

**FRACTURING FLUID (GUAR POLYMER GEL)
DEGRADATION STUDY BY USING OXIDATIVE AND
ENZYME BREAKER**

By

Bibi Syabila Binti Nor Azahar

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Petroleum Engineering)

JANUARY 2011

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan.

CERTIFICATION OF APPROVAL

**FRACTURING FLUID (GUAR POLYMER GEL)
DEGRADATION STUDY BY USING OXIDATIVE AND
ENZYME BREAKER**

By

Bibi Syabila Binti Nor Azahar

A project dissertation submitted to the
Petroleum Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(PETROLEUM ENGINEERING)

Approved by,



(Assoc Prof. Aung Kyaw)

Associate Professor
Geoscience & Petroleum Engineering Department
Universiti Teknologi PETRONAS
Bandar Seri Iskandar, 31760 Tronoh
Perak Darul Ridzuan, Malaysia.

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JANUARY 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



BIBI SYABILA BINTI NOR AZAHAR

**Petroleum Engineering Department,
Universiti Teknologi PETRONAS.**

ABSTRACT

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 aim for sand control while hydraulic fracturing is to stimulate the well. 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 facilitates the flowback of residual polymer providing rapid recovery of polymer from proppant pack. Ineffective breakers or misapplication of breakers can result in screenouts or flowback 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 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 paper provides a guideline of how to mix the fracturing fluid, the compositions of the fracturing fluid, and how to conduct the crosslink and break test. Crosslink test gave the optimum crosslinker 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. Also, for enzyme breaker, increasing temperature does not mean more reduction in viscosity. Observation from experiment also revealed that small concentration of enzyme breakers provides rapid break compare to oxidative breakers.

ACKNOWLEDGEMENT

The author wish to express her appreciation to Halliburton Energy Services for allowing author to use the facilities, consumables and chemicals in their Kemaman laboratory for authors' first phase experiment. Also, an utmost gratitude to BJ Services for providing enzyme breaker for this project. Besides, the author would like to give her appreciation to AP Aung Kyaw (author supervisor), Indran Pathmanathan and Geok Cheen Woon (Halliburton engineers), for their guidance throughout the research project. Lastly, the author also wants to thank the lab technologist Amirul Qhalis from UTP Drilling Fluid Lab for his assistance in guiding author to use the laboratory facilities.

TABLE OF CONTENTS

CERTIFICATE OF APPROVAL	i
CERTIFICATE OF ORIGINALITY	ii
ABSTRACT.....	iii
ACKNOWLEDGMENT	iv
CHAPTER 1 - INTRODUCTION	1
1.1 Background Study	1
1.2 Problem Statement	2
1.2.1 Problem Identification	2
1.2.2 Significant of The Project	3
1.3 Objectives And Scope Of Study	3
1.4 The Relevancy Of The Project	4
1.5 Feasibility of Project within scope and time frame	5
CHAPTER 2 - THEORY & LITERATURE REVIEW.....	6
2.1 Introduction To Fracturing Fluid	6
2.2 Fracturing Fluid Properties	7
2.3 Selection Of Fracturing Fluids	9
2.4 Fracturing Fluids Chemical Additives	10
2.5 Breaker	12
2.5.1 Enzyme Breaker	13
2.5.2 Oxidizing Breaker	14
2.5.3 Acid Breaker	14
CHAPTER 3 - METHODOLOGY	15
3.1 General Project Flow Chart.....	15
3.2 Consumables And Equipments	16
3.3 Experiment Procedure	18
3.3.1 Crosslink Time Test Procedure	18

3.3.2	Break Test Procedure	20
3.4	Gantt Chart for Fyp-2	22

CHAPTER 4 - RESULTS & DISCUSSION

4.1	Data Gathering From Lab Experiment And Analysis	23
4.1.1	Crosslink Time Test	23
4.1.2	Break Test for Oxidative Breaker (ViCon NF) At 200°F....	25
4.1.3	Break Test of Combination Oxidative Breaker (ViCon NF).. and Breaker Activator (CAT-3) At 200°F	26
4.1.4	Break Test for Oxidative Breaker (ViCon NF) At 140°F	27
4.1.5	Break Test for Enzyme Breaker (GBW 12-CD) At 200°F	28
4.1.6	Break Test for Enzyme Breaker (GBW 12-CD) At 140°F	29
4.1.7	Break Test for Enzyme Breaker (GBW 12-CD) At Ambient Temperature And At 200°F	31
4.2	Data Gathering From Research and Analysis.....	32
4.2.1	Paper (1) : SPE 140520	32
4.2.2	Paper (2) : H05000 Halliburton Bulletin	35
4.2.3	Paper (3) : Vol.4, No.7, September 2009; ARPJ Journal.. of Engineering And Applied Sciences	36

CHAPTER 5 – CONCLUSIONS & RECOMMENDATION 40

5.1	Conclusion.....	40
5.2	Recommendation	42

REFERENCES 43

LIST OF FIGURES

Figure 1 : pH Scale	10
Figure 2 : GBW 12-CD breaker	16
Figure 3 : LGC-16 gelling agent.	16
Figure 4 : Waring Blender	17
Figure 5 : Fann Viscometer	17
Figure 6 : Weighting Scale	17
Figure 7 : Water Bath	17
Figure 8 : pH measurement by using pH electronic meter	18
Figure 9 : Vortex form during high speed mixing	19
Figure 10 : Vortex Closure	19
Figure 11 : Lip Jar Test	20
Figure 12 : Viscosity measurement by using Fann-35A Viscometer.	21
Figure 13 : Gantt chart for FYP-2. Current standing at week 8.	22
Figure 14 : Over cross-linked gel. It looks lumpy.	24
Figure 15: Good cross-linked gel.	24
Figure 16 : Cross-linked gel.	29
Figure 17 : Stringy gel.	29
Figure 18 : Break test profile for thermagel using ViCon NF (oxidative) breaker at 275°F	35
Figure 19 : Effect of temperature on the break time at breaker concentration of 5gpt at 300rpm (cp).	37
Figure 20 : Effect of temperature on the break time at breaker concentration of 10gpt at 300rpm (cp).	37
Figure 21 : Effect of temperature on the break time at breaker concentration of 15gpt at 300rpm (cp).	38

LIST OF TABLES

Table 1 : Fluid recipe based on Halliburton Chemicals Trade Products.	16
Table 2 : Main equipments for laboratory preparation and testing.	17
Table 3 : Crosslinker and crosslinker accelerator concentration.	19
Table 4 : Fracturing fluid sample.	20
Table 5 : Classification of gel stages.	21
Table 6 : Crosslink time test data.	23
Table 7 : Pilot test 1 at 200°F using ViCon NF (oxidative breaker).	25
Table 8 : Pilot test 2 at 200°F using combination of ViCon NF. (oxidative breaker) and CAT-3 (breaker activator)	26
Table 9 : Pilot test 3 at 140°F using ViCon NF (oxidative breaker).	27
Table 10 : Pilot test 4 at 200°F using GBW 12-CD (enzyme breaker).	28
Table 11 : Pilot test 5 at 140°F using GBW 12-CD (enzyme breaker).	29
Table 12 : Pilot test 6 at ambient temperature and 200°F using GBW 12-CD (enzyme breaker).	31
Table 13 : Percentage of residue generated after the gel has been broken using oxidizers at 125°F.	33
Table 14 : Percentage of residue generated after the gel has been broken using oxidizers at 150°F	33
Table 15 : Percentage of residue generated after the gel has been broken using enzyme at 125°F and 150°F.	34
Table 16 : Effect of temperature on the break time at breaker concentration of 5gpt at 300rpm (cp).	36
Table 17 : Effect of temperature on the break time at breaker concentration of 10gpt at 300rpm (cp).	37
Table 18 : Effect of temperature on the break time at breaker concentration of 15gpt at 300rpm (cp).	38
Table 19 : Effect of temperature and concentration on break time.	38

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND STUDY

The use of fracturing fluids has evolved greatly over the past 60 years and continues to evolve. Fracturing fluids are commonly used for frac pack jobs and hydraulic fracturing. A frac pack technique combines the stimulation advantages of a highly conductive hydraulic fracture with the sand control of a gravel pack to improve productivity in low to moderate permeability, unconsolidated formations. Frac pack and hydraulic fracturing treatments are accomplished by injecting a fracturing fluid into the well and imposing sufficient pressure on the fracturing fluid to cause the formation to break down with the attendant production of one or more fractures. (Hainey et al., 1992)

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. Generally, a gelation agent and/or an emulsifier is used to gel or emulsify the fracturing fluid to provide the high viscosity needed to realize the maximum benefits from the fracturing process. (Gupta et al., 1993)

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 hydrocarbon 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. 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. (Gupta et al., 1993)

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

The viscosity of fracturing fluids is increased when gelling agents and crosslinkers are used to aid proppant transport and placement. This increased viscosity is desirable during pump-in procedures. However, **if this viscosity is not reduced the treated well may not flow.** The stimulation fluid must have the capability to decrease in viscosity (break) following proppant placement. The decrease in fluid viscosity is necessary to

- minimize return of proppant
- maximize return of stimulation fluids to the surface

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.** (Gupta et al., 1993)

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 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.

1.2.2 Significant of the Project

This project with the title of “Fracturing Fluid (Guar Polymer Gel) Degradation Study by Using Oxidative and Enzyme Breaker” is significant in understanding the degradation pattern with according to the oxidative and enzyme breaker. As the fracturing fluid viscosity need to be reduced at the desired time depends on the job or treatment requirement, the selection of breaker that can totally break the fracturing fluid after fracture has been created plays a big role in a success of fracturing process. The decrease in the fluid viscosity is usually achieved using chemicals referred to as gelling agent breakers or gel breakers. The gel breaker functions by breaking the long chain polymers into shorter chain segments, allowing the fluid more mobility with controlled and predictable viscosity decrease. The degree of reduction in viscosity is controlled by the **breaker type, pH, gel concentration, breaker concentration, time, and temperature**. (Halliburton, 2005). Thus, this project in the end is hoped to give a clear understanding on the comparison of the oxidative and enzyme breaker to the degradation of fracturing fluid (guar polymer gel).

1.3 OBJECTIVES AND SCOPE OF STUDY

The objectives of this research are:

- i. To determine the composition cross-linked fracturing fluid (guar polymer gel).
- ii. To conduct a comprehensive study to evaluate the degradation pattern of fracturing fluid (using oxidative and enzyme breaker) as a function of time, temperature and breaker concentration.
- iii. To make a comparison study on oxidative and enzyme breaker properties based on the experimental and researches results obtained.

The scope of study cover:

- i. The literature review on the fracturing fluid properties, fluids chemical additives, and the selection of fracturing fluids and breakers.
- ii. A thorough study on oxidative and enzyme breakers from Halliburton's Product Bulletin, SPE papers and United States Pattern research paper.
- iii. Frac pack and hydraulic fracturing stimulation treatment since these are the jobs that using high viscous gel to fracture the formation. Understanding the treatment purpose and how the fracturing process takes place will help author to formulate the fracturing fluid recipe.
- iv. Laboratory experimental to produce the fracturing fluid and test with different type of breakers to obtain the break time and degradation pattern.

1.4 THE RELEVANCY OF THE PROJECT

This project is relevant to petroleum engineering field since fracturing fluid system has been a constant research and development focus in fracturing process to increase gross permeability or conductivity of subterranean formation. This project is relevant for author as a final year student majoring in Drilling & Production as well because author can apply the fundamental knowledge learnt from Well Stimulation Technique course. Other relevancies are this project is reliable to be done individually, produce from experiment, the product is visible and the result can be analyze from structure of the gel itself whether it is still cross-linked or break. These justify the relevancy of this project.

1.5 FEASIBILITY OF PROJECT WITHIN SCOPE AND TIME FRAME

The first phase (FYP-I) of the project involves the literature review on current utilization and properties of fracturing fluid for frac pack and hydraulic fracturing job, the fracturing fluid chemical additives and also the criterion to select a breaker. Laboratory works will also be performed to design the fluid recipe that can produce good crosslink fracturing fluid.

The second phase (FYP-II) of project will still involves the laboratory experiment with this time break time test will be carried on for each type of breakers. Results obtain from research on SPE papers will also be analyzed and used to support and to be compared with the result obtained from the lab experiment. Following these would be a thorough discussion and finally the conclusion for the overall project findings. This project is expected to be done by end of March 2011.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 INTRODUCTION TO FRACTURING FLUID

Fracturing fluid is the fluid used in hydraulic fracturing or frac pack by injecting the fracturing fluid at pressure higher than the formation pressure to create conductive path that will bypass the damage zone and extend to a greater depth into the reservoir.

Economides and Nolte (2000) points out that the “fracturing fluid is a critical component of the hydraulic fracturing treatment” (p.7-1). According to them, fracturing fluid functions are to open the fracture and to transport propping agent along the length of the fracture. Successful hydraulic fracturing treatments require that the fluids have other special properties. In addition to exhibiting the proper viscosity in the fracture, they should break and clean up rapidly once the treatment is over, provide good fluid-loss control, exhibit low friction pressure during pumping and be as economical as is practical.

2.2 FRACTURING FLUID PROPERTIES

There are varieties of fluids available for use in hydraulic fracturing. It is necessary to understand the properties of fracturing fluid in order to select the proper fluid for a specific well.

Chemtotal (2010) have identified several properties that a fracturing fluid should possess. There are low leakoff rate, the ability to carry the propping agent, low pumping friction loss, easy to remove from the formation, compatible with natural formation fluids, minimum damage to the formation permeability, and break back to a low viscosity fluid for clean up after the treatment.

➤ **Low leakoff rate**

According to Howard and Fast (1970)

Low leakoff rate is the property that permits the fluid to physically open the fracture and one that controls its areal extent. The rate of leakoff to the formation is dependent upon the viscosity and the wall-building properties of the fluid. Viscosity and wall-building properties can be controlled with appropriate additives. (p.50)

➤ **Ability of the fluid to carry the propping agent**

According to Howard and Fast (1970)

Essentially, this property of a fluid is dependent upon the viscosity and density of the fluid and upon its velocity in the pipe or fracture. Density and velocity are not hard to describe; however, viscosity is difficult to measure and describe properly since many fracturing fluids are non-Newtonian. Two different fluids such as an emulsion and gelled water, can appear to have the same viscosity by one measurement, but may have widely varying abilities to carry propping agents in suspension. This aspect of propping agent suspension is frequently overlooked. The rate of movement is a major factor in the ability of fluid to carry the propping agent. Plain water with its low viscosity will carry proppants satisfactorily if it is pumped at a high rate.(p.50)

➤ **Friction loss**

According to Howard and Fast (1970)

Friction loss has become more important in recent years because it is controllable and because higher pumping rates have proved effective in fracturing treatments. The ability to reduce friction loss in pumping has been one of the governing factors in the present trend toward the use of water-base fracturing fluids.(p.50)

➤ **Easy to remove from the formation**

According to Howard and Fast (1970)

To achieve the maximum benefits from fracturing, the fracturing fluid must be removed from the formation. This is particularly true with the very viscous fracturing fluids such as viscous oils, gels, or emulsions. Most of the gelled-oil and water-base fracturing fluids have built-in breaker systems that reduce the gels to low viscosity solutions upon exposure to the temperatures and pressures existing in the formations. When the viscosity is lowered, the fracturing fluid may be readily produced from the pay formation and no flow restrictions remain.(p.50)

2.3 SELECTION OF FRACTURING FLUIDS

This project require author to select a correct fracturing fluid before it is bring to lab for testing on different temperature and breaker concentration. Halliburton (2005) state that “the selection of a fracturing fluid depends upon the particular formation to be treated and the tubular goods in the well”.

Halliburton (2005) have identified five considerations in fluid selection which are the formation rock properties, the formation fluid properties, friction properties of the treating fluid, fluid loss properties of the treating fluid, and proppant transport.(p.6.3)

Howard and Fast (1970) points out the selection of a fracturing fluid depends primarily on the nature of the formation encountered and the fluids in place in the formation. Not only the chemical nature (carbonate, sandstone or other), but also the physical nature of the rock itself must be considered. The chemical nature of the fluids in the reservoir - whether gas, oil, brine, etc.- and their physical nature, from the standpoint of what will influence their movement, also play a vital role in the selection of the fracturing fluid. Finally, the physical properties of the reservoir, such as temperature, pressure, wettability, and fluid saturation, can influence the choice of liquid.(p.55)

Other resource found from Chemtotal website (2008) says that to select the proper fluid, concerns such as fluid-loss control, fracture conductivity, formation damage, and proppant transport must be considered. Extensive testing should be conducted to promote better understanding of fracturing-fluid behavior in treatments of high-permeability formations. The fluids are evaluated for fluid-loss properties, regained permeability (formation damage), and fracture conductivity. The results from these tests would help in making the best fluid selection for a given well. The results from various formation-damage tests and fracture-conductivity tests around the world have shown hydroxyethyl cellulose (HEC) to be the most applicable linear gel for fracture treatments. Borate-crosslinked hydroxypropyl guar (HPG) gels are found to be the most effective crosslinked fluid system for Fracture Completion Services. The use of either a linear gel or a crosslinked gel is dependent on permeability of formation, reservoir fluid and reservoir pressure of candidate well.

2.4 FRACTURING FLUIDS CHEMICAL ADDITIVES

Halliburton (2005, p.6.3) grouped the chemical additives used in fracturing fluid into nine classifications. Their uses are explained below.

d) pH control agents

Function: Addition of pH control agents in stimulation treatment fluid control variables such as crosslinker function, temperature stability, iron problems, polymer hydration, clay control, and gel break.

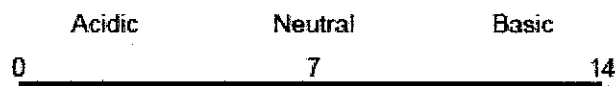


Figure 1 : pH Scale

b) Clay Control

Problem: Presence of clay can cause many problems in the production of hydrocarbons, particularly where stimulation processes are employed. Where a water swelling clay is contacted by foreign water in the formation, an increase in clay swelling can reduce the size of flow channels and thus decrease the flow capacity of the rock.

Solution: Addition of clay control into water base treatment fluid prevent the alteration of the natural water retention of the clay when it get contacts to a clay bearing formation.

c) Fluid Loss Control Additives

Problem: Fluid loss into the formation reduces the size of the fracture as well as the fluid pressure inside the fracture.

Solution: Traditionally, finely powdered solids have been used to control fluid loss. As the fluid moves into the pores of the formation, the fluid loss additives build up on the fracture face and form a filter cake. This reduces fluid loss. Some of the solids are inert while others go into solution and/or degrade. Another

approach to fluid loss control uses liquid additives that deposit droplets along the fracture face to control the loss of fluid. A major advantage of this approach is that no solids that might impair productivity are left in the formation or fracture. Fluid loss control additives can be water based fluid or oil based fluid.

➤ Surfactants

Function: Surfactants (“surface active agents”) have been developed to reduce fluid retention in a formation. Through the wise use of surfactants, these chemicals can aid in stimulation fluid recovery and reduce the possibility of emulsions forming in the formation.

Surfactants have been used in conjunction with fracturing treatments for several years. There are four important effects of these chemicals in fracturing:

- helps prevent water blocks
- helps prevent the creation of emulsions between the injected fluid and the formation fluid
- helps stabilize emulsions when using an emulsified treatment fluid
- aids in fluid recovery

➤ Gelling Agents

Function: Used for increasing viscosity, reducing friction, controlling fluid loss, etc. Viscosity (resistance to motion) is the most important condition derived from the use of gelling agents. Gelling agents can be divided into water based and oil gelling agents.

➤ Crosslinker

Function: Crosslinker are used to provide additional viscosity in a fracturing fluid system. Crosslinking agents commonly used in stimulation fluids are metals (antimony, zirconium, aluminum, chromium, titanium) and boron.

➤ Breakers / Stabilizer

Breakers: Used to reduce viscosity of guar and derivatized guar polymers are generally grouped into three classes: oxidizers, enzymes, and acids.

Stabilizers: Used to stabilize gels at high temperature because at high temperatures, either pH or temperature may break the viscosity of the gel prematurely. Example of stabilizer that Halliburton use is Gel-Sta.

➤ **Bactericides / Biocides**

Function: Used to destroy or control bacteria. Bacteria can cause viscosity instability in batch mixed gels. When conditions are favorable, sufficient numbers of bacteria can be the chief cause of gel degradation.

2.5 BREAKER

Relatively high viscosity fluids are used to transport proppant into the fracture. Leaving a high-viscosity fluid in the fracture would reduce the permeability of the proppant pack to oil and gas, limiting the effectiveness of the fracturing treatment (Penny, 1987; Brannon and Pulsinelli, 1992).

Gel breakers are used to reduce the viscosity of the fluid intermingled with the proppant. Breakers reduce viscosity by cleaving the polymer into small-molecular-weight fragments. It has been estimated that fluid loss during the treatment and during closure increases the polymer concentration in the fracture after closure 5-7 times (Penny, 1987) to as much as 20 times (Hawkins, 1988) higher than the surface concentration. The increased polymer concentration causes a major increase in viscosity.

For Example, the viscosity of an unbroken guar fluid containing polymer at 400 lbm/1000 gal gel concentrated 10 times because of fluid loss on fracture closure) has been estimated to be in excess of 1000 poise (Pope *et al.*, 1994).

Economides and Nolte (2000) say that significant effort has gone into designing breakers to address this problem. Ideally, a gel breaker put into the fluid at the surface should have minimal effect on the gel until pumping ceases (and the fracture closes) and then should react rapidly with the gel. The viscosity of the gel and the

molecular weight of the polymer should be significantly reduced to allow rapid cleanup of the sandpack (Almond et al., 1984; Gall and Raible, 1985).

According to Halliburton (2005)

The decrease in the fluid viscosity is usually achieved using chemicals referred to as gelling agent breakers or gel breakers. The gel breaker functions by breaking the long chain polymers into shorter chain segments, allowing the fluid more mobility with controlled and predictable viscosity decrease. The degree of reduction in viscosity is controlled by the breaker type, pH, gel concentration, breaker concentration, time, and temperature. (p.6.26)

Halliburton (2005) grouped the breaker used to reduce viscosity of guar and derivatized guar polymers 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. (p.6.26)

According to Halliburton (2005), a breaker should be selected based on its performance in the temperature, pH, time, and desired viscosity profile for each specific treatment.

2.5.1 Enzym Breaker

Halliburton (2005)

Enzymes are referred to as Nature's catalysts because most biological processes involve an enzyme. Enzymes are large protein molecules. Proteins consist of a chain of building blocks called amino acids. In Oilfield applications, breaker enzymes cause hydrolysis, or the addition of water, to the guar polymer. This causes viscosity to decrease. However, because of the characteristics of enzymes, they are only effective in a relatively narrow range of temperatures and pH levels. (p.6.26)

2.5.2 Oxidizing Breaker

Halliburton (2005)

Sodium, potassium, and ammonium persulfate have been used effectively as breakers for over 30 years. In these types of breakers, oxidation-reduction chemical reactions occur as the polymer chain is broken. (p.6.27)

2.5.3 Acid Breaker

Halliburton (2005)

Acid also provides the same break via hydrolysis as an enzyme. Acid, however, poses various difficulties for practical applications. Acid is not used as a guar polymer breaker very often because of cost, poor break rate control, chemical compatibility difficulties, and corrosion of metal goods. Another difficulty with acid breakers is that the formation may act as a buffer. A small amount of acid introduced as a breaker may be totally consumed by the formation water and minerals. This absorption could quickly change the pH of the fracturing fluid to a point where breaking may not occur. Most formation brines have a pH between 6 and 8. (p.6.28 – p.6.29)

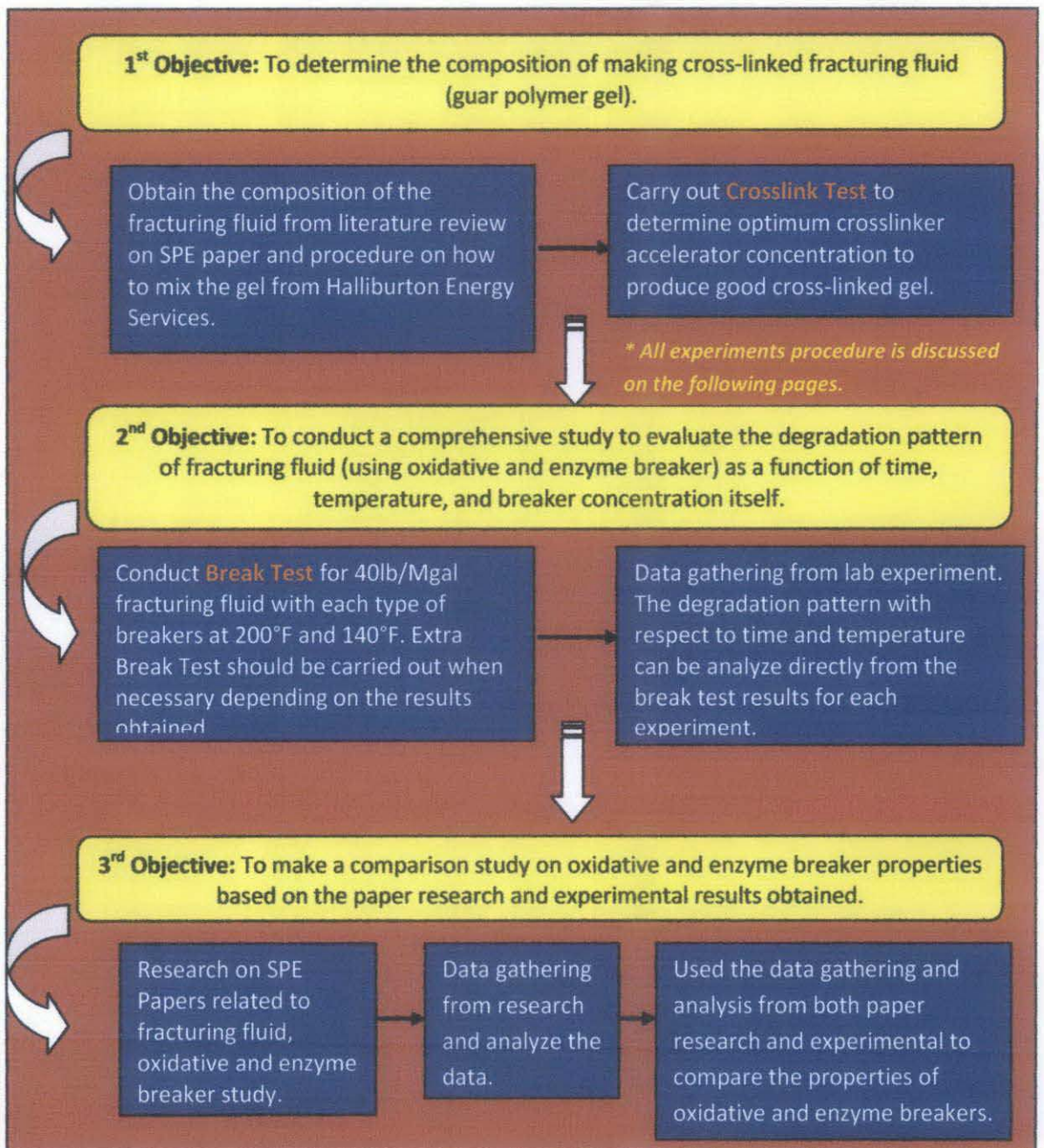
The applications for acid breakers are limited, with two exceptions that involve delayed-release type acids. First, a delayed-release acid may be used to un-crosslink a borate. Second, delayed-release acid may also be useful with enzyme breakers. Especially at low temperatures, the use of enzymes in borate crosslinked fluids is often effective. To allow the enzyme to be effective in the pH 9 to 11 borate fluid, delayed-release acids can be used to lower the fluid pH value to a range where the enzymes are effective. (p.6.29)

CHAPTER 3

METHODOLOGY

3.1 GENERAL PROJECT FLOW CHART

The flow chart below shows the activity sequence of the project and progression to achieve all three project's objectives.



3.2 CONSUMABLES AND EQUIPMENTS

The consumable materials which are required to make the linear gel in the first stage of this project are guar polymer which is classified as the gelling agent, NaCl solution, acidic and alkaline buffer. The following stage is to prepare crosslinked fracturing fluid and the consumable materials needed are crosslinker, crosslinker accelerator and a breaker. Below is the initial formulation for 40 lb/Mgal gel loading.

Table 1 : Fluid recipe based on Halliburton Chemicals Trade Products.

Types of Consumable	Trade Product Name	Approximate Quantity (on a basis of 1000ml)
Fresh Water	-	985ml
NaCl solution	-	6%
Gelling Agent	LGC-16	40lb/Mgal
Acidic Buffer	BA-20	1 gal/Mgal
Alkaline Buffer	MO-67	1 gal/Mgal
Crosslinker	CL-28M	3.0 gal/Mgal
Crosslinker accelerator	CL-31	10% solution from 0.8 gal/Mgal
Oxidizer Breaker	VICON NF	1, 5, 10 gal/Mgal
Enzym Breaker	GBW-12CD	1, 5, 10 gal/Mgal



Figure 2 : GBW 12-CD



Figure 3 : LGC-16 gelling agent.

The laboratory equipments listed below are used for fracturing fluid preparation and also for break time testing. Below are the equipment and the primary functions.

Table 2 : Main Equipments for Laboratory Preparation and Testing

Main Equipment(s)	Functions
WARING Variable Speed Laboratory Blender	Mixing of gel fluid
OHAUS Adventurer [®] Pro Electronic Weighting Scale	Measuring required amount of NaCl
FAAN [®] MODEL 35A Viscometer	Measuring the viscosity of the fluid
JULABO TW12 Water Bath	Heating the gel fluid to obtain the viscosity profile from break time test

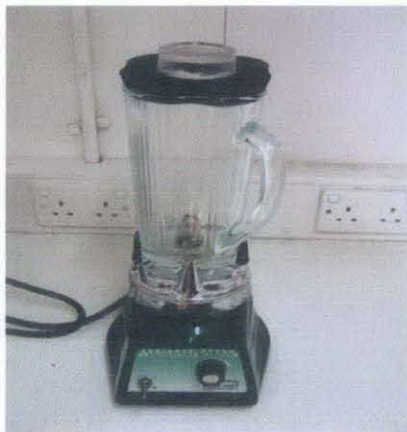


Figure 4 : Waring Blender



Figure 5 : Fann Viscometer



Figure 6 : Weighting Scale



Figure 7 : Water Bath

3.3 EXPERIMENT PROCEDURE

3.3.1 Crosslink Time Test Procedure

1. Measure out the proper amount of gel and mix it into 6% NaCl brine.
2. After stirring for a while, add the required amount of acidic buffer to bring the pH to about 5-6.



Figure 8 : pH measurement by using pH electronic meter.

3. Continue stirring for 15-20 minutes to make sure that the gel is fully hydrated. (Can feel the liquid to be slick).
4. Add the proper amount of alkaline buffer to bring the pH up to about 10-11 for proper cross-linking.
5. For the crosslink test, fix the crosslinker concentration of 3.0 gal/Mgal and vary crosslinker accelerator concentration.
6. Prepare the crosslinker and crosslinker accelerator based on concentration given in the table below. Crosslinker accelerator need to be diluted in water since it is recommended to use 10% mixture.

**CL-31 is 10% mixture : 10ml CL-31 + 90ml water*

Table 3 : Crosslinker and crosslinker accelerator concentration.

CL-28M Concentration gal/Mgal	CL-31 Concentration gal/Mgal
3	0.4
3	0.5
3	0.8
3	1.5

7. Turn on the blender as high as possible without entraining air in the gel.
8. Add the breakers **FIRST!**

Note: If breaker is add after the crosslinker, the breaker could not dissolved properly since the molecular chains in the gel has been crosslinked to each other.

9. Start the watch immediately after adds the crosslinker and crosslinker accelerator.
10. Record the time it takes the vortex in the gel to close over.



Figure 9 : Vortex form during high speed mixing.



Figure 10 : Vortex closure.

11. After the vortex has closed, pour the gel into a glass sample jar.
12. Perform a lip test until the gel has a strong crosslink, which is usually shown by the gel hanging at least one inch of over the mouth of the jar and returning easily.

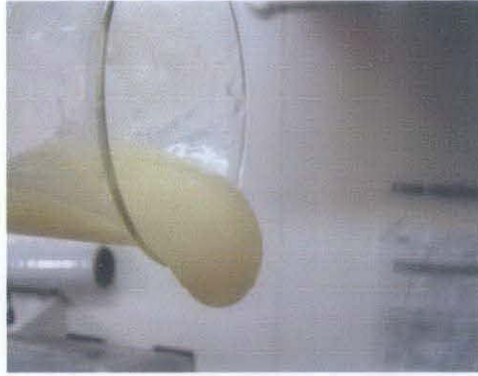


Figure 11 : Lip Jar Test

13. Record the time when the gel passes the lip test (crosslink time).

3.3.2 Break Test Procedure

1) Repeat the procedures as stated in the “Crosslink Test Procedure” with varying the breaker concentration as shown in table below.

Table 4 : Fracturing fluid sample.

Label	LGC-16 (gal/Mgal)	Breaker Type	Concentration (gal/Mgal)
A	40	VICON NF	1
B			5
C			10
D		GBW-12CD	1
E			5
F			10
Control		No Breaker	-

2) Place the sample into a water bath at 200°F.
 3) Perform lip test for every 15 minutes for the first 2 hours and 30 minutes after that. A viscosity test is also performed whenever possible.



Figure 12 : Viscosity measurement by using Fann-35A Viscometer.

4) Classification of the gel stages are as follows:

Table 5 : Classification of gel stages.

<u>Symbol</u>	<u>Stage</u>	<u>Description</u>
C	Cross-linked	When it can still be poured over the lip of the jar and returns cleanly.
WC	Weak Crosslink	When it can be poured over the lip, but has difficulty returning back to the jar.
S	Stringy	When it will not return to the jar when it is poured over the edge, but still sticks together like slime.
SP	Stringy and Pourable	When it almost like water but it still stick together like slime with apparent viscosity $> 10\text{cp}$ at 300rpm (511sec^{-1}) by Fann-35A Viscometer.
B	Break	When it almost like water with apparent viscosity $< 10\text{cp}$ at 300rpm (511sec^{-1}) by Fann-35A Viscometer.

5) Repeat the “Crosslink Test Procedure” and “Break Test Procedure” for 140°F.

3.4 GANTT CHART FOR FYP-2

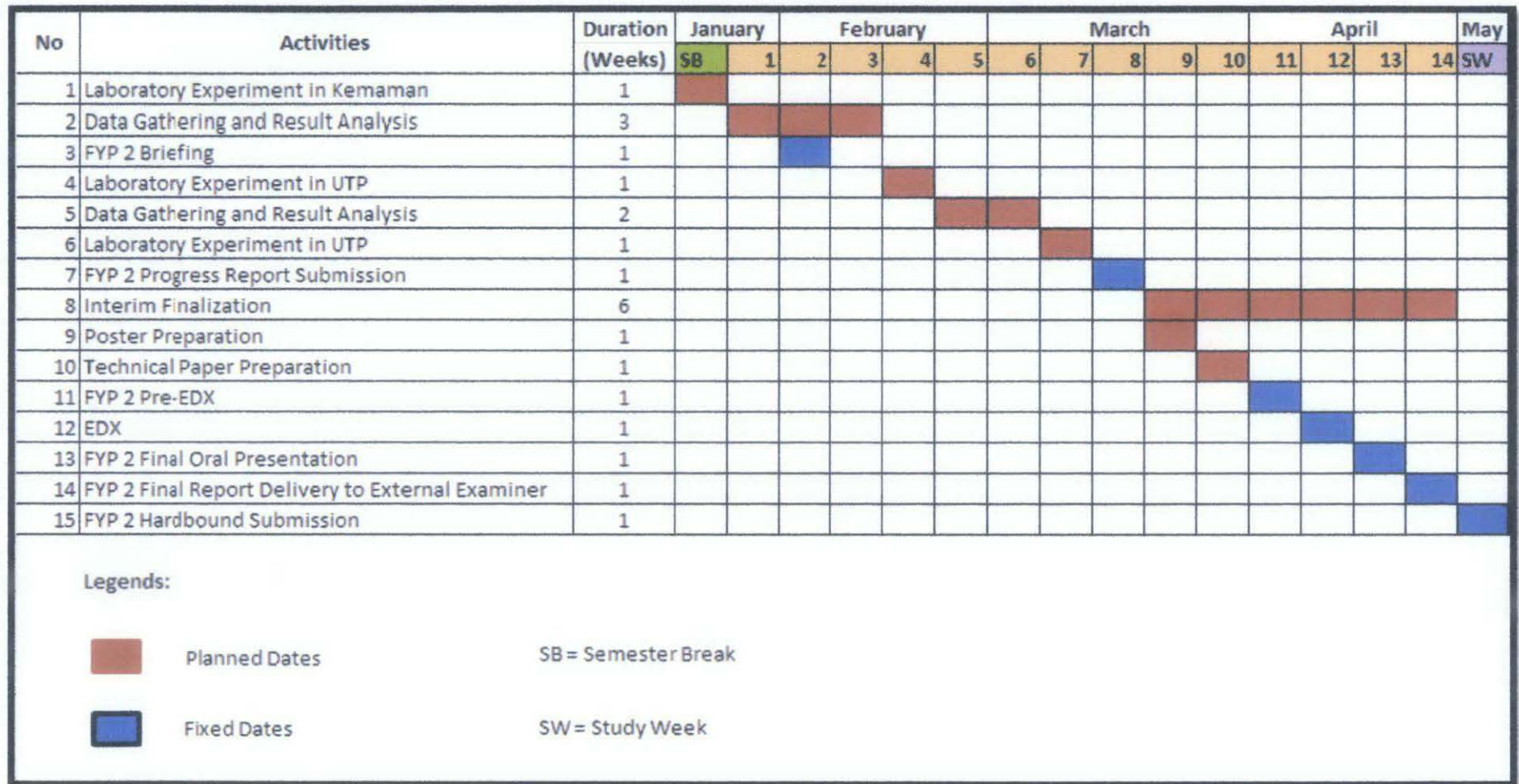


Figure 13 : Gantt chart for FYP-2. Current standing at week 11.

CHAPTER 4

RESULTS & DISCUSSION

4.1 DATA GATHERING FROM LAB EXPERIMENT AND ANALYSIS

4.1.1 Crosslink Time Test

Date: 18th January 2011

Purpose

To determine the optimum crosslinker concentration to produce good crosslink gel.

Result

Table 6 : Crosslink time test data.

CL-31 Conc (gal/Mgal)	Gel Crosslink Condition	Vortex Closure Time	Clean Test Time	Lip Jar Test
0.4	Crosslink but not clean	-	-	-
0.5	Crosslink but not clean	-	-	-
0.8	Good Crosslink	4 s	25 s	1.35 min
1.5	Over Crosslink	-	-	-

Note:

- Vortex Closure Time
The time for the vortex form during gel mixing start to close.
- Clean Test Time
The time acquires when the gel is no more stick to the beaker.

- **Lip Jar Test**

The time acquires when the gel can be poured over the lip of the jar and returns cleanly. It indicates the gel is fully crosslink.



Figure 14 : Over cross-linked gel. It looks lumpy.



Figure 15: Good Cross-linked gel.

Discussion

The initial crosslink concentration of 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-28™. Thus, CL-31 concentration of 0.8 gal/Mgal will be fixed to be used in preparing all samples required for break test.

4.1.2 Break Test for Oxidative Breaker (ViCon NF) At 200°F

Date: 18th January 2011

Purpose

1. To observe the break time pattern with ViCon NF (oxidative) as breaker at 200°F.
2. To observe the effect of breaker concentration on the break time of fracturing fluid.

Result

Table 7 : Pilot test 1 at 200°F using ViCon NF (oxidative breaker).

No	Breakers Conc.	Gel Description @ 200°F, minutes								
	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

Discussion

Result show that a break-time of 4 hours cannot be achieved by using the oxidative breaker (ViCon NF) alone. Thus, another test is conducted to see the break behaviour of the gel when 10gal/Mgal of oxidative breaker is 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.

4.1.3 Break Test of Combination Oxidative Breaker (ViCon NF) and Breaker Activator (CAT-3) At 200°F

Date: 19th January 2011

Purpose

To determine gel's break time when breaker activator is use together with the breaker.

Result

Table 8 : Pilot test 2 at 200°F using combination of ViCon NF (oxidative breaker) and CAT-3 (breaker activator).

No	Breakers Conc. (gal/Mgal)		Gel Description @ 200°F, minutes								
	ViCon NF	CAT-3	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)

Discussion

The result revealed that ViCon NF (breaker) concentration at 10 gal/Mgal 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 hours.

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).

4.1.4 Break Test for Oxidative Breaker (ViCon NF) At 140°F

Date: 20th January 2011

Purpose

1. To observe the break time pattern with ViCon NF (oxidative) as breaker at 140°F.
2. To observe the effect of breaker concentration on the break time of fracturing fluid.

Result

Table 9 : Pilot test 3 at 140°F using ViCon NF (oxidative breaker).

No	Breakers Conc.	Gel Description @ 200°F, minutes								
	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

Discussion

Result from this 3rd pilot test is as expected. The fluid system did not break within 4 hours since ViCon 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 hours, 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 is influenced by breaker concentration.

4.1.5 Break Test for Enzyme Breaker (GBW 12-CD) At 200°F

Date: 18th February 2011

Purpose

1. To observe the break time pattern with GBW 12-CD (enzyme) as breaker at 200°F.
2. To observe the effect of breaker concentration on the break time of fracturing fluid.

Result

Table 10 : Pilot test 4 at 200°F using GBW 12-CD (enzyme breaker).

No	Breakers Conc.	Pilot Test 1 – Gel Description @ 200°F, minutes									
	GBW 12-CD (gal/Mgal)	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	S	SP (11cp)	B (9cp)							

Discussion

As can be observed from the result, 5gal/Mgal and 10gal/Mgal concentration of GBW 12-CD broke the fluid in just 30 minutes. 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 are no more cross-linked at 0 minute before the fluids are left heated in the oven.

4.1.6 Break Test for Enzyme Breaker (GBW 12-CD) At 140°F

Date: 10th March 2011

Purpose

1. To observe the break time pattern with GBW 12-CD (enzyme) as breaker at 140°F.
2. To observe the effect of breaker concentration on the break time of fracturing fluid.

Result

Table 11 : 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, minutes									
		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)								



Figure 16 : Cross-linked gel.



Figure 17 : Stringy gel.

Discussion

The enzyme reaction in breaking the fracturing fluid is 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 to. 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 is a bit low from the concentration used in the previous one. Thus it take less time for the gel to break.

4.1.7 Break Test for Enzyme Breaker (GBW 12-CD) At Ambient Temperature And At 200°F

Date : 11th March 2011

Purpose

1. To observe the reaction pattern of GBW 12-CD (enzyme breaker) with the gel at ambient temperature and when heated at 200°F.

Result

Table 12 : 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 temperature, minutes			Gel Description @ 200°F, minutes							
		0	15	30	0	15	30	45	105	165	240	
Control	0	C	C	C	C	C	C	C	C	C	C	C
A	2				W C	S (23cp)	S (35cp)	S (50cp)	S	S	S	S
B	3				W C	S (21cp)	S (31cp)	S (49cp)	S	S	S	S
C	4	WC	S (24cp)	SP (20cp)	SP	B (10cp)						
D	8	S (24cp)	B (7cp)									

Discussion

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

4.2 DATA GATHERING FROM RESEARCH AND ANALYSIS

4.2.1 Paper (1) : SPE 140520

Title : Gel Degradation Studies of Oxidative and Enzyme Breakers to Optimize Breaker Type and Concentration for Effective Break Low Profiles at Low and Medium Temperature Ranges

Inventors : M.U. Sarwar, SPE, K.E. Cawiezel, SPE, BJ Services, H.A. Nasr-El-Din, SPE, Texas A&M University

This paper contained evaluation on the breaker activity of low to medium temperature range oxidative and enzymatic breaker systems, including ammonium persulfate, sodium persulfate, calcium and magnesium peroxides, and galactomannanase enzyme in linear gel fluids at temperatures from 75°F - 300°F. Two test were conducted which are Break Test and Residue-After-Break (RAB) Tests. **The Residue-After-Break (RAB) test result from this research can be used as the aid data to support our study on this project.**

Residue-After-Break (RAB) Test

Purpose

1. To determine the amount of unbroken gel and residue generated after gel was broken.

Materials

- Tap water
- Guar polymer : dry powder for 30 ppt loading
- Oxidative breaker : Ammonium persulfate, sodium persulfate
- Enzymatic breaker : Galactomannanase

Procedure

30 ppt gels were first prepared using three breakers which have similar working ranges (130-200°F). Ammonium persulfate, sodium persulfate and galactomannanase enzyme were tested. All three breakers were tested with 30 ppt gels at two different working temperature, i.e 125°F and 150°F. After adding breaker, the samples were left overnight to allow for maximum break time. The next day, the amount of unbroken polymer and residue for these samples were calculated.

Result

Table 13 : Percentage Of Residue Generated after the gel has been broken using oxidizers at 125°F

Conc. (ppt)	% RAB	
	Ammonium Persulfate	Sodium Persulfate
	125°F	125°F
10	6.580556	6.430556
5	7.694444	7.653
1	74.38889	35.91667
0	79.875	79.875

Table 14 : Percentage Of Residue Generated after the gel has been broken using oxidizers at 150°F

Conc. (ppt)	% RAB	
	Ammonium Persulfate	Sodium Persulfate
	150°F	150°F
10	5.375	4.763889
5	5.25	5.875
2	4.875	6.875
1	6.736111	5.527778
0.5	44.56944	27.55556
0	75.13889	75.13889

Table 15 : Percentage Of Residue Generated After The Gel Has Been Broken Using Enzyme at 125°F and 150°F

Conc. (ppt)	% RAB	
	Ammonium Persulfate	Sodium Persulfate
	125°F	150°F
1	5.638889	7.166667
0.5	8.555556	5.847222
0	79.875	75.13889

Discussion

The oxidative breakers produce very similar results. The enzyme was found to produce less residue than the ammonium and sodium persulfate breakers especially at lower concentrations (0.5ppt, 1ppt of oxidizer). The amount of residue for the oxidizers for the lower concentrations was very high. Thus it can be say that enzyme provide better break than the oxidizers.

4.2.2 Paper (2) : H05000 Halliburton Bulletin

Title : ViCon NF™ Fracturing Fluid Breaker ; Improved Fracture Fluid Cleanup Capability Provides Virtually 100% Retained Permeability with Mid-to-High-Temperature Fracturing Gel Systems

Purpose

1. To acquire the viscosity profile of Termagel fracturing fluid system using ViCon NF (Oxidative) breaker at various concentration.

Result

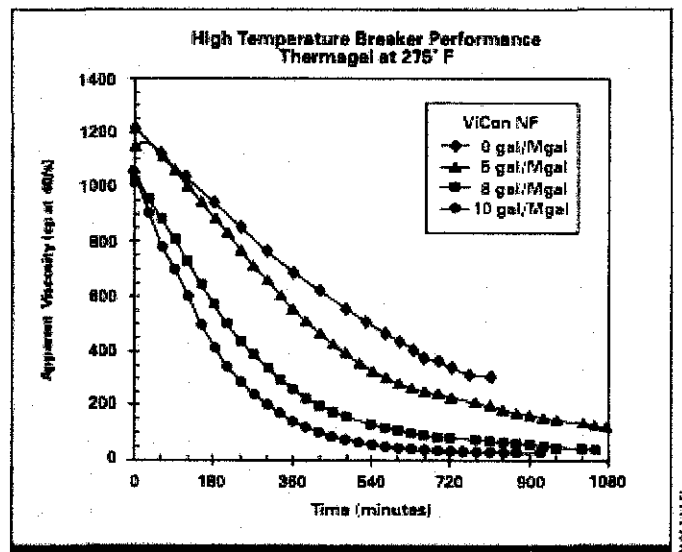


Figure 18 : Break Test Profile for Thermagel Using ViCon NF (oxidative) Breaker at 275°F

Discussion

The break profile figure found in Halliburton Bulletin shows that the time required to degrade the gel was a function of breaker concentration. Gels degrade faster as high breaker concentrations are used. As stated in the Bulletin, “Viscosity can be easily controlled by adjusting the concentration of ViCon NF breaker to provide the desired break profile”.

4.2.3 Paper (3) : Vol.4, No.7, September 2009; ARPN Journal of Engineering And Applied Sciences

Title : Modelling Break Time On Gravel Pack Fluid At Different Breaker Concentrations And Temperatures

Inventors : Joel O.F. , Ademiluyi F.T. and Iyalla M.C

This paper aims to investigate the effect of gel breakers on 60lbs/Mgals gravel pack fluid at different temperatures and concentrations. Thus, tests were conducted at temperatures of 190°F, 210°F and 230°F with high temperature (HT) breaker of concentrations 5.0gal/Mgal, 10gal/Mgal and 15gal/Mgal.

Purpose

Author purpose on studying this paper is to look for the effect of temperature and breaker concentration on gravel pack fluid. Even though gravel pack fluid is made up of linear gel which is different from fracturing fluid where we add crosslinker to the linear gel, but the fundamental objective of using breaker in those two types of fluids are the same. Thus this paper is applicable for author study to investigate the properties which influence breaker function.

Result

Table 16 : Effect of temperature on the break time at breaker concentration of 5gpt at 300rpm (cp).

Time (minutes)	0	30	90	120	180	210	270	300	360	390	420	450	510	540	600
190°F	40	34	30	29	28	27	26	26	25	24	22	20	16	14	10
210°F	40	34	30	29	27	25	18	15	10						
230°F	40	32	28	24	10										

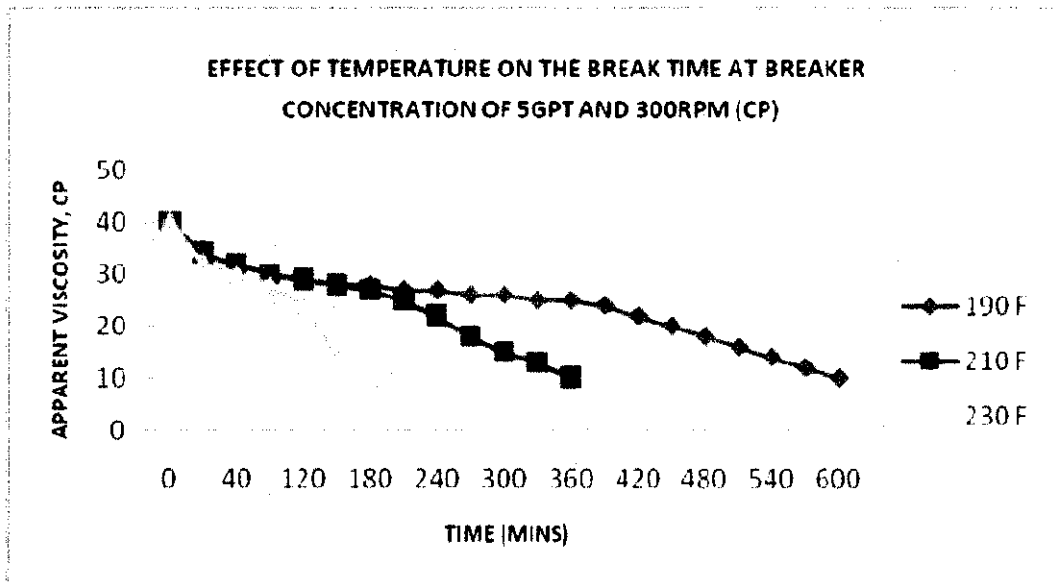


Figure 19 : Effect of temperature on the break time at breaker concentration of 5gpt at 300rpm (cp).

Table 17 : Effect of temperature on the break time at breaker concentration of 10gpt at 300rpm (cp).

Time (minutes)	0	30	60	90	120	150	180	210	240	270	300	330	360
190°F	40	34	32	30	29	28	27	25	22	18	14	12	10
210°F	40	33	31	29	28	22	14	10					
230°F	40	32	10										

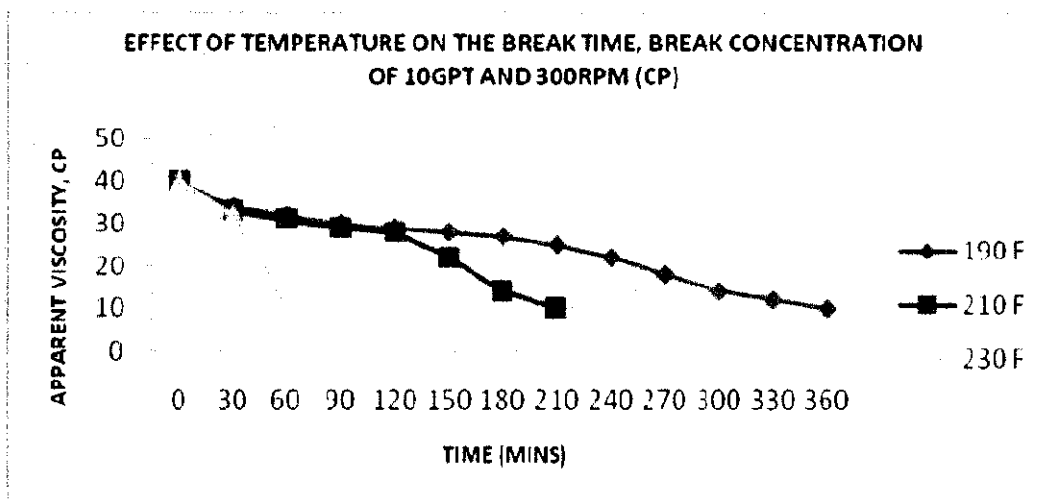


Figure 20 : Effect of temperature on the break time at breaker concentration of 10gpt at 300rpm (cp).

Table 18 – Effect of temperature on the break time at breaker concentration of 15gpt at 300rpm (cp).

Time (minutes)	0	30	60	90	120	150	180	210	240
190°F	40	34	31	28	25	20	16	13	10
210°F	40	30	22	14	10				
230°F	40	32	8						

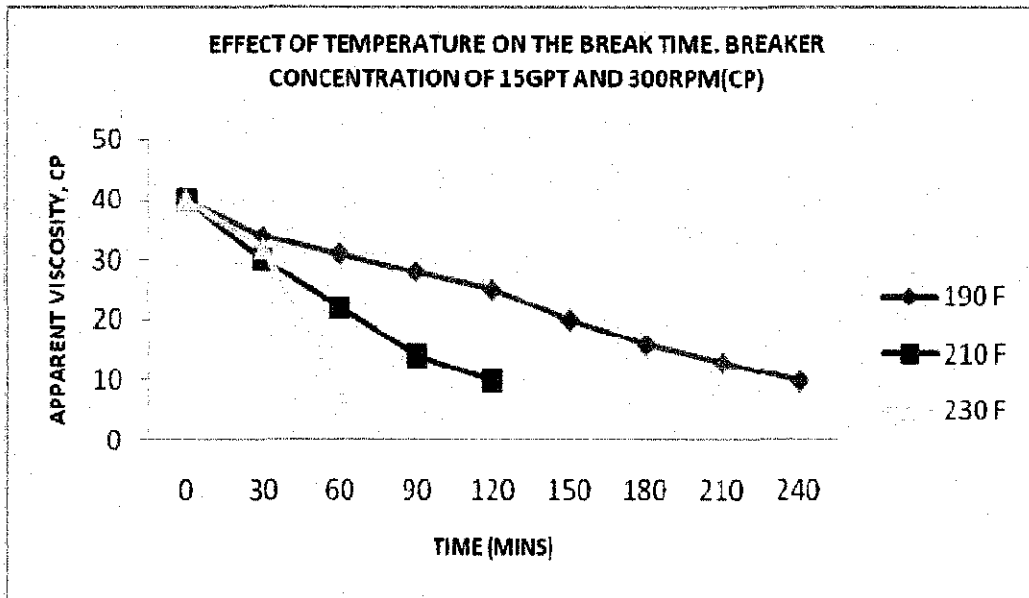


Figure 21 : Effect of temperature on the break time at breaker concentration of 15gpt at 300rpm (cp).

Table 19 : Effect of temperature and concentration on break time.

Breaker concentration (gal/1000gal)	190°F	210°F	230°F
5	600mins	360mins	180mins
10	360mins	210mins	60mins
15	240mins	120mins	40mins

Discussion

1. The researchers who produce this paper state that the gel “was considered broke when viscosity of 10cp or less is obtained from 300rpm dial reading of Fann Viscometer”. This is similar to author assumption which author had used 10cp as the bench mark viscosity to identify whether or not the gel was broke.
2. Results from table 5 drawn conclusions to us that the gel break is a function of temperature and concentration of breaker. These can be clearly seen when the breaker concentration increased from 5gal/Mgal to 15gal/Mgal at respective temperatures, the less time took for the fluid to break. Same goes to temperature as temperature increased from 190°F to 230°F at the respective breakers concentration, the less time took for the fluid to break.

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

5.1 CONCLUSIONS

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 conclusion can be drawn from this study:

1. 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.
2. Break time test using oxidative (ViCon NF) breaker showing that the guar polymer gel degradation time was 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 meaning, the breaker activator is used to expedite the break time of fracturing fluid.

3. Break time test using enzymatic (GBW 12-CD) breaker, a hemicelluloses class 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 enzymes concentrations are required due to denature of the enzyme. The break time test also showed more degradation viscosity with increase in enzyme breaker concentration.
4. 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.
5. Based on the residue-after-break tests from Paper 1, 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.

5.2 RECOMMENDATIONS

These are some of the recommendations to further enhance the research project in future work:

1. Conduct residue-after-break (RAB) and regained permeability tests to support the results. Residue after break test will give the amount of unbroken gel and residue generated after the gel was broken. Regained permeability test will give the permeability of the core after fracturing fluid has been clean up after breaker activity takes place. Thus, the effectiveness of the breaker in breaking the fracturing fluid and thus enhance the permeability could be obtained from this test.
2. Add acid breaker for this research project. Though acid breaker is not widely used because of the rapid rate and some time resulted instantaneous break upon the addition of it into the fracturing fluid but a delayed-release acid type may be useful with combination of enzyme breakers.
3. Increase the temperature range for testing to 300°F. This will give more accurate data analysis and breaker activities comparison.
4. More breakers from low to high temperature range can be used from both type of oxidative and enzyme breakers to support the fracturing fluid degradation comprehensive study.

REFERENCES

1. Chemtotal, 10 May 2008 <http://www.chemtotal.com/fracturing-fluid-systems.html>.
2. Economides, Michael J. and Nolte, Kenneth G. 2000. *Reservoir Stimulation*, John Wiley & Sons, New York.
3. Howard, G.C. and Fast, C.R. 1970, *Hydraulic Fracturing*, New York, Society of Petroleum Engineers of AIME.
4. Halliburton Energy Services, 2005. *Stimulation I*.
5. Joel O.F. , Ademiluyi F.T. and Iyalla M.C., 2009, "Modelling Break Time On Gravel Pack Fluid At Different Breaker Concentrations and Temperatures," *ARPN Journal of Engineering and Applied Sciences* 4 (7): 2006-2009.
6. Brannon, H.D. and Pulsinelli, R.J.: "Breaker Concentrations Required to Improve the Permeability of Proppant Packs Damaged by Concentrated Linear and Borate-Crosslinked Fracturing Fluids," paper SPE 21583, SPE Production Engineering (November 1992) 7, No.4, 338-342.
7. Penny, G.S.: " An Evaluation of the Effects of Environmental Conditions and Fracturing Fluids upon the Long-Term Conductivity of Proppants," paper SPE 16900, presented at the SPE Annual Technical Conference and Exhibition, Dallas, Texas, USA (September 27-30, 1987).
8. Hawkins, G.W. : "Laboratory Study of Proppant-Pack Permeability Reduction Caused by Fracturing Fluids Concentrated During Closure," paper SPE 18261, presented at the SPE Annual Technical Conference and Exhibition, Houston, Texas, USA (October 2-5, 1988).

9. Pope, D.S., Leung, L.K.-W., Gulbis, J. and Constien, V.G.: "Effects of Viscous Fingering on Fracture Conductivity," paper SPE 28511, presented at the SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana, USA (September 25-28, 1994).
10. Almond, S.W., Bland, W.E. and Ripley, H.E.: "The Effect of Break Mechanisms on Gelling Agent Residue and Flow Impairment in 20/40 Mesh Sand," paper CIM 84-35-30, presented at the 35th Annual Technical Meeting of Petroleum Society of CIM and Canadian Association of Drilling Engineers, Calgary, Alberta, Canada (June 10-13, 1984).
11. Sarwar, M.U., Cawiezel, K.E., Nasr-El-Din, H.A., : "Gel Degradation Studies of Oxidative and Enzyme Breakers to Optimize Breaker Type and Concentration for Effective Break Profiles at Low and Medium Temperature Ranges," paper SPE 140520, presented at the SPE Hydraulic Fracturing Technology Conference and Exhibition, Woodlands, Texas, USA (January 24-26, 2011).
12. Gall, B.L. and Raible, C.J.: "Molecular Size Studies of Degraded Fracturing Fluid Polymers," paper SPE 13566, presented at the SPE Oilfield and Geothermal Chemistry Symposium, Phoenix, Arizona, USA (April 9-11, 1985).