

Influence of Acidity in Paste Properties of Modified Corn Starch Through Natural Fermentation

Maiara P Mendes^a, Crislayne T Vasques^a, Denise M B Silva^b, Claudia C F Monteiro^c, Ivo M Demiate^d, Antonio R G Monteiro^{b*}.

^aFood Science Post-Graduation Program, State University of Maringá, Av Colombo, 5790.87020-900, Maringá-PR, Brazil.

^bFood Engineer Department, State University of Maringá, Av Colombo, 5790.87020-900, Maringá-PR, Brazil.

^cDepartment of Design, State University of Maringá, Av Colombo, 5790.87020-900, Maringá-PR, Brazil

^dFood Engineer Department, State University of Ponta Grossa, Av. Carlos Cavalcanti, 4747 84030-900 Ponta Grossa-PR Brazil.

argmonteiro@uem.br

The objective of this research was to carry out the fermentation of corn starch in the same manner as cassava starch fermentation and to study its behavior during the fermentation process, analysing acidity and paste properties. CoS (corn starch) and CaS (cassava starch) were used. The sample was analysed by paste properties and acidity, at time 0, at every 7 days until the end of fermentation and after sun-drying. Regarding viscosity peak, CaS samples showed higher values, in the resistance attribute when comparing CoS and CaS samples those that had the same fermentation time did not present significant difference between them. CoS samples showed no significant difference between break results, but they did differ when compared to CaS samples. Only NCaS (native cassava starch) had greater retrogradation compared to CoS samples. However, the initial samples NCoS (native corn starch) and NCaS did not present differences in final viscosity results. However, they presented the highest values for this parameter with results of 171.50 and 180.50 RVU (Rapid Visco Units), respectively. Correlating results of acidity with paste properties it was observed that with fermentation time and consequent acidity increase, paste properties had important changes, decreasing the values of the measured parameters, only the paste temperature remained constant. It is concluded that the natural fermentation modification of corn starch compared with cassava starch had similarities about acidity. However, for pasting properties were no significant differences and should be better clarified through functional analysis and application product.

Keywords: Modified Starch; production; structure; paste properties.

1. Introduction

Starch is one of the most used polymers in the food industry. Currently, it stands out for its excellent utility in various food products. Its use is prevalent among food manufacturers because of its low price and availability. The primary sources of starch are corn, cassava, wheat and rice (Waterschoot et al., 2015).

During the last years, the gluten-free products market showed a remarkable expansion. This has occurred due to the demand of celiac patients, increasing digestive health issues, changes in consumer's eating habits and awareness about other food intolerance issues (Díaz et al., 2019).

The starches most used in the production of gluten-free products are those of corn and some roots and tubers, such as potatoes and cassava (Masure, Fierens&Delcour, 2016). In South America, it is used very starch fermented cassava and dried in the sun.

Fermentation in cassava starch is a type of enzymatic modification. The production of modified starches is an alternative that has been used to overcome one or more limitations of native starches. Native starches have unstable functional properties, i.e., low resistance to changes in pH, temperature and mechanical treatment. To avoid such undesirable changes, native starch is modified by physical, chemical or enzymatic methods (Alcázar-alay&Meireles, 2015).

By using different starch modification technologies, it is possible to obtain different characteristics in the final product. For this reason, selecting the appropriate modification process is vital in food production (Roznowska & Fortuna, 2017).

Fermented cassava starch is a product obtained from natural fermentation of native cassava starch or sweet starch. This modification occurs after the fermentation process and sun-drying. Starch modified by fermentation (enzymatic modification), acquires functional properties of industrial interest, such as increase in nutritional value and decrease of toxicity (Lopez-Diago et al., 2018). Besides conferring characteristic properties and flavor to the product. Fermentation may also change paste temperature and peak viscosity in comparison with native cassava starch (Cereda, 1983; Gomes et al., 2005).

To find starch sources which could behave similarly to that of cassava under fermentation and sun-drying. Fermented corn starch is a possible substitute for sour cassava starch. Its production may expand alternatives for the processing of gluten-free products in regions where cassava cultivation is not traditional.

Native corn starch can be modified to obtain a paste with specific attributes that can withstand extreme food processing requirements such as heat, agitation, and low pH conditions — making it a very suitable raw material for food production (López et al., 2010; Aquino et al., 2015).

Thus, the objective of this study was to carry out the fermentation of corn starch in the same way as the fermentation of cassava starch and to study its behavior during the fermentation process, analysing acidity and paste properties.

2. Materials and methods

Fermentation

Fermentations of cassava starch and corn starch were carried out separately. In the starch fermentation, 3 kg of each sample were used, and 4.8 L of water was added. The mixtures were subjected to a controlled temperature chamber at 30 °C.

During fermentation, sample acidity was analyzed weekly. The fermentation end was determined according to the acidity following Brazilian legislation that determines the maximum acidity for fermented cassava starch (CaS) of 5.0 mL of NaOH 100g⁻¹ (Brazil, 1978). With that, the fermentation of CaS lasted 21 days, and the corn starch (CoS) lasted 28 days. At the end of the fermentation, the excess water was drained. The samples were dried exposing them to the sunlight until reaching a moisture content of <14% (Brazil, 1978).

Sampling

During the fermentation period, portions of each sample were separated for analysis of paste properties and acidity at time 0, at every 7 days until the end of the fermentation and after sun-drying. The earlier separated samples were also sun-dried.

Acidity

The acidity was determined according to AOAC (1990) and the results expressed in mL of NaOH.100g⁻¹.

Paste properties

The determination of paste properties was performed using the methodology described by Pumacahua-Ramos et al. (2015) using an RVA-4 Rapid Viscosity Analyzer (Newport Sci., Australia). The results were expressed in RVU (Rapid Visco Units).

Statistical analysis

The data obtained were statistically evaluated from the analysis of variance (ANOVA), with a subsequent analysis of means by Tukey test at 5% probability using the software Sisvar 5.6 (Ferreira, 2011).

3. Results and discussion

The results in Tables 1 and 2 show the evolution of fermentation for CoS and CaS respectively, comparing the results of the same sample with each other during fermentation time.

Cereda and Vilpoux (2002) indicate that a titratable acidity greater than 7.0 mL of NaOH 100 g⁻¹ indicates very intense fermentation. In contrast, acidity lower than 3.0 mL of NaOH 100 g⁻¹ indicates no fermentation or no intense fermentation. It is observed that the fermentation of corn starch can only be confirmed with 14 days of fermentation, with sample CoS2 (Table 1) presenting acidity of 3.90 mL of NaOH 100 g⁻¹. CaS showed evidence of fermentation at 7 days, with sample CaS1 (Table 2) presenting acidity of 3.62 mL of NaOH 100 g⁻¹.

Table 1: Acidity of corn starch samples (CoS). Native corn starch (NCoS), fermented corn starches for 1, 2, 3 and 4 weeks of fermentation CoS1, CoS2, CoS3 and CoS4 respectively, and corn starch fermented for four weeks post sun-drying (FCoS).

Sample	Acidity (mL of NaOH 100 g ⁻¹)
CoS	2.92 ± 0.18 ^{bc}
CoS1	2.59 ± 0.18 ^c
CoS2	3.90 ± 0.04 ^a
CoS3	3.46 ± 0.06 ^{ab}
CoS4	3.82 ± 0.02 ^a
FCoS	4.13 ± 0.10 ^a

Equal letters in the same column indicate that there was no significant difference between the means of the results by ANOVA and Tukey tests, at 5% significance level.

Table 2: Acidity of cassava starch (CaS) samples. Native cassava starch (NCaS), cassava starch fermented for 1, 2 and 3 weeks of fermentation CaS1, CaS2, and CaS3 respectively and cassava starch fermented for three weeks post-sun-drying (FCaS)

Sample	Acidity (mL of NaOH 100 g ⁻¹)
NCaS	2.81 ± 0.21 ^c
CaS1	3.62 ± 1.05 ^{bc}
CaS2	4.10 ± 0.15 ^{abc}
CaS3	5.09 ± 0.31 ^a
FCaS	4.26 ± 0.17 ^{ab}

Equal letters in the same column indicate that there was no significant difference between the means of the results by ANOVA and Tukey tests, at 5% significance level.

Aquino et al. (2016) analysing the productive process of sour cassava starch from eight manufacturers observed that the titratable acidity of the samples of sour cassava starch varied between 1.66 and 7.05 mL of NaOH 100 g⁻¹. It is observed in the two fermented samples an increase in acidity according to the time of fermentation about native starches.

Since lactic acid bacteria are responsible for this process, as fermentation progresses, there is an increase in the production of organic acids, mainly lactic acid and acetic acid by bacteria (Adegunwa et al., 2011). Some studies indicate that sun exposure induces photochemical oxidation of fermented cassava starch in the presence of lactic acid, which is evidenced by a reduction in the concentration of these organic acids (Dufour et al., 1996). This may have happened to FCaS sample, which after sun-drying showed no significant difference with CaS1, CaS2 and, CaS3, considering that CaS3 had higher acidity than CaS1.

Table 3 compares the acidity results of AM and FM samples through fermentation time.

Table 3: Acidity comparison between samples during fermentation.

Sample	Acidity (mL of NaOH 100 g ⁻¹)					
	Native	7 days	14 days	21 days	28 days	Final
CoS	2.92 ± 0.18 ^a	2.59 ± 0.18 ^a	3.90 ± 0.04 ^a	3.46 ± 0.06 ^b	3,82±0.02	4,13±0,10 ^a
CaS	2.81 ± 0.21 ^a	3.62 ± 1.05 ^a	4.10 ± 0.15 ^a	5.09 ± 0.31 ^a	-	4,26±0,17 ^a

Equal letters in the same column indicate that there was no significant difference between the means of the results by ANOVA and Tukey tests, at 5% significance level.

It was observed in Table 3 that only in 21 days of significant fermentation differences between the samples were observed, with CaS having 5.09 mL of NaOH 100 g⁻¹ and CoS 3.46 mL of NaOH 100 g⁻¹, this acidity of CaS in 21 days is the maximum allowed by Brazilian legislation, thus CaS fermentation was interrupted.

The fermentation of CoS lasted 28 days with the acidity of 4.13 mL of NaOH 100 g⁻¹.

After fermentation and sun-drying the samples of CaS and CoS obtained 4.26 mL of NaOH 100 g⁻¹ and 4.13 mL of NaOH 100 g⁻¹ of acidity respectively and did not present significant differences between them. This final acidity is within the current Brazilian legislation (Brazil, 1978). In this way, it is noticed that although the CoS took longer to complete fermentation about CaS, after drying both products had the same characteristic acidity.

Table 4: Paste properties of native corn and cassava starch samples and treatments.

Sample	Paste temperature (°C)	Viscosity peak (RVU)	Resistance (RVU)	Break (RVU)	Retrogradation (RVU)	Final viscosity (RVU)
NCoS	80.30 ± 0.80 ^a	166.58 ± 1.08 ^e	95.50 ± 1.75 ^a	71.08 ± 2.83 ^d	76.00 ± 3.54 ^b	171.50 ± 1.78 ^a
CoS1	80.80 ± 0.64 ^a	154.42 ± 0.24 ^f	87.04 ± 0.41 ^{ab}	67.38 ± 0.65 ^d	60.92 ± 5.07 ^{bc}	147.96 ± 4.66 ^{bc}
CoS2	79.50 ± 0.00 ^a	156.29 ± 0.06 ^f	89.54 ± 1.00 ^{ab}	66.75 ± 1.06 ^d	63.42 ± 1.18 ^{bc}	152.96 ± 0.18 ^b
CoS3	79.40 ± 1.98 ^a	135.54 ± 1.47 ^{gh}	71.80 ± 2.30 ^{cd}	63.75 ± 3.77 ^d	42.05 ± 3.71 ^{de}	113.83 ± 1.41 ^{de}
CoS4	77.98 ± 0.60 ^a	143.63 ± 2.53 ^g	66.42 ± 3.30 ^d	77.21 ± 5.83 ^d	50.13 ± 4.18 ^{cde}	116.55 ± 0.88 ^d
FCoS	80.75 ± 0.80 ^a	131.67 ± 1.08 ^h	67.25 ± 1.75 ^d	64.42 ± 2.83 ^d	38.25 ± 3.54 ^e	105.50 ± 1.78 ^e
NCaS	65.90 ± 0.29 ^b	297.92 ± 1.39 ^a	85.83 ± 2.18 ^{ab}	212.08 ± 1.69 ^a	94.67 ± 1.55 ^a	180.50 ± 0.63 ^a
CaS1	66.50 ± 0.35 ^b	237.00 ± 1.41 ^b	81.96 ± 2.42 ^{bc}	155.04 ± 1.00 ^b	56.88 ± 2.06 ^{cd}	138.83 ± 0.35 ^c
CaS2	66.93 ± 0.25 ^b	243.29 ± 2.53 ^b	85.09 ± 1.18 ^{ab}	158.21 ± 1.36 ^b	55.29 ± 1.12 ^{cd}	140.38 ± 0.06 ^c
CaS3	66.45 ± 0.28 ^b	217.59 ± 0.24 ^c	70.59 ± 2.95 ^d	147.00 ± 2.71 ^{bc}	44.38 ± 1.47 ^{de}	114.96 ± 1.47 ^{de}
FCaS	66.30 ± 0.29 ^b	191.58 ± 1.39 ^d	53.50 ± 2.18 ^e	138.08 ± 1.69 ^c	36.42 ± 1.55 ^e	89.92 ± 0.63 ^f

Equal letters in the same column indicate that there was no significant difference between the means of the results by ANOVA and Tukey tests, at 5% significance level.

Evaluating the results of Table 4, where all samples are compared to each other, it is observed that paste temperatures of all CoS samples were statistically different from all CaS samples, but CoS samples among themselves had statistically the same paste temperatures, the same results were obtained for CaS. The paste temperature indicates the gelatinisation time during processing, where the first detected viscosity is measured. It is an index characterised by the initial change due to starch swelling. A higher paste temperature indicates higher water-binding capacity, higher gelatinisation and lower starch property due to the high degree of association between starch granules (Ezeala, 1984; Oyewole, 1990).

The CoS samples presented higher paste temperature compared to CaS samples, ranging from 77.98 to 80.80 °C. This may have occurred by the conversion of starch to simple sugars through fermentation by microorganisms, reducing the structural stability of starch (Adegunwa et al., 2011).

About viscosity peak, CaS samples presented higher values during the entire fermentation time and after drying compared to CoS samples. The highest peak value was 297.92 RVU for NCaS and the lowest of 131.67 RVU for FCoS. Peak viscosity is the maximum viscosity value of starch during the heating cycle. It is related to the quality of the final product and reflects the molecular degradation of starch (Wani et al., 2012; Dias et al., 2011). As temperature increases, starch granules swell and increase paste viscosity until viscosity peak is reached. A higher viscosity peak corresponds to a higher thickening starch power (Adegunwa et al., 2011).

For the resistance attribute, it was observed that comparing CaS and CoS samples in time, those with the same fermentation time did not present significant differences between them. Except for FCoS and FCaS samples that showed differences and had resistance values of 67.25 RVU and 53.50 RVU, respectively.

The CoS samples did not present significant differences between them in breakage results. However, had differences when compared to CaS samples. The highest break value was 212.08 RVU for NCaS and the lowest of 63.75 RVU for CoS3. The heat treatment followed by mechanical agitation on the starch granules leads to structural breaks and, consequently, loss of granule integrity. The breakage indicates the resistance of the starch under high temperature and stirring (Dias et al., 2011; Aquino et al., 2016). The lower the break value, the higher is the damaged starch content, in this way corn starch was the most damaged by fermentation (Dias et al., 2011; Aquino et al., 2016).

Only NCaShad greater retrogradation compared to CoS samples, which at all fermentation times had higher values than CaS samples. This may have occurred because CoS contains more amylose than CaS. With cooling, amylose molecules rearrange trying to return to their original structure, causing them to increase viscosity, forming a precipitate or gel, leading to retrogradation or setback (Asante et al., 2013). Retrogradation varies with temperature, shelf life, pH and starch source; it influences the acceptability and digestibility of food containing starch and the aging of bakery products (Denardin & Silva, 2009). Amylose is more involved in retrogradation properties because the linear chain structure of amylose helps to form hydrogen bonds between the molecules, which contributes to the formation of gels (Gani et al., 2013).

The initial samples NCoS and NCaS did not present differences in final viscosity results. However, they presented the highest values of this parameter with results of 171.50 and 180.50 RVU respectively, in comparison with the other samples. The samples FCoS and FCaS presented final viscosity values of 105.50 and 89.92 RVU respectively. The final viscosity indicates firmness of the heated starch and ability to form the gel. The firm gel texture is related to amylose present in the granule (Kong et al., 2015). Common corn starches have higher final viscosity value compared to waxy corn starches because they have a higher

amount of amylose. This fact was evidenced by Teixeira (2016) who studied the fermentation of waxy corn starch and Dias et al. (2007) that evaluated the fermentation of ordinary corn starch. These studies obtained values of final fermented starch viscosity of 158.8 RVU and 207.83 RVU respectively. Dias et al. (2007) also observed a drop in final viscosity between native and fermented starches.

Observing the individual fermentations of CoS and CaS, it was observed that in both fermentations there was a decrease of viscosity peak during fermentation. After fermentation and drying the samples of FCoS and FCaS showed the lowest viscosity peaks with 131.67 and 191.58 RVU, respectively. This can be explained by the fact that the fermentative process promotes changes in starch granules that interfere with its rheology. For this reason, the characteristic viscosity peaks have a lower maximum viscosity than the native starch (Diniz, 2006). Adengunwa et al. (2011), analysing different fermentation times in paste properties of sour starch samples from different cassava varieties also verified that viscosity peak decreased as fermentation time increased. For the cassava variety 30572, it decreased from 466.63 to 360.38 RVU at the end of fermentation, for 4(2)1425, decreased from 460.09 to 333.17 RVU, for 93B/00061, decreased from 357.25 to 342.29 RVU, for 96/0603, decreased from 395.75 to 362.96 RVU and for TME1, decreased from 458.36 to 380.75 RVU (Adengunwa et al., 2011).

By analogy of acidity results with paste property results, it was observed that with fermentation time and consequent acidity increase, the paste properties had important changes, decreasing their values for parameters in both samples, only paste temperature remained constant.

The results of acidity and paste properties indicate that there is a connection between the acidity increase of the samples and the decrease of viscosity peak, especially when looking at the values in the end of fermentation and post-drying. Acidity and fermentation reduce the viscosity peak, the fermentation disintegrates some starch granules, reducing the swelling capacity, because acids and enzymes attack amorphous regions of granules (Putri et al., 2012). This fact was also evidenced by Teixeira (2016), which obtained viscosity peak values of 528.49 RVU for native waxy corn starch and 489.18 RVU for fermented waxy corn starch. Decreased retrogradability can be observed during fermentation. Being that at the end of fermentation and after drying both fermented starches had the lowest values of retrogradation. This can be attributed to the changes caused by acid or enzymatic action on starch granules during fermentation due to starch structural modification (Rivera, 1997).

Conclusion

Based on the considerations it is concluded that corn starch was intensively modified by the fermentation process. The natural fermentation of corn starch makes the characteristics of this starch similar to those obtained by the natural fermentation of cassava starch about acidity. There were significant differences concerning paste properties that should be evaluated more deeply. There is a need to evaluate more functional characteristics of fermented corn starch. Apply the fermented corn starch products are now produced with fermented cassava starch. In this way, the differences pointed out in the study could be evaluated in practice and if they are relevant when applied in the product.

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