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Carboxymethylation of Icacina trichantha Oliv.Tuber Starch and Its Use as a Viscosifier and Fluid Loss Control Agent in Water Based Mud

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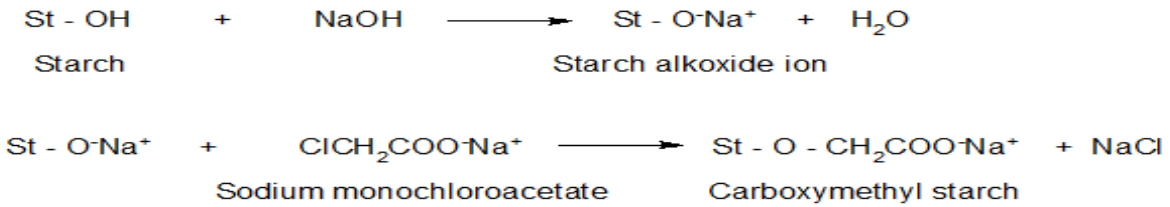
Abstract
Starch from a non-food wild plant- *Icacina trichantha oliv*.tuber was extracted, characterized and chemically modified by carboxymethylation to produce two new derivatives of two different degrees of substitution. The derivatives were used in the preparation of water based muds. The rheological and filtration properties of these new muds were compared to those of muds prepared with the underivatized native starch and a commercial drilling starch using viscometric and fluid loss methods. Experimental results showed that the new muds have better filtration control behavior and viscosity than those of the native and commercial drilling starches. The values of flow index of the new muds were found to be less than 1.0, showing non-Newtonian and Pseudoplastic flow behavior of drilling muds. Yield stress of the muds increased with the modification. Viscosity decreased with increasing shear rate, showing shear thinning behavior of drilling muds. The new muds were found to obey the API models for static filtration as well as Power law and Herschel–Bulkley models for fluid rheology.
Keywords: *Icacina trichantha oliv*.;Carboxymethyl starch; drilling mud; filtration; rheology.

1. INTRODUCTION

Starches for drilling and other industrial operations are mostly sourced from the staple food crops such as rice, wheat, corn, millet, potato, cassava etc. This has undoubtedly contributed to the recent global food shortage.In the bid to tackle this, many developed and developing countries haveshifted attention to alternative resource and local content development. Sources of industrial raw materials that would not compete with food are now encouraged. This has made researchers to go as far as even utilizing agricultural waste for industrial raw materials. Akaranta and Osuji, (2009) utilized orange mesocarp cellulose in drilling mud formulation. Corn cob cellulose has also been successfully used in drilling mud formulation used by Nmegbu and Bekee, (2014).Omojola, (2013) studied the production and modification of wild Taccastarch for industrial purposes. Appropriate agro waste modifications has conveniently been utilized as binding agents, viscosity enhancers, antioxidants, inhibitors, resins pigments etc. in industries (Akaranta, 2007).

Icacinatrichanthaoliv.(ITO) plant is a non-food small shrub which has climbing stem of about 1.5m and produces an oval tuber that weighs up to 3kg at full maturity (Ogunwa *et al.*, 2016). The use of carboxymethyl starches as fluid loss agent and viscosifier is well documented probably because of their excellent swelling ability. They are water soluble polysaccharides which are biodegradable and non-toxic, hence they are widely used as additives serving as thickener, binder and emulsifying agent. However, carboxymethylstarch derivatives of different starches differ in their physicochemical attributes. The major contributing factors to this differences isthe native starch origin (Jie*et al.* 2004; Moorthy*et al.* 2006) and chemical modification conditions such as reaction conditions and degree of substitution(Xie*et al*., 20015).

Chemical modification by carboxymethylation is in essence etherification reaction (Carey, 2003). This reaction inserts the hydrophilic carboxymethyl group into the glucose unit of the starch molecules to stabilize it in aqueous media and also prevent retro-gradation at low temperature (Simon *et al.* 2012). It involves two successive steps as shown in scheme1. The first step involves generation of reactive starch alkoxide ion in a strong alkaline medium and second step isreaction of Sodium monochloroacetate(SMCA) to form carboxymethyl starchderivative.



Scheme 1: Carboxymetylation of Starch with SMCA

Studies on biodegradable polymers such as starches and their use in water-based drilling fluids (muds) have been carried out (Chike-Onyegbula*et al.*, 2012;Kok and Alikaya, 2003; 2005; Alderman et al., 1988; Gray and Darly, 1980). Most of these studies focused on the effects of temperature, concentration and pressure on the

rheological and filtration behavior of these polymers when used in drilling muds. Gray and Darly, 1980 drew a conclusion about two filtration parameters of a given mud, thatsoptivity and diffusivity are dependent on temperature. This work considered a novel non-food starch source (ITO tuber) and studied on the suitability of its carboxymethyl starch derivative as viscosifier and fluid loss agent in Water Based Muds (WBMs). The carboxymethyl starch derivatives were compared with the unmodified native starch and a commercial drilling starch in terms of their physicochemical properties and the rheological-filtration performances as viscosity enhancer and fluid loss agent in water based mud. The effect of two different degree of substitution was also considered.

The concept of sorptivity and diffusivity aids the use of mathematical models to describe the filtration behavior of drilling muds whereas that of shear stress and shear rate and their measurement aids the mathematical description of the flow of drilling muds.The API static filtration model which states that for any static filtration, the total fluid loss is directly proportional to the square root of time was used to characterize the filtration property of the various muds prepared. On the other hand, Power law- a two parameter model which relates shear stress to shear rate in a non-linear manner (Alderman et al., 1988; Okafor, 1992) and Herschel-Bulkley- a three parameter model which describes the behavior of yield-pseudoplatics fluids (Mewis et al., 1989) were used for the rheological properties of the various muds.

The API model;$V = St^{1/2}$……1

Where V is total fluid loss volume, S is sorptivity of the fluid and t is time of filtration.

Power law model; $\tau = K\dot{\gamma}^{n}$ ……..…2

Where: τ = shear stress, $\dot{\gamma}$ = shear rate, K = consistency index and n= flow behavior index.Taking logarithm of equation 2, we have: $\log \tau = \log k + n \log \dot{\gamma}$……..3

Thus, n = slope and k = intercept.

Herschel- Bulkley model; $\tau=\tau_o+ K\dot{\gamma}^{n}$ 4

Whereτ is the shear stress,$\tau_o$is the yield stress,k is the consistency index,$\dot{\gamma}$is the shear rate, and n is the flow index.

2. EXPERIMENTALS

2.1 Sample Collection/Starch Extraction: Fresh ITO tubers were harvested in Obe and Odidama the village forest in Agulu town, Anaocha Local Government Area of Anambra State, Nigeria. The starch was extracted by wet milling process as described by Ogunwa *et al.*, (2016). The physicochemical properties; starch granule Size (µm), pH,IR Spectroscopy, Water Absorption Capacity WAC (%), Swelling Power SP(%), Gelatinization Temperature GT (^oC) and Amylose Content (%) were determined on the starch and recorded in table 2.

2.2Synthesis of ITO CarboxymethylStarch: Carboxymethylation was conducted by the combined methods ofNattapulwat*et al,* 2009 and Stojanovic*et al,* 2005. 40g of ITO native starch was suspended completely in 120ml Isopropanol and 7ml of aqueous 11.5M NaOH was added in drop-wise manner with continuous stirring for 1hr at room temperature. Sodium monochloroacetete (SMCA) was added at two different concentrations of15 and 28g. The reaction mixture was then heated and held at 50^{o}C for 2hrs. The pH of the mixture was then adjusted to about 5 by adding 50% glacial acetic acid. The resulting Carboxymethyl starch mass was recovered and washed with aqueous ethanol (80%). The modified starch was dried in oven at 50^{o}C for 6hrs. The Degree of Substitution (DS) done by the method of Stojanovic*et al,* 2005. The carboxymethyl groups substituted on the starch were first converted to acid form by adding 30ml of 6M HCL per 10g of modified starch suspended in Methanol with continuous stirring for about 30mins. The acidified starch was recovered with Buchner funnel and vacuum pump, washed thoroughly with Methanol and was then dried in the oven at 50^{o}C. About 2-5g of the modified starch was weighed into 30ml distilled water to make a suspension and was then made alkaline by adding 20ml 0.2M NaOH. The whole mixture was transferred to a 100ml volumetric flask and made up to mark with distilled water. 25ml of the solution was taken in a conical flask and titrated with 0.04M HCl using phenolphethalein indicator. The titration was replicated three times and average titer value used for calculation. A blank was conducted following the same procedure but without the starch sample.

$$DS = \frac{162 \times nCOOH}{md_s - 58 \times nCOOH} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

$$md_s = \frac{(1 - W_{water})ms}{100} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 6$$

$$nCOOH = (V_b - V)C_{HCl} \times 4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 7$$

Where: 162 – Molar mass of anhydrous glucose unit (g/mol), nCOOH – Amount of COOH (mol), md_s – Mass of dry sample (g), ms – Mass of sample taken (g), W_{water}– Moisture content of sample (%), V_b– Volume HCl used for blank (ml), C_{HCl}– Concentration of HCl (mol/l), V – Volume of HCl used for sample (ml), and 4 – Ratio of total solution volume (100ml) and the volume taken for titration (25ml). Two different degree of substitution were achieved for this study.

2.3Formulation Technique

The industry standard measurement for preparing water based drilling fluid sample is based on pound per barrel (lb/bbl) units. One lb/bbl is the equivalent of pound of additive in 42 US gallons of mud. The SI unit is kg/m^{3}for clarity i.e. 10lb/bbl = 28.5 kg/m^3**.** Base on this, the proportions of other additives would be determined. The additives and concentrations and their functions in the drilling fluid as used for this work were patterned after Hamilton (2001).

Table1: Formulation for One Barrel of mud

Additive	**Concentration/Quantity**	**Function**
Water	316.4	Base fluid
Caustic Soda	0.2g	Alkalinity control
Soda ash	0.2g	Calcium ion removal
Modified, unmodified and a commercial starch	2.0g	Filtration control
Xanthum gum	2.8g	Viscosifier
Potassium Chloride	18g	Inhibition control
Barite	76.8g	Weighting agent

2.4 Preparation of Drilling Mud Samples with various Additives.

The method of preparation described by Egun *et al*., 2013 was used with some variations. Appropriate quantities of additives (table1) were measured into the base fluid in the order listed in table1 while stirring continuously with a beach mixer. The additives were added at a control mixing time of 2mins for each. The preparations were done in turns with the unmodified native starch, the new starch derivatives and the commercial drilling starch giving rise to four different mud samples.The mud samples were coded as ITON; Mud with native starch, ITO-CMS1; Mud with lower DS carboxymethyl starch, ITO-CMS2; Mud with higher DS carboxymethyl starch, and C-STARCH; Mud with commercial starch.

2.5 Rheological Tests by Viscometric method

The rheology was measured with Fann viscometer (model 35) fitted with spring and bob.The drilling fluid was prepared according to the specified recipe. The fluid was poured into the viscometer cup and rheological readings measured at room temperature.The readings were taken with Fann model viscometer at 3, 6, 100, 200 and 600rpm.The Plastic viscosity PV and Yield point YP were calculated using these expressions:

$PV = \theta_{600} - \theta_{300}$……8

$YP = \theta_{300} - PV$……9

2.6 Determination of Gel Strength

Fann viscometer (model 35) fitted with standard spring and bob was used for this measurement.Each of the prepared drilling mud was poured into the viscometer cup at room temperature and the rotor sleeve immersed to the scribed line.The fluid was agitated for 10s at 600rpmand then at 3rpm. The maximum reading attained at 3rpm was noted as the initial gel strength at 10s. This was also repeated for 10mins at 600rpm and at 3rpm and the maximum reading attained at 3rpm was noted as the gel strength for 10 minutes.

2.7 Filtrate (Fluid loss) Measurement

Fann Low Temperature Low Pressure (LTLP) Filter Press was used for this measurement.Each part of the cell was put together as specified in the equipment operations manual.The mud samples were placed in the sample cell and operating pressure set at 100psi. The filtrate volume collected at 5minutes intervals until 30minutes elapsed at thispressure were measured with a graduated cylinder and recorded in table 3.

3. Results and Discussions

The difference in the FT-IR Spectrum of ITO Carboxymethyl Starch and that of the native starch indicating modification is clearly seen in figure 1. The presence of a new peak at 1743.65cm^{-1}and strong absorption band at 1610.56cm^{-1} are due to the COO^-group (Carey, 2003). Nattapulawat*et al.*, 2009 recorded such peaks for the IR analysis of carboxymethyl yam starch.This is an evidence that hydroxyl group of the native starch was replaced with the carboxyl group during modification.

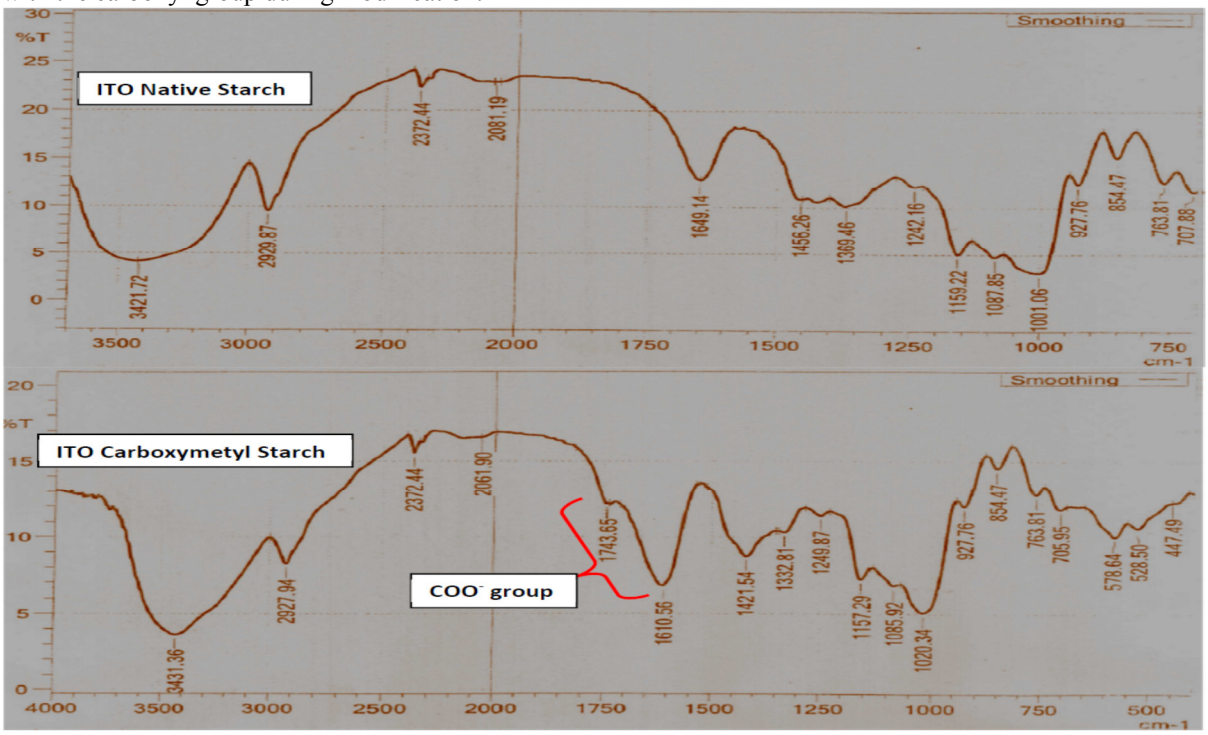


Fig. 1: IR-FT Spectra of ITO native starch and ITO carboxymethyl starch.

3.1 Physicochemical properties

The physicochemical properties of native ITO starch and its carboxymethyl derivative are recorded in table 2 below.

Table 2: Physicochemical properties of native ITO starch and its carboxymethyl derivative

Samples/Products	WAC (%)	Gelatinization Tempt (^oC)	pH	DS
ITON	108.93	77	5.01	0
ITO-CMS1	457.35	68	5.06	0.41
ITO-CMS2	521.30	62	7.52	0.59

Samples/Products	Swelling Power (SP)				
	50ºC	60ºC	70ºC	80ºC	90ºC
ITON	11.71	11.95	12.73	23.72	30.77
ITO-CMS1	27.93	32.67	36.58	80.12	82.70
ITO-CMS2	29.92	39.22	40.63	82.02	82.76

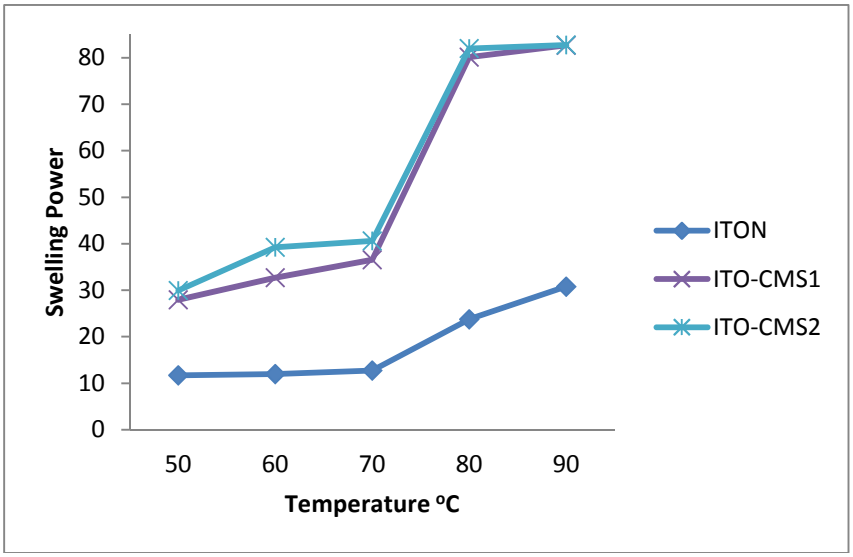


Fig. 2: Swelling Profile of ITO native Starch and Carboxymethyl Derivatives

From table 2, tremendous increase was observed %WAC and the SP, and more so, these parameters increased with increase in DS. The marked increase in the SP with temperature can be seen on the swelling profile in figure 2. This agreed with Nattapulawat*et al.*, (2009) and Wurzburg, (1986)that the swelling power of carboxymethyl starches generally increases with the DS due to the hydrophilicity of the carboxymethyl groups which makes it possible for more water to penetrate into the starch structure. This thickening and the stabilizing ability makes it widely used in the oil and gas industry as mud additive. On the other hand, gelatinization temperature was found to reduce with the modification and even further at higher DS.Tatongjai and Lumdubwong, (2010) suggested that this could possibly be due to the reduction in the melting point by higher density of negatively charged carboxymethyl groups which tend to cause greater electrostatic repulsion between the substituted starch chains.

3.2 Rheological Tests

Rheology describes the flow properties of a drilling mud and is necessary for removal of cuttings while drilling. The rheometerdial readings were obtained for Mud ITON, C-STARCH, ITO-CMS1 and ITO-CMS2 are recorded in table 3. From the dail readings, the Plastic Viscosity PV and Yeild Point YP were calculated with equations 8 and 9 respectively.

Table 3: Viscometer Dial Readings of the various Mud samples

Samples	ITON	ITO-CMS1	ITO-CMS2	C-STARCH
Rheology Tests				
Speed (rpm)	Viscometer Dial Reading			
600	63	71	76	62
300	54	61	65	55
200	50	56	58	50
100	42	45	48	43
6	24	24	24	22
3	15	21	20	19
PV	9	10	11	7
YP	43	51	54	48

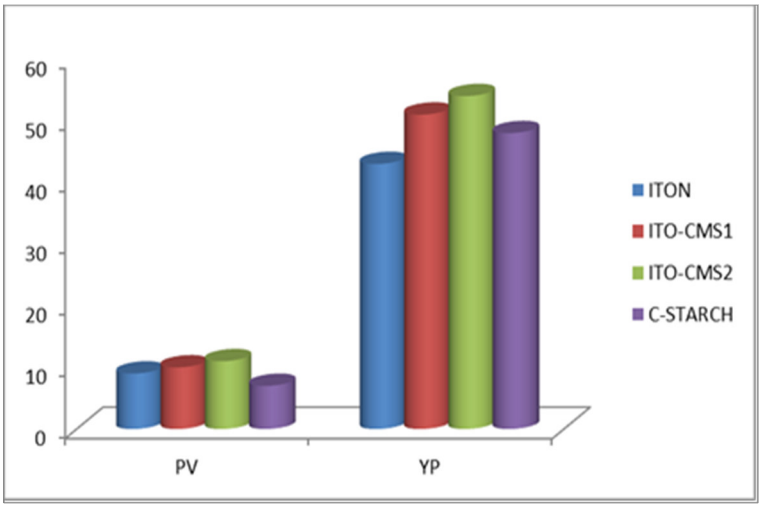


Fig. 3: PV and YP of the various Mud samples

The PV of a mud is a measure of the resistance to flow caused by the shearing action of the liquid itself, the mechanical friction between the mud solid content, and between the solids and the liquids surrounding them. In a given mud system, a change in the PV usually indicates a change in the solids content. It is an indication of inter-particle attraction while the mud is in motion. Functions such as carrying cuttings out of the hole are influenced by YP (Biltleston and Guillot, 1991; Beroid, 1997). Figure 3 showed that the modification was able to improve both the PV and YP of the native starch.

Power law and Herschel -Bulkley models of shear stress versus shear rate curves (figures 4)were produced for each mud sample to test their fitness with the actual measurement, determine the Flow index (n) and the Consistency index (k).The curves showed little or no difference between the power law and the Herschel-Bulkley model's estimations for each mud. It can be seen that the rheological curve (dotted lines) formed by the actual measurement showed very good fitness with those of the test models. The high level of fitness are evident in the values of R^2 (coefficient of determination), and also in the very low values of standard error SE recorded for each mud. The curves showed that the shear stress and shear rate were related in a non-linear manner; hence the muds obeyed the power law model and Herschel- Bulkley model for non-Newtonian fluids (Equations 2 and 4 respectively).

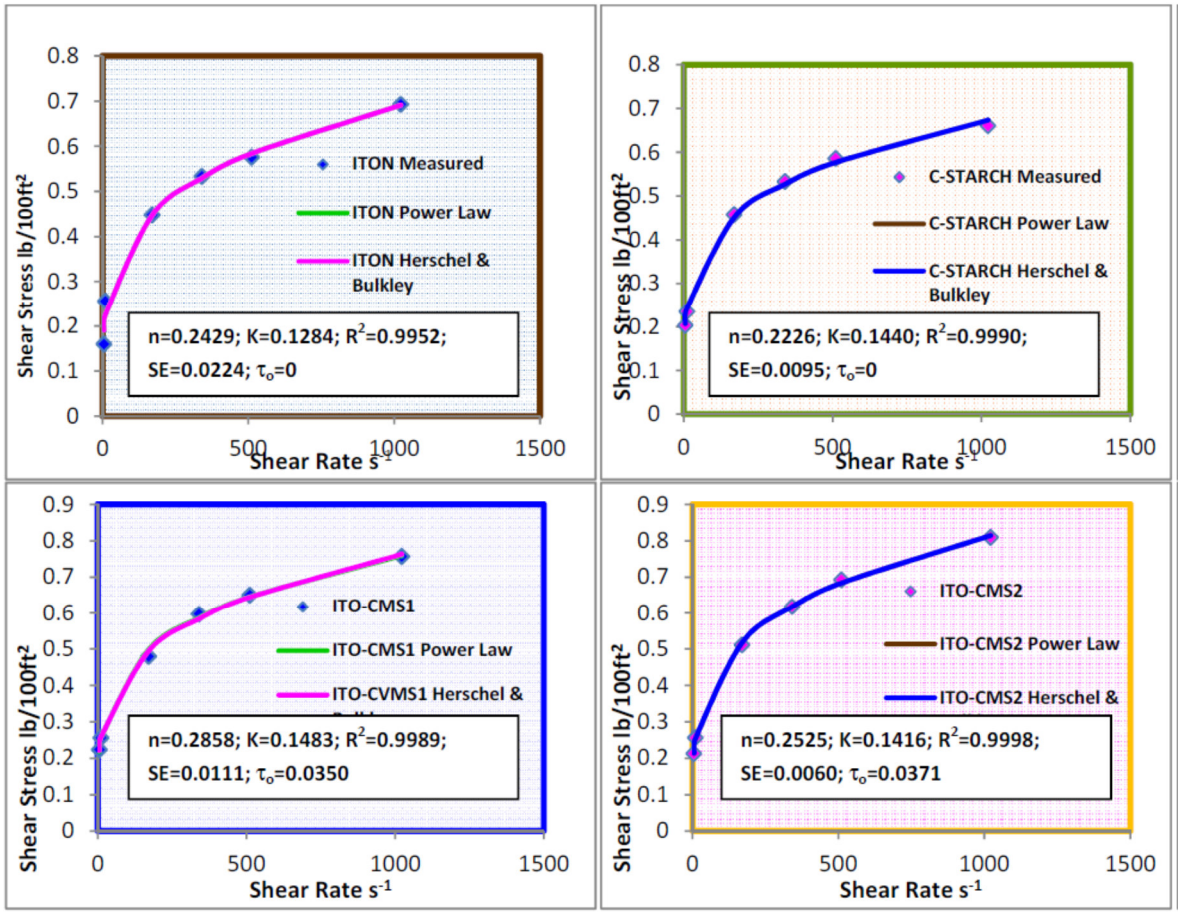


Fig. 4: Modeling of the rheological behavior of the various muds

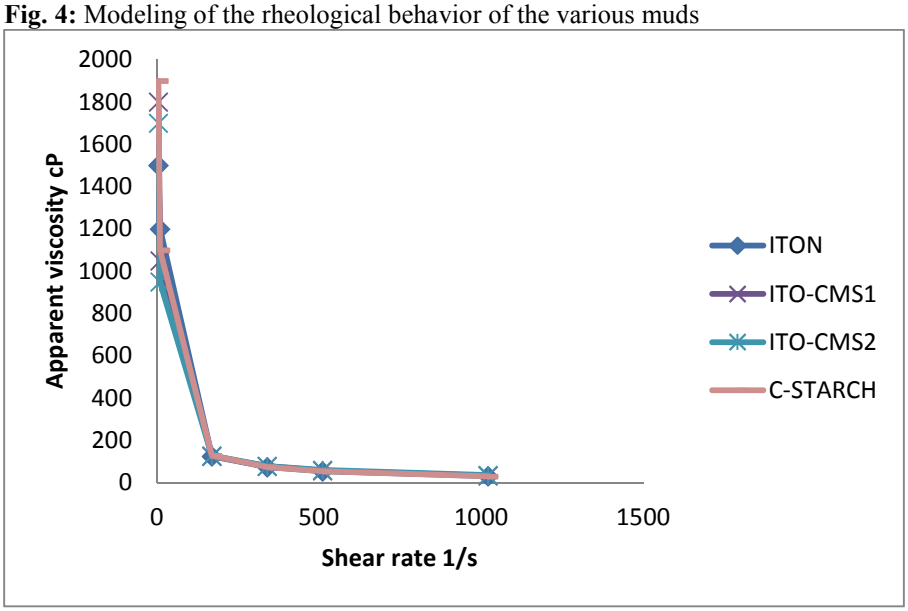


Fig. 5: Plot of Apparent viscosity vs. Shear rate

According to Mewis*et al*., (1989), fluids for which n value is less than 1 (n < 1) is said to have pseudo plastic flow behavior which is typical of drilling muds. Further examination of figure 4showed that muds with modified starches have higher *k*values. This may be due to the fact that the chemical modification caused increase in the viscosity of the mud samples, which increased their resistance to the applied rate of shear or force (shear stress), which then gave rise to an increase in consistency index. The low *k* index of all the muds generally indicates high pumpapility(Beroid, 1979),which improves mud circulation and down hole cleaning.

The yield stress $\tau_o$increased with starch modification and even increased further with higher DS.Plot of Apparent viscosity against shear rate (figure 5) revealed that the muds exhibit thixotropic property, the shear-

thinning behavior of drilling muds.

Gel strength values at 10secs and 10mins are presented in table 4. Gel strength relates to functions like suspension of cuttings when circulation is lost. From the table 4, it is obvious that carboxymetylation lowered the gel strength of the mud. However, the lower the gel strength, the lower the pump pressure needed for circulation start up after rest.Lower pump pressure would mean lower energy consumption and reduced frequency of pump break down.

Table 4: Gel Strength

Samples	ITON	ITO-CMS1	ITO-CMS2	C-STARCH
		GEL STRENGHT		
10 Seconds	21	20	19	24
10 Minutes	26	24	24	26

The amounts of filtrate collected for Filtration test on each mud sample at different time are recorded in Table 5. A good drilling mud must not have filtrate loss above 15ml at 30mins (API, 1993).Mud prepared with ITO-CMS2 had the best fluid loss control which seen in the lowest sorptivity value, followed by that of ITO-CMS1. It is seen that higher DS ITO-CMS had positive effect on the mud regarding the filtration behavior. Mud prepared with C-STARCH recorded lower filtrate loss than that with the native raw starch.

Table 5:Filtration test

Samples		ITON	ITO-CMS1	ITO-CMS2	C.STARCH
		FILTRATION TEST			
Time (mins)	$t^{1/2}$	**Amount of Filtrate (cc)**			
0	0	0	0	0	0
5	2.2361	4	2	1	3
10	3.1622	5	3	2	4
15	3.8729	6	4	3	5
20	4.4721	7	4	3.5	6
25	5.0000	8	5	4	7
30	5.4772	9	5	4	7
Sorptivity (ml/mins^2) from modeling		**1.5877**	**0.9504**	**0.8110**	**1.3293**

The curve modeling in figure 6 followed linear regression for all the mud samples confirming the API law of static filtration (equation 1) which states that volume of filtrate loss is directly proportional to the square root of time taken. The new model equation becomes:

$$Q = \boldsymbol{a}T + \boldsymbol{b} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 10$$

Where Q is the quantity of filtrate, ***a*** corresponds to the sorptivity value which is different for each mud sample, T is square root of time and ***b*** is a correcting value. When the Coefficient of determination (R^2)approaches one and percentage error (%E) is less than 10% as shown in figure 6 for the various muds, it is an indication of good fit of the predicted values with the actual measurement.

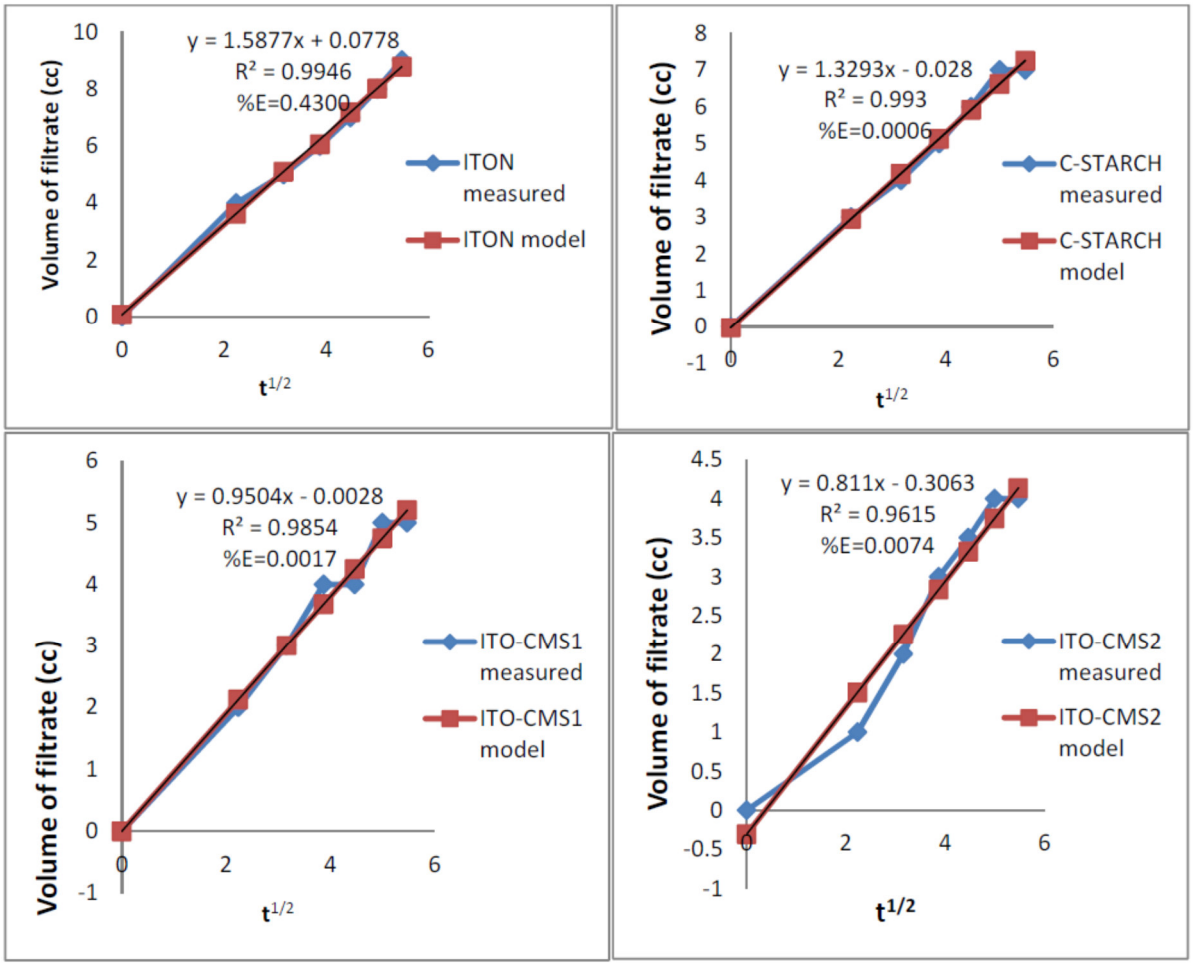


Fig 6: Modeling of the filtration behaviour of the various muds

4. Conclusions

Starch from*Icacinatrichanthaoliv*.tuber and its carboxymethyl derivative are suitable for preparing water based muds. It is quite remarkable to note that the raw native starch showed similar behaviors to the commercial drilling starch used for this work. The carboxymethyl derivatives readily enhanced the viscosity, sorptivityindex, consistency index, yield stress and filtration control of the new muds prepared with them, but had negative effect on the gel strength when compared with the native starch and the commercial starch.The flow index of the new muds prepared with the starch and its carboxymethyl derivatives were less than one, indicating that the various muds are non-Newtonian and has pseudo-plastic flow of typical drilling fluids. If the starch from this non-food source is utilized more for drilling operations, there will be less exploitation of the staple food crops for drilling starches.

5. Acknowledgements

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