International Journal of Advanced Engineering and Technology
www.newengineeringjournal.com
ISSN: 2456-7655
Received: 16-09-2021, Accepted: 02-10-2021, Published: 19-10-2021
Volume 5, Issue 2, 2021, Page No. 35-42

Modeling the effect of modified local polymer on the rheological and filtration properties of water-based drilling fluid

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Abstract
In order to achieve a successful drilling operation, the drilling fluid used must be properly designed. Water based drilling muds that are formulated to suit drilling requirements include additives like clays for higher viscosity and starch for better filtration control properties. Locally available yams (Dioscorea) are a good source of starch, with good absorbent properties that give its good filtration control properties but poor gelling properties due to the easily soluble branched chained Amylopectin molecules which causes it to easily degrade. While mud samples treated with Carboxylmethyl cellulose (CMC) was used as control.
Chemical modification of starch has been researched to be a good method of improving its gelling properties in water based mud which in turn improves the rheological properties of the mud. Cross linking agents like sodium acetate and ammonium phosphate are used to cross-link the Amylopectin and Amylose molecules in the starch thus making them less degradable.
An experimental study was carried out to reduce the yams starch bio-degradable nature via chemical modification with some cross-linking agents (sodium acetate and ammonium phosphate). The results from the rheological and filtration control test carried out on the formulated mud samples treated with modified yams starch additive gave higher gel strength and yield point, exceptional shear thinning ability, lower plastic viscosity and a good but lower fluid loss control when compared to with the control samples. A Factorial design was developed to predict the rheological properties of the mud system at different temperatures and varying starch quantities. The results of the mud samples treated with the non-modified starches, modified yam starches and imported viscosifier (CMC) are indicators that the modified starches improved its gelling nature thereby giving the drilling mud a better rheological properties.

Keywords: yam starches, crosslinking agents, rheological properties, fluid loss, water-based mud

Introduction

Oil and gas Exploration and Production involves a series of operations; amidst the operations carried out, Drilling confirms the presence of prospective resources in a field and provides the conduit for production to the surface. One of the fundamental materials required while drilling a well is the Drilling Fluid. The drilling fluid is formulated and designed to suit the requirement of the well and formation. There are three major classes of drilling fluid used in the industry as classified on the basis of the distribution or base fluid. Of the three classes, i.e. water based, oil based and pneumatic muds, the water based mud preserves the environment of the surrounding formations best and is easy to formulate.
The, success in drilling operations requires that drilling fluids possess desirable qualities which depend on their rheological and fluid filtration properties [1].
The conventional drilling fluids require a large amount of sodium montmorillonite to achieve the desired rheological and filtration properties [2]. Additives are chemicals added to the drilling fluid to help it perform its functions effectively. These chemicals additive are used in large quantity annually in the oil field [3]. Several of them have been formulated and synthesized for various applications in drilling fluids [4, 5].
Starch polymer can serve as additive that can be used to enhance the properties of the drilling fluid, but it is degrades with increase in temperature and exposure with time. However this can be reduced to a large by modification Modification helps make the material in the mud more stable at higher temperatures in downhole conditions.
Yam (*Dioscorea* spp) is the most important staple food in West Africa after cereals [6] and Nigeria is the leading producer producing over 34 million [7]. There are about ten species of *Dioscorea* spp economic significance as food [8]. In this study, only three species were used they are the white yam (*D. rotundata)*, water yam *(D. alata) and* bitter yam (*D. dumetorum)* Modification of starch is the alteration of the physical and chemical properties of starch to improve the inherent physio-chemical properties of native starch. Sodium acetate and Ammonium phosphate are two chemical reagents used for the chemical modification in this study. The main components of starch are amylose and amylopectin, with the amylose content reaching as high as 30% and amylopectin molecules larger in size and greater in proportion from 75 – 85%. It is reported that the short branching chains in the amylopectin component are the main crystalline component in granular starch while the amylose component of starch controls its gelling behaviour as gelling is the result of re-association of the linear molecules [9]. Cross-linking agents were introduced into the different starches to modify its gelling and absorption characteristics as this will help reduces the biodegradation of the starch molecules. Manipulating the composition of the straight and branched chained molecules causes a modification in the behaviour of the product. An increase in the typical level of the amylopectin content from 75% up to 99% was discovered to have better thermal stability [10]

Starch and cellulose-based polymers degrade thermally by the same mechanism. The polymer chains are broken, and the glucopyranose units are converted to other compounds. The decomposition rate can be determined by use of chemical kinetics methods.
The mud samples apparent viscosity, plastic viscosity and yield point were evaluated with the Bingham Plastic model equations as shown in the equations 1.0, 2.0 and 3.0, respectively

$$Av = \Theta_{600} / 2.0 \qquad 1.0$$

$$\mu_p = \Theta_{600} - \Theta_{300} \qquad 2.0$$

$$\gamma_y = \Theta_{300} - \mu_p \qquad 3.0$$

His paper went further to describe the experiments that determined the stability of these polymers at various temperatures using kinetic methods. A 2^2 Factorial design was used to create an experimental design that predicts the mud properties at different temperatures and starch quantities with their interaction effect also inclusive Predictive model was proven to give rheological properties with minimal standard deviations when fitted model response was compared to the actual experimental response
Flow indices for the mud samples were calculated using the power law model equation 4

$$n = 3.322 \log\left(\frac{\phi_{600}}{\phi_{300}}\right) \qquad 4$$

A Factorial design was developed for the experimental setting to estimate the properties (yield point and plastic viscosity) at other varying conditions temperature and quantities of modified starch.

$$N = L^K \qquad 5$$

L = value levels e.g. low level and high level
K = number of variables (factor variable)

Experimental Settings
$N = 2^2 = 4$
N = no. of experimental runs
Response variable = Plastic viscosity and Yield Point
Factor variables = Temperature and Quantity of Modified starch

$$Y = B_o + B_1X_1 + B_2X_2 + B_{12}X_1X_2 + e. \qquad 6$$

$$X_i = \frac{V_c - V_o}{V_f - V_o} \qquad 7$$

V_c = current value
V_o = centered value
V_f = high value
e = error term

The four runs represent the high and low levels for the temperature and modified starch quantities combination. The factor level settings and the high and low level values for X_1, X_2 and their interaction X_1X_2 are seen in Tables 4 and 5.

$$\text{Effect}, B_i = \frac{A}{2^{K-1} x\, 2} \qquad 8$$

Using the expression from equation 2,

$$Y_P = B_o + B_1X_1 + B_2X_2 + B_{12}X_1X_2 + e \qquad 9$$

Where; Y_P= yield point
$B_o, B_1. B_2, B_{12}$ are Coefficient effects as shown in the Table 9.
X_1, X_2 are main effects for temperature and modified starch quantities respectively
X_1X_2 is Interaction Effect between X_1 and X_2

Materials and Methods

Starch Extraction and Modification

Three species of *diaoscorea spp* white yam (*dioscorea rotundata*), water yam (*dioscorea alata*), bitter yam (*diaoscorea dumetorum*), were obtained from a local market and the procedure below was carried out for each sample to obtain starch as the end product. The procedure comprises: The yam tubers were peeled and grated into flake-like fractions. Water was added and mixed with the yam flake-like fractions then left for 3-4days to ferment. The fermented yam solution was sieved with a sieve (150 µm) to obtain a starch solution. The solution was left for 72 hours to enable settling of the starch at the bottom and was separated from the water using process of decantation and sedimentation and left to dry. The dried starch was ground with a pestle and mortar into powdered starch and kept in an air tight container. The materials used for the experiments are: Distil water, bentonite, starch (bitter yam, white yam and water yam), hamilton beach multimixer: digital weighing balance, mud balance: rotational viscometer, measuring cylinder, spatula: digital weighing balance: and thermometer, ammonium phosphate sample, sodium acetate sample: The properties of the mud samples were determined within the temperature range of 30- 60°C.

Starch Modification: The modification of the starch obtained from the *dioscorea spp* involved the following procedure:

Use of Sodium Acetate

1. 35g of native water yam starch was weighed and placed in a plastic container.
2. 5ml of Potassium Hydroxide (KOH alkaline catalyst) with 1 mol/dm^3 concentration was added and mixed thoroughly.
3. 2.5g of sodium acetate, a cross linking agent, was added and mixed for 15 minutes.
4. The sample was dried in an oven at 85°C for 5 hours and stored in a plastic air-tight container at room temperature.

Use of Ammonium Phosphate

1. 35g of native water yam starch was weighed and placed in a plastic container.
2. 5ml of Potassium Hydroxide (KOH alkaline catalyst) with 1 mol/dm^3 concentration was added and mixed thoroughly.
3. 2.5g of ammonium phosphate, a cross linking agent, was added and mixed for 10 minutes.
4. The sample was dried in an oven at 85°C for 6 hours and store in a plastic air-tight container at room temperature.

Determination of Amylose Content

The amylose and amylopectin content of the three yam samples, were obtained as outlined below:

1. Weigh 0.2g of sample and place in a beaker and Measure 1ml of pure ethanol acid using a pipette
2. Add 9ml of 0.1 molar concentration of KOH and heat in a water bath for 20 minutes at 100°C and then allow to cool. And add distilled water to make 100ml and shake properly.
3. Take 5ml into a volumetric flask and add 1ml of acetic acid and 2ml of iodine solution.
4. The sample was transferred into the photo-spectrometer analogue device where the absorbent was read.
5. Using the standard amylose curve, the amylose content was obtained in percent.
6. The amylose value was subtracted from 100% to obtain the amylose content in percentage.

The results of the Amylose and Amylopectin content for the yam starches are presented in Table 2.0.

Statistical Analysis

A 2^2 Factorial design was created to estimate experimental responses at different effects combination. The Factor level settings are set while the High and Low level combinations for Temperature and Starch quantity are also set for the fitted responses.

Results and Conclusion

Starch Modification: The modified starch was kept in an air tight container and labelled as presented in the Table 1

Table 1: Yam Starches Nomenclatures

Mud Sample Type	Sample
Bitter yam starch	A
White yam starch	B
Water yam starch	C
Bitter Yam Modified With Sodium Acetate	A1
Bitter Yam Modified With Ammonium Phosphate	A2
White Yam Modified With Sodium Acetate Sample	B1
White Yam Modified With Ammonium Phosphate	B2
Water Yam Modified With Sodium Acetate	C1
Water Yam Modified With Ammonium Phosphate	C2

Amylose Content

The Amylose content and absorbent capacity for the different starch samples were determined in the laboratory and the results presented Table 2.

Table 2: Amylose and Amylopectin Content of Local Yam Starches

Starch	Sample Wt(g)	Absorbent (@ 365µm Wavelength)	Amylose Content (%)	Amylopectin Content (%)
Water yam	0.2	0.927	26.98	73.02
White yam	0.2	0.681	28.85	71.15
Bitter yam	0.2	0.540	18.78	81.22

Rheological Properties

In Figure 1, the slope of each plot indicate the shear thinning rate of the mud sample. It is observed that sample A1 possesses the greatest slope indicating a high shear thinning rate while sample C possess the lowest slope with the control mud sample – CMC possessing the second lowest slope. Also, it can be observed that the shear thinning rates of the mud samples between 30 – 600 rpm are close but vary largely at a lower shear rate of 6rpm.

The Figure 2 shows the apparent viscosity of the tested samples after aging at different shear rates with a similar trend like that shown in Figure 1 but it is observed that the apparent viscosity values are far greater A1 with the highest shear thinning rate compared to that of about 650cp before aging. Figure 2 also indicates that sample A1 has the highest thinning rate with the control mud sample having the lowest thinning rate.

The plastic viscosity of the muds with the control sample, CMC and one of the best performing modified starch (A1) at different temperatures before and after aging are represented in Figure 3. From the chart it is noticeable that CMC has a greater plastic viscosity compared to A1 before and after aging at the different temperatures. The effect of aging gives the mud samples better properties. It is observed that the plastic viscosity of the mud with A1 tend to either increase or remain the same with initial increase in temperature, after which it begins to decrease but the mud with CMC decreases more rapid with temperature though possessing higher plastic viscosities.

The yield point of the mud with CMC and A1 before and after aging shown in Figure 4. It is observed that the mud with CMC has lower yield point before and after aging as temperature increases but that of the mud with A1 increases with initial increase in temperature before it begins to decrease. Depending on the yield point requirement in the mud design, the modified starches can be used as an additive to increase the yield point of the mud.

The gel strength of the muds with CMC and sample A1 shown in Figure 5 indicates that mud sample A1 gives higher gel strength than sample CMC before and after aging thus proving that the mud with modified starch provide better gel strength compared to the control sample when left quiescent.

The Plastic viscosity, yield point and gel strength performance of the different mud samples indicate the modified starch relatively have good ability to serve as an added viscosifier depending on the design requirement of the drilling mud.

$$Y_P = 14.963 + 3.2X_1 + 4.625X_2 - 0.65X_1X_2 - 0.125 \quad 10$$

Equation 10 describes the Factorial design on the experimental setting for the yield point. The coefficients for the temperature and starch effects are positive indicating an increase in the yield point of the mud sample with increase in the temperature and quantity of starch in the mud sample. The interaction effect of the two main effects is negative, hence causing a decrease in the yield point. With the coefficient of the starch greater than that of temperature, it indicates that the quantity of starch in the mud sample has more effect on the yield point than temperature.

$$\mu_p = 4.4 - 0.3X_1 - 0.2X_2 + 0.25X_1X_2 \quad 11$$

Equation 11 describes the Factorial design on the experimental setting for the plastic viscosity. The coefficients for the temperature and starch effects are negative indicating a decrease in the plastic viscosity of the mud sample with increase in the temperature and quantity of modified starch in the mud sample. The interaction effect of the two main effects is positive, hence causing an increase in the plastic viscosity. With the coefficient of the starch smaller than that of temperature, it indicates that the quantity of starch in the mud sample has a less effect on the plastic viscosity compared to temperature but is compensated with the greater positive interaction effect of the two factor variables. The error term in the factorial design is zero thus giving a fitted model that is a replica of the experimental response.

Noting, the degree of accuracy of the model is dependent on the number of factor variables in the model. Figures 8 and 9 show the experimental and fitted model profile with their degree of correspondence.

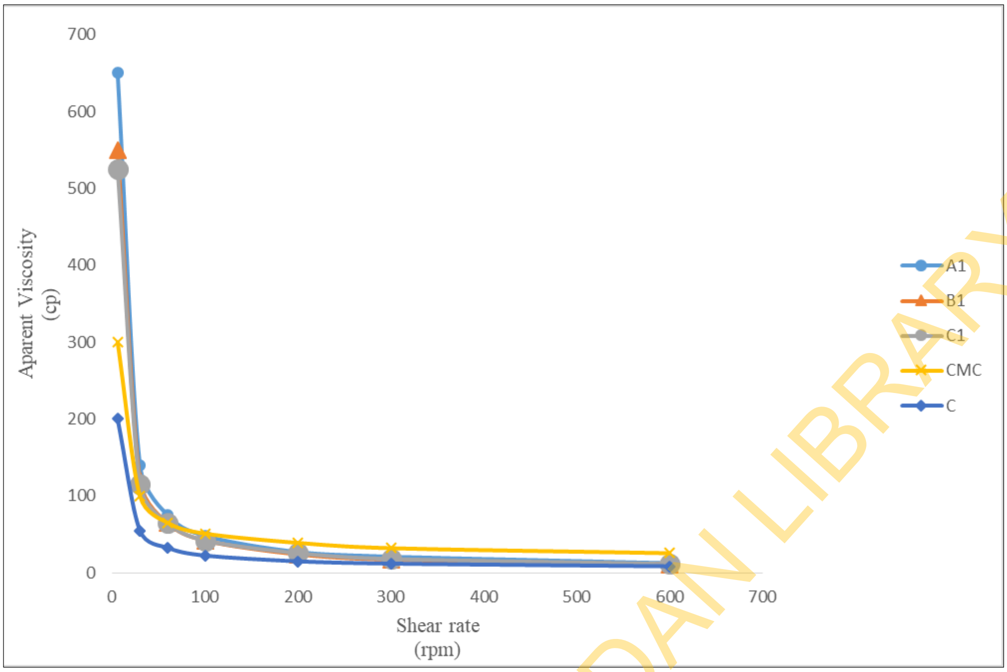

Fig 1: Apparent viscosity of Mud samples at different shear rates before aging at 30°C

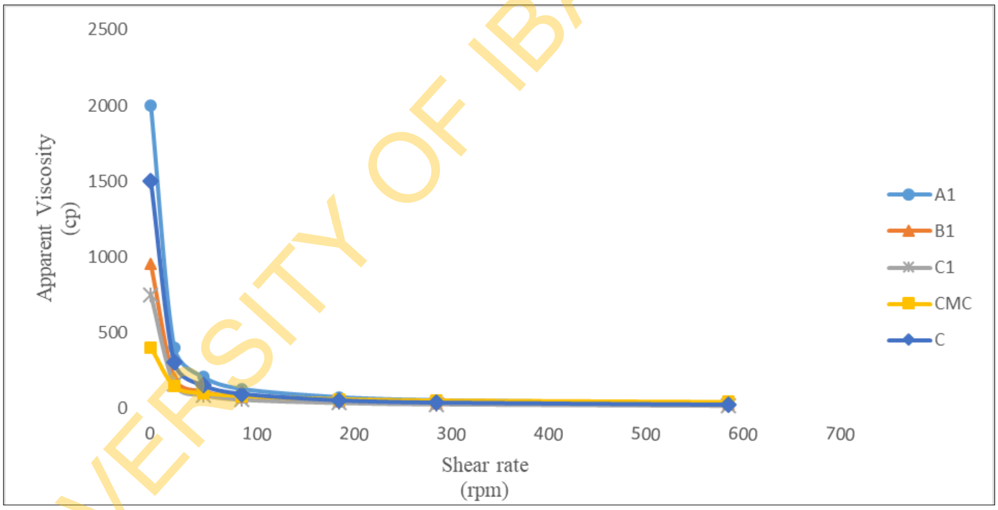

Fig 2: Apparent viscosity of Mud samples at different shear rates after aging at 30°C

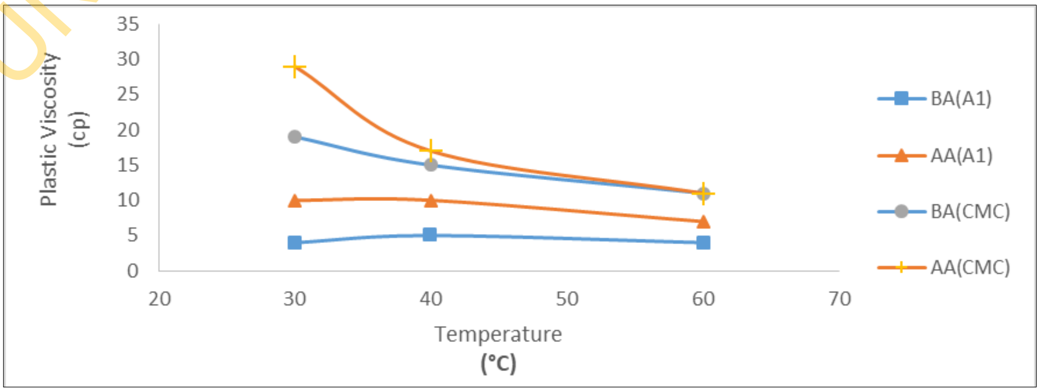

Fig 3: Plastic viscosity of Mud samples before and after aging against temperature

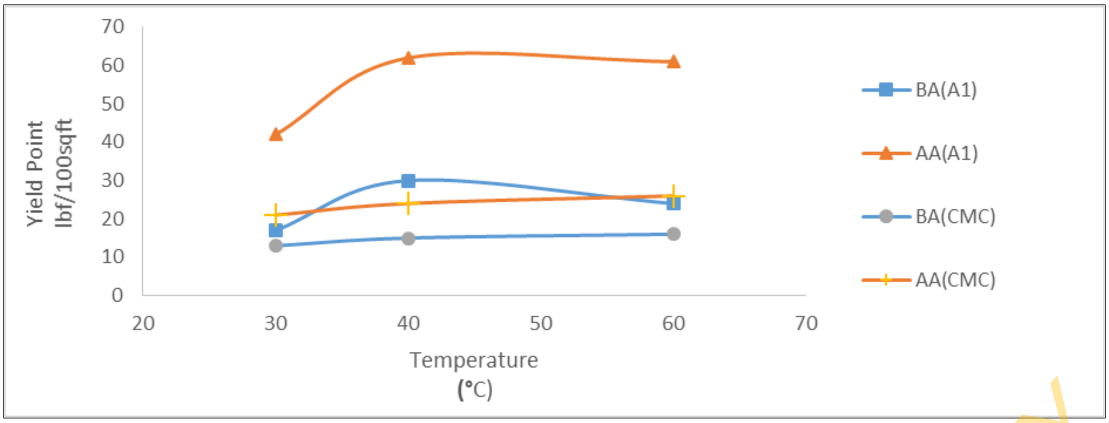

Fig 4: Yield Point of Mud samples before and after aging against temperature

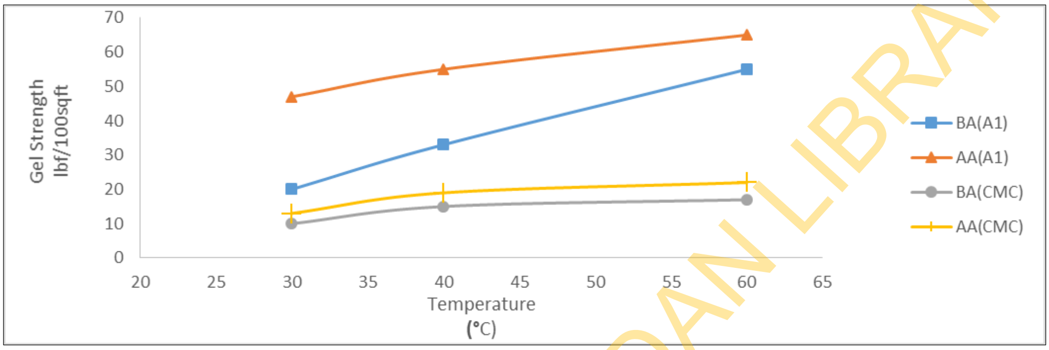

Fig 5: Gel strength of mud samples with and without aging effect at 30°C

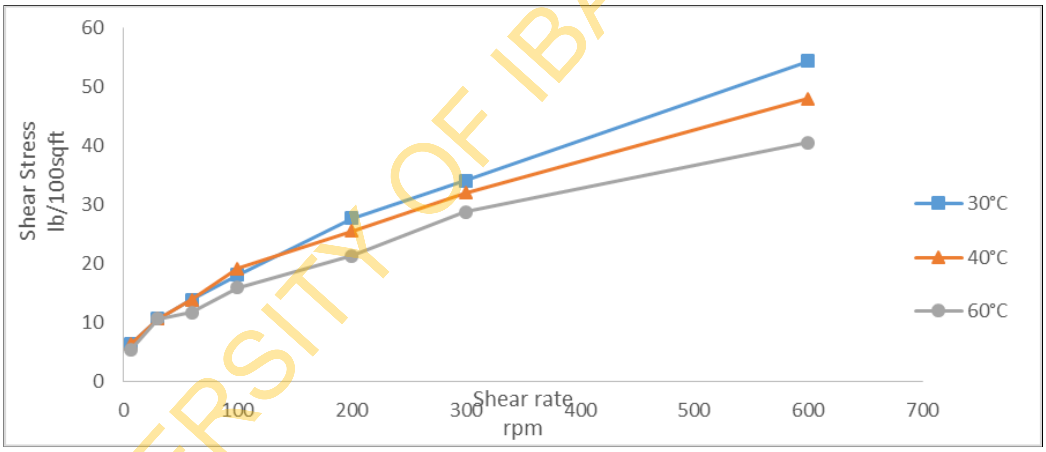

Fig 6: Shear stress against Shear rate for Sample CMC

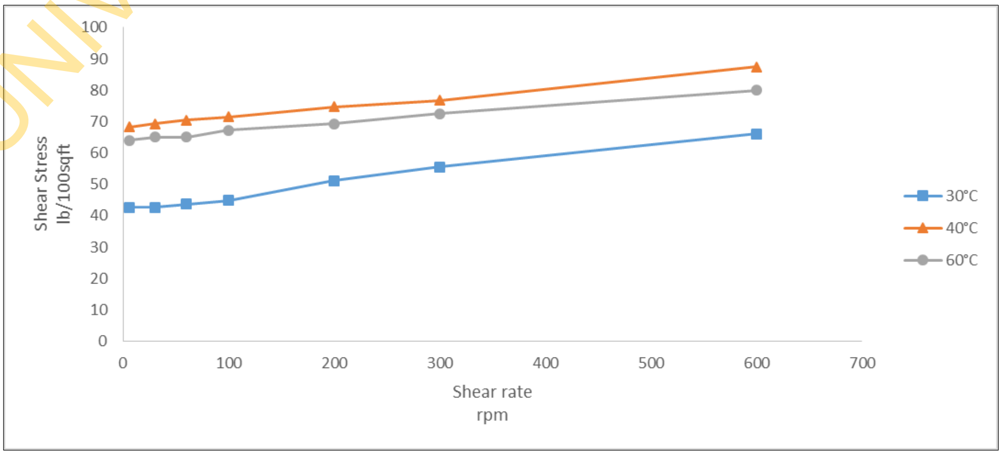

Fig 7: Shear stress against Shear rate for Sample A1

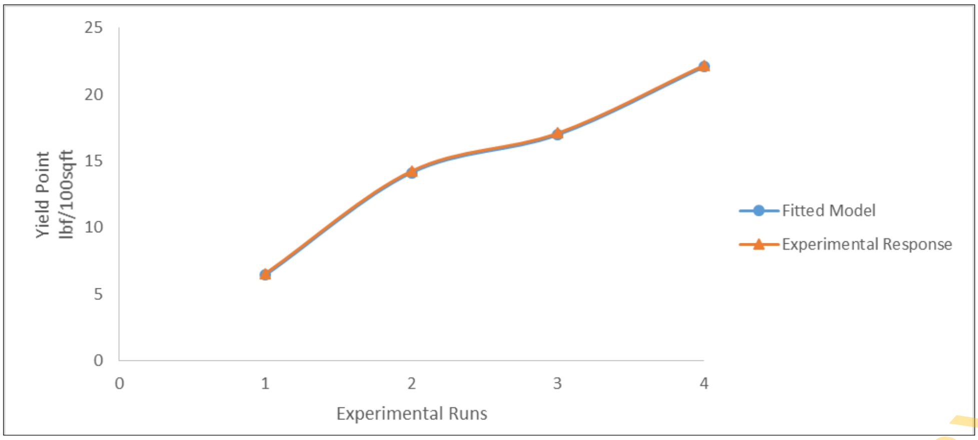

Fig 8: Comparison of Experimental response and fitted model for Yield Point

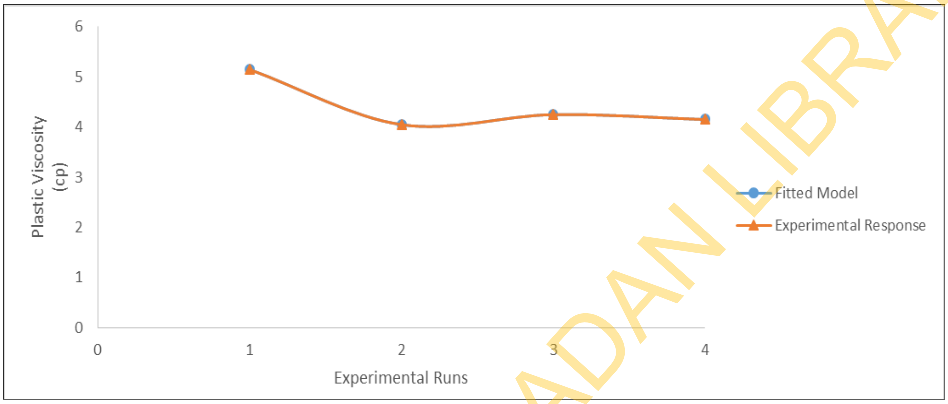

Fig 9: Comparison of Experimental response and fitted model for Plastic Viscosity

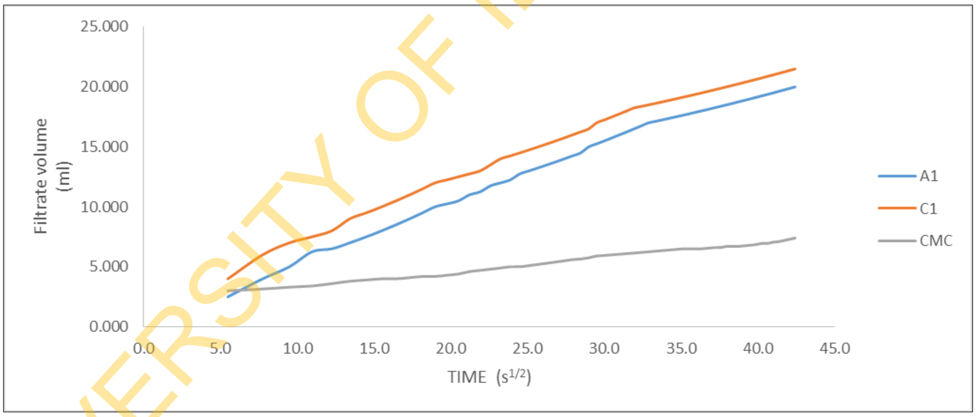

Fig 10: Filtrate loss volume of mud samples against time

Yield Point

Standard error = residual = 0.125

Sum of squares, SSQ $= \frac{contrast^2}{2^k X\ 2}$ 12

Variance of effects $= \frac{4\sigma^2}{2^{k-r}}$ 13

Where

r = no. of replications

σ^2= variance

Where k = 2, r = 2;

Variance of effects = $4\sigma^2$

$\sigma^2 = \frac{SSQ_{residual}}{2^k}$ 14

$SSQ_{residual} = SS(Totals) - SS(X_1 + X_2)$ 15

$SSQ_{residual} = (1031.215 - 903.003) - (5.12 + 10.6953)$

= 112.397

$\sigma^2 = 112.397/2^2$

= 28.0993

Variance of effect = 4 x 28.0993

= 112.397

Plastic viscosity

Standard error = 0

$SSQ_{residual} = (74.7281 - 73.74516) - (0.0013 + 0.005)$

= 0.9667

$\sigma^2 = 0.9667/2^2$

= 0.2417

Variance of effect = 4 x 0.2417

= 0.9667

The flow indices of the mud samples before and after aging at 30º and 60°C is shown in Table 3. The flow indices indicate that the mud sample with CMC has the highest index therefore tending more to a Newtonian fluid behaviour when compared to the other the others. The results of the flow indices for the fluid show that all the mud samples still behave as pseudoplastic fluid (n< 1) thus utilising a Non-Newtonian model.

It is noticeable that sample A2 has a higher flow index at 60°C than at 30°C which is unusual with the trend. This may however be attributed to experimental error.

Table 3: Flow index of mud samples before and after aging at 30°C and 60°C

	At 30º C		At 60 º C	
SAMPLE	(n) B/A	(n) A/A	n) B/A	(n) A/A
A1	0.252	0.254	0.193	0.141
A2	0.415	0.407	0.474	0.226
B1	0.372	0.303	0.193	0.160
B2	0.415	0.280	0.241	0.222
C1	0.354	0.273	0.322	0.188
C2	0.476	0.379	0.372	0.290
CMC	0.672	0.660	0.493	0.376
A	0.515	O.279	0.284	0.166
B	0.521	0.290	0.290	0.170
C	0.503	0.322	0.282	0.202

Table 4: Factor level Settings

Factor		LEVELS	
	Low(-)	Standard	High(+)
Temp.(˚F)	86.0	113.0	140
Starch(g)	0.0	2.5	5.0

Table 5: High and Low level combinations for Temperature and Starch Quantity

Run no.	V_c (Temp) (°F)	V_c (Starch) (g)
1	86	0
2	140	0
3	86	5
4	140	5

Table 6: Analysis Matrix for 2^2 full Factorial Design for the high and low levels

Run No.	I	X_1	X_2	X_1X_2
1	+1	-1	-1	+1
2	+1	+1	-1	-1
3	+1	-1	+1	-1
4	+1	+1	+1	+1

Table 7: Experimental results for Plastic Viscosity

RUN No.	Temp(°F)	Modified starch(g)	μ_p(I)	μ_p (II)	$\mu_{pI} + \mu_{pII}$
1	86	0	5.0	5.3	10.3
2	140	0	4.0	4.1	8.1
3	86	5	4.0	4.05	8.05
4	140	5	3.9	4.0	7.9

Table 8: Experimental results for Yield Point

RUN No.	Temp(°F)	Modified starch(g)	y_p(I)	y_p (II)	$y_{pI} + y_{pII}$
1	86	0	6.5	6.6	13.1
2	140	0	14.2	14.3	28.5
3	86	5	17.1	17.1	34.2
4	140	5	22.1	22.3	44.4

Table 9: Factorial Effects using Yates Algorithm for Yield Point

RUN No.	Treatment totals	1st time	Effect Total	Est. Effect	Coeff. value(B_i)	Effect name
1	13.1	41.6	119.2	14.963	14.963	I
2	28.5	78.6	25.6	6.400	3.200	X_1
3	34.2	15.4	37.0	9.250	4.625	X_2
4	44.4	10.2	-5.2	-1.300	- 0.650	X_1X_2

Table 10: Factorial Effects using Yates Algorithm for Plastic Viscosity

RUN No.	Treatment totals	1st time	2nd time (A)	Effect Total	Coeff. Value	Effect name
1	10.3	18.4	35.2	4.4	4.40	I
2	8.1	16.8	-2.4	-0.6	-0.30	X_1
3	8.5	-2.2	-1.6	-0.4	-0.20	X_2
4	8.3	-0.2	+2.0	0.5	0.25	X_1X_2

Fluid Loss

The filtrate loss for three mud samples are represented in figure 6 which show the filtrate volume loss for the samples plotted against the square root of the time for which pressure was exerted on the filter press. Sample A1 and C1 having modified starch additives give filtrate loss volumes with small difference between them, but the sample with CMC (control sample) gives better filtrate loss volumes. The mud cake thickness for Sample A1 and C1 is 1/5 inch, Sample C1 while that of CMC was 1/8 inch

Recommendation

The experimental study carried out on the behaviour of modified starch on the rheological properties of water-based mud presents some interesting results which are comparable with a widely used viscosifier, CMC which was used as the control mud sample. The mud samples with modified starch give a higher yield point, lower plastic viscosity, higher gel strength and exceptional shear thinning ability when compared to the mud with CMC and yet retains its good filtration ability. Dioscorea yam species are readily available in the local market, affordable and rich sources of starch thus the required raw materials are present. Improving the rheological properties of the drilling mud with starch modification helps the starch to serve as a good rheological and filtration control additive. More experimental work can be carried out on the modification of yams starch to verify this experimental study and further prove its ability to improve the viscosities of water-based muds while yet retaining its good filtration control ability. This will reduce the cost of viscosifiers that can be added to water-based muds and also reduce the amount of solids in the mud.

Abbreviations

°C = Degree Celsius
°F = Degree Fahrenheit
ϕ_N = Dial reading/deflection at N
N = Rotary speed
μ_a = Apparent viscosity
μ_p = Plastic viscosity
t_r Shear thinning rate
B_o = Intercept coefficient
B_1; and B_2 = Main coefficient on factor 1 and 2, respectively
B_{12} = Interaction coefficient of factor 1 and 2
X_1X_2 = Interaction Effect of factor 1 and 2
t = Shear stress

Ɣ = Shear rate
y_p = Yield point
P = Pressure
ϱ_m = Mud density
H = Depth
CMC = Carboxymethylcellulose
PAC = Polyanionic cellulose
AA = after aging
BA = before aging
RPM = Revolutions per minunte

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