BREAKER EFFICIENCY CHARACTERIZED BY EVALUATION OF POLYMERIC FRAGMENT SIZE DISTRIBUTION

Harold D. Brannon and Robert M. Tjon Joe Pin
BJ Services Company

Abstract

Fluid viscosity reduction is commonly used to gauge polymer degradation. Although viscosity reduction indicates polymer degradation, it is misleading to conclude that this reduced viscosity equates to improved fracture conductivity. Polymer fragments which are desolubilized from the gelled fluid no longer contribute to fluid viscosity but do, unfortunately, contribute significantly to proppant pack damage.

Several new breaker technologies have been introduced in efforts to improve polymer degradation, and thereby, improve fracture conductivity and ultimately, well productivity. Many production case histories have been offered as evidence of the utility of the new technologies to improve well productivity. However, the facility to quantitatively determine the polymer degrading efficiency of the breakers has heretofore been lacking.

Laboratory procedures, both wet chemical and instrumental, have recently been developed to address characterization of the relative degrading efficiency of the various breakers. The analysis of the combined data provide a quantitative profile of the polymer fragments. Extensive studies were conducted employing the new procedures to compare the degrading efficiency of various oxidative and enzymatic breakers. Detailed analysis of the results are provided.

Introduction

Viscosity reduction of the gelled fluid is commonly used to gauge the polymer degradation, with the assumption that the observance of a "broken gel" viscosity at the surface upon return flow is proof positive optimum gel degradation. The definition of a "broken gel" in terms of viscosity has been a moving target for several years. As recently as 15 years ago, a broken gel was defined as one having the viscosity reduced to a value of less than 15 cps as measured at 511 sec^{-1} on a Fann 35 viscometer. Subsequent reports on the high degree of fracture conductivity damage caused by fracturing fluid residues led to the broken gel criteria being reduced to less than 10 cps.

Although viscosity reduction indicates polymer degradation, it is misleading to conclude that this reduced viscosity will equate to fracture cleanup and improved conductivity. Solution viscosity is a function of both the polymer concentration and the molecular weight of the polymer. At a given constant concentration, solution viscosity exhibits an exponential relationship with the molecular weight of the polymer used to viscosify the fluid.[4] Cleavage to reduce the polymeric molecular weight results in an exponential reduction in the solution viscosity. Guar solutions broken at 160°F with an oxidative breaker to a viscosity 3 cps have been reported to have average polymer molecular weights in the range of 250,000 to 500,000, with as much as 20% of the polymer remaining essentially unbroken at a molecular weight of greater than 2 million.[5] Viscosity reduction may also occur due to the creation of insoluble polymeric fragments by undesirable reactions. The polymer

fragments which are desolubilized from the fluid no longer contribute to fluid viscosity but do, unfortunately, contribute significantly to proppant pack damage.

New technologies have been introduced in recent years in efforts to reduce residual polymeric damage, and hence, improve fracture conductivity and ultimately, well productivity. Many production case histories have been offered as evidence of the utility of the new technologies to improve well productivity.[6-9] A multitude of parameters, over which the engineer has little control or absolute knowledge, also impact well productivity, serving to mask the contribution of a modification, good or bad. Unfortunately, this masking frequently serves to bring into question the reliability of any conclusions based upon relative well productivities. Consequently, much confusion and controversy over the true direct benefits of newly introduced concepts, products, and techniques have occurred. The benefits of the recently introduced guar linkage-specific enzyme breakers relative to the conventional breakers have been a particularly controversial issue. In order to address the existing controversies and provide insight to relative performance of the various fracturing fluid systems and gel breaker additives, a direct method for characterization of breaker efficiency was needed.

Several authors have discussed the results of various laboratory studies to evaluate the molecular weight reduction of fracturing fluid polymers and breaker performance.[4-5,10-12] Almond observed that broken fracturing gels can cause significant flow reduction in porous media. He also observed that the break temperature or break mechanism plays an important role in determining the amount of flow impairment obtained with guar polymers [10,11]. Volk and Gall, et.al. reported on molecular size studies of degraded fracturing fluids in conjunction with the DOE Multi-Well Experiments in the mid-80's.[4,5] The work was very insightful, utilizing Size Exclusion Chromatography to relate the relative average molecular weight reduction with the effects on fluid viscosity. They observed that degradation of the fluid viscosity did not ensure fluid return, because the broken fluids contained sufficient amounts of partially degraded residues to damage and restrict the fracture permeability. They also confirmed that the viscosity of degraded solutions is a function of polymer concentration and molecular weight and derived a correlation between the log of the polymer average molecular weight and the inverse of the solution viscosity.

Unfortunately, the previously published studies have been narrow in scope and have not been related in a manner to guide optimized selection of the current polymer systems and breaker products. The studies were also short-term, limited to evaluation of the status of polymer degradation after, at most, 72 hours. Often times load recovery continues for several weeks after the placement of the stimulation treatment. Continued reduction of the molecular weight of the polymer versus time is thought to be beneficial to the ultimate removal of a greater volume of the residual polymer from the fracture and thus, important to optimize long-term well productivity.

A broad-based study was undertaken to characterize breaker efficiency in terms of molecular weight reduction. Further, evaluations were conducted versus time to provide insight to the long-term implications of utilizing various systems. An extensive test matrix was constructed to evaluate the polymer degrading efficiencies of the various oxidative and enzymatic breakers on guar-based fracturing fluids at temperatures of 75°F to 210°F over a period of up to 8 weeks. The initial "baseline matrix" included testing in excess of 500 gelled fluid samples on which many as 20 measurements were conducted per sample. The data provided herein are limited to the baseline matrix and thus, are confined to uncrosslinked natural guar-based fluids at pH 5.

Laboratory Procedures

Fluid Preparation

The fluids tested in this study were comprised of 40 pounds per thousand gallons (lbm/1000 gal) natural guar polymer hydrated in deionized water. The fluids were buffered with acetic acid to pH 5.

The oxidative breakers used for the evaluations was ammonium persulfate and ammonium persulfate activated with copper EDTA. The oxidative breaker concentrations used in the study were dependent upon the test temperature. At 75°F, an ammonium persulfate concentration of 4 ppt was used with 0.5 ppt of the activator. The tests at 125°F were run with 4 ppt persulfate and 0.5 ppt activator as above and with 4 ppt persulfate breaker alone. This was done in order to distinguish any differences between oxidizer and activated oxidizer breaker efficiency at 125°F. The oxidative breaker loading used in the 175°F and 210°F tests was 0.1 ppt of ammonium persulfate.

Two enzyme breakers were evaluated. The conventional hemicellulase enzyme loadings were added at 0.1 ppt. The 0.1 ppt loading provides an enzyme concentration of 30,340 International Units per liter. A loading of 1.0 gal/1000 gal of the Guar-Linkage-Specific Enzyme (GLSE) was used at all temperatures. The 1.0 gpt loading of GSLE provides an enzyme concentration of 30,000 International Units/liter.

Sample Preparation and Conditioning

The fluids were hydrated in 20-gal master batches. Once hydrated, the 20-gal batches were split into 4-gal batches. The various breakers were mixed into the 4-gal batches from which 200 mL samples were decanted into 8-oz bottles and sealed. This procedure was implemented to ensure consistent additive loadings in all samples. The samples were then placed in heated water baths and allowed to equilibrate to the respective test temperature.

Eight samples were prepared for each breaker/temperature condition. The testing schedule dictated that evaluations be performed after 4 hours, 24 hours, 48 hours, 1 week, 2 weeks, 4 weeks, and 8 weeks exposure time at temperature. At the appointed time, one sample was pulled from the bath and cooled to room temperature. A suite of tests was then performed on the sample, including: Brookfield viscosity, Fann 35 viscosity, pH, Barfoed's test for monosaccharides, Benedict's test for disaccharides, ultracentrifugal separation for molecular weight distribution evaluation, and Total Organic Carbon content of the filtrate from the centrifugations.

Viscosity Measurement

Viscosity measurements were made at 75°F using both Fann 35A and Brookfield viscometers. The Fann 35 viscosities were measured with an R1:B1 rotor:bob configuration at 300 rpm which provides the fluid viscosity at 511 sec^{-1}. This Fann 35 measurement is standard for the evaluation broken gel viscosity. The Brookfield measurements, conducted to evaluate the viscosity a low shear rates, were determined with a #2 spindle at 60 rpm, which provides a shear rate of 12.7 sec^{-1}. The initial viscosity (@ 0 hours) of the 40 ppt linear guar solution at 75°F was 38 cps at 511 sec^{-1} as measured with the Fann 35 and 342 cps at 12.7 sec^{-1} as measured on the Brookfield viscometer.

Disaccharide and Monosaccharide Evaluations

The disaccharide and monosaccharide evaluations were carried out by standard qualitative biochemical methods.[13] The Benedict's test indicates the presence of disaccharides above the minimum detection limit of 0.0048% (0.4 ppt). Barfoed's test, which is specific for the presence of monosaccharides, has a minimum detection limit 0.024% (2 ppt) for positive monosaccharide indication.

Molecular Weight Distribution Analysis

Molecular weight distributions were evaluated by using an Ultra-Filtration Molecular Weight Cut-off technique. This analysis provides a measure of the weight percentage of soluble material present in various size ranges. The testing involves separation of the variously-sized polymer fragments in the broken gel solutions by filtration across semi-permeable membranes using centrifugation. The fragments which are too large to pass through the membrane are thus excluded from the filtrate passing through.

The ultra-filtration membranes used were Millipore Ultrafree-CL filters which are calibrated to known molecular weight dextrans. The molecular weight cutoff membranes utilized were selected to separate the fragments to 300, 100, 30, 10 and 5 thousand nominal molecular weight. The ultrafiltration membranes were flushed twice with de-ionized water and centrifuged for one hour each time before the addition of the sample. Each molecular weight cutoff membrane tube was weighed before the addition of the sample. One milliliter of the sample was then added to the tube and centrifuged at 2500 G's for 30 minutes. The weight was measured after centrifugation to arrive at the weight of the filtrate which passed through the membrane. A margin of $\pm 6\%$ error was observed for the MWCO analysis, based upon reproducibility.

Analysis of these data provide an average molecular weight distribution of those polymer fragments degraded to 300,000 (300K) or less. Since fragments of a size of 300K or greater are excluded on the largest membrane, calculation of average molecular weight for all polymer fragments is biased to the minimum. The fragments excluded by the 300K membrane are sized in a distribution between 300K and the unbroken molecular weight of the polymer which ranges to greater than 2 million. Therefore, two values are presented from the MWCO analyses, the average molecular weight of polymer fragments 300K and less ($AvMW_{300}$) and, the weight percent (wt %) of those fragments sized greater than 300K.

Total Organic Carbon Analysis by CHNS-O

CHNS-O Analysis may be used for quantitative determination of Carbon, Hydrogen, Nitrogen, Sulfur, and Oxygen content present in a wide range of organic and inorganic samples. The samples are subjected to flash combustion at 1200°C in a reactor which converts organic and inorganic substances into combustion products. The resulting combustion gases are passed through a separation column, then a thermal conductivity detector which transmits a response signal proportional to the concentration of the elements in the sample. The specific interest with respect to this study was the Total Organic Carbon (TOC) content within the filtrate of the Ultra-Filtration Molecular Weight Separation analyses.

The filtrate was analyzed for the TOC content using a CHNS-O EA 1108 Elemental Analyzer from Fisions Instruments. The system was preconditioned by spiking the column with bypasses and blanks. A calibration curve was generated from testing with known standards and calculations using the K-factors method incorporated in an EAGER 2000 automation work station.

Once calibrated, a known volume of centrifuged Ultra-Filtration filtrate was transferred to a tared tin container. The sample was then purged with helium gas to displace atmospheric nitrogen and sealed to prevent sample leakage. The sample weight was recorded, and the sealed tin was placed in the auto-sampler for analysis. The results were recorded as percent carbon with an experimental error of 0.004%, based on reproducibility.

Results and Discussion

Effects of Breakers on Guar-Based Fluids at 75°F

The viscosity reduction provided by the various breakers versus time at 75°F is shown in Figure 1. The GLSE breaker was observed to reduce the Fann 35 viscosity from the initial 38 cps to 3 cps within 4 hours. More than 48 hours were required with both the activated persulfate and the conventional enzyme to reduce the viscosity to less than 10 cps.

Only the samples degraded with the GLSE indicated a presence of disaccharides or monosaccharides above detection limits at any time. As shown in Table 1, disaccharides were detected in all 75°F samples broken with the GLSE breaker. Monosaccharides were detected in all GLSE degraded samples after 24 hours at 75°F.

The molecular weight distributions of the degraded guar fragments observed after 24 hours at 75°F as measured by the MWCO technique are shown in Figure 2. The distributions observed after two weeks is shown in Figure 3. The calculated average molecular weight for the fragments ($AvMW_{300}$) and the weight percent of the fragments greater than 300K (wt %) are shown in Table 2. The degradation provided by the activated persulfate breaker within 24 hours resulted in an $AvMW_{300}$ of 251K with 83% of the fragments greater than 300K. Additional reduction over time was minimal with an observed 8-week $AvMW_{300}$ of 233K with 77% greater than 300K. The conventional enzyme was slightly better at 24 hours with an $AvMW_{300}$ of 211K and 69% greater than 300K. However, continued degradation of the polymer by the conventional enzyme was observed, resulting in an 8-week $AvMW_{300}$ of 153K with 48% greater than 300K. The most effective molecular weight reduction was provided by the GLSE breaker with an observed $AvMW_{300}$ of 106K after 24 hours with 32% of the fragments greater than 300K. The GLSE as well continued to function as time passed, reducing the $AvMW_{300}$ after 8 weeks to 24K with only 2% of the fragments greater than 300K.

TOC evaluations of the 2-week samples provided results very similar to those observed in the MWCO analyses. The size distributions from the TOC analyses are shown graphically in Figure 4, and the calculated average molecular weight values are provided in Table 3. An $AvMW_{300}$ of 212K with 68% of the fragments greater than 300K was observed for 75°F fluids degraded with activated persulfate. The conventional enzyme reduced the $AvMW_{300}$ to 142K with 44% greater than 300K. An $AvMW_{300}$ of 10K with 0% fragments than 300K was observed after 2 weeks at 75°F for the samples degraded with the GLSE enzyme breaker.

Based upon these evaluations, one could readily conclude that GLSE breaker provides the best breaker efficiency in terms of molecular weight reduction for the conditions and breaker concentrations evaluated. However, given the lethargic viscosity reduction observed with the activated persulfate and conventional enzyme breaker tests, higher concentrations should be evaluated to determine whether improved molecular weight reduction can be achieved with those breaker species.

Effects of Breakers on Guar-Based Fluids at 125°F

Viscosity reduction to less than 10 cps at both 511 sec^{-1} and 12.7 sec^{-1} was observed within 24 hours with each of the breakers at 125°F, as shown in Figure 5. Viscosity reduction appeared to cease after 24 hours in the samples degraded with oxidizers and activated oxidizers, suggesting that the persulfate-initiated free radical degradation terminates in less than 24 hours. The conventional enzyme and GLSE breakers were observed to continue to reduce the viscosity for extended periods, with the viscosity of the GLSE broken fluid approaching 1.0 cps within a 48 hours.

Neither disaccharides nor monosaccharides were detected in samples degraded with oxidizers, activated oxidizers, or the conventional enzymes. Disaccharides were detected in the GLSE broken samples after 4 hours, and monosaccharides were present after 24 hours at 125°F. Molecular weight reduction effectively ceased after about 24 hours for both the persulfate and activated persulfate breakers to an $AvMW_{300}$ of about 240K with 80% greater than 300K. The $AvMW_{300}$ after 8 weeks was 237K for activated persulfate and 232K for persulfate alone with 78% and 75% greater than 300K, respectively, as shown in Figures 6 and 7.

Molecular weight reduction with conventional enzyme breaker continues over a long period of time as evidenced by the $AvMW_{300}$ of 246K at 24 hours with 82% greater than 300K and the $AvMW_{300}$ of 82K after 8 weeks with 21% over 300K. The GLSE breaker was observed to provide the most efficient 125°F molecular weight reduction of the guar-based fluid. After 24 hours, the $AvMW_{300}$ of GLSE broken fluid was 75K with 21% of the polymer fragments greater than 300K. The molecular weight reduction was observed to continue over the 8 weeks of testing to an $AvMW_{300}$ of 23K with only 4% greater than 300K.

The TOC results on 2-week samples, as shown in Figure 8 and Table 3, generally substantiated the MWCO data. An $AvMW_{300}$ of about 205K with 66% greater than 300K was observed for the oxidative breaker systems. The conventional enzyme breaker provided reduction to an $AvMW_{300}$ of 89K with and 25% greater than 300K. An $AvMW_{300}$ of 14K with only 2% greater than 300K was calculated from the TOC measurements of the samples containing the GLSE breaker.

It is interesting to note that the breaker efficiency trends observed at 125°F correlate extraordinarily well with previously reported fracture conductivity data at 125°F comparing the retained permeabilities observed utilizing these same breakers.[14-15] In the 48-hour MWCO data, the GLSE breaker was indicated to provide average molecular weight reduction almost 3-fold better than the oxidative or conventional enzyme breaker ($AvMW_{300}$ of 89K vs. ~ 250K). When tested in guar-based fluids, the GLSE was observed to yield a retained permeability of 98% as compared to the 31%, 55%, and 65% observed with the persulfate, activated persulfate, and conventional hemicellulase breaker systems at concentrations similar to those in this study.

Effects of Breakers on Guar-Based Fluids at 175°F

The viscosity reduction provided by the selected breakers at 175°F is shown in Figure 9. The viscosity of the samples containing the persulfate breaker were reduced to 15 cps after 24 hours, but the viscosity continued to fall over time, approaching 10 cps after two weeks. The viscosity of the fluids containing conventional enzymes was broken to 6 cps in 24 hours and 4 cps after 1 week. The GLSE breaker was observed to reduce the fluid viscosity more effectively than either the persulfate or the conventional hemicellulase enzyme. The viscosity of the fluid containing the GLSE was reduced to 3 cps within 4 hours.

Only the GLSE breaker provided degradation of the pH 5 fluids at 175°F to the extent that a presence of disaccharides or monosaccharides could be detected. As shown in Table 1, disaccharides were observed in the GLSE degraded samples after 4 hours and monosaccharides were noted after 24 hours.

The molecular weight reduction provided by the oxidative breaker effectively ceased within 24 hours, at which time the $AvMW_{300}$ was 253K with 84% of the fragments greater that 300K, as illustrated in Figures 10 and 11. The conventional hemicellulase enzyme was less effective at 175°F than was observed at the lower temperatures. An $AvMW_{300}$ of 235K with 77% greater than 300K was observed after 24 hours by the MWCO technique. However, the molecular weight reduction was not observed to continue as it had in the lower temperature evaluations, with an $AvMW_{300}$ of 251K and 82% greater than 300K measured after 48 hours. The samples containing the GLSE enzyme breaker, however, were observed to exhibit continued molecular weight reduction versus time at 175°F. The $AvMW_{300}$ at 24 hours was 90K with 20% greater than 300K and at 48 hours was 33K with only 8% greater than 300K.

Whereas, the TOC evaluations after 2 weeks at 175°F yielded results with the persulfate and conventional hemicellulase breakers somewhat different from those generated by the MWCO technique, the data from the GLSE containing fluids agreed very well. As shown in Figure 12, the GLSE sample was observed to have an $AvMW_{300}$ of 33K with only 2% of the fragments greater than 300K. The values for the oxidative breaker at 175°F after two weeks were reduced to an $AvMW_{300}$ of 92K with 28% greater than 300K. An $AvMW_{300}$ of 186K with 59% greater than 300K was observed for the conventional enzymes after 2 weeks by the TOC method. These TOC data appear to conflict with those observed by the MWCO technique after 48 hours as well as the observations at 125°F. The discrepancies are believed to be due to thermally induced hydrolysis of the polymer at the higher temperature of 175°F.

Effects of Breakers on Guar-Based Fluids at 210°F

The viscosity reduction of the guar-based fluids at 210°F is illustrated in Figure 13. Each of the breakers reduced the 511 sec^{-1} viscosity to less than 10 cps within 24 hours. The GLSE breaker provided the most effective viscosity reduction, to less than 5 cps within 24 hours. Disaccharides and monosaccharides were detected only in the GLSE degraded samples. Disaccharides were present in the 48-hour sample and monosaccharides were detected in GLSE samples after 1 week. The longer time to detection with the GLSE relative to the lower temperatures is an indication of reduced activity of the GLSE complex at the higher temperature. Note, however, that the activity was not terminated, but rather retarded, as evidenced by the continual reduction to generate monosaccharides.

The MWCO molecular weight distributions observed at 210°F after 24 and 48 hours are shown in Figures 14 and 15, respectively. MWCO evaluations were not conducted at longer times as it was anticipated that the thermal degradation would increasingly mask the contributions of the breakers as time passed. The molecular weight distribution of the persulfate-containing fluid was reduced after 24 hours to an $AvMW_{300}$ of 243K with 80% of the fragments greater than 300K. The values observed after 48 hours at 210°F were essentially unchanged at an $AvMW_{300}$ of 236K with 78% greater than 300K. The samples with the conventional enzyme breaker were observed to exhibit distributions similar to those seen with the oxidative breaker. An $AvMW_{300}$ of 242K with 80% greater than 300K was observed at 24 hours and 238K with 78% after 48 hours. Effective molecular weight reduction was observed only in the fluids containing the GLSE enzyme breaker. The 24-hour values of the GLSE broken fluid at 210°F were an $AvMW_{300}$ of 127K with 40% of the fragments at greater than 300K. Further reduction to an $AvMW_{300}$ of 107K and 32% greater than 300K was observed after 48 hours. TOC testing was not conducted on the 210°F samples.

Assuming that thermal degradation contributes similarly to the degradation each of the fluids at a given temperature and exposure time, the best breaker efficiency in terms of molecular weight reduction was exhibited by the GLSE enzyme.

Conclusions

Laboratory procedures have been developed and implemented to characterize the efficiency of gel breakers based upon the size distribution of the generated polymeric fragments.

Reduced viscosity is not fully indicative of molecular weight reduction as exhibited by fluids with "adequately reduced viscosity" containing gross concentrations of fragments with average molecular weights exceeding 300,000.

Degradation by oxidative breakers was observed to terminate rapidly as evidenced by minimal reduction of average molecular weight observed after 24 hours.

Enzyme breakers in general were observed to provide more efficient molecular weight reduction than oxidative breakers. Both the GSLE breakers and the conventional hemicellulase enzymes were observed to continue catalyzing molecular weight reduction for up to 8 weeks.

Guar-Linkage-Specific Enzyme breakers were observed to outperform the conventional enzyme and oxidative breakers, in terms of the molecular weight reduction, at all conditions evaluated. The GLSE breaker was observed to consistently degrade the average molecular weight of guar to less than 30,000 over the 8-week study. Reduction to produce monosaccharide or disaccharide fragments was observed only with the GLSE breakers.

Additional evaluations are needed to characterize the relative breaker efficiency in crosslinked fluids, at other environmental conditions, and with other breakers.

Acknowledgement

The authors wish to acknowledge the management of BJ Services for their continuing support, Chris Elliff and Beth Prasek for their contributions toward gathering the necessary data and Doris Porter for preparing the manuscript.

References

1. Hawkins, G.W.: "Laboratory Study of Proppant Pack Permeability Reduction Caused by Fracturing Fluids Concentrated During Closure," paper SPE 18261 presented at the SPE 63rd Annual Technical Conference and Exhibition, Houston, October 2-5, 1988.

2. Van Poolen, H.K., Tinsley, J.M., and Saunders, C.D.: "Hydraulic Fracturing - Fracture Flow Capacity vs. Well Productivity," *JPT* (May 1958) 91-95; Trans, AIME, 213.

3. Tannich, J.D.: "Liquid Removal From Hydraulically Fractured Gas Wells," *JPT* (November 1975) 1309-1317.

4. Volk, L.J., Gall, B.L., Raible, C.J., and Carroll, H.B.: "A Method for Evaluation of Formation damage Due to Fracturing Fluids," paper SPE/DOE 11638 presented at the 1983 SPE/DOE Symposium on Low Permeability, Denver, March 14-16.

5. Gall, B.L. and Raible, C.J.: "Molecular Size Studies of Degraded Fracturing Fluid Polymers," paper SPE 13566 presented at the International Symposium on Oilfield and Geothermal Chemistry, Phoenix, April 9-11, 1985.

6. Small, J., et.al.: "Improving Fracture Conductivities with a Delayed Breaker System : A Case Study," paper SPE 21497 presented at the 1991 SPE Gas Technology Symposium, Houston, January 23.

7. Tjon Joe Pin, R.M., Brannon, H.D., and Martinez, A.D.: "Increased Well Productivity Utilizing Improved Fracturing Fluids and High pH Enzyme Breakers: A Case Study on San Andres Formation Well in the Permian Basin," paper presented at the 1994 Southwest Petroleum Short Course, Proceedings of the 41st Annual Meeting, Texas Tech University, Lubbock, April 22-23.

8. Brannon, H.D. and Tjon Joe Pin, R.M.: "Biotechnological Breakthrough Improves Performance of Moderate to High-Temperature Fracturing Applications," paper SPE 28513 presented at the SPE 69th Annual Technical Conference and Exhibition, New Orleans, September 25-28, 1994.

9. Tjon Joe Pin, R.M., Brannon, H.D., and Handren, P.J.: "Improved Fracturing Technologies Provide Increased Well Productivity: A Case Study on Red Fork Formation Wells," paper SPE 29446 presented at the 1995 Production Operations Symposium, Oklahoma City, April 3-5.

10. Almond, S.W.: "Factors Affecting Gelling Agent Residue Under Low Temperature Conditions," paper 10658 presented at the SPE Formation Damage Symposium, Lafayette, March 24-25, 1982.

11. Almond, S.W. and Bland, W.E.: "The Effect of Break Mechanisms on Gelling Agent Residue and Flow Impairment in 20/40 Mesh Sand," paper SPE 12485 presented at the SPE Formation Damage Control Symposium, Bakersfield, February 13-14, 1984.

12. Hawkins, G.W.: "Molecular Weight Reduction and Physical Consequences of Chemical Degradation of Hydroxypropyl Guar in Aqueous Brine Solutions," Proc. ACS Division of Polymer Materials: Science and Engineering (1986) 55.

13. Strong, F.M. and Koch, G.H.: *Biochemistry Laboratory Manual*, Wm. C. Brown Company Publishers, Dubuque, (1981) 66.

14. Proppant Consortium Report, Fluids 1991.

15. Report SL 2395, Stim-Lab, Inc., July, 1991.

Table 1

Guar/pH 5	4 hrs		24 hrs		48 hrs		168 hrs	
75°F	MS	DS	MS	DS	MS	DS	MS	DS
OXI/ACT	-	-	-	-	-	-	-	-
ENZYME	-	-	-	-	-	-	-	-
GLSE	-	+	+	+	+	+	+	+
125°F								
OXI/ACT	-	-	-	-	-	-	-	-
ENZYME	-	-	-	-	-	-	-	-
GLSE	-	+	+	+	+	+	+	+
175°F								
OXIDIZER	-	-	-	-	-	-	-	-
ENZYME	-	-	-	-	-	-	-	-
GLSE	-	+	+	+	+	+	+	+
210°F								
OXIDIZER	-	-	-	-	-	-	-	-
ENZYME	-	-	-	-	-	-	-	-
GLSE	-	-	-	-	-	+	+	+

Table 2 - MWCO

Linear Guar pH 5.0	24 Hours		48 Hours		2 Weeks		8 Weeks	
	$AvMW_{300}$	Wt% >300K	$AvMW_{300}$	Wt% >300K	$AvMW_{300}$	Wt% >300K	$AvMW_{300}$	Wt% >300K
75°F								
GLSE	106K	32%	89K	25%	27K	21%	24K	2%
ENZYME	211K	69%	250K	83%	231K	77%	153K	48%
OXI/ACT	251K	83%	255K	84%	250K	83%	233K	77%
125°F								
GLSE	75K	21%	55K	12%	48K	10%	23K	4%
ENZYME	246K	82%	247K	82%	151K	46%	82K	21%
OXIDIZER	247K	78%	252K	84%	249K	82%	232K	75%
OXI/ACT	238K	82%	265K	86%	250K	82%	237K	78%
175°F								
GLSE	90K	20%	33K	8%	-	-	-	-
ENZYME	235K	77%	251K	82%	-	-	-	-
OXIDIZER	249K	83%	253K	84%	-	-	-	-
210°F								
GLSE	127K	40%	107K	32%	-	-	-	-
ENZYME	242K	80%	238K	78%	-	-	-	-
OXIDIZER	243K	80%	236K	78%	-	-	-	-

Table 3 - TOC

GUAR pH 5.0	2 Weeks					
	75°F		125°F		175°F	
	$AvMW_{300}$	Wt% >300K	$AvMW_{300}$	Wt% >300K	$AvMW_{300}$	Wt% >300K
GLSE	10	0%	14	2%	27	8%
ENZYME	142	44%	89	25%	186	59%
OXIDIZER	-	-	202	65%	92	28%
OXI/ACT	212	58%	207	67%	-	-

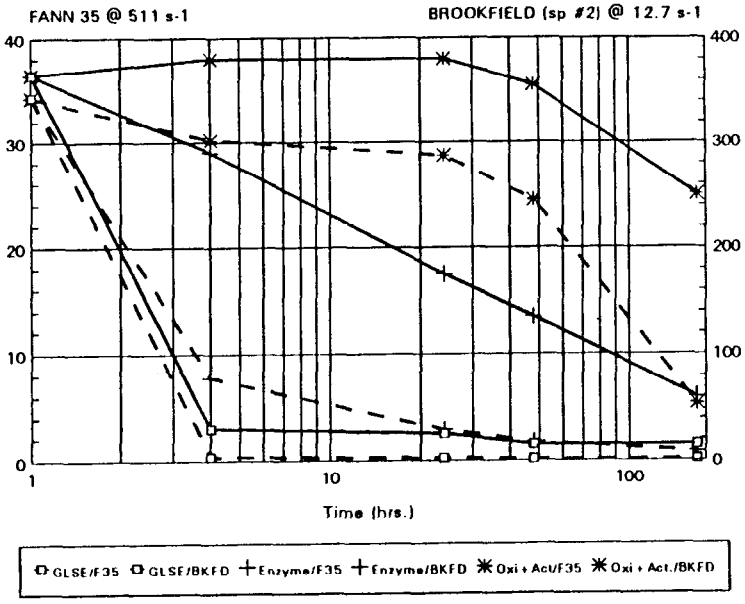

Figure 1 - Guar Viscosities @ 75^{0}f (ph 5)

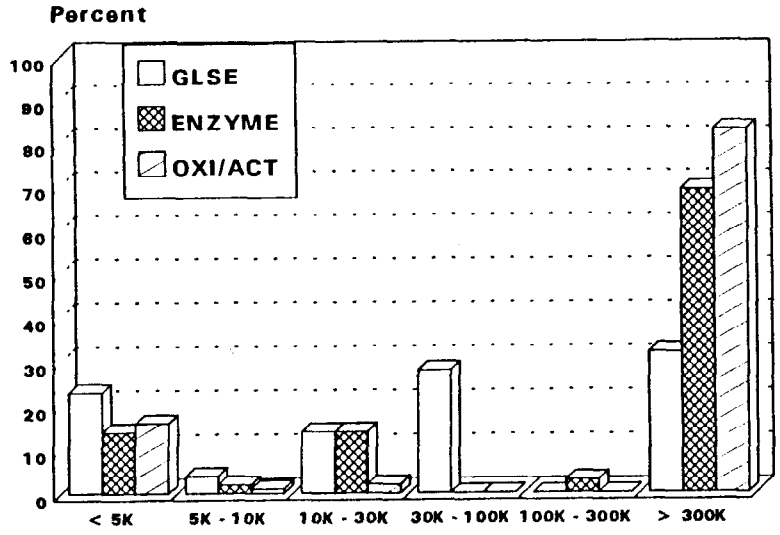

Figure 2 - AvMW $_{300}$ Distribution by MWCO of Guar @ ph 5 after 24 hours @ 75^{0}f

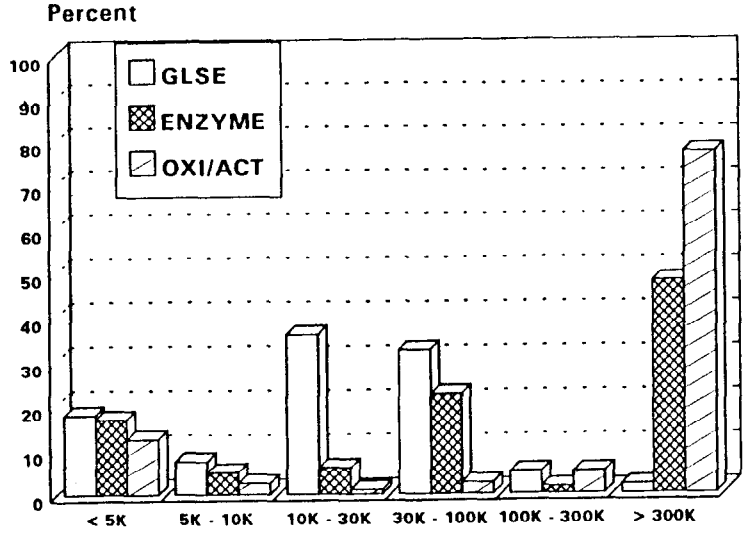

Figure 3 - AvMW $_{300}$ distribution by MWCO of Guar @ ph 5 after 8 weeks @ 75^{0}f

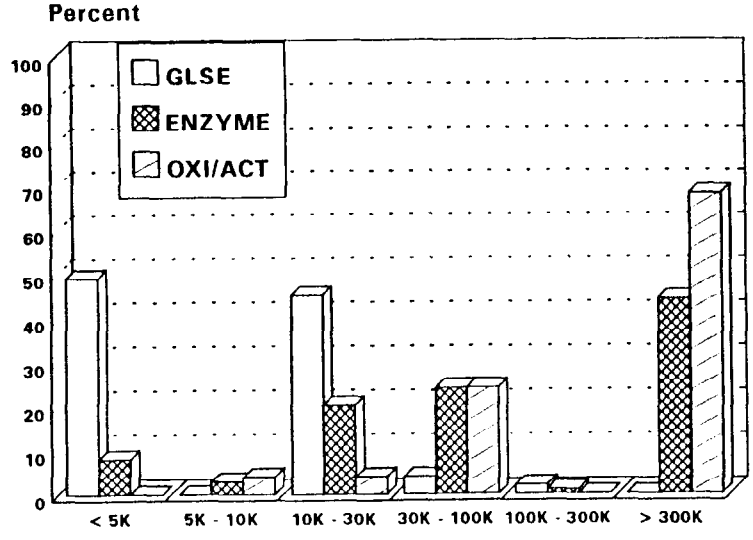

Figure 4 - AvMW $_{300}$ distribution by TOC of Guar @ ph 5 after 2 weeks @ 75^{0}f

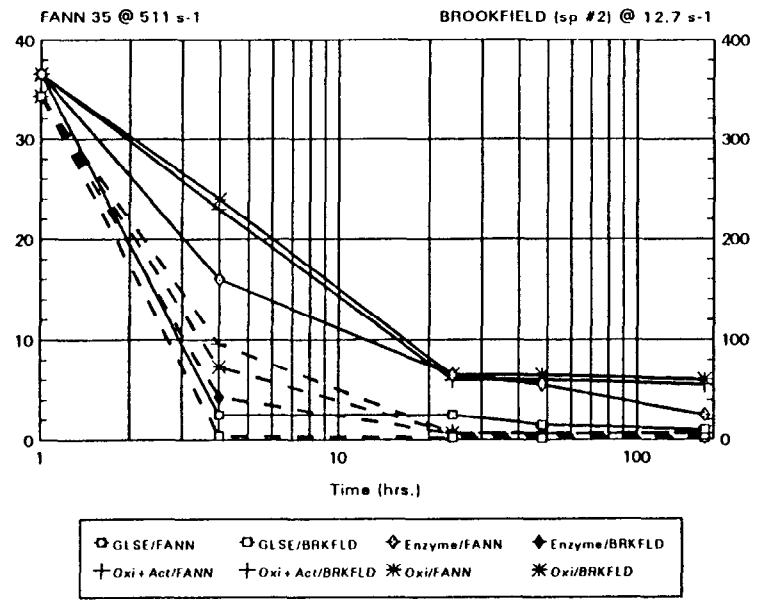

Figure 5 - Guar Viscosities @ 125^{0}f (ph 5)

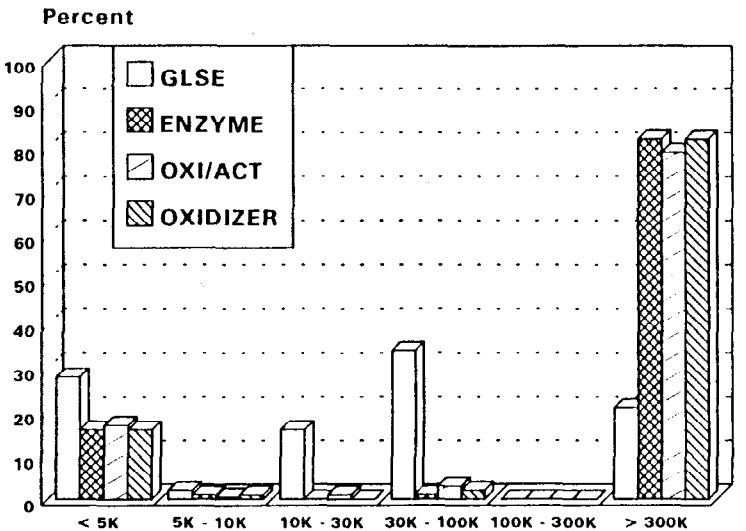

Figure 6 - AvMW $_{300}$ distribution by MWCO of Guar @ ph 5 after 24 hours @125^{0}f

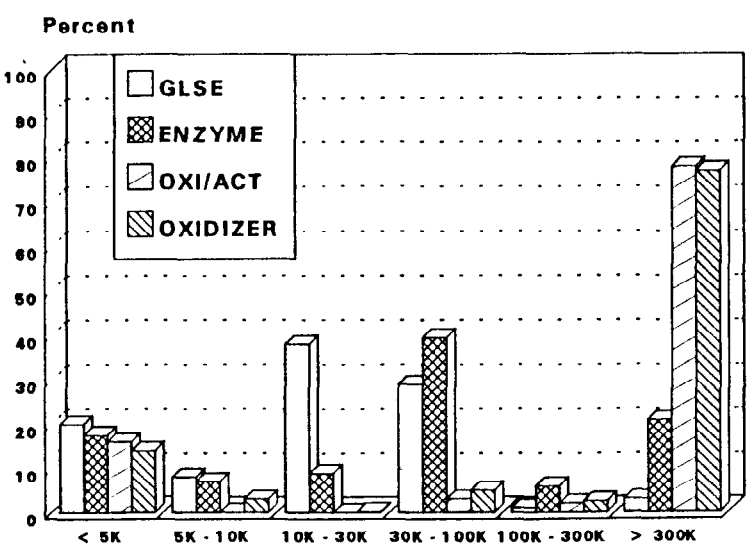

Figure 7 - AvMW $_{300}$ distribution by MWCO of Guar @ ph 5 after 8 weeks @ 125^{0}f

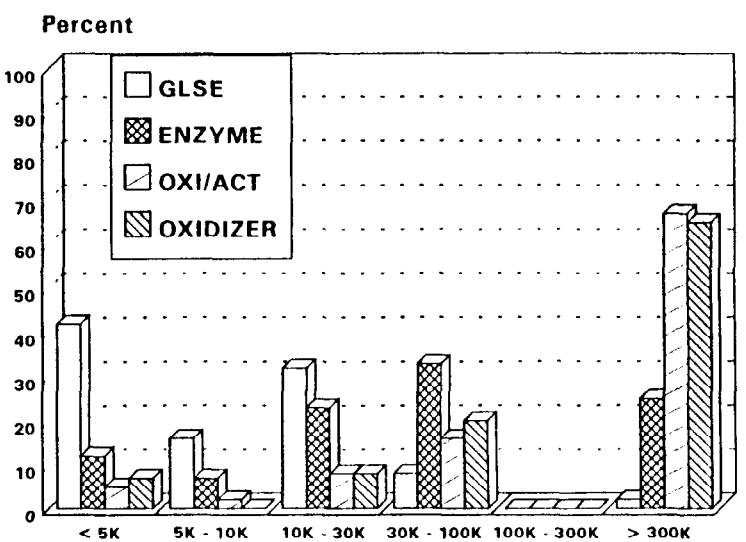

Figure 8 - AvMW $_{300}$ distribution by TOC of Guar @ ph 5 after 2 weeks @ 125^{0}f

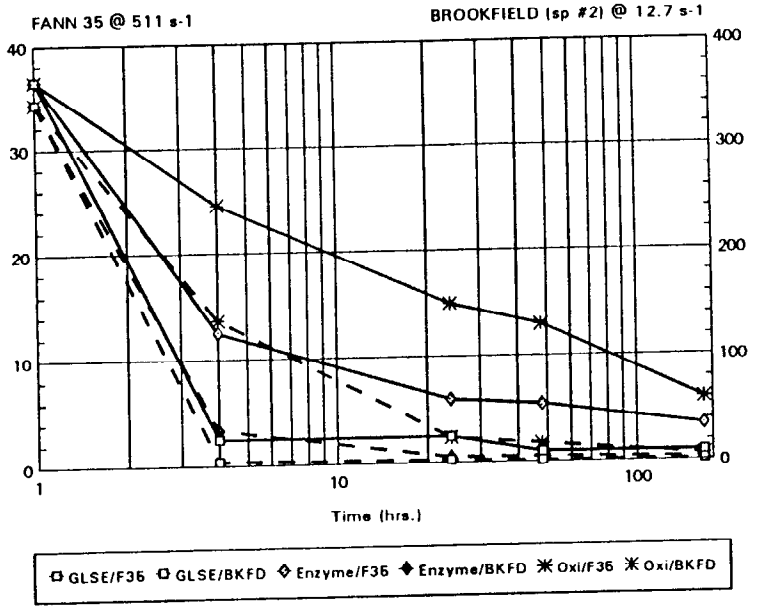

Figure 9 - Guar Viscosities @ 175^{0}f (ph 5)

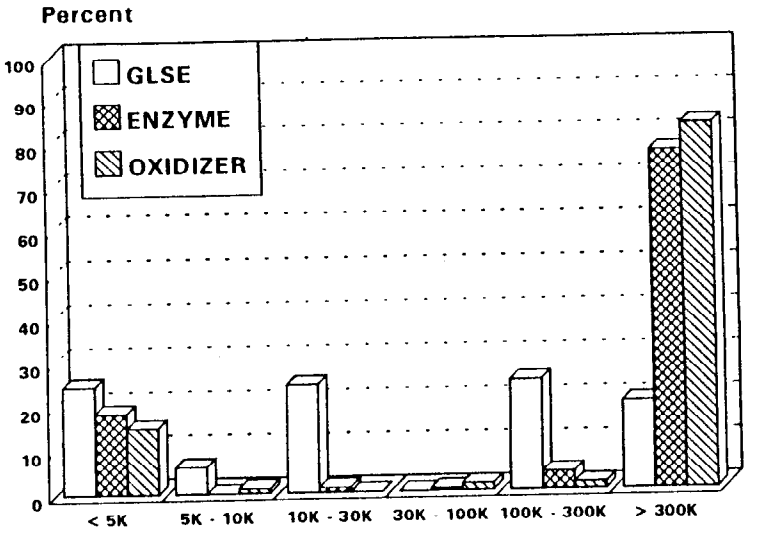

Figure 10 - AvMW $_{300}$ distribution by MWCO of Guar @ ph 5 after 24 hours @ 175^{0}f

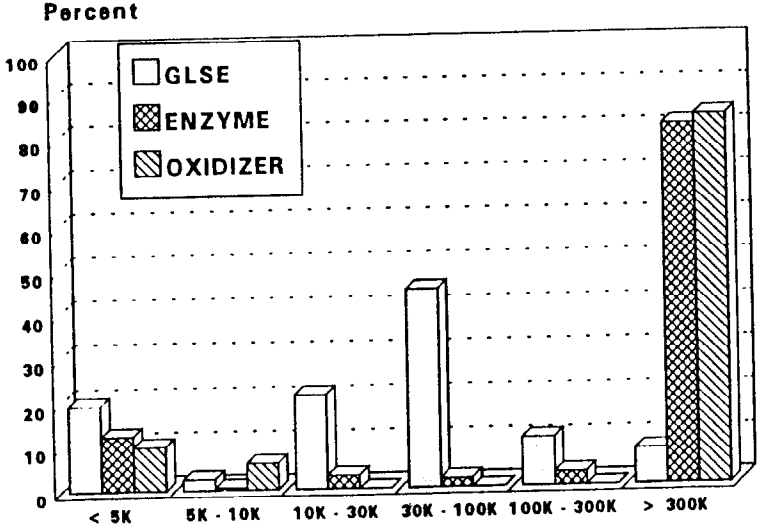

Figure 11 - AvMW $_{300}$ distribution by MWCO of Guar @ ph 5 after 48 hours @ 175^{0}f

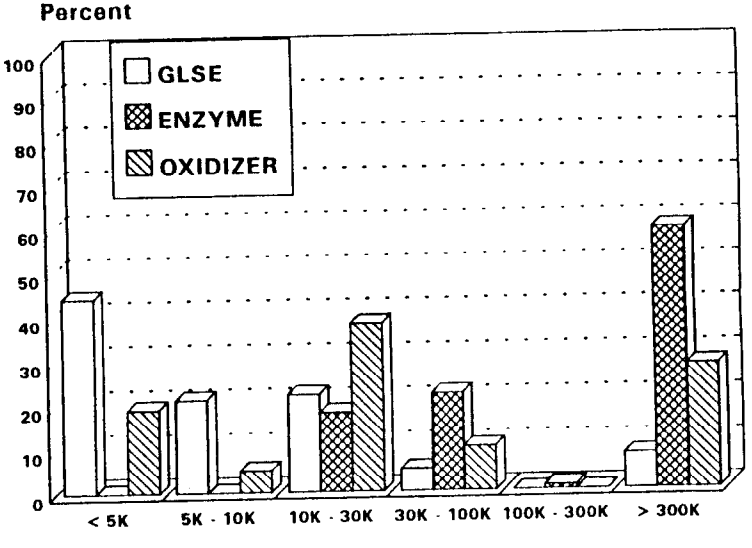

Figure. 12 -AvMW $_{300}$ distribution by TOC of Guar @ ph 5 after 2 weeks @ 175^{0}f

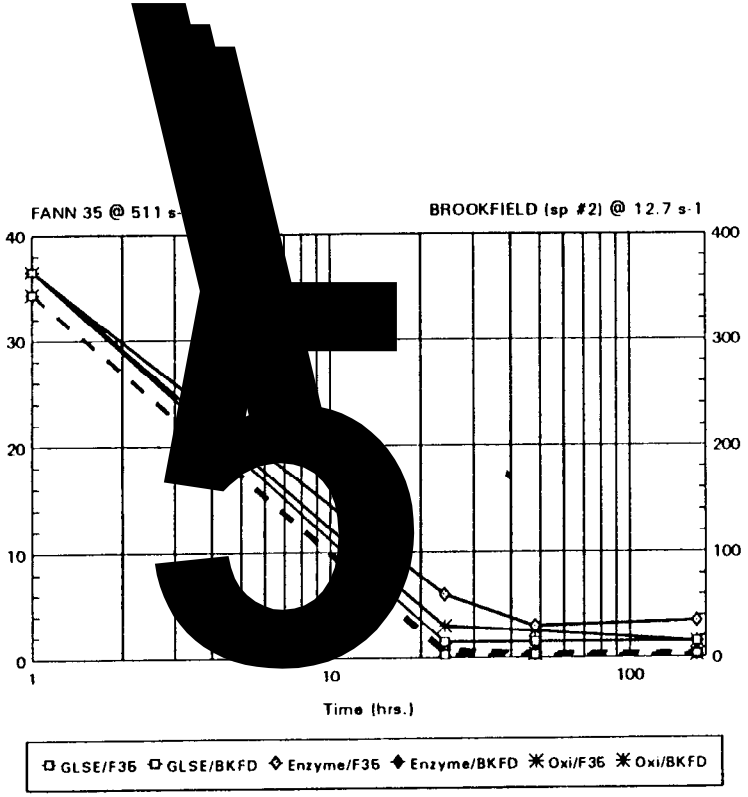

Figure 13 - Guar Viscosities @ 210^{0}f (ph 5)

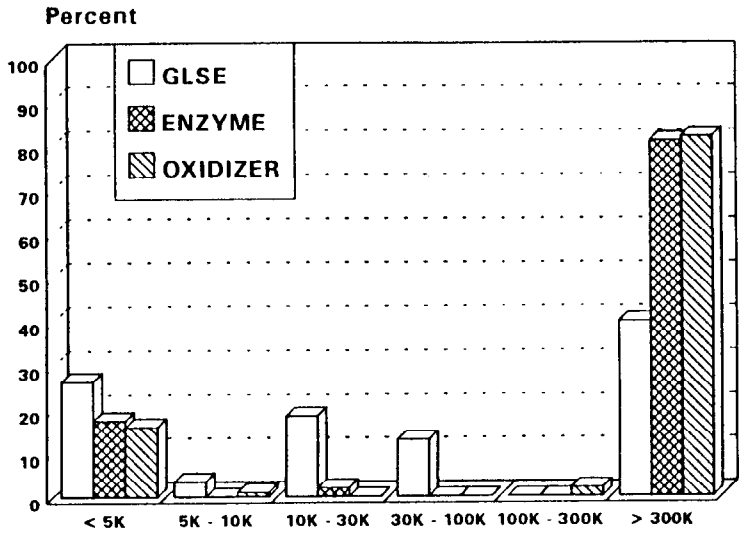

Figure 14 - AvMW $_{300}$ distribution by MWCO of Guar @ ph 5 after 24 hours @ 210^{0}f

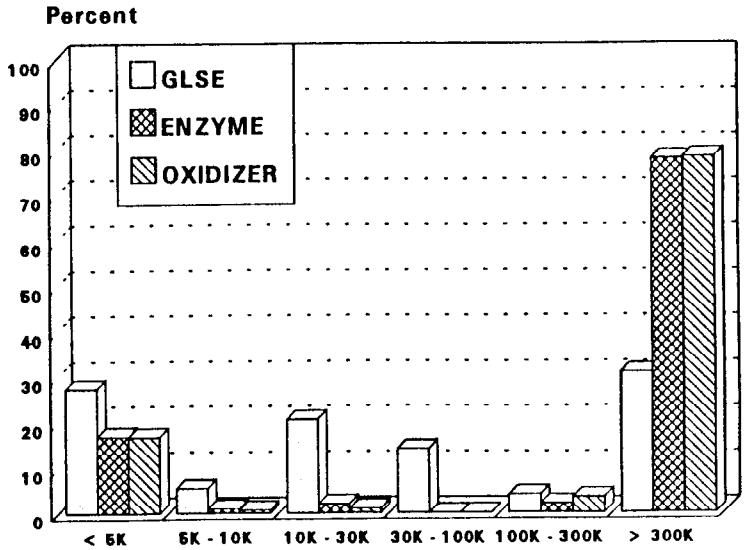

Figure 15 - AvMW $_{300}$ distribution by MWCO of Guar @ ph 5 after 48 hours @ 210^{0}f