Appraisal of Esters of Non-Edible Oils For Synthetic Mud Formulation

Onungwe, O. S., Ayuba, I.

Abstract: SBM is highly dispersible and biodegradable unlike WBM and OBM whose use somewhat endangers the biosphere. Oils from edible seeds have been a major source of SBM's base fluid (biodiesel). This threatens food's demand and supply as human population is not commensurate with investment or interest in agriculture. Edible oils are expensive to non-edible oils. This research is to appraise SBM from esters of non-edible oils.

Oils were extracted from non-edibles: Hura crepitans and Enterolobium cyclocarpum. The oils were characterised for their Physico-chemical properties; and fatty acid content using the GC-FID. Results obtained were utilised to synthesize the esters. The esters were characterised for its properties using the GC/MS and FTIR. 350ml mud for each was with 80/20 ester water ratio with other requisite additives and their attendant rheological properties, electrical stability and retort tests were carried. Control, fossil Diesel Based Mud was formulated and the Ester Based Mud were compared.

H. crepitans and E. cyclocarpum, yielded 51 and 7% oil respectively. Similarly, the ester yield of H. crepitan 97% while E. cyclocarpum was 23%. The two best yield was due to esterification before transesterification unlike E. cyclocarpum. The pH values were greater than 8 an indicator that they would not corrode the drilling equipment. The gel strength of the mud, oil, water and solid content of the mud, and the rheological properties of the mud are acceptable. The electrical stability of OBM was 468 Volts and SBM-HC was measured to be 399 Volts. Although, the difference from the control is not much, this can be improved by the addition of thermally stable emulsifiers.

SBM-HC measured at 30°C has n < 1 (0.86) while K is 38.73 an indication that it is a non Newtonian fluid. This relationship is similar to others hence, the formulated muds were non Newtonian and conform to the Bingham Plastic and the Power Law Models.

The results from these analyses show that the mud would perform well technically and environmentally if prudently utilised in the field while the issue of economics should be re-examined.

Common words: synthetic base mud, SBM, oil, ester, Gas Chromatography/Mass Spectroscopy, GC/MS.

— — — — — — — — — ◆ — — — — — — — — —

1. INTRODUCTION

As environmental regulations governing the disposal of drilling fluids become increasingly restrictive, use of conventional OBM's is being curtailed [1]. SBM being highly dispersible, degradable and less toxic certainly would be a preferred solution. Though they act like petro-leum-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 [2]. Although there are many types of synthetic fluids, esters have been reported to most degradable, dispersible and less toxic [3]. Oils/lipids are main source of biodiesel, the base fluid of SBM. These oils can be obtained principally from four main sources namely: (1.) vegetable oils (edible and non edible), (2.) animal fat, (3.) waste cooking oil – used oil materials and (4.) algae oils. Each of these have been examined by different researchers and vegetable oils appear more appealing due to their availability and low cost of processing into biodiesel.

Currently, according to [3] edible oils are the main resources for world biodiesel production (more than 95%). The following reasons have been presented to caution the use of edible oils for this purpose:

1. Edible oils adversely affects food price as its the reduces food sources and growth of commercial plant capacities.
2. Oils from these resources are as a rule, unsuitable for human consumption due to the presence of toxic compounds. For example, the main toxic compounds in

jatropha plants are protein curcin and purgative agents, protein ricin in castor plant, glucoside cerberin in fruits of sea mango and flavonoids pongamiin and karanja oil.

3. Non edible oil producing plants abounds across the world.

4. The non edible oil plants can easily be cultivated in barren lands (lands unsuitable for human crops) with much lower cost than those of the edible oil crop plantation.

5. The growing plants reduce the concentration of CO_2 in the atmosphere – a major contributor to global warming as well as acid rain.

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. 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 by product, glycerol. The main factors affecting trans-esterification reaction and produced ester yield are: (1.) the molar ratio of 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 [5].

Molar Ratio of Alcohol and Oil: Although there are several reports on the mole ratio of the reactants, generally, oil/alcohol ratio of 1:6 respectively is most favoured. Usually, it the ratio ought to 1:3 but since the reaction is reversible, to favour FAAE production, more of the alcohol is needed to forestall its reversal. Some have even used more alcohol up to the ratio of 1:8, 1:10 etc.

Temperature: biodiesel can be synthesised at room temperature but higher temperature fastens its rate of reaction. It has been reported that temperatures between 40 – 60°C highly favours biodiesel formation. Optimum result is guaranteed at 60 Celsius. Temperature should not be increased above the boiling point of the alcohol. This would lead to the loss of the alcohol

by evaporation especially when the system is open and reduce the ester yield [4].

Time: increase in time yields better result. Studies have shown that biodiesel can be synthesised in five minutes however, best yield is favoured between 30 – 60 minutes.

Type/Amount of Catalyst: generally 1% weight of the oil is acceptable for transesterification. While H_2SO_4 is useful for esterification, NaOH/KOH is for transesterification. Sulphuric acid can be utilised for both esterification and transesterification however, this would take a longer time of about 2 days (48hrs) to get the process through. This implies higher cost for electricity generation and staff to monitor.

Type of Alcohol: This affects the type of product synthesised as well as the cost of the synthesis. For example, the use of methanol results in the synthesis of FAME while the use of ethanol results in the synthesis of FAEE. Methanol is costs less than ethanol.

Mixing intensity: the better mixing the faster the reaction and of course ester yield. However the rpm of the magnetic stirrer bar should be such that the bar is allowed to rest in the reactor on magnetic bar without jumping about. 1000 rpm has been used successfully for 350 ml of oil sample [4].

Free Fatty Acid: free fatty acid can be regarded as an enemy of the transesterification hence, the need to reduce it to the barest minimum to guarantee good yield. Oils with FFA higher than 0.5 mg KOH/g should be esterified (pre-treated) before transesterification. Esterification reduces the amount of FFA in the oil sample and acid catalyst (sulphuric acid) is used for this purpose. Although some literatures say provided it is less than 1 KOH/g transesterification can be utilised without recourse to esterification. The presence of FFA in the feedstock consumes more catalyst and ultimately affects the yield of biodiesel and cost of production.

Water in Oils: The presence of water of water in the feedstock during trans-esterification deactivates the catalyst. The total water content must be 0.1–0.3 wt% or less. This is because the presence of water in the feedstock promotes the hydrolysis of alkyl esters to FFAs and soap formation [7]. Dehydration or removal of water

can be achieved by passing nitrogen gas through the oil. The effect is negligible using supercritical transesterification. [7], [8].

2.   EQUATION OF REACTIONS
1.   Esterification

$$ROH_{(l)} + R' - COOH_{(l)} \underset{<--}{-->} R'COOR_{(l)} + H_2O_{(l)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$
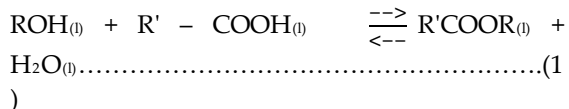
Carboxylic acid reacts alcohol to produce ester and water. It is an endothermic hence, it absorbs heat to shift the equilibrium position to the right and favour forward reaction. This reaction can proceed on its own without a catalyst but at a slow rate due to its high activation energy barrier at this instance.

Hydrogen in the oil is replaced by R and the hydrogen combines with the hydroxyl group to form water. This reversible reaction is esterification in the forward direction and hydrolysis in the opposite direction.

Since they are in the same phase of liquid, according Le Chatelier principle, pressure has no effect on this reaction [12]. However, an increase in the concentration would definitely favour the forward reaction.

2.   Transesterification

$$ROH_{(l)} + R'COOR_{(l)} \underset{<--}{-->} R'COOR''_{(l)} + C_3H_8O_{3(s)} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$
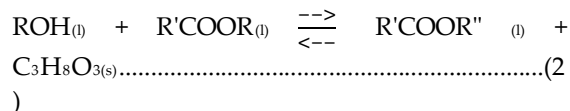
Ester reacts with alcohol to yield fatty acid alkyl ester (biodiesel) and glycerol. This is an endothermic reaction [11]. Hence, increase in heat beyond its equilibrium position would reverse the reaction. Similarly, positive catalyst would speed up the reaction.

Transesterification: alcohol + ester → different alcohol + different ester [11].
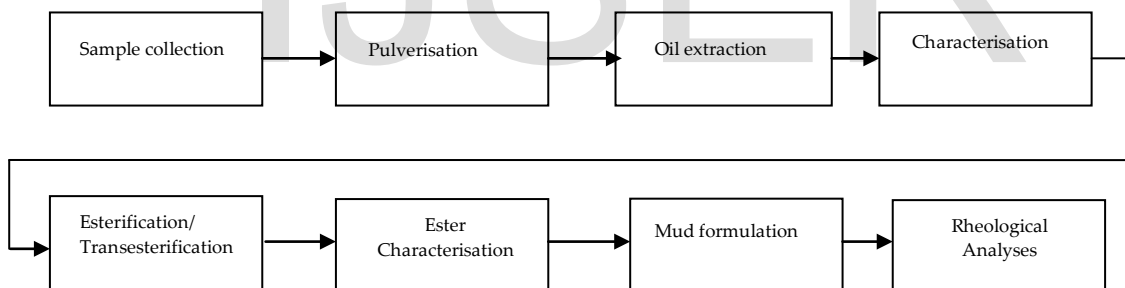
3. METHODOLOGY

Fig. 1. Block Diagram of the entire process.

Scores of feedstock for the production of biofuel abounds, but the most appropriate ones should not compete with food, have high yield per unit area of growth and require a minimum input (water, fertilizer, energy) to grow [9]. Seeds chosen for this research were: (i.) *Hura crepitans* [Sandbox tree] and (ii.) *Enterolobium cyclocarpum* meets these conditions.

The samples were collected at the UI-Botanical Garden, dried, de-husked and pulverised. Oils were extracted using n-hexane as solvent and the

Soxhlet Extractor equipment at the UI- Petroleum Engineering Department.

Characterisation for the Physico-chemical properties of both the oils and the esters were conducted at the Kappa Biotechnology. Laboratory, Ibadan. Preceding transesterification were the Methylation and Gas Chromatographic analysis of the oils at the UI-Multidisciplinary Lab., Ibadan, to determine their Fatty Acid Composition using internal standard of GC-FID. Esterification and transesterification of the oils were carried out at

Forestry Research Institute of Nigeria, Ibadan. Transesterification was carried using oil/methanol ratio of 1:6 and about 1% weight of catalyst. The catalysts used were liquid sulphuric acid (H_2SO_4) for esterification and (NaOH) sodium hydroxide for transesterification. The magnetic stirrer bar was set at about 1000 rpm for 350 ml of oil sample.

Fourier Transform Infrared Spectroscopy, FTIR and the Gas Chromatography/Mass Spectroscopy, GC/MS of samples were analysed at the UI, Ibadan and OAU, Ile-Ife respectively for the purpose of identifying their bonds and functional groups; and composition and possible structures, in that order. Esters were analysed for their Physico-chemical properties.

Laboratory mud was formulated using ester/water ratio of 80/20 with – 3g of organophilic clay, 3g of lime, 10g of barite and 5g of emulsifier.

3.1 Synthetic Mud Formulation

Procedure

TABLE 1.
MAKEUP OF THE MUD

Components	Unit	Mass /Volume
1. Base fluid	(ml)	280
2. Water	(ml)	70
3. Organophilic clay	(g)	3
4. Lime	(g)	3
5. Barite	(g)	10
6. Emulsifier	(g)	5

The mud was designed using the listed components listed in the table 1 and the multimixer was utilised for mixing the mixture.

1. The base fluid was mixed with water in the multimixer cup
2. Primary emulsifier was added and mixed for 15 – 20 minutes.
3. Lime was added and the mixture was again sheared for 15 – 20 minutes.

4. Secondary emulsifier was added and mixed for 15 -20 minutes.
5. Organophilic clay was added with maximum possible shear applied.
6. Weighting agent was added and the entire system was stirred for enough time.
7. Rheological properties were determined.
8. The mud was aged for 24hours and stirred with the multi-mixer.
9. Rheological properties determined.

Rheological, gel strength, pH, electrical stability and oil-water-contents analyses were determined using the Rheometer, pH meter, Electrical stability and Baroid Retort Kit in that order.

3. RESULTS AND DISCUSSIONS

4.1 Oil yield expressed in percentage: *Hura crepitans – 51%* and *Enterolobium cyclocarpum – 7%*. *E. Cyclocarpum* uneconomical. The results show that *Hura crepitans* is suitable for oil extraction while the *Enterolobium cyclocarpum* is highly uneconomical for this purpose.

4.2 Ester yield expressed in percentage: *Hura crepitans – 97%* - esterification before transesterification were used. *Enterolobium cyclocarpum – 23%* - no esterification preceded transesterification. This affirms that the presence of free fatty acid in oil sample decreases its ester yield and that to guarantee better ester yield, esterification should precede transesterification.

TABLE 2
PHYSICO-CHEMICAL PROPERTIES OF THE OIL SAMPLES

Parameter	HC	EC
Density (g/ml)	0.95 ± 0.00	0.91 ± 0.00
Flash Point (°C)	253.33 ± 1.27	178.67 ± 1.77
Pour Point (°C)	6.33 ± 1.58	12.33 ± 0.76
Acid Value (mg KOH	1.40 ± 0.08	1.13 ± 0.13
Sapon. Value (mg/g)	134.90 ± 1.44	126.37 ± 0.13
Iodine Value (mg/100g)	63.83 ± 0.12	72.17 ± 0.29
Moisture Content (%)	0.73 ± 0.06	1.77 ± 0.08
Viscosity (CentiStokes)	380.53 ± 0.17	225.33 ± 0.13
Kinematic Viscosity	456.33 ± 0.25	270.43 ± 0.13

Table 2 shows the mean Physico-chemical properties of the oils extracted after analyses and their standard deviation. *H. crepitans* is denser than *E. cyclocarpum* and with a difference of 0.04 g/ml.

Their flash points in centigrade also vary, 235.33 $\pm$ 1.27 for *H. crepitans* and 178.67 $\pm$ 1.77 for *E. cyclocarpum.* The high flash points of these oil samples show that they can be effective at high temperatures because they cannot easily flash or burn. Table 1 also, shows that H. *crepitans* has a better pour point than E. *cyclocarpum* meaning; it still retains its fluidity above this temperature whereas the other would tend to be semi solid or solid.

The FFA content of all the oil samples is less than one hence, one step transesterification method would suffice for their biodiesel production. Contrary to this would imply that a two-step approach be applied and this is more expensive when compared to the former. However, some authors recommend that FFA should be less than 0.5 before a transesterification can be used to assure success.

Table 2 reveals the saponification values of the samples as 126.37 and 134.90 for *E. cyclocarpum* and *H. crepitans* respectively. Similarly, their iodine values are 72.17 and 63.83 respectively. The moisture content of this these oil samples are 0.73 for *E. cyclocarpum* and 1.77 for *H. crepitans*. Too much deactivates our catalyst.

Viscosities of these oils in CentiStokes ranged between 200 and 500. 225.33 is for *H. crepitans* and *E. Cyclocarpum* is 380.53. The kinematic viscosity in table 2 is similar to that of viscosity since they can be easily converted to each other by the use of density.

From table 2, the flash points of the synthetic oils are 182.3, 135.3 and 90.5 for *H. crepitans, E. cyclocarpum* and diesel respectively. This is in consonance with literature which puts the flash point of biodiesel to be greater than 130°C while that of the diesel being 90.5 is acceptable as it falls with 52 and 96 °C. The high flash point of biodiesel above that of the conventional diesel makes the biodiesel less susceptible to ignite in the event of fire outbreak. Similarly, the cloud points are good enough as the fall with the conventional range of -60 °C to +49 °C and this biodiesel is often used in high pressure and temperature conditions, it means it will remain its right state. In the same vein, the smoke points are 153.6, 110.6 and 179.6, in the earlier order. Syn-HC is 0.3, 5.6 and 9.6 are for Syn-HC, EC and diesel respectively.

TABLE 3
PHYSICO-CHEMICAL PROPERTIES OF THE BIODIESEL

Property	Syn-HC	Syn-EC	Diesel (CST)
Flash Point (°C)	182.3 $\pm$ 2.0	135.3 $\pm$ 1.5	90.5 $\pm$ 2.0
Cloud Point (°C)	10.3 $\pm$ 1.5	7.6 $\pm$ 0.5	5.5 $\pm$ 0.5
Smoke Point (°C)	153.6 $\pm$ 2.0	110.6 $\pm$ 1.6	179.6 $\pm$ 2.0
Pour Point (°C)	0.3 $\pm$ 0.5	5.6 $\pm$ 0.5	9.6 $\pm$ 0.5

Table 4 shows that variation in temperature varies the viscosity of the esters and this relationship is not linear.

TABLE 4
TEMPERATURE VERSUS VISCOSITY

Temp (°C)	Syn-HC	Syn-EC	Diesel(CST)
40	38.50 $\pm$ 0.36	51.83 $\pm$ 0.15	37.33 $\pm$ 0.35
100	28.40 $\pm$ 0.	39.60 $\pm$ 0.26	26.30 $\pm$ 0.31

Similarly, Table 5 temperature variation affects the time density.

TABLE 5
TEMPERATURE VERSUS DENSITY

Temp (°C)	Syn-HC	Syn-EC	Diesel (g/ml)
40	0.8422	0.8283	0.8281
100	0.8106	0.7987	0.7952

This result shows that stearic acid and pentadecyclic acid are the dominant acids in this oil occupying about 69.46% and 17.52% respectively while lauric acid appears as the least with 0.75% concentration.

The appearance of C17 can be attributed to its presence in the GC standard.

TABLE 6
FATTY ACID CONTENT OF *ENTEROLOBIUM*

Type of fatty acid	Mean Percentage

C10:0	Saturated Capric acid	3.48
C12:0	Saturated Lauric acid	0.75
C15:0	Saturated Pentadecyclic acid	17.52
C15:1		1.16
C18:0	Saturated Stearic acid	69.46
C18:2n6t	Unsaturated Linolelaicdic acid	1.31
C18:2n6c	Unsaturated Phenomenex acid	2.52
C21:0	Saturated Heneicosanoic ac	2.33
C22.2	Unsaturated Docosadienoic acid	1.49

TABLE 7

FATTY ACID CONTENT OF *HURA CREPITANS* OIL

Type of fatty acid		Mean Percentage
C10:0	Saturated Caprylic acid	5.55
C12:0	Saturated Lauric acid	2.03
C15:0	Saturated Pentadecyclic	13.55
C18:0	Saturated Stearic acid	74.59
C18:2n6	Unsaturated Linoleic	2.54

Two runs where obtained during the GC-FID and their mean determined. In cases where there were two different compounds at a particular position, the name of the compound that had the greater concentration was retained while the other was ignored even though its value was considered.

C17 was found in the result at high concentration, this is not too suitable for ester synthesis and should not be a major component a vegetable oil. However, it was discarded or not considered during the computation of the results. C17 was a component of the standard (fatty acid standard) and so its appearance in the result does not deserved to be utilised in the computation of the result (Senn and Johnson, 2007).

4.3 Gas Chromatography/Mass Spectroscopy Results
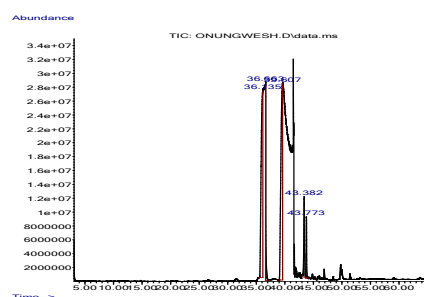
Fig. 2. GC/MS spectrum of *Hura crepitans* ester

A breakdown of these results indicates that H. *crepitans* contains about 99% hexadecanoic acid, methyl ester; 99% 9,12-Ocyadecadienoic acid, methyl, Methyl 10-trans, 12-cis-octadecadie at 99%. The H. *Crepitans* results indicates that Methyl 9-eicosenoate is 96% likely to be in the ester and lastly, Methyl 18-methylnonadecanoate probability in the sample is 99%.

4.4 Fourier Transform Infrared Spectroscopy (FTIR)
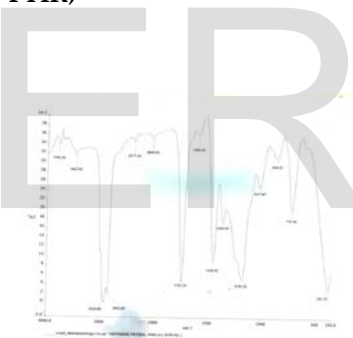
Fig. 3. Syn-*Hura crepitans* FTIR Spectrum

A careful examination of the FTIR chromatogram of the *Hura crepitans*, it can be observed that most of the peaks below fall 3000cm-1 wavelength, an indication of alkyl group (organic molecules).

Comparing the peaks of these spectra, the three sample between 3500 – 3200 cm-1 and having O – H stretch, H – bonded with the alcohol functional group. 3400 – 3250 cm-1 lies the N – H stretch bond and primary, secondary amines, amides.

Also, C – H stretch bond with the alkanes as its functional group and this appears between 3000 – 2850 cm-1. C = O stretch and this exists between 1750 – 2850 cm-1 and has esters, saturated aliphatic as its functional group. 1500 – 1400 cm-1 lies C – C stretch (in – ring) with an aromatic

functional group. Similarly, the 1370 – 1350 cm^{-1} has C – H rock bond, alkanes as a functional group and finally between 1300 – 1150 cm^{-1} is C – H (-CH2X) alkyl halides as its functional group. 900 – 675 cm^{-1} has C – H "oop" aromatics functional group and finally 725 – 720 cm^{-1} goes with the C – H rock bond, alkanes as functional group.
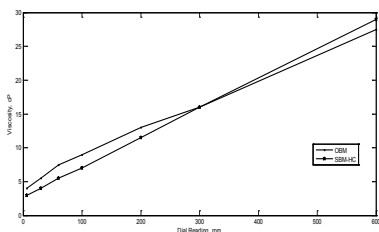

Fig. 4. Dial Reading Versus Viscosities of the Muds At 30°C

Fig. 4 shows that SBM formulated at 30°C with H. *crepitans* ester has the higher viscosity the control (OBM).
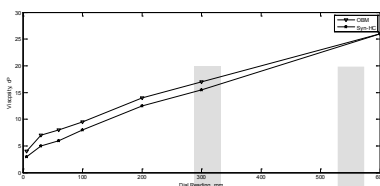
Fig. 5. Dial reading versus viscosities of the muds at 50°c

Similarly, Fig. 8 gives the viscosity reading of the various temperature 50°C indicating that at the climax, OBM and mud made with H. *crepitans* ester measures virtually the same.
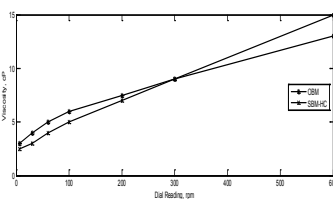
Fig. 6. Dial reading versus viscosities of the muds at 70°c

Fig. 6 gives the viscosity reading of the various temperature 70°C. Here between the control and H. c*repitans* ester, the ester has higher viscosity.
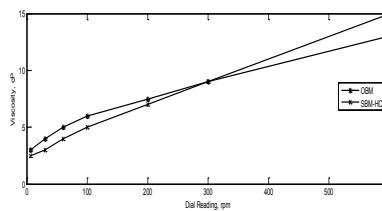

Fig. 7. Dial reading versus viscosities of the muds at 90°c

This fig. 7 indicates that at 90°C, H. *crepitans* has higher, 15 cP while the control at 13 cP. So far, the result shows that temperature increase has the least effect on fossil diesel based mud which is a common trend in drilling mud engineering (Onungwe, 2015).

TABLE 8
pH/TEMPERATURE AND ELECTRICAL STABILITY

Sample	OBM	SBM-HC
pH /Temperature	8.10 @ 28.9°C	8.05 @ 33.7°C
Electrical Stability @ 50°C	468 Volts	399 Volts

Table 8 shows that pH of the mud samples fall within the acceptable range of 8 – 12 otherwise, the mud could corrode drill pipes and valves.
The electrical stability of H. *crepitans* fall a little below the recommended 400 volts of oils based mud. This may be attributed to its synthetic nature and or formulation however, such mud can be bettered by formulating it with an emulsifier that is more resistant to thermal degradation.

TABLE 9
POWER LAW MODEL ANALYSIS

Sample/Parameter	OBM	SBM-HC
n @ 30°C	0.70	0.86
K @ 30°C	84.04	38.73
n @ 50°C	0.61	0.91
K @ 50°C	193.16	13.99
n @ 70°C	0.55	0.70
K @ 70°C	231.27	51.86
n @ 90°C	0.53	0.74
K @ 90°C	168.44	30.31

Table 9 shows that HC mud sample conforms to the Power Law Model of fluids recommended by the API. The fluids are shear thinning (Non Newtonian) with 0.70 and 0.85 as the slope or n for OBM (control), Synthetic Base Mud – HC while their intercepts are 84.04, and 38.73 in that

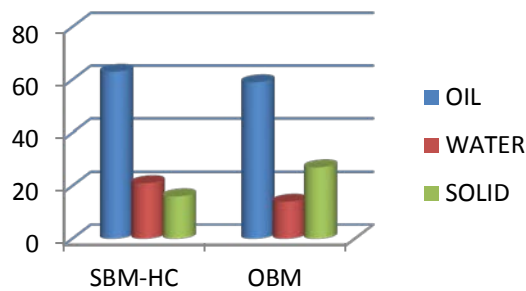order, for the values examined at 30°C. Others are as in the table.

Fig. 8. Oil, Water and Solid Content

Fig. 8 shows the water content of the formulated muds: OBM posses 14% and SBM-HC contained 21%. For sand content OBM was 27% and 16% represented that of SBM-HC.

Also, SBM-HC has the higher oil content of 63%while OBM's oil content was 59%.

4. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

1. The oil yield of the pulverised samples were 51% for *Hura crepitans* and 7% for *Enterolobium cyclocarpum.* This clearly shows that *Enterolobium cyclocarpum* is economically unviable for oil extraction.
2. Ester yield for *Hura crepitans* was 97% while *Enterolobium cyclocarpum* was 23%. The better yields resulted from two-steps process of esterification (pre-treatment) preceding transesterification.
3. OBM had a pH of 8.10 at 28.9°C and SBM-HC was measured to be 8.13 pH. The alkalinity of the formulated muds indicates that they would not corrode or damage downhole equipment.

REFERENCES

1. Growcock, F. B., Andrews, S. L. and Frederick, T. P. "Physicochemical Properties of Synthetic Drilling Fluids" IADC/SPE 27450 Drilling Conference, 1994.

4. The muds aged at 30, 50, 70 and 90 degrees Celsius each exhibited variation in their deformation with fossil or convention diesel based mud most stable.
5. Measurements show that the OBM has 468 Volts and SBM-HC was measured to be 399 Volts. Although the difference from the control is not much, this can be improved by the addition of thermally stable emulsifiers.
6. The retort analysis of the formulated muds shows that SBM-HC had an oil content of 63% 59% for OBM. Their water content vary OBM had 27% and 16% for SBM-HC.
7. The formulated muds conform to the Bingham Plastic and Power Law Models and have acceptable rheological properties.

a. **Recommendations**
1. Further research should be carried on the muds' toxicity, dispersibility and biodegradation to ascertain their true effect on the environment.
2. The mud should be subjected to field test to determine its applicability for drilling operations.
3. The mud were aged at 30°C, 50°C, 70°C and 90°C and the feasibility of older muds may not be guaranteed. Hence, the need to utilise advance technology to age the mud at elevated temperatures to ascertain its true behaviour before a recourse to field application.
4. High pressure high temperature equipment should be used to determine the mud filtration property.

5. Growcock, F. B. and Frederick, T. P. "Operational Limits of Synthetic Muds", Omoco Corp, EPTG Drilling, 1996.
6. Neff, J. M., McKelvie, S and Ayers, Jr. R. C. "Environmental Impacts of Synthetic Based Drilling Fluids", U.S. Department of the Interior Minerals Management Service Gulf of Mexico OCS Region. 1 – 67, 2000.

7. Bankovic-llic, I. B. Stamenkovic, O. S. and Veljkovic, V.B. "Biodiesel Production from Non edible Plants Oils", Renewable and Sustainable Energy Reviews – 16, 3621-3647, 2012.

8. Onungwe, O. S. "Evaluation of Synthetic Mud from Esters of Selected Non-Edible Oils", University of Ibadan, M.Sc. Project. Pp 1 – 129, 2015.

9. Ding, J, He, B and Li, J "Biodiesel Production from Acidified Oils via Supercritical Methanol" energies, ISSN 1996-1073 pp. 1-12, 2011.

10. Da Silva, C. and Oliveira, J. V. "Biodiesel production through non-catalytic supercritical transesterification: current state and perspective." 2014

11. Jiuxus Liu "Biodiesel Synthesis via Transesterification Reaction in Supercritical Methanol: a) A Kinetic Study, b) Biodiesel Synthesis Using Microalgae Oil." M.Sc. Project, Syraccuse University, pp. 1-149, 5-1-2013.

12. Babatunde, A.A., Egmba K.C., Kehinde, A.J. and Falode O.A. "Issues, Trend And Opportunities For The Production Of Bio- Synthetic Paraffinic Kerosene (SPK)", SPE 167542, 2013.

13. Senn, R. B, and Johnson, M. S. (2007) "Interpretation of Gas Chromatography: A tool in subsurface hydrocarbon investigation" Amco Corporation Tulsa Oklahoma, pp.1-27.

14. www. wikipedia.com (February, 2015 and March, 2016).

15. Ababio, O. Y., "New School Chemistry" Africana-Fep Publishers Limited in association with FEP International Private Limited, Onitsha, Nigeria, 2000.
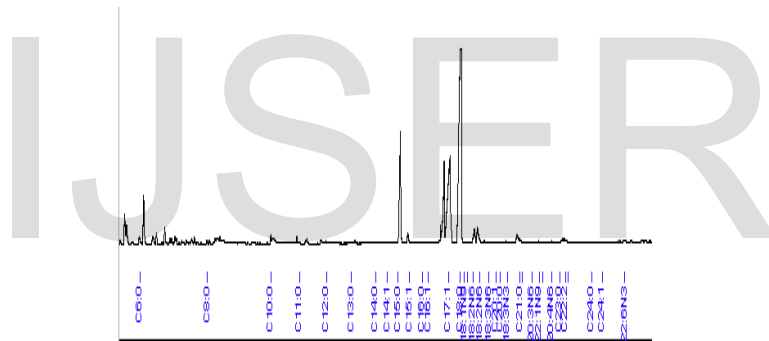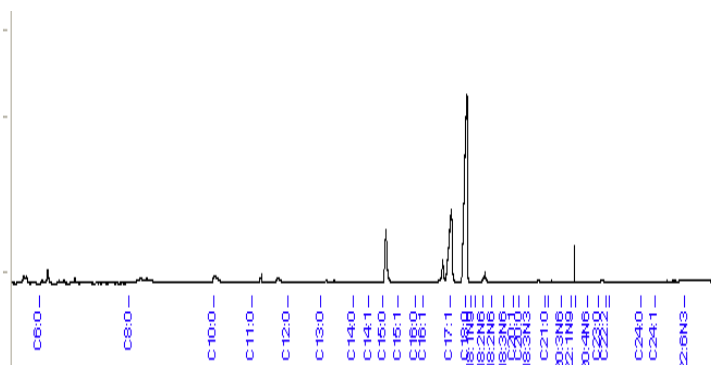
Appendices

Appendix A
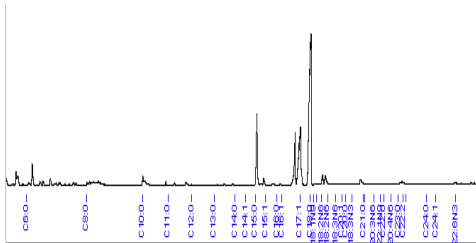
First Fatty Acid Chromatogram of *Enterolobium cyclocarpum* oil

Appendix B

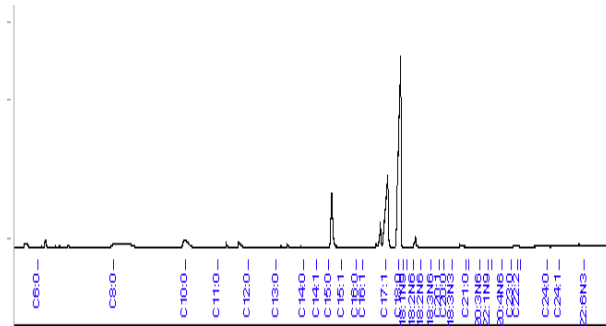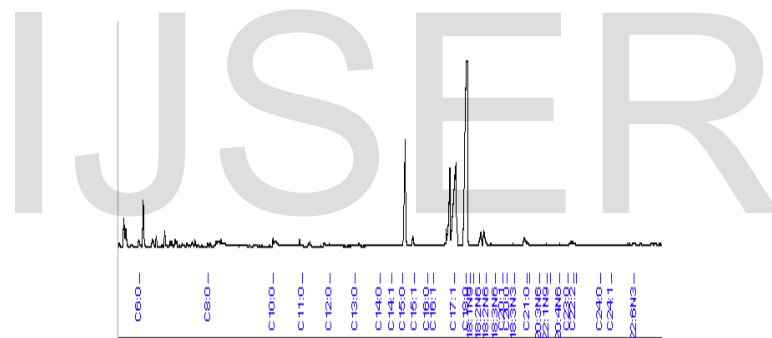Second Fatty Acid Chromatogram of *Enterolobium cyclocarpum* oil

Appendix C

First Fatty Acid Chromatogram of *Hura crepitans* oil

Appendix D

Second Fatty Acid Chromatogram of *Hura crepitans* oil

Appendix B: Fatty Acid Chromatogram of *Enterolobium cyclocarpum* oil