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Laboratory Investigation of Esters from Beef Oil for the Synthetic Based Mud

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Key Words
SBM -synthetic based mud, OBM – oil-based mud, WBM – water-based mud, M-Bio-M – mud formulated with ester from methanol, M-Bio-E – mud formulated with ester from ethanol, M-Diesel – mud formulated using conventional diesel. LTLP – Low Temperature Low Pressure HTHP – High Temperature High Pressure.

ABSTRACT

87% oil yield was obtained from beef fat after rendering and the oil was characterised. Transesterification was carried out after esterification between alcohols (methanol and ethanol) and from beef oil. The ester yields were 60% and 65% for the ratios of 1:6 and 1:9 respectively using methanol and were 63% and 70% for the ratios of 1:6 and 1:9 respectively using ethanol. These esters were characterised and used to formulated synthetic-based muds, SBM. These SBMs were compared with oil-based mud formulated with the conventional diesel. The pH of each mud was 8.0, 9.5 and 9.0 for M-Bio-M, M-Bio-E and M-Diesel respectively. The rheological properties reveal that M-Bio-M performed best followed by M-Bio-E and lastly by M-Diesel. The filtration test shows that all of them fell within range as none showed the tendency of causing undesirable filter cake on the wall of the well.

Introduction

Rotary system of drilling is a common drilling technique and requires the use of drilling fluids. Drilling fluid is a composite fluid which is circulated through a well for the ease of cuttings' generation and evacuation from the wellbore to surface. The term fluid is interchangeable with mud although fluid is preferred when the base is air. There are several functions of the drilling fluid and these have been discussed by (Queensland, 2013), (Onungwe, 2015 and 2022), among others. The performance of the drilling mud is dependent on the type of formation being drilled and the various properties of the drilling fluid. IADC Drilling Manual (2014) states that the selection and design of a particular drilling fluid and its properties depends on the complexity of the well being drilled, subsurface pressures and temperatures, logistics, cost and local experience. Drilling fluid is affected by the drilling equipment being used and the skills of the personnel using it.

Purpose of drilling

Drilling is the act of making a hole (Onungwe, 2015). The purpose of drilling may be for (i.) extraction of natural resources such as ground water, brine, natural gas and petroleum (ii.) the injection of fluids from the surface to the subsurface reservoir (iii.) subsurface exploration, formation valuation and monitoring and (vi.) mining and construction.

How to drill

During drilling, the drilling fluid is pumped from the mud tank down the hollow drill pipe and through nozzles in the drill bit. The flowing mud sweeps the crushed rock cuttings from beneath the bit and carries them back up the annular space between the drill pipe and the borehole or casing to the surface. The mud is then passed through solids control equipment (an integrated system of shale shakers screens and hydroclones) to remove the cuttings. It is circulated back to the mud tanks where the cycle is repeated.

Why was synthetic based mud formulated?

There are different types of fluid. Each was developed as a solution to an identified problem at a particular point in time (Onungwe, 2015). The cable may not need the drilling fluid however; the rotary system cannot operate efficiently without the fluid as it needs the fluid to carry and suspend cuttings and lubricate the bit and drillstring. Hence, water-base mud (WBM) was formulated to meet these needs. Advances in drilling later discovered that WBM was unsuitable for (a.) highly deviated wells, (b.) high temperature and cold temperatures (c.) swelling clays and therefore, the oil-base mud (OBM) was built to meet these challenges. The setback of the OBM is that the cuttings and mud disposal as OBM rarely degrade and constitutes a threat to the ecology. Therefore, direct discharge (without treatment) of the OBM into the environment is highly prohibited. To forestall sanctions from the government and host communities, drilling companies were compelled to spend their fortunes to treat these fluids. This also affects the overall profit by the companies.
The synthetic base mud (SBM) promises to tackle this problem. Studies reveal that SBM has the capacity of surpassing or rather equaling the operational performance of OBM while maintaining its environmental friendliness. This is because SBM is not only biodegradable but also, possesses low toxicity when compared to the conventional OBM (diesel and mineral oil or non-vegetable oil).

1.2 Synthesis and Synthetic Base Muds (SBMs)

The Longman dictionary of contemporary English defines the term synthesis as the act of making chemical or biological substance by the combination of different things.
SBM is a relatively, new class of drilling mud that is particularly, useful for deep-water and deviated hole drilling. They were developed to combine the technical advantages of OBM with the low persistence and toxicity of WBM. In WBM, the continuous liquid phase is a well characterised synthetic organic compound. A salt/brine usually is dispersed in the synthetic phase to form an emulsion. The other ingredients of an SBM and include emulsifiers, barite, clay, lignite, and lime. SBM contains the same metals as WBM. All are tightly complexed with the barite and clay fractions of the mud and have a low bioavailability and toxicity.

SBM is a subcategory of the OBM. In contrast to diesel and mineral oils which are refined from crude, synthetic fluids are all made from organic compound (Growcock and Federick, 1996). Though they act like petro-luem-derived oils with respect to drilling but biodegrade readily. By design, they contain none of the myriad of products found in refined oils such as aromatics, naphthenics and thiophenics. Typically, they possess similar average molecular weights to low-toxicity mineral oils (LTMO) but have much narrower molecular weight distributions (carbon chain lengths generally range from C_{14} to C_{22}).

The main challenge with oil-based fluids in conventional OBM is that the based fluid being of fossil product such as diesel and mineral oil tend to persist for many years in marine environment. In the past, cuttings generated in offshore drilling operations were discarded into the ocean and these settle to form pile. Seabed surveys revealed that oily residue on cuttings generated from OBM degrades infinitesimally. Plants and animals' life beneath the cuttings pile would suffocate. Perhaps even worse, ocean life in the vicinity of the pile suffers a similar fate because of slow aerobic biodegradation process that the oil undergoes depletes the surrounding water of oxygen for many years.

Today, oily cuttings generated offshore are disposed of by (a.) shipping them to shore and discarding or treating them there with other wastes, (b.) downhole injection (down the annulus or into another well) or (c.) cleaning them on the site via solvent extraction or distillation.
All of these options are expensive. An alternative is to find a drilling fluid that performs as much as the conventional OBM but can be discarded into the ocean without causing harm to workers and damage to the environment. SBM has that potential. Operationally, SBM performs as much as conventional OBM. Although, SBM is environmentally friendly, it is rather expensive than OBM. However, if thoroughly formulated and properly handled, it pays off on the long run.

1.3 Oils for Biodiesel Synthesis

Oils are the main resources for the world biodiesel production and biodiesel is often used as the based fluid for SBM. Oils for SBM can be obtained from (1.) Vegetable sources (edible and non-edible), (2.) animal fat, (3.) waste cooking oils – used oil materials including food and contaminated oils and (4.) algae.

Esters are organic compounds made by replacing the hydrogen of an acid by an alkyl or other organic group. Many naturally occurring fats and essential oils are esters of fatty acids. Ester is a product of the reaction between oil with alcohol and usually, glycerol is the by-product. This ester is called synthetic fluid having resulted from the reaction of oil and alcohol and speeded by catalyst.

Biodiesel is a mixture of fatty acid alky ester (FAAEs) most often methyl or ethyl (FAMEs and FAEEs) respectively, obtained by the alcoholysis of triacylglycerols (TAGs) from vegetable oils and animal fats or more precisely alcoholysis with an alcohol (methanol or ethanol). Triacylglycerols or simply triglycerols are major constituents of lipid (fats and oils). Lipids are made up of building blocks called triglycerides which results from the combination of one unit of glycerols and three units of fatty acid. The triglyceride molecule is the major component of oils even though monoglycerides and diglycerides may be or are present as minor components (Prah, 2010).

Techniques for biodiesel synthesis

There are different techniques for biodiesel synthesis and this includes **pyrolysis** – thermal degradation in the absence of oxygen such that gasification does not occur to an appreciable extent. The process has been abandoned due to viscosities of pyrolysed oils were considered too high, **micro-emulsion** – which is a heterogenous mixture of immiscible liquids dispersed in each other. These can be achieved by mixing oil and alcohol until homogenous however, the diesel from this may not serve well in diesel engines as it results in incomplete combustion and formation of carbon deposits akin to the use of neat oil and **transesterification –** the OH group in the alcohol is removed making the alcohol an alkyl group and the H in the OH in the fatty acid is removed from the fatty acid together with the OH from the alcohol to form water.
Thus, the alkyl group combines with the fatty acid less of a hydrogen atom to form its alkyl-acid compound. It is a condensation reaction, and heat is given out in the process, making it an exothermic reaction. However, the heating of the reactants is to set it to temperature of reaction. This paper focuses on transesterification which is the most widely accepted method of biodiesel production.

Transesterification is the process of exchanging the organic alkyl group of an ester with the organic alkyl group of an alcohol. This reaction his reversible and requires the use of catalyst. The result of this is the modification of vegetable oils viscosity from high to acceptable range comparable to mineral diesel suitable as a substitute for diesel (Prah, 2010). Apart from viscosity, the free fatty acid and water content need to be put in check.

Factors that affect trans-esterification reaction in the course of producing good esters yield are:

1. The molar ratio of the alcohol and oil.

2. Type of alcohol
3. Type and amount of catalyst
4. Reaction temperature
5. Pressure
6. Time
7. Mixing intensity
8. Free fatty acid – FFA content and
9. Water in oils

The presence of water in the feedstock during transesterification deactivates the catalyst and the presence of FFA in the feedstock consumes more catalyst and ultimately affects the biodiesel yield and the cost of production. Dehydration of the feedstock is achieved by passing nitrogen through the oil while FFA can be reduced by esterification with the use of an acid catalyst. The alcohol and the catalyst also have to meet specifications. Water content should not be more than 0.3 wt% as it promotes hydrolysis of alkyl esters to FFA and soap formation (Ding *et al.*, 2011).

1.4 Statement of the Problem

Oil based mud and water-based mud have been found to be non-degradable and or toxic in composition. Synthetic based mud is a substitute to these muds because it is environmentally friendly and operationally efficient. Synthetic based mud formulated with esters are organic in nature meaning, they are degradable and less toxic. Esters from beef oil have not been utilized to formulate synthetic based mud despite their potentials and availability. Beef oil is not classified as food due to its high cholesterol content and this makes it cheap. The need to utilise it for synthetic based mud formulation rather than discarding it is the focus of this study.

1.5 Properties of SBMs

Though SBMs and OBMs share common properties in performance in the field, the distinct chemical composition of the SBMs does not eliminate certain differences in their behaviour. Growcock in 1996 identified some special properties of the SBMs as:

Environmental Effect – SBMs appear to be less toxic to aquatic life, easier to handle and more biodegradable aerobically than LTMOs and LTMO base muds.

Rheological and Thermal Stability – At ambient temperature, SBM are 2 – 4 times more viscous than LTMOs: 3 – 5 cP versus 1 – 2 cP. Likewise, at ambient temperature, SBMs are several folds more viscous than OBMs. However, the viscosity of synthetics is affected by temperature more strongly. Growcock *et al.* (1994) noted that SBMs thin with increasing temperature to a greater extent than does an LTMO base mud. The strong effect that temperature has on the rheology of synthetics raises the question of whether it is possible to formulate high temperature SBM's that have satisfactory carrying capacity at elevated temperatures, yet are pumpable at low temperatures. However, one must address the issue of the effect of temperature on emulsion stability. SBMs have been limited to lower temperatures (250-350˚F) or (121.11 – 176.67°C) than conventional OBMs (400-500˚F) or (204.44 – 260°C). The reason(s) for this have not been clear; apparently arise from the chemical composition of SBMs. To determine which constituents are responsible for low thermal stability of these muds, chemical degradation experiments were conducted. First, the synthetic fluids themselves were tested: these were heated to 425˚F (218.33°C) for 16 hours under ultra-pure argon in a Teflon-lined stainless steel rolling cell. The result showed that synthetic fluids are themselves stable at least at 425˚F(218.33°C). Of all the other constituents present in SBMs, emulsifiers (surfactants) and low shear rheology modifiers (oligomers of fatty acid emulsifiers are probably most susceptible to thermal degradation. Differential Scanning Calorimetry (DSC) test also conducted on 10 emulsifiers show that the limiting factor for thermal stability for SBMs is probably the emulsifiers. To measure emulsion stability of muds, high temperature and high pressure, HTHP fluid loss is required. Generally, a mud is considered to have high emulsion stability if it has low HTHP fluid loss <15 cc/30 min and little or no free water.

Shale Dehydration Potential – SBMs do not hydrate or dehydrate shale just like conventional OBMs but, water transport can be increased by adjusting the emulsifier package.

Material Compatibility – ether and aliphatic hydrocarbons appear to be similar to LTMOs with regards to elastomers but a more limited

choice of elastomers is available for use with ester and LAB.

Lubricity – Synthetic fluids themselves are good lubricating agent and can improve lubricity of WBMs.

1.7: Advantages of SBMs

1. OBM and SBM have similar performance hence would generate similar volume of waste material. However, synthetic fluid has no aromatic as compared to 30-60% and less than 0.2% for diesel oil and mineral oil respectively. This characteristic makes SBM to be highly environmentally friendly and could be discharged directly into the environment. This does not apply to OBM and some WBMs. Since OBMs are by regulation required to be hauled to shore for discharge, the possibility of toxic organics in diesel and mineral oil base muds leaching into the drinking water supply from landfills poses a long-term potential threat to the environment.

2. Having no contaminated cuttings from diesel OBM eliminates the possibility of future environmental impacts associated with onshore disposal. The EPA (2021) listed numerous priority pollutants and toxic organics in diesel oil. These pollutants were identified after the combustion of this fuel and they are: (1) soot or particulate matter (PM), (2) Oxide of Nitrogen (NOx) which contributes to the production of ground level ozone (smog) and acid rain, (3) Hydrocarbons (HC) and other Hazardous Air Pollutants and air toxics (HAPs) Candler *et al.* (1993) state that these savings by not using diesel can be quantified by multiplying the concentrations of toxic pollutants found in diesel by the volume of material generated from the rig.

3. SBM has been identified to possess the following drilling performance: 1.) increased rate of penetration; 2.) fewer wiper trips; and 3.) a decrease in unscheduled events, such as stuck pipe. This in turn translated into fewer rig days and thus economic saving in rig time alone.

4. Reduction in air pollution from not hauling cuttings is another significant non-water quality issue discussed in EPA development document as a basis for the utilization of SBM. This is because SBM as earlier mentioned can be discharged directly into the environment.

5. Synthetic fluids have higher flash points than diesel and mineral oil reducing the possibility of fire or explosion on the rig.

6. Increased hours of crane use, forced loading under rough seas, large numbers of boxes loaded on each boat, and the size and weight of cuttings boxes all contribute to making loading and hauling of cuttings dangerous. Discharging cuttings instead of hauling cuttings will prevent accidents associated with handling cutting boxes. This is possible with SBM.

7. SBMs are safer for worker health because they do not produce toxic fumes in the mud pit room or the shaker area. Living and working in an environment where OBM is used exposes worker to vapours which may have adverse effects on their health. Some mineral and diesel oils are known carcinogens and have strict personal exposure limits. SBM can be safer to work around.

8. The use of SBM eliminates the possibility of spilling OBM to and from rig. It also, eliminates the possibility of spillage of OBM and cuttings during transportation to a landfill.

1.8: Limitations and Optimization of the SBMs

1. (Candler *et al.*, 1993) put the cost of SBMs at 4 – 5 times higher than OBMs while (Growcock, 1996) rate them at about 3 – 5 times that of OBMs. However, this could be more; high cost of SBM is occasioned by high cost of synthetic which is its based fluid however, overall cost is lowered as a result of fewer drillings days.

2. It has been realized in the North Sea that although conventional OBM provides the same benefits, further mud management of SBM by optimising surface solids-control equipment and general fluids handling would result in substantial savings and reduced waste volumes. This will make the SBM available for proper reuse. Implementation of similar programmes in the Gulf of Mexico led to similar cost savings and ecological benefits.

3. The loss of SBM for example, by the means of lost circulation, is highly detrimental to the economics of drilling operations than is to an LTMO and is prudent to avoid the use of SBM where high losses are expected.

4. Growcock (1996) highlighted the need to maximize the concentration of water or brine in SBM because it lowers the cost of the mud and decreases the amount of the synthetic-fluid left on drill cuttings.

5. Despite the fact that the synthetic fluids have higher viscosity than oils in conventional OBM at ambient temperatures, they thin rapidly with increasing temperature.

6. Synthetic fluids are stable to about 425˚F (218.33˚C). It has been observed that their temperature limits are not imposed by the synthetic fluids themselves but rather the other components especially, the emulsifier as they may not tolerate high temperatures. In fact, most of the emulsifiers chemically begin to degrade at 65-148.89˚C. Field muds of the same composition are expected to have higher emulsion stability and carrying capacity than laboratory muds because the stabilizing effects of the added solids and circulation of the mud through the bit. Consequently, in the field, it may be possible to extend the temperature of the SBM further. To possess

acceptable properties, laboratory prepared SBM needs to be formulated with (1.) concentrations of conventional emulsifiers that are considerably higher than – 14 to 24 lbm/bbl or (2.) emulsifier that are more resistant to thermal degradation.
7. Gas solubility makes detection more difficult and critical than water-based mud. Oil contamination in SBM system makes the mud unacceptable as SBM. Addition of synthetic-based.

1.9: The choice of Ester

In today's market, concerns about toxicity, biodegradation rates, environmental impacts and cost have essentially eliminated all synthetic-based fluids except olefins or alkynes and esters from use in offshore drilling. Olefins are less costly than esters, more stable at higher temperatures, less viscous at low temperature and more adaptable to deep water drilling environment. Olefins are preferred usually if only drilling properties are considered. However, esters are much more biodegradable than olefins, giving the impression that they are more environmentally compatible than olefins Neff *et al.* (2000).

2.0: Biodegradability

The desire of any responsible drilling engineer or supervisor is to safely carry out his drilling operations at minimum cost without compromising on the environment. This is why before drilling activity is done; the Environmental Impact Assessment, EIA and of course, Job Hazard Analysis, JHA for the entire operation should be carried out. Indeed, it is inevitable that economic, social or political factors will outweigh environmental factors in many instances however, if one cannot improve on the environment after an operation, then he is morally bound to leave it as he met it. Again, this may be difficult to achieve and therefore it becomes necessary to put in place systematic mitigation programme as a minimum requirement. This must meet set standards to avoid litigations and sanctions from host communities and regulatory bodies. One of the mitigation programmes apart from the avoidance of drilling fluids spillage, wrong disposal, and treatment before disposal is to design the drilling mud such that it can be biodegradable.

Biodegradation has been defined by Glossary of Environment Statistics (1997) as the process by which organic substances are decomposed by micro-organisms (mainly aerobic bacteria) into simpler substances such as carbon dioxide, water and ammonia. (Sardrood *et al.,* 2013) have defined biodegradation as an aspect of bioremediation which they also defined as the use of life to solve problem. This biological technique involves the decontamination of the environment through the use of microorganisms such as bacteria and fungi to act on the contaminant. Drilling fluid is not natural substance as it is a product of the mixture of different components. When this is biodegradable, it makes it easier to restore the impact environment naturally with minimum aid. A substance in this case, a drilling fluid can be set to be biodegradable when they degrade on exposure to microbes be it naturally or artificially. This is observed when microbes on exposure to contaminants such as a drilling fluid increase in numbers and when the contaminants are degraded, the biodegradative population declines. This can be likened to a parabolic curve. (Sardrood *et al.,* 2013) say that the residues for the treatment are usually harmless products and include carbon dioxide, water and cell biomass. Another method of testing for biodegradation is the examination of a sample for an increase in torpidity. When this is positive, it means biodegradation is taking place and the reverse means it is not taking place.

Microbial degradation of pollutants or contaminants is a sustainable way to recover or clean up a contaminated area. This is achievable because microorganisms have enzyme systems to degrade and utilize different hydrocarbon as a source of carbon and energy (Nrior and Inweregbu, 2019). They noted that microorganisms are capable of converting these poisons into harmless products by mineralization, generation of CO_2 and water or by conversion into microbial biomass by exploiting its diverse metabolic abilities known as bioremediation. The use of bioremediation technique is cheap compared to chemical and mechanical methods.

Several bacteria have been identified for feeding exclusively on hydrocarbons thus degrading drilling mud wastes and spills. *Pseudomonas aeruginos*, Aeromonas *hydrophila*, *Alcaligenes xylosoxidans*, *Gordonia* sp., *Pseudomonas_fluorescens*, *Pseudomonas_putida*, *Rhodococcus equi*, *S. maltophilia*, and *Xanthomonas* sp. have been found to be useful according to Xu *et al.,* (2018). Ogbonna *et al.,* (2020) recently carried out a study on bioremediation of drilling fluid in a marine environment and confirmed that *Pseudomonas, Bacillus, Micrococcus and Enterobacter* were useful *with Pseudomonas having the very best frequency of 35.7%, followed by Bacillus with the frequency of 30.7%, Micrococcus had 15.4% and Enterobacter 15.4%.Fungi genera* used for the study revealed that *Aspergillus, Penicillium* and *Rhizopus Mucor* and discovered that water based mud was more biodegradable than oil based mud.

2.1: The Formulation of Drilling Fluid

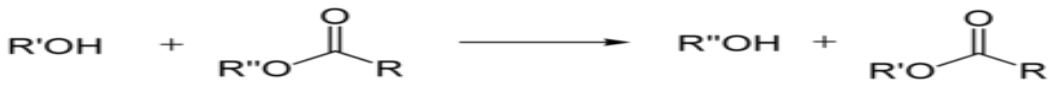
From the work of Bloys *et al.*, (1994), where they worked on WBM, the following ingredients may be needed in the design of a typical drilling fluid: **Based fluid** is major component of the drilling fluid. **Weighty agents** are added to control formation fluid pressure. The most common is barite. **Clay** – bentonite is used for the provision of viscosity and creates a filter cake on the borehole wall in order to control fluid loss. Clay is frequently replaced by organic colloids such biopolymer, cellulose polymer or starch. **Polymers** – are used to reduce filtration, stabilize clays, flocculate drilled solids and increase cuttings carrying capacity. Cellulose polacrylic and natural gum polymers are used in low-solids mud to help maintain hole's stability and minimize dispersion of cuttings. Long chain polymers are absorbed on the cuttings, thereby preventing disintegration and dispersion. **Thinners** – are added to the mud to reduce its resistance to flow and stifle gel development. They are typically plants tannins, polyphosphate, lignite materials, lignosulfonates or synthetic polymers. **Surfactants** – serves as emulsifiers, foamer and defoamers, wetting agents, detergents, lubricators and corrosion inhibitors. **Inorganic chemical** – there are variety of this and they are added to mud for various reasons. For instance, calcium hydroxide is used in lime mud and calcium chloride in OBM; sodium hydroxide and potassium hydroxide (caustic soda and caustic potash) to increase mud pH and solubilise lignite; sodium carbonate (soda ash) to remove hardness, sodium chloride for inhibition. Sodium chloride has other uses such as increasing salinity, increasing density and preventing hydrate formation. **Bridging materials** – calcium carbonate, cellulose fibres, asphalts and gilsonite are added to build up a filter cake on the fractured borehole and help prevent filtration loss. **Lost circulation materials** – are used to pore block large openings in the wellbore. These include walnut shells, mica and mud pills containing high concentration of xanthum and modified cellulose. **Specialized chemicals** – scavengers of oxygen, carbon dioxide and hydrogen sulfide are sometimes needed as they are biocide and corrosion inhibitors.

Biodiesel Synthesis

Bankovic-llic (2012) notes that the main challenge with non-edible plants is that they contain high content of free fatty acids (FFA) or non-esterified fatty acid (NEFA) which increases the cost of biodiesel production. Thompson and Asla (2019) say animal fats are attractive feedstock for biodiesel production because they are cheaper than vegetable oil. This is partly because the market for animal fat is limited than that of vegetable oil since the much of them are not considered edible. Animal fat has been found to have rich cholesterol content and medical experts taught us that cholesterol has negative effect on human body.

Waste fat from animal carcasses is removed and then made into oil using rendering process. Rendering consists of grinding the animal by-product to a fine consistency and cooking them until the liquid fat separates and pathogens are destroyed. The solids are usually passed through a screw press to complete the removal of the fat from the solid residue. The cooking process removes water, which makes fat and solid material stable against rancidity. The end products are fat and high protein feed additive known as meat and bone meal.

Animal fats are highly saturated which means that the fat solidifies at a relatively high temperature therefore biodiesel made from animal fat has a high cloud point of 55-60˚F (12.77 -15.55°C) B100 (pure biodiesel) and it is recommended for warm climate. That of animal fat experiences tendencies to form soap. However, biodiesel from animal fat can be blended with petro-diesel. At lower blends such as B5 (a blend of 5% biodiesel with 95% petro-diesel) the high cloud point of the animal fat biodiesel does not have much effect on the cloud point of the blend. Even when the animal fats are made into biodiesel, the challenge of solidification at lower temperature is possible and they have high melting point. Transesterification is the main method of synthesising biodiesel. During this process, alcohol is reacted with oil (triacylglycerol) to produce fatty acid alkyl ester and a byproduct, glycerol.



Transesterification: alcohol + ester → different alcohol + different ester (Wikipedia, June, 2021).

2.2 Methods

1 Oil Extraction

Beef fat of 2.3kilograms was obtained from Nchia Market; Rivers State in Nigeria was shredded into smaller pieces and poured into a pot for melting. The pot was covered but not airtight and heated by an electric burner. The shredding was done to speed up fat melting process. The process took about 60 minutes to get all the fats melted. The hot melted tallow (oil) was then strained from the residue using a sieve to remove particles and preserved for biodiesel synthesis.

Percentage oil yield = $\frac{mass\ oil\ after\ the\ filtration\ from\ solid\ residue}{mass\ of\ the\ beef\ tallow}$ x 100% (1)

2 Synthesis of Biodiesel

Two-step process were adopted for the synthesis of the biodiesel due to the nature of the sample which has high free fatty acid content above 2 KOH /mg

Oil: alcohol ratio of 1: 6 and 1: 9 were adopted for the transesterification as calculations were done based on established GC/fatty analyses.

Procedure:

The mass/volume of the alcohol was determined and poured into a conical flask. The calculated mass of sodium hydroxide, NaOH (catalyst) about 1% required was weighed and dissolved in methanol by manually stirring. The calculated mole ratio and alcohol sample was measured and added in the flask. The flask and its content were heated to 60˚C for a period of 1 hour with continuous stirring such that the mixture did not separate in two layers. While still warm, the mixture was poured into separating funnel and was allowed to cool and separate into two layers. The upper layer is the biodiesel and the lower is mostly the glycerin. This was not allowed to stand for too long in order to prevent the lower layer from solidifying. The lower layer was drained into a graduated beaker. This solution contained glycerin, unreacted alcohol, unreacted sodium hydroxide, a trace of water and salts. Note: In commercial process, the glycerin and alcohol can be collected for reuse. In this experiment, it was a waste container labeled for glycerin and alcohol.

The top layer in the separation funnel was labeled biodiesel. It would be contaminated with traces of alcohol, glycerin, unreacted NaOH and soap which is a byproduct of the reaction. (Soap is the sodium salt of fatty acid). The biodiesel was washed by adding 10 ml of tap water to the separation funnel. The mixture was gently swirled for about 1 minute to dissolve the alcohol, glycerin, NaOH and any soap. Note: This was not shaken to avoid formation of emulsion. The mixture was allowed to separate, drained and the bottom layer was discarded. Note: If an emulsion were formed, the addition of a few grams of sodium chloride and swirling the mixture for 1 to 2 minutes and allowing the mixture to stand makes it form two layers. This can be drained of the lower layer and discarded in the waste container labeled for glycerin and alcohol. The biodiesel layer was then drained into a clean, dry beaker. The biodiesel was vacuum filtered using a Buchner filtration apparatus into a clean, dry side arm flask. The traces of water from the biodiesel were removed by adding a few grams of anhydrous sodium sulfate and the mixture was swirled for 1 to 2 minutes. The biodiesel was poured into clean, dry, weighed graduated cylinder.

The mass was determined, the volume too.

Oil Yield = $\frac{Mass\ of\ Biodiesel}{Mass\ of\ oil\ used}\ x\ 100\%$ (2)

Oil Yield = $\frac{Volume\ of\ Biodiesel}{Volume\ of\ oil\ used}\ x\ 100\%$ (3)

Mole = $\frac{Mass\ (g)}{Molar\ Mass\ \left(\frac{g}{mol.}\right)}\ x\ 100\%$ (4)

3. Synthetic Mud Formulation

Table 1: Components of the Formulated Mud

Components	Unit	Mass/Volume
Based fluid	ml	200
Water	ml	100
Barite	g	76.8
Xylene emulsifier	ml	50
Lime	g	1.5

4. Mud Rheology Test

Rheology refers to the deformation and flow behaviour of all forms of matter. Some rheological properties of measured are viscosity and gel strength and these help to determine the fluid flow under a various condition.

The Baroid (Model 286) Rheometer is a coaxial cylindrical rotational viscometer, used for the determination of single or multi-point

viscosities. It has fixed speeds of 3 (Gel), 6, 30, 60, 100, 200, 300, and 600 RPM that are switched selectable with the RPM knob. In addition, that same switch set at the VAR position, enables speed selection of between 3 and 625 RPM, by manual adjustment of the variable knob.

Procedure

A recently, agitated sample was placed in the cup, the upper housing of the Rheometer was tilted back, the cup was located under the sleeve (the pins on the bottom of the cup fit into the holes in the base plate) and the upper housing was lowered to its normal position. The knurled knob was turned between the rear support posts to raise/lower the rotor sleeve until it was immersed in the sample in the scribed line. The sample was stirred for 5 seconds at 600 rpm, and then the subsequent RPMs were selected as preferred. The dial reading was allowed to stabilize (the time depends on the sample's characteristics). The dial reading and rpm were recorded.

Rheological Calculations

Plastic Viscosity, PV (in centipoises) = 600 rpm reading – 300 rpm reading (5)

Apparent Viscosity, AV (in centipoises) = 600 rpm reading /2 (6)

Yield Point, YP (in lb/100ft2) = 300 rpm reading – Plastic Viscosity (7)

Gel Strength

Theory: The Baroid Rheometer is also used to determine the gel strength, in lb/100 sq.ft. of mud. The gel strength is a function of the intermolecular forces. An initial10-second gel and a 10-minute gel strength measurement indicate the amount of the gellation that will occur after circulation is ceased and the mud remains static. The more the mud gels during shutdown periods, the more pump pressure is needed to initiate its circulation. Most drilling muds are either colloids or emulsions which behave as plastic or non-Newtonian fluids. The flow characteristics of these differ from those of Newtonian fluids (that is water, light oils, etc.) in that their viscosity is not constant but varied with the rate of shear. Therefore, the viscosity of plastic fluid will depend on the rate of shear at which the measurements were taken.

Procedure

A sample at 600 rpm was stirred for about 15 seconds. The rpm knob was turned to the stop position. The desired rest time of wait (about 10 or 10 minutes) was observed. The rpm knob was switched to Gel position. The maximum deflection of the dial before the Gel broke was recorded as the Gel Strength in $lb/100ft^2$. Note: $lb/100ft^2$ x 5.077 = Gel Strength in $dynes/cm^2$.

Yield Point

Theory: This is the measure of the electrochemical or attractive forces in the mud underflow (dynamic) conditions. These forces depend on (1) surface properties of the mud solids, (2) volume concentrations of the solids, and (3) the electrical environment of the solids. The yield point of the mud reflects its ability to carry drill cuttings out of the hole.

Procedure

A recently agitated mud sample was obtained. Using the Baroid Rheometer, dial readings were obtained at 3, 300, and 600 rpm. Calculation Yield Point, YP (in lb/100ft2) = 300 rpm reading – Plastic Viscosity.

Filtration or Fluid Loss

The Procedures for Drilling Mud Fluid Loss Testing

Equipment: API LTLP filter press

The following procedure was used for measuring fluid loss control at ambient temperatures: It was checked that the rubber gasket was seated correctly in the base of the filter press mud chamber and circular gauze frame was inserted and Whatman No. 50 filter paper was placed on top of the gauze frame. A rubber gasket was placed on top of the filter paper; the pins on the cylindrical body of the mud chamber were engaged with the slots in the base of the chamber and twist firmly to lock the assembly together. The mud chamber was filled with mud, keeping the air gap at the top to a minimum. The mud chamber was placed in the filter press frame; the rubber gasket was seated correctly in the mud chamber lid and placed over the cylindrical body of the mud chamber. The screw in the filter press frame was turned to lock and seal the lid firmly down on the mud chamber.

A graduated/measuring cylinder was placed on the adjustable platform below the mud chamber and adjusted the height so that filtrate can be collected from the discharge tube at the base of the mud chamber. A new CO_2 cartridge was inserted into the pressure assembly on the lid of the mud chamber. The pressure regulator was adjusted to apply a pressure of 100 psi to the mud chamber and the start time was recorded. The spurt loss volume recovered was measured in the graduated measuring cylinder during the first few seconds, if it is significant. The pressure gauge at regular intervals was checked to ensure that 100 psi pressure is maintained throughout the 30-minute test period. When the 30-minute test period was over, the pressure regulator was closed, the red bleed-off knob was pulled to release the pressure in the mud chamber and the volume of filtrate collected was recorded in the graduated measuring cylinder. This was reported as fluid loss in milliliters.

Carefully, the mud chamber was dismantled without damaging the filter cake on the filter paper.

The filter paper was removed and gently rinsed off the surface mud on the filter cake. The thickness of the filter cake to the nearest 1/32 nd of an inch and any relevant observations were noted about filter cake quality (e.g., firm, slick, etc.). The filtrate collected in the graduated measuring cylinder was used for the chemical analysis part of the mud checks. The used CO_2 cartridge was removed from the pressure assembly. The filter press components were thoroughly washed and allowed to dry, in preparation for future tests.

RESULTS AND DISCUSSION

1. Oil Yield from Beef Tallow

2300 grams of beef tallow yielded 2000 grams amounting to 87% oil yield from the beef tallow. This resulted in 2,128 ml of oil. This mass of beef tallow was obtained at 500 naira, approximately 1$ at the time it was obtained. Although Ali *et. al* (2012) obtained 89.01%, the result obtained in this analysis is not far from it. Thus, giving a form of validity.

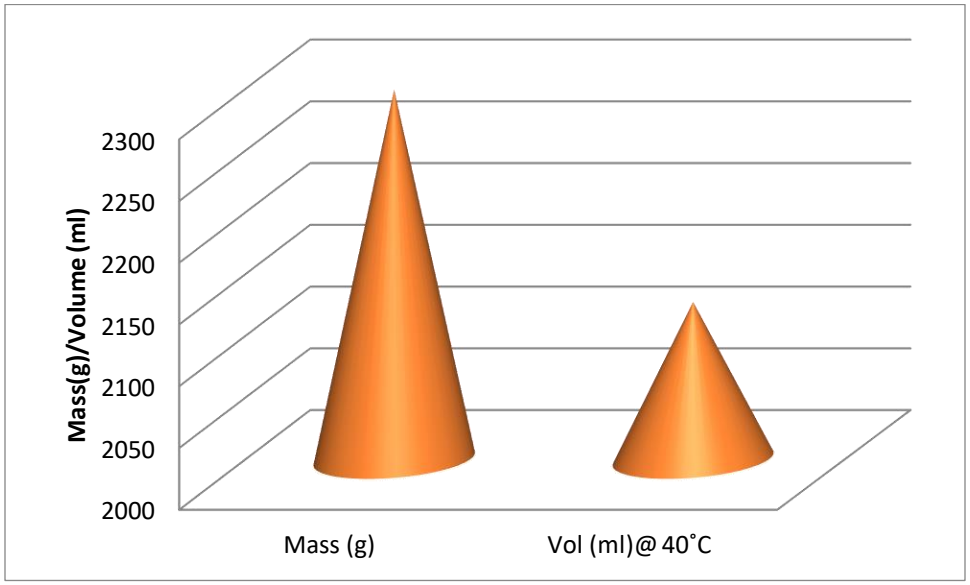


Figure 1: Percentage oil yield per gram of weight of sample

2: Physico-chemical properties of oil samples

Table 2: Physico-chemical properties of oil samples

Parameter	Value
Density (g/ml) @ 40˚C	0.94
Flash Point (˚C)	171
Pour Point (˚C)	10
Water content (%)	1.5
Viscosity @ 26˚C	-

Table 3: Results of Sample Pretreatment: Esterification

Sample	Methanol	Ethanol
Oil	68%	70%

The oil sample was esterified using both methanol and ethanol in molar ratio of 1:20 with 10% w/w of the oil sample each and the results are as shown in the table 3 above. Theoretically, molar ratio should be 1:3 however, scientifically, it has been established that the forward reaction is favoured when there is an excess of alcohol. Hence, the choice of 1:20 was preferred considering the high free fatty acid composition of the oil sample which is also rich in saturated acids such as C18:0 stearic acid, C16:1 palmitoleic acid and C14:0 myristic acid which together makes it difficult to transform this solid at room temperature to liquid (biodiesel).

Table 4: Volume of Ester Yield

Sample (vol.)	Methanol	Ethanol
400 ml	272 ml	280ml

From the table above, after pre-treating (esterifying) 400ml of the oil sample each with methanol and ethanol the result was 272ml for ester produced with methanol and 280ml for ester produced from ethanol. The outcome is as defined in table 4 above.

Table 5: Ester Yield after Transesterification

Sample + Alcohol	1:6	1:9
Oil + Methanol	60%	65%
Oil + Ethanol	63%	70%

The results show that using ethanol for the transesterification resulted in more ester yield than methanol as shown in the table 5 above. Similarly, the molar ratio of 1:9 gave an improved result as compared to those of 1:6. This is because it has been experimentally proven that an increase in alcohol to oil ratio results in better ester yield. Although, the results would have been far better than these were the reactor used was airtight to prevent the possible evaporation and escape of the alcohol used. The vaporizing and subsequent escape of the alcohol reduces the available alcohol for the reaction. However, caution was taken to ensure that the temperature used for the process was less than the boiling temperatures of the alcohol. The boiling temperature of methanol is 64.7˚C and that of 78.37˚C but in both reactions, reaction temperature adopted was 60˚C. This reaction temperature is closer to the boiling temperature of methanol than that of ethanol thus making methanol to be more susceptible to vaporization and escape when compared to ethanol. This explains why the ethanol gave a better yield against methanol.

Table 6: Physico-chemical Properties of the Biodiesel

Sample	Diesel	Bio-M	Bio-E
Density @40˚C	0.89	0.91	0.92
Dynamic Viscosity (CST)	37.3	21.87	41.61
Kinematic Viscosity (CST)		0.83	1.58
Flash Point	90.5	120	138
Pour Point		9.6	12

The properties of the synthesized ester were compared with the European standard – EN 14214 and ASTM D6751 – American Society for Testing and Materials which stipulates that the flash point of biodiesel should not be less than 101˚C and the ester produced conform to this model with 120˚C and 138˚C for Bio-M and Bio-E respectively. The pour point determined is in conformity with the work of Gandure *et al.* (2017).

Table 7: The pH of the formulated drilling muds

pH of the muds	M-Bio-M	M-Bio-E	M-Diesel
	8.0	9.5	9.0

The pH values of the formulated drilling muds show that formulated with M-Bio-E has the best pH value which is 9.5; M-Bio-M and M-Diesel 8.0 and 9.0 respectively. This can always be can be adjusted to a desired range using hydrated lime to forestall possibility of causing corrosion and ensuring that the mud mixture is stable. The lime when added usually reacts with the hydrogen ions (acidic components) of the mud and to yield water, carbon dioxide and calcium in case of using $CaCO_3$ thereby, neutralizing the acidic component of the mud according to Anderson *et al.* (2013).

Table 8: Mud Density in Different Units

Density	PPG	SG	lb/ft^2	lb/100ft
Bio-E	9.6	1.15	72	500
Bio-M	9.7	1.17	73	510
Diesel	9.7	1.16	72	500

Table 9: Showing the rheological properties of the drilling mud formulated.

RPM/Dial Reading	M-Bio-M	M-Bio-E	M-Diesel
600	35	82	94
300	27	62	75
200	23	54	66
100	17	42	54
60	14	37	47
30	11	28	40
6	7	14	23
Apparent Viscosity, cP	35	82	94
Plastic Viscosity, cP	8	20	19
Yield Point, lb/100 sq.ft.	19	42	56
10-sec. Gel, lb/100 sq ft.	7	14	23
10-min. Gel, lb/100 sq ft.	7	14	23

The data obtained from the rheological test of the invert emulsion mud was plotted using Microsoft Excel and the model obtained is as presented below.

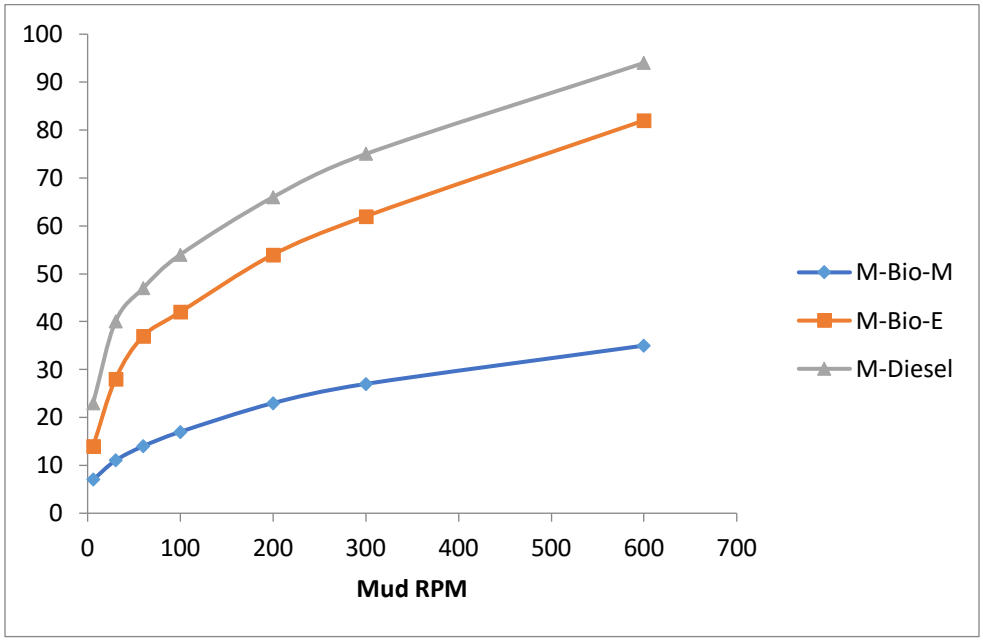


Fig. 2: RPM vs Dial Reading of the SBMs

From the figure 2 above, it could be observed that the use of ethanol formulated biodiesel is seems to mimic better the rheological properties of the control fluid (fossil diesel formulated mud). The outcome of this result can be attributed to molecular weights of the alkyl group as ethyl has a higher molecular weight than methyl. However, all the mud conforms to Bingham plastic model.

Table 10: Result of the filtration Test in Mililitres

Time (Minutes) / Sample	30	60	90	120	150	180
M-Bio-E	3.5	5.0	6.0	7.0	8.0	9.0
M-Bio-M	2.8	4.0	5.0	6.0	6.8	7.6
M-Diesel	2.4	3.2	4.4	5.2	6.0	6.4

The results obtained with an interval of 30 minutes are presented in the table 10 above. From left to right, it shows the expected increase in the filtrated, measured in cubic centre. According to (Koya, 2015), anything below 10 mililitres is low filtration. This result obtained is good because it will neither result in high formation damage nor tendencies of stuck pipe during drilling operations.

Conclusions

The oil yield from beef tallow was 87%. This result shows that beef tallow is filled with oil. However, it contains high concentration of saturated fatty acids makes it readily solidify at room temperatures.

Beef tallow of 2300grams and worth 500 naira only able to yield 2128 ml which is very profitable.

Esterification using both methanol and ethanol in the molar ratio of 1:20 each yielded 68% and 70% esters respectively.

Transesterification using methanol and ethanol using molar ratio of 1:6 and 1:9 showed that ethanol gave a better yield.

The synthetic mud formulated using the esters synthesized were tested for rheological behaviours comparing with a fossil diesel formulated mud as a control. It was observed that ethanol synthesized ester better mimics the behaviour of the fossil diesel.

The pH of the muds were measured and found to be 8.0, 9.5 and 9.0 for M-Bio-M, M-Bio-E and M-Diesel respectively. These results are acceptable according to standards as the pH would guarantee the stability and proper dispersal of the constituent additives.

The formulated synthetic muds conform to Bingham plastic and Power law models and have acceptable rheological properties.

Contribution to Knowledge

1. Biodiesel was synthesized from beef oil.
2. This research shows that biodiesel synthesized from beef oil can be used to formulate Synthetic Based Mud for drilling operations.

Even though oil samples obtained from waste oil, edible, non-edible, alage and animal fats can be used for biodiesel synthesis, only

samples with high unsaturated fats could guarantee high yield and profitable returns. Thus, those with high content of saturated fatty acids are better used for polish, deodorant and cream.

3. Biodiesel synthesized using ethanol is less toxic compared to that synthesized using methanol and it is appropriate to prefer ethanol to methanol for biodiesel synthesis when it is needed for mud formulation.

Recommendations

This laboratory formulated mud should be subjected to field test to determine its true applicability.

Further research should be carried out on its toxicity, dispersibility and biodegradation of the formulated muds.

The mud was aged at room temperature however; this can be extended to higher and even elevated temperatures to examine their behaviours. Also, longer aging can be adopted to determine has aging affects the synthetic muds.

Beef oil has been found to have high saturated fatty acid content about 45 – 52% and these are dominated by C18:0 stearic acid, C16:1 palmitoleic acid and C14:0 myristic acids easily coagulate at room temperature. This makes this oil very useful for the soap, hair cream, deodorant and shoes polish formulation as it may require little or no refining unlike in the case of ester or biodiesel formulation which requires pretreatment to remove these compounds in the oil mixture. Oghome and Kamalu (2012) in a study to characterised the fatty acids used in the manufacture of various soaps in Nigeria, mainly antiseptic, toilet and laundry soaps found out that after carrying out a chromatography on these soaps and discovered that Delta soap has 40.48% of palmitic acid, C16:0, 34.35% of oleic. In temosol they found out that oleic has 39.35% and palmitic acid, C16:0 has 29.11%. For Carex antiseptic soap, C18:1 and C16:0 were 36.06% and 29.96% respectively. In Jumbo and truck bar which are both laundry soaps, C18:1 and C16:0 were prominently found in them. C16 was 43.47% and C18:1 was 36.20%. In truck bar, 43.89% and 31.73% for oleic and palmitic acids respectively. In Lux, oleic acid was 41.51% and palmitic, 26.70%. In Joy, oleic was found to be 40.60% and palmitic, 24.99%.

It is also important to pay attention to C18:0 stearic acid, C16:1 palmitoleic acid and C14:0 myristic acids in any oil sample and as much as possible avoid samples with high concentrations of those fatty acids as it cost much to refine before it can be used and though the oil itself is readily available and cheap, the cost of pretreating it can high rocket its price. Allard (2018) stated that beef tallow has been used in manufacturing deodorant, creams and polish.

Subsequent synthesis should be carried out in an airtight reactor as this will enable the reaction to be carried out a preferred temperature without necessarily losing the alcohol as this will enhance its ester yield.

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