Research Article

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Native Cassava (Yuca) Starch Physically Modified By Cryogenic and Conventional Milling for Its Application as Api Fluid Loss Control Additive In Water-Based Drilling Fluids

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Abstract
In this work, the physical modified of native cassava (yuca) starch (Manihot esculenta crantz) was studied as API fluid loss control additive. Physical pregelatinization of native yuca starch can be carried out without the need to use water or heat; they were used only with pressure cutting at cryogenic temperatures and environment. Pregelatinized native yuca starch samples obtained from these two processes, show physical and rheological properties similar to chemically pregelatinized potato starch sample. However, physical pregelatinized yuca starch sample obtained by convectional milling at room temperature was the one provided the best API fluid loss control with 2.5 mL ± 0.1 mL in water-based drilling fluids (WBDF).

Keywords: Gelatinized Starch, Yuca Starch, Potato Starch, Cryogenic Milling, Filtrate Control Api Test In Water-Based Drilling Fluids

Introduction
Potato, maize or yuca starches are used to control fluid loss and viscosity in WBDF ranging from freshwater to saturated-salt to high-pH lime fluids [1-7]. Starches (polymers) are chemically modified to solubility and viscosity increase at room temperature [8, 9]. Unmodified native yuca starch has been effectively used in oil wells Venezuela as an API fluid loss control additive in WBDF however its use at room temperature is limited by low solubility in water, requiring more time and an activation temperature of about 160 °F to be solubilized and exhibit the functional properties: viscosity and swell develop (fluid loss control and viscosity) in WBDF [8, 10-13]. Chemical modification of starches is expensive and their technology is foreign.

On the other hand, the high quality of these products is unnecessary in drilling operations. Physical modification by milling or extrusion is a pressure cutting mechanical process that releases heat, which must be eliminated or minimized so that the starch does not absorb it and cause undesirable structural and color changes [14]. Maintaining a low or ambient temperature during the milling process would minimize structural damage in the starch granules [14, 15]. Techniques application of cryogenic and conventional (room temperature) milling to native starch could slightly alter the physical structure of the starch granules and facilitate the release at room temperature of amylose and amylopectin, responsible of fluid loss control and viscosity in WBDF [16,17]. If instead starch is physically modified (pregelatinized), the minimum properties required in water-based drilling fluids with local technology and lower costs can be achieved. This research opens the possibility of manufacturing with local technology a physical pregelatinization module for native yuca starch, environmental friendly and suitable for WBDF [12, 18-21].

Materials and Methods
Materials
Native cassava (yuca) starch sample *(Manihot esculenta Frantz)* was obtained from INVEYUCA factory, El Tigre, Simon Rodriguez municipality of Anzoategui state, Venezuela.

Sample treatments
Native yuca starch pregelatinization, was realized by means of an equipment of cryomilling, model 6770 Freezer/mill with liquid nitrogen bath to -196 °C and conventional (room temperature) milling there was in use the Rock lab equipment, LA model.

Milling conditions
1. **Cryomilling with variable milling and constant cooling time** Five samples of yuca starches were weighed, each one (2.0± 0.1 g) into the milling tube and placed in the simple holder of Freezer/Mill 6770 SPEX with liquid nitrogen (-196 °C). Five milling times were used (3, 6, 9, 12 and 15 minutes) with 2 minutes at constant cooling. Recharge times per sample of approximately 8 min.
2. **Cryomilling with variable milling and constant cooling time** Five samples of yuca starches were weighed, each one (2.0} 0.1 g) into the milling tube and placed in the simple holder of Freezer/Mill 6770 SPEX with liquid nitrogen (-196 °C). Five cooling times were used (10, 20, 30, 40 and 50 minutes) with

6 min at constant milling time. Recharge times per sample of approximately 8 min.

3. Conventional at room temperature milling

Yuca starch samples seven were weighed, each one (2.0}0.1 g) into the tungsten mortar with concentric rings and placed in the Rock labs LA. Seven samples were milled with milling times different of (2, 2.5, 3, 4, 6, 12 and 24 minutes) at room temperature. Vessel sample recharge times per sample of approximately 10 min.

Determination of water solubility (WSI) and water absorption (WAI) indexes

WSI and WAI were measured according to a modified analytical method [22]. Native yuca starch samples of 0.9000 g it was placed inside a pre-weighted 15 mL centrifuge tube, after was added 13 mL of distilled water at room temperature, along with a magnetic stirring bar and it is closed hermetically. The samples was vortexes for 15 min, magnetic bar was removed and then was centrifuged a 5,000 r/min for 10 min at room temperature [22]. For the determination of WSI, an aliquot between 500-1000 mL of supernatant was weighed into a tared aluminum capsule and dried at 80 °C for 24 hours in a fan-forced oven. Dried supernatants as well as the centrifuge tube with formed gel were weighed. WSI and WAI were estimated using the equations 1 and 2 [15, 23-24]. After the supernatant was transferred into canisters, the centrifuge tube with gel sediment was weighed. All analyses were made by duplicate.

WSI = g Starch supernatant (soluble)/g native starch (1)
WAI = g water absorbed /g native starch (1- g soluble fraction) (2)

Differential scanning calorimeter analyses (DSC)

Gelatinization degree reached by native yuca starch samples, there was used a Jade DSC/ differential scanning calorimeter, Perkin Elmer. By measuring the endothermic heat flow, gelatinization process enthalpy is found. For each starch sample was weighed 5 mg and placed into of open capsule DSC pan. Pans were heated from 25 °C to 140 °C at 5 °C/min. Initial, peak and conclusion temperatures (T_o, T_p, T_c; expressed in °C) and gelatinization enthalpy were determined. Gelatinized fraction was calculated according to equation 3.

GF (%) = [(ΔH_G native starch - ΔH_G treatment starch)/ΔH_G native starch] x100 (3)

Fourier Transform Infra-red spectroscopy (FTIR)

FTIR spectroscopy was done at a resolution 4 cm^{-1}, from 4000 cm^{-1} to 650 cm^{-1}. Starch fractions were evaluated for the regions between 1022 cm^{-1} and 1047 cm^{-1} [15, 25- 26].

Scanning Electron Microscopy analyses (SEM)

SEM analyses were done using a JOEL JSM-6490LV. There were realized the micrographies of native yuca starch and modified native yuca starch samples. To observe some visible alteration of granule starches, such as fissures/ruptures or texture changes.

Evaluation of modified native yuca starch samples as fluid loss controller and viscosifier in Standard WBDF

Modified native yuca starch sample evaluations as fluid loss controller and viscosifier additive in water-based drilling fluids, according to the methodology of the American Petroleum Institute (API) (ISO 10416: 2008 and API RP 13B-1/ISO 10414 -1). Rheological properties to be considered are Plastic Viscosity (PV), Yield Point (YP) and gel strength; as well as, API fluid loss test. Filtering control consists in measure static filtration behavior of WBDF at room temperature and a 100-psi differential pressure.

Results and discussion

Effect of cryogenic milling on the particle size and native yuca starch color

Yuca starch samples subjected to cryogenic grinding, do not present to the naked eye increase in granule size and change in the characteristic white color. Textures of pregelatinized yuca starch samples are similar to the texture of native yuca starch sample. Solubility and water absorption rates of pregelatinized yuca starch samples by grinding with constant cold and variable time increased the water solubility and absorption rates compared to the native yuca starch sample (Table 1). In contrast, yuca starch pregelatinized samples by grinding with variable cold and constant time, the solubility and absorption rates increase with respect to pregelatinized by grinding with constant cold and variable time; however, there is no clear trend with the contact time (Table 2).

Table 1: Cryomilling with constant cold and variable contact time

#	Yuca starch sample	Grinding time (min)	Cold contact time (min)	Solubility index	Gelatinization index
1	Native	0	0	0.0161	0.5944
2	M (2x3)	3	2	0.5056	1.5946
3	M (2x6)	6	2	0.7504	2.6390
4	M (2x9)	9	2	1.6079	1.8985
5	M (2x12)	12	2	1.5206	1.9288
6	M (2x15)	15	2	3.0193	2.8470

Table 2: Cryomillig with variable cold and constant contact time

#	Yuca starch sample	Grinding time (min)	Cold contact time (min)	Solubility index	Gelatinization index
1	Native	0	0	0.0161	0.5944
2	M (10x6)	6	10	0.4736	1.5812
3	M (20x6)	6	20	2.5135	1.7800
4	M (30x6)	6	30	2.0389	1.8930
5	M (40x6)	6	40	2.9951	1.3330
6	M (50x6)	6	50	2.1189	1.5139
7	M (60x6)	6	60	2.5861	1.8218

In Figures 1 and 2 shown formed amylose films (soluble fraction of starch) and amylopectin gels (fraction that absorbs water).

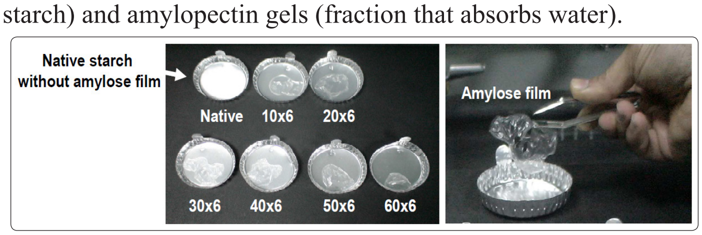

Figure 1: Amylose films obtained from modified native yuca starch sample soluble fractions

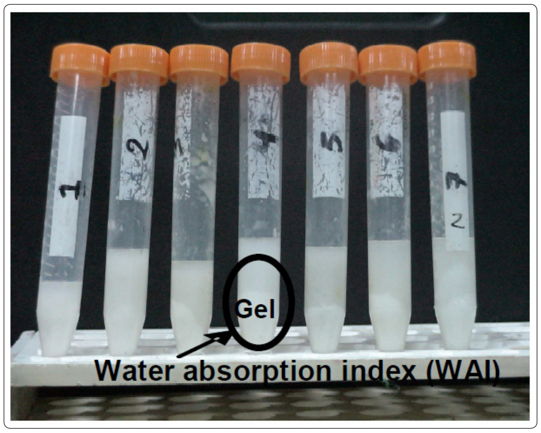

Figure 2: Amylopectin gels and amylose remains (supernatant liquid)

Milling apparent effect with non-cryogenic pressure on particle size and native yuca starch color

Native yuca starch samples previously cooled were milled at room temperature at milling time different, with an increase in the water solubility and absorption indexes with the increase in milling time, with the solubility index being more consistent with this variable (Table 3).

Table 3: Convectional milling at room temperature and variable contact time

#	Yuca starch sample	Grinding time (min)	Cold contact time (min)	Solubility index	Gelatinization index
1	Native	0	0	0.0161	0.5944
2	M (0x2)	2	0	1.8343	2.5493
3	M (0x2.5)	2.5	0	2.8259	4.3832
4	M (0x3)	3	0	2.9741	3.6345
5	M (0x4)	4	0	4.6732	4.5529
6	M (0x6)	6	0	4.4485	3.9971
7	M (0x12)	12	0	4.5981	4.4593
8	M (0x24)	24	0	5.5471	4.4740

Differential scanning calorimetry (DSC)

During the shear milling process it causes the fragmentation of the starch granules, which is evidenced by the increase in solubility and viscosity at room temperature, given by hydrogen bonds breaking between amylopectin and amylose, forming a structurally less crystalline starch, therefore more amorphous. As gelatinization is an endothermic process it is expected that enthalpies decrease with increase in the gelatinization degree [8]. Results obtained according to processing conditions different of native and modified yuca starch samples are presented below (Table 4).

Table 4. Gelatinization enthalpy for native yuca starch samples

#	a) Condiction Yuca starch sample	ΔH (J/g)	b) Condiction Yuca storch sample	ΔH (J/g)	c) Condiction Yuca storch sample	ΔH (J/g)
1	Native	321.9	Native	321.9	Native	321.9
2	M (3x2)	292.8	M (6x10)	294.9	M (0x2)	344.2
3	M (6x2)	339.9	M (6x20)	262.0	M (0x2.5)	302.5
4	M (9x2)	392.7	M (6x30)	320.3	M (0x3)	298.9
5	M (12x2)	385.5	M (6x40)	284.4	M (0x4)	290.5
6	M (15x2)	379.0	M (6x50)	293.7	M (0x6)	339.6
7	--	--	M (6x60)	329.9	M (0x24)	283.2

Infrared spectroscopy (FT-IR)

Infrared spectra (FT-IR) of native yuca starch and modified starch samples by cryogenic and convectional (room temperature) milling are shown (Figures 3 and 4).)

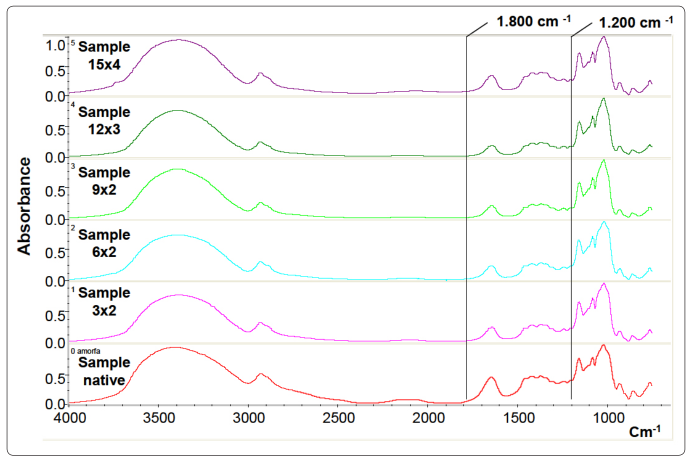

Figure 3: Native and modified yuca starch sample FT-IR spectral by cryomilling with constant cold with variable contact time: (a) condiction

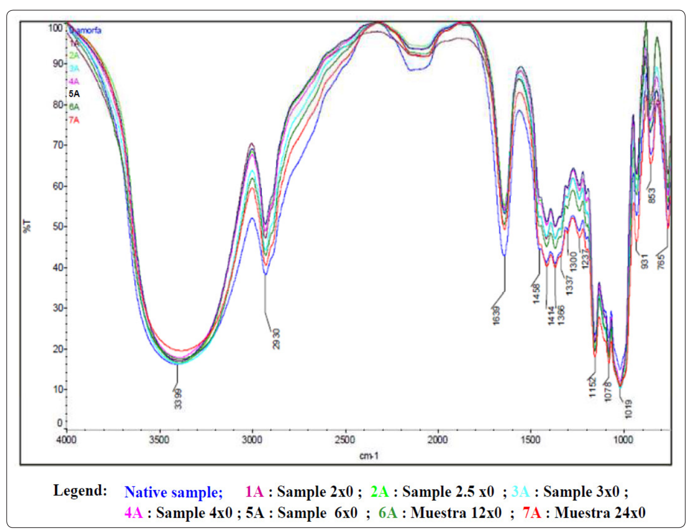

Figure 4: Native and modified yuca starch samples FT-IR spectral by convectional milling (room temperature with variable contact time: (c) condiction

Scanning electron microscopy (SEM)

Pregelatinized native starches by cryogenic and conventional milling were observed by scanning electron microscopy to observe the alterations that occurred to the granules that make up the crystalline-amorphous matrix of these yuca starches. It is shown in Figure 5, native yuca starch granules without modification, where it can be seen that the spherical and ovoid granules do not present cracks on their surface or amorphous granules. In some granules the characteristic cross of the birefringence, indicative of starch crystalline matrix, can be observed. Figure 6 shows cryogenically pregelatinized yuca starch micrograph, in which yuca starch granules are shredded and cracked, compared to native yuca starch granules, which facilitates the release of amylase by partial breakdown of amylopectin structure. In Figure 7, the micrograph of pregelatinized yucca starch granules at room temperature is presented, where the sheared and melted yuca starch granules are observed, providing amorphous and amorphous granules with rupture.

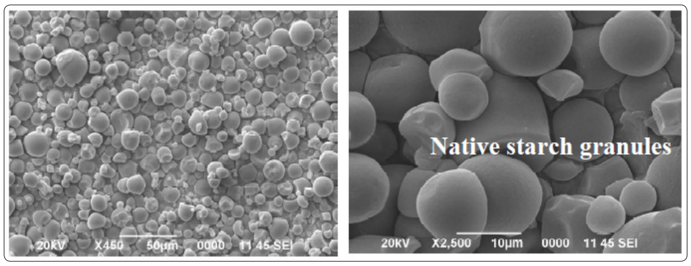

Figure 5: Native yuca starch granule micrographs

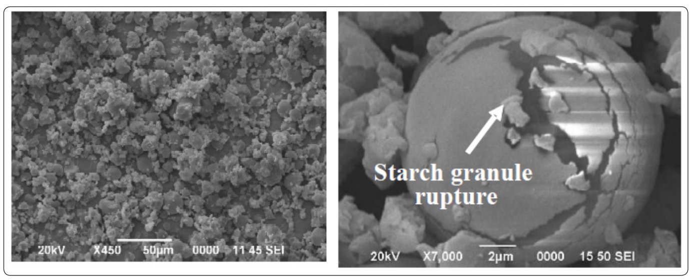

Figure 6: Modified native yuca starch granule micrographs by cryomilling

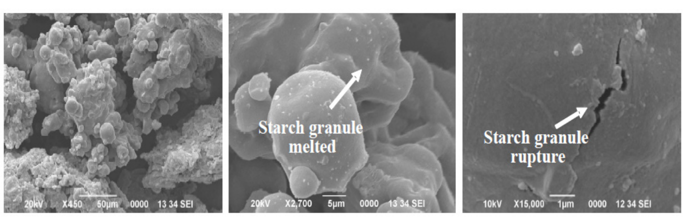

Figure 7: Modified native yuca starch granule micrographs by convectional milling at room temperature

Evaluation of modified native yuca starch samples as fluid loss controller and viscosifier in Standard WBDF

Evaluation of modified native yuca starch samples by cryogenic and conventional (room temperature) milling as fluid loss additive, WBDF six formulations were prepared as follows: a base fluid without any type of starch (F0), base fluid with native yuca starch (F1), F0 with commercial modified potato starch without sodium bisulfite (F2), base fluid with commercial additive of modified potato starch with sodium bisulfite (F3), F0 with pregelatinized native yucca starch with cryomilling (F4) and FO with native yuca starch with convectional milling at room temperature (F5) [11, 27, 28] (Tables 5a, 5b and 5c).

Table 5a: Rheological properties and fluid loss control of modified native yuca starch samples by cryogenic and conventional (room temperature) milling

Formulations	UN	F0	F1	F2	F3	F4	F5
Water	mL	283.5	283.5	283.5	283.5	283.5	283.5
Potassium chloride	g	7	7	7	7	7	7
Clarified xanthan gum	g	1.5	1.5	1.5	1.5	1.5	1.5
Native yuca starch	g	0	4	0	0	0	0
Commercial modified potato starch	g	0	0	4	0	0	0
Commercial modified potato starch	g	0	0	0	4	0	0
Cryogenically pregelatinized yuca starch (native)	g	0	0	0	0	4	0
Yuca starch pregelatinized at room temperature	g	0	0	0	0	0	4
Monoethanolamine (MEA)	g	1	1	1	1	1	1
Sodium bisulfite		0	0	0	0.5	0	0
Calcium carbonate	g	60	60	60	60	60	60
Barite (Density fluid =12 lpg)	g	144	144	144	144	144	144

Table 5b: Rheological properties at 120 °F (16 hours x dynamic-aging test before)

Lectures Fann 35A	UN	F0	F1	F2	F3	F4	F5
L600	rpm	52	65	62	51	58	65
L300	rpm	41	52	50	40	47	52
L200	rpm	35	43	41	34	40	42
L100	rpm	27	33	32	27	31	29
L6	rpm	10	11	12	10	11	9
L3	rpm	09	9	09	8	9	7
Plastic Viscosity (PV)	cP	11	13	12	11	11	13
Yield Point (YP)	(*)	30	39	38	29	36	39
10s/10min gel strength	(*)	8/9	9/10	10/10	8/8	9/9	8/8
pH		10	10	10	10	10	10

Table 5c: Rheological properties at 120 °F (16 hours x dynamic-aging test after)

Lectures Fann 35A	UN	F0	F1	F2	F3	F4	F5
L600	rpm	57	56	55	64	50	55
L300	rpm	45	47	45	46	42	46
L200	rpm	38	39	32	39	31	35
L100	rpm	28	26	23	29	22	24
L6	rpm	7	6	6	8	6	5
L3	rpm	5	4	4	6	4	4
Plastic Viscosity (PV)	cP	12	9	10	18	8	9
Yield Point (YP)	(*)	35	38	35	28	34	37
10s/10min gel strength	(*)	5/5	4/4	5/5	6/6	23/65	4/4
API fluid loss (± 0,1 mL)	mL	3.0	2.9	3.3	2.8	3.5	2.5
pH		10.1	9.9	10.0	10.3	9.8	9.9

(*) lb/100 ft^2

Modified yuca starch samples by cryomilling increased their solubility and viscosity in WBDF at room temperature. Pregelatinization native yuca starch samples to dissipate the flow of heat to the cryogenic medium, modified native yuca starch samples with textures and organoleptic properties similar to the native starch; without granules fused with a certain percentage of cracked granules that are those that allow the incorporation of amylose to the aqueous medium to improve the solubility in water at room temperature and avoiding imbibition. Pregelatinized native yuca starch samples by milling at room temperature, also increase their solubility and viscosity in WBDF at room temperature, however pregelatinization native yuca starch samples at room temperature dissipate the heat flow to the environment, causing some yuca starch granules to melt and others to rupture, changing the texture and organoleptic properties of native yuca starch precursor to a granular texture due to heat absorbed in the endothermic process of gelatinization, causing a regrowth of the yuca starch granules; however, they allow the incorporation of amylose into the aqueous medium, facilitating its solubility in water at room temperature and avoiding imbibition. Solubility and water absorption indexes of native yuca starch samples by grinding at room temperature are slightly higher than native yuca starch sample indexes provided by cryomilling. Rheological and API fluid loss control behavior of modified native yuca starch samples by cryogenic and convectional milling (F5) are similar to those provided by commercial pregelatinized potato starch sample (F3), however, API fluid loss control best with 2.5 mL ± 0.1 mL was achieved by modified native yuca starch sample with convectional milling (F5) (Figure 8).

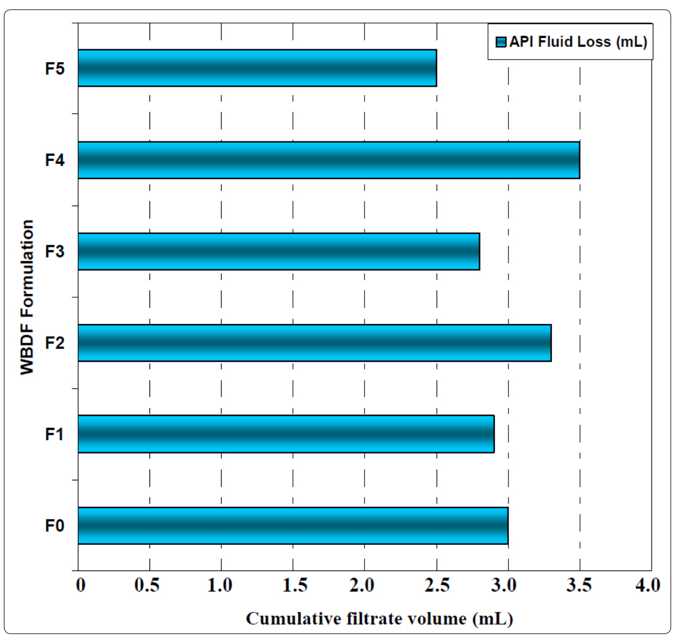

Figure 8: API Fluid loss control of the WBDF formulations

Conclusions

1. Modified of native yuca starch sample can be done without using water, heat or pressure shear, both cryogenic and convectional (room temperature) milling.
2. Solubility in water of modified native yuca starch samples at room temperature increases with respect to native yuca starch sample.
3. Best API fluid loss control with 2.5 mL was achieved by modified native yuca starch sample with convectional (room temperature) milling.
4. Rheological behavior of modified native yuca starch samples are similar to rheological behavior of commercial chemically modified potato starch sample.

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