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Review

Trend of Modification by Autoclave at Low Pressure and by Natural Fermentation in Sweet Potato and Cassava Starches

Giselle de Lima Paixão e Silva *, Juliana Aparecida Correia Bento, Manoel Soares Soares Júnior and Márcio Caliari

Department of Food Engineering, School of Agronomy, Federal University of Goiás (UFG), Campus Samambaia, Rodovia GO-462, CP 131, Goiânia CEP 74690-900, Brazil; julianaap.ufg@gmail.com (J.A.C.B.); manoel@ufg.br (M.S.S.J.); macaliari@ufg.br (M.C.)

* Correspondence: xpaixao@hotmail.com

Abstract: Sweet potatoes (*Ipomoea batatas* L.) and cassava (*Manihot esculenta* C.) are part of the largest food crops in many countries. They have good nutritional value because, in addition to containing vitamins, minerals, carotenoids, and anthocyanins in varied contents, due to the existence of various colors of their pulps, they have starch as their major constituent. As such, they are considered valuable raw materials for the food factory. The starch granules have distinct morphologies and properties, related to the type of cultivar, planting conditions, storage, and processing, which in turn can affect the quality of the final products to which they have been added. The use of native starches in the food industry has limitations, which can be improved by modifications. Physical methods, as they are associated with green technology, and do not pollute the environment, have demonstrated great potential for this purpose. Both modifications—by autoclave at low pressure and natural fermentation—have shown potential in modifying these starches.

Keywords: physical treatment; autoclaving starch; spontaneous starch fermentation; *Ipomoea batatas* L.; *Manihot esculenta* C.

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1. Introduction

Sweet potato (*Ipomoea batatas* L.) is a tuberous root from Central and South America that has great economic importance and is easy to grow [1]. It has high nutritional value, with starch as its major component (70–80% d.w.), in addition to fibers, proteins, vitamins, minerals [2], and bio components (such as carotenoids, phenolics, and anthocyanins) [3]. Its pulp can display white, beige, orange, purple, and other colors [4] and its starch granules may exhibit different morphologies and pasting properties, presenting the potential for application in different products [5]. These differences, in both morphology and properties, may be associated with the cultivar, climatic conditions, and physiology of the sweet potato plant [6,7]. In this way, its starch (or its flour) is widely used in some countries, such as China, as ingredients in the food industry for contributing to the textural properties of soups, sauces, pasta, bread, and snacks [2,8,9].

Cassava (*Manihot esculenta* C.) is an important crop in the tropical and subtropical regions of the world, exhibiting good adaptability to poor soil and drought. It is a staple food at low cost and is rich in starch (on average 84.5% d.w.) [10]. Genetic factors and cultivation conditions influence the properties of cassava starch. The application of flour and starch from this root in food formulations being guided by the composition, physical–chemical and functional properties of these components. Cassava products include fermented and non-fermented (such as chips), which contribute to their growing industrial applications [11].

Starches in native form have limitations of use in the food industry, such as instability to changes in temperature and tendency to retrograde. Thus, the modification of native starches has been studied to expand and improve the use [12]. Modification methods

that do not use chemicals are the most attractive today [13] because they do not harm the environment [14], among them, are the autoclave modification methods [15] and fermentation [16]. Products modified by these methods (starch or flour) can be used as ingredients in food formulations, unlike those resulting from chemical methods that are classified as additives [17].

Previous research with autoclave modification has shown changes in granule morphology, increased absorption and solubility in water, increased thermal stability (with increased crystalline portion), and reduced retrogradation, in arrowroot starches [15], oats [18], rice [19], and sweet potatoes [20].

Regarding the fermentation in which the selected microorganisms are added, in spontaneous fermentation there is a staggering multiplication of the microorganisms inherent and natural to the raw material itself, thus being more practical and simpler. Microbial metabolites alter the structure of starch granules, giving them specific functional properties [21]. The "puba" is an example of typical food from the north of Brazil and of indigenous tradition, produced from the natural fermentation of cassava in domestic conditions [22]. However, there are few studies on the modification of starch and/or sweet potato flour through natural fermentation [23,24].

Therefore, and given the feasibility of modification by both autoclave and natural fermentation, this study aimed to show through the bibliographic review the feasibility of modification by autoclave at low pressure and by natural fermentation in cassava and sweet potato starches.

2. Sweet Potatoes (*Ipomoea batatas* L.)

Sweet potato (*Ipomoea batatas* L., *Convolvulaceae*) is a crop of great nutritional importance (Figure 1) after rice, maize, wheat, potatoes, millet, and cassava [3]. It is grown in many tropical and subtropical countries, such as Asia, Africa, and Latin America. They are dicotyledonous plants belonging to the *Convolvulaceae* family, in which there are approximately 50 genus and more than 1000 species [25]. The composition and content of nutrients in cultivars vary widely; depending on genetic and environmental factors [26]. Its cultivation is not seasonal, having a short vegetative cycle (3.5 to 5.5 months) and good adaptability to various climates and agricultural systems, which allows its wide supply and low cost [27,28].

Figure 1. Sweet potato, *Ipomoea batatas* L. Source: Personal archive.

Sweet potato presents diversified nutritional properties due to its white, beige, purple, and orange pulps [8], as well as variation in the content of its components, on a dry basis, such as starch (42.4–77.3%), crude fiber (1.9–6.4%), protein (1.3–9.5%), ash (1.1–4.9%), lipids (0.2–3.0%), and total sugar content, which is approximately 3.8%, with sucrose, maltose, and

glucose representing the predominant free sugars, which provide the sweet taste of this tuberous root [3]. It is usually consumed roasted, boiled, steamed, or fried as direct food [29].

It is also considered a highly nutritious vegetable because it contains vitamins (such as vitamin C, riboflavin, pyridoxine, and tocopherol), minerals (such as zinc, potassium, magnesium, copper, calcium, and iron), and fibers (such as pectin, cellulose, and hemicellulose). Depending on the color of its pulp, it has an expressive content of bioactive compounds, such as carotenoids, phenolic acids, and anthocyanins [9,13].

Carotenoids and anthocyanins are pigments synthesized by plants and are fat-soluble and water-soluble, respectively. The former is responsible for the yellow to orange colors, and the latter for the light pink to purple colors. Both can be used in foods, such as dyes, flavorings, and nutritional supplements [30]. Carotenoids are polyisoprenoid compounds classified into hydrocarbon carotenes (such as β-carotene) and xanthophylls [31].

Phenolic compounds are antioxidant molecules with at least one aromatic ring and one or more hydroxyl groups; flavonoids are a group of phenolics that consists of two aromatic rings linked by three carbons that are in an oxygenated heterocyclic ring [32,33]. As simple phenols, there are derivatives of hydroxycinnamic acid, and as polyphenols (or flavonoids), there are anthocyanins [31,34].

3. Orange and Purple-Fleshed Sweet Potatoes

In recent years, orange and purple-fleshed sweet potatoes (Figure 2) have been the focus of research due to the high content of carotenoids and anthocyanins, respectively [7,29,30,35].

Figure 2. Purple and orange-fleshed sweet potatoes. Source: Personal.

The purple sweet potato stands out mainly for its high content of anthocyanins (approximately 580.0 μg/g) and the presence of other phenolics [36]. The total phenolic content, simple phenolic acids, as well as total anthocyanins, are more concentrated in purple sweet potatoes, compared to orange, white, and beige sweet potatoes [37,38]. Antioxidant, cardioprotective, neuroprotective, antidiabetic, antihypertensive, anti-inflammatory, anti-hepatotoxic, and anti-tumor effects have been associated with the consumption of purple sweet potatoes [38–40].

The orange sweet potato contains a mixture of phenolic acids (such as hydroxycinnamic acids) and stands out for its high content of β-carotene (approximately 282.0 μg/g) and, consequently, its pro-vitamin A activity [2,3,38], that contributes to the prevention of deficiencies of vitamin A and night blindness [37]. Carotenoids and hydroxycinnamic acid derivatives have antioxidant capacity [39], neuroprotective effect [41], and anti-inflammatory [37].

4. White and Beige-Fleshed Sweet Potatoes

The white and beige-fleshed sweet potatoes (Figure 3) contains the luteochrome pigment [33,42], in addition to small amounts of β-carotene (approximately 16 μg/g) [37,43] and nothing or small amounts of anthocyanins (less than 45.0 μg/g) [36], having less beneficial effects associated with consumption than colored ones [44].

Figure 3. White and beige-fleshed sweet potatoes. Source: Personal archive.

Due to its production capacity, high consumption, nutritional value due to its bioactive components (especially orange and purple-fleshed sweet potatoes), and its correlation with disease prevention, sweet potatoes are considered a good food choice [38,45]. In this way, both its flour and its starch have great potential to be explored by the nutraceutical and food industry [7,13,28,46].

Because starch is the major constituent of sweet potatoes (about 80% d.w.) it is an important resource of the food industry for its use in pasta, soups, snacks, creams, baby foods, and bakery products [2,8,9,35,47].

5. Cassava (*Manihot esculenta* C.)

The cassava (*Manihot esculenta* C.; *Euphorbiaceae*) [48] (Figure 4) is one of the main staple food crops in Africa and South America [49]. It is a perennial crop and can be grown in poor soil and withstands adverse weather conditions [50]. This root has white, cream, yellow, and brown colors [51]; and nutrients such as vitamin C, carotenoids, calcium, potassium, iron, magnesium, cuprum, zinc, and manganese [52] and contains a high starch content (65–91% d.w.), although this content may vary in different cultivars [53]. In general, the nutrient composition of cassava and other fresh tubers has a high moisture content (greater than 70–80%), with intermediate levels of carbohydrates (20–30%) and low levels of proteins, lipids, and minerals (1–2%) [54].

Figure 4. Cassava, *Manihot esculenta* Crantz. Source: Personal archive.

In South America, the agricultural exploitation of this crop is intended for the horticultural market and the processing industries. The commercialization of cassava roots for use in human consumption occurs mainly in the fresh form. However, in Brazil, the market for cassava products for culinary use, such as frozen precooked, products processed from the cooked dough, such as croquettes, breaded, dumplings, and chips, is growing [55].

Cassava flour and starch have exceptional quality attributes that have been explored mainly in bakery and noodles products [56,57], for example, their native starch has high viscosity and transparency, in addition to freeze–thaw stability [58].Thus, for the various

industrial applications of starch, which can be obtained from different raw materials, it is important to investigate its structural, functional, and chemical properties [8,35,59].

6. Starch

Starch is presented in the form of individual aggregates, called granules, which are organized in growth rings, which originate from a central point or *hilum* [60]. These growth rings alternate in crystalline and amorphous regions/lamellae that are possible to view by X-ray diffraction [61,62]. They can present spherical and semi-spherical, oval, or polygonal shapes, with small and large sizes that can be observed through scanning electron microscopy [1,45]. The schematic representation of the organization, as well as the forms of sweet potato starch granules, can be seen in Figure 5A,B and Figure 6.

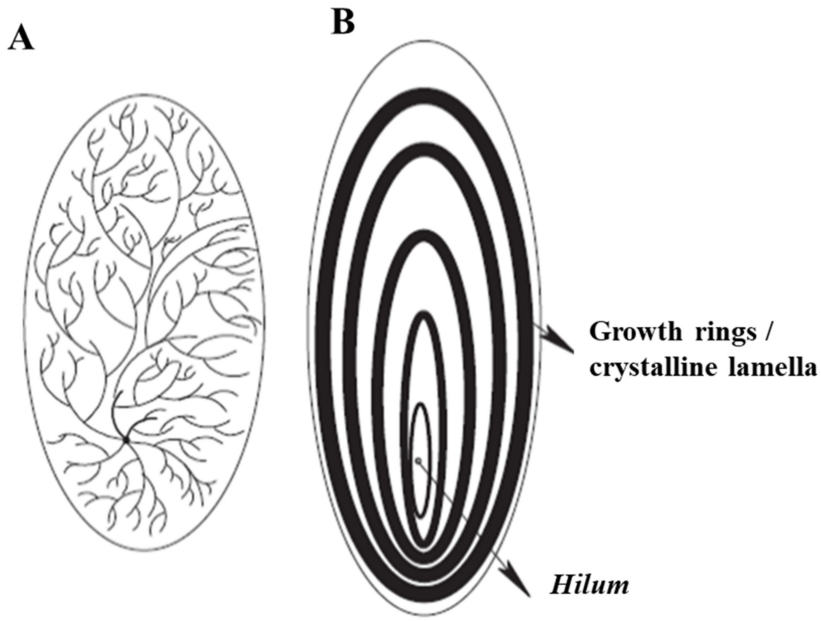

Figure 5. (**A**) Schematic organization of the sweet potato starch granule; (**B**) Central *hilum* and sweet potato starch granule growth rings. Reproduced from Xijun, Lin [61]; with some modifications.

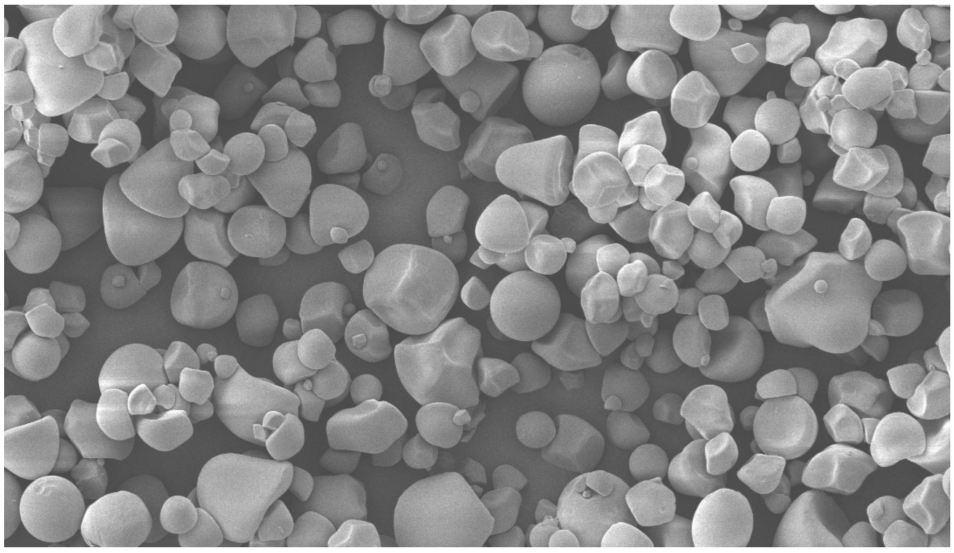

Figure 6. Scanning electron microscopy (500× magnification) of sweet potato starch granules. Source: personal archive.

Some factors, such as environmental conditions, the type of soil where the plant was cultivated, and the genotype, influence the morphology and properties of the starch granules [63].

Although the basic form of starch is a glucose monomer, its exact structure is extremely complex. However, the model called multi-scale structure has been universally accepted (Figure 7) where various parts of the starch are presented gradually on a scale from micrometer (10^{-3}) to nanometer (10^{-9}). With granules of 2–100 µm, growth rings of 120–500 nm, blocks of 20–50 nm, amorphous and crystalline lamellae ~9 nm, and molecular structure (amylose and amylopectin branches) 0.1–1.0 nm [64,65].

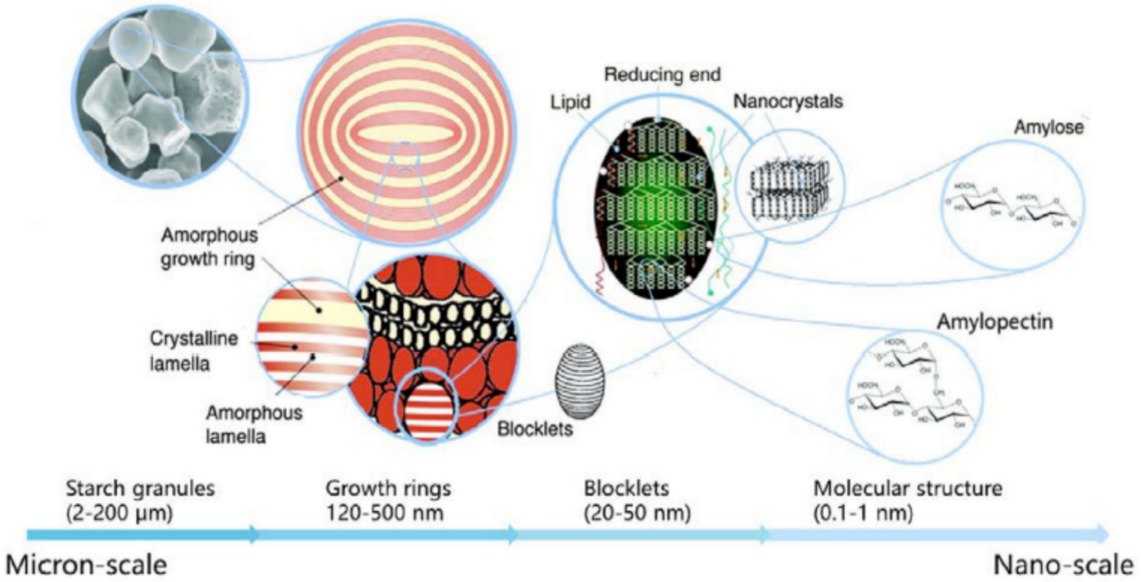

Figure 7. Multi-scale starch structure. Reprinted (adapted) with permission Le Corre, Bras [64] Copyright American Chemical Society and Gallant, Bouchet [65]

7. Amylose and Amylopectin

Amylose (Figure 8) is an essentially linear polymer that consists of D-glucopyranose linked by α-1,4 glycosidic bonds and is slightly branched (0.3 to 0.5%) by α, 1–6 glycosidic bonds [66]. Amylopectin (Figure 8) has the same basic structure and is a highly branched polymer containing around 6% α, 1–6 glycosidic bonds [64]. It has been reported that the molecular weight of amylose ranges from 10^5 to 10^6 and that of amylopectin is on the order of 10^7–10^9 [67].

Amylose has long branches with hundreds or thousands of glucose units, while amylopectin is extensively branched and has comparatively short branches (less than 100 glucose units) [68]. Amylose molecules tend to form helical structures, due to the axial → equatorial position of coupling D-glucopyranose molecules [69].

The coexistence of these two molecules joined by hydrogen bonds results in the appearance of crystalline and amorphous regions, and the linear part of amylopectin also forms a double helical structure; from which the crystalline regions of the granules originate. The amorphous region is formed by the branches of amylose and the branches of amylopectin [60,68,70].

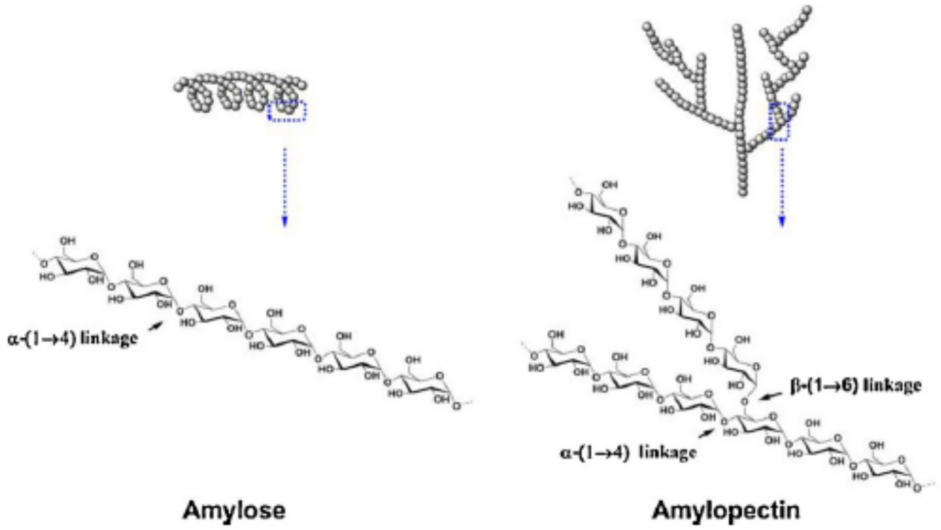

Figure 8. Illustration of the structure of amylose and amylopectin. Reproduced from Fan and Picchioni [66].

According to the crystallinity, the starch granules are classified in A, B, C, and V, and can be visualized in X-ray diffraction. Tuber starches are commonly type B, type A cereals, and type C roots and legumes, which is a mixture of standards A and B [71]. The type V pattern is observed when amylose is complexed with lipids [72], which can happen in native starch, but that possibly this complex is formed to a greater extent during heat treatment or gelatinization [60].

The difference in the structures of amylose and amylopectin makes these two components distinct in physical and chemical properties, for example, amylopectin is easier to dissolve in hot water, and amylose can complex with iodine and change the color of the solution to violet [66]. Amylopectin contributes to swelling, while amylose inhibits [7].

The amylose and amylopectin content have a decisive influence on the technological properties of starch, such as on the temperature of gelatinization, water solubilization, recrystallization or retrogradation, swelling, and viscoelastic properties [6,60]. Thus, understanding the structural and compositional basis for variations in the physicochemical properties of starch is essential for its better use [73].

8. Solubility, Swelling, Gelatinization, and Retrogradation

Starch has limited solubility in cold water, but when heated, it solubilizes and forms a paste or gel. This occurs due to the formation of hydrogen bonds between water molecules and hydroxyl groups in amylose and amylopectin molecules [74].

Gelatinization is the irreversible rupture of the granular structure of starch and occurs with its heating (60–70 °C) more than water, which leads to maximum swelling [6]. Initially, the separation of amylose and amylopectin occurs, by breaking the intermolecular hydrogen bonds and double helices, causing the loss of crystallinity. This process begins in the amorphous region because of the ease of water seepage. Sequentially, amylose leaches out of the granule, which contributes to solubilization [74]. Factors, such as the amount of water, the amylose/amylopectin ratio, and granular architecture, affect the gelatinization temperature and the quality of the paste [75]. This is a parameter widely explored by the food industry, and its study is important due to its relationship with the functionality of starch [27]. Some techniques and equipment, such as differential scanning calorimetry (DSC), x-ray diffraction, and the rapid visco analyzer (RVA) are used to assess the behavior of the granule against gelatinization [76].

When the gelatinized starch is cooled, the secreted amylose and amylopectin realign themselves in a crystalline structure, in a process known as retrogradation. It is usually accompanied by water loss or syneresis and increased viscosity. Besides, at the same time,

several amylose glucose molecules are bound to form the double helix and amylopectin chains crystallize [77]. The characteristics of retrogradation of amylose and amylopectin are distinct. This process in amylose is faster because of the reassociation by forming hydrogen bonds with other adjacent amylose molecules, forming crystalline structures of double helices when the solution cools and maintains for a long period. On the other hand, amylopectin retrogradation happens at a much lower rate over a long period [78]. Protein content, as well as the botanical origin, duration, and storage conditions, and quantity of water influence the retrogradation process [79].

9. Modification of Starch by the Physical Method of Autoclave at Low Pressure

In its native form, starch is insoluble in water at room temperature, has a strong tendency to retrograde, and low thermal stability or inability to withstand high temperatures, forms a weak, cohesive, and elastic paste when heated, and forms an unwanted gel when cooled or stored, which limits its direct application in food processing [12,80,81]. To overcome these disadvantages and adapt them to wider industrial applications, chemical, physical, and enzymatic modifications have been studied to significantly alter the functional properties of starch [74,82]. Physical changes include different combinations of temperature, humidity, pressure, irradiation, and shear [83]. They are simple, low-cost, and safe, as they do not use chemical agents, being the current focus of research as they are considered a technique for producing starch derivatives in a "green" way [66].

Among the most used methods for the physical modification of sweet potato starch are heat moisture treatment (HTM) [84–86] and high hydrostatic pressure (HPP) [87,88]. HMT is a modification that involves low levels of humidity, (usually in a range of 10–30%), and heating at high temperatures in an autoclave or oven (90–120 °C) for a period ranging from 15 min to 16 h [89]. In the HPP, different combinations of pressure (above 100 MPa) and temperature can be used to achieve the desired effect on the texture, color, and flavor of food [87].

Previous studies report that the physical modification using an autoclave, has, as the main characteristic, the pre-gelatinization of starches, allowing their dispersion in cold water and reducing the energy necessary for the process to occur, which is correlates with the breakdown of the granular structure, resulting in the alteration of the paste, thermal and functional properties (such as absorption and solubility in water) [15,19,20].

Changes in sweet potato granules modified by HPP have been reported in studies by Carballo Pérez, Mu [87] with a 56.80% reduction in particle size (Table 1). Moreover, researchers using HTM in different conditions of exposure time, temperature, and humidity to modify sweet potato and cassava starches showed a reduction in the water absorption index of 16.66–68.08% [84–86]) (Table 2). However, concerning the water solubility index, Jyothi, Sajeev [84] obtained an increase of more than 100% in this index, and Trung, Ngoc [85], Huang, Zhou [86]) obtained a reduction of 50.00–76.48%.

Table 1. Particle mean size of granules and amylose content of native and modified starches by high hydrostatic pressure (HPP), autoclave and fermentation, and pH of fermentation broth of native and fermented starches.

Starch Source	Modification	Mean Diameter (μm)		Amylose (%)		pH	Reference
		Native/Modified Starch	% **	Native/Modified Starch	% **		
Sweet potato	HPP (100, 200, 300 and 400 MPa; 20 min, 25 °C)	34.86–14.95 *	56.80	-	-	-	Carballo Pérez, Mu [87]
Sweet potato	Autoclave (1.1 Kgf.cm^{-2}, 1 h, 121 °C	-	-	18.17–24.98	37.50	-	Babu and Parimalavalli [20]
Sweet potato	Fermentation (natural of sour liquid) (24 h, 25 °C)	12.81–11.44	10.69	25.61–24.27	5,23	-	Deng, Mu [23]
Cassava	Fermentation (natural in a tank) (30 days, 35 °C)	15.30–13.90	9.15	-		-	Alvarado, Grosmaire [90]
Sweet potato	Fermentation (natural in a tank) (3.8 and 12 months; 30 °C)	-	-	29.40–6.10	79.25	-	Ye, Xiao [91]
Cassava	Fermentation (natural) (20 days, 20 °C)	-	-	20.00–17.00	15.00	-	Díaz, Dini [21]
Sweet potato	Fermentation (natural) (120 h, 30 °C)	-	-	-	-	6.49–4.50	Yuliana, Nurdjanah [24]
Cassava	Fermentation (artificial: *L. amylophyllus*) 48 h, 30 °C)	-	-	-	-	6.16–6.95	Putri, Haryadi [92]
Cassava	Fermentation (natural) (7 days, 40 °C)	-	-	-	-	6.42–4.95	Paixão e Silva, Bento [93]
Cassava	Fermentation (natural) (72 h, 25 °C)	-	-	-	-	5.40–4.60	Oyeyinka, Adeloye [48]

* at 200 Mpa; ** percentage of reduction or increase of native to modified starch.

Table 2. Water absorption index (WAI) and water solubility index (WSI) of native and modified starches by heat moisture treatment (HTM), autoclave, and fermentation.

Starch Source	Modification	WAI (g/g)		WSI (%)		Reference
		Native/Modified Starch	% [1]	Native/Modified Starch	% [1]	
Sweet potato	HTM (6, 10 and 14 h, 80, 100 and 120 °C; 15.20 e 25% of moisture)	25.10–15.30 ****	39.04	15.70–31.90 ****	103.19	Jyothi, Sajeev [84]
Cassava	HTM (6, 10 and 14 h, 80, 100 and 120 °C; 15.20 e 25% of moisture)	36.60–19.70 ****	46.17	22.30–48.20 ****	116.14	Jyothi, Sajeev [84]
Sweet potato	HTM (6 h, 100 °C; 35% of moisture)	12.00–10.0 ****	16.66	8.00–4.00 ****	50.00	Trung, Ngoc [85]
Sweet potato	HTM (2 h, 100 °C; 30% of moisture)	21.01–6.71 ***	68.08	11.44–2.69 ***	76.48	Huang, Zhou [86]
Sweet potato	Autoclave (1.1 Kgf.cm^{-2}, 15 to 60 min, 121 °C	5.00–10.00 *	50.00	2.00–8.00 *	300.00	Paixão e Silva, Bento [94]
Sweet potato	Autoclave (1.1 Kgf.cm^{-2}, 15 to 60 min, 121 °C	6.70–14.80 *	120.90	1.00–9.00 *	800.00	Silva, Bento [95]
Sweet potato	Fermentation (natural) (120 h, 30 °C)	4.50–6.00 **	33.33	21.00–13.00 **	38.09	Yuliana, Nurdjanah [24]
Cassava	Fermentation (natural) (72 h, 25 °C)	24.00–12.00 **	50.00	-	-	Oyeyinka, Adeloye [48]

* at 60 °C; ** at 70 °C; *** at 80 °C; **** at 90 °C; [1] percentage of reduction or increase of native to modified starch.

Regarding the thermal and pasting properties, some authors who used the HTM modification in sweet potato and cassava starches obtained a reduction of 30.60–69.14% in peak viscosity and 10.28–62.05% in gelatinization enthalpy, as well as an increase of 21.98%, 13.98%, and 20.59% in final viscosity, in pasting temperature and peak temperature respectively [84,85] (Tables 3 and 4). Besides, the HPP method in sweet potato starch reduced the peak temperature by 1.62% and the gelatinization enthalpy by 3.8% [87] (Table 4).

Table 3. RVA parameters (pasting temperature, peak viscosity and final viscosity) of native and modified starches by high hydrostatic pressure (HPP), heat moisture treatment (HTM), autoclave, and fermentation.

Starch Source	Modification	Pasting Temperature (°C)		Peak Viscosity (cP)		Final Viscosity (cP)		Reference
		Native/Modified Starch	% *	Native/Modified Starch	% *	Native/Modified Starch	% *	
Sweet potato	Autoclave (1.1 Kgf.cm^{-2}, 1 h, 121 °C	70.68–50.07	29.15	4906.66–381.00	92.23	3558.33–581.50	83.65	Babu and Parimalavalli [20]
Sweet potato	Autoclave (1.1 Kgf.cm^{-2}, 15 to 60 min, 121 °C	74.60–82.00	9.92	-	-	2682.00–450.00	83.22	Paixão e Silva, Bento [94]
Sweet potato	HTM (6, 10 and 14 h, 80, 100 and 120 °C; 15.20 e 25% of moisture)	-	-	2723.00–873.50	67.92	-	-	Jyothi, Sajeev [84]
Cassava	HTM (6, 10 and 14 h, 80, 100 and 120 °C; 15.20 e 25% of moisture)	-	-	2826.50–872.00	69.14	-	-	Jyothi, Sajeev [84]
Sweet potato	HTM (6 h, 100 °C; 35% of moisture)	71.50–81.50	13.98	1778.00–1074.00	30.60	1592.00–1942.00	21.98	Trung, Ngoc [85]
Sweet potato	Fermentation (natural of sour liquid) (24 h, 25 °C)	79.50–82.70	4.02	178.00–189.00	6.18	-	-	Deng, Mu [23]
Cassava	Fermentation (natural in a tank) (30 days, 35 °C)	61.60–62.00	0.65	835.00–777.00	6.95	844.00–522.00	38.15	Alvarado, Grosmaire [90]
Sweet potato	Fermentation (natural in a tank) (3.8 and 12 months; 30 °C)	78.60–78.80	0.25	5346.00–2246.00	58.00	3737.00–1237.00	66.89	Ye, Xiao [91]
Sweet potato	Fermentation (natural) (120 h, 30 °C)	93.87–84.30	10.20	430.00–947.00	120.00	-	-	Yuliana, Nurdjanah [24]
Cassava	Fermentation (artificial: *L. amylophyllus*) 48 h, 30 °C)	85.10–91.40	7.4	2169.60–1209.60	44.25	1984.00–1561.00	21.32	Putri, Haryadi [92]
Cassava	Fermentation (natural) (7 days, 40 °C)	63.37–61.22	3.40	3035.88–5540.76	82.50	2088.84–2529.36	21.10	Paixão e Silva, Bento [93]
Cassava	Fermentation (natural) (72 h, 25 °C)	74.00–75.00	1.35	5930.00–5210	12.15	3450.00–5260.00	62.89	Oyeyinka, Adeloye [48]

Table 3. *Cont.*

Starch Source	Modification	Pasting Temperature (°C)		Peak Viscosity (cP)		Final Viscosity (cP)		Reference
		Native/Modified Starch	% *	Native/Modified Starch	% *	Native/Modified Starch	% *	
Cassava	Fermentation (natural in a tank) (15 to 90 days; 25 °C)	63.48–64.52	1.64	24,000.00–10,000.00	58.33	-	-	Alonso-Gomez, Niño-López [14]
Cassava (tapioca)	Fermentation (artificial: *L. plantarum*) 24 h, 37 °C)	65.00–65.80	1.23	1650.00–1218.30	26.16	1304.00–901.70	30.85	Qi, Hong [96]
Sweet potato	Fermentation (artificial: *L. plantarum*) 3 days, 37 °C)	79.25–79.90	0.82	5227.20–4722.00	9.67	3219.60–3417.60	6.15	Liao and Wu [97]

* Percentage of reduction or increase of native to modified starch.

Table 4. DSC parameters (peak temperature and gelatinization enthalpy-ΔH) of native and modified starches by high hydrostatic pressure (HPP), heat moisture treatment (HTM), autoclave, and fermentation.

Starch Source	Modification	Peak Temperature (°C)		Gelatinization Enthalpy/ΔH (J/g)		Reference
		Native/Modified Starch	% [1]	Native/Modified Starch	% [1]	
Sweet potato	HPP (100, 200, 300 and 400 Mpa; 20 min, 25 °C)	78.59–77.32	1.62	0.79–0.76	3.80	Carballo Pérez, Mu [87]
Sweet potato	Autoclave (1.1 Kgf.cm^{-2}, 15 to 60 min, 121 °C	-	-	11.24–22.00	95.73	Silva, Bento [95]
Sweet potato	Autoclave (1.1 Kgf.cm^{-2}, 15 to 60 min, 121 °C	73.35–86.00	17.24	-	-	Paixão e Silva, Bento [93]
Sweet potato	HTM (6, 10 and 14 h, 80, 100 and 120 °C; 15.20 e 25% of moisture)	-	-	10.70–9.60	10.28	Jyothi, Sajeev [84]
Cassava	HTM (6, 10 and 14 h, 80, 100 and 120 °C; 15.20 e 25% of moisture)	-	-	11.80–7.30	38.13	Jyothi, Sajeev [84]
Sweet potato	HTM (6 h, 100 °C; 35% of moisture)	71.88–86.65	20.59	12.36–4.69	62.05	Huang, Zhou [86]
Sweet potato	Fermentation (natural of sour liquid) (24 h, 25 °C)	77.77–78.66	1.14	8.22–4.49	45.37	Deng, Mu [23]
Sweet potato	Fermentation (natural in a tank) (3.8 and 12 months; 30 °C)	73.90–74.40	0.67	12.30–12.70	3.25	Ye, Xiao [91]
Cassava	Fermentation (natural) (20 days, 20 °C)	68.50–67.20	1.89	15.40–13.85	10.06	Díaz, Dini [21]
Cassava	Fermentation (natural) (7 days, 40 °C)	68.87–67.69	1.71	10.43–11.96	14.67	Paixão e Silva, Bento [93]
Cassava	Fermentation (natural) (72 h, 25 °C)	72.00–80.00	11.11	4.00–3.00	25.00	Oyeyinka, Adeloye [48]
Cassava	Fermentation (natural in a tank) (15 to 90 days; 25 °C)	-	-	2.18–3.47	59.17	Alonso-Gomez, Niño-López [14]

[1] percentage of reduction or increase of native to modified starch.

Although there are many works of HTM with autoclave, there are few studies with physical modification of sweet potato starch using an autoclave at low pressures (0.107 MPa, 121 °C) with different exposure times and moisture [20,98].As shown in Tables 2–4 Paixão e Silva, Bento [94], Paixão e Silva, Bento [95] in their studies with modification of sweet potato starch using low pressure (0.107 MPa, 121 °C) they observed a 50.00–120.90% increase in the absorption index, a 300–800% increase in the water solubility index (Table 2), a 17.24% increase in peak temperature, a 95.73% increase in gelatinization enthalpy (Table 4) and a 9.92% increase in pasting temperature (Table 3). Babu and Parimalavalli [20] also used low pressure in an autoclave to modify sweet potato starch and noticed a 37.50% increase of amylose content (Table 1), a 29.15% reduction in pasting temperature, a 92.23% reduction in peak viscosity, and an 83.65% reduction in final viscosity (Table 3).

10. Modification of Starch by Spontaneous Fermentation or "Puba" Production

Modification of starch by fermentation is also an alternative method to chemical modification [14]. With the growing interest in green technology and the demand for starches with new features, the modification of starch using fermentation is promising for specific food applications. Fermentation has been commonly applied to the modification

of cassava starch to improve functionality and can produce starches with characteristic flavors [48].

The growth of microorganisms in the fermentation medium, conditioned by the availability of nutrients, enables the production of enzymes and acids (such as lactic acid) that, in turn, alter the structure of the starch granules, their physicochemical properties [21], as well as their gelatinization behavior [90].

Some results of the previous research with fermentation in sweet potato and cassava starches can be seen in Table 1. These results showed that the pH of the fermentative broth decreased from 5.40–6.49 to 4.50–4.95 [24,48,92,93]. Similarly, there was a 5.23–79.25% reduction in the amylose content of fermented starches [21,23,91]. This table also shows a 9.15–10.69% reduction in the granule size in fermented sweet potato and cassava starches [23,90].

Table 2 shows that natural fermentation under different conditions and sources can present different results regarding swelling and solubility, which Yuliana, Nurdjanah [24] obtained a 33.33% increase in swelling and a 38,09% reduction in solubility with fermented sweet potato starch, but Oyeyinka, Adeloye [48] obtained a reduction of 50.00% in swelling with fermented cassava starch.

Commonly in the northern regions of Brazil, fermented cassava flour, called "puba", is widely used in artisanal cake making. The process is usually done by immersing the peeled roots of cassava in water for an average of seven days or until softening by natural fermentation, then washing the mass and exposing it to the sun to dry the flour [22]. The microorganisms associated with this type of fermentation are *Lactobacillus*, *Streptococcus*, *Enterococcus*, *Leuconostoc*, *Pediococcus*, and *Lactococcus* [92].

Studies with a spontaneous fermentation of cassava for seven days demonstrated that the process can slightly change the thermal properties and markedly the paste properties of its flour [93]. The natural fermentation (for seven days) of corn starch has also been shown to alter its pasting properties. In addition to making the acidity characteristics of this component similar to those obtained by the natural fermentation of cassava starch [99].

However, recent studies using natural (or spontaneous) fermentation to modify sweet potato starch are rare in the literature, and the few that exist have reported depolymerization of the granular structure with modification of the thermal and pasting properties of their flours; thus, suggesting that a greater number of researches being carried out to evaluate this method [23,24].

Previous research presented in Tables 3 and 4, which aimed to modify sweet potato and cassava starches under various conditions (form of inoculation of the microorganism, time and temperature of fermentation) both by natural and artificial fermentation found an increase of 0.25 to 4.02% [14,23,48,90–92,96,97] or a reduction of 3.40 to 10.20% [24,93] in pasting temperature, an increase of 6.18 to 120.00% [23,24,93], or a reduction of 6.95 to 58.33% [14,48,90–92,96,97] in peak viscosity, an increase of 6.15 to 62.89% [48,93,97] or a reduction of 21.32 to 66.89% [90–92,96] in final viscosity (Table 3), an increase of 0.67 to 11.11% [23,48,91] or a reduction of 1.71 to 1.89% [21,93] in peak temperature and an increase of 3.25 to 59.17% [14,91,93] or a reduction of 10.06 to 45.37% [21,23,48] in gelatinization enthalpy (Table 4).

According to the data summarized in Tables 1–4, a divergence between the surveys can be observed. This can be explained due to the variations of the methodologies used for the different modifications presented here, as well as the type of cultivar of the sweet potato or manioc used, and the way of extracting the starch and or flour.

11. Conclusions

Due to the economic importance of cultivation in various regions of the world, the high nutritional value, and because they are rich sources of carbohydrates, starches and flours from sweet potato and cassava have great potential for use in the food processing industry. However, the direct application of starch in its native form has limitations that encourage the

growing exploration of methods to modify this component. Physical modifications have been preferred over chemical ones because they are simple, safe, and produce green starches.

Among the methods commonly used for this purpose are HTM and HPP in different combinations of parameters, but with the use of a low pressure autoclave (0.107 MPa, 121 °C), studies are few. Significant changes in amylose content, water absorption and solubility, peak temperature, gelatinization enthalpy, paste temperature and peak and final viscosities have already been reported through the use of this low pressure autoclave treatment.

Fermentation has also been described as an alternative to methods that use chemical agents. Researcher studies reported here, in regards to fermentation of sweet potatoes and cassava, obtained a reduction in the pH of the fermentation broth, a reduction in the granular size, changes in the technological, thermal, and paste properties of their starches. However, studies on starch modification through natural fermentation of sweet potatoes are also rare. In the few that exist, they described the depolymerization of the granular structure and changes in the thermal and paste properties.

Thus, the development of research aimed at the modification of sweet potato or cassava starch, by autoclave at low pressure, and by natural fermentation, are necessary to provide a greater scientific basis for this area of study.

Moreover, due to the relevance of these changes, caused in sweet potato and cassava starches, both by low pressure autoclave and natural fermentation, to replace chemically modified ones, future research with the purpose of testing these modified products in various industrial applications (as in sauces, baby foods, snacks, soups, creams and pastas) are suggested.

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