maintained viscosity for more than 4 h. Thus, it was determined that this fluid system, at the given temperature, can only be broken by a combination of ViCon NF (breaker) and CAT-3 (breaker activator).

Pilot test 3 (Table 4): ViCon NF (oxidative breaker) at 140°F.

Result from this 3rd pilot test was as expected. The fluid system did not break within 4 h since ViCon NF is premiere breaker at temperatures above 200°F. Stated in Halliburton breaker bulletin, ViCon can be run below 200°F with an activator. Thus to achieve break time within 4 h, it is needed to combine the ViCon NF with any activator for example CAT-3. Again from this test also, it can be seen that the degradation of the fluid system was influenced by breaker concentration.

Pilot test 4 (Table 5): GBW 12-CD (enzyme breaker) at 200°F.

As can be observed from the Table 5 result, 5 and 10 gal/Mgal concentration of GBW 12-CD broke the fluid in just 30 min. This bring to the conclusion, lower concentrations are required for GBW 12-CD (enzyme) to achieve the same results as the ViCon NF (oxidative breaker) at the same temperature. GBW 12-CD also effective at temperature close to ambient temperature (equal to room temperature) as the fluids were no more cross-linked at 0 min before the fluids were left heated in the oven.

Pilot test 5 (Table 6): GBW 12-CD (enzyme breaker) at 140°F.

The enzyme reaction in breaking the fracturing fluid was found to be very fast. It causes an almost immediate reduction in viscosity when added to the fluid system. However compared to Pilot Test 4, the degradation of the gel in this test seems to be faster than it supposed to be slow. It is predicted the gel will take longer time to break in 140°F temperature compared to 200°F. It was probably because the concentration of CL-31 (crosslinker accelerator) used for this test was a bit low from the concentration used in the previous one. Thus it took less time for the gel to break.

Pilot test 6 (Table 7): GBW 12-CD (enzyme breaker) at ambient and 140°F temperature.

From the observation in sample C & D, enzyme breaker reacts actively at ambient temperature as it degraded instantaneously over the gel after breaker was injected into it. This is because enzyme breakers are protein based so they will react at room temperature. However, the gel from sample A and B seems to regain viscosity when they were heated and maintained stringy when subjected to longer heating. Therefore, we can

Table 5: Pilot test 4 at 200°F using GBW 12-CD (enzyme breaker)

No	Breakers conc. GBW 12-CD (gal/Mgal)	Pilot test 1 - gel description @ 200°F, (min)									
		0	15	30	60	90	120	150	180	210	240
Control	0	C	C	C	C	C	C	C	C	C	C
A	1	C	C	C	WC	WC	WC	S	S	S	S
D	5	WC	SP(13cp)	B(10cp)							
E	10	SSP(11cp)	B(9cp)								

Table 6: Pilot test 5 at 140°F using GBW 12-CD (enzyme breaker)

No	Breakers conc. GBW 12-CD (gal/Mgal)	Pilot test 1 - gel description @ 140°F, (min)									
		0	15	30	60	90	120	150	180	210	240
Control	0	C	C	C	C	C	C	C	C	C	C
A	5	S(20cp)	B(10cp)								
B	10	S(19cp)	B(7cp)								

Table 7: Pilot test 6 at ambient and 200°F temperature using GBW 12-CD (enzyme breaker)

No	Breakers conc. GBW 12-CD (gal/Mgal)	Gel description @ ambient			Gel description @ 200°F, (min)						
		0	15	30	0	15	30	45	105	165	240
Control	0	C	C	C	C	C	C	C	C	C	C
A	2				WC	S(23cp)	S(35cp)	S(50cp)	S	S	S
B	3				WC	S(21cp)	S(31cp)	S(49cp)	S	S	S
C	4	WC	S(24cp)	SP(20cp)	SP	B(10cp)					
D	8	S(24cp)	B(7cp)								

conclude that the higher the temperature and the longer the heating is continued, the less efficient for the fluid to break as the enzymes has been denatures.

Research from SPE 140520 paper: This research study designed a residue-after-break test to determine the amount of unbroken gel and residue generated after the gel is broken. The final result found that enzyme breaker provides an overall better break than oxidizers and generate less amount of residue. This support the observation seen in the break test experiment for ViCon NF and GBW 12-CD that GBW 12-CD breaker gave a cleaner and homogeneous break of the polymer compared to ViCon NF breaker.

CONCLUSION

The first objective of this research was to determine the composition of cross-linked fracturing fluid (guar polymer gel). The second objective was to conduct a comprehensive study to evaluate the degradation pattern of fracturing fluid (using oxidative and enzyme breakers) as a function of time, temperature and breaker concentration itself. The third objective was to make a comparison study on oxidative and enzyme breaker properties based on the research and experimental results obtained.

An initial testing to determine optimum crosslinker accelerator concentration from crosslink test was carried out as a part to determine right composition of cross-linked fracturing fluid. An extensive amount of testing was done with oxidative breaker (ViCon NF) and enzymatic breaker (GBW 12-CD). A wide range of

breaker concentrations and two different temperatures were used. Break test and viscosity measurement were done to evaluate breaker activity. The following conclusions can be drawn from this study:

- Thorough study on the composition of fracturing fluid resulted out that the main composition of the fracturing
- fluid (guar polymer gel) were water, a guar gelling agent, crosslinker and a breaker. Other important chemical used were acidic buffer to hydrate the linear gel to pH 5 and alkaline buffer to bring up the pH to pH 10 for proper cross-linking. The concentration of crosslinker/crosslinker accelerator is determined from crosslink time test for the final fluid recipe design.
- Break time test using oxidative (ViCon NF) breaker was showing that the guar polymer gel degradation time is a function of breaker concentration and temperature. This information can be used as a guideline for designing fracturing fluids with specific break times using this breaker. ViCon NF was also found to be less reactive at temperature below 200°F. Thus for temperature below 200°F, ViCon NF usage should be combined with breaker activator or breaker catalyst such as CAT-3 (a Halliburton trade product) to activate ViCon NF or otherwise the degradation process would be very slow. In other words, the breaker activator is used to expedite the break time of fracturing fluid.
- Break time test using enzymatic (GBW 12-CD) breaker, a hemicelluloses class was showing that enzymes were active at ambient temperature as they begin to degrade the polymer immediately upon

mixing. The results also revealed that at upon longer and high temperature heated (200°F), the polymer degradation reduced slowly because of denaturing (permanent loss of the 3D structure) of the enzyme. Above 200°F, (Economides and Nolte, 2000) high enzyme concentrations are required due to denature of the enzyme. The break time test also showed more degradation viscosity with increase in enzyme breaker concentration.

- The used of enzyme alone in frac pack and hydraulic fracturing treatment will probably result a premature viscosity loss because of it is extremely reactive when first introduced into the fluid, before it heats up in the reservoir. The result obtained from pilot test 4 can be used to prove this probable phenomenon in a real fracturing treatment as the polymer gel with 5gal/Mgal of enzyme breaker was prematurely lost the viscosity and exhibit weak crosslink before being heated at 200°F.
- Based on the residue-after-break tests from SPE 140520, a clear comparison between oxidative and enzymatic breaker can be seen where enzyme was found to produce less residue than the oxidative breakers. These tests indicate that the enzymatic breaker can provide a cleaner, more homogenous break of the polymer compared to oxidative breakers, used at the same temperatures. This finding was clearly in line and support the theoretical fact pointed

out by Economides and Nolte (2000) that polymer degradation by enzyme breaker might go on for a longer time and be more complete than with an oxidizer.

ACKNOWLEDGMENT

The author(s) wish to express their appreciation to Halliburton Energy Services and BJ Services for supporting this research project by providing the chemicals. Also, the authors would like to thank Universiti Teknologi PETRONAS, Indran Pathmanathan and Geok Cheen Woon (Halliburton engineers) for providing assistance throughout this research.

REFERENCES

- Economides, M.J. and K.G. Nolte, 2000. Reservoir Stimulation. John Wiley and Sons, New York.
- Gall, B.L. and C.J. Raible, 1985. Molecular Size Studies of Degraded Fracturing Fluid Polymers. Paper no. SPE 13566, Presented at the SPE Oildfield and Geothermal Chemistry Symposium, Phoenix, Arizona, USA (April 9-11, 1985).
- Halliburton Energy Services, 2005. Retrieved from: www.halliburton.com/public/pe/contents/Data_Sheets/web/H/H05000.pdf.