

Stabilizing biopolymers in water-based drilling fluids at high temperature using antioxidants, a formate salt, and polyglycol

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Abstract: Biopolymers degrade in water-based drilling fluids when exposed to high temperatures for some time, thus leading to hole-cleaning problems such as stuck pipe. To stabilise biopolymers in drilling fluids, the mechanisms by which they degrade at elevated temperatures must be understood. The degradation mechanisms of thermally labile biopolymers, therefore, include acid-catalysed hydrolysis and oxidation-reduction (redox) reactions. In this paper, an attempt is, therefore, made to investigate whether the combination of anti-oxidants, formate salt, and polyglycol could stabilise biopolymers in water-based drilling fluids with pH 8 to 10 above 200°C. Novel clay-based drilling fluids were formulated with sodium carbonate, sodium bicarbonate, biopolymers, antioxidants, a formate salt, a defoamer and polyglycol. The rheological properties of the drilling fluid formulations were measured using Model 800 and Model 1100 viscometers before and after hot-rolling dynamically in a roller oven for sixteen hours to condition the fluids. Presented results showed that xanthan gum in bentonite-water suspension remained stable up to 100°C, and konjac gum in bentonite-water suspension remained stable up to 65°C. Experimental data also indicated that after dynamic aging for 16 hours, the antioxidant, formate salt and polyglycol increased the stability temperatures of the biopolymers - konjac gum and xanthan gum – in water-based drilling fluid formulations above 200°C. The best additives package that increased the stability temperatures of the biopolymers was potassium formate, sodium erythorbate, and 0.7% polyethylene glycol. This additive package also maintained the suspension capability of the drilling fluid formulations. These additives can, therefore, be used to stabilise water-based drilling fluids containing biopolymers in the 150-232°C temperature range without using expensive and formation damaging synthetic polymers.

Keywords: Konjac gum; xanthan gum; stability temperature; drilling fluid; oil-based mud.

1. Introduction

Biopolymers are used in drilling fluids to provide viscosity, suspension, and fluid-loss control. They are non-toxic and less expensive and can improve the rheological and fluid loss properties at small concentrations of water-based fluids [1]. In addition, biopolymers in water-based drilling fluids do not impair reservoir rocks adversely [1,], [2], and are biodegradable and environmentally friendly [3]; they can either be run separately or combined to improve bentonite performance [4]. Despite all their advantages in water-based drilling fluids, biopolymers degrade

under high-temperature conditions. This degradation of the biopolymers at elevated temperatures leads to the loss of viscosity, and suspension and fluid loss capacity of drilling fluid, thereby causing hole cleaning problems such as stuck pipe. The low stability temperatures of biopolymers, therefore, make them unsuitable for high-temperature drilling operations. According to Roger J. Bradshaw et al. [5], it is challenging to select additives that can give water-based mud the rheological and fluid-loss properties required in a formation with temperature exceeding 300°F(150°C) as some additives degrade at elevated temperatures. Consequently, most water-based fluids formulated with biopolymers can only be deployed in formations with temperatures lower than 300°F (150°C) [6]. To stabilise biopolymers in drilling fluids, the mechanisms through which biopolymers degrade at elevated temperatures, therefore, must be understood. The degradation mechanisms of thermally labile biopolymers, therefore, include acid-catalysed hydrolysis at the acetal linkages present in the biopolymer backbone [7] as well as oxidation-reduction (redox) reactions and early onset of the helix-coil conformation transition [8]. These mechanisms can be exploited to stabilise biopolymers in water-based fluids under high-temperature conditions by deploying additives that can retard the degradation processes. Many researchers have undertaken research work to stabilise water-based fluids using antioxidants, formate salts, and polyethylene glycol. To stabilise water-based fluids at temperatures above 150°C, Howard et al. [9] screened numerous additives to formulate water-based drilling fluids. The best mud formulation that increased the temperature stability of xanthan in potassium formate was made up of magnesium oxide and 5% v/v of polyethylene glycol. The magnesium oxide was used as an antioxidant and pH control agent. Antioxidants protect biopolymers and increase their thermal stability at high temperatures, by inhibiting oxidative reactions and reacting with hydroxyl free radicals that contribute to the degradation of polymers. They pointed out that the polyethylene glycol likely acted as a sacrificial scavenger, which mopped up free radicals before they could attack the biopolymer. This investigation was not done above 210°C, and the mud formulations were clay-free. Formate brine is usually used in water-based drilling muds in high-temperature drilling operations as they act as an anti-oxidant, which preserves biopolymers [10], [9]. They are found to stabilise water-based fluid systems by raising the T_m (transition temperature) of a biopolymer and providing free-radical properties, capable of retarding an oxidative process [11]. Formate brines, therefore, increase the thermal stability of biopolymers by increasing their T_m . J. D. Downs [12] in his investigation observed that formate salts are potent antioxidants and can prevent polymers from thermal degradation up to a temperature of at least 150°C. This finding by J. D. Downs et al. is supported by Howard et al. [9] who reported that formate brine could only raise the thermal stability of biopolymers up to around 175°C at best. It is, therefore, not recommended to use formate salts alone to stabilise water-based fluids above 175°C. Eric van Oort et al. [13] investigated a new method to improve the High-Pressure High Temperature (HPHT) stability of conventional rheology modifiers and fluid-loss controlled polymers used in water-based drilling fluids. The technique exploited the interactions of polysaccharides (e.g. xanthan gum, scleroglucan), cellulose (e.g. CMC, PAC) and starches with polyglycols. The biopolymer and polyglycols were found to associate by intermolecular hydrogen bonding and hydrophobic interactions. This association was found to stabilise the biopolymers at higher temperatures. This finding by Eric van Oort et al. is supported by Howard

et al. [9] who reported that polyglycol stabilised biopolymers at high temperatures. Dissolved oxygen in drilling fluid is not only responsible for thermal degradation of biopolymer at high temperatures, but it is also responsible for corrosion of drill pipes. Consequently, in the industry, oxygen scavengers are used to remove dissolved oxygen from drilling fluids. According to J.D. Downs [14], to protect biopolymer from degradation at high temperature, some users used pH preserving agents and antioxidants to prevent the polymer degradation processes. In addition, Scott L. Wellington et al. [15] investigated the chemical stability of biopolymers. Oxidation/reduction (redox) reactions involving free radicals were highlighted as the probable cause of polymer degradation and concomitant viscosity loss. R.S. Seright and B. J. Henrici [18] investigated the relative importance of hydrolysis, oxidation, and helix-coil transition in xanthan degradation. In the absence of oxidising agents (i.e., dissolved oxygen), results indicated that free-radical, oxidation/reduction reactions were not the dominant mechanism for xanthan degradation. This finding by R.S. Seright and B. J. Henrici supports the conclusion drawn by J.D. Downs [14] and Scott L. Wellington et al.[15] on the use of antioxidants to stabilise biopolymers in water-based drilling fluids at high temperatures.

The literature survey reveals the advantages of stabilising biopolymers in water-based fluids with antioxidants, formate salts, and polyglycols. However, none has considered the combination of pH stabilising agents with the additive package used in this study. This study objective, therefore, was to investigate whether the combination of antioxidants, potassium formate, polyethylene glycol could increase the stability temperatures of biopolymers in water-based drilling fluids. The scope of the study included the examination of thermal stability of the biopolymers in bentonite-water suspension and in drilling fluid formulations buffered with sodium carbonate and sodium bicarbonate. Howard et al. [9] in their investigation defined thermal stability of biopolymers to be the temperature at which they retain 50% of their viscosity when hot-rolled for 16-hours in a roller oven. This same discretionary measurement was used in this experimental study. The goal of this study was to determine the mud properties through laboratory measurements and to find the additive package that would extend the 16-hour thermal stability of the biopolymers above 200°C (396°F) in drilling fluid formulations with pH 8 to 10.

2. Materials, and experiment apparatus and procedure.

2.1 Materials

Konjac gum, a perennial herbaceous herb, mainly grows in the South East of Asia [16]. It is high molecular weight, non-ionic, linear glucomannan consisting of D-mannose and D-glucose units in the ratio 1.6:1. It has a molecular weight range of 200,000 to 2,000,000 Daltons [17]. Its high molecular weight accounts for its high viscosity in solution. Xanthan gum (XC), a polysaccharide, made from carbohydrates, is made commercially by using microbial fermentation with the *Xanthomonas campestris* bacterium. Xanthan gum structure is based on cellulose backbone having alternate glucosyl residues substituted by a trisaccharide chain of D-mannose, D-glucuronic acid and a terminal D-mannose. Some of the properties of xanthan gum include high viscosity at low concentrations, pseudo plasticity and insensitivity to a wide range of

temperature, pH, and electrolyte concentrations [18]. It is used in pharmaceuticals, food, paper, cosmetics, paint, textiles, and petroleum industries as a result of its desirable properties [19]. It has an average molecular weight of 3×10^5 to 7.5×10^6 g mol⁻¹ or greater, thus indicating the ability of xanthan molecules to aggregate [20].

2.2 Experiment apparatus and procedure

All the mud samples were stirred for 30 minutes using the Hamilton Beach mixer (Fig. 1a). The additives were gradually added to 350 ml (one lab barrel) of water and stirred for 30 minutes at room temperature. The base muds were aged to hydrate thoroughly at room temperature for sixteen hours before testing for their rheological properties at 25°C (before the hot rolling test (BHR)), using Model 800 (Fig. 1b) and Model 1100 (Fig. 1c) viscometers. Other test muds were pressurised in ageing cells (Fig. 1d) and were aged dynamically in a roller oven (Fig. 2) at different temperatures for sixteen hours and were allowed to cool to 25°C before testing for their rheological properties (after the hot rolling test (AHR)). Model 800 viscometer uses the principle that the force, which turns an object in a fluid, can indicate the viscosity of the fluid [21]. The speed accuracy (RPM) of the instrument is 0.1 [22].



(a)



(b)



(c)



(d)

Fig.1: Experimental equipment. (a): Model 1100 viscometer and laptop. (b): Aging cells. (c) Model 800 viscometers. (d): Hamilton Beach Mixer



Fig. 2: The roller oven

Plotting shear rate vs shear stress on a graph requires the calculation of the shear stress values as shown in the equations below:

$$\gamma = \text{RPM} \times 1.70 \quad (1)$$

$$\tau_{OFU} = \theta \times 1.067 \quad (2)$$

$$\tau_{SI} = \tau_{OFU} \times 0.4788 \quad (3)$$

$$\mu_{eff} = \frac{\tau_{SI}}{\gamma} \quad (4)$$

Where OFU= oil field unit, SI= SI unit, and μ_{eff} is effective viscosity. The RPM-values are multiplied by a constant 1.703 to convert to a shear rate with the unit per second(s^{-1}). The instrument was calibrated before running tests. The Model 1100 Pressurized Viscometer is fully-automated. It is used to measure the shear stress, shear rate, time, and temperature of fracturing fluids and drilling fluids at pressure up to 2500 psi. The instrument is operated with ORCAD[®] software portable. The speed (RPM) accuracy is 0.001 [25]. The device was calibrated before the tests were carried out. With the Model 1100 viscometer, the ‘RP 13D’ - Bingham Plastic Analysis Model - was selected and the test results were exported to Excel Spread Sheet. From the dial readings of the Model 800 viscometer, plastic viscosity, yield point, and effective viscosity were calculated. The plastic viscosity (PV) and yield point (YP) were calculated from two dial readings at 600rev/min and 300rev/min respectively.

$$PV = \theta_{600} - \theta_{300} \quad (5)$$

$$YP = \theta_{300} - PV \quad (6)$$

Apparent viscosity μ_a was calculated as follows:

$$\mu_a = \frac{600RPM}{2} \quad (7)$$

Where θ is the dial reading at ω rev/min. It is usually reported at the 600 revs/min reading. The effective viscosity was calculated by the equation below:

$$\mu_e = \frac{300\theta \text{ (at any RPM)}}{RPM} \quad (8)$$

The viscometer was calibrated before starting the test.

2.2.1 Fluid formulations

Twelve different test fluids were formulated in total to determine their rheological properties. The first test fluids, the base fluids, were prepared by adding each of the biopolymers to pre-hydrated bentonite-water suspension. The concentrations of materials in the test muds were similar to those used in previous studies on polymer-based fluids [1], [2], [9]. Clay solid contents in freshwater-based mud should not be more than 7% [26]. It should be less than 7% for efficient solids control to prevent pipe sticking and to reduce drag and torque [4]), 10.5 Ibm of bentonite was, therefore, added to 1bbl of fresh water ((3% w/v concentration was used in this study). The other test muds were prepared by mixing each of the biopolymers –xanthan gum and konjac gum – with the other mud additives. The other additives used were as shown in Table 1, and the drilling fluid formulations are shown in Tables 2 and 3. The additive concentrations were within the range used in similar studies [1], [2], [9].

Table 1: Additives tested for their effects on the temperature stability of biopolymers

Additives	Primary function	Amount
Potassium formate	Temperature stabilizer/Anti-oxidant	1 – 3 (lbm)
Sodium erythorbate	Antioxidant/ Oxygen scavenger	1 –3 (lbm)
Polyethene glycol 8000(PEG)	Shale stabiliser	1 –3 (lbm)
Sodium carbonate	Buffer	1 – 3 (lbm)
Sodium bicarbonate	Buffer	0.1-1.2 (lbm)
Dispelair Se574	Defoamer	0.003-0.03 (bbl)

Table 2: Drilling fluid formulations with xanthan gum and other additives

Mud Name	MudA1	Mud A2	Mud A3	Mud A4	Mud A5
Additives					
Water(bbl)	1.0	1.0	1.0	1.0	1.0
Bentonite(Pre-hydrated)(Ibm)	10.5	10.5	10.5	10.5	10.5
Xanthan Gum (Ibm)	1.0	1.0	1.0	1.0	1.0
K-Formate (Ibm)	-	-	-	3.0	3.0
Sodium Erythorbate (Ibm)	-	-	-	1.5	1.5
Na carbonate (Ibm)	-	-	-	1.5	0.7
Na Bicarbonate	-	-	-	1.2	1.2
DispelairSE 574(bbl)	-	-	-	0.01	0.01
PEG(8000) (Ibm)	-	-	-	1.0	1.5

Table 3: Drilling fluid formulations with konjac gum and other additives

Mud Name	Mud B1	Mud B2	Mud B3	Mud B4	Mud B5	Mud B6	Mud B7
Additives							
Water(bbl)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Bentonite(Pre-hydrated) (Ibm)	10.5	10.5	10.5	10.5	10.5	10.5	10.5
Konjac gum	1.0	1.0	1.0	1.0	1.0	1.0	1.0
K-Formate (Ibm)	-	-	-	-	3.0	3.0	3.0
Sodium Erythorbate (Ibm)	-	-	-	-	1.0	1.0	1.5
Na carbonate (Ibm)	-	-	-	-	1.0	1.5	1.2
Na Bicarbonate	-	-	-	-	0.8	1.2	0.7
DispclairSE 574(bbl)	-	-	-	-	0.01	0.01	0.02
PEG(8000) (Ibm)	-	-	-	-	1.0	1.0	2.5

3. Results and discussion

3.1 The base fluid formulations

Hot-rolling tests were used to investigate the thermal stabilities of the biopolymers. The stability temperature was defined as the temperature that a fluid can be exposed to for 16 hours without losing more half of its viscosity [9]. The viscosities of drilling fluids formulated with the additives were compared with the control fluid formulations comprising just the biopolymer in bentonite-water suspension to evaluate the fluids stabilities and performance. The fluid control formulations were Mud A1 and Mud B1.

Table 4: Properties of muds formulated with xanthan gum before and after dynamic aging

Muds	A1	A2	A3	A4	A5
	(BHR@ 25°C)	(AHR@1 00°C)	(AHR@1 10°C)	(AHR@2 00°C)	(AHR@2 10°C)
Properties					
Shear stress @511s ⁻¹	21.0	12.0	8.0	18.0	15.0
Shear stress @1021s ⁻¹	30.0	16.0	12.0	22.0	20.0
Apparent viscosity (cP)@511s ⁻¹	20.0	11.0	8.0	17.0	14.0
10-sec Gel	9.0	4.0	4.0	11.0	4.0
10-min Gel	11.0	4.0	6.0	14.0	5.0
Plastic viscosity (PV)(cp)	6.0	3.0	2.0	2.0	2.0
Yield Point (YP) (Ib/100ft ²)	11.0	9.0	6.0	15.0	5.0

Table 5: Properties of muds formulated with konjac gum before and after dynamic aging

Muds		B1	B2	B3	B4	B5	B6	B7
		(BHR @25°C)	(AHR@ 60°C)	(AHR@ 65°C)	(AHR 70°C)	(AHR@1 70°)	(AHR@2 00°C)	(AHR@2 32°C)
Properties								
Shear stress	@511s ⁻¹	30.0	18.0	15.0	12.0	25.0	16.0	29.0
Shear stress	1021 s ⁻¹	47.0	27.0	23.0	20.0	28.0	19.0	32.0
Apparent Viscosity (cP)@	@511s ⁻¹	28.0	17.0	15.0	11.0	23.0	15.0	27.0
10-sec Gel		7.0	4.0	3.0	1.0	13.0	9.0	12.0
10-min Gel		9.0	4.0	3.0	2.0	15.0	11.0	16.0
Plastic viscosity (PV)(cP)		7.0	4.0	4.0	4.0	3.0	2.0	4.0
Yield Point (YP) (lb/100ft ²)		9.0	14.0	11.0	9.0	22.0	14.0	24.0

Table 6: The apparent viscosities (AVs) of drilling fluid formulations with xanthan gum at different shear rates

Shear rate (s ⁻¹)		1021	511	341	170	102	51	10
(Mud A1 BHR@25°C)	AV(cP)	14	20	25	42	65	119	500
(Mud A2AHR @100°C)	AV(cP)	8	11	15	15	34	62	210
(Mud A3AHR@110°C)	AV(cP)	6	8	9	14	21	37	100
(Mud A4 AHR@200°C)	AV(cP)	10	17	22	44	75	150	700
(Mud A5 AHR@210°C)	AV(cP)	10	15	20	36	60	100	570

Table 7: The apparent viscosities of drilling fluid formulations with xanthan gum at different shear rates

Shear rate (s ⁻¹)		1021	511	341	170	102	51	10
(Mud B1 BHR@25°C)	AV(cP)	22	28	32	47	66	110	400
(Mud B2AHR@60°C)	AV(cP)	13	17	20	30	39	58	200
(Mud B3AHR@65°C)	AV(cP)	11	15	19	28	37	57	190
(Mud B4 AHR@70°C)	AV(cP)	9	11	13	16	21	30	75
(Mud B5 AHR)@170°C)	AV(cP)	13	23	29	53	86	167	800
(Mud B6 AHR@200°C)	AV(cP)	9	15	20	39	65	130	500
(Mud B7 AHR@232°)	AV(cP)	15	27	38	74	123	243	800

Rheological properties – PV, YP, and 10-sec and 10- min Gel strengths – were measured and presented in Tables 4 and 5. The apparent viscosities (AVs) were measured and presented in Tables 6 and 7. The apparent viscosities of the based fluids before hot-rolling (BHR) tests indicated as follows (Tables 4 and 5):

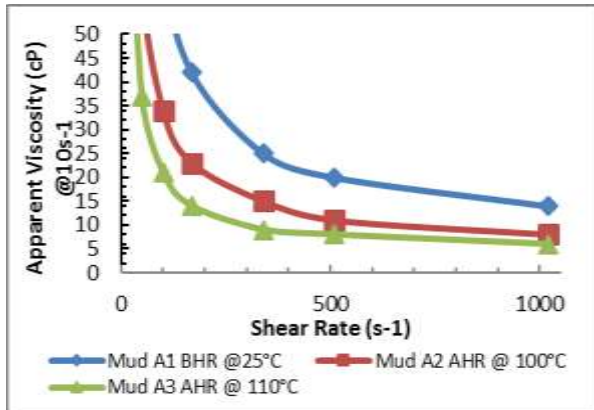
- Mud A1 viscosity @ 511s^{-1} and 25°C was 20 cP.
- Mud B1 viscosity @ 511s^{-1} and 25°C was 28cP.

After that, the control samples were aged dynamically to mimic drilling fluid circulation in a wellbore annulus. Fig. 3 shows the rheological properties of mud formulations; Fig. 3a shows the apparent viscosity of the base sample (Mud A1) at different shear rates. It can be seen that the base fluid sample (Mud A3) hot rolled at 110°C did not exhibit similar rheological properties to those of the base fluid sample (Mud A1). It (Mud A3) lost more than half its viscosity, thus indicating thermal degradation. Its apparent viscosity, when aged at 110°C for 16 hours, was 8cp at 511s^{-1} while the apparent viscosity of the base fluid sample before hot rolling at 25°C was 20cP at 511s^{-1} .

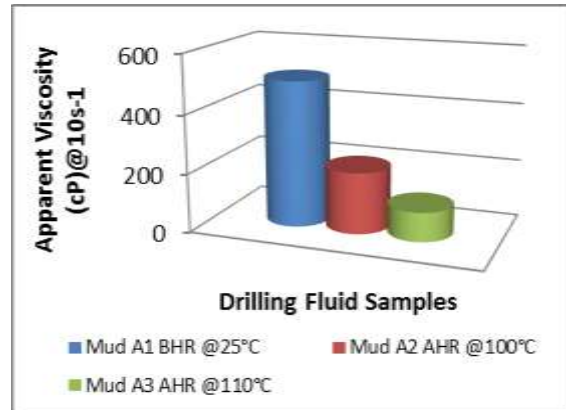
A stable mud will indicate that its rheological parameters are almost the same before and after hot rolling tests. In addition, a mud is said to be stable if it does not lose more than half of its viscosity after being hot-rolled for sixteen hours [9]. After being hot rolled at 100°C for 16 hours, Mud A2 lost 50% of its viscosity (Table4). Consequently, and from the discretionary measurement adopted in this study, xanthan gum stability temperature in bentonite water-suspension is, therefore, 100°C . In addition, the base fluids low shear rate viscosity after being hot-rolled at 110°C for 16 hours was very low (Fig. 3b), thus indicating its inability to suspend cuttings when drilling operations are stopped temporarily. Fig. 3c shows the apparent viscosity of the base fluid sample (Mud B1) at different shear rates. It can be seen that the base fluid sample hot rolled at 70°C for 16 hours did not exhibit similar rheological properties to those of the base fluid sample before the hot rolling tests. The base fluid (Mud B1) formulated with konjac gum after being hot-rolled up to 70°C lost more than half its viscosity, indicating thermal degradation (Table 5). For Mud B1, after being hot-rolled at 65°C for 16 hours, it lost 50% of its viscosity. However, after being hot-rolled at 70°C , the fluid lost more than half its viscosity, thus indicating thermal degradation. Its apparent viscosity when hot-rolled at 70°C for 16 hours was 11cp at 511s^{-1} while the apparent viscosity of the base fluid before being hot-rolled at 25°C was 28cP at 511s^{-1} . It can be seen that the stability temperature of konjac gum in bentonite-water suspension is 65°C . The base- fluid low shear rate viscosity after being hot-rolled at 70°C for 16 hours was very low (Fig.3d)). It can be observed that for 16 hours at 70°C , the base fluid containing konjac gum will degrade, thereby losing its capacity to suspend cuttings and weighting material during quiescence. In addition, the xanthan gum and konjac gum developed excellent viscosities in the bentonite-water suspension and underwent thermal thinning as the aging temperatures were increased. It is clear, therefore, that the xanthan gum and konjac gum were in their transition phases from 100°C and 65°C upwards respectively. Above the stability temperatures of the biopolymers after sixteen hours of aging, the effects of temperatures on the biopolymers were irreversible.

As the aging temperatures were increased above the stability temperatures, the bonds in polymer chemical structure were damaged. This damage led to the breakage of the side chains of the polymer backbone, hence the reduction in their viscosities [27]. It is clear therefore that the base fluid samples lost their

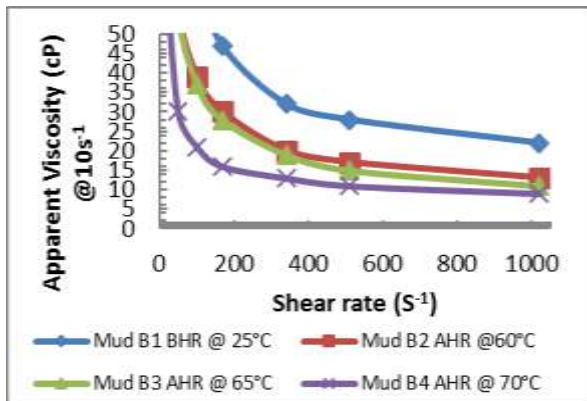
viscosities at high temperatures as there was no additive to offer them protection from oxidative and hydrolytic degradation. More so, all the viscosities of the base fluids reduced after hot rolling, thus showing thermal degradation. The base fluids underwent thermal thinning as it was heated to high temperatures. In addition, The rheological properties (YP and Gel strengths) of the base fluids measured after hot rolling at different temperatures decrease sharply (Tables 3 and 4), thus showing their instabilities at high temperatures. A stable mud retains most of its rheological properties at high temperatures. For this reason, the low stability temperatures, the poor low shearing viscosities, and unstable rheological properties of the base fluids show that they are not suitable for use in high-temperature drilling operations. Above their temperature stabilities, the base fluids would experience total failure, regarding the loss of their viscosities, and suspension, and fluid loss control capacity. Consequently, the base muds are not suitable for use above their stability temperatures. The mud formulations, therefore, require further modification and protection at high temperature, hence the need to deploy antioxidants, formate salts, and polyglycol as shown in Table 1. It has been reported in previous works that the best thermal stabiliser for biopolymers include a solution containing a concentrated salt brine, glycol, and an oxygen scavenger [9], [15]



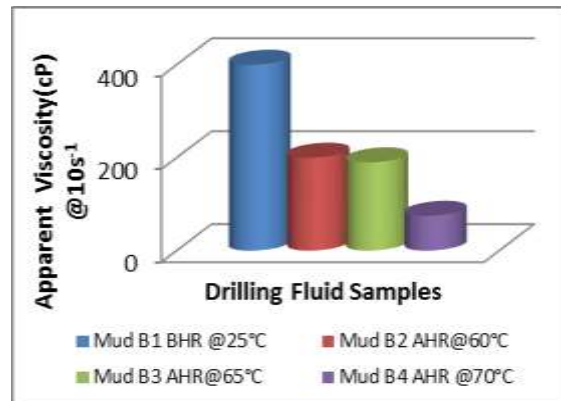
(a)



(b)



(c)



(d)

Fig. 3: Rheological properties of base mud formulations. **(a):** Viscosity of base fluids formulated with xanthan gum at different shear rates before and after dynamic aging at different temperatures for 16 hours. **(b):** Low shear rate viscosity of base fluids formulated with xanthan gum before and after dynamic aging at different temperatures for 16 hours. **(c):** Viscosity of base fluid formulated with konjac gum at different shear rates before and after dynamic aging at different temperatures for 16 hours. **(d):** Low shear rate viscosity of base fluids formulated with konjac gum before and after dynamic aging at different temperatures for 16 hours.

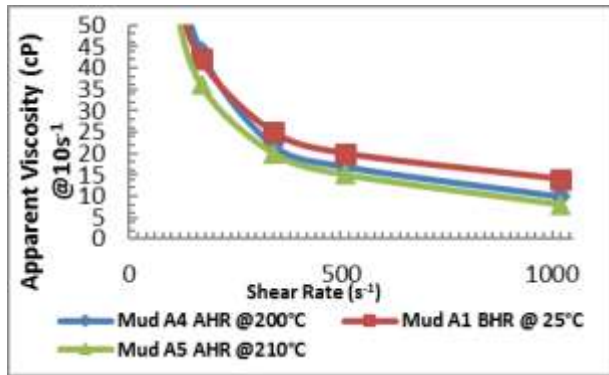
3.2 Effects of antioxidants, formate salt, and polyglycol on biopolymers

Biopolymers in water-based drilling fluids degrade when exposed to high temperatures for a long period. This degradation of the biopolymer can lead to total failure of a water-based drilling fluid. The additives deployed in this study to retard the degradation of biopolymers in water-based drilling fluids were potassium formate, sodium erythorbate, and polyethylene glycol. The additives were tested to find out if they could extend the 16-hour stability temperature of konjac gum and xanthan gum in drilling fluid formulations buffered with sodium carbonate and sodium bicarbonate. Since one of the mechanisms through which bio-polymers degrade at high temperature is acid-catalysed hydrolysis, the mud formulations were buffered with buffering agents. Since oxidation reaction is one of the mechanisms through which biopolymers degrade at high temperatures, sodium erythorbate, an antioxidant, was added to the drilling fluids formulations. Potassium formate was added to the mud formulations, as it is the best promoter of polymer stability at high temperature. It also serves as an antioxidant in drilling fluids. Antioxidants protect biopolymers and increase their thermal stability at high temperatures. They inhibit oxidative reactions and react with hydroxyl free radicals that contribute to the degradation of polymers [9]. The thermal stabilities of the mud formulations with the additives at high temperature were examined through hot-rolling tests. The rheological properties such as YP, PV, gel strength, and apparent viscosity (AV) were measured and presented in Tables 3, 4 and 5. From Section 3.1, the low stability temperatures, the poor low shearing viscosities, and unstable rheological properties of the base fluids show that they are not suitable for use in high-temperature drilling operations. When aged for 16 hours above their stability temperatures, xanthan gum and konjac gum would experience total failure regarding the loss of their viscosities and suspension and fluid loss control capabilities. Consequently, the biopolymers in bentonite-water suspension are not suitable for use in drilling operations above their stability temperatures. The mud formulations, therefore, require further modification and protection at high temperature, hence the need to deploy antioxidants, salt brine, and polyglycol as shown in Table 1. It has been reported in previous works that the best thermal stabiliser for biopolymers includes a solution containing a concentrated salt brine, glycol, and an oxygen scavenger [9], [24]. Howard et al.[9] in their investigation used different types of additives to formulate a clay-free water-based fluid that remained viscous for 16 hours at 194°C. In this study, the additives were screened to determine their ability to extend the thermal stability of biopolymer in bentonite-water suspension over a period of 16 hours and for temperatures up to 232°C. The Newtonian viscosities of the additives were measured and did not increase by more than 1cP. Konjac gum and xanthan gum developed excellent viscosity with the additive package. The fluid formulations were hot rolled at different temperatures to condition them before testing.

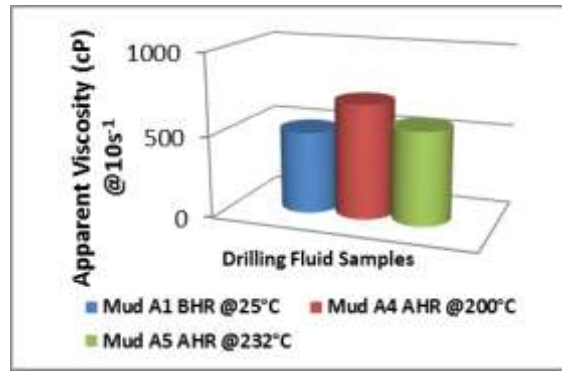
Fig. 4 shows the rheological properties of drilling muds formulated with additives. Figs. 4a and 4c show

the viscosities of the fluids formulated with the additives at different shear rates. It can be seen that the fluid formulations have viscosities close to or higher than those of the base fluids (Mud A1 and B1) after being hot rolled for 16 hours at high temperatures. These results confirm that the additive package used in this study is effective regarding the reduction of polymer degradation or retention of biopolymer viscosities at high temperatures. In Figs. 4a and 4c, the fluid formulations showed shear thinning characteristics: The viscosities of the fluids decreased with increasing shear rate. The slope of the curves was high at low shear rates, and the reverse was the case when the shear rate increases. This characteristic of the fluids confirms that polymer solutions are shear thinning. It can also be seen that the viscosities of the fluid formulations decrease sharply at low shear rates with a small increase in shear rate. The build-up and dissociation of solid particles in the fluids were reversible, and the dissociation of solid particles in the fluids can be timely built up when the shear rate is reduced. The viscosities of the fluid formulations, therefore, decrease sharply at low shear as the shear rate increases but decrease slowly at high shear rates. This sharp decrease in viscosity with a small increase in shear rates indicates that the drilling fluid formulations with the additives will transmit high horsepower through the bit nozzle to clean the bit face and carry drilling cuttings and weighting materials effectively through the wellbore annulus. Additionally, the low viscosities of mud formulations at high shear rates are desirable as low pump pressure will be required to reduce formation fracture potential. In addition, during testing, the fluid formulations all showed excellent thixotropic behaviour at low shear rates. Figs. 4b and 4d show the low shear rate viscosities of drilling fluids formulated with xanthan gum and the additives before and after dynamic aging at different temperatures for 16 hours. The high viscosities at low shear rates show that the mud formulations with the additives have good suspension properties which help prevent drilled cuttings and weighting materials from settling to the bottom of the wellbore during quiescence (Figs. 4b and 4d).

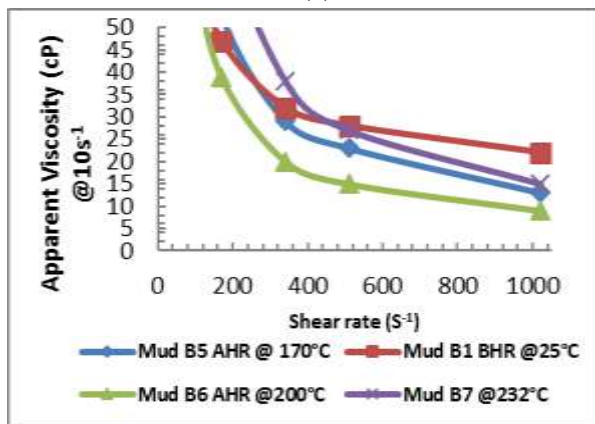
The PVs of the mud formulations decreased as the temperature increased while the YP remain mostly stable (Tables 4 and 5). The stable YP indicates that the fluid formulations have drilled cuttings and weighting materials carrying capabilities. The decrease in PVs could be attributed to the dispersion of additives in the fluids at high temperature. Since high PV is not desirable, the low PV indicates that the mud formulation could be more lubricious at high temperatures. From Tables 4 and 5, it can be seen that the fluid formulations have flat gel strengths, which is a desirable property of drilling fluids. Gel strength is said to be flat when there is no mark difference between the 10-seconds and 10-minutes gel. When the difference between the 10-seconds and 10-minute gel readings is wide, the gel strength is said to be progressive, and the progressive gel is an indication of a drilling problem. It is quite evident from the experimental results that the additive package – sodium erythorbate, polyethylene glycol 8000, and potassium formate – protected the biopolymer and promotes the dispersion of solid particles in the fluids at high temperatures. The dispersion of the solid particles could be attributed to flat gel strengths of the mud formulations. The results above show the excellent thermal stability of the biopolymers – xanthan gum and konjac gum- in the drilling fluids formulated with the additives when compared to the base fluids (Muds A1 and B1). The best additive package that stabilised the mud formulations when aged dynamically at high temperatures for 16 hours was the combination of potassium formate, sodium erythorbate and 0.7% polyethylene glycol. The test could not be carried out beyond 232°C, which is the maximum operating temperature of the roller oven used for the laboratory test.



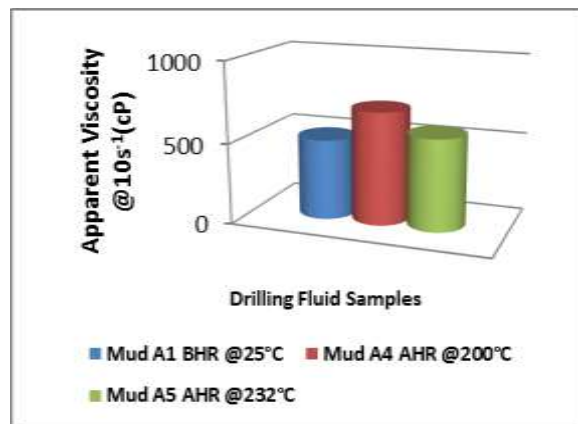
(a)



(b)



(c)



(d)

Fig. 4. Rheological properties of drilling muds formulated with additives. (a): Viscosities of the base fluid before dynamic aging at 25°C compared with those of drilling fluids formulated with xanthan gum and the additives after dynamic aging at different temperatures for 16 hours. (a): Low shear rate viscosity of drilling fluids formulated with xanthan gum and additives before and after dynamic aging at different temperatures for 16 hours. (c): Viscosities of the base fluid before dynamic aging at 25°C compared with those of drilling fluids formulated with konjac gum and the additives after dynamic aging at different temperatures for 16 hours. (d): Low shear rate viscosity of drilling fluids formulated with konjac gum and additives before and after dynamic aging at different temperatures for 16 hours.

4. Conclusion

Biopolymers are used almost in all water-based drilling fluids. They are non-toxic, less expensive biodegradable, and environmentally friendly. However, when exposed to high temperatures for a some time, biopolymers in water-based drilling fluids degrade. This degradation of the biopolymer can lead to total failure of water-based drilling fluid under high-temperature conditions. Synthetic polymers are stable at high temperature, but they are expensive and cause formation damage, hence the need to stabilize biopolymers in water-based drilling fluids. To stabilize biopolymers in drilling fluids, the mechanisms through which they degrade at elevated temperatures must be understood. The degradation mechanisms

of biopolymers in solutions at high temperatures include acid-catalysed hydrolysis and oxidation-reduction (redox) reaction. These mechanisms were exploited to stabilise biopolymers in water-based drilling fluids by deploying additives to retard the degradation processes. The objective of conducting this study was, therefore, to determine the effects of anti-oxidant, formate brine, pH control agents, and polyglycol on the stability temperatures of biopolymers in water-based drilling fluids with pH 8 to 10. This investigation involved laboratory tests to identify the additives package that would extend the 16-hour thermal stability of the biopolymers in water-based drilling fluids. Based on the analyses of the results obtained, the following can be concluded from the study:

- The anti-oxidant, potassium formate, pH control agent, and polyglycol stabilised biopolymers – konjac gum and xanthan gum - for 16 hours up to 232°C. The best additive package combination was potassium formate, sodium erythorbate, and 0.7% polyethylene glycol. The additives were, therefore, able to protect the polymer from oxidative and hydrolytic degradation.
- From this study, it is possible to formulate water-based drilling fluids containing clay and biopolymers for high-temperature drilling operations in the 150-232°C range without using expensive and formation damaging synthetic polymers.
- The measured mud samples exhibited a pseudo-plastic shear thinning characteristics.
- All the biopolymers developed viscosity in all the mud formulations.
- Konjac gum in bentonite suspension water suspension (base mud) remain stable up to 65°C after dynamic aging for 16 hours.
- Xanthan gum in bentonite suspension water suspension (base mud) remain stable up to 100°C after dynamic aging for 16 hours.
- The sodium carbonate and sodium bicarbonate pH buffer did not affect the fluid formulations negatively as they have a flat rheological profile.
- The finding of this study confirms the suggestions by other researchers that the best additives to stabilise biopolymers in water-based drilling fluids at high temperatures include salt brine, polyglycol, and an antioxidant [8], [9], [28].

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