AGRO-Wastes Utilization in Oilfield Operations for Sustainable Development

Uzoho. C. U, Akaranta. O

***Abstract*— Oilfield chemicals are expensive and essential in oil and gas operations. Over 10% of the cost of drilling is apportioned to drilling fluids; therefore, there arises a need to substitute conventional chemicals with agro-wastes as additives in drilling operations. This paper appraises the use of oil palm empty fruit bunch (EFB), rice husk, walnut shell powder, coconut shell powder, groundnut husk, cassava mesocarp, orange mesocarp, corn cob, palm bunch and plantain peel as loss circulation materials, thinning agents, defoamers, filtration control additives, flocculants and deflocculants, dispersants, viscosifiers/thickeners, emulsifier and pH control agents in drilling mud formulations. Publications showed that 20g of rice husk to 350ml of mud gave a decrease in fluid loss and the addition of rice husk to a drilling mud increased its density and viscosity. Soda lignin was also extracted from black liquor of oil palm empty fruit bunch (EFB) by 20%v/v sulphuric acid and used as dispersant in drilling mud. The utilization of agro-wastes will reduce cost of production, maximize profit, and create job opportunities for sustainable development.**

***Index Terms*— Oilfield Operations, Drilling fluid additives, Agro-wastes**

I. INTRODUCTION

Oilfield operation is the economic backbone of oil and gas producing nations globally. It comprises of drilling and production. Drilling is the major aspect of oilfield operation and entails the search of the hydrocarbon pay zone in an economic quantity. Twenty five (25%) percent of the oilfield exploitation cost is attributed to drilling whereas over 10% of this drilling cost is apportioned to drilling fluid/mud. Drilling mud is the mixture of drilling fluid with additives that are specially formulated to serve various functions for smooth successful drilling operations. These functions are transportation of the cuttings and caving to the surface, suspends the cuttings and caving when circulation stops, cools and lubricate the drilling bit and string, prevents formation damage, suspends the drilling string and casing, protects the drilling string and casing from corrosive, strengthens the walls of the well bore/supports the walls of the wellbore, transmit hydraulic energy, provides a medium for wireline logging, controls subsurface pressure/maintain hydrostatic pressure, seal permeable formations and inhibit gas hydrate formation. Most of the oilfield chemicals used to accomplish the above-mentioned functions are imported, expensive and toxic both to the environment and human health. Publications showed that agro-wastes can also function as drilling fluid additives [1, 2, 3, 4, 5 and 6]. Agro-wastes are abundant, inexpensive and bio-degradable, thus, non-toxic to the environment and human health.

Most developing nations generate so much agro-wastes. The semi-processing of various agricultural crops in Africa generates about 300 million tons of agro-wastes annually. For example, the quantity of maize cob, groundnut shell, rice husk and sugar cane bagasse generated annually in Africa is estimated to be over 12 million metric tons and Nigeria being the most populous nation in Africa generates over 3 million metric tons of these four agro-wastes as at 2001 [7]. Nigeria is one of the fastest growing economic in the world, it is the most densely populated in Africa and the 9th most densely populated in the world. Nigeria has the largest oil and gas reserve base in sub-Saharan Africa, the largest oil producer in Africa and the 12th largest in the world. Nigeria is the 8th world largest exporter of crude oil with a proven reserve of above 30 billion barrels of oil and 180Tscf of natural gas. This makes it the 10th largest proven reserve in the world. Its oil and gas industry accounts for 75% of government revenue and 95% of total export revenue. Nigeria is a country blessed with natural resources and its agricultural products are abundant, which include groundnuts, oil palm, cocoa, coconut, citrus fruit, maize, rice and sugar cane [8]. Over 60% of its populace are engaged in agriculture [9]. Despite all these, the rate of importation of goods into the country remains high which directly and indirectly affects the nation's economy and increases the level of poverty and unemployment.

Oil field chemicals are among imported items that drain our foreign reserve and thereby contribute to the poor state of Nigeria economy. It is time for the government and the stake holders to consider substantial development initiatives in Nigeria as a way forward towards achieving a better tomorrow. This paper appraises the utilization of agro-wastes in oilfield operations for sustainable development. This will lead to a greener environment, healthier people, reduction in waste management issues, job creation and the conversion of agro-wastes to wealth.

II. OILFIELD OPERATIONS

An oilfield is defined as a region of abundance of wells extracting crude oil and natural gas from the sub-surface. Its operation is expensive but highly rewarding. Nigeria, whose coast lies in the Gulf of Guinea, is richly endowed with oil and gas proven reserves. The natural gas reserves are three times the crude oil reserves, yet Nigeria losses $18.2M daily to gas flaring. According to the Ministry of Petroleum Resources, Nigeria has a total of 159 oilfield and 1481 wells. Seventy eight (78) of the one hundred and fifty-nine (159) oilfields are located in the coastal Niger Delta basin of South South,

Manuscript received Sep 21, 2016

Uzoho. C. U, World Bank African Centre of Excellence, Institute of Petroleum Studies, University of Port Harcourt, Rivers State, Nigeria.

Akaranta. O, Department of Pure and Industrial Chemistry, University of Port Harcourt, Rivers State, Nigeria.

Nigeria. Most of the oilfields are small and scattered, producing 2.3million barrels per day [10].

2.1. Drilling:

Drilling is the first step in oilfield exploration. It involves the drilling of deep borehole in the subsurface. This process is the most expensive practice in oil and gas industry. During drilling, challenges are encountered which are cushioned using drilling mud additives. Drilling mud additives are chemicals added to drilling mud to optimize operational conditions for a successful drilling operation. The use of drilling mud without additive will not give a satisfactory rheological properties needed for an optimum performance in drilling operations [11].

Drilling mud is the suspension of solids like clays, barite and small cuttings for drilling a wellbore. The term drilling mud and drilling fluid are used interchangeably in the industry. The drilling fluid is circulated from the surface via the mud pit, down the drill string, through the drill bit and back to the surface through the annulus [12]. Drilling fluids are thixotropic in nature, which aids their viscosity to increase during static condition. This enables the cuttings to suspend during shut-in period. Drilling fluids are carefully selected to avoid formation damage and corrosion problems. Its additives must be compatible with the drilling fluid for an excellent performance. The drilling fluids are classified based on its carrier fluid (base fluid), depth of interest and use.

Types of drilling fluid:

- Water-based mud (WBM) – In WBM, the carrier fluid is water. It represents the continuous phase and provides the initial viscosity needed to modify the desired rheological properties. It is composed of bentonite clay (gel) with barium sulphate (barite), calcium carbonate or hematite (Fe_2O_3) and additives. WBM also helps to suspend reactive colloidal solids (bentonite) and inert solids (barite). Clay used in WBM are montmorillonites (bentonite), kaolinites and illites. Thickeners or dispersants are used to increase or reduce viscosity in WBM respectively. Conventional thickeners are xanthan gum, guar gum, glycol, carboxymethyl cellulose (CMC), polyanionic cellulose (PAC) or starch while dispersants are clay-based muds, anionic polyelectrolytes (e.g. acrylates, polyphosphate, lignosulfonates or tannic acid). WBM are used in about 80% of all wells because they are inexpensive and non-toxic to aquatic organisms. Though they have their disadvantages, the major is still linked to the instability of the wells, mainly due to the interaction of clays with the formation water [11]. In WBM, the carrier fluid may be fresh water, sea water, brine, saturated brine, or formate brine. Drilling fluid based on formate brine had been suggested as being more environmentally friendly than traditional fluids. They are created by reacting formic acid with metal hydroxides. WBM are readily disposable on site and are not suitable for wells drilled in reactive shales, deep wells, horizontal and extended reached wells.
- Oil Based Mud (OBM) – OBM are selected when severe drilling problems are encountered. Such a problem could be a reliable shale inhibition, excellent lubricity, drilling a deviated well, High temperature High pressure (HTHP) formation, wash-out of cuttings produced during drilling process, drilling of water sensitive and water-soluble formation such as salt. Apart from these specific features difference of OBM, the additional difference between it and a WBM is that the required viscosity is attained by emulsification of water in the oil and the use of clay [12]. Its composition is suitable oil, water, asphalt, surfactants, emulsifiers, calcium hydroxide, weighting materials and other chemical additives. Organophilic bentonite is the primary viscosifier in most oil-based systems. Oil Based Muds are expensive and toxic to aquatic life.
- Synthetic based mud (SBM) – SBM was formulated to reduce the environmental impact of offshore drilling operations. This is achieved by reducing the toxicity of these chemicals by its chemical formulation. Its oil phase has been replaced by synthetic fluids such as ether, ester or linear alkyl benzene. It is more expensive than OBM but less toxic (and also reduces drilling waste volume and fastens biogradability in drilling waste).
- Air or Foam – This type is used when drilling fluid is not a desirable circulating medium. Foam drilling is gaining popularity now as it increases the rate of penetration when compared to a typical mud motor setup [13]. Drilling foam combined with bentonite and polymers creates the filter cake which helps to control zones of unconsolidated soils.

There are factors to consider when using any additives. These factors are the drilled hole size, compatibility of the drilling fluid with the additive, well depth, well depth in relation to the pay zone (zone of interest), drill bit nozzles and drill string [11]. Fundamental measures must be put into consideration when selecting a good drilling fluid. These control measures are as stated below:

1. Viscosity Control Agent – This control measure employ the use of viscosifiers and thinners. The viscosifier increases the viscosity, gel strength and yield point of the drilling fluid while the thinners reduce the viscosity, gel strength and yield point of the drilling fluid. Thinners are in two forms namely, the organic and inorganic thinners. Examples of an inorganic thinner are phosphates which are useful in most bentonite WBM at shallow depth of less than 130^oF. Organic thinners are lignites, tannins, and lignosulfonates. Lignites serve both as dispersants and fluid loss control agents due to their colloidal structure. They have thermal stability at 400^oF. Tannins are effective in thinning lime muds and cement contaminated mud while lignosulfonates, thermal stability ranges from 300^oF to 350^oF. Lignosulfonates and lignites are used to keep the mud in a fluid state.
2. Fluid Loss Control Agent – These are bentonite, starch (degrades at temperature above 200^o F), CMC

(Thermal stability up to 400°F), CYPAN (Thermal stability at 400°F), XC polymer and lignites and tannins (Thermal stability at 300 to 350°F).

3. Weighting Control Agent – They are fluid loss circulation materials like fibrous materials (used for seepage losses and in combination with other materials), flake materials (for seepage losses only) and slurries that develops strength over time.
4. Corrosion Control Agent – Because of the interaction between the acidic nature of some drilling fluids and the operating pH of some mud systems, it is necessary to introduce materials that will help maintain the pH of the mud system. This is important to inhibit corrosion on the drilling equipment. Conventional pH adjusters are caustic soda, potassium hydroxide, calcium hydroxide, sodium chloride, sodium carbonate and potassium carbonate.

Drilling fluids have various properties that help it function as designed. They are:

1. Viscosity – Is a measure of the fluids resistance to flow. It shows the thickness or thinness of the mud system. This property aids the removal of the cuttings from the well drilled. If the viscosity of the fluid is low, it could make the cuttings settle at the bottom of the well. This eventually leads to stuck pipe and lost circulation.
2. Gel Strength – This is a measure of the suspension properties of a drilling fluid. It enhances the cuttings suspension function of the mud.
3. Fluid Loss – The drilling mud is subjected to hydrostatic pressure which presses it against the walls of the wellbore. The liquid phase enters the formation as mud filtrate while the solid phase sticks on the walls of the wellbore as mud cake. This property enhances the wall bore stability and prevents the well drilled from collapsing.
4. Mud Density – It is the weight per unit volume of the drilling mud. It determines the hydrostatic pressure exerted by the drilling mud and determines the muds ability to control formation pressure.
5. Mud pH – Is a measure of the drilling muds hydrogen ion content. It balances the formation pH which aids the control of corrosion of drilling equipment. This is an important property because corrosion is a major challenge in oilfield and drilling operations.

2.2 Drilling fluid additives

- Bentonite – Bentonite is a naturally occurring clay mineral (montmorillonite) that forms a mud when mixed with water [12]. It is a non-Newtonian fluid and its application is universal, from a reactive to a non-reactive soil, consolidated or unconsolidated soils. It has high gel strength. It removes the cuttings from the wells and forms a filter cake on the walls of the wellbore. At higher temperature, the electrochemical charge of hydrate dispersion makes bentonite becomes unstable and it tends to flocculate and thickens [3].
- Barite – Is a weighting agent that is added to increase the drilling fluid density. It maintains hydrostatic pressure, thus preventing the influx of unwanted fluid from the formation into the wellbore and facilitates pulling. Other examples of weighting agents are calcium carbonate and Hematite (Fe_2O_3). Hematite is used as an excellent weighting additive for oil-based mud. Wells have also been drilled using ilmenite ($FeTiO_3$) instead of barite.
- Defoamers – Used to reduce foaming action particularly in brackish and saturated salt water drilling fluids [14, 15].
- Emulsifiers – helps create a homogeneous mixture of two insoluble liquids. e.g. Detergents, soaps, organic acid and water based surfactant for WBM and fatty acid and amine based chemicals for OBM.
- Filtration control additives – They are used to reduce fluid loss of a drilling fluid into permeable formations that might be under-pressurized [14] e.g. CMC (Non-toxic) reducing human hazards substantially, PHPA (Partially hydrolysed polyacrylamide, poly anionic cellulose (PACLV (low viscosity), PACHV (high viscosity)), Drilled Amyl, modified starch for WBM, Asphalt and bitumen for OBM. Mud filtrate and formation fluids form an emulsion reducing reservoir porosity.
- Flocculants – They are used to increase bentonite yield. It increases viscosity for improved hole cleaning, cause colloidal particles in suspension to group into clusters causing solids to settle out from the fluid at the surface [16]. It is also used to clarify or de-water low solids drilling fluids. E.g. Drill salt, potassium chloride, hydrated lime, calcium hydroxide, gypsum, calcium sulphate, soda ash, sodium carbonate, sodium bicarbonate, tetra sodium pyrophosate (TSPP) and polyacrylamide (polymers).
- Gelling agent and viscosifiers – Are used to increase viscosity for a better hole cleaning and suspension of solids. The viscosity at the bit affects penetration rate, so it better when the viscosity is lower but the mud has to be viscous enough in order to be able to lift the cuttings out through the annulus to the surface which must not also be too high in order to minimize friction pressure loss; e.g. Xanthan gum, guar gum, PACHV, glycol, CMC, and starch (for WBM) and organophilic bentonite for OBM.
- Loss circulation materials – Used to physically plug the zone in the formation that is losing drilling fluids e.g. Nut plug, mica, ultra seal, fibrous materials, cellophane, crushed walnut shell and graphitic materials.
- Lubricants and spotting agents – used to reduce the coefficient of friction in drilling fluid systems. To decrease torque and drag e.g. Drilling detergents, stuck free pipe oils, EP lube and biocides. Tiny glass or polymer beads can also be added to the drilling fluids to increase its lubricity.
- Thinning agents – It modifies the relationship between viscosity and percentage of solids in the drilling fluid. They are used to reduce gel strength, improve pumpablity of a drilling fluid. Most function as a deflocculant to prevent the flocculation of clay particles which produces high viscosity and increase in gel strength; e.g. Lignosulfonates and lignites.

- Demulsifier or emulsion breaker – used to separate emulsions. That is water in oil emulsion e.g. Polyols, polyamides, epoxy, resins. Methanol and isopropanol are demulsifier. They are usually ethoxylated (increase water solubility e.g. Ethylene oxide) or propoxylated (decreases water solubility e.g. Propylene oxide).
- Dispersants – Helps in breaking up solid clusters into smaller particles that can be easily carried by the drilling fluid without causing unnecessary obstruction. e.g. Iron lignosulfonates, lignitic additives and tannins. Dispersed system requires addition of caustic soda to maintain a pH of 10 to 11 [15].
- Deflocculants – Are used to reduce viscosity of clay-based muds. e.g. Tannic acid, Anionic poly-electrolytes (e.g., acrylates and polyphosphates), lignosulfonates derivatives as quebracho.
- Surfactants – These are substances like soap or fatty acids used to emulsify and defoam the drilling mud or fluid.
- Biocides – Used to inhibit and thwarf the growth of bacteria that could cause reservoir souring. e.g. Cholorophenols, formaldehydes or organic amines.

III. Agro-wastes

The word waste is most times mistaken to be useless materials, but this is not true. Waste is better defined as an un-used resource or a product looking for a market. They are usually by-product of agricultural or industrial processes.

Agro-waste is a term used for waste from agricultural processes. They could be grouped into crop, animal, lignocellulose and carbohydrate residues [17] which are obtained from organic sources such as corn, wheat, rice, sugarcane, fruits, vegetables, potatoes, coconut, oil and oil seed. There wastes are generated in abundance as a result of the processing of these organic sources [17, 18].

In Nigeria, over 3 million metric tons of wastes from rice husk, corn cob, groundnut shells and sugar cane bagasse are generated annually and about 50% of these wastes are potential low-cost sources of cellulose. It has been reported that cellulose yield of about 33% is realizable from these wastes. If full-scale commercial extraction of cellulose were to be embarked on a theoretical production of one million metric tons of cellulose will be produced annually [7].

Cellulose is the most abundance renewable and biodegradable polymer followed by starch [19]. It is the promising feed stock for the production of chemicals for industrial applications. The primary occurrence of cellulose is the existing lignocellulosic materials in forests (with wood as the important source). Other cellulosic materials include agricultural residue, water plant, grasses and other plant substances. Besides cellulose, they contain hemicellulose, lignin, and a comparably small amount of extractives [20].

Corn cob, rice husk, groundnut husk, peanut husk were used as sources of cellulose for the production of carboxymethylated cellulose (CMC) and related products [17]. Carboxymethylated cellulose, the sodium form, swells in cold water to give a highly viscous gel. Most of the waste products of the cellulose extraction process are solubilised lignins and degraded biomolecules which are bio-compatible and/or biodegradable in the environment [7].

Research had shown that agro-wastes such as oil palm empty fruit bunch, rice husk, walnut shell powder, coconut shell powder, groundnut husk, cassava mesocarp, orange mesocarp, corn cob, palm bunch ash, plantain peel ash, sugar cane bagasse, coconut coir can serve as good performance drilling fluid additives; most especially in Nigeria where these agro-wastes are in abundance constituting a form of nuisance everywhere; since there are no proper waste management programme laid out for its recycling. As a result of the toxic and non-degradable nature of petroleum based polymer, there arises the need to consider the use of non-conventional sources of cellulose biomass as a raw material for the production of cellulose and its derivatives. China, India and Malaysia are among the fore-front nations that through sustainable development initiatives have converted most of its waste to resourceful products of great economic significance. In India, industrial and agro-based products are converted as stated below in Table 1.

A large percentage of wastes generated in Nigeria are from agriculture [21]. Nigeria generates substantial volume of agricultural waste in all its ecological zones [22] and these wastes are vastly under-utilized. Agricultural waste can be classified as all forms of plant derived or animal derived materials that are considered useless either because they have no known positive economic importance or because they are not grown or raised for any specific purpose [23]. One of the ways of utilizing these agricultural wastes is in oilfield operations as drilling fluid additives.

Table 1
Agro-wastes to valuable products

Agro-wastes	Use
Coconut shell, saw dust, rice husk, cotton yarn, coir path	Activated carbon
Corn cob, peat, wheat husk	Bio-fertilizers
Cotton waste	Carpet
Rice husk	Cement
Coconut shell powder	Drilling additives
Groundnut shell, Bagasse, Saw dust, Palm husk, Soya beans husk, Rice husk, Wood chips, Coir pitch	Fuel briquettes
Vegetable Oil waste	Fatty acid
Rice hull/husk	Furfural
Crude oil bleaching	Petroleum jelly
Rice husk	Hard board
Sugar cane fibre (bagasse)	Kraft paper and hard board
Waste carton boxes	Kraft paper

Waste paper	Kraft paper
Rice husk, saw dust	Oxalic acid
Tea waste	Caffeine
Charcoal, saw dust, wood chips, peat or paper	Coal fuel briquettes
Agricultural cellulosic wastes	Bio-coal briquettes
Dried banana leaves	Fuel briquettes
Oil palm empty fruit fibre	Fibre mattress

IV. AGRO-WASTES UTILIZATION AS DRILLING FLUID ADDITIVES

4.1. Oil palm empty fruit bunch (Elaeis guineensis)

Oil palm is native to West Africa and of relative abundance in Southern Nigeria. Apart from palm oil production from the oil palm tree, its fronds, trunks and empty fruit bunches/fibres are all valuable and raw materials [24]. In Nigeria, oil palm is imported from Malaysia, the very country that got its first seedlings from her in the early 1970's [9] while in Malaysia; an estimate of 2.28 million ha of land is used for oil palm plantation which makes them account for 39% of World oil palm production and 44% of World exports [25]. Oil palm empty fruit bunch (ETB) is a by-product in oil palm mill and its disposal is a major challenge. It contains 45 to 50% cellulose, 25% hemicellulose and 35% lignin [24] and its shredded fibre has become a major source biomass media. About 18 million tons of ETB fibre was available as at 2010 and it is currently in higher demand as a new raw material for pulp and paper production. Publications showed that these fibres can be used as fluid loss materials in drilling operations. Loss circulation is one of the major challenges encountered during drilling operations. This occurs when drilling fluid flows into formation uncontrollably, which leads to loss of drilling fluid into formation until an efficient thick mud cake is formed on the walls of the well bore [11]. ETB fibres plug the drilling fluid from further entering the formation. This fibrous material promotes an excellent filter cake formation.

An environmentally friendly drilling mud thinner known as Fe-tannin-lignin (FTL) was successfully formulated from oil palm lignocellulose waste [3]. Thermal decomposition of lignin based mud additives above 121^{o}C was accomplished by copolymerization with acrylamide to produce poly-lignin acrylamide (PLA). This poly-lignin acrylamide had thermal stability of 190^{o}C. It is more tolerant than lignosulfonate towards salt contamination. At an optimum dosage of 0.3% total mud volume, PLA performed effectively as a thinner and also as an agent of controlling filtration loss than lignosulfonates. Lignin was also extracted from soda pulping process of oil palm ETB fibres and used as loss control materials (LCM). The EFB fibres were first soaked into water for two days to remove dirt before the pulping process. Then the fibres were pulped in a 20 L stainless steel rotary digester unit with 25% (w/w) NaOH (cooking liquor) for three hours at the maximum cooking temperature of 170^{o}C. The mixture of cooking liquor to the EFB fibre was in the ratio of 10:1. In this pulping process, the pH of black liquor was measured as 12.45 and its density was 1.02 g/ml. The soda lignin was then precipitated from the concentrated black liquor by acidifying it to pH 2 using 20% (v/v) sulphuric acid. The precipitated lignin was filtered and washed with pH 2 water, which was prepared using the same acid in the earlier step. The soda lignin was then dried in vacuum oven at 55^{o}C for 24 hours [26, 24]. It was also reported the effect of lignin purification on the performance of iron complex drilling mud thinner [3]. Here, soda lignin was extracted from black liquor of oil palm EFB fibres by 20%v/v sulphuric acid. The yield of lignin which is 3.016grams/200ml of black liquor was purified by n-pentane using soxhlet apparatus for six hours. The result showed that purification process was not required to increase performance of chelated ferrous ion drilling mud thinner. The rheological properties was compared with that of a commercial thinner, lignosulfonate (LS) and the lignin was reacted with ferrous ions to form ferrum-tannin-lignin (FTL). The purified and unpurified samples of lignin comprises of 0.345% and 5.75% ash respectively. The graft lignin depicts high potential in viscosifying and gelling abilities at high temperatures. It also performed well with fresh and saline drilling mud.

The polymerization of lignin as a raw material could produce a new compound. And lignin graft copolymer (LGC) can be used in oilfield operations to solve fluid loss problems. Experiment shows that the combination between water based drilling mud and lignin graft copolymer provides an optimum rheological performance and gelling effect for the water based drilling mud. The rheological performance of LGC shows that it gives good gelling, viscosity building and pH controlling abilities at low concentration of 0.5%w/w with a thermal stability at high temperature up to 200^{o}C [11]. Lignin is non-toxic, inexpensive with a potential of high value. It is available in large amount. There is a potential of using modified lignin as drilling mud additive in oilfield operations especially in high temperature and high pressure conditions. This combines its ability as a drilling mud viscosifying and gelling agent.

Oil palm empty fruit bunch fibre is a renewable biomass; it is non-toxic, abundant and cheap and has high lignocellulose content. The lignin recovered from it has high potentials as a raw material for value added products [26, 11]. Lignin graft copolymer was prepared by grafting itaconic acid onto soda lignin recovered oil palm empty fruit bunch via condensation polymerization.

An experiment [26] compared the filtration performance of LGC and a commercial fluid (Ressinex II). The result showed that LGC can be used as a fluid loss additive for drilling operations at temperature of about 190^{o}C. It also provides more tolerance to salt contamination at room temperature and high temperature. After extraction of lignin from soda black liquor, nitrobenzene oxidation was carried out by adding 50mg of dry ETB lignin into a mixture of 7ml of 2M NaOH and 4ml nitrobenzene in a15ml steel autoclave heated to 160^{o}C for 3h. A yield of 1.6% vanillin was isolated from 50mg lignin sample. This vanillin is used in the production of vanilla, a flavour used in most confectionaries, pharmaceuticals, and as fragrance in perfumes and odour-masking products.

Xylose is produced from EFB fibre using sulphuric acid. Xylose is a raw material for the production of xylitol, a high value product. Batch hydrolysis of ETB fibre at 120^{o}C with 2-6% sulphuric acid produced 29.4, 0.87 and 1.25g/l of xylose, glucose, furfural and acetic acid respectively. Palm fruit fibres are used for the production of furfural through acid hydrolysis and the furfural is a raw material for the production of phenol-furfural resins used to produce some plastic wares [17].

4.2 Rice husk (Oryza sativa)

Rice husk is the outer layer of the paddy grain, separated during the milling process from the rice grains. During milling of paddy, about 78% of weight is received as rice, broken rice and bran. The rest 22% is rice husk [18]. Rice bran contains about 15-25% oil that can be used for the production of vegetable oils and protein based animal feeds [17]. Rice husk is an agricultural waste abundantly available in rice producing nations. It contains 75% organic volatile matter and 25% of it is converted to ash. Rice husk ash (RHA) contains 85-90% amorphous silica and its moisture content ranges from 8.68 to 10.44% with its bulk density from 86 to 114kg/m3. It has a high ash content of 92-95% silica and it's highly porous and has a light weight. About 10^{8}tons of rice husks are generated annually in the world with an approximate of 120 million tons produced in India. It can be used to manufacture paper, activated carbon, particulate silica from its ash, cement, strawboard, mill board, extraction of ultra-pure silicon, sodium silicate, concrete fibre, insulating materials, particle board and fossil fuel substitute to generate electricity.

Nigeria is one of the producers of rice but still rice imports consumes half a trillion naira yearly [9]. Rice husk can be used as fluid loss control additive in water based mud. It has thermal stability and high resistance to water penetration. It is slightly acidic and its effectiveness as a drilling mud viscosity agent in oil based mud was investigated [15]. The mud density increased from 9.5 to 10ppg for an increment in weight from 5 to 25g. The apparent viscosity also increased from 55 to 115cp with same weight increment. Rice husk added to the drilling mud increased its densities, plastic viscosities and apparent viscosities. Hence, it can serve as a good viscosifying and weighting agent and filtration loss material in oil based mud. A research was done [15] on the evaluation of rice husk as FLC additive in WBM and its results compared with conventional FLC additive called sodium carboxymethyl cellulose (CMC) and polyanionic cellulose (PAC). 20g of rice/350ml of mud gave a decrease of 64.89% fluid loss compared to 62.77% CMC and 59.57% PAC at a content of 10g/350ml mud. This research showed that rice husk is a good substitute for CMC and PAC as fluid loss control additives. The filter cake thickness obtained were 3.2mm, 3.5mm and 3.3mm for rice husk, PAC, and CMC respectively.

Rice husk contains approximately 20% Opaline silica and phenyl propanoid structural polymer called lignin. The combination of silica and lignin makes rice husk high resistance to water penetration, thermal and fungal decomposition. In addition, rice husk particles are compressible at high pressure, thus preventing stuck pipe due to increased mud cake thickness during drilling operations.

4.3 Walnut shell (Juglans spp.)

Walnut shells are non-toxic, biodegradable agro-waste materials that are used as loss circulation material [14]. It does not alter the drilling fluid consistency and is compatible with both WBM and OBM. They are used for control of filtration loss circulation in drilling muds, water remediation, exfoliation in cosmetics, dynamite, anti-slip additives and as plywood. The larger the size of crushed walnut shells the better its use to minimize fluid-loss by sealing perforations [22]. This helps to create a secure and less permeable well environment [23]. Walnut shells are also used to reduce cement density. The walnut shells of 2mm, 4mm and 6mm samples and their equal weight mixture of 2-4mm and 4-6mm were added to the drilling fluid samples in different concentration. It was observed that the polymer has the optimum effects on the water based mud. The optimum concentration of polymer with 6mm walnut shell was determined as 0.4g/350ml [24].

4.4 Groundnut husk (Arachis hypogaea)

The base materials for the production of CMC are agricultural waste e.g. Groundnut husk, rice straw/husk, sugar cane waste (bagasse), saw dust, orange mesocarp, cotton stables and weeds (Eichoria crassipes). The etherification of cellulose through methylation, carboxymethylation, cynaothylation, hydroxy propylation, single or mixed is among the most important routes of cellulose formulation [19]. Various concentration of cellulose was processed from groundnut husk and the result was compared with PAC. The rheological properties determined showed that pH, mud density, specific gravity of the mud formulated from groundnut husk cellulose was higher than that of PAC. Better result was achieved with higher concentration. 2g groundnut husk cellulose had a fluid loss of 7.6mls as against 4g groundnut husk cellulose with a fluid loss of 6.5mls. This shows that groundnut husk is a better fluid loss control agent than PAC in drilling mud formulation.

4.5 Cassava mesocarp (Manihot esculenta) and orange mesocarp (Citrus sinensis)

Cellulose isolated from orange mesocarp has been carboxymethylated to a degree of substitution of 0.45-0.63 and used in the formulation of drilling mud [17]. The cellulose reacts with monochlooroacetic acid and caustic soda (NaOH) to form sodium carboxymethyl cellulose, sodium chloride and water. Carboxymethyl Cassava Mesocarp (CMCM) is also used as a thickener in water based mud to influence viscosity of the fluid. Cassava mesocarp is also used for preparation of activated carbon used as adsorbents for dyes and metal ions [25].

4.6 Corn cob (Zea mays) and sugar cane bagasse (Saccharum officinarum)

Corn cob is a major agro-waste in most West Africa nations. The most important characteristic of corn cob is its absorbency. It has the capacity to hold up to four times it weight in fluid. Corn cobs are excellent carriers for vitamins and antibiotics in animal feed or as carriers for herbicides and pesticides in lawn care products. An evaluation of the use of corn cob cellulose as drilling mud formulation was carried out. The results showed that corncob is an effective drilling fluid additive used as fluid loss control agent. The water loss analysis showed that the drilling fluid formulated from corn cob had a lower fluid loss of between 5.2 to 5.8mls as compared to 6.6mls for PAC. The mud density was higher than that of standard mud by 27% and the rheological properties of the prepared mud were lower than that of the standard by 50%. This showed that corn cob can suitably replace PAC and it's cheap, available and environmentally friendly [26].

Corn cob and sugar cane bagasse are used as viscosifiers in drilling fluid. A publication reported [27] that plastic viscosity and yield point have direct relationship with the amount of materials added. As the amount of corn cob and sugar cane bagasse increased; the density, plastic and viscosity and yield point of mud increased also. From their analysis, the optimal quantity of corn cob and sugar cane bagasse obtained was 6.45lb/bbl and 9.43lb/bbl respectively. This showed that the addition of corn cob and sugar cane waste was able to improve the rheological properties of the hydrocarbon drilling fluid.

4.7 Palm bunch ash (Elaeis guineensis), plantain peel ash (Musa sapientum) and banana peel ash (Musa paradisiaca)

Oil palm empty fruit bunch ash contains high silicon dioxide (SiO_2), which can be used to reduce cement density. A report showed [16] that cement losses into formation could lead to zonal isolation problem. This may happen in weak formation when equivalent circulation density (ECD) of the cement exceeded formation pressure. Low density cement helps to avoid cement losses thus providing complete zonal isolation. An experiment was carried out on the use of indigenous material like palm bunch ash and plantain peels (ripe and unripe) as corrosion inhibitors [28]. The result indicates that these indigenous materials can maintain the pH values of a typical water based drilling system. The results were further compared with that of conventional NaOH and KOH; the indigenous materials had similar alkaline properties on WBM as the conventional ones.

Banana peel ash and plantain peel ash contain oxides of potassium and sodium which when dissolved in water forms its hydroxides. They also contain poly phenols, carotenoids and other bio-active compounds that are beneficial to human health. The peels of banana and plantain were burnt to ash in a furnace, grinded and sieved with mesh sieve of 205 microns size. These local materials when added to the mud were able to increase its pH value from 8 to 12 and from 8 to 13 for banana peel ash and plantain peel ash respectively. These indicate that these local materials can serve as pH adjusters to control the danger of corrosion on down-hole equipment.

4.8 Coconut husk/coir (Cocos nucifera)

When drilled hole penetrates a fracture, the drilling fluid may be lost completely in worse cases to the fracture which might lead to the loss of the well. Coconut coir (a mixture of short fibres, flakes, granular pieces and powder from coconut husk) has been used as loss circulation material (LCM) in drilling fluid to prevent loss of drilling fluid into fractures of rock formation. It can also serve as an emulsifier. 75-25% concentration of oil-water ratio was stable for a 5% emulsifier and the adsorption of oil was better at smaller particle size of 630µm unmodified coir as compared to larger sizes of above 630µm to 2mm [29].

CONCLUSION

Agro-wastes have great potentials for use as drilling fluid additives. They can efficiently and effectively substitute convention drilling fluid additives especially those used as thinners, viscosifiers, gelling agents, pH adjusters, loss circulation materials and deflocculants. Developing countries like Nigeria should consider the use of these agro-wastes for sustainable development.

REFERENCES

1. Lim Say Liang and Mohamad Nasir Mohamad Ibrahim, Preparation of Lignin Graft Copolymer as a Fluid Loss Additive for Water-Based Mud. Journal of Engineering Science, Vol. 9 (2013) 39–49.
2. Mohamad Azir Syazwan Bin Sufri, Mohamad Azir, *Study on Rice Husk as Lost Circulation Material,* Universiti Teknologi Petronas, (Unpublished) 2012.
3. Mohamad Ibrahim M. N., Azian H. and Mohd Yusop M. R., The Effects of Lignin Purification On The Performance Of Iron Complex Drilling Mud Thinner, Jurnal Teknologi, 44(F) (2006) 83–94
4. Adebowale,A.O.J. and Jamiudeen Kayode Raji, Local Content Suplements as an Alternative to Imported Corrosion Control Additives for Drilling Mud Treatment (A Case Study of the Use of Burnt Plantain and Banana Peels), Proceedings of the International Academic Conference for Sub-Sahara African Transformation and Development, University Of Ilorin, Ilorin, Kwara State, Nigeria, Vol. 3 (Issue 4) (2015).
5. Iscan A. G. and Kok M. V., Effects of Walnut Shells on the Rheological Properties of Water Based Mud in Drilling Fluids, Energy Sources, Part A, Vol. 29 (2007).
6. Adebayo, Thomas Ayotunde Chinonyere and Precious C., Sawdust as a Filteration Control and Density Additives in Water-Based Drilling Mud, International Journal of Scientific and Engineering Research Vol. 3 (Issue 7) (2012).
7. Okhamafe Augustine O. Inaugural Lecture, From Rubbish To Riches, Trash To Treasure, (Series 66) 2006.
8. Addax Petroleum Report (Nigeria).
9. Falaye, A. E., Utilization of Agro-Industrial Wastes as Fish Feedstuffs in Nigeria, 10th Annual Conference of the Fisheries Society of Nigeria (Fison), Vol. 10 (1993) 47-57.
10. Environmental Resources Managers Limited (ERML) Niger Delta Environmental Survey Final Report Phase 1; Vol. 1: Environmental and Socio-Economic Characteristics (Lagos: Niger Delta Environmental Survey, September 1997).
11. Mohamed Khodja, Malika Khodja-Saber, Jean Paul Canselier, Nathalie Cohaut and Faïza Bergaya, Drilling Fluid Technology: Performances and Environmental Considerations, 2013.
12. Nabel A. Negm, Salah M. Tawfik, and Mahmoud I. Abdou, Evaluation of Nonionic Surfactants in Drilling Muds, 2014.
13. Trenchless Technology, Bentonite Drilling Fluids vs. Foams (Surfactants/Soap), 2011.
14. Rasheed Performance Minerals: Drilling Fluid Additives.

15. Anietie N. Okon, Francis D. Udoh, Perpetual G. Bassey , Evaluation of Rice Husk as Fluid Loss, Society of Petroleum Engineers Journal, 2014.
16. Wan Zairani Wan Bakar, Arina Sauki, The Effect of Ash from Oil Palm Empty Fruit Bunch to Cement Properties, Engineers Australia, (2014) 1628
17. Akaranta Onyewuchi Inaugural Lecture, Agro-Wastes Utilization – The Chemist Input, (No. 55) 2007.
18. NIIR Project Consultancy Services, Rice Husk, Rice Hull, Rice Husk Ash (Agricultural Waste) Based Projects, (An ISO 9001: 2008 Company).
19. Varshney V. K. and Sanjay Naithani, Chemical Functionalization of Cellulose Derived from Non-Conventional Sources, Chapter 2, 2011.
20. Dagde, Kenneth Kekpugile and Nmegbu, Chukwuma Godwin Jacob, Drilling Fluid Formulation using Cellulose Generated from Groundnut Husk, Scirespub, Ijoart, 2014.
21. Edewor-Kuponiyi Theresa I. and Omotayo Amuda S., Evaluation of Production of Oxalic Acid from Some Solid Industrial Wastes in Nigeria, International Journal of Basic and Applied Science, Insan Akademika Publications.
22. Civil and Environmental Research, Agricultural Waste Pulping in Nigeria – Prospects and Challenges, Vol. 6 (No. 10) 2014.
23. Adeyi, Oladayo, Proximate Composition of Some Agricultural Wastes in Nigeria and Their Potential Use in Activated Carbon Production, Journal of Applied Sciences and Environmental Management,Vol. 14 (No. 1) 2010.
24. Mohamad Nasir Mohamad Ibrahim, Mohamad Yusof Nor Nadiah, Mohd Salleh Norliyana,Coswald Stephen Sipaut, Sollehuddin Shuib, Pulau Pinang, Separation of Vanillin from Oil Palm Empty Fruit Bunch Lignin, Clean 2008, 36 (3) (2008) 287 – 291.
25. Lim Say Liang and Mohamad Nasir Mohamad Ibrahim, Preparation of Lignin Graft Copolymer as a Fluid Loss Additive for Water-Based Mud. Journal of Engineering Science, Vol. 9 (2013) 39–49.
26. Nmegbu, Chukwuma Godwin Jacob and Bekee Bari-Agara, Evaluation of Corn Cob Cellulose and its Suitability for Drilling Mud Formulation, Int. Journal of Engineering Research and Applications Vol. 4, Issue 5(Version 7) (2014) 112-117.
27. Sonny Irawan, Sonny and Ismail B. Saaid, Ismail, Corncob and Sugar Cane Waste as a Viscosifier in Drilling Fluid, Pertanika Journal Science and Technology, Vol.17 (1) (2009) 173-181.
28. Oriji A. Boniface and Boma Kinigoma, Performance of Indegeneous Materials as pH Control Agents to Minimise Corrosion Caused by Water Based Mud to Drilling Equipment, Cenresin Publications, Journal of Sciences and Multidisciplinary Research, Vol. 3, 2011.
29. Aimuni Izzati Binti Mohammad Yatim, Separation of Oil and Water by Using Coconut Coir. Universiti Malaysia Pahang, Faculty of Chemical and Natural Resources Engineering, 2012.