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Analysis of Enzymatic Degradation of Polymer Additives

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ABSTRACT

The objective of this study was to investigate the ability of a complex enzyme (LIQ 1) to degrade two polymer compounds Sesbania gum and Guar gum. The study was based on an assumption that the polymer compounds dissolved in water would increase viscosity and be able to plug an artificial rock sample (made of pulverized coal) placed in a pressured chamber. The study also based on an assumption that complex enzyme (LIQ 1) would slowly degrade the polymer compounds there by reducing their viscosity and hence forth unplug the artificial rock. Viscosity of Sesbania gum solution basing on 600 rotations per min on the Fann V-G meter, Model 35 without complex enzyme was 40, after 6 h, the value did not change. The viscosity of Guar gum solution was 34 and after 6 h was still the same. This showed the polymer compounds were not auto degradable at room temperature. Mixtures of polymer compounds and enzyme mixture however, showed a decrease in viscosity after 1 h, Sesbania gum had reduced to 30 and Guar gum 26. The artificial rock sample was plugged with Guar Gum additive 20 min into the experiment and later degraded by the complex enzyme 30 min into the experiment. Sesbania gum plugged the rock after 20 min and was degraded after a longer time of 300 min into the experiment.

Key words: Sesbania gum, guar gum, complex enzyme, plugging, degradation

INTRODUCTION

This study is a laboratory experiment model on reservoir protection technology. It's an investigation on the use of enzymes to degrade polymer cake deposited on the earth formation during the drilling process. Filter cakes or face plugs form during various procedures done within a well bore (Watson *et al.*, 2003). Filter cakes are composed of precipitates, such as silicates formed from drilling muds or residue formed after using polymer-containing gelatable fluids. The residue can contain either poly acrylamide or polysaccharides, depending on the polymer used (Joseph *et al.*, 2001). Polymers have been used in drilling fluids since the 1930s, when cornstarch was introduced as a fluid-loss-control additive. Since that time, polymers have become more specialized and their acceptance has increased accordingly. Polymers are part of practically every water-base system in use today (Swaco, 2001) A variety of polymers have been used in designing a drilling mud to meet some functional requirements such as appropriate mud rheology, density, mud activity, fluid loss, control property, etc (Amanullah and Yu, 2005). Natural polymers such as starch are widely used in drilling, completion and stimulation applications as additives to provide friction reductions, viscosification, particle transport, fluid loss control and zonal isolation (Kameda, 2007).

The drilling fluid is forced into porous zones by differential pressure, displacing or commingling with a portion of the virgin reservoir fluids. This may create blockages due to one or more of several mechanisms that may reduce the permeability or restrict the flow due to relative permeability or viscosity effects. Viscosity effects include emulsions but also plugging by high viscosity treating fluids which for some reason do not "break" or is not sufficiently diluted to readily return to the wellbore under the influence of the available differential pressure (Growcock *et al.*, 2006). Increased water saturation causes water blocking or reduced permeability to oil and gas. Liquid filtrate may create a viscous emulsion with the virgin reservoir oil or water may tend to oil-wet/water-wet the formation rock, reducing the relative permeability to oil. Enzyme systems are known to degrade the types of polysaccharides used in fracturing, blocking gels and other oil industry applications. Enzyme breaker systems have been designed to break gelled fracturing and blocking fluids used in the industry. Enzymes, for example the cellulases, hemi-cellulases, amylases, pectinases and their mixtures are familiar to those in the well service industry when used in fracturing gel breaker systems (Shahriarinour, 2011). Some of these enzymes break the bonds that connect the monosaccharides into a polysaccharide backbone, for instance, the (1,4)-α-D-galactosiduronic linkages in pectin. Instead of fragmenting almost completely into much smaller fragments, these enzymes break the polysaccharide backbone into a mixture of fragments consisting of monosaccharides, disaccharides and polysaccharides. Natural polymers used in drilling fluids are composed of polymerized sugar molecules and belong to a class of compounds called polysaccharides. The monomers are the sugar units and they contain carbon:hydrogen:oxygen in the ratio of 6:12:6 (Growcock, 2010).

Various methods have been used to remove damage in an effort to increase well productivity, including either strong acids or oxidizing agents to cause polymer degradation and removal. However, these agents are partially effective in removing filter-cake damage (Kameda, 2007). Oxidizers as well as strong acids are considered non-specific reactive types. They can react with many different materials, including treating lines, downhole tubulars, formation components, including hydrocarbons (Suhy and Harris, 1998; Luyster and Ali, 2000).

The main objective of this study is to investigate the ability of an enzyme to degrade a filter cake formed, particularly unplugging cross linked polymer bonds formed on an artificial rock sample thereby increasing its permeability. Polymer additives in use today increase viscosity of water when dissolved in solution (Ptasinski*et al.*, 2001).

Sesbania gum is a natural polysaccharide growing only in China with an average molecular weight of 2.3×105-3.4×105. Sesbania gum is a galactomannan and its main structure involves β (1→4) glycosidic bonds linked mannose and α (1→6) glycosidic bonds linked galactose on the side chains (Zhang *et al.*, 2008). The mannose: galactose ratio of the galactomannan is 2:1. Physicochemical properties and chemical construction of Sesbania gum are similar to guar gum (Ma and Pawlik 200; Rwddy and Tammishetti, 2004). The molecular structure of Sesbania gum is shown in Fig. 1 (Fan *et al.*, 2000; Wang *et al.*, 2005). Like other galactomannans, Sesbania gum is insoluble in organic solvents but partially soluble in water.

Guar gum is a polygalactomannan obtained from the seeds of a leguminaceae plant, *Cyamopsis tetragonalobus*, grown mainly in northwestern India and Pakistan. It is a water-soluble polysaccharide and because of its low cost and excellent viscosifying properties, it and its derivatives are extensively used in industrial applications including food, oil recovery, personal care, etc. Guar gum remains highly viscous even at high temperatures (Jain-Raina and Babbar, 2011) Structurally it has a backbone of α-1, 4-linked mannose units with α-1,6-linked galactose units attached as side chains to almost every alternate mannose unit. Molecular structure of Guar gum is shown in Fig. 2 (Rwddy and Tammishetti, 2004).

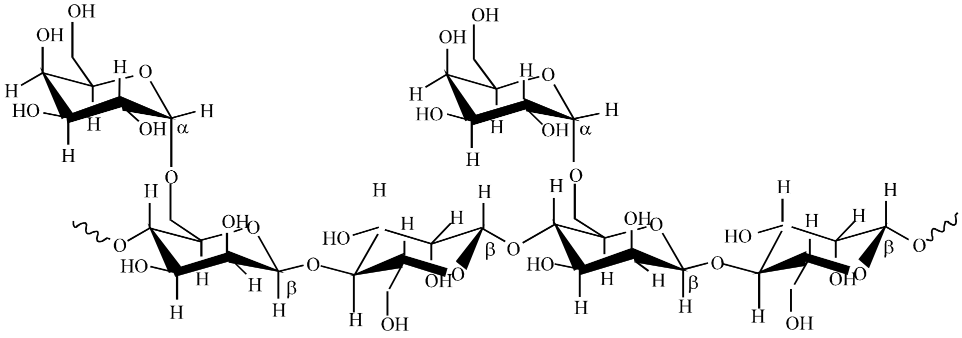

Fig. 1: Molecular structure of sesbania gum

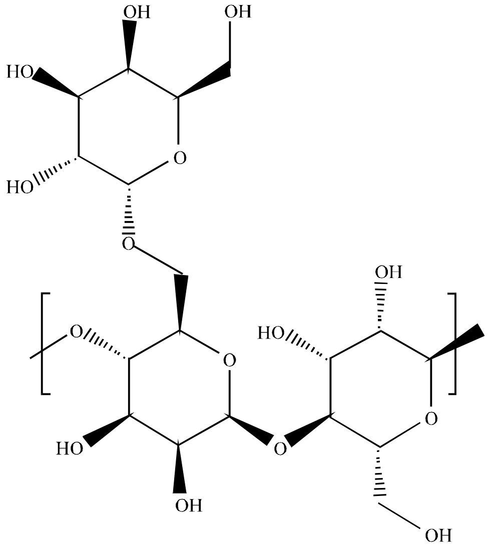

Fig. 2: Molecular structure of guar gum

Drilling polymer additives will gelatinize when meeting with water producing high quantity of viscosity, shear stress and strong adhesion. They have strong adhesive properties and net structural ability. These quantities do well to leakage plugging (Zhenbin *et al*., 1996).

The objective of this study is to investigate the ability of a complex enzyme (LIQ1) to degrade two polymer compounds sesbania gum and guar gum when they are used to plug an artificial rock.

MATERIALS AND METHODS

Polymer additives: Two polymer additives were used namely Guar gum and Sesbania gum powder. The polymers were obtained from the drilling fluids laboratory at China University of Geosciences (Wuhan) Hubei Province China between May and October 2010.

Artificial rock sample and rock permeability characterization: Rock samples were prepared in the laboratory for the study on permeability changes using a core press machine at controlled pressure of 20 Mpa for a period of 30 min.

Pulverized coal was used to make the rock samples (Adedosu *et al*., 2007). Coal grain size (20-40 mm) was purchased from Shaanxi coal and chemical industry group, Shaanxi Province, China. The rock samples were prepared by mixing the 20 gm of coal grains with 0.5ml Sodium silicate and 1 mL of calcium chloride solution.

The length and cross sectional area of the rock sample was recorded. Permeability was determined using Darcy's law (Amiri, 2001) of fluid flow in porous media.

Complex enzyme: Complex enzyme, LIQ 1 (20 mL) was obtained from Longhua Biotechnology Company limited, Wuhan, Hubei province China. The enzyme is active for low to moderate temperatures and works in the pH range of 2.0 to 10.0.

Experiment to determine Viscosity of polymer solution: One set of two plastic beakers was filled with water up to the 500 mL mark. Two grams of each of the polymer additives Sesbania and Guar gum were weighed and mixed uniformly in the water for 20 min using an electric mixer. The solutions were maintained at room temperature.

Viscosities of the solutions were measured using a Fann V-G meter, Model 35 at 600, 300, 200, 100, 6 and 3 rpm at intervals of one h for five h and then after 24 h.

A second set of two plastic beakers was filled with water to 500 mL mark. Two grams of each of the additives Sesbania and Guar gum were weighed and mixed uniformly. Three drops of complex enzyme was added to the mixture and mixed uniformly for 20 min using an electric mixture. The solutions were maintained at room temperature.

Viscosities of the solutions were measured using Fann V-G meter, Model 35 at 600, 300, 200, 100, 6 and 3 rpm at intervals of one h for five and then after 24 h.

Experiment to determine permeability and extent of plugging: A return permeameter (Lake *et al*., 2006), a device made up of flow lines for fluids and gases and gauges to measure pressures and flow rates were used. Artificial rock made of pulverized coal of unit length L and diameter D, was placed in an enclosed pressure chamber in a Return Permeameter device. The rock sample was saturated with nitrogen gas at pressure of 2 MPa to simulate the conditions of the earth. A cylinder in the return Permeameter was filled with 500 mL of water and used to flood the rock core from one side at a pressure of 4 MPa; the amount of water that passed through the rock was recorded at intervals of five min until a constant flow of water was determined. The permeability of the sample in its natural state was then measured.

A solution of 500 mL water, 2 g Guar gum and 3 drops of complex enzyme was well stirred in an electric stirrer for 20 min. The solution was then placed in the cylinder in the return permeameter and used to flood the rock sample at a pressure of 4 MPa .The amount of liquid that passed through the rock was recorded every 5 min for the first thirty min and then at intervals of 10 min for the next period of 5 h.

The flow lines in the return permeameter were then washed clean, the rock sample in the pressured chamber was replaced with a new one. The procedure described above for Guar gum was repeated for Sesbania gum. The solutions contained 500 mL of water, 2 g of additive and 3 drops of complex enzyme well mixed for a period of twenty min in an electric stirrer. The amount of liquid that passed through the rock samples for the periods was recorded until a constant flow rate was obtained. Schematic diagram of experimental set up is shown in Fig. 3.

RESULTS AND DISCUSSION

Table 1 shows results from experiment to investigate the auto degradability of the polymer additives at room temperatures. The length of time it took for viscosity of additive to reduce was directly proportional to the rate of auto degradability (Cai *et al*., 2009).

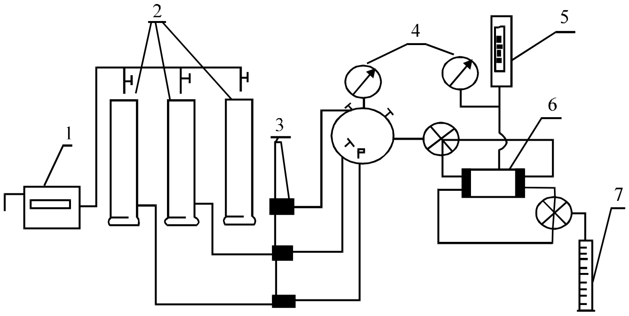

Fig. 3: Schematic diagram of the experimental set up; 1: Nitrogen gas cylinder, 2: Liquid cylinders, 3: Flow valves, 4: Liquid pressure gauges, 5: Hydraulic oil pressure gauge, 6: Pressured chamber for rock sample, 7: Test tube to collect liquid that has flowed through rock sample

Table 1: Viscosity measurements of polymer additive solution at varying shear rates in the absence of complex enzyme

		Viscosity at varying RPM values (Ib/100 sq.ft)			
Polymer additive	Interval of experiment (h)	600	300	200	100
Sesbania gum	0	40	30	24.5	17.5
	6	40	30	25	18
	24	37	26	21	14.5
	30	34	23	18	12
	48	23	14	10	6
	54	21	11.5	8	4
	72	11	6	3	2
Guar gum	0	34	24	20	14.5
	6	34	24	20	14
	24	33	24	19	13
	30	33	23.5	19	13.5
	48	32	22	17	11
	54	30.5	20	15.5	10
	72	22	13.5	9	6

RPM: Rotations per min

From the results, the viscosities of the two polymer additives under room temperature were found to be constant for over a period of 24 h. Casas *et al.* (2000) found out that apparent viscosity of guar gum solution increased with gum concentration and decreased with temperature. Considering viscosities at shear rate of 600 rpm, Guar gum had a small change in viscosity value from 33 to 30.5 after 54 h, after 72 h it however, almost halved to 22. Sesbania gum had its value of viscosity slightly constant for a period of 30 h, after it started to steadily drop. By 72 h, it was as low as 11. When Guar gum is dispersed in water, the galactose side chain of the molecule interacts with water molecule, leading to inter-molecular chain entanglement of the guar gum in aqueous solutions and causing the increase in viscosity of the solution. With the increase in concentration of guar gum, the degree of inter-molecular chain interaction or entanglement would be enhanced which results in increased viscosity (Zhang *et al.*, 2005).

From the above, it can be concluded that polymer additives under room temperature and in the absence of an enzyme are able to maintain their cross linked structure and not degrade for a period of at least 30 h.

The results of viscosity of the solutions and enzyme mixture in Table 2 showed a gradual decrease in viscosity with time. Considering viscosity values at shear rate of 600 rotations per min (RPM) the initial result of Sesbania gum and complex enzyme was 34. After a period of 1 h, the value dropped to 30. The viscosity value continued to drop at a steady rate and after a period of 24 h, the value was 6. Wang *et al.* (2005) reported a steady decrease in viscosity of less than 10% at varying temperatures. This shows that the complex enzyme was able to gradually break down the cross linked bonds in the Sesbania gum after a period of 1 h, the longer the time of contact with the complex enzyme, the more bonds broken up.

The results for Guar gum degradation showed a high value of viscosity at 34, after a period of one h, it dropped to 26 and after a period of 24 h, it had dropped to 15. Shell and Hitzman (1992) reported an initial viscosity of 49, the value dropped to 23 after 1 h and then 10 after 24 h. This showed the complex enzyme was able to break down the cross linked bonds in the polymer. Salyers (1979) found that guar gum can be degraded by enzymes in faecal bacteria leading to a total abolition of its viscous properties.

From Table 3, it shows that the Guar gum-complex enzyme solution was able to flow through the artificial rock at an increasing rate for the first 20 min. After, the cross linked structure of polymer formed a plug on the artificial rock. Flow was inhibited for a period of 5 h. During this time, the complex enzyme was slowly breaking down the cross-linked polysaccharide bonds in the Guar gum into monosaccharide bonds. The enzymes rapidly reduced the viscosity of guar gum solutions while breaking only a limited number of glycosidic bonds (Ahmed *et al.*, 2001). The molecular weight (versus dextran standards) of the guar gum decreased sharply as the viscosity

Table 2: Viscosity measurements of polymer additive - complex enzyme solutions at varying shear rates

		Viscosity at varying RPM (Ib/100 sq.ft)			
Polymer additive	Interval of experiment (h)	600	300	200	100
Sesbania Gum + Complex Enzyme	0	34	26	22	18
	1	30	20	17	11
	2	26	18	14	9
	24	16	10	8	5.5
Guar Gum + Complex Enzyme	0	33	24	19	13.5
	1	26	17	13	8
	2	23	11	9	5
	24	15	8	6	3

RPM: Rotations per min

Table 3: Volume of liquid that flowed through rock sample when guar gum and complex enzyme was used

Time (min)	Volume (mL)
0	0
2	20
32	20
62	20
120	20
180	20
240	20
300	22
330	27

Table 4: Volume of liquid that flowed through rock sample when sesbania gum and complex enzyme was used

Time (min)	Volume (mL)
5	14.00
15	14.50
25	14.75
35	14.75
55	14.75
75	14.75
95	14.75
115	15.00
135	15.25
155	15.75
175	16.25
195	16.50
215	16.75
235	17.00
255	17.25

decreased (Balascio *et al.*, 1981). The linear structure of the polymer as a result of the degradation unplugs the artificial rock thus solution of guar gum-enzyme complex resumes flow at the 300 min as illustrated in Fig. 1 with the steady rise in the graph. The complex enzyme was able to totally unplug the Guar gum polymer after 5 h.

From Table 4, it shows that the Sesbania gum-complex enzyme solution was able to flow through the artificial rock at an increasing rate for the first 5 min. After, the cross linked structure of the sesbania polymer formed a plug on the artificial rock. Flow was then inhibited. The netted structure of sesbania completely plugged the rock. The complex enzyme unplugged the rock after 115 min but the rate of flow of liquid was very slow. Less than 3 mL of liquid flowed through the rock sample 140 min after it was unplugged. This shows that despite the complex enzyme being able to unplug the porous structure of the rock, the polymer netted structure of Sesbania gum makes it work as a plugging agent for longer period of time.

CONCLUSION

Based on the results of this laboratory experiment carried out at room temperature, the polymer additives were able to plug the coal rock sample. Sesbania gum polymer plugged the coal rock sample employed after 20 min while guar gum plugged the rock sample 25 into the experiment. The complex enzyme employed also degraded the polymer bonds of the two polymers used. Sesbania gum and Guar gum were degraded after 300 and 95 min, respectively. Overall, the research on the use of enzymes to degrade polymer bonds used as drilling fluid additives was achieved at laboratory level.

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