MODELLING THE EFFECTS OF MODIFIED LOCAL STARCHES ON THE RHEOLOGICAL AND FILTRATION PROPERTIES OF A WATER – BASED DRILLING FLUID

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Abstract

This study is designed for the comparative analysis of chemically modified local starches used as additive in improving the rheological and fluid loss properties of a water- based drilling fluid. Additives are added to a drilling fluid in order to enhance the various functions of the drilling mud. Different drilling fluid samples were formulated without additive and with various concentrations modified starches. A laboratory investigation on the drilling fluid rheological and filtration properties using the API recommended standard procedures, pressure were studied at 1000 psi with a temperature range of 40.0 to 180.0 ° C, using a High Pressure High Temperature, (HTHP) rheometer and Fann Model 35A respectively From the analyses of the experimental results, it was observed that effective viscosity, plastic viscosity and yield point decrease steadily with increase in temperature. The experimental results, water based drilling fluid treated with chemically modified local starches improves the filtration and rheological properties of the drilling mud. Finally, this paper also presents a predictive model equation good enough to analyse trends and predict future values for effective and plastic viscosities.

Key words: CMC, Etherification, Filtration properties, Rheology properties; Native starches

Introduction

Since the advent of drilling fluid in the US, drilling fluid have passed through different technological evolution. It has evolved from the simple mixture of water and clays to a complex mixture of various specific organic and inorganic products for specific operations. The principal functions of the drilling fluids are to: carry cuttings from beneath the bit, transport them up the annulus, and permit their separation at the surface; cool and clean the drilling bits; (3) reduce friction between the drilling string and the side of the hole; (4) maintain the stability of uncased sections of the borehole; (5) prevent inflow of fluids from permeable rocks penetrated; (6) form a thin, low permeable filter cake which seals pores (Apaleke *et al.*, 2012), Hossain and Al-Majeed,(2012.) The drilling fluid rheological properties such as apparent viscosity, plastic viscosity, yield point and gel strength play important role in designing efficient and optimized drilling operation.

The success of any drilling operation is based on how well the drilling fluid is formulated. Small chemicals or materials called additives are often added to this to give specific properties to the mud. Polymeric additive from starch is mostly applied in water based drilling muds (WBMs) as a fluid loss control additive as a result of its low cost and easy accessibility.

Starch is a naturally occurring, inexpensive, biodegradable, and abundantly available polysaccharide molecule found in stems, roots, grains, and fruits of all forms of green leafed plants. It is one of the polymer commonly used in the oil industry (Baba Hamed and Belhadri 2009), Starches from different sources have different granular structures that affect their physical properties. Starch consist of two major weight components, amylose linear polymer with molecular weight between 100, 000 to 500, 000 and branched amylopectin with a molecular weight between 1 to 2 million depending on its botanical source (Wing, 1988). It functionality depends on the average molecular weight within the granule

The amylose component controls the gelling behavior which is the result of re-association of the linear chain molecules while amylopectin reduce the mobility of the polymer and its orientation in a aqueous environment (Amanullah. *et al*. 1997). The ratios of amylose and amylopectin vary depending on the origin and nature of the starch, and this variation changes the behavour of the starch. However, in starch in it native state exhibits limited applications due to thermal decomposition, low shear stress resistance, high retrogradation and syneresis, In addition to poor processability and solubility in common organic solvents. And also susceptible to biological or microorganisms attack. In order to overcome this shortfall, numerous methods of modification such as chemical modification, physical degradation, genetic alteration or enzymatic conversion have been proposed.

Chemical modification involves the introduction of functional groups into the starch molecule, in order to alter the physico-chemical properties of the starch. Modifications is aimed to improve the water solubility, thermal stability, as well as its resistance to bacterial attack of the starch and consequently improve the drilling fluid filtration properties (Guo, and Peng, .2012). In the quest for the applicability of locally available material for use as drilling fluid additives in Nigeria, several researches have been conducted. Okumo and Isehunwa (2007) studied the prediction of the viscosity of a water -base mud treated with cassava starch and potash at varying temperatures using factorial design. Ikegwu *et al*.(2009) in their study, showed variations observed in the functional properties of the starch samples of about 13 cassava cultivars by studying; water absorption capacity ranged from 59.75- 68.02%; oil absorption capacity 60.70 - 80.01%; swelling power 5.49 - 6.92% and solubility index 4.25 - 5.96%. Onitilo, (2007) carried out test on 40 cassava varieties and observed a significant differences ($P<0.05$) in the functional properties of the starch A research on the rheological behavior of polymer-extended water-based drilling muds at high temperatures and high pressures was carried out by Salimi, *et al*,(2007) and they observed that temperature had a detrimental effect on the rheological properties of the test fluids while the effect of pressure on these properties was realized to be less significant (specially at pressure above 300 psi).

Andreas et al (2009) investigated the effects of shear rejuvenation, aging and shear banding in yield stress fluids in order to provide a common framework to describe the behavior of yield stress materials and also simulate shear rejuvenation and aging effects in shear thinning yield stress fluids in a typical rotational rheometer. Their work revealed the existence of time-dependent shear banding that occurs within the gap when the macroscopically imposed shear rate is below a certain critical value. The effect of temperature and time –dependent behavior of a water base mud treated with maize (*zea mays)* and cassava (*manihot esculanta*) starches was investigated by Akintola and Isehunwa (2015), they observed that both native maize (*zea mays)* and cassava (*manihot esculanta*) are good materials for use as drilling fluid additive.This paper seek to examine the effects of chemical modified starch as suitable fluid loss additive in a water based drilling fluid.

Materials and Methods

Materials

The fresh maize (*Zea Mays*), cassava tubers TME 419 (*Manihot Escalanta*) and potash , were obtained locally, Sieves (180 µm and 400 µm), Distil water, Analytic grade Sodium monochloroacetic acid (MCA acid, 40% w/v), Ethylene Diamiet Tetra acetic Acid solution, Sodium Meta Bisulphate, Iso-propanol: water - 80:20, 2N NaOH solution, 0.05 M H_2SO_4, Nitrogen atmosphere Sodium Carboxymethyl Cellulose (CMC) and Wyoming Bentonite were obtained from Mi-Swaco, Port-Harcourt

Apparatus

Mud balance, Fann 35, Fann Roller Oven (Model 705ES); Incubator, pH meter, three neck flask, Fann HPHT filter press and the HPHT Viscometer, Spatula, Electric Weighing Machine, Hamilton Bench Mixer,

Extraction of Starches

(i) Maize starch

The maize is coarsely sieved to separate contaminations, e.g. stones, cobs, dust particles, foreign grain material, and fine material. Maize starch was extracted by steeping in the presence of 0.05 M H_2SO_4 at 50 ° C for 48 hrs. followed by grinding and centrifugation of the resultant mash that resulted into settling of starch which was obtained after removing the supernatant and drying the remaining residue at 40 ° C in an air tight oven. The maize starch was obtained after steeping in hot water for 8 hrs and subsequent grinding. The resultant mash was centrifuged to allow the starch to settle down. The starch was then washed several times using clean distilled water. Starch obtained was then dried in an air forced oven at 40 ° C and then stored at room temperature.

(ii) Cassava starch

Starch separation was carried out according to the method described by Takeda, *et al* (1987) with slight modifications. Fresh tubers were washed, peeled, diced, and dipped in ice water containing 100 ppm sodium meta bisulphate to minimize browning. Diced sample was wet milled at low speed in a laboratory scale blender with 1: 2w/v of tap water for 2 minutes and filtered through a gauze cloth. The residue was repeatedly wet milled and filtered for thrice, and suspension was kept overnight for settling of starch. The supernatant was decanted, and the settled residue was further purified with repeated suspension in tap water (1:2v/v) followed by the settling for 3 hours. The purified starch was dried at 35 ° C, sieved through a 300 μm sieve, sealed, and packed into an air tight container for analysis.

Preparation of MCS and CMS

The method of Khalil, *et al* (1990) with slight modification was used for the chemical modification of the two native starches. Each of the starch (30.0 g) was suspended in aqueous solution (iso- propanol: water - 0:20) (300 ml) in a round bottom flask and an aqueous sodium hydroxide solution was added. The resulting mixture was stirred for 10 min. at a controlled temperature of 30 °C Sodium monochloroacetate was added and stirring was continued up to the designated time.

The pH adjusted with 2N NaOH solution to about 5.0. The process of Carboxymethylation was carried out under nitrogen atmosphere. The carboxymethyl starch was filtered and washed with aqueous ethanol (80:20) with the excess alkali neutralized using acetic acid, after the washing, the Carboxymethylated starch samples were filtered, oven dried at 50°C. The dried carboxymethyl starches were passed through a 100-mesh sieve and then stored in an air tight labeled containers.

Preparation of Water-Based Drilling Fluids

The following materials were used for the formulation of the water base drilling fluid. 22.5g of Wyoming bentonite was added to 350ml of distil water. And a Hamilton mixer was used to mix the mixtures for 20 min. The prepared mud samples were kept for 24 hours to hydrate and its properties such as density, rheological properties and pH value were determined. Four drilling mud samples were prepared and labelled as simple water- base drilling fluid without additive,; another 2 mud sample treated with the modified starches additive (MCS and CCS) and finally the control mud sample treated with CMC

Experimental Procedure

The modified starches were characterized using the AOA .The drilling mud experiments were conducted in accordance with the API 13A recommended drilling procedure

Mud balance:

The mud balance was calibrated with water and 8.3 ppg was obtained, before the mud weight was read at the edge of the rider towards the mud cup**.**

Mud pH

The drilling mud samples pH were determined using the pH meter

Rheological Parameter

The Fann35A Rheomete was also calibrated and then the dial readings obtained for the different mud samples were taken. The plastic viscosity and the yield point of the mud samples was determined using the equation s 1,0 and 2.0

$$\mu_p (cp) = \theta_{600} - \theta_{300} \qquad 1.0$$

$$y_b = \theta_{300} - \mu_p \qquad 2.0$$

Fluid Loss

The HPHT fluid loss test was conducted using the Ofite HPHT filter press. The various mud samples were placed an aging cell, pressurized to 1000 psi and heated to 302 °F. The amount of filtrate collected at 30 minutes using a graduated measuring cylinder were recorded.

Determination of Aging

Since the properties of the drilling fluid obtained at the surface does not correlate with the bottom-hole conditions, the aging of the drilling fluid is carried out. This help in the simulation of the properties of the drilling mud at bottom-hole conditions. Aging is done under conditions which vary from static to dynamic and from ambient to highly elevated temperatures. A Baroid roller oven was used to determine the aging properties of the mud samples after being placed in a n high-pressured aging cells and rolled in an oven for a 16 hours

Results and Discussion

To provide us with the actual properties of the modified starches which in turn improves the behavior of the drilling mud, some of the physicochemical properties of both the native and modified starches were determined using the standard methods. The results for the amylose and amylopectin ration content of the native and modified starches are presented in the Table 1.0.

Table 1.0: Amylose and Amylopectin Content of Both Native and Modified Starches

Sample	Amylose %	Mean Amylose %	Amylopectin%	Mean Amylopectin %
Maize Starch	25.31		74.69	
	25.24	25.47	74.76	74.53
	25.87		74.13	
Maize Carboxyl	20.35		79.65	
methyl Starch	20.37	20.36	79.63	79.64
Cassava Starch	22.06		77.94	
	22.20	22.13	77.80	77.87
	22.13		77.87	
Cassava Carboxyl	22.25		77.55	
methyl Starch	22.25	22.25	77.55	77.55

The results for total degree of substitution (DS) Protein content, Fat content Moisture content, Carbohydrate and Ash content are presented in the Table 2.0. Higher DS results in higher solubility of the starch. Although both modified starches (MCS and CCS 0.20 and 0.19, respectively) were not high, which can be attributed to the distribution of the etherifying agents along the starch molecule, they both were completely soluble in cold water.

Table 2.0: Chemical composition dry weight basis of the two Modified Starches

Sample	Maize Carboxyl methyl Starch	Cassava Carboxyl methyl Starch
Degree of Substitution	0.2	0.19
Protein content	0.425	0.17
Fat Content	0.08	0.05
Moisture content	8.88	7.87
Carbohydrate	90.27	91.62
Ash content	0.356	0.296

The results for the starches functional properties of both the native and the modified starches of the maize and the Cassava starch is presented in the Table 3.0

Table 3.0: Functional properties of Modified Starches.

Sample	Maize Carboxyl methyl Starch	Cassava Carboxyl methyl Starch
Water absorption %	350.26	330.26
Swelling power %	18.35	20.26
Solubility	16.64	18.56
Least gelation Conc	6.00	6.00
Bulk density g/cc	0.49	0.47
Emulsion Capacity %	38.85	39.55

The mud density and pH of the drilling mud treated with 5.0 and 10.0 g of the modified starches, respectively, at temperature of 80 and 302 ^{o} F before and after hot rolling are presented in the Tables 4.0 and 5.0 respectively.

Table 4.0: 5.0 g Modified Starches BHR and AHR at 80 and 302 ^{o}F

Sample	5.0 g Modified Starch BHR @ 80 ^{o} F		5.0 g Modified Starch AHR @ 80 ^{o} F		5.0 g Modified Starch BHR @ 302 ^{o} F		5.0 g Modified Starch AHR @ 302 ^{o} F	
	Density (ppg)	pH	Density (ppg)	pH	Density (ppg)	pH	Density (ppg)	pH
MCS	8.6	8.07	8.6	8.07	8.6	8.07	8.6	8.07
CCS	8.6	8.18	8.6	8.18	8.6	8.18	8.6	8.18
CMC	8.6	8.38	8.6	8.38	8.6	8.38	8.6	8.38

Table 5.0: 10.0 g Modified Starches BHR and AHR at 80 and 302 ^{o}F

Sample	10.0 g Modified Starch BHR @ 80 ^{o} F		10.0 g Modified Starch AHR @ 80 ^{o} F		10.0 g Modified Starch BHR @ 302 ^{o} F		10.0 g Modified Starch AHR @ 302 ^{o} F	
	Density (ppg)	Ph	Density (ppg)	pH	Density (ppg)	pH	Density (ppg)	pH
MCS	9.1	8.27	9.1	8.27	9.1	8.27	9.1	8.27
CCS	9.1	8.32	9.1	8.32	9.1	8.32	9.1	8.32
CMC	9.1	8.40	9.1	8.40	9.1	8.40	9.1	8.40

3.1 Effects of Temperature

The effect of temperature on Mud sample without additive is presented in the Figure 1.0. and it was observed that as the temperature increased, the viscosity decreases this could be attributed to the complicated interplay of factors such as reduction in the degree of hydration, and viscosity of the suspending medium, increased thermal energy of the clay and dispersion of associated clay micelles.

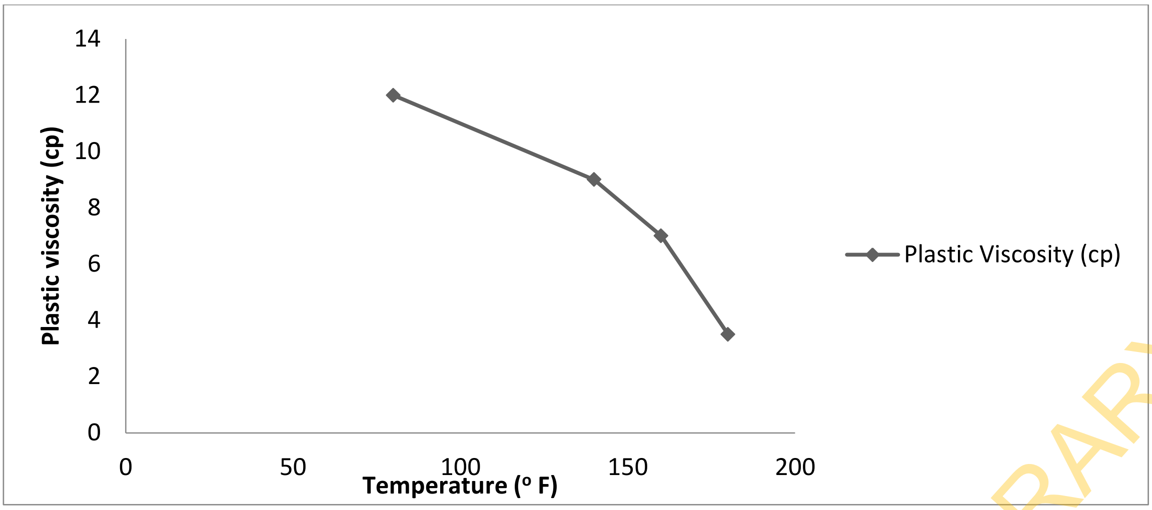

Figure 1.0: Mud sample without additive.

One of the component of a drilling fluid rheological properties is the drilling fluid plastic viscosity (PV) Plastic viscosity is an indication of the fluid solid content, solid content increment in drilling mud will result in higher PV. In order to improve the performance of the simple water – base drilling fluid without additives different concentrations of the modified starches were added (Figure 2.0).

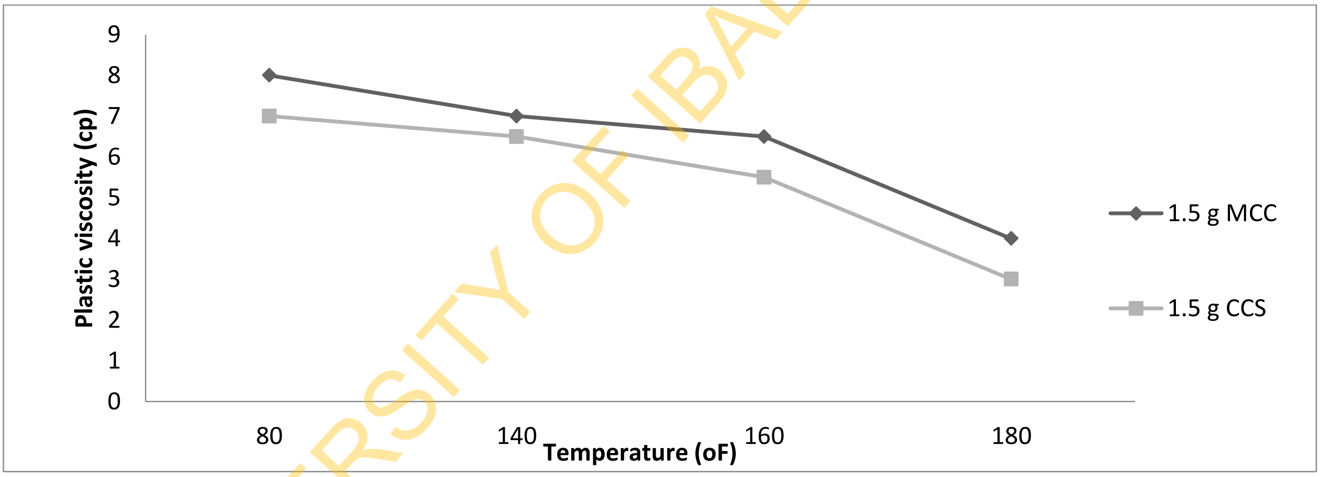

Figure 2.0: Plastic viscosity against Time for a 1.5 g Carboxymethyl starches

The addition of more of the modified starches (Figure 3.0) resulted in a further increase in the plastic viscosity values but CMC shows a decrease in plastic viscosity value whereas the modified starches had an increasing value in plastic viscosity.

Although the viscosity of the two mud samples as temperature increased tends to decrease steadily, this is in support of the work carried out by Annis (1997) who noted that high temperature causes flocculation of bentonite clays resulting in high viscosities at low shear rates and high gel strengths

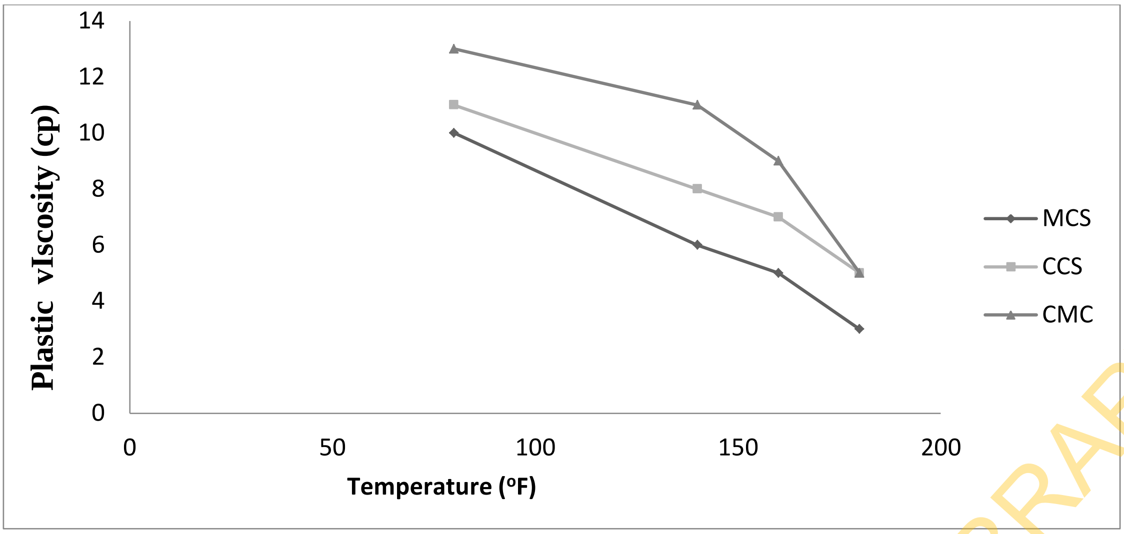

Figure 3.0: Plastic viscosity against Time for a 2.5 g Carboxymethyl starches

The effect of the addition of potash as a thinner in different concentrations and quantity of modified starches is presented in the Figures 4.0 to 7.0. From the profile of these results, it was observed that there was a change in the profile of the graphs

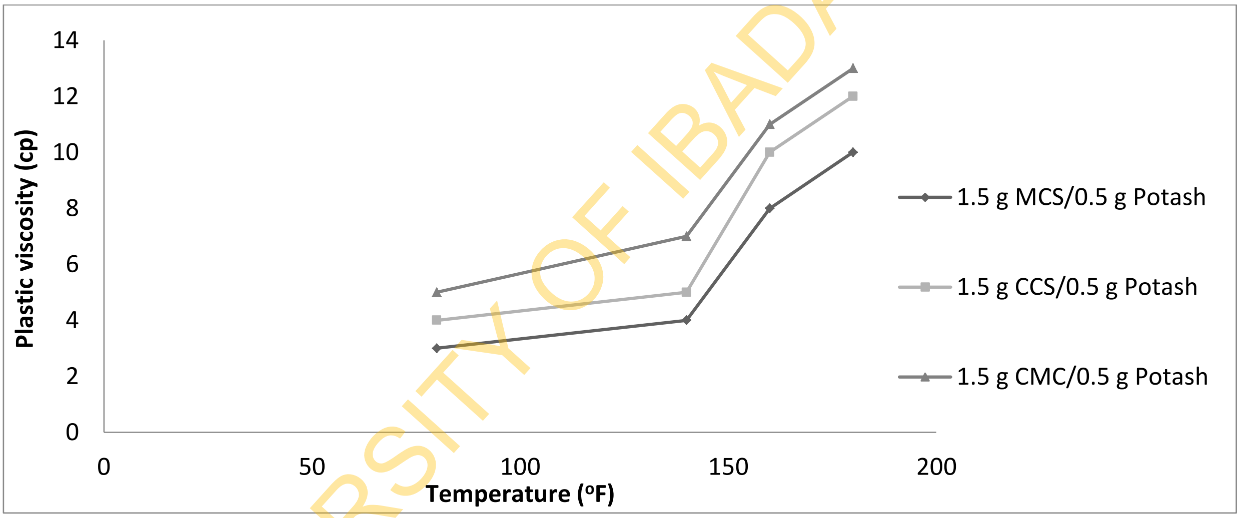

Figure 4.0: Plastic viscosity against Time for1.5 g Carboxymethyl starches and 0.5g Potash

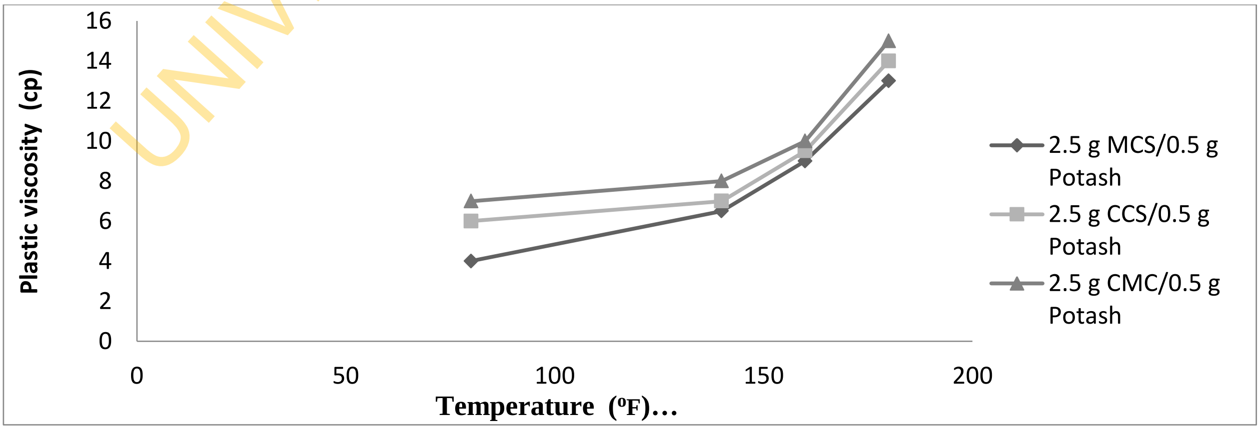

Figure 5.0: Plastic viscosity against Time for 2.5 g Carboxymethyl starches and 0.5 g Potash

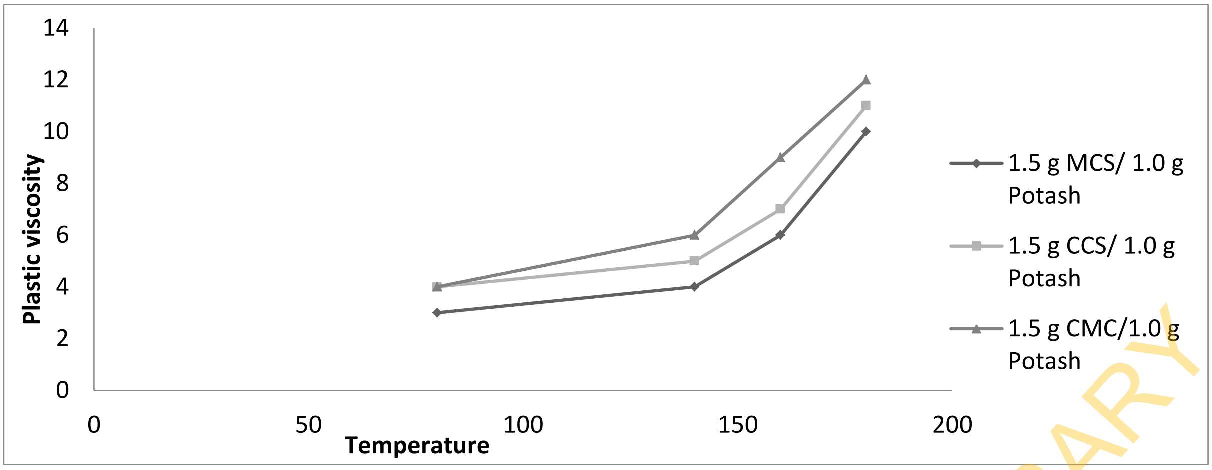

Figure 6.0: Plastic viscosity against Time for 1.5 g Carboxymethyl starches and 1.0 g Potash

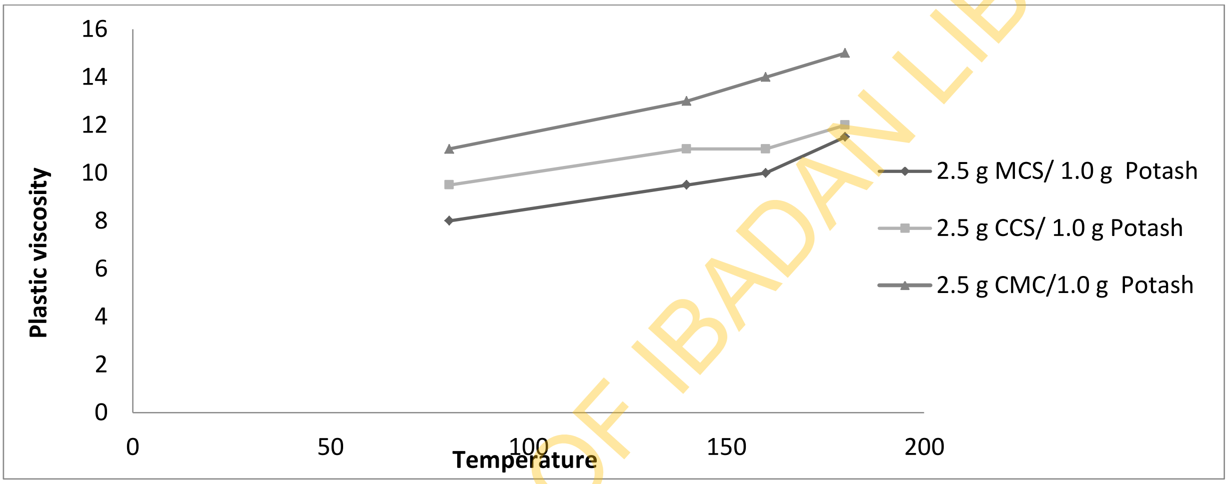

Figure 7.0: Plastic viscosity against Time for 2.5 g Carboxymethyl starches and 1.0 g Potash

3.2 Effect of Aging

To simulate the performance of the drilling fluid when being circulated while drilling, the various mud samples were placed in a Fann 705ES, rolling oven for 16 hours. The mud rheological characterization were carried out by the use of a Fann 35 viscometer in six different speeds (600, 300, 200, 100, 6 and 3 rpm) and the rheological properties (apparent viscosity (AP), plastic viscosity (PV), yield point (YP), and gel strength (GS)) were obtained for the treated mud sample before and after hot rolling . 5.0 grams each of the modified starch was used to treat the simple water - base drilling fluid separately at temperature of 80 and 302 ^{o} F. The result shows that viscosity decreases with increase in aging time.

3.3 Filtration Loss

The Table 6.0 presents the HPHT filtration test for the drilling mud fluid loss and mud cake were tested under pressure of 1000 psi at 302 °F over 30 minutes. From the HPHT test result, it was observed that at low quantity of starch MCS (14.0 ml.) has the value close to the range of the API specification but when the modified starch quantity was increased to 10 gram CCS (11.0 ml.) presented the least value of fluid loss. For the mud cake of the drilling fluid it was observed that the cake thickness for CCS has the lowest thickness at 5 g while at 10 g MCS was lowest

Table 6.0: 5.0 g and 10.0 g of Modified Starches HPHT fluid loss, (ml) and Filtrate cake thickness, (mm)

Sample	5.0 g HPHT fluid loss, (ml)	5.0 g cake thickness, (mm)	10.0g HPHT fluid loss, (ml)	10.0g cake thickness, (mm)
MCS	14	9.27	20.5	4.39
CCS	25	4.74	11	6.7
CMC	24	6.58	12	4.67

Model Development

The SPSS was used to obtain a predictive model equation 3.0 and 4.0 for viscosity and 5,0 to 6.0 for fluid loss, to enable the analysis and prediction of values for viscosity and fluid loss

$$P_v(MCS) = 7.56 + 3.93X_1 + 2.12X_2 - 1.44X_3 + 1.75X_1X_2 - 0.56X_1X_3 - 0.25X_2X_3 - 0.13X_1X_2X_3 \quad 3.0$$

$$P_v\,(CCS) = 7.47 + 3.84X_1 + 1.72X_2 - 1.09X_3 + 1.59X_1X_2 - 0.47X_1X_3 - 0.47X_2X_3 - 0.09X_1X_2X_3. \quad 4.0$$

$$\mathrm{Fl\,(MCS)} = 8.12 - 0.72X_4 + 0.65X_5 - 1.24X_6 + 2.63X_7 - 0.23X_4X_5 + 0.10X_4X_6 - 0.21X_4X_7 - 0.03X_5X_6 + 0.15X_5X_7 - 0.47X_6X_7 + 0.02X_4X_5X_6 + 0.15X_4X_5X_7 + 0.13X_4X_6X_7 - 0.07X_5X_6X_7 + 0.15X_4X_5X_6X_7 \quad 5.0$$

$$Fl\,(CCS) = 7.78 - 0.76X_4 + 0.68X_5 - 1.34X_6 + 2.50X_7 - 0.05X_4X_5 + 0.03X_4X_6 - 0.27X_4X_7 - 0.03X_5X_6 + 0.38X_5X_7 - 0.54X_6X_7 + 0.34X_4X_5X_6 + 0.02X_4X_5X_7 + 0.03X_4X_6X_7 - 0.05X_5X_6X_7 + 0.23X_4X_5X_6X_7 \quad \mathbf{6.0}$$

4.0 Conclusions

The following conclusions were made based on the results obtained from the laboratory investigation,

The samples with higher amylose content and high water absorption capacity produced drilling fluid with higher viscosity and lower fluid loss

1. The viscosities, of the polymeric fluid decrease with increase in temperature
2. Modified Local starch (Maize or cassava) could be used as a substitute for imported sample to control viscosity and fluid loss in water based drilling fluid
3. The developed models can be used to predict future values for viscosity since there is a good correlation
4. This will provide economic benefit to Nigerian economy

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