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Research paper

Evaluation and suitability of a biomaterial as oil-based drilling fluids viscosifier using chemical structural properties approach

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Abstract

Mucuna solannie is a locally sourced material in Nigeria and other parts of Africa that enhances the viscosity of a drilling fluid. Due to its effectiveness, studies have been carried out on the structural properties of its seed flour for suitability as additive in oil-base mud. The chemical structures, name and other physiochemical properties of Mucuna solannie were determined using X-Ray Diffraction method, and the Fourier Transform Infrared Spectrometer. The scanned sample of Mucuna solannie was used to confirm the molecular bonding form, chemical structures and certain functional groups as basis of spectrum type. The result showed that Mucuna solannie was close to chitosan with covalent bonded molecular structure having calcium salt alone. It is a crystalline polymer and would require high calorific value to break the bonding energy existing in the molecules. Then, the FTIR discovered some functional groups and the position of carbon-carbon, carbon-hydrogen indicating the double bond.

Keywords: *Mucuna solannie; Chemical Structural Properties; Viscosity; Chitosan Structure; Double Bond.*

1. Introduction

The classification of oil based fluids used for drilling operations is dependent on formation type, and also its requirements. In drilling most intense wells, special kinds of drilling fluids are considered and because of the core firmness of the formation, the term, mud is used [1]. Drilling fluids are made up of different chemical compounds that will perform various functions in drilling operations. It is monitored by the mud engineer to ensure cost effectiveness and that efficiency is at optimum.

Some basic functions of the drilling fluid as relates to rheological properties include; solids removal while drilling or circulating, solids suspension when stationary, pressure drop optimization through annular hole cleaning, and maintain equivalent circulating density.

Hole cleaning, which relates to cuttings removal and suspension depends on the following rheological properties: yield point, yield stress, gel strength and plastic viscosity. Classifications of drilling muds are mostly either water base muds (WBMs) or oil base mud (OBMs), which is determined by the continuous mud phase. Therefore, OBMs can accommodate water and WBMs can also accommodate oil [2]. The drilling muds with oil as its continuous phase are more preferable to those which use water as continuous phase to prevent interaction between the rocks and the drilling muds, particularly drilling under harsh pressure and temperature conditions or reservoir rocks where permeability and porosity are low [3]. For any material to be suitable for oil-base mud viscosity additive, it must contain some percentage of fatty acids. Mucuna called velvet beans contains some fatty acids as shown on the proximate composition measurements (Table 1).

Table1: Proximate Composition (%) [4]

Composition	Value (%)
Moisture	6.02 ± 0.11
Ash	3.60 ± 0.01
Ether extracts	4.52 ± 0.05
Crude protein	25.65 ± 0.14
Crude fiber	7.23 ± 0.05
Carbohydrate (by difference)	42.98
Fatty acids	12.49

Also, according to [5], Mucuna solannie has 20.0 – 25.4% crude protein, 43.5% - 49% carbohydrate, 5.05 – 7.0% fatty acids, 25.0 – 27.4% crude fiber, 46.0% - 14.0% moisture and contains fat (%); raw (dehulled) 6.5±0.26 and cooked 8.3±0.21 [6].

Before experimental analysis is carried out, it is highly recommended to firstly carry out chemical structural properties measurements. Experimental analysis should also be carried out on the reservoir fluid. Also, to determine the reservoir fluid chemical makeup, it should be analyzed and the level of damages that can occur by predictable problems can be modified [7].

The demand for cost efficiency and effectiveness of a drilling fluid using different alternative materials is as old as engineering as a profession [8]. Different local materials have been sourced and experimentally proven to be effective for drilling operations. There are so many local materials in Nigeria and across Africa that researchers have proven to be suitable for drilling fluid formulation, but many are not in use because of the inability to meet American Petroleum Institute (API) requirements as drilling fluid additives.

All functions of a drilling mud are influenced by two most important properties [9]

i) Density; oil and water have various densities hence imported or local materials are also added to increase their densities, such as barite.

ii) Viscosity; oil and water have their own measure of viscosities in which other materials imported or locally made can be added to increase the viscosities, such as Mucuna solannie and snail shell etc.

The proper selection of the drilling fluid additives will determine the success of the operation, so if the fluid system is not properly chemically and structurally analyzed, formulated and monitored, it will be hazardous to the environment and possess a greater danger to the personnel. In the petroleum industry, high pressure and temperature additive material has to be well analyzed for drilling operations [10]. Drilling fluids and their additives are used so as to increase the life span of drilling equipment and reduce the cost of drilling the oil and gas well [11]. The beneficiation of Nigerian bentonite using local materials such as periwinkle, snail shell and Mucuna solannie, according to previous research, has discovered that in order to beneficiate the rheological characteristics of drilling fluids, Mucuna solannie has the ability to do so in the presence of calcium to sodium base composition [12, 13]. Bentonite is the major substance that is used to enhance viscosity and provide the control of fluid loss in a drilling mud. But, with the addition of other additives during the formulation, fluid loss into the formation is minimized and viscosity controlled. It was discovered that these additives help to reduce formation damage, minimize log analysis problems, maintain hole integrity, protect shale sensitivity to water, fluid loss control in the shielded formation and minimize the washing out of hole to attain better job of casing and cementing [14].

Mucuna solannie is a leguminous plant found in Nigeria and other parts of Africa. Mucuna solannie serves different purposes, such as use as additive in local food. It is made up of high percentage of carbohydrates, protein, fiber, low lipids, sufficient minerals, and meet the essential amino acids requirement [8]. The family of Mucuna solannie comprises M. Veracruz, M. sloanei, M. pruries and M. Urensi [15] and as such Mucuna solannie is mostly in use because it is thicker than others in terms of viscosity in culinary. Also, it is used as an additive for the formation of drilling mud since it contains sizeable quantity of sodium and calcium molecules [16]. Experimentation using Mucuna solannie, periwinkle and snail shell as additives to Nigerian bentonite [12], [13] also proves that suitable fraction of nanoparticles and inhibitive ions that are very essential in the stability of wellbore effectiveness and fluid loss control are found in them. The sizes of nanoparticle range less than 100nm shows new or enhanced properties that depend on sizes in relation to the particle of large size having the same material [17]. In another research [18], it was observed that nanoparticles prevent shale swelling as a result of their power to seal smaller holes in shale formation by establishing packed filter cake for the control of fluid loss and the prevention of downhole change in pressure.

Organophilic clay is used in the oil-based drilling mud as a viscosifier and gelling agent to aid support for weight materials and enhance cuttings carrying capacity and cuttings removal. The inclusion of organophilic clay gives a high thermal firmness to oil based drilling fluid, and the potential to swell in an organic medium (gas-oil), and some preferred rheological characteristics including high shear thinning behavior, viscosity, thixotropy and yield stress [19]. Mucuna solannie is a viscosifier having different chemical and structural properties. The viscosifier controls the rheological properties to transmit cuttings through the annulus to the surface and suspend cuttings at low rate of circulation or when the pumps are off for barite sag prevention and cuttings residing at the bottom [20].

Organic polymers are important in drilling mud for fluid loss control, increased viscosity and encapsulation of solids. The sustainability to provide some of the above functions is governed by its molecular structure. Molecular sizes and shapes in the presence of charged sites and stability are particularly important in large molecules (typically 5×10^6) and provide viscosity and some fluid loss control. Some molecules (typically 100×10^3) provide fluid loss control such as carboxyl methyl cellulose. Polymers are anisotropic in nature. The polymer chains have much weaker dispersive forces between them and are covalently bonded along the polymer chain. As a result, polymers can expand by differing amounts in different directions. Conventional molecules in comparison with the different side molecules, the polymer is allowed with hydrogen bonding and ionic bonding which gives rise to proper cross-linking stability. The high flexibility of polymer is dependent on the dipole-dipole bonding side chains. Polymers with Van der Waals forces connecting chains make the melting point of a polymer to be low because of its known weakness.

2. Materials and method

Laboratory equipment/materials used are given in Table 2.

Table 2: Laboratory Equipment and Materials Used for the Measurements

Equipment/Material	Function/Use
X-ray diffraction	Structural analysis
Electronic weighing device	Weight measurement
Measuring cylinder	Base fluid quantity measurement
Mucuna solannie	Viscosifier additive
Fresh water	Used in bomb calorimeter
Pycnometer	Specific gravity determination
FTIR	Chemical bond identification
Variable speed mixer	Mixing of samples
SEM-EDS	Qualitative chemical analysis
Bomb calorimeter	Heat of combustion measurement
Spectrophotometer	Compound concentration measurement
Gas Chromatography Mass Spectrometry (GC-MS)	Detection and analysis of samples
Anhydrous Potassium bromide	Halide salt

2.1. Experimental procedures

2.1.1. Bond length determination using FTIR and SEM-EDS

To determine the bond length, the elements present in the sample were first detected using Scanning Electron Microscopy with Energy Dispersion X-ray Spectroscopy. When used, the SEM-EDS indicated the element present while the FTIR indicated the bond present. A table of bond length was then used to determine the length of each compound that form the whole substance analyzed.

2.1.2. Molecular weight

This was calculated based on the result realized from the X-ray diffraction that was carried out. The XRD brought out the chemical structure which was then used to detect the total compound present and was then used to calculate the molecular weight.

2.1.3. Determination of calorific value using bomb calorimeter

The combustion of a known mass, m, of standard benzoic acid was carried out using the procedure given, with a calibrated instrument known as bomb calorimeter. The heat of combustion of benzoic acid is known to be 26.453KJ/g. According to standard procedure, ASTM D2382-88, oxygen bomb calorimeter (model 6100, Parr instrument Co. Illinois, Moline) was used to measure the gross net of combustion. 1 milliliter of deionized water mixed with approximately 0.1gram of the weighed sample was placed in an adiabatic bomb calorimeter being calibrated. The two electrodes in the pressure (bomb) were connected to a chromel (chromium nickel alloy) wire and ignition takes place when in contact with the sample. The bomb was setup, fastened and removed twice by increased pressure to 0.5MPa with pure (99.99%) oxygen after which it was vented. It was later pressurized to 2.0MPa with pure oxygen to carry out the experiment and 2 liters of water bath in an insulated jacket was used. A uniform temperature was created by circulating the water around the bomb with a motorized stirrer inserted inside the water bath. The electric current was then passed through the chromel wire causing the sample to ignite and burn completely the presence of oxygen with high pressure. The bucket and the bomb were then kept in a calorimeter jacket and used for thermal protection. The result was displayed in the display section (Cal/g) or (MJ/kg) or depends on which unit the user selected. This method was repeated for other samples.

2.1.4. Chemical name and structure

This was gotten by searching through the National Library of Medicine, National Centre for Biotechnology Information data by typing in the molecular formula. Also the structure was realized from the same library.

2.2. Equipment procedure

2.2.1. FTIR

The Shimadzu Fourier Transformation Infrared Spectrophotometer-FTIR 8400S was used to determine the functional unit of the sample. Sample was weighed to 0.01g using a mortar agate. Transparent pallets were obtained when the mixtures were pressed by vacuum hydraulic (Graseby specac) at 1.2psi. The description of the test sample spectrum is done by passing through infra-red the scanned sample, where its continuous signal by indicator that is attached to a computer. The absorption area of 600 to 4000cm-1 was where the sample was normally scanned as seen in Fig. 9. The chemical structure, molecular binding form and definite functional units are the results obtained from the tested and analyzed sample as basic of spectrum type.

2.2.2. SEM and XRD procedures

The procedures are similar in accordance with published works [13].

2.2.3. Spectrophotometer

The T70 PG Instruments' UV-spectrophotometer was used to analyze the samples at different wavelength and absorption. The spectrophotometer was first switched on and allowed to stabilize before the calibration was done using distilled water and a black body. After calibration the wavelength was set to 330nm and the corresponding absorption was displayed after pressing the key for absorption. This step was followed for other wavelengths until it got to 900 nm.

2.2.4. Gas chromatography - mass spectrometry (GC-MS)

GC analysis sample was carried out with the aid of gas chromatography (Perkin-Elmer 8500). Temperature programme and column requirements are outlined in this manner; column material- stainless steel (S.S), column SE30 (10%) on chromosorb® W, internal diameter- 1/8 inch, column length- 4 meters, injector temperature- 300^{o}C, FID temperature- 300^{o}C, flow rate of N_2- 30ml/minute, temperature programming- 100-250^{o}C with 5^{o}C/minute increase in temperature and finishing hold time of 5 minutes.

2.2.5. Specific gravity procedure

Washed, dried and weighed 50ml Pycnometer bottle was used for the test. The bottle was filled with water and weighed, and the reading was taken. The sample was also weighed by emptying, drying and filling the bottle with the sample. The reading was also taken.
The procedure is as follows:

i) First the Pycnometer was completely filled with liquid, and the mass of the liquid in the Pycnometer determined. Once this value has been determined, the volume of the Pycnometer V_{ges} is known.

$$V_{ges} = \frac{m_{1fl}}{\rho_{fl}} \quad (1)$$

ii) Next (after the Pycnometer was emptied, cleaned, dried and brought to the required temperature), the Pycnometer was filled to about 2/3 with sample material; this yields the mass of the powder ms.
iii) The next step was to fill the Pycnometer the rest of the way with liquid and weighed again, which gave the combined mass of the sample with the liquid m(fl+s).
iv) The difference between Step iii and Step ii gave the mass of the liquid.
v) The volume of the liquid, was, hence determined by the ratio of the mass of the liquid and the its density
vi) The volume of the powder was then found as the difference between Step i and Step v.

3. Results and discussion

The chemical structures and other properties are given in Table 3 and the data were obtained from Figures 8 and 9 as shown in the appendix. The chemical structure properties of Mucuna solannie are similar to that of chitosan and the closest is Tricosanol with the covalent bonded molecular structure as shown in Fig. 10. The covalent bonded molecular structure shows that it is a good candidate for viscosity builder additive. Also the percent fatty acids content and elemental composition as shown in Figs.11 and 12 signifies that Mucuna solannie is also good for emulsion stability because of fatty acids concentration and borehole inhibition and stability due to the quality of the elemental composition of Mucuna solannie.

Table 3: Structural Properties of Mucuna Solannie

Botanical name	Mucuna solannie
Chemical name	Tricosanol
IUPAC Name	Tricosan-12-ol
Chemical formula	$C_{23}H_{48}O$
Specific gravity	0.4806
Molecular weight	340.627g/mol
Bond length (Å)	0.625
Total bond	71
Surface area	20.2 m^2/g
Calorific value	17.2186 MJ/kg

The main reason for the determination of the structural properties such as the bond length, molecular weight, calorific value was to know or evaluate the suitability of Mucuna solannie mud as a viscosity additive in an oil base mud.
Fig.1, Fig.2, Fig.3 and Fig.4 show the effect of calorific value, bond energy, bond length and molecular weight on viscosity respectively for Mucuna solannie mud.
Mucuna solannie exists in a covalent bond as seen in Table 4 because of the ability of the carbon– hydrogen–oxygen molecular bond to share valence electrons at their outermost shell during polymerization. Figs. 6 and 7 show the degree of bond length and bond energy respectively for each of the bonded elements in their chemical composition. The lower the bond length, the higher the bond energy as shown in Fig. 5. Oil well drilling fluids such as organophilic clay has similar characteristics with Mucuna solannie due to the presence of nanoparticles.
For the Mucuna solannie mud, the viscosity increases as a result of;
i) Increase in the calorific value. It was calculated in terms of energy, the stronger the bond the more energy required to form or break the bond. Since Mucuna solannie is a crystalline polymer, similar to polyethylene which has high melting point, it will require high calorific or heating value as seen in Table 5 to break the bonding energy existing in the molecules. It also has high carbon content that gives temperature stability.

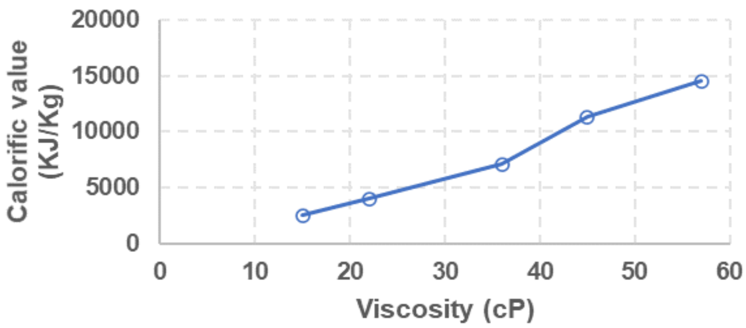

Fig. 1: Effect of Calorific Value on Viscosity for Mucuna Solanine.

ii) Increase in the bond energy. It is ruled by the power of intermolecular forces and mostly by the shapes of the fluid molecules. Fluids that can form hydrogen or whose molecules are polar tend to be more viscous than fluids of non-polar substance. The dynamics of hydrogen bond dominates the intermolecular forces as hydrogen bonds form or break during the motion of the molecules and thereby influences the shear viscosity.

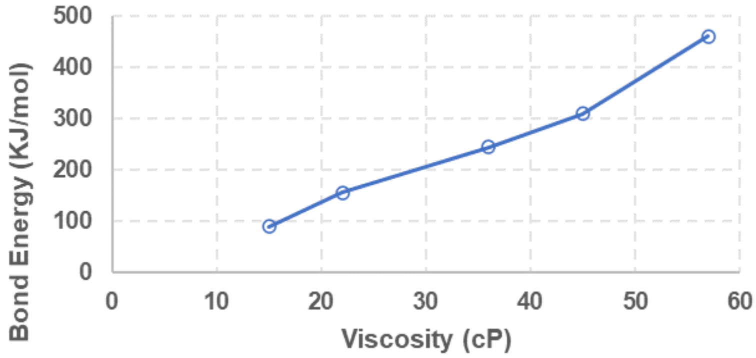

Fig. 2: Effect of Bond Energy on Viscosity for Mucuna Solanine.

iii) Decrease in the bond length. The shorter the bond, the stronger the strength. Larger particles do not slide pass each other more easily than the smaller molecules. The larger molecules have strong intermolecular forces known as London forces that bring them together to one another with greater power. This obstructs molecular flow which gives rise to higher viscosity. It is the length the electrons share to reach the equilibrium distance. Bond length occurs when there is overlap between valence orbit. Electron being shared or transferred form a cloud around the nucleus of the atom.

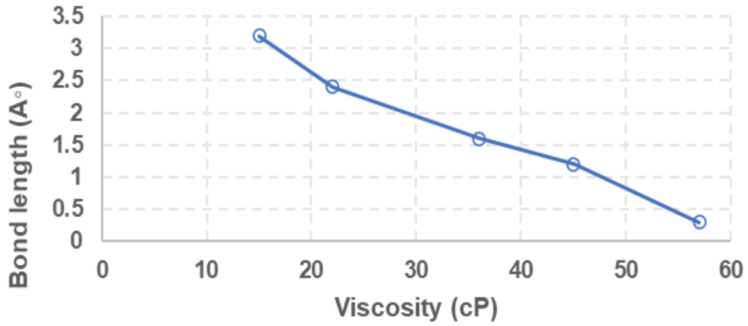

Fig. 3: Effect of Bond Length on Viscosity for Mucuna Solanine.

iv) Increase in the molecular weight. The viscosity of Mucuna solannie mud increases with high molecular weight using conventional method. The larger the chains, the harder it is to get them to flow because they are more entangled.

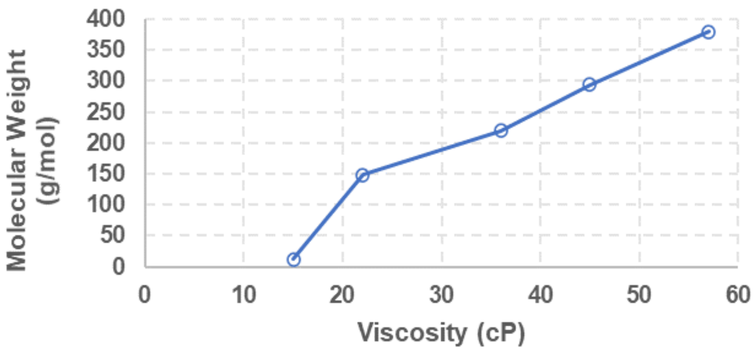

Fig. 4: Effect of Molecular Weight on Viscosity for Mucuna Solanine.

Fig. 5 shows the relation between the bond length and the bond energy. The higher the bond length, the lower the bond energy. The point of intersection between the bond length and bond energy is called equilibrium distance. At this point, there is equal attraction and repulsion. From the graph, at 1.44Å and 355KJ/mol, the viscosity is high.

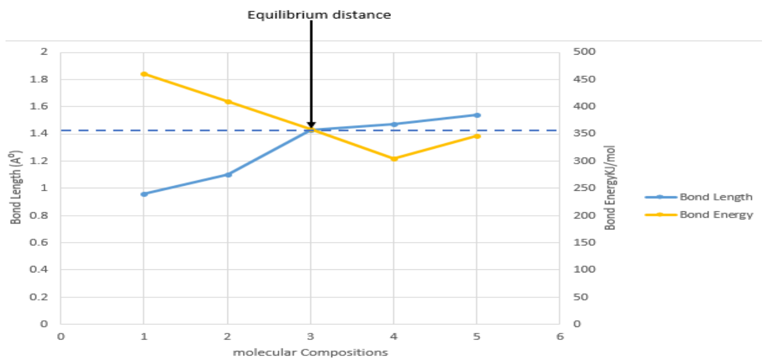

Fig. 5: Comparing the Bond Length and Bond Energy as A Function of Their Molecular Compositions.

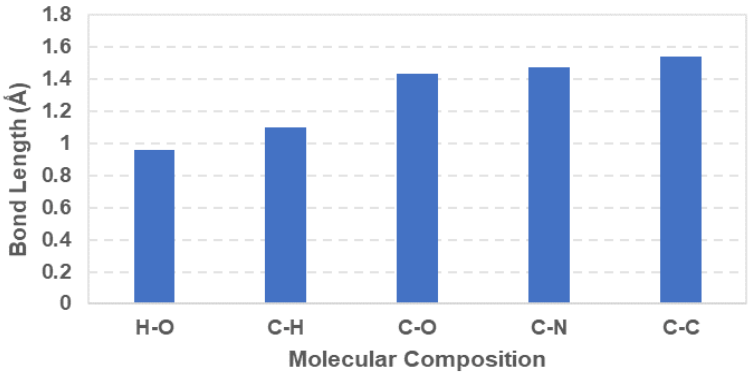

Fig. 6: Molecular Compositions of Mucuna Solannie at Different Bond Lengths.

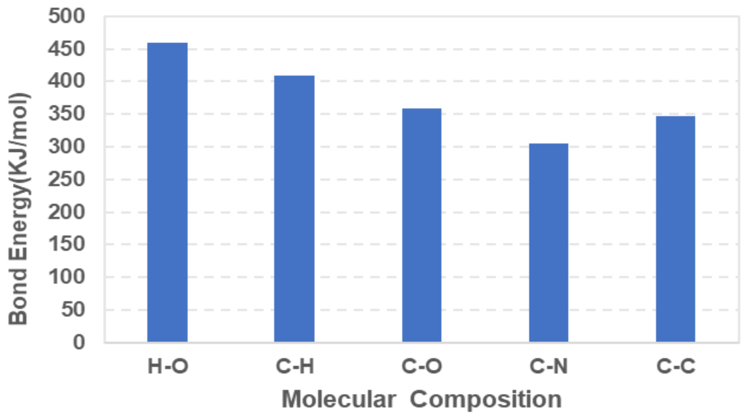

Fig. 7: Molecular Compositions of Mucuna Solannie at Different Bond Energies.

4. Conclusion

From the chemical evaluation, it has been shown that Mucuna solannie mud additive is an organic polymer which belongs to the family of the simplest polymer with high melting point. The larger the bond chain to increase the molecular weight, the higher the resistance to flow (viscosity). Similarly, the bond that exists in the chemical composition of Mucuna solannie is covalent in nature which gave rise to higher bong energy with lower bond length. Also, the calorific value is high because of the possession of stronger bonded energy. Mucuna solannie is a double bonded additive which makes it similar to organophilic clay which is a drilling fluid additive that increases viscosity. Some of the findings also show that Mucuna solannie contains some fatty acids which makes suitable for oil base mud additive. Moreso, the qualitative elemental composition of Mucuna solannie makes it a good candidate for borehole stability. Finally, equilibrium distance of Mucuna solannie makes it very suitable as a viscosity builder oil base mud additive.

5. Declaration of interest

No conflict of Interest has been declared by the authors

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Appendix

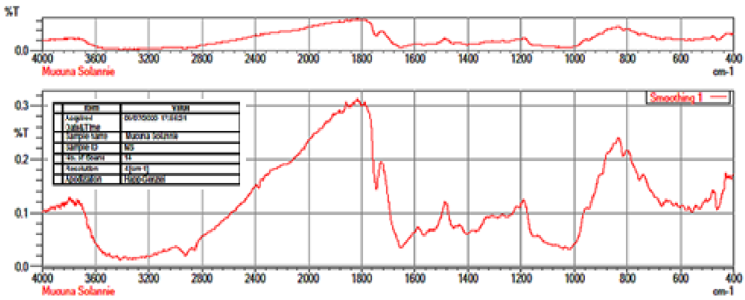


Fig. 8: Absorption Area of Mucuna Solannie During Scanning.

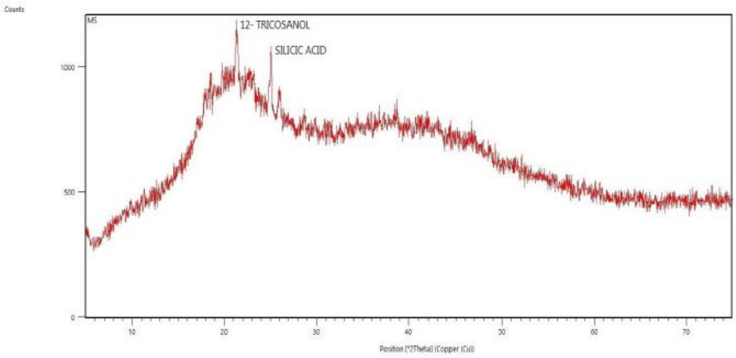


Fig. 9: 12-Tricosanol Graphics Representation.

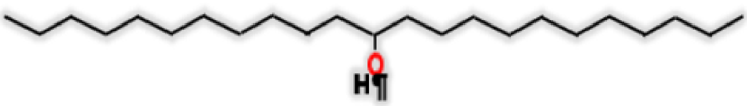
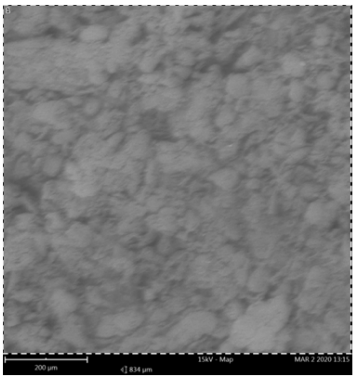


Fig. 10: Molecular Structure of Tricosan-12-Ol Covalently Bonded.



Element Name	Element Symbol	Element Number	Atomic Conc.	Weight Conc.
Potassium	K	19	28.87	39.17
Carbon	C	6	35.26	14.70
Phosphorus	P	15	7.35	7.88
Zinc	Zn	30	2.80	6.38
Iron	Fe	26	2.64	5.10
Sulfur	S	16	4.53	5.06
Calcium	Ca	20	3.26	4.54
Yttrium	Y	39	1.16	3.55
Titanium	Ti	22	1.83	3.07
Chlorine	Cl	17	2.18	2.71
Oxygen	O	8	3.75	2.07
Silicon	Si	14	2.01	1.94
Aluminium	Al	13	1.88	1.78
Magnesium	Mg	12	1.38	1.18
Sodium	Na	11	1.07	0.85

Fig. 11: Scanning Electron Micrograph Mucuna Solanine.

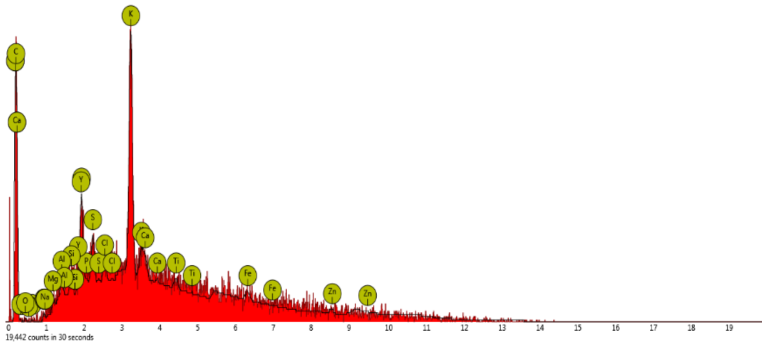


Fig. 12: Elemental Composition of Mucuna Solanine.

Table 4: Bonding Nature of Molecules of Mucuna Solannie

Bond	Bond order	Bond length (Å)	Bond energy (KJ/mol)
H-O	1	0.96	460
C-H	1	1.10	410
C-O	1	1.43	358
C-N	1	1.47	305
C-C	1	1.54	347

Table 5: Structural Properties of Mucuna solannie

Viscosity (cP)	Calorific value (KJ/mol)	Bond energy (KJ/mol)	Bond length (Å)	Molecular weight (g/mol)
15	2500	90	3.2	12
22	4000	156	2.4	148
36	7100	245	1.6	220
45	11300	310	1.2	294
57	14500	460	0.3	380