Experimental Study of Wood Ash (WA) and Lignosulphonate (LS) in Drilling Fluid Design

Emeka Iloke ^{1,*}, Ndubuisi, E.C ², Ikeh, Lesor³, Obeta, P.O⁴ Joel Ogbonna⁵

^{1,2,3,5} University of Port Harcourt, Faculty of Engineering, Department of Petroleum and Gas Engineering, P.M.B 5323, Choba, Uniport.

⁴Igbinedion University Okada, Benin City, Nigeria * Corresponding author email address: emeka_iloke@uniport.edu.ng Received 10 April 2023; Accepted 25 April 2023

Abstract

The conditioning of drilling mud is very essential in improving its rheological properties. As a result, oil and gas companies spend millions of US Dollars to import oilfield additives. This adds greatly to the total drilling cost. However, these additives can be sourced from locally sourced biomass. This has always been at the front burner of research at the local content level, as many of these wastes constitute environmental pollution. Hence, recycling them, especially the wood ash which is the end-product of the combustion of wood wastes into useful oilfield cement additives becomes very important. Wood wastes are on top of the list of biomass-raising environmental concerns over decades. Its conversion to wood ash by incineration has not abated the challenge posed by it because wood ash (WA) accumulation is hard to manage, the need for this work. In this work, the interest in this study was to experimentally study the performance of wood (WA) with polymer-lignosulphonate (LS) as drilling mud additives. A mud slurry of 15.8g was prepared with 0.1% concentration and 0.2% concentration and with 0.1% of LS and 0.2% of LS. The rheological properties of the formulated mud slurries were determined using a viscometer at 80°F, 120°F, and 150°F. The result shows that the mud samples treated with WA had decreased viscosity with increasing temperature at both 0.1% and 0.2%. The sample treated with LS has a reversal effect on viscosity at 0.2%. Also, WA polymer reduced gel strength in mud slurries at 0.1% but at 0.1% of LS, the gel strength was increased and reduced at 0.2%. WA polymer also improved the pH of mud slurries as the slurries treated with LS had a pH of 7.0 while WA-based slurries had a pH of 8.0. Therefore, going by the above results, WA performed excellently with LS as an oilfield additive and could serve as a substitute.

Keywords: lignosulphonate, wood ash, rheology, polymer, viscosity, additive, biomass

I. Introduction

Wood ash (WA) is a non-agro-waste that is generated when the wood wastes are combusted. Combustion of wood waste is commonplace in wood mills. Burning biomass wastes such as sawdust from paper mills is one of the conventional methods of waste disposal. In the process of burning agro-wastes, a considerable amount of ash is generated (Füzesi, et al., 2015). Wood Ash (W A) is a waste and its generation is fast growing, resulting in a serious environmental concern. It was gathered that the estimated amount of wood ash in Hungary was 30 thousand tons and its volume was 50 thousand m³ ((Tóth, et al. 2011). In Nigeria, a large volume of wood waste is churned out annually. Saw mills in Nigeria produces more than one million meter cubes (100000m³) of waste wood and the plywood industry produced five thousand meters cube of waste in 2010 (Jacob, et al., 2016). It was equally gathered that they generate over 1.8 million tons of sawdust and 5.2 million tons of wood waste yearly (Jacob, et al., 2016). Population growth and urbanization have also continued to increase the growth of wood ash at an alarming rate through electric power generation by wood-burning industries utilizing woodchips, wood barks, sawmill scraps, hardships, and wood sawdust as a fuel sources (Eric, et al., 2020) and by so produce a large of quantity of wood ash, which can pose a risk of health threat to the biotic environment are accumulated (Barathan and Gominath, 2013), if not properly managed. The only known and effective wood ash disposal method is landfill which takes care of about 70% of wood ash disposal (Campbell, 1990; Etiegni and Campbell, 1991; NCASI, 1993) and it has been in use over the decades. In the landfill disposal method, there is an inherent respiratoryrelated issue for the people living around the dumpsite due to the highly fine particles which WA has that get easily airborne (Eric, et al, 2020). It also causes pollution of the underground water through the leaching of its heavy metal components (Udoeyo, et al., 2006). Hence, the landfill method of WA disposal has not sufficiently addressed the problem of pollution and economics. Finding the industrial use of wood ash in the oil and gas industry would go a long way to solve the problem of pollution and hence take advantage of the useful components for monetization of WA, thereby adopting the most economic approach to wood ash disposal. WA is rich in SiO₂, P₂O₅, SO₃, K₂O, CaO, TiO₂, V₂O₅, MnO, Cr2O₃, Fe₂O₃, ZnO, CuO, Y₂O₃, Ag₂O, BaO, Eu2O₃, Re2O₇, HgO,

and CeO while Al₂O₃ was found in both X-ray fluorescence (XRF) and Scanning Electron Microscopy (SEM) tests carried out (Eric, et al., 2020).

Wood ash has various uses which have been explored by some researchers, though not exhaustive. WA is used in agriculture, horticulture, and forestry as a source of manure for soil amelioration (Demeyer et al., 2001; Steenari and Lindqvist 1997; Zimmermann et al., 2010) as a result of its micro-element and macro-element components. The aforementioned use of wood ash has not been able to address the environmental concerns posed by the enormous quantity produced annually.

It also has high lignin and cellulose contents, making it a veritable locally sourced material for oil field additives. For instance, wood ash is used in the bioremediation of soil polluted with oil spills (Essien, et al., 1995). WA has been used in the improvement of the fertility of the soil for high productivity but can release heavy metals like sodium and the like. Sodium (Na) poses unfavorable conditions for cultivated crops by excessively raising the salinity of the soil as high as 60mg/kg (Füzesi, et al., 2015). Wood ash was experimentally examined to ascertain its ability to treat oil-contaminated soil in comparison with the chemically synthesized surfactant, Tween 80. WA achieved 94.54% success while Tween 80 had 90.28% success (Akan, et al., 2013). This is a clear indication that WA is a good surfactant. However, the application of WA has not been harnessed in the area of cement and mud additives, specifically, oil field cement and mud dispersant. The surfactant ability of wood ash in oil spill clean-up shows that it could do well serving as an oil field additive. Hence, this work focused mainly on experimentally studying AW as oil field cement and mud additives. This is to help abet the problem of environmental pollution, and health hazards to man and optimize cement and mud slurry designs.

Wood Ash Effects on the Environments

Wood ash has been proven to have some useful applications in the agricultural sector to improve the fertility of the soil, reduce the acidity of the soil (Füzesi, et al., 2015), pollution control i.e bioremediation procedure (Akan, et al., 2013). As of 2012, forest biomass, of which wood waste contributed a very high portion was expected to hit 231 million tons in the United State of America and grow more to 286 million tons in 2017 (U.S. Department of Energy, U.S. Billion-Ton Update, 2015; Clarke and Preto, 2015). It was gathered from some research works that WA has different components as observed in the SEM and XRF tests conducted. These constituents include: SiO₂, P₂O₅, SO₃, K₂O, CaO, TiO₂, V₂O₅, MnO, Cr₂O₃, Fe₂O₃, ZnO, CuO, Y₂O₃, Ag₂O, BaO, Eu₂O₃, Re₂O₇, HgO, and CeO but lacks Al₂O₃ (Francisco, et al., 2015; Eric, et al., 2020). The components mentioned above contribute to the characteristic functions of wood ash for different purposes. Wood ash is in abundance globally and it could pose health challenges to the biotic environment and edaphic factors through the release of heavy metals. It has the potential to chemically alter the composition and PH of the soil, especially the top layer (Mandre et al., 2006; Ozolincius et al., 2007). However, it was also gathered that the wood ash reduces the mobility of the heavy metals when it is released into the soil (Vance 1996; Campbell 1990), making it less toxic but still limiting its use coupled with the fact that urbanization and population have added so much the increased production wood ash globally (Eric, et al., 2020), making a potential threat to environments and lives. It was however argued that the chemistry of the wood ash is dependent on the species of wood burnt, the nature of the combustion process, and conditions at the application site. In the UK, it was discovered that recycling wood ash is posing a big challenge in management and requires carefully tailor-made biomass project design (Étienne, 2020).

Also, wood ash has been studied by many researchers to evaluate its capacity to be used for engineering projects like construction (Athanasopoulou, 2013), concrete mixtures (Sumer, 2012), and soil stabilization (Tastan, *et al.*, 2011; Kumar, *et al.*, 2007) but other applications of wood ash have not been delved into, which could be economical and equally solve the problem of pollution which still remains unsolved as the production of wood ash is on the increase due the human activities such as industrialization and urbanization... Recycling wood ash for use in the oil and gas industry is gradually gathering global interest but unharnessed. For instance, geotechnical projects always need a large amounts of biomass, and using recycled wood ash would be a good move (Francisco, *et al.*, 2015). Wood ash and sugar cane ash have been used as a pozzolanic material in the concrete mixture (Udoeyo, *et al.*, 2006). This pozzolanic characteristic of wood ash makes it a very good material for the conditioning oilfield additives. WA has the ability to increase the strength of materials from various studies by researchers (Dutta, 2008). Another work revealed that WA has a comparably high specific surface area suitable for a good adsorption process (Genty, *et al.*, 2012). Wood ash is generally in a powdered form and has fine particles. Its particle size is responsible for the attribute. Dry sieve analysis done by some researchers showed that it has two-grain sizes; the fine grain which is below 100μm and the coarse grain size which is above 100μm (Danuta and Mariola, 2021).

Table 1 Chemical Composition of Wood Ash (WA) (American Coal Ash Association, 1995; Abdullahi, 2006;

CONSTITUENTS	WOOD ASH (WA)
SiO ₂ ,	31.8
Fe_2O_3	2.34
Al_2O_3	28
CaO	10.53
Na_2O	6.5
SO_3	-
K_2O	10.38
MgO	9.32

Wood ash has been used as a surfactant and its performance was compared with that of Tween 80. WA achieved 94.54% success while Tween 80 had 90.28% success (Akan, *et al.*, 2013). This result showed succinctly that WA is a good surfactant. However, it has not been explored in the area of oilfield additives, creating a gap for further studies.

Factors Affecting the Quantity and Quality of Wood Ash

The quantity and quality of wood ash depend largely on a number of factors such as temperature, wood type, and others. The temperature at which the ash is obtained affects the quality and quantity of ash after combustion. High temperatures yield low quality and quantity of wood ash. It reported that a combustion temperature of 1000.4° F to 1999.4° F would reduce ash production to 45% and the temperature above 1832° F would lead to the decomposition of carbonates and bicarbonates but at the combustion temperature of 932° F results in a high concentration of bicarbonates and carbonates, especially calcite (CaCO3) in ash (Cheah and Ramli, 2011). Some elemental components such as potassium, zinc, and sodium decrease in quantity as the temperature increases to 1999.4° F leaving more oxides like quicklime (CaO) in the ash (Etiegni and Campbell, 1991). The use of ash is dependent on its quality and components (chemical characteristics). Wood ash contains carbonate which could be carbonate of sodium or calcium. According to work done by Campbell (Etiegni and Campbell, 1991), wood ash contains other elemental components at different percentages such as carbon (5 – 30%), calcium (7- 33%), potassium (3 – 4%), magnesium (1 – 2%), manganese (0.3 – 1.3%), phosphorus (0.3 – 1.4%), and sodium (0.2 – 0.5%). In comparison with lignosulphonate, wood ash shares the carbonate component property with lignosulphonate which is responsible for the dispersing characteristic of both polymers.

Lignin Structure and Components

Lignin is a veritable raw material for the production of paper in the pulp and paper industry and it is the most abundant biopolymer known globally (Zakzeski, *et al.*, 2010). Rini, *et al.*, (2020) categorically stated that unreacted lignin has three basic functional group components which include: phenolic O-H functional group, aliphatic and aromatic -CH- stretching functional groups, and C=C aromatic groups as shown in fig. 1.1. The extraction loop which is done using NaOH is not stopped until the lignin meets the standard required before the process is halted, else, the loop continues until the desired result is obtained. As soon as the sulfonation process which yields lignosulfonate is successfully carried out, there will be alteration in the functional group components as shown in fig.2.2. The new functional groups resulting from the displacement reaction will be alkene functional group (-C=C- aromatic), stretching sulfonate functional group (S=O), carboxyl functional group (C=O) and ester functional group (S-OR) as revealed in the recent work by Rini, *et al.*, (2020b). Lignosulfonates are highly branched macromolecules and are formed from phenylpropane units connected in a non-regular manner by ether or C-C bonds, the latter between the aromatic rings' (Flatt and Schober, 2012), as shown in fig.2.2. Lignin with high purity α-cellulose is a veritable raw material for the production of the cellulose ester for making plastics as investigated by Varma AJ (2013).

Figure 1 Schematic of Lignosulfonate

The recent study by Rini, *et al.*, (2017) shows that sodium lignosulfonate can be obtained from the Bagasse plant through a two-stage process of hydrolysis with NaOH and sulfonation process using bisulfide (NaHSO₃). The recent study by Rini, *et al.*, (2017) shows that sodium lignosulfonate can be obtained from the Bagasse plant through a two-stage process of hydrolysis with NaOH and sulfonation process using bisulfide (NaHSO₃). Also, Guterman, *et al.*, (2019) found out that unmodified lignosulfonate could produce undesirable substances because it cannot maximize interfacial contact and complexation with cellulose and protein.

Carbonate component of Wood Ash and Modified Lignosulphonate

The chemical compositions and structures of modified lignosulphonate (see figure 2.6) and wood ash (Etiegni and Campbell, 1991) show that both of the polymers have carbonates which are responsible for their dispersing characteristics. Calcium carbonate in calcium-modified lignosulphonate is responsible for the anionic surfactant property of lignosulphonate containing hydrophilic end (sulphoric, phenolic, and hydroxyl groups) and hydrophobic end (carbon chain) (Strydom, *et al.*, 2018). This makes it have some level of surface activity (Fredhein, et al., 2003; Chen and Wu, 1994). Wood ash obtained at a regulated temperature of about 932°F (Cheah and Ramli, 2011) also contains carbonate which could be carbonate of sodium or calcium according to work done by Campbell (Etiegni and Campbell, 1991). The viscosity of the cement is reduced to the barest minimum using dispersants (Boughton, *et al.*, 1962).

II. Materials and Methods

Materials and apparatus used for the study include the following; weighing balance, Atmospheric consistometer, Hamilton beach mixer, Fann viscometer, mud cup, measuring cylinder, measuring cup, oven, syringe, wood ash sample, lignosulphonate, water, defoamer, Pack-R, (thickening agent), Bentonite, XCD, Barite KCl, CaCO₃



Figure 3 Lignosulphonate Sample



Figure 2 Wood Ash Sample

Preparation Mud Slurry

270 ml of fresh water was measured out and stirred for 5min using a Hamilton mixer, 12g of bentonite was added and allowed to mix for 30min, then Pac-R (2g) was added as well and allowed to stir for 5min, XCD (2g) was added and mixed for 5min, KCl (10g), CaCO3 (0.2g), and barite (53.89g) for two samples having 0.1% and 0.2% concentrations for both wood ash and lignosulphonate.

Rheological Property Determination

Fresh drilling mud slurry samples treated with wood ash and lignosulphonate following the design (API standard) in Table 3 and Table 4 respectively were set for the rheological test. The rheological properties of the two samples were measured at 600rpm, 300rpm, 200rpm, 100rpm, and 6rpm at 80°F and 120°F. The gel strengths of the wood ash and lignosulphonate treated samples were determined at 80°F and 120°F at the first deflection of 600rpm and recorded. The PV and YP were obtained by calculation using equation 1 and equation 2. The mud density was determined using the mud balance and the pH values of both wood ash and lignosulphonate-treated samples were measured and recorded.

The rheological values obtained from the viscometer and various calculations obtained from test results are shown below. The reference for measuring and calculating viscosity was done based on the specifications of API (API RP-13B-1/ISO10414-1, 2016). The features and specifications of the Model-35 Fann direct-indicating viscometer used are equipped with the standard R1 rotor sleeve, B1 bob, F1 torsion spring, and stainless-steel sample cup. The constant values used for the calculation are based on the stipulated standard for R1-B1-F1. The readings obtained from the viscometer were converted to the oilfield units to get the values for shear stress and shear rate by employing equation 1 and equation 2.

Determination of the Plastic Viscosity (PV) and Yield Point (YP)

The plastic viscosity (PV) and yield point (P) of both oil field cement and drilling mud slurries were calculated using the equations (3.4) and (3.5)

PV (cP) =
$$(\theta 300 - \theta 100) \times 1.5$$

YP $(1b/100ft^2) = (\theta 300 - PV)$

Where;

 $\boldsymbol{\theta}$ = dial reading

The gel strength at 10 seconds and gel strength at 10 minutes were obtained from the Fann Viscometer immediately after the required duration, at the first deflection. This was according to the America Petroleum Institute Specification and procedures (API RP 13B-1/1SO 10414-1, 2016).

Calculation of Shear Stress and Shear Rate

According to the R₁-B₁-F₁ specification

Shear stress (
$$1b/100ft^2$$
) = 1.065 x 10Fann 3
Shear rate (sec-1) = 1.7023 x rpm, N 4

N = Rate of revolution of the outer cylinder, rpm

 θ = Fann viscometer reading

Viscosity was obtained by the equations (5a. 5b, 5c) and the conversion factors as listed in table 3.4.

$\mu = k_1 k_2 / k_3 (100) \theta / N$	5a
$\mu = kf^{\theta}/N$	5b
$\mu = \tau/\gamma (100)$	5c

Where;

 μ = viscosity in centipoise (cP)

N = Rate of revolution of the outer cylinder (rpm)

 θ = Fann Viscometer reading

 τ = shear stress, dynes/cm² which is calculated as $k_1k_2\theta$

 γ = shear rate, sec-1, which is calculated as k_3N

Note: 1Poise = 100cP

III. Results

Tabulated readings of Fann Viscometer (RPM) at Varied Temperatures.

Table 1 to **Table 4** show the viscometer reading is obtained at different temperatures for both the LS-based cement mud and WA-cement mud. PV and YP were obtained analytically using **equation 1** and **equation 2** while the gel strength values were obtained at the first deflection at 10sec and 10min.

Table 1 Results of Rheological Properties of Wood Ash-based Mud Slurry at 0.1%

RPM (θ)	80°F	120°F	150°F
Θ600	245	250	254
$\Theta 300$	177	185	191
$\Theta 200$	148	152	155
Θ100	111	115	118
Θ6	46	47	48
$\Theta 3$	40	41	42
PV (cP)	102	97.5	94.10
YP (lb/100ft2)	75	87.5	21.90
Gel Strenght at 10sec	46	45	44.30
Gel strength at 10min	60	50	42.5

Table 2 Results of Rheological Properties of Wood Ash Based Mud Slurry at 0.2%

RPM (θ)	80°F	120°F	150°F	
Θ600	300+	300+	300+	
$\Theta 300$	214	212	211	
$\Theta 200$	175	172	170	
Θ100	130	128	127	
Θ6	53	55	55	
Θ 3	47	47	47	
PV (cP)	129	132	134	
YP (lb/100ft2)	85	80	73.3	
Gel Strength at 10sec	45	50	53.8	
Gel strength at 10min	76	70	65.5	

Table 3 Results of Rheological Properties of Lignosulphonate-Based Mud Slurry at 0.1%

	U		
RPM (θ)	80°F	120°F	150°F
Θ600	300+	300+	300+
Θ300	233	232	231
Θ200	148	152	194
Θ100	152	150	149
Θ6	67	65	64
Θ3	66	65	47
PV (cP)	100.5	102	103.10
YP (lb/100ft2)	132.5	130	128.1
Gel Strength at 10sec	80	86	90.5
Gel strength at 10min	59	57	56

Table 4 Results of Rheological Properties of Lignosulphonate-based Mud Slurry (144ppg) at 0.2%

RPM (N)	80°F	120°F	150°F
Θ600	275	275	275
$\Theta 300$	230	196	171
$\Theta 200$	190	165	146
Θ100	145	122	105
$\Theta 6$	60	50	43
Θ 3	50	42	36
PV (cP)	67.5	118.5	156.8
YP (lb/100ft2)	162.5	77.5	13.3
Gel Strength at 10sec	48	46	44.5
Gel strength at 10min	55	45	37.5

Effect of Temperature on Shear Stress and Shear Rate Relationship on Imported Polymer (Lignosulphonate) and Local Polymer (Wood Ash) Based Cement and Mud Slurries

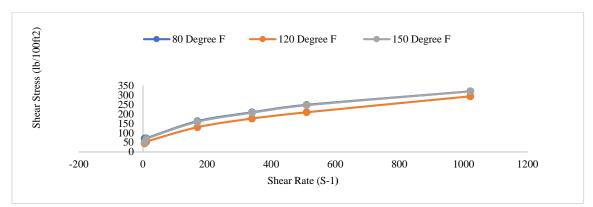


Figure. 4 Variation of Shear Stress versus Shear Rate at 0.1% of Lignosulphonate of mud Slurry of 15.8ppg at Different Temperatures

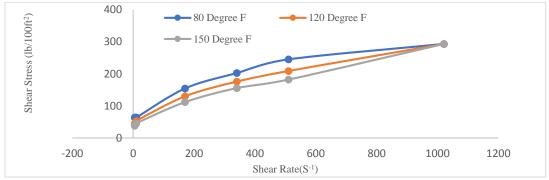


Figure 5 Variation of Shear Stress versus Shear Rate at 0.2% of Lignosulphonate of Mud Slurry of 15.8ppg at Different Temperatures

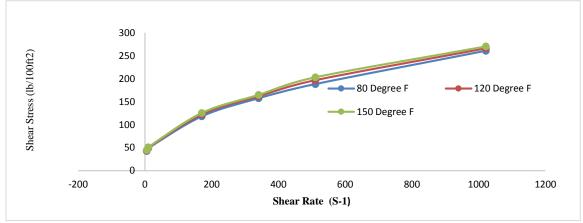


Figure 6 Variation of Shear Stress versus Shear Rate at 0.1% of Wood Ash of Mud Slurry of 15.8ppg at Different Temperatures

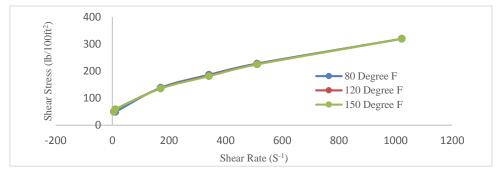
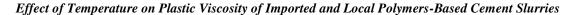


Figure 7 Variation of Shear Stress versus Shear Rate at 0.2% of Wood Ash of Mud Slurry of 15.8ppg at Different Temperatures

LS-based mud slurry with a concentration of 0.1% showed maximum shear rate and maximum shear stress at 80°F and 120°F. There was an overlap between values of shear stress and the shear rate at 120°F and 80°F (**figure 4**). The maximum shear rate and shear rate values were obtained at 80°F for 0.2% concentration lignosulphonate (LS) (**Figure 5**) and an overlap of shear stress – shear rate for at 80°F, 120°F and 150°F. The WA-based mud slurry showed a close-range increase in the shear stress and shear rate and overlapped afterward (**Figure 6**). At 0.2 % concentration of WA, the shear stress versus shear rate increase overlapped from the start.

The results show explicitly the increasing trend of shear stress versus the shear rate at different temperatures of the various samples for mud and slurries at 0.1% and 0.2%. The graphs implied a direct relationship between shear stress and shear rates, meaning that mud slurry will not flow until the yield point (critical value) is exceeded. From the graphical presentation of shear stress against shear rate, it is therefore established that the fluid flow is in line with the Bingham plastic model.



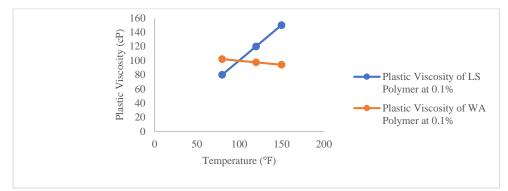


Figure 8 Variation of Plastic Viscosity at Different Temperature Values for 0.1% of LS Polymer and WA Polymer in 15.9ppg of Mud Slurry

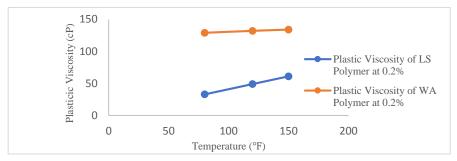


Figure 9 Variation of Plastic Viscosity at Different Temperature Values for 0.2% of LS Polymer and WA Polymer in 15.9ppg of Mud Slurry

Mud slurries formulated with 0.1% of wood ash (WA) polymer and Lignosulphonate Polymer (Imported) experienced an increase in plastic viscosity as the temperature increased while the mud slurry treated had its plastic viscosity slightly decreased as the temperature increased from $80^{\circ}F - 150^{\circ}F$ (**Figure 8**). When the concentration of each polymer (local and imported) was 0.2%, their viscosities both increased as the temperature increased from $80^{\circ}F - 150^{\circ}F$ as shown in **Figure 9** This implied that both WA and LS polymers are viscosifiers at a concentration range of 0.1 - 0.2%.

The Variation of Gel Strength with Imported Polymer (LS) and Local Polymer (WA) at Different Concentrations in Cement Slurries

The effects of temperature on gel strengths of wood ash polymer-treated mud slurry and lignosulphonate polymer-treated mud slurry are shown in **Figures 10** to **Figure 11**

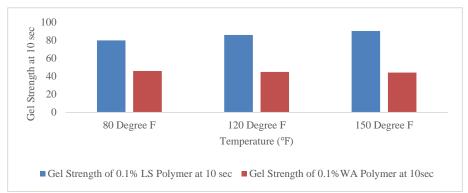


Figure 10 Variation of Gel Strength of 0.1% LS Based and 0.1% WA Based Mud Slurries at Different Temperatures for 10sec

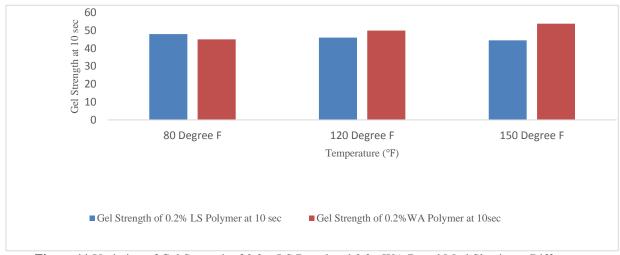


Figure 11 Variation of Gel Strength of 0.2% LS Based and 0.2% WA Based Mud Slurries at Different Temperatures for 10sec

Figure 10 to **Figure 11** show the change in gel strength of mud slurry formulated with wood ash and lignosulphonate polymers as the temperature increases at different concentrations of the polymers under study. The gel strength at 10secs of WA-based slurry decreased slightly from 46 – 44.30 as the temperature increased from 80°F 150°F and LS-based mud slurry had its gel strength at 10secs increased from 80 – 90.5 at 0.1% (see fig. 3.7). At 0.2%, the gel strength at 10secs of LS-based mud slurry slightly increased with increasing temperature while WA-based mud slurry increased with increasing temperature (Fig.3.8). Gel Strength at 10mins of both LS-based mud slurry and WA-based mud slurry decreased with an increase in temperature at 0.1% (See fig. 3.7). Increase in temperature brought about a decrease in the gel strength at 10mins of LS-based and WA-based polymer at 0.2% (See fig. 3.8). This implies that WA-based polymer performed favorably with LS-based polymer as an oilfield mud additive

IV. Conclusions

An experimental study was done to investigate wood ash as a drilling mud additive. Based on the results obtained, the following conclusions were drawn:

The ability of local polymer (WA) to thin or disperse mud depends on its concentration just as the imported sample (LS) does.

Wood ash increased the pH of mud slurries (pH of 8) and Lignosulphonate made the slurries neutral and that is an advantage WA has over the imported sample.

The study reveals that wood ash could serve as a substitute for lignosulphonate in drilling mud.

The graph of shear stress against shear rate for wood ash-based mud slurries is in tandem with Bingham Plastic model.

Gel strength was improved more in WA-based mud slurry than in LS.

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