

# Turning Industrial Waste into a Valuable Bioproduct: Starch from Mango Kernel Derivative to Oil Industry

## Mango Starch Derivative in Oil Industry

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**Abstract:** After industrial mango processing, tons of residues such as peels and kernels are discarded as waste. Nevertheless, almost 60% of the mango kernel is due to starch on a dry weight basis. Herein, starch from mango (*Manguijera Indica L.*) kernel was applied to obtain a starch fatty ester with vinyl laurate, in DMSO, under basic catalysis. FTIR, <sup>1</sup>H and <sup>13</sup>C NMR confirmed that a starch ester with a degree of modification of 2.6 was produced. TGA showed that the modified starch has higher thermal stability than its precursors and higher than a vinyl laurate/starch physical blend. SEM data showed that granular shape and smooth surface on mango starch changed after chemical modification to a continuous and shapeless morphology. This industrial reject derivative behaved as an efficient alternative environmentally friendly fluid loss controller in oil drilling fluids, even in conditions of high temperatures and high pressures (HTHP) drilling.

**Keywords:** Mango Starch; oil drilling fluid; transesterification; vinyl laurate

## 1 Introduction

Starch is a biomass mostly obtained from corn, cassava, tapioca, wheat and potato [1], which comprises a mixture of two polysaccharides, amylose, a mainly linear polymer constituted by (1→4)- $\alpha$ -D-glucopyranose units ( $M_w = 10^5$ - $10^6$  g/mol), and amylopectin, which has (1→4)- $\alpha$ -D-glucopyranose units with 5-6% of  $\alpha$ -(1→6) branches ( $M_w = 10^7$ - $10^8$  g/mol) [2]. It has been used in food and non-food applications [3], but some of its properties, as its hydrophilic nature, low shear and low temperature resistance have motivating the physical or chemical modification of starch [4-17].

One of the major problems in oil industry is the influx of the drilling fluids through the rock, blocking pores of the rock and decreasing the production of oil. Multifunctional additives, such as polymers, are added to filtration control. Modified starch products, in particular, have effectively acted as filtration reducers in water-based drilling fluids [18-21]. Nevertheless, in some cases, such as in water sensitive clays/shales, wells with high temperature and high pressure, oil-based drilling fluids are required. Then, it would be interesting to apply bio-based materials with good compatibility in organic media to act on filtration control of oil drilling fluids. Corn starch esters, for example, were prepared previously by Dias et al [22] and acted as fluid loss additives on invert emulsion oil drilling fluids [23].

Taking into account sustainability, it would be also attractive to apply other sources of starch that could meet starch demand and support the inestimable possibility of applications, without the need to increase local production of starch sources or their importation. In special, solid waste beneficiation is

mandatory to protect environment and turn industrial rejects into high-value materials [24-26]. In this context, mango (*Manguifera Indica L.*) industry rejects 40-60% of this fruit, being 12-15% due to peels and 15-20% of kernels, without further waste beneficiation to commercial purposes [27]. About 60% of the mango kernel on a dry basis is constituted by starch [28, 29]. Mango (*Manguifera Indica L.*) is one of the most important valuable tropical fruits [30], which has been cultivated in more than 100 countries around the world [31]. Nevertheless, few studies have been made about mango starch and no chemical modification to petroleum industry interest was found in literature.

In this scenario, the exploration of alternative natural sources, which are largely rejected by industry, in order to develop bioproducts with commercial importance, is crucial on the crescent demand to add value to industrial waste. Herein is demonstrated the utilization of starch from mango kernel in producing a starch ester, as well as is investigated its potential as an eco-friendly fluid loss control additive in invert emulsion oil drilling fluids.

## 2 Experimental

### 2.1 Materials

Starch was extracted from mango (*Mangifera indica L.*) kernel (SISGEN: AD3DC70), according to the procedure described previously [30]. Vinyl laurate (ethenyl dodecanoate) was acquired from Tokyo Kasei. Potassium carbonate ( $K_2CO_3$ ), deuterium dimethyl sulfoxide (DMSO- $d_6$ ) and deuterium chloroform ( $CDCl_3$ ) were provided by Sigma-Aldrich. Chloroform, dimethylsulfoxide (DMSO) and isopropyl alcohol were supplied by Synth. Methanol and toluene were purchased from ISOFAR. Sodium hydroxide (NaOH) was obtained from Éxodo Científica.

Organophilic clay, commercial grade n-paraffin (named hereafter as n-paraffin), emulsifier, hydrated lime ( $Ca(OH)_2$ ), barite ( $BaSO_4$ ) and a commercial fluid loss control additive were gently donated by Petrobras. Pharmaceutical grade n-paraffin (PG n-paraffin) was acquired from União Química Farmacêutica Nacional S/A. All the compounds were used without further purification.

### 2.2 Synthesis of the Mango Starch Fatty Ester

Acylation of mango starch with vinyl laurate was performed under basic catalysis, according to described in literature to corn starch [22,32], but with some modifications. Specifically, 5 g of mango starch was added to 50 mL of DMSO, at room temperature ( $\sim 25^\circ C$ ), under magnetic stirring, for 24 hours. The solution was then transferred to a three-necked flask coupled to a reflux condenser, mechanical stirring, thermometer and a heating mantle, under  $N_2(g)$  atmosphere. Potassium carbonate (2% w/w with respect to starch) dissolved in 15 mL of DMSO and vinyl laurate (3 mol/1 mol anhydroglucose unit in starch) were added and the reaction was kept at  $110^\circ C$ , for 3 hours. The acetaldehyde gas by-product was removed from the system by absorption in 1M NaOH, with the aid of a bubbler coupled to the reflux condenser outlet. The system was then cooled to room temperature and the modified starch was precipitated with methanol. Subsequently, the product was washed three times with methanol and then once with isopropyl alcohol. Finally, the sample was filtrated under vacuum and dried in an oven, at  $65^\circ C$ , for 24 hours.

A vinyl laurate/starch (3:1 mol) physical mixture was also prepared in order to compare it with the chemically modified starch behaviour.

### 2.3 Infrared Spectroscopy

Infrared (IR) spectroscopy was performed on an IRAffinity-1S FT-IR Spectrometer from Shimadzu. The samples were analyzed with an attenuated total reflectance (ATR) accessory and scanned from  $700\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ .

## 2.4 Solubility Tests

Solubility tests were performed in solvents of different polarities: water, DMSO, chloroform, toluene, pharmaceutical grade n-paraffin and crude n-paraffin, in order to evaluate the change in starch hydrophilicity with chemical modification. Each sample (0,1 g) was slowly added to the solvent (10 mL) vortex and left at constant magnetic stirring, during 24 hours, at room temperature (~25°C).

## 2.5 NMR Spectroscopy

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained with a 600 MHz Bruker Biospin spectrometer, at 60 °C. Native starch was solubilized in dimethyl sulfoxide-d<sub>6</sub> whereas vinyl laurate and starch derivative were dissolved in chloroform-d (CDCl<sub>3</sub>). Chemical shifts were reported in ppm and calibrated against residual solvent signal as internal standard.

## 2.6 Thermal Analysis

Thermogravimetric analyses (TGA) were carried out on a SDT Q600 thermal analyzer, from TA Instruments, in a temperature ranging from ambient (~25) to 750°C, with a heating rate of 10 °C/min and under nitrogen flow of 30 mL/min.

## 2.7 Scanning Electron Microscopy (SEM)

The morphological features of the samples were observed using a HITACHI TM 3000 scanning electron microscope, operating at an accelerating voltage of 15 kV.

## 2.8 Preparation of the Drilling Fluids

The water/oil drilling fluids were prepared from a standard composition (Table 1) in a Hamilton Beach blender from Fann, and then submitted to dynamic aging for 16 hours, at 93°C (200 °F), in a Fann roller oven, in order to simulate the wellbore conditions. Their behaviour was studied in the light of the tests recommended by the API RP 13B-2 standard [33]

**Table 1:** Composition of the drilling fluids

Order of addition	Constituents	Function	Amount	Stirring time (min)
1	N-Paraffin	Continuous phase	230.0 mL	5
2	Emulsifier	Stabilize the emulsion	8.0 g	5
3	Calcium hydroxide	Activator	10.0 g	10
4	Brine (35 wt% NaCl)	Aqueous phase	120.0 mL	5
5	Commercial fluid loss additive or starch ester	Filtration control additive	1.5 g	10
6	Organoclay	Thickener	2.0 g	10
7	Barium sulphate	Weighting agent	50.0 g	10

## 2.9 High Temperature and High Pressure (HTHP) Filtration Tests

Static filtration tests were performed in a Fann HTHP filter press, at 93°C (200°F) under a pressure differential of 500 psi, during 30 minutes. The fluid was placed into the filter cell with a filter paper no. 50 from Whatman, which was then inserted into a preheated heating jacket. The system was sealed and pressurized with gaseous nitrogen. The filtrate was collected in a graduated test tube.

## 2.10 Electrical Stability

Electrical stability measurements were made in a Fann model 23-E electrical stability tester, at 49°C (120 °F).

## 2.11 Rheology

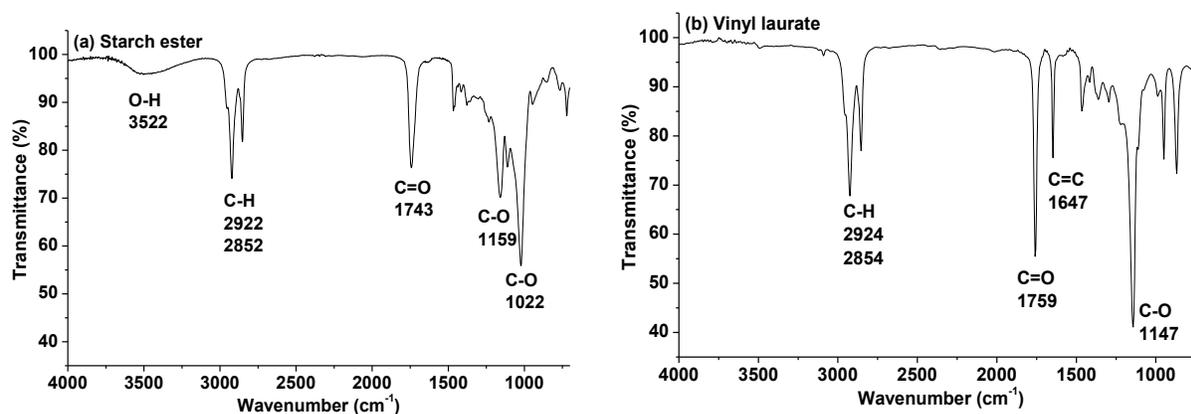
Rheological measurements were performed in a Fann viscometer model 35-A, equipped with coaxial cylinders, at 49°C (120°F). The fluid was submitted to the following decreasing rotational velocities: 600 rpm, 300 rpm, 200 rpm, 100 rpm, 6 rpm and 3 rpm, equivalent to shear rates of 1021.8 s<sup>-1</sup>, 510.9 s<sup>-1</sup>, 340.6 s<sup>-1</sup>, 170.3 s<sup>-1</sup>, 10.2 s<sup>-1</sup>, and 5.1 s<sup>-1</sup>, respectively. The corresponding values obtained in the dial of the equipment were employed to determine the rheological parameters apparent viscosity, plastic viscosity and yield point. To obtain the gel strength, the sample was submitted to 600 rpm for 60 seconds and subsequently measured at 3 rpm after resting for 10 seconds (to initial gel) and resting for 10 minutes (to final gel), respectively.

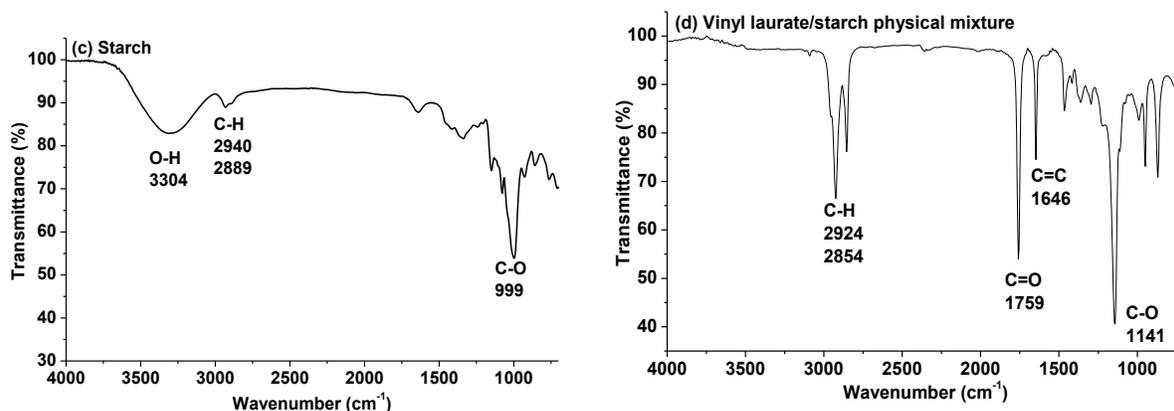
## 3 Results and Discussion

### 3.1 Infrared

The synthetic strategy followed in this work for acylation of mango starch with vinyl laurate involves a nucleophilic substitution mechanism, by using potassium carbonate as basic catalyst. Analogous to what was shown in literature, herein is proposed that the reaction of carbonate with starch formed a starch alkoxide, followed by its addition to the C = O of vinyl laurate, producing a tetrahedral intermediate. Starch ester was then obtained by the elimination of the gaseous leaving group, acetaldehyde [34-36].

The chemical modification of starch by the reaction with vinyl laurate was demonstrated on its IR spectrum (Fig. 1(a)) by the appearance of a peak at 1743 cm<sup>-1</sup>, related to C = O stretching vibration of saturated ester, lower than the absorption frequency observed for carbonyl vinyl ester (Fig. 1(b)). As similarly seen for native starch (Fig. 1(c)), starch ester presented a band centered at 3425 cm<sup>-1</sup> related to O-H stretching vibration and a peak at 1022 cm<sup>-1</sup> attributed to C-O stretching of the polysaccharide structure. The peaks at 2924 cm<sup>-1</sup> and 2854 cm<sup>-1</sup> can be ascribed respectively to C-H asymmetric and symmetric stretching of both anhydroglucose units and laurate portions in the modified starch. The peak at 1159 cm<sup>-1</sup> can be assigned to C-O stretching of saturated ester (modified starch), that is higher in frequency than the one seen for vinyl ester (vinyl laurate) C-O stretching frequency [22, 37]. It was also noted that when a physical mixture between vinyl laurate and native starch were studied by FTIR, the resulted spectrum (Fig. 1(d)) presented essentially the same peaks observed for vinyl laurate, probably because of the great amount of the vinyl ester in the sample (mixture with the same proportion used for the synthesis of starch ester).





**Figure 1:** Infrared spectra of (a) starch ester, (b) vinyl laurate, (c) native starch and (d) vinyl laurate/starch physical mixture

### 3.2 NMR Analysis

The introduction of long aliphatic side chains turned starch into a material insoluble in solvents of higher polarity, namely water and DMSO, whereas was soluble in more hydrophobic solvents, i.e. pharmaceutical grade n-paraffin, chloroform and toluene (Tab. 2). This is the opposite behaviour founded for native mango starch, indicating the higher hydrophobic character on starch derivative. For this reason, NMR spectra were performed in DMSO- $d_6$  for native starch and in  $CDCl_3$  for starch ester and vinyl laurate.

**Table 2:** Solubility behaviour for starch, vinyl laurate and starch ester under different solvents

Solvent	Starch	Vinyl laurate	Starch ester
Water	+	-	-
DMSO	+	-	-
PG N-paraffin*	+/-	+	+
Chloroform	-	+	+
Toluene	-	+	+

+ Soluble; - insoluble; +/- partially soluble

\*Pharmaceutical grade n-paraffin chosen to solubility test in order to eliminate the influence of some impurities typically present on the commercial n-paraffin employed

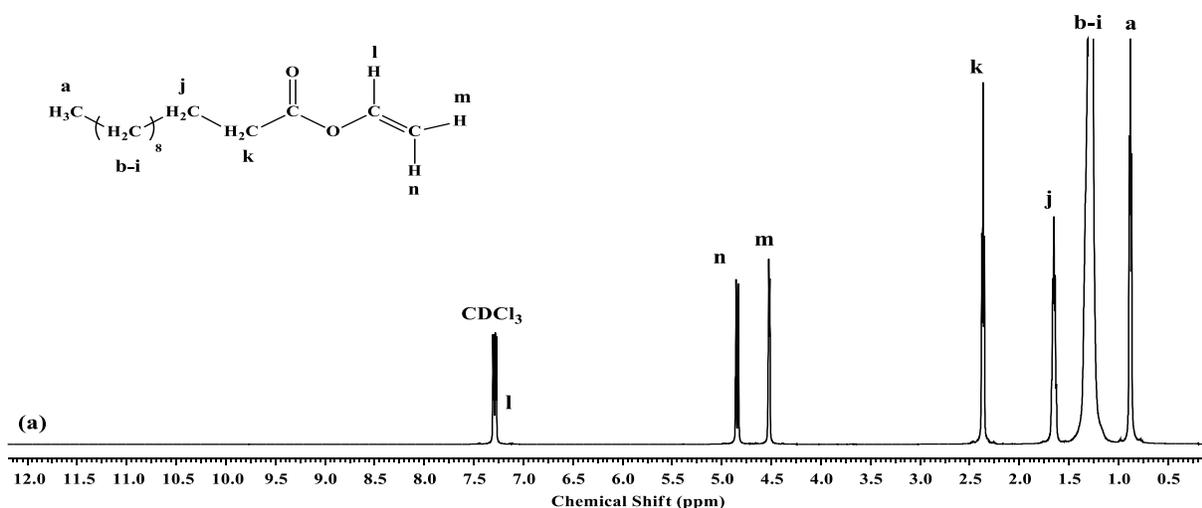
A typical  $^1H$  NMR spectrum for vinyl laurate is presented in Fig. 2(a). The peak at 0.88 ppm can be assigned to methyl protons. The signals at 1.65 ppm and 2.37 ppm are due to H-j and H-k methylene protons, respectively. Other methylene protons appeared overlapped at 1.27 ppm. The peaks at 4.53 ppm and 4.83 ppm can be ascribed to vinyl terminal protons, whereas the  $COOH-CH_2$  vinyl proton is probably superposed with solvent sign at 7.27 ppm. Hydrogen associated to anhydroglucose units in starch and modified starch  $^1H$  NMR spectra appeared at a region between 3.0-5.8 ppm (Figures 2b and 2c). Peaks arising from aliphatic hydrogen atoms of the fatty acid chain on modified starch spectrum appeared at 0.88-2.6 ppm, being the peak at 0.88 ppm attributed to  $-CH_3$  protons, the broad sign at 1.12-1.54 ppm is attributed to H-b-i methylene protons, whereas the peak centered at 1.60 ppm and the one at 2.30 ppm can be assigned to H-j and H-k methylene protons, respectively [22, 36, 38-40]. The degree of substitution (DS) of modified starch is the average number of hydroxyl groups that were substituted by acyl groups in each anhydroglucose repeat unit. Since each anhydroglucose unit has three hydroxyl groups, the DS value can vary from 0 to 3. In this work, the DS was of 2.6 and was determined from integration values of proton sign

from acetate methyl group ( $I_{\text{CH}_3}$ ) and proton sign from anhydroglucose unit ( $I_{\text{Hstarch}}$ ) [36, 41], according to the following equation:

$$\text{DS} = (7I_{\text{CH}_3}) / (3I_{\text{Hstarch}}) \quad (1)$$

Fig. 3 shows a clear difference on the  $^{13}\text{C}$  NMR spectra of starch ester and its precursors. The absence of resonance of the olefinic carbon at 140 ppm indicates that the product is free from vinyl laurate impurities and that the purification was effective. The peak at 14.02 ppm is assigned to  $-\text{CH}_3$  (C12'). The carbons C-4'-9' give the signals at 29.36-31.94 ppm. The peaks at 22.67, 24.73, 34.01 and 38.25 ppm can be attributed to the carbons C-11', C-3', C-10' and C-2', respectively [32, 40].

As also observed in literature, the resonances arising from the anhydroglucose unit on acetylated starch were broadened and lower in intensity when compared to native starch. In addition, the peaks related to C-1 and C-4 were shifted upfield on starch ester spectrum. C-1 appeared at 97.37 ppm, C-2, C-5, C-3 and C-4 were superposed at 71.28 ppm and the signs at 59.67 and 61.81 can be assigned to unsubstituted and substituted C-6, respectively [32, 42-44]. As expected, C = O from starch ester appeared downfield (173 ppm) in comparison with vinyl laurate (170 ppm), due to the absence of the conjugation of the single bonded oxygen with C = C [37]. The solubility tests, together with FTIR and NMR results proved that the synthesis of starch ester was successful.



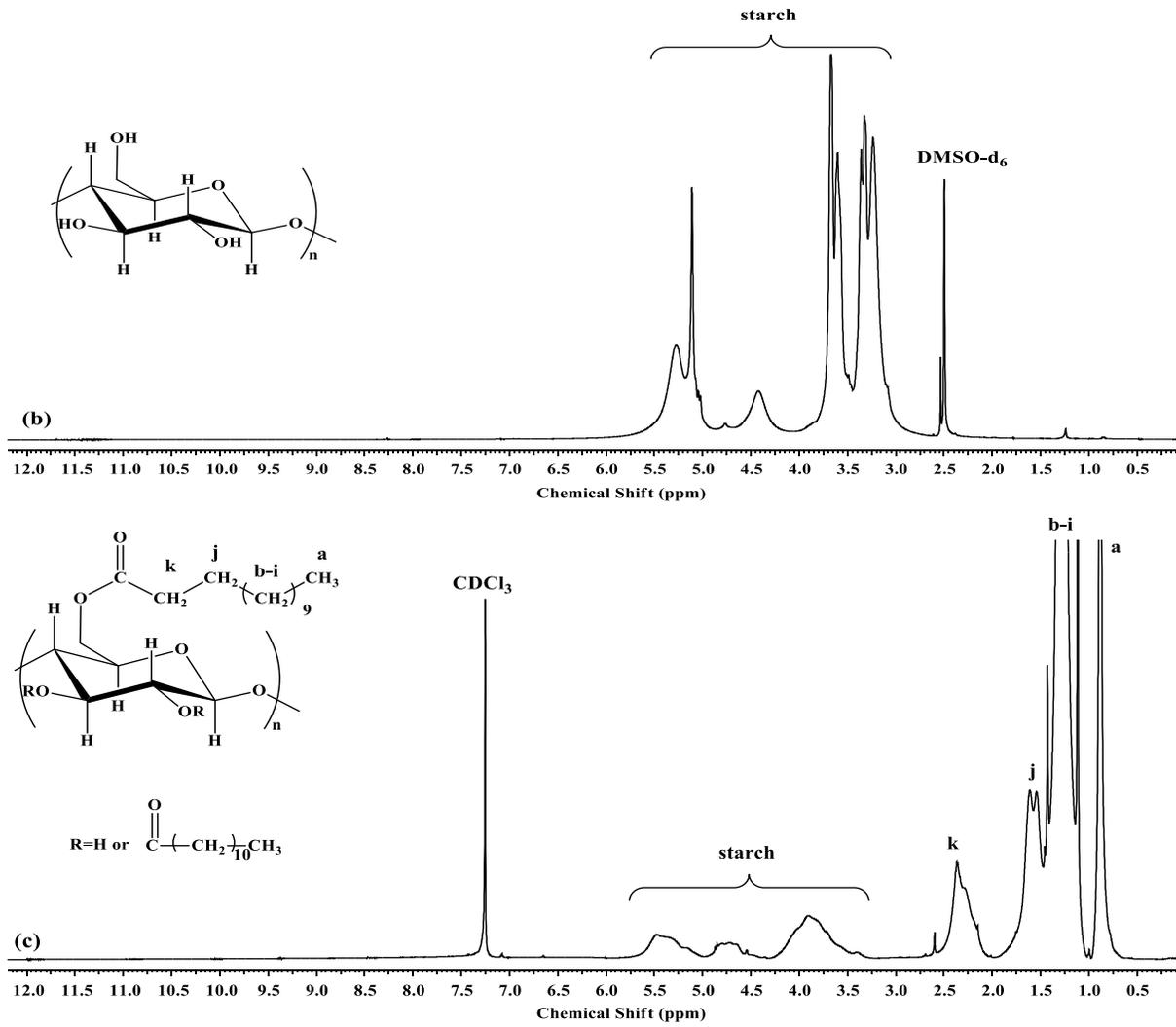
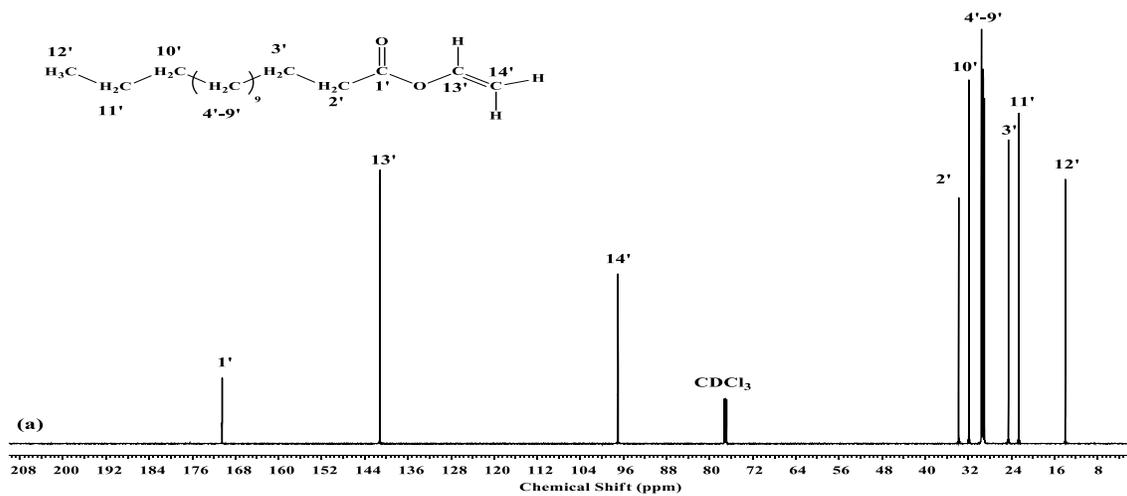
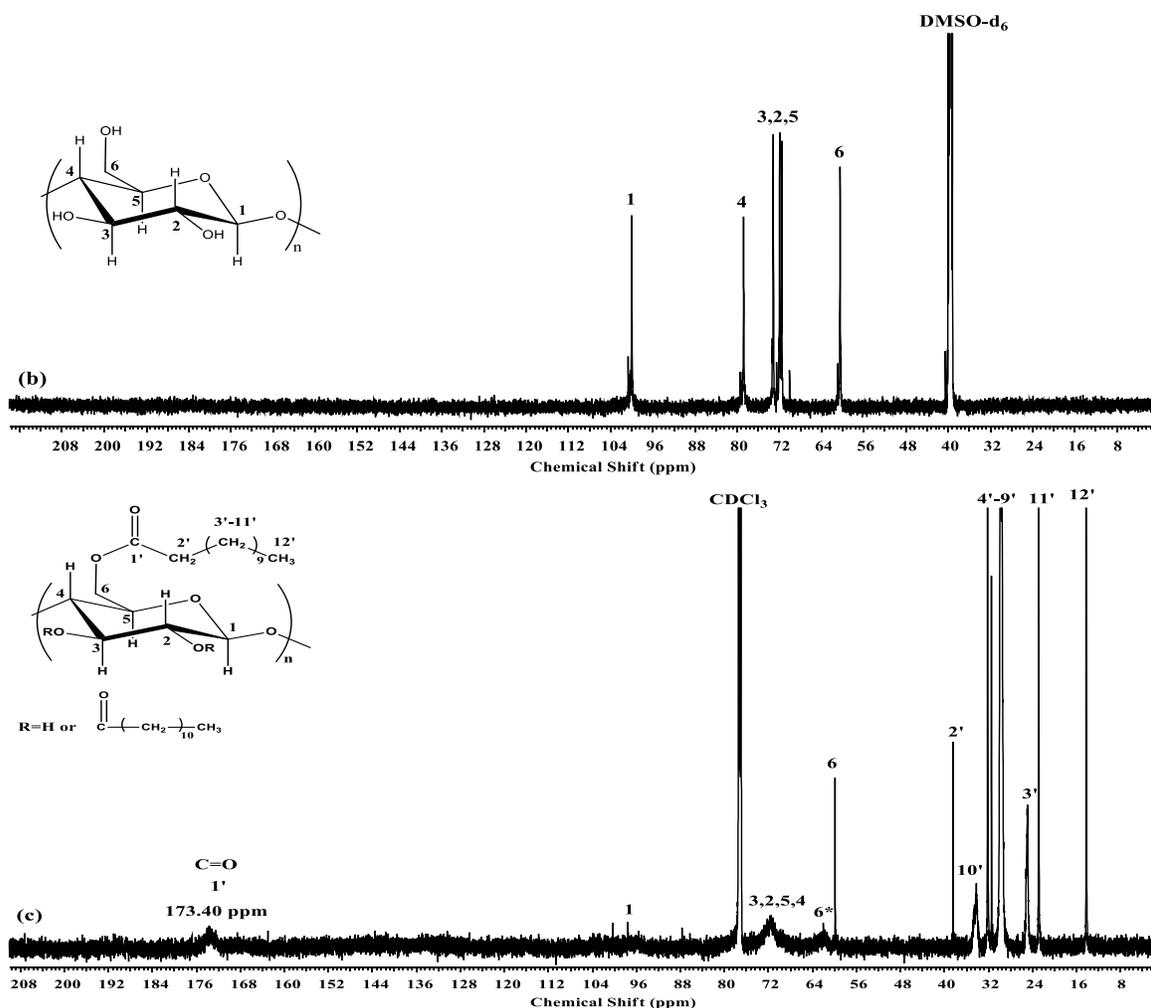


Figure 2:  $^1\text{H}$  NMR spectra of (a) vinyl laurate, (b) starch and (c) starch ester



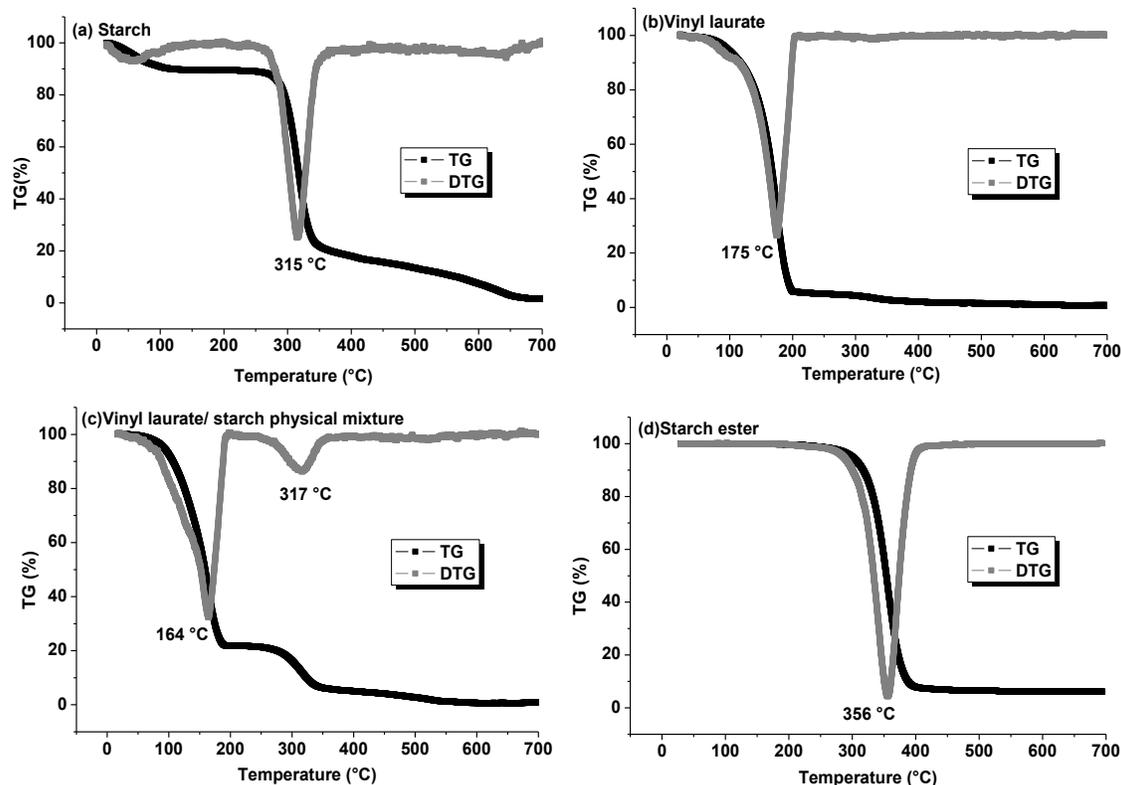


**Figure 3:**  $^{13}\text{C}$  NMR spectra of (a) vinyl laurate, (b) starch and (c) starch ester

### 3.3 Thermal Analysis

Fig. 4 presents the thermogravimetric curves of starch, vinyl laurate, vinyl laurate/starch physical mixture and starch ester. Native starch exhibited a mass loss below  $100^\circ\text{C}$ , which was attributed to moisture, indicating that the sample is hygroscopic. Starch displayed a thermal degradation process in the  $262\text{--}361^\circ\text{C}$  temperature range, with a DTG peak of  $315^\circ\text{C}$ , related to intramolecular and intermolecular dehydration of starch chains [45-47].

Vinyl laurate exhibited a mass loss step at  $82\text{--}207^\circ\text{C}$ , with a DTG peak at  $175^\circ\text{C}$ , due to sample evaporation. Starch/vinyl laurate physical mixture showed a two thermal degradation steps, at  $60\text{--}198^\circ\text{C}$  and  $266\text{--}363^\circ\text{C}$ , with DTG peaks at  $165^\circ\text{C}$  and  $315^\circ\text{C}$ , respectively. The first peak can be attributed to vinyl laurate and corresponds to roughly 80% in mass loss, due to the higher amount of vinyl laurate in the mixture. The second peak can be ascribed to thermal degradation of starch. Both thermal events are very close to the ones obtained for pure vinyl laurate and starch separately, showing no improvement on thermal stability with the simple mixture of those two components.

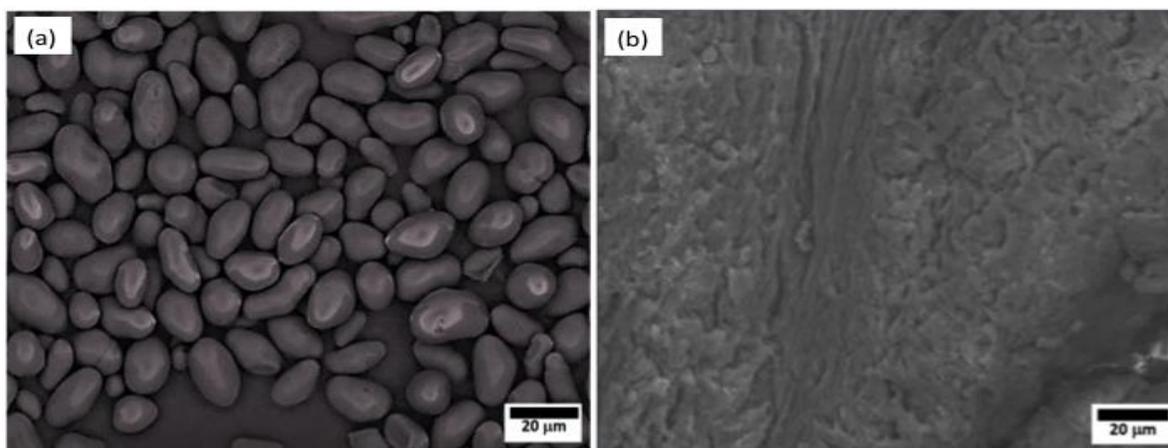


**Figure 4:** TG (black symbols)/DTG (gray symbols) curves for (a) native starch, (b) vinyl laurate, (c) vinyl laurate/starch physical mixture and (d) starch ester

Contrary to native starch, starch ester did not exhibit mass loss below 100°C, possibly due to the higher hydrophobic character after the introduction of aliphatic chains on the polysaccharide structure. The sample showed a single degradation step at the 270–411°C temperature range, with a DTG peak at 356°C, which demonstrates that the starch ester is thermally more stable than its precursor. This behaviour is analogous to what was found on literature for starch esters with  $DS > 1$  and has been attributed to the lower number of hydroxyl groups, higher number of covalent bonds and higher molar mass of the products after esterification of starch [22,36,47].

### 3.4 Scanning Electron Microscopy (SEM)

Fig. 5 exhibits the morphology of mango starch and starch ester, obtained by SEM analysis. Native mango starch presented an oval to ellipsoid granular shape and smooth surface with size ranging from 5  $\mu\text{m}$  to 12  $\mu\text{m}$  and mean diameter of 10.6  $\mu\text{m}$  [27,29,30]. On the other hand, smoothness and granular aspect were lost on starch derivative. This change of appearance to a continuous and shapeless morphology can be related to the acylation process that separate the macromolecules by introducing a long hydrophobic chain onto starch, leading to a disorganized molecular network after precipitation and drying [38,48,49].



**Figure 5:** Surface morphology of (a) native mango starch and (b) starch ester via SEM (x1000)

### 3.5 HTHP Filtration Test

The volume of filtrate obtained on HTHP filtration tests is an important parameter to demonstrate the fluid loss control capacity's on reducing the invasion of the fluid through the rock formation under conditions of high pressure and high temperature, normally found when oil-based fluids are required. In this study, the drilling fluid with starch ester exhibited a lower volume of filtrate than those where the commercial additive was applied (Tab. 3). It indicates that the mango starch derivative is able to minimize the influx of fluid through the porous rock, probably by interactions among its hydrophobic portions and the components that form the filter cake, such as the organophilic clay [23]. Higher volumes of filtrate are not desired, because it can induce problems on well drilling operation, such as decrement of hydrostatic pressure [50].

**Table 3:** Volume of filtrate, electrical stability, plastic viscosity, yield point and gel strength for drilling fluids prepared with commercial additive and starch ester

Property	Commercial additive	Starch ester
Volume of filtrate (mL)	8	7.2
Electrical stability (Volts)	435	364
Plastic viscosity* (mPa.s)	10.8	13.4
Yield point* (Pa)	1.4	2.1
Gel strength** (Pa)	0	1.02

\* Obtained from the Bingham model plot of curves on Fig. 6(a).

\*\* Obtained from the shear stress difference between final gel and initial gel.

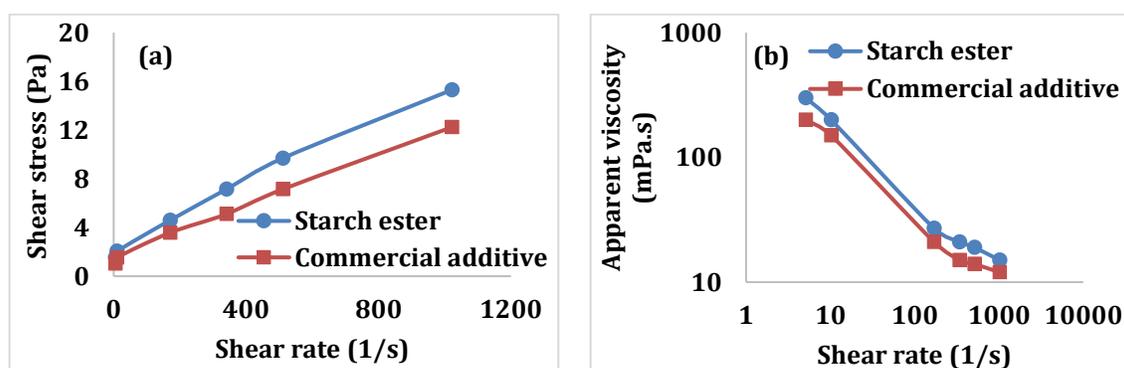
### 3.6 Electrical Stability

Emulsion breakage must be prevented in water-in-oil emulsion drilling fluids to assure viability of drilling operations [51]. Herein, fluids prepared with both starch ester and commercial filtrate controller exhibited much bigger stability values (Tab. 3) than the minimum of 200 V recommended by the API RP 13B-2 standard. The chemical structure of commercial additive is unknown, but the amphiphilic nature of the modified starch may have contributed effectively to the stability of the emulsion drilling fluid, as literature showed that under comparable conditions an drilling fluid with unmodified corn starch had electrical stability value lower than 200 V [23].

### 3.7 Rheology

Flow and viscosity curves for the drilling fluids are exhibited at Fig. 6, whereas the corresponding plastic viscosity, yield point and gel strength are presented in Tab. 3. Both fluids showed pseudoplastic behaviour, which means that the apparent viscosity decreases as the shear rate is increased. Low viscosity at the highest shear rates is required to clean the wellbore from drilled rock cuttings, to decrease pumping pressures and limit flow properties, promoting the increase of penetration rates. Whereas high viscosity at the lowest shear rates, help to carry cuttings from the well bottom to the surface, avoiding cutting accumulation in the borehole and proceed drilling [52, 53].

Fluid prepared with starch ester as filtration control additive displayed higher rheological parameters than the one prepared with the commercial additive. Starch ester based fluid presented higher viscosity, which can promote a better cleaning of the wellbore and, differently of commercial additive based fluids, presents gel strength and a higher yield point, that can help on maintaining cuttings in suspension in static conditions [52]. As also demonstrated in Tab. 2, the higher hydrophobicity of the derivative in relation to native mango starch allowed good interaction with the continuous phase of the drilling fluid, which contributes to its good rheological properties.



**Figure 6:** (a) Flow curves and (b) viscosity curves of the drilling fluids prepared with starch ester and commercial additive

### 4 Conclusion

Starch ester from mango starch kernel was successfully produced, as confirmed by solubility tests, FTIR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR. It was thermally more stable than its precursors and than a physical blend between mango starch and vinyl laurate, probably as a result of the lower number of hydroxyl groups, higher number of covalent bonds and higher molar mass of the products after esterification. The granular morphology was completely lost after acylation reaction in DMSO that separates the macromolecules by introducing a long hydrophobic chain onto starch, leading to a disorganized molecular network after precipitation and drying. The oil drilling fluid prepared with starch ester as additive presented excellent electrical stability as well as higher rheological parameters and lower volume of filtration under HPHT conditions when compared to the one prepared with the commercial additive. Therefore, starch ester fluid can promote a better cleaning of the wellbore and prevent problems related to fluid loss to the rock formation, which makes of this industrial waste bio-based derivative a promising candidate as additive for fluid loss control of oil drilling fluids.

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