

Marina F. de Escalada Pla
Carolina E. Genevois *Editors*

Designing Gluten Free Bakery and Pasta Products

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Chapter 3

Non-cereals Starch Resources



Cecilia Dini, Silvia Flores, María Gabriela Kupervaser, Carola Sosa, Maria Victoria Traffano-Schiffo, and Sonia Zulma Viña

Abbreviations

CS	cassava starch
DHT	dry heat treatment
DSC	scanning differential calorimetry
FTIR	fourier transform infrared
GF	gluten-free
GI	glycaemic index
HMT	heat-moisture treated
HPMC	hydroxypropyl methylcellulose
PS	potato starch

C. Dini · S. Z. Viña

Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA), UNLP-CONICET-CICPBA, La Plata, Argentina

e-mail: cdini@biol.unlp.edu.ar; soniavia@quimica.unlp.edu.ar

S. Flores (✉)

Universidad de Buenos Aires (UBA), Facultad de Ciencias Exactas y Naturales (FCEN), Departamento de Industrias, Intendente Güiraldes 2160 (1428), Ciudad Autónoma de Buenos Aires, Argentina

CONICET – Universidad de Buenos Aires, Instituto de Tecnología de Alimentos y Procesos Químicos (ITAPROQ), Buenos Aires, Argentina

e-mail: sflores@di.fcen.uba.ar

M. G. Kupervaser · C. Sosa

Grupo de Investigación en Biotecnología y Alimentos (BIOTEC), Universidad Tecnológica Nacional. Facultad Regional Resistencia, Resistencia, Chaco, Argentina

e-mail: g_kupervaser@ca.fre.utn.edu.ar; departamentoiq@fre.utn.edu.ar

M. V. Traffano-Schiffo

Instituto de Química Básica y Aplicada del Nordeste Argentino, IQUIBA-NEA, UNNE-CONICET, Corrientes, Argentina

e-mail: m.traffanoschiffo@conicet.gov.ar

R&T	roots and tubers
RS	resistant starch
RVA	rapid visco analyser
RVU	rapid visco units
SEF	soybean extruded–expelled meal
SEM	scanning electron microscopy
WS	waxy starches
XG	xanthan gum

3.1 Introduction

To produce bakery goods, the gluten protein is the key factor due to its contribution to water absorption capacity and because it provides extensibility, elasticity and cohesiveness to bread dough. This allows the fermentation gas remains occluded and maintained in the liquid phase during dough development, leading to obtain high-grade breads (Wieser 2007). However, gluten has been identified as the responsible of celiac disease (Ronda et al. 2009), and the only effective treatment for patients is to follow strictly a gluten-free (GF) diet (Witczak et al. 2016). It has been observed that, if formulation is not properly adjusted, baked products without gluten could result in lower quality attributes, reduced nutritional characteristics and consumer acceptance (Naqash et al. 2017). Therefore, the development of GF products appropriate for consumers with disorders related to gluten intake was growing in importance (Zhang et al. 2017).

Formerly, hydrocolloids and starch were the major ingredients in GF diets (Shi and Bemiller 2002). From last decades, the demand of new food ingredients suitable for GF products is expanding in order to obtain more foods for a wider diet without potentially allergenic proteins. Among those ingredients, alternative starches resources are intensely searching. Starch is one of the most abundant and consumed natural polysaccharide in human diet. It is a biopolymer composed of glucose and it is obtained from plants such as grains, legumes, and tubers (Karmakar et al. 2014). Despite its high abundance, commercially sustainable sources of starch are limited to corn, wheat, cassava, potato and rice. With respect to corn, the global market reached 78 million tons (Mt) in 2020, being mainly produced in the United States, Europe and China (70–80%), whereas wheat is produced (6.3 Mt) mostly in Europe China and India (98%). The cassava starch (CS) production (6.9 Mt) comes from Asian Pacific region (Thailand, China and Indonesia) and Brazil (75%). Finally, potato starch (PS) which global market attained 3.4 Mt, accounting the highest productions from China, India, United States and Europe (80%); while rice is produced particularly in Asia (Expert Market Research 2020; Murphy 2000). Each region has a more convenient source of starch production mostly determined by climatic and logistic requirements (Semeijn and Buwalda 2018).

For food production (noodles, baked goods, etc.), starch is widely used as a gelling, thickening, and/or stabilizing agent (Fonseca et al. 2021; Rożnowski et al. 2014), besides being processed and used as binder, sweetener and as emulsifier (Mahmood et al. 2017; Bello-Pérez et al. 2006).

In particular, natural starches with low or without gluten are intensely requested because of their possibility to be used in the formulation of GF bakery products. In this context, corn and potato are the most commonly used starches, together with cassava and rice (Masure et al. 2016), due to their beneficial characteristics, such as neutral taste, soft texture, and high digestibility. They are frequently used in combination with proteins and hydrocolloids to counter their minimal structure-building potential, contributing to the structure, texture and stability of food through their thickening or gelling behaviour and surface properties (Capriles and Arêas 2014; Doublier et al. 2000). Other cereals, like minor or pseudo-cereals, like sorghum, millet, quinoa, amaranths and buckwheat, are being tested as alternative ingredients tolerated by celiac patients (Comino et al. 2013). In addition, new sources of non-cereal starch are being explored including beans (pea, chickpea), sweet potato and other ethnical tubers, carrots, nuts and some fruits as banana or mango (unripe pulp and kernel) (Witzcak et al. 2016; Punia Bangar et al. 2021; Lagunes-Delgado et al. 2022). Till the moment, many reports are found describing general properties of such novel starches but there are not clear applications yet.

To better understanding the functionality of starch in food production, some general aspects about structure, functional, nutritional properties and a brief mention to available techniques to modify starches is described in the following sections. A special description and some applications of potato, cassava and others non-conventional resources starches is also exposed.

3.2 Native Starch

3.2.1 Morphology and Chemical Structure

Starch is usually stored during photosynthesis in the amyloplasts of tubers, seeds of cereals and legume crops, rhizomes and other reserve organs of some plants (Emmambux and Taylor 2013).

Regarding to the morphology and surface properties (smooth or dented) of starch granules (different shapes such as spherical, polygonal to splits or lenticular), depends on the starch source and the lipid, protein and phosphorus contents, which influence the behaviour in terms of functional characteristics such as pasting properties and water binding capacity. For example, smaller and angular starch granules, show higher resistance to amylolysis and to gelatinization than large and spherical granules (Przetaczek-Rożnowska et al. 2018; Malumba et al. 2017). Additionally, starch granules can present different types of size distribution (unimodal, bimodal, or trimodal) (Schmiele and Sampaio 2019). As it can be observed in Fig. 3.1, rice

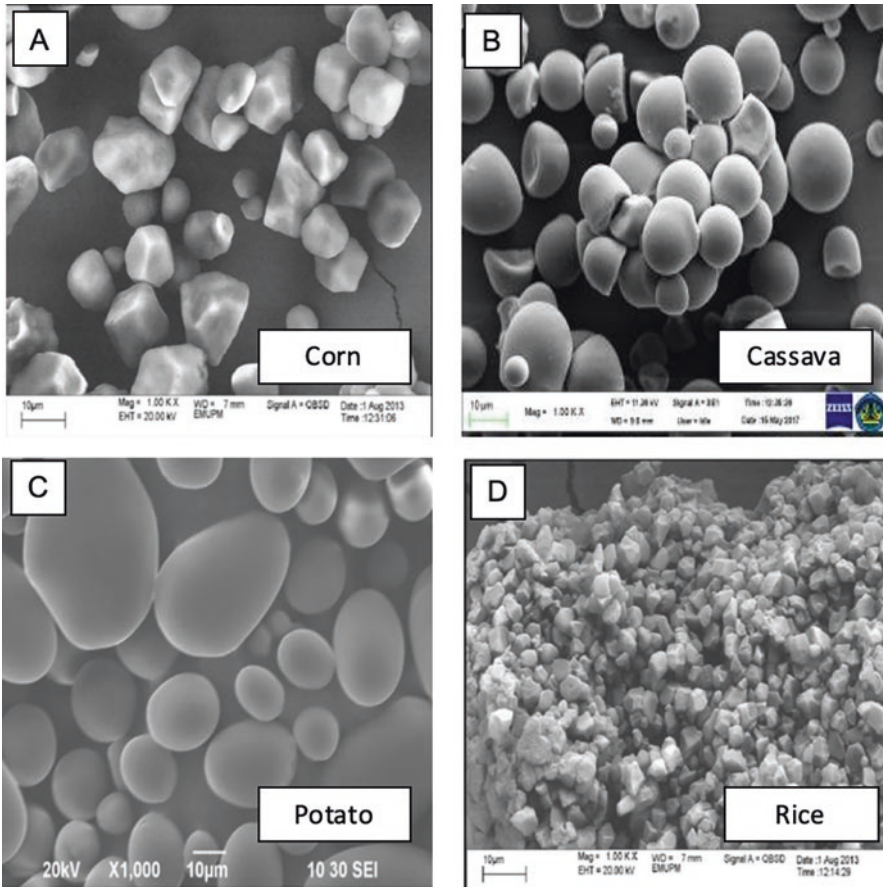


Fig. 3.1 Scanning electron microscopy (SEM) of starch granules (a) corn, (b) cassava, (c) potato and (d) rice with $\times 1000$ magnification at 20 kV. (Reprinted with permission from: (a) and (d) Aghazadeh et al. 2017; (b) Yulianto et al. 2020, Copyright © 2020 by the authors. This is an open access article distributed under the Creative Commons Attribution License which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited; (c) Liu et al. 2016)

starch granules (3–8 μm , are very small polygonal) are considerably smaller than those of potato (20–50 μm large, are round or oval), cassava (8–20 μm , are round or truncated) and corn (10–15 μm , are polygonal) (Semeijn and Buwalda 2018; Waterschoot et al. 2014).

There is a consensus regarding starch granule structure, however researchers are continuously proposing more suitable models. The most consolidated structure suggests a multiscale granule organization (Fig. 3.2).

From the highest to lowest scale, the whole granule (2–100 μm) is composed by amorphous and semi-crystalline growth rings (120–500 nm thick) which are built for ovoid blocklets (20–50 nm). They support nanometric crystalline regions

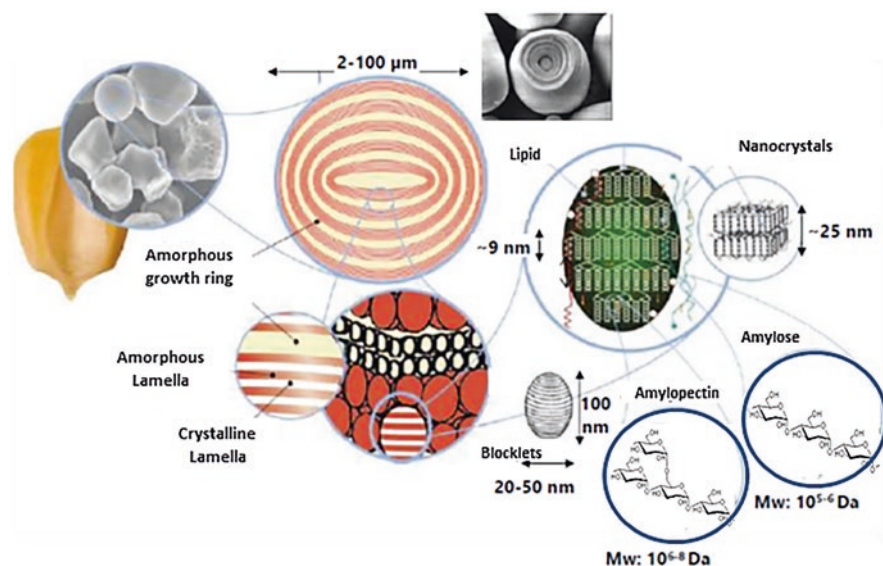


Fig. 3.2 Starch granule and its hierarchical structure. (Adapted with permission from Le Corre et al. 2010; Copyright 2010. American Chemical Society)

disposed as lamella, called starch nanocrystals. Both amorphous and ordered zones are conforming by two main biopolymers, amylopectin and amylose in different arranges (Lu and Tian 2021; Yu et al. 2021a; Goren et al. 2018). Amylose and amylopectin chains occupy approximately 98% granule dry matter and the content of each one depends on the botanical source of starch (Tester et al. 2004). The ratio of amylose and amylopectin can vary between 20–30% and 70–80%, respectively (Jane 2009). Moreover, although they are composed of the same glycosidic monomer (glucose), linked by hydrogen bonding which maintains the integrity of the granule, they exhibit totally different characteristics (solubility and paste formation-gel) and are radially arranged with their terminal reducing groups oriented toward the centre or hilum, point of origin of the ring structure (Swinkels 1985; Pérez and Bertoft 2010). Amylose is conformed by D-glucose units linked by α -(1→4) glycosidic linkage, resulting in a long chain linear polymer, whereas amylopectin also present α -(1→4) D-glucose linked units but branched with numerous short chains which are linked through α -(1→6) glycosidic linkage to the linear parts of the macromolecule (Fan and Picchioni 2020). Both are deposited to form the starch granule, defining a semi-crystalline structure made up of alternating amorphous (amylose) and crystalline (amylopectin) shells, which are called “growth rings” as was previously described (Fig. 3.1) (Jane 2009; Donald et al. 2001).

The genetic modification into the plant can generate starches with high amount of amylopectin, called starches (WS) (brittle, above 85% amylopectin) and also starches with high amylose content (resistant to amylases activity, difficult to gelatinize- above 40% amylose) (Jane 2009; Tester et al. 2004). Physical and chemical characteristics of both structures vary considerably due to their conformational

space, while the functionality is significantly dependent on its fraction. Pure amylose is insoluble in cold water and contributes to increase the gelatinisation capacity of starch, while not degraded amylopectin is water soluble; and contributes to increase the adhesion characteristics of starch (Hernández-Carmona et al. 2017).

3.2.2 Extraction, Functional Properties and General Characterisation

Starch can be extracted from various parts of plants such as fruits, leaves, seeds, and roots (Makroo et al. 2021). Conventionally, extraction methods can be classified as wet and dry milling, being the last one the most appropriate technically, but the extract obtained showed weaker functional properties compared to the first one (Lee et al. 2007). Once vegetable raw material was milled, starch extraction usually consists of four main steps: washing, cleaning from fat and protein, centrifugation and drying, producing a large amount of waste, which could contain high quality compounds (Moorthy 2002; Bernardo et al. 2018). In order to overcome the shortcomings of traditional methods, novel technologies have been employed such as enzyme and carbon dioxide assisted extraction (Buksa 2018), high hydrostatic pressure, ultrasound, and moderate electric field for the extraction (Makroo et al. 2021).

The extracted and dried starch granules are highly robust and impermeable to water at ambient temperature, preventing the interaction between starch and water molecules and, therefore, avoiding swelling and caking. When aqueous suspension of granules is heated, at above the melting point of starch crystalline structure (≥ 60 °C), granules can absorb water and gelatinise through an endothermic and irreversible process (Tester et al. 2004). Gelatinisation generates the swelling of particles, water absorption, loss of crystallinity, leaching of amylose and solubilisation of granular content resulting in viscosity development (Sciarini et al. 2015; Silva Nykänen et al. 2014). Furthermore, the gelatinisation process is not only influenced by starch source characteristics, such as the growing conditions, cultivar, maturity and amylose-amylopectin ratio, but also, processing conditions and the amount of water used (Brunt et al. 2002). For instance, when starch is cooked in a given process and leaves behind remnants of the parent starch granules it is defined as “ghosts”, leading to a product with less surface shine, affecting the final starch-based products characteristics (Li and Wei 2020; Debet and Gidley 2007). After cooling and storage, the viscosity increases dramatically as starch undergoes gelation and molecular re-crystallisation being undesirable in some gels and bakery products as it causes texture hardness and moisture loss, known as staling. In bakery products, it is defined as “retrogradation process” (Šmídová and Rysová 2022). Pasting characteristics are important quality parameters (texture, hardness and taste) in starch further processing.

On the other hand, besides food formulation, starch is being profusely studied as one of the most convenient biopolymer matrix to constitute edible coatings to be applied on food surface and also to generate self-supporting biodegradable

packaging materials. The starch matrix can provide an effective barrier against hazards by reducing moisture migration, gas exchange (mainly O₂ and CO₂), respiration and oxidative reaction rates; suppressing physiological disorders; delaying changes in textural properties; and improving mechanical integrity or food handling characteristics (Versino et al. 2016). The edible matrix can be added with other compounds such as plasticizers (glycerol, propylene glycol, etc.) to obtain a flexible film, or active agents (antimicrobial, antioxidants, colourants, etc.) to become the film or coating in functional, with the aim to extend food shelf-life (Díaz-Montes and Castro-Muñoz 2021; Campos et al. 2011). Chapter 7 gives a deeper insight about this important filmogenic property of the starch.

Regarding to the methodology to characterize starch morphology, structure, physical, chemical, or functional properties, there is a wide range of methods that have been used. Once starch granules were separated and purified, their size distribution can be determined using sieving, light or SEM, laser light scattering, among other techniques (Lindeboom et al. 2004). Colour is usually determined by reflectance spectrophotometers (Soison et al. 2015), while shape and surface morphology can be analysed by SEM or atomic force microscopies, with the properly sample preparation (Chakraborty et al. 2020). Information about strength of granules can be obtained through a compression test (Molenda et al. 2006). Since granules present an anisotropic character, it can be observed the birefringence phenomenon using a polarization microscope showing the characteristic Maltese cross and the hilum position (Chakraborty et al. 2020). More information about long-range ordered structure or repetitive crystalline and amorphous lamellae fraction are obtained by wide angle X-ray diffraction or small angle X-ray scattering respectively (Wang et al. 2015). Other basic assays used to describe starch functionality are swelling, solubility, water retention or holding capacity tests (Ačkar et al. 2010). The molecular weight of amylose and amylopectin can be determined by high-performance size-exclusion chromatography (Kobayashi et al. 1985) and by field-flow fractionation coupled to multi-angle light scattering (Rübsam et al. 2012). Amylose content is determined by a colorimetric method using standards of amylose and amylopectin after association with I₃⁻ to form the known amylose/iodine recognized for the typical blue colour of the solution (Alzate et al. 2020). The presence of chemical groups, their connectivity and spin–spin relaxation time has been studied with spectroscopic techniques such as Fourier transformed infra-red, near-infrared reflectance, Raman and H¹ and C¹³ nuclear magnetic resonance spectroscopies (Wang et al. 2015). The thermal characterisation involves the determination of the gelatinisation temperature in presence of water, loss mass during heating and decomposition temperature, are commonly performing by scanning differential calorimetry (DSC) and thermogravimetric analysis (Wu et al. 2019). The viscous capacity of starch is one of the most important properties that must be exploited. The pasting viscosity profiles of starch solutions when are submitted to a standardised heating and cooling cycles under stirring can be performed in Rapid Visco Analyser (RVA) instrument (pasting test) (Gupta et al. 2009). Once gelatinised, the rheological characteristics of the starch slurries, which are strongly dependent on concentration and storage time, can be performed under large deformations applying tangential forces

(flow behaviour) in a viscometer or uniaxial compression in a texture-meter or press device. On the contrary, assays using small perturbations have been developed to determine the viscoelastic properties of starchy systems using a dynamic rheometer. In general, oscillatory test are carried out to describe gelation mechanisms, molecular interactions, and starch retrogradation (González et al. 2021; Li et al. 2020; Gupta et al. 2009). Moreover, when starch is used to prepare dough, the properties such as resistance, extensibility, consistency, viscosity, mixing time and tolerance are usually studied by extensigraph, farinograph, alveograph and development time tests (Rasper 1993), in addition to DSC and dynamic rheology studies (Witczak et al. 2012). Several freezing-thermal cycles to observe the water presence (syneresis) and compression of the gelling system are used to test retrogradation level (Karim 2000). It is important to remark that no single method can provide a complete information about starch structure and the changes during gelatinisation or retrogradation at both macroscopic and molecular level, being necessary to perform parallel some of the mentioned tests (Wang et al. 2015).

Other important aspect of starch that must be analysed is the amount of resistant starch (RS) because of the nutritional implications (Bojarczuk et al. 2022). The RS is defined as a portion of starch that cannot be digested by human amylases in the small intestine and passes to the colon to be fermented by the microbiota (Nugent 2005). Although the cooked raw material is highly digestible by healthy humans, after cooking and under certain conditions, part of the starch may not be digested. Some possible causes be the retrogradation due to re-association of amylose chains in double helices, the lipid-amylose interaction forming inclusion complexes and the chemical modification of starches (Birt et al. 2013). Due to the recent recognition of incomplete digestion and absorption of starch in the small intestine as a normal phenomenon, interest in RS has increased. Several studies have shown that RS has physiological functions similar to those of dietary fibre (Sajilata et al. 2006). Regarding methodology to determine RS, it can be classified as *in vivo* and *in vitro* methods. The most used *in vivo* methodology consists of evaluating undigested starch at the end of the ileum in healthy human models with ileostomy (McCleary 2013). However, this method is difficult, laborious, expensive and ethically controversial (Iacovou et al. 2017). More practical are the *in vitro* tests that attempt to simulate gastrointestinal digestion, but results depend on the types of enzymes and the experimental conditions used (Li and Hu 2022; Maningat and Seib 2013; Perera et al. 2010).

3.3 Methods for Modifying Starch Structure

It was observed that performance of native starch in food-industry processing is often limited by some of its physical and chemical properties. Viscosity of cooked native starch is often relatively high or unstable to be used in certain products. In addition, low mechanical, acid, and thermal resistance, as well as high tendency toward retrogradation are the main limitations of native starches. In such sense,

rheological properties of some starch dispersions such as potato, tapioca, and maize WS affect the final product characteristics, providing a gummy, stiff structure thus deteriorating their sensory properties. Therefore, starches need to be modified to enhance their properties and make them more functional in wider applications (Punia Bangar et al. 2022a). Aforementioned drawbacks can be overcome by starch modification through different methods as chemical, enzymatic, physical, and a combination of them, in order to improve its functional characteristics. According to the changes introduced in starch structure, it is possible to decrease the viscosity, increase the stability in dispersions and hot paste stability, decrease gelatinisation temperature and breakdown viscosity, improve cold-water dispersibility and contribute to new starch characteristics by substituting the molecule with different functional groups (Gilet et al. 2018; Hadnadev et al. 2018; Molavi et al. 2018; Lacerda et al. 2019).

Chemical methods are the most used for starch modification and can be grouped as: conversion, cross-linking, and substitution (including esterification and etherification) (Cui 2005). Starch conversion treatment and final properties can be described as: (a) acid converted (thin-boiling starches), the granular starches that are partially acid hydrolysed, reduce hot-paste viscosity forming strong gels upon cooling due to shortening of starch macromolecules; (b) oxidised (bleached starches) treated with sodium hypochlorite and yielding high paste clarity, low paste viscosity, short and good paste stability; and (c) pyroconverted (dry heating treatment, 140–200 °C, with or without acid), as pyrodextrins (white and yellow dextrins, British gums), giving low viscosity, good film-forming ability, high solubility, good hot-paste stability.

In the other group are cross-linked starches: (a) di-starch phosphates by sodium trimetaphosphate or phosphorus oxychloride treatment; (b) di-starch adipate using adipic anhydride; both with the same final desirable properties, high stability, and resistance to processing conditions (increased temperature, shear, low pH stability).

Finally, stabilised starches obtained by esterification or etherification. These can be: (a) acetylated starch (esterified with acetic anhydride) resulting in increased paste clarity and stability, reduced starch retrogradation, lower gelatinization temperature; (b) monostarch phosphated starch (esterified with *ortho*-phosphoric acid, sodium/potassium *ortho*-phosphate, or sodium tripolyphosphate) obtaining higher paste viscosity and stability, improved clarity, cohesive texture, high resistance to retrogradation, lower gelatinization temperature, high freeze–thaw stability; (c) sodium octenyl succinate starch (esterified with octenylsuccinic anhydride and octenylsuccinate) and (d) hydroxypropylated starch (etherified with propylene oxide) causing in both cases, increased peak viscosity, lower gelatinisation temperature, good freeze–thaw stability, film-forming ability and emulsifying properties (Semeijn and Buwalda 2018; Hadnadev et al. 2018).

On the other hand, physical modification consists of the application of mechanical friction to change starch granules size or temperature/moisture, pressure, shearing, milling, UV-radiation, and some novel techniques, such as ultrasound (Alzate et al. 2020), pulsed electric fields, superheating, iterated syneresis and instantaneous controlled pressure drop process (Kaur et al. 2012). To obtain pre-gelatinised

(instant cold-water swelling) starches, suspension is treated by drum drying, spray cooking, or extrusion. Heat/moisture treatment consists of applying heat to starch at a temperature above their gelatinisation point with insufficient moisture to cause gelatinisation, in contrast annealed starches heat at a temperature below from gelatinisation point for prolonged periods of time (Singh et al. 2007). Continuously, alternative, sustainable and eco-friendly techniques are investigated to replace traditional and polluting methodology to obtain modified starches. In this sense, the use of microwave radiation, cold plasma, ultrasonication, supercritical CO₂, ionic liquids, mechano-chemistry, etc., were reported as unconventional and green technologies (Otálora González et al. 2020; Gilet et al. 2018).

Another green approach to produce starch with altered molecular mass, branch chain-length distribution and amylose/amylopectin ratio is the employment of hydrolytic enzymes (α -amylase, pullulanase, glucoamylase and, less frequently, transferases). The modification can be performed in a single, dual, triple, and quadruple enzymatic reaction using combinations of several enzymes. As a result of the enzymatic modification, freeze-thaw stability and retrogradation effects on gels were improved during storage. In addition, cyclodextrin glycosyltransferases have been used to obtain cyclodextrins. Despite the benefits obtained by enzymatic modification, the technology is quite expensive and new sources of safe enzyme should be provided (Punia Bangar et al. 2022b).

Chemical modified starch production is regulated by the American Food and Drug Administration. Backwards, physically modified starches are not considered food additives and therefore, they could be used to develop “clean label” products, which are highly demanded by the consumers nowadays. Locally, the Argentine Food Code rules in relation to levels and labelling of native and modified starches (Argentine Food Code 2021). In Table 3.1. it is described recent developments of modified starches for food application.

3.4 Native and Modified Potato Starch – Different Alternatives and Applications

Potato (*Solanum tuberosum*) is a rich source of starch (79 % dry base) among other nutritional components such as protein, dietary fibre, vitamins and minerals, being the fourth most well-known food crop after rice, wheat and corn worldwide (Gui et al. 2022). There are thousands of potato varieties that grow in temperate, tropical, and sub-tropical regions. The world production (359 Mt, 2020 data) is shared among Asia (48%), Europe (32%), Americas (17%) and Africa (7%) (FAOSTAT 2021). The potatoes are milled to extract the starch granules from the cellulose cell wall compartments (amyloplasts) (Fig. 3.3, panel a). After removing the protein and the fibre subsequent washing and drying steps yields to the starch as final product (Semeijn and Buwalda 2018). Starch from potatoes is a very significant commodity that has a wide inclusion in food and non-food industry and a high economical

Table 3.1 Recent developments of modified starches for food application

Starch modification method	Food application	Benefit in functionality/ physicochemical characteristic	Reference
Sour/fermented starches physical modification	Bread, noodles.	Improve swelling and solubility. Less susceptible to hydrolysis and thermally stable. Increase gelling potential. Decrease aging ability. Adjuvant or as a main ingredient in GF foods	Punia Bangar et al. (2022a)
Instant starches/ cold-water swelling starch	Desserts, cake or muffin batters with particles, puddings, sauces, salad dressings, dry soups, baby foods, pie fillings, jellies. Foods with bioactive materials, heat-sensitive colourants, cold desserts and microwavable.	Increase viscosity and produce a soft paste without heating. Prevent sinking to the bottom during baking of particles (chocolate chips or fruit pieces). Reduce or eliminate cooking time and act as thickening agent, stabiliser and emulsifier in instant foods and non-thermal processing. Used as encapsulating material for the encapsulation of bioactive materials and nutrients. Improved freeze-thaw stability.	Majzoobi and Farahnaky (2020)
Degraded starches	Confections, cheese analogues, surimi, glazing, toppings, drinks, soups.	Gelling agents.	Semeijn and Buwalda (2018)
Enzyme-treated starches	Bread, low fat yogurt.	Fat replacer, mouthfeel enhancer, fillers, and in co-spray drying of flavours. Emulsifier. Gelling agent.	Punia Bangar et al. (2022b)
Acid-degraded	Gum candies, jellies, pastilles baked goods. Confections, Cheese analogues.	Reduce gelatinisation temperature and increase the solubility. Loss of swelling capacity and viscosity. Improve gelling or gel strength. Favour the retrogradation that leads to slowly digestible and RS formation. Reduces the tolerance to refrigeration, storage and freeze-thaw cycles.	Semeijn and Buwalda (2018) and Wang et al. (2022)

(continued)

Table 3.1 (continued)

Starch modification method	Food application	Benefit in functionality/ physicochemical characteristic	Reference
Oxidised starches	Coating, sealing, batter binding, emulsification, and dough conditioning in baking. Clear drinks, soups. Battered meat and breading, film former. Crispy coating in fried foods and texturizer in dairy products.	Low viscosity, high stability, clarity, film-forming, and binding properties. Reduce retrogradation of the cooked paste, enhanced stability at low temperature. Higher adhesion and improved film-forming properties	Chakraborty et al. (2022)
Cross-linked starches/ inhibited starches.	Snacks, sauces, food coatings, mashed potatoes, GF breads.	Prevention of full disintegration of the starch during gelatinisation. Form strong and stable gels with limited susceptibility to staling and retrogradation	Roman et al. (2020) and Witzczak et al. (2012)
Acetate starches	Meat, oriental noodles, ready meals Pulping pies, gravy, salad dressing and pies.	For extended shelf-life and refrigeration are required. Better freeze-thaw stability, expansion, and dissolution characteristics. Have no heat and shear stability.	Lin et al. (2019)
Octenylsuccinate starches	Drinks (clouding agent), salad dressing, creams, mayonnaise style products, butter, margarine.	Emulsifier: adjust viscosity levels for products and processes. Encapsulating agent for enzymes, fatty acids, salt, fragrances, and flavours. Biodegradable edible packaging. Fat replacer or flour substitute for bread dough formulation.	Altuna et al. (2018)
High Hydrostatic Pressure (HHP) treated sweet potato starch	Doughs	Higher water absorption, dough development time, and stability with the increase of HHP The dough height, maximum gaseous height, total gas production, and retention capacity were significantly increased for at 500 MPa. More consistent and uniformed network structure.	Rahman et al. (2022)
Heat-Moisture-treated sweet potato starch	Noodles	Similar acceptability scores for raw starch noodles, plain boiled, comparing to the commercials.	Collado et al. (2001)

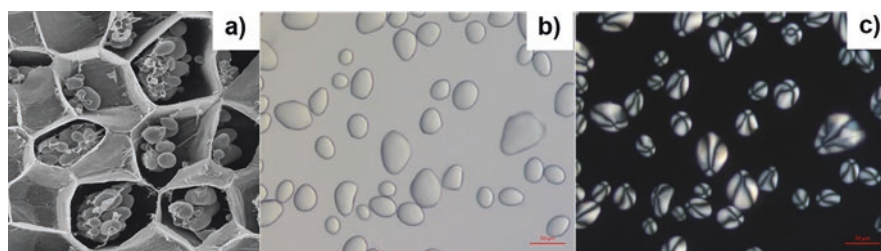


Fig. 3.3 PS granules: (a) SEM of potato cells (magnification: 50x), (b) bright field microscopy (scale bar: 50 μm) and (c) polarized light microscopy (scale bar: 50 μm). (Image (a) is from <https://render.fineartamerica.com/images/rendered/share/24341696&domainId=1> which property release is not required. Images (b) and (c) are reprinted with permission from Dupuis and Liu 2019; Springer Nature)

Table 3.2 Characteristics, composition and pasting properties of starch granules

Starch source	Shape	Diameter (mm)	Amylose (%)	Lipids (%)	Proteins (%)	Phosphate (nmol/mg)	T_m^a ($^{\circ}\text{C}$)	Peak Viscosity (RVU) ^b
Potato	Round, oval	5–100	18–29	0.02–0.2	0.1–0.4	23.2	62.6	510
Maize	Round, polygonal	2–30	23–32	0.6–0.8	0.3–0.4	0.11	68.9	250
Wheat	Round, lenticular	1–40	23–29	0.3–0.8	0.3	0.20	61.6	230
Barley	Round, lenticular	2–40	22–27	0.6–0.9	0.1	0.12	58.0	100
Tapioca	Oval, truncated	4–45	17–33	0.03–0.1	0.2	1.11	67.5	220
Rice	Polygonal	3–8	14–29	0.6–1.4	0.1–0.5	$\sim 1^c$	70.1	239 ^d

^a T_m is the mid-point temperatures measured by DSC, ^bRVU are Rapid Visco Units measured in a Rapid Visco Analyser (RVA) instrument. Reprinted with permission from Vamadevan and Bertoft (2015) (John Wiley and Sons), ^cChen et al. (2017b); ^dBaxter et al. (2004)

relevance. From human nutrition point of view, its main role is to provide the metabolic energy for a large portion of the world's population. Native potato starch is quite resistant to digestion, but it becomes digestible after cooking, resulting food products with a high glycaemic index (GI). There is an interest in elucidating how nutritional properties of starch could be modified under specific conditions of composition, structure, or processing of food stuff (Dupuis and Liu 2019). Table 3.2. summarises some properties and components of several starch granules sources for comparison reasons. Potato starch (PS) is one of the biggest in size (Fig. 3.3, panels b and c). Regarding PS composition, it has a very low amount of lipids and proteins as many others starch sources. However, the high number endogenous phosphate in PS is another distinctive characteristic. The principal constituents of PS are amylose (18–29%) and amylopectin (Vamadevan and Bertoft 2015). In addition, PS pastes

show low temperature of gelatinisation, better transparency and very high viscosity compared to other sources. Such properties have been related to the phosphate groups esterified to the amylopectin fraction and the superior granule integrity (Xu et al. 2017).

PS is commonly used as a thickener, colloidal stabilizer, gelling, bulking and water-retention agents (Li et al. 2021). These properties are adequate for food formulation such as clear soups, meat (Joly and Anderstein 2009), Asian style noodles (Chen et al. 2003), confections (Buwalda et al. 2014; Woltjes et al. 2004), fillings and snacks. Regarding the latter, PS is responsible for the balance between crunchy and crispy characteristics (van der Sman and Broeze 2013). On the other hand, PS is naturally GF, satisfying consumers with gluten-related disorders and people searching for non-allergenic ingredients, contributing to the growing GF market (Villanueva et al. 2018). Normally, PS is used in GF pasta production since its addition could increase the overall quality (including appearance, colour, odour, and hardness) of GF pasta made from corn, rice, and sorghum flours (Rodrigues Ferreira et al. 2016). In addition, the incorporation of different GF ingredients such potato flours can simulate the viscoelastic properties of gluten, retain gas, and improve the maintenance of structure, texture and shelf life of bakery products (Gallagher et al. 2004; Arendt et al. 2002).

It is known that the larger size of the native PS granules and their high swelling capacity lead to extremely bulky swollen granules, which result in a high viscosity but also in a less smooth texture. Despite native PS can meet several requirements in food applications (particularly high viscosity, low off-taste and clarity), starches with modified properties are highly required because processes and storage conditions become more demanding on characteristics of final product (Semeijn and Buwalda 2018). Due to the higher fragility of the swollen PS granules, their pastes are prone to disperse or solubilize on heating and shearing, giving a weak-bodied, stringy, and cohesive slurries (Singh et al. 2016). As other native starches, PS can be modified using a chemical, physical or enzymatic method, single or combined, as was previously described (Morikawa and Nishinari 2000). In addition, modification of PS could increase their resistance to enzymatic hydrolysis rendering in a novel and high RS content product (Dupuis and Liu 2019). Therefore, different kinds of PS are successfully used in a broad range of food products. Table 3.3. describes some examples where the incorporation of native and modified PS was performed to obtain GF bakery products.

3.5 Native and Modified Cassava Starch – Different Alternatives and Applications

Cassava (*Manihot esculenta* Crantz) also known as tapioca or yucca, is a tuberous root vegetable of the Euphorbiaceae family. Although cassava is a crop native to Latin America (mainly Brazil, Paraguay and Colombia) and the Caribbean, this region contributes only 11% (2010–2020 average) of world production (251–303 Mt,

Table 3.3 Formulation of GF bakery and pasta goods with native and modified potato starch (PS)

Native or modified PS inclusion in formulation	Food	Main findings	Reference
High protein brown rice flour + tapioca starch + PS	Cupcake	PS increased cupcakes specific volume and decreased hardness	Aleman et al. (2021)
PS + Hydroxypropyl methylcellulose (HPMC)/ Carboxymethylcellulose, xanthan gum (XG) /apple pectin.	Bread	Hydrocolloids increased the gelatinization temperature and water absorption capacity of potato dough. Bread had higher specific volume, lower hardness and rapidly digestible starch.	Liu et al. (2018)
Modified PS (acidification acetic and lactic acid) + caseinate or soy-protein isolate + HPMC.	Dough	Proteins structured and strengthened the protein isolate-PS dough. Increased pasting viscosities with protein addition. Acidification of protein-enriched starch matrices modulates dough rheological properties.	Villanueva et al. (2018)
PS	Bread	Decreased protein levels, an increased moisture content (about 2%) and carbohydrates levels due to the composition of potato. Sensory analysis (80% PS) bread with better characteristics: taste, colour and odour.	Nemar et al. (2015)
PS + powdered sugar + artificial colour + vanilla flavour	Pudding	Sensory evaluation showed non-significant difference between non cereal pudding mix and control (corn starch). PS-based pudding mix can be stored for 12 months without impacting quality.	Singh et al. (2021)
PS + Potato protein + Potato fibre + Potato flour + Fresh tube	Bread	By balancing the strong swelling power of PS, was resolved the cracks on the crust. The breads showed a typical appearance, loaf size, low porosity but high cell density crumb structure and unique favourable sensory qualities (2% potato fibre or 30% fresh tuber). Breads staled quickly during storage.	Lu et al. (2021)
Corn/PS mix + Waxy corn/ waxy PS mix	Bread	WS increased the storage and loss moduli due to the increased swelling capacity. The presence of WS (10–15%) reduced the hardness and chewiness of crumb, limiting the increase of these parameters during storage and reducing staling.	Witczak et al. (2019)

(continued)

Table 3.3 (continued)

Native or modified PS inclusion in formulation	Food	Main findings	Reference
Heat-Moisture Treated (HMT) PS + Sodium Chloride as a binder paste.	Noodles	Dough owned higher hardness and noodles exhibited less solid loss and broken noodles, firmer texture, and better elasticity.	Yang et al. (2022)
Rice flour, Corn starch and PS blends + XG or Guar gum	Flat bread	Gums improved the weight and roundness. Formulations Rice flour: Corn starch: PS 40%:20%:40% and 40%:40%:20% with 3% XG showed higher moisture retention, lower hardness and remained softer up to 72 h.	Mahmoud et al. (2013)
Sorghum, rice, Corn flours and PS mix + egg + oil	Pasta	Sorghum, rice flours and PS (40:20:40) showed the best cooking quality, density, yield, weight increase and the lowest solids loss.	Rodrigues Ferreira et al. (2016)

2010–2020 data). Africa (mainly Nigeria, Congo) and Asia (mostly Thailand, Indonesia) share almost all the world cassava production with of 60% and 30%, respectively (FAOSTAT 2021). Cassava represents the third most important source of calories in the tropics, after rice and maize (Zhu 2015a) and continues its transition towards a market oriented to products and raw materials for the processed food industry. Mature roots have an average composition of 60–70% water, 30–35% carbohydrate, 1–2% fat, 1–2% fibre and 1–2% protein, with trace quantities of vitamins and minerals. Cassava also contains different amounts of cyanogenic glucosides depending on varieties. Proper processing of roots can eliminate such toxic compound (Wang and Guo 2020). Starch content in mature cassava parenchyma (Fig. 3.4a, b) ranges from 15% to 33% (up to approximately 80% of dried weight of tuber), depending on the climate and harvest time. For starch extraction, roots must be firstly washed, chopped and grated in sulfur-containing water to separate starch from pulp. Then, the separated starch fraction is reduced in water content by centrifugation or filtration, before final drying (flash dryer) and packaging (Breuninger et al. 2009). Typically, cassava starch (CS) present granules with a medium size and contains 17–33% amylose and minimal amounts of proteins, lipids, ashes and phosphates (Fig. 3.4 and Table 3.2).

In addition, amylose from cassava has a higher molecular weight than other starches. The swelling power of CS is moderate compared to potato and cereal starches but has a higher solubility, which can be attributed partially to the high swelling power. Regarding, gelatinisation properties, CS has low gelatinisation temperature and higher water-binding capacity, viscosity and shear resistance making it a suitable option in food, feed, chemicals and pharmaceutical products (Wang et al. 2022). The CS gels trend to be more stable than starch gels from cereals, which is of importance in food applications (Wang and Guo 2020). The mentioned characteristics of CS (low content of amylose, lipids and proteins, high molecular weight

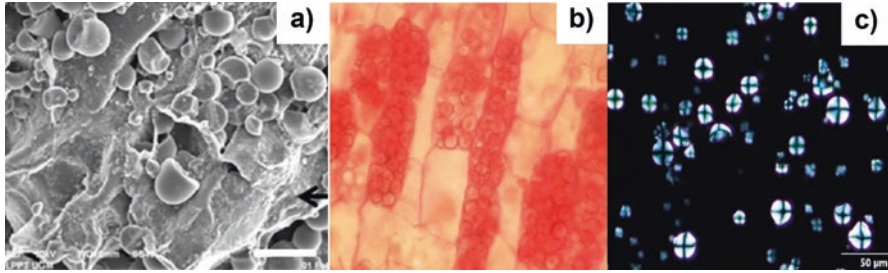


Fig. 3.4 CS granules: (a) SEM of cassava parenchyma (scale bar: 10 μm), (b) light microscopy (Objective: 40X) and (c) polarized light microscopy (scale bar: 50 μm). (Images (a) and (b) from Maherawati et al. (2017); Asian Network for Scientific Information. Copyright ©2017: Maherawati et al. This is an open access article distributed under the terms of the creative commons attribution License, which permits unrestricted use, distribution and reproduction in any medium, provided the original author and source are credited. Image (c) is reprinted from Grace and Henry (2020). Copyright © 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>))

amylose), make it a unique native starch for direct use. The CS is also distinguished by its gel-forming ability and bland taste (Breuninger et al. 2009). Concerning nutritional aspects, CS has high digestion rate and, consequently, a rapid increase of glucose in blood is observed. There is a great interest to increase the RS content in CS to develop improved functional foods for particular health requirements (type 2 diabetes, obesity, etc.).

Native CS is used in many applications in food industry such as raw material for sweeteners production (high-fructose syrup, glucose, dextrin and monosodium glutamate), for obtaining bakery and pastry products, noodles, soups, soft drinks, ice creams, and yoghurts as well as feedstock for microbial fermentation in the bioethanol, butanol, L-lactic acid and trehalose production. As other starches, technological limitations of CS include low cold solubility, freeze-thaw stability, shear and thermal resistance, poor enzymatic hydrolysis, high syneresis, high tendency towards retrogradation and high digestibility. Particularly, chemical modification can convert CS into a rich RS starch with many health benefits (Wang et al. 2022). Table 3.4 summarises some applications of native and modified CS to produce GF products.

3.6 Native and Modified Non-conventional Starches. Different Alternatives and Applications

Added to conventional starch sources such as cereal grains, potato tubers and cassava roots, starches from minor or geographically circumscribed crops, with diverse functional properties, are becoming relevant in food manufacturing. One of the significant characteristics of these raw materials is their natural lack of gluten proteins and, therefore, their suitability to be used in GF products.

Table 3.4 Formulation of GF bakery and pasta goods with native and modified cassava starch (CS)

Native or modified CS inclusion in formulation	Food	Major Findings	Reference
Sorghum starch + gelatinised CS + cellulose derivatives + emulsifiers + egg white powder	Bread	Emulsifiers strengthened the doughs (increased elastic recovery) and decreased crumb firmness and staling rate when compared to the control (without emulsifiers and cellulose derivatives). Particularly, at 2.4% w/w emulsifiers. The effect of cellulose derivatives on dough strength was influenced by the type, concentration and ionic character.	Onyango et al. (2009)
CS + corn flour (80:20) + vegetable fat + hen egg + soybean flour	Bread	The optimum bread (highest levels of fat and soybean flour and one egg), presented low values of firmness (≤ 100 N) and elasticity ($>65\%$) and the lowest variation of these parameters with storage. Overall acceptability was 84% for habitual consumers and 100% by celiac people. Bread was enriched in proteins due to soybean flour.	Milde et al. (2012)
Cassava (flour, native and sour starch) + maize starch/rice flour	Bread	CS and, to a lesser extent, flour can help to improve the quality of GF breads. The addition of CS in small percentages (10%) can help to improve its texture and mouth feel, as well as its specific volume. Sour CS give slightly affect taste and texture in the mouth.	Sigüenza-Andrés et al. (2021)
Flour, coarse and bran rice + Pre-gelatinised CS + hydroxypropyl methylcellulose (HPMC) + soybean extruded–expelled meal (SEF) + sucrose + salt	Bread	Lower pre-gelatinised CS and SEF levels presented loaves with higher specific volume, softer crumb with faster recuperation of springiness and less susceptibility to being disintegrated during chewiness. SEF decreased lightness, increased the colour intensity and gave a more uniform microstructure. Optimal formulation was: Pre-gelatinised CS 15 g/100 g, SEF 6 g/100 g and water 160 g/100 g. SEF addition would increase the intake of dietary fibre and proteins in 1.4 and 3.7fold, respectively.	Genevois and de Escalada Pla (2021)

(continued)

Table 3.4 (continued)

Native or modified CS inclusion in formulation	Food	Major Findings	Reference
Cassava flour + Sucrose + NaCl + Extra-virgin olive oil + Egg white	Bread	Baking trials were carried out by using egg white or/and olive oil, due to their high nutritional value. Significant improvements of loaf specific volume (from 2.24 to 3.93 mL/g) and crumb firmness (from 9.14 to 4.67 N) were achieved by contemporarily including egg white and olive oil. Cassava breads containing both these ingredients obtained the best scores from panellists and resulted attractive as the wheat bread.	Pasqualone et al. (2010)
Heat-moisture-treated CS, sorghum flour, amaranth flour (50:40:10) + sugar + baker's fat + salt + amaranth malt	Bread	Heat-moisture-treated CS had higher crystallinity, onset pasting temperature and water absorption index; and lower swelling power, water solubility index and peak viscosity, affecting properties and crumb texture of GF batter and bread, respectively. Batter consistency increased but crumb hardness and chewiness decreased with increasing moisture content and incubation time of starch modification and increasing amaranth malt content.	Onyango et al. (2013)
Bread: maize starch + rice flour + CS + sugar + salt + yeast + ice cream neutral mixture (guar gum, Carboxymethylcellulose, emulsifiers) + soybean extract powder + margarine + emulsifier + eggs Muffin: idem bread (maize starch) but using brown sugar + baking powder + cinnamon + chocolate	Breads and muffins	A comparative analysis of specific volume, elasticity, firmness, and triangular test was performed with pre-baked, baked, and frozen bread. From sensory analysis of acceptance, it was concluded that the formulation relating to the optimal simultaneous point between instrumental measurements (20% rice flour + 30% CS + 50% maize starch) obtained the best results. The sensory evaluation of the muffin conducted by common and celiac consumers showed good acceptability and buy intention. The addition of the soybean extract powder enriched in protein both products.	Schamne et al. (2010)

(continued)

Table 3.4 (continued)

Native or modified CS inclusion in formulation	Food	Major Findings	Reference
Modified CS (oxidised, modified, sour) + cheese + corn starch + pre-cooked corn flour + whole milk	Cheese bread	All doughs were prepared and frozen previous elaboration. The chemically modified starches had higher resistance to freezing and resulted with lower hardness and number of pores than sour CS. A better overall appearance, higher softness but higher compaction and hardness, and less salty in taste were observed for samples with oxidised CS, detectable by panellists in comparison with fresh dough.	Mesa et al. (2019)
Damaged cassava + sugar + peanut oil + salt	Crackers	The increase in damage level led to a slight increase in amylose content and reduction in crystallinity. Also exerted a major influence on the pasting properties and interaction between damaged cassava and water. Damage (>11.5%) rendered texture properties similar with those of wheat flour. Cracker made with damaged cassava had acceptable sensory qualities comparable to control.	Liu et al. (2019)
Cassava WS + wild-type CS fermented for up to 30 days and oven or sun dried + cheese + sunflower oil	Baked or fried expanded products.	The specific volume after baking for cassava WS was 3.5 times higher than that in wild-type starches. There was a synergistic combination of fermentation (10–14 days) and sun-drying. Fermentation reduced viscosities and the weight average molar mass led to denser macro-molecules and increased branching degree, which were linked to a high loaf volume. Cassava WS can emerge as a cheaper, GF, clean label, and neutral taste alternative.	Dufour et al. (2022)

(continued)

Table 3.4 (continued)

Native or modified CS inclusion in formulation	Food	Major Findings	Reference
Defated marama flour + CS	Bread-type dough	Defated marama flour and CS (33:67) can produce a dough of similar strength but less stability to wheat flour dough, but which can produce an alveograph dough bubble and has good gas-holding capacity during proofing. The presence of the dietary fibre in the defated marama flour and the inclusion CS appear to favourably modify the marama protein rheological properties. Defated marama flour have considerable potential as a functional gluten replacement.	Nyembwe et al. (2018)
Pre-gelatinized cassava flour + CS and amaranth flour	Pasta	The use of pre-gelatinized cassava flour, native CS and amaranth flour (10:60:30), allowed a pasta similar in quality as commercial wheat products: light yellowish colour, fibre rich [9.37 g (100 g) ⁻¹], source of protein [10.41 g (100 g) ⁻¹], adequate firmness (43.6 N) and low stickiness (3.2 N). In addition, the use of cassava bagasse improved the fibre content.	Fiorida et al. (2013)
CS and corn flour (80:20) + Whole milk powder + Vegetable fat + Whole egg fresh + XG	Pasta	0.6% XG concentration developed the highest potential to improve the pasta capacity to prevent structure disintegration with the lowest cooking loss and the lowest values for firmness, cohesiveness, chewiness, springiness and cutting force.	Milde et al. (2020)
CS and corn flour (80:20) + Whole milk powder + Vegetable fat + Whole egg fresh + XG + Salt + Egg albumen	Pasta	Egg albumen was used to fortify dry GF pasta. 1.5 g egg albumen/100 g showed great potential in prospective for industrial development, with intermediate cooking time, low cooking loss, firm texture, low adhesiveness and good sensory evaluation. Also it increased protein and fibre content, and maintained high protein digestibility. In addition, shelf life was determined of up to 8 months.	Milde et al. (2021)

(continued)

Yields higher than 30% are expected for these unconventional sources to be considered for commercial purposes (Tagliapietra et al. 2021). Applied extraction methods depend on the complexity of the matrix, including solvents, acid/base reagents, enzymes or physical treatments such as ultrasound, shear forces, etc., and could lead to modifications of the starch granules and the rheological properties of their pastes.

Considering the growing consumer demand for food products made with natural, unmodified ingredients, the starches obtained from these sources may allow to bypass or reduce the use of chemically modified starches in several industries. Chemical modifications are usually designed for the increasing of starch shear resistance, the reduction of retrogradation and syneresis and the stabilization of the macromolecules during heating, shearing, freezing and/or storage (Mason 2009). These features might be at least partially achieved by little-explored natural sources which could, in consequence, boost the production worldwide of such alternative native starches. These starches could also serve as new starting points to attain technological properties different from those of traditional sources (mainly cereal starches) upon chemical or physical modifications. Diverse gel strengths, gelatinisation temperatures or swelling degrees are demanded by the food industry depending on the process and the desired characteristics of the final product but, as a general rule, starches with high whiteness index and low retrogradation tendency are sought.

Non-cereal GF starch sources include fruits, seeds, roots and tubers, and pulses, from which starch can be readily extracted with acceptable yield and purity. Among them, some extraction paths are sheared for matrices with similar characteristics, which may include processing steps such as pericarp removal, dehulling, wet or dry milling, or grinding in water. Some examples are discussed in more detail below.

3.6.1 Non-traditional Root and Tuber Starches

Starchy roots and tubers (R&T) are excellent alternatives to cereal crops. These are high in water and usually contain low quantity of proteins and lipids compared to cereals, which eases starch extraction and enables R&T to be directly crushed in water without the need for a pre-soaking, turning the milling and the beginning of the extraction into a single step. Furthermore, the negligible content of lipids (<0.1%) in starches from R&T leads to a tasteless product compared to those from cereals, which is desirable for food applications (Moorthy et al. 2018).

Among the R&T, only potato and starch have a worldwide commercial distribution. However, non-traditional R&T starches are gaining increasing attention related to production sustainability, use of by-products, its regional availability which derives in foods typical of each local gastronomy, as well as the diverse technological properties that can distinguish them from common starches (Tagliapietra et al. 2021). Some of these starch-rich non-traditional crops are listed in Table 3.5.

Due to the high moisture content of starchy R&T, processing installations for starch extraction must be close to cropping areas, as described for cassava, to avoid

Table 3.5 Content and characteristics of starches from non-traditional sources

Common name	Scientific name	Starch content (% db)	Starch characteristics					References		
			Lightness (L*)	Granule size (µm)	Granule morphology	Crystallinity degree	Amylose content (%)		Resistant starch (%)	Gelatinisation temperature (°C)
Arracacha	<i>Arracacia xanthorrhiza</i>	46–64	86	7–23	Round, polygonal, irregular and elliptical	24.0–31.5	3–39	10.1–15.3	57.8–61.2	Salazar et al. (2021), Castanha et al. (2018), López Calderón (2017), Pinzon et al. (2020), Santacruz et al. (2002).
Taro	<i>Colocasia esculenta</i>	64–85	88–96	3–6	Round irregular and polygonal	23.9–45.1	2.5–35.9	10.3–23.7	54.4–107	Wongsagnon et al. (2021), Singla et al. (2020), Salazar et al. (2021), Martins et al. (2020), Nagar et al. (2021), Setiarto et al. (2020)
Achira	<i>Canna indica</i> <i>C. edulis</i>	55–80	95–96	20–100	Round, oval and elliptical	23.4–36.6	24.8–31.5	20–26.7	63.4–67.9	Salazar et al. (2021), Fuentes et al. (2019), Zhang et al. (2018), Lan et al. (2016a, b), Cabrera-Canales et al. (2021), Yamadevan et al. (2018), Wu et al. (2020), Mendez-Montealvo et al. (2022)

(continued)

Table 3.5 (continued)

Common name	Scientific name	Starch content (% db)	Starch characteristics					References		
			Lightness (L*)	Granule size (µm)	Granule morphology	Crystallinity degree	Amylose content (%)		Resistant starch (%)	Gelatinisation temperature (°C)
Kudzu or kuzu	<i>Pueraria spp.</i>	30–80	94	2–20	Spherical and polygonal	34.8–48.2	20.0–24.3	24.1–68.5	65.6–83.7	Zhao et al. (2017, 2021), Guo et al. (2016), Li et al. (2019a), Chen et al. (2017a), Liu et al. (2021), Reddy et al. (2017), Guo et al. (2021)
Sweet potato	<i>Ipomoea batatas</i>	38–80	91–97	16–24	Spherical, oval, irregular and polygonal	32.8–39.6	17.7–34.2	1.4–49.9	68.3–79.3	Guo et al. (2020), Wang et al. (2020b), Na et al. (2021), Bajaj et al. (2021), Sun et al. (2022)
Yam	<i>Dioscorea spp.</i>	20–85	97	1–90	Round, oval, polygonal and irregular	25.1–53.0	10–36	15.6–55.8	66.0–85.1	Zhu (2015b), Lovera et al. (2017), Chen et al., (2019), Liu et al. (2020), Ribeiro Oliveira et al. (2021), Yu et al. (2021b)
Andean yam bean, ajipa or asipa	<i>Pachyrhizus ahipa</i>	43.7–65	93–96	2–20	Spherical and polygonal	41.9–44.5	11.6–16.8	N/D	64.8–67.2	Dini et al. (2013), López et al. (2010), Diaz et al. (2016), Doporito et al. (2012, 2014), Forsyth and Shewry (2002)
Jicama or Mexican yam bean	<i>Pachyrhizus erosus</i>	83	N/D	5–35	Spherical and polygonal	34.3	16.9–25.1	N/D	61.7	Stevenson et al. (2007), Forsyth and Shewry (2002)

Sago starch	<i>Metroxylon sagu</i>	79–88	55.2–93.3	10–50	Polygonal or oval, some truncated oval	23.0–50.4	21.4–30.0	62.61	69.5–72.5	Karim et al. (2008), Abdorreza et al. (2012), Othman et al. (2015), Azfaralariff et al. (2020), Arshad et al. (2018), Ahmad et al. (1999), Grace and Henry (2020), Mustafa Kamal et al. (2017), Zhu (2019)
Bean/ Common Bean	<i>Phaseolus vulgaris</i>	36.8–40.3	85.4–87.7 ^a	24–47 length; 23–32 width	Round to oval, with smooth surface	27.7–30.3	38.0–41.5	32.4–36.0	73.7–74.5	Chung et al. (2008), Shimelis et al. (2006)
Pea/Field pea/ Dry pea	<i>Pisum sativum</i>	27.22–57.53 ^b	N/D	3–20	Oval or kidney-like, round, spherical, irregular or polygonal	25.1–30.0	40.7–82.6	35.5–37.9	63.5–79.8	Li et al. (2019b), Shen et al. (2016)
Lentil	<i>Lens culinaris</i>	35–53	N/D	6–37 length; 6–32 width	Oval, round, elliptical	26.2–30.6	23.5–38.0	41.3	65.2–76.1	Hoover et al. (2010), Keskin et al. (2022), Li et al. (2019b), Romano et al. (2021)

(continued)

Table 3.5 (continued)

Common name	Scientific name	Starch content (% db)	Starch characteristics					References		
			Lightness (L*)	Granule size (µm)	Granule morphology	Crystallinity degree	Amylose content (%)		Resistant starch (%)	Gelatinisation temperature (°C)
Chickpea	<i>Cicer arietinum</i>	29.1–46.0	N/D	14–30 length; 9–30 width	Oval, spherical	23.0–27.6	23.0–35.2	N/D	63.5–77.3	Hoover et al. (2010), Keskin et al. (2022), Tan et al. (2021)
Acom	<i>Quercus spp.</i>	50–60	83–91	2.5–126.2	Spherical and elliptical	22–28	16–39	31–41	59–88	Taib and Bouyazza (2021), Correia et al. (2021), Yoo et al. (2012)
Chestnuts	<i>Castanea spp.</i>	42–82	>93	10.8–111.7	Spherical, elliptical and irregular	9–51	17–57	4–85	61–69	Guo et al. (2019), de La Montaña Miguelez et al. (2004), Liu et al. (2015), Correia and Beirão-da-Costa (2012), Cruz et al. (2013), Yoo et al. (2012), Zhang et al. (2011), Yang et al. (2010)

starch degradation due to enzymatic processes and root rotting (Manthey 2016). With some modifications, starch extraction from non-traditional R&T at laboratory scale was successfully applied in similar way to that used for industrial starch extraction. The process mostly consists in washing, peeling, chopping and crushing the roots with water, alkali or other aqueous solutions (e.g., sodium bisulfite) in a blender, and then washing the slurry on screens where fibre bagasse is retained and the starch slurry passes through (Manthey 2016; Zhao et al. 2021; Zhu 2015b). After separation of the fibre fraction, other steps for removing small non-starch material can be required.

According to Opara (2003) R&T can be divided into three groups (a) those that are grown worldwide and used in large quantities, such as potatoes; (b) tropical crops that are staple foods in developing countries: e.g. cassava, aroids (such as taro), and yams; and (c) lesser-known crops such as the Andean R&T (like some from the *Pachyrhizus*, *Canna* and *Arracacia* genera) or certain specialty vegetables (e.g. Chinese water chestnut and Kudzu). Except for potatoes, R&T are grown in warmer areas of the world (Opara 2003; Dini et al. 2012).

Among the second group, sweet potato (*Ipomoea batatas*) is one of the most widespread crops, grown in many tropical and subtropical countries in Asia, Africa, and Latin America (Tong et al. 2020), being China the world's biggest producer and consumer (FAOSTAT 2021). Flour is the mostly used ingredient derived from sweet potato roots. Starch separation carries a difficulty due to the presence of fibrous material and latex, which prevents easy settling of the granules, and the high amount of sugars in the slurry which makes it susceptible to fermentation (Moorthy et al. 2018). Also, if not properly processed, starch may have an off-colour due to the phenolic compounds present, mainly in exocarp, which diminishes its lightness value (L^*). Sweet potato starch has lipid and phosphorus content similar to cassava starch, and hence exhibits similar properties (Moorthy et al. 2018).

Taro (*Colocasia esculenta*) also known as pituca or Malanga, is widely cultivated in Asia, India and other tropical and subtropical regions. Taro flour is scarcely available on the international market while starch is almost non-existent. Nip et al. (2007) used taro flour as major component to formulate snap and drop cookies, tested different ratios of ingredients and reached a highly acceptable formulation as indicated by a taste test. Analogous to the difficulty that latex provides to sweet potato starch extraction is that produced by mucilage in taro. The strong binding of starch with protein in mucilage may produce loss of starch granules during the filtration step and results in lower yields of taro starch (Wongsagonsup et al. 2021). Taro starch is distinctive from other R&T starches in its small granule size, which derives in enhanced emulsion stabilizing properties and a good performance as a filler in edible films (Singla et al. 2020). Taro starch was also assayed to improve textural properties in yogurt and ketchup, and α -amylase treated starch was successfully applied as stabilizer in ice cream (Singla et al. 2020).

Yam is a root vegetable and comprises several species of the genus *Dioscorea*. The most commonly cultivated species include *D. alata* (water yam), *D. cayenensis* (yellow yam), *D. esculenta* (lesser yam), *D. opposita* (Chinese yam), *D. rotundata* (white yam), and *D. trifida* (cush-cush yam) (Zhu 2015b). Starch yield at lab scale

has been reported to reach up to 88% (db) (Zhu 2015b). Starch is almost unavailable in the global market, but some studies assayed the incorporation of yam starch in pasta and bread (Zhu 2015b), the latter exhibiting good quality attributes by 30% wheat flour replacement with yam starch (Zhu 2015b; Nindjin et al. 2011).

The group of lesser-known crops include Andean R&T such as arracacha, achira, and the Andean yam bean. Arracacha (*Arracacia xanthorrhiza*) is a tuberous root popular in several South American countries (Bolivia, Brazil, Colombia, Peru, Ecuador, and Venezuela), and traditionally used for the preparation of soups, stews and purees, and for making bread, cakes and drinks (Leidi et al. 2018). Starch is the main carbohydrate present in arracacha, with high resistant starch and significant FOS contents reported for these roots (Lovera et al. 2017; Sancho et al. 2017); thus, arracacha could provide suitable ingredients for low glycaemic index foods with potential prebiotic properties (Leidi et al. 2018). Arracacha roots may be used for starch extraction and because of its properties (low gelatinisation temperature and low retrogradation and syneresis) may have specific uses in the food industry (e.g., milk-based drinks or soups). The industrial use of arracacha starch has led to a complete characterisation of its physicochemical and rheological properties (Leidi et al. 2018).

Pachyrhizus ahipa (Andean yam bean) from the Andean region and its closely related Mesoamerican species *P. erosus* (jicama) are another tuberous-root producing crops. The starch content in ahipa roots reaches 44–65% (Dini et al. 2013) while *P. erosus* has more than 80% db of this carbohydrate (Stevenson et al. 2007). Starches from both sources exhibit similar morphological and physicochemical properties (Table 3.5). Jicama is a popular dietary staple in Mexico, Central and South America (Stevenson et al. 2007) while ahipa is only consumed locally in some Andean regions of Bolivia, and the north of Argentina (Dini et al. 2012). This crop has higher crude protein content than other R&T (6.5–9.4%) (Dini et al. 2021), and these are non-prolamins thus ahipa is suitable for GF products (Dopporto et al. 2011). Ahipa proteins are highly hydrosoluble and have low molecular weight thus most of them are removed during the starch extraction process (Dini et al. 2012). Similar to *Ipomoea batatas*, some *P. ahipa* accessions have anthocyanin pigments which provide a dark layer of a protein and anthocyanins mixture over the sedimented starch cake (Dini et al. 2021), which is reflected in a lower L^* value of the starch powder compared to *P. erosus* (Table 3.5), the latter being non-pigmented roots. Native ahipa starch exhibits better expansion properties during baking than native CS (Díaz et al. 2019). Modifications such as natural fermentation and protein enrichment were assayed in this starch, which provided mainly modifications in the rheological properties (fermentation) (Díaz et al. 2019) and in the texture and crumb alveolar distribution of GF baked products (Malgor et al. 2019).

Pueraria (kudzu) root starch is only popular in China, Japan and other East Asian countries. Starch is an important component of kudzu root, accounting for ~50% of its dry weight, and can be extracted in high purity (up to 99%) (Zhao et al. 2021). Industrial root processing is established in these countries and starch is commercially available. Furthermore, kudzu starch can be purchased as a specialty in western countries. In artisanal produced starches, relatively high isoflavones levels can

be detected, which are stated to enhance its nutritional value (Zhao et al. 2021). Native kudzu starch has some intrinsic limitations such as low solubility, thus, various physical, chemical, and enzymatic modifications have been assayed, attempting to improve and broaden its food applications, such as emulsification properties and film forming capacity (Zhao et al. 2021).

3.6.2 Legume Starches

Legume dicotyledonous seeds (Fabaceae botanical family) such as beans, peas, chickpeas, cowpeas, and lentils are a good source of total carbohydrates, which represents 65–72% of the weight of dried legumes. This fraction comprises starch (about 85%) and dietary fibre (between 10 and 20%) (Fabbri and Crosby 2016). Oligosaccharides (α -galactosides) are also present (Carpenter et al. 2017). Galactooligosaccharides were held as flatulence-causing compounds, so that soaking, and processing treatments have been suggested to remove them or significantly reduce their content. Recently, these kinds of carbohydrates have been recognized as prebiotics and promoters of beneficial intestinal bacteria (Affrifah et al. 2021).

Although starch is the major component of legume seeds, its content varies significantly depending on species and cultivars, from 35% to 60% of the total mass of pulses (Kringel et al. 2020). Likewise, the starch yield could reach 84.7% as reported for faba bean, or be relatively low as informed for black bean (16.4–22.2%) (Ashogbon et al. 2021) depending on the different methods of dehulling, the seed coat hardness, soaking procedures, etc.

The fact that most of legume total carbohydrates is represented by starch and, at the same time, legumes are good sources of dietary fibre can be explained by the relatively high proportion of resistant starch in these seeds.

Starch extraction processes are generally classified into wet and dry milling (Fig. 3.5). The isolation of proteins from defatted legume flours also yields starch as a by-product (Wani et al. 2016). Dry milling is principally used for industrial processing and wet milling is commonly applied at the laboratory, allowing the isolation of purer pulse starches (Hoover et al. 2010).

The obtaining of starch from legume seeds performed by wet milling method implies the co-decantation of proteins, small fibre components and the starch granules (Wani et al. 2016). Thus, starch isolation from legume grains is challenging because of the insoluble accompanying macromolecules that interfere in the sedimentation and co-settles with the starch to form a brownish cake (Hoover et al. 2010).

The main steps for isolating starch from legumes by wet milling (Fig. 3.5) are soaking, dehulling, washing, blending, screening, centrifugation or sedimentation, to end with the drying, grinding up and sieving of the obtained starch (Hoover et al. 2010; Lawal and Adebowale 2005). Wet milling is performed in alkaline conditions, being the pH used for the extraction in the range 8.5–10. In some cases, dehulled seeds are soaked in water with the addition of sodium chloride (6 g L^{-1} ; solid to liquid ratio 1:5) for the extraction of salt soluble proteins (Abu et al. 2006) or

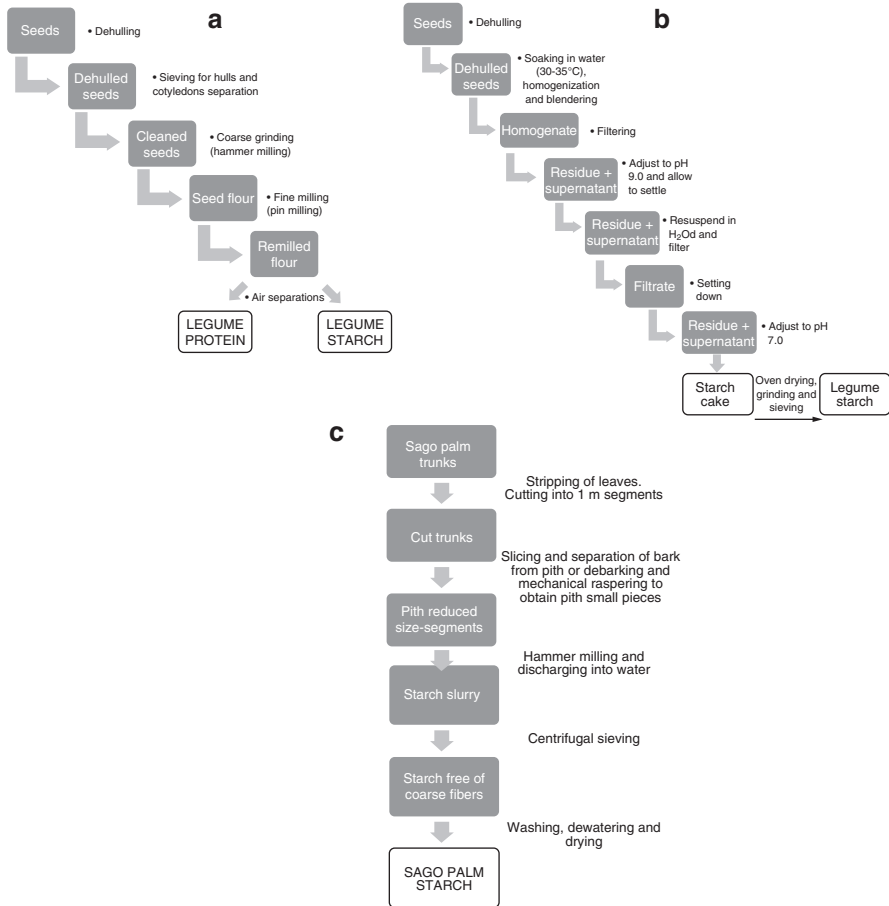


Fig. 3.5. Dry (a) and wet milling (b) processes for obtaining legume starches and sago starch extraction process (c). (Flow diagrams were adapted from Hoover et al. 2010 and Kringel et al. 2020)

potassium metabisulfite, to avoid occurrence of browning phenomena (Aggarwal et al. 2004).

Hoover et al. (2010) have pointed out that the starches of several pulses such as smooth and wrinkled peas (*Pisum sativum* subsp. arvense), faba bean (*Vicia faba*), mung bean (*Vigna radiata*), lentil (*Lens culinaris*), navy bean (*Phaseolus vulgaris*), lima bean (*Phaseolus lunatus*) and cowpea (*Vigna unguiculata*) have been obtained by dry milling, using hammer and/or pin mills and air sorting. A high degree of particle size reduction is demanded to separate the starch granules from the protein matrix and, as it was previously mentioned, air separation does not allow to achieve a complete fractionation of these components. Even after repetitive milling and air classification, the starch obtained by this method shows lower purity than that

coming from wet milling process, and a water washing step must be implemented to reduce the remnant attached protein to approximately 0.25% in the separated starch.

Table 3.5 shows the main morphological and physicochemical characteristics of the starches obtained from bean, pea, chickpea and lentil grains.

Most pulse starch granules are oval, although spherical, round, elliptical and irregularly shaped granules were also described (Hoover et al. 2010). Based on its X-ray diffraction pattern, legume starches are often classified into the C-crystallinity type, which indicates that the granules contain both A-crystalline structures forming the outer layers, and B-crystalline types found in the centre of the granules (Manthey 2016). Some pulse starches, such as pea, lentil and bean starches, are typically rich in amylose, show relatively low swelling power, deficient dispersibility in water, and tend to retrograde. These starches possess strongly bonded chains, which is reflected in their high gelatinisation transition temperatures and enthalpies (Ashogbon et al. 2021).

Total amylose content of legume grain starches has been reported to be in the range 14–88% (Tayade et al. 2019). These wide differences are generally related to inter and intra specific genetic variability, climate and soil growing conditions, physiological status of the plants, and analytical methods. In this sense, amylose content can be determined spectrophotometrically and, sometimes, under or overestimated if defatting is not previously carried out, and/or the iodine complexing phenomena of long external amylopectin chains are not considered.

Pulse starches present a relatively high proportion of resistant and slowly digestible starch fractions, which are the preferable forms of dietary starch due to their slow glycaemic response and relative control of the plasma insulin levels (Keskin et al. 2022). Thus, functional and healthier food products can be developed using legume starches as ingredients.

On the other hand, the relatively high amylose content of some legume starches usually causes detriment to desired functional properties in many food applications as compared to prevalent cereal and root starch sources. Nevertheless, with the development of starch modification agents and techniques, it is possible to restructure practically all starches to meet targeted uses. γ -Irradiation is an alternative to preserve and functionally modify the starches obtained from different sources. Abu et al. (2006) analysed the physicochemical and thermal properties of the starch isolated from 2, 10 and 50 kGy irradiated cowpea flours and pastes. The authors reported that pasting and swelling properties were significantly decreased in a γ -irradiation dose-dependent way. Differential scanning calorimetry of cowpea starch showed increments in peak gelatinisation temperature with higher irradiation doses. On the other hand, scanning electron microscopy and Fourier transform infrared (FTIR) spectroscopy revealed that, up to a 50 kGy dose, irradiation did not cause visible physical effects on cowpea starch granule surface.

3.6.3 Palm Starch

Sago palm (*Metroxylon sagu* Rottb.) is a tropical plant species belonging to the *Areaceae* botanical family, grown in Southeast Asia and Oceania (Malaysia, Indonesia, Papua New Guinea, Philippines, Thailand and the Solomon Islands) (Chua et al. 2021). The plant produces an upright trunk ~10 m high and 0.75 m in diameter. During the vegetative phase (10–15 years), the stem stores starch to a maximum level up to the development of a huge inflorescence at its top. This energy and carbon storage is then consumed during fruiting, and the plant dies after mature fruit falls from the palm (Manthey 2016). Although the long harvesting time of sago palm discourages its cultivation, this crop presents high-starch producing capability: 25 tons per hectare per year (i.e., amongst 4–5 times that of rice, corn and wheat, and about 17 times that of cassava) (Chua et al. 2021).

The storage parenchyma of the trunk pith contains simple, 10–50 µm in size, oval or polygonal shaped starch granules in its cells. Sago palm starch comprises about 27% amylose and its gelatinisation temperature varies from 69.5 to 70.2 °C (Karim et al. 2008). Abdorreza et al. (2012) have shown that hydrolysing sago starch with hydrochloric acid at 50 °C for 6, 12, 18, and 24 h significantly augmented gelatinisation temperature and enthalpy with increasing degree of hydrolysis.

Othman et al. (2015) applied γ -irradiation (6, 10 and 25 kGy) to sago starch and observed that the apparent amylose content and swelling power of irradiated-sago starch was significantly reduced, while the starch solubility increased due to degradation. Although there was no physical damage to sago starch even at the highest dose assayed, the treatments induced a decrease in the relative crystallinity, but did not alter the crystalline type.

Recently, Azfaralariff et al. (2020) analysed the physicochemical properties of starch nanocrystals extracted from sago starch and their performance as a Pickering emulsifier agent. The authors concluded that significant differences in morphological, thermal and pasting properties were derived from the conventional acid hydrolysis method applied for obtaining de starch nanocrystals (3.16 M H₂SO₄ at 40 °C for 5 days, then rinsing with distilled water until pH 7). Nevertheless, no major chemical changes were identified by FTIR analysis when compared to the native sago starch. Required sago starch nanocrystals concentration was at least 3.5% (w/v) to produce Pickering emulsions that showed good stability and no sign of creaming during 2 months of storage at room temperature (Azfaralariff et al. 2020).

To improve starch functionality for the formulation of food products, Zailani et al. (2022) exposed previously washed or cold-soaked sago starch to microwave heat treatment and found that the modified starches exhibit better solubility in hot water, oil and water binding capacity, and higher resistant starch content of cooked samples compared to the control. The authors also reported an increase in amylose content as well as morphological changes on the previously washed starch granules.

3.6.4 Nut Starches

Among starchy nuts, acorns and chestnuts stand out in their high proportion of this carbohydrate. Acorns is the general name given to the nuts from oak trees (*Quercus* spp.), being starch the main component of its kernels (Taib and Bouyazza 2021). Among the available commercial products made from acorn starch or flour, are snacks, noodles, breads, cakes, soups, and jelly. Particularly, a traditional jelly product made from acorn starch known as *mook* is a highly popular food in Korea (Kim and Yoo 2011).

Chestnuts are the fruits of trees of the genus *Castanea*, from the *Fagaceae* family. These are widely consumed in many countries, especially from Asia, Europe and America (Guo et al. 2019), toasted (as snack) or included in food preparations. Starch is the main component of chestnuts, with percentages up to ~80% depending on the variety and genotype (de La Montaña Míguez et al. 2004; Liu et al. 2015). Commercial availability of chestnut starch is rather scarce while the flour is a little more easily found.

Starch extraction from these sources is similar to that of pulses, involving dehulling and wet or dry milling of the kernels (Fig. 3.5), but includes as a preliminary step the removal of the outer shell (pericarp). At laboratory scale, kernels are grinded into a flour which is then suspended in an alkaline (NaOH) or enzymatic (protease) solution, screened and/or centrifuged, rinsed with distilled water and dried (Correia et al. 2021; Deng et al. 2020; Zarroug et al. 2020), reaching yields up to 88.5% and 83.9% for acorns and chestnuts, respectively, and high purity (>96%) (Correia and Beirão-Da-Costa 2012). Cruz et al. (2013) proposed the use of sodium bisulfite solution for chestnuts starch extraction, and purification by sedimentation. Authors reported yields of 94% and high purity (93%) and stated that granules integrity was more preserved this way than using alkali as extractant (Cruz et al. 2013).

Chestnut starch has acceptable whiteness, showing lightness (L^*) values above 92 (Guo et al. 2019; Cruz et al. 2013), while acorn starch exhibit average L^* values around 88 (Correia et al. 2021; Deng et al. 2020) leading to a more grayish product (Table 3.5).

Starch granules are predominantly spherical and elliptical for both nuts, but in the case of chestnuts, some authors also observed irregular and triangular forms (Guo et al. 2019; Liu et al. 2015; Cruz et al. 2013; Moreira et al. 2015; Yoo et al. 2012).

Acorn starch granules size ranged from 2.5 to 126.2 μm , depending on the genotype and the extraction method used (Taib and Bouyazza 2021; Correia et al. 2021), while for chestnuts starch, mean sizes ranged between 10.8 and 18.1 μm (Liu et al. 2015; Cruz et al. 2013). Particularly, starches from 21 cultivars of *C. mollissima* Blume from different regions of China showed a bimodal distribution, with mean particle sizes ranging from 21.5 to 111.7 μm (Guo et al. 2019).

According to Cruz et al. (2013) the crystallinity degree of chestnut starch is directly related to the moisture content, varying from 9% to 51% for moisture contents rising from 5% to 29%. Likewise, amylose content of chestnut starch varies greatly among species and extraction methods, with high (~41–57%) (Guo et al. 2019; Correia and Beirão-Da-Costa 2012) and intermediate (17–30%) (Liu et al. 2015; Cruz et al. 2013; Yoo et al. 2012; Zhang et al. 2011) values reported. Acorns starch crystallinity degree and amylose values were reported in a narrower range (Table 3.5).

Chestnuts resistant starch percentage is also strongly dependent on the species and the extraction method, for which values from extremely high (84.9%) (Liu et al. 2015) to extremely low (4.3%) (Zhang et al. 2011) were informed.

Acorn flour has low digestibility, partially attributed to its tannin content (approx. 6%) (Soni et al. 1993) which can act as endogenous starch hydrolysing enzyme inhibitors (Lin et al. 2018). Additionally, acorn starch has a high proportion of resistant starch (30.8–41.4%) (Taib and Bouyazza 2021). This may position acorn flour and starch as promising ingredients for the formulation of low-glycaemic index foods.

When used as an additive, it has been reported that native acorn starch in concentrations lower than 1%, can provide improved functional properties, enhanced viscosity and reduced syneresis in a fermented dairy product (Zarroug et al. 2020).

Kim and Yoo (2011) studied the effect of the addition of guar gum and locust bean gum in the rheological and thermal properties of acorn starch and found that galactomannans increased the viscoelastic properties, lowered the gelatinisation enthalpy and raised the gelatinisation temperature compared to the native starch, attributed to a phase separation due to a low interaction between different polymers. Increased gel strength and decreased freeze-thaw stability were reported for the mixture of acorn starch with other hydrocolloids (e.g., carrageenan, xanthan gum) (Saleh et al. 2016).

Regarding starch modifications, physical treatments such as heat moisture treatment (HMT, heating starch at low moisture values) and annealing (heating a starch slurry below the gelatinization temperature) were assayed, individually and combined, on native Persian acorn starch (Molavi et al. 2018). More noticeable changes were produced by individual HMT treatment. Changes included increasing starch solubility, decreasing swelling power and amylose leaching, raising the gelatinisation temperature and lowering the gelatinisation range and enthalpy. Particularly, the changes produced by HMT in the pasting properties of starch could provide increased resistance to conditions such as prolonged heating and/or acidic medium. Furthermore, starch retrogradation was also limited on HMT starches (Molavi et al. 2018).

In the case of chestnuts starch, physical modifications such as dry heat treatment (DHT), addition of XG (Liu et al. 2022), and ultrasonic and microwaves treatments (Wang et al. 2020a) were assayed separately and combined. The DHT plus XG increased in 2% the amount of resistant starch compared to the native sample (Liu et al. 2022), and the microwave treatment followed by ultrasonication increased the freeze-thaw stability of chestnut starch pastes, which could be useful in frozen

foods (Wang et al. 2020a). Likewise, chemical modifications such as acetylation and hydroxypropylation also provided increased freeze-thaw stability to chestnut starch, while crosslinking showed better performance in reducing the retrogradation tendency of the starch pastes (Oh et al. 2019).

3.6.5 Some GF Food Application

As was expressed in previous sections, much research was made to obtain new and GF resources of starches. A complete physical and chemical characterisation of granules from non-conventional resources has been reported and is available. However, studies related to applications as food ingredient are scarce, particularly to demonstrate the suitability of new starches or for production of GF items. Table 3.6 shows some developments where non-conventional resources were used to produce bakery and pasta items.

Table 3.6 Some non-conventional starch resources used in bakery and pasta production

Starch resource	Food application	Main findings	Reference
Native or hydrothermally modified bean starch	GF bread	Modified starch reduced the hardness and the retrogradation enthalpy. Improved the chemical composition and quality of fresh bread but did not extend its freshness during storage.	Krupa et al. (2010)
Pea starch	Noodles	Noodles prepared by twin-screw extrusion exhibited similar brightness in colour and cooking time to, but firmer texture. The conventional starch noodle-making procedures was simplified.	Wang et al. (2012)
Lentil starch	Noodles	Noodles were less bright in colour, but had superior texture when cooked as compared to commercial mung bean starch noodles	Wang et al. (2014)
Chestnut flour	GF bread, cakes, snacks	In addition with structuring agents, various quality attributes of the bread including hardness, specific volume, colour and sensory scores were improved.	Zhu (2017)
Sweet potato	GF noodles	Fortification with protein and/or another starches enhanced the acceptability as well as functional value. Reduced starch digestibility and enhanced protein content.	Menon et al. (2016)
Sweet potato	Noodles	Addition of hydrocolloids with high water binding capacity was necessary to control the degree of swelling of starch granules.	Silva et al. (2013)

(continued)

Table 3.6 (continued)

Starch resource	Food application	Main findings	Reference
Sweet-potato Starches	Noodle	Starch with high firmness and elasticity of its gel, result in good quality starch noodle. Suitability of sweet-potato for starch noodle making depends on variety.	Chen et al. (2002)
Sweet-potato	GF model doughs	In combination with HPMC reduced the dough development time, strength against mixing but increased gelatinisation temperature.	Zhang et al. (2017)
Green banana flour	Pasta	Greater acceptance and similar appearance, aroma, flavour and over-all quality than whole-wheat flour pasta. Modified pasta had ~98% less lipids.	Zandonadi et al. (2012)
Banana starch	GF sugar-snap cookies	30% replacement of rice flour improved starch digestion rate and consumer's acceptance. RS was increased. Gelatinised starch inclusion increased the water fraction that shifted cookie from brittle to soggy.	Roman et al. (2019a)
Green banana flour	GF muffins	Muffins were rich in minerals, less firm, had more volume and overall acceptability. Physicochemical, baking, texture and sensory evaluation showed that the use of 100% GBF had a favourable effect on muffin quality.	Kaur et al. (2017)
Pre-gelatinized unripe banana flour	GF bread	Volume and specific volume increased with the addition of HPMC and flour, while the hardness decreased. The addition of flour and water increased the number and size of alveoli and affected their distribution in crumbs.	Hernández-Aguirre et al. (2019)
Ripe banana flour	GF bread	The highest specific volume was obtained with 2-week ripening and 70% water. The flour was shown to have good potential as a substitute for gluten. The swelling ability on GF breadmaking was achieved with 10% flour.	Hosokawa et al. (2020)
Banana starch	GF bread	Slowed down the starch digestibility of bread crumb and crust	Roman et al. (2019b)
Banana flour and starch	GF cookies	Sensory profiling of cookies meet consumer requirement but also compared favourably with conventional cookies.	Olawoye and Gbadamosi (2020)

3.7 Conclusions

Starch is a substantial ingredient for the development of GF foods. Depending on the physical and chemical properties of starch, baking products and pasta will have characteristics. Amylose content and minor compounds, such as lipid, protein and phosphorus modulate the suitability of the starch in bread or pasta making. The pasting, gelatinisation, swelling and solubility behaviour of starch affect the development of volume and texture integrity in the GF breads and pasta. It is also important, the response of starch to fermentation process in which amylase enzyme must reach the starchy substrate. In these sense, physically damaged starches improve the rate of the fermentation process under amylase action. Resistant starch (RS) amount is an important nutritional aspect to take into account. It is considered that RS enhance the nutritional properties of GF breads by reducing the digestion rate of starch and, consequently, glycaemic index. Upon modification, the physicochemical and functional properties of starch could be adjusted in order to obtain improved foods with better texture and more stable products, since most of the modified starches reduce the retrogradation rate and the staling. When gluten is take off from formulation, natural GF non-cereal starches can be used as gelling, thickening, adhesion, moisture-retention, stabilizing, film forming, texturizing, and antistaling ingredients. However, other compounds may be added to achieve optimal expansion, integrity and stability of GF breads and pasta. Although many different sources of starch have been studied, as an alternative to cereal ones, the reports give information about properties of granules and scarce results were found in relation to accessibility and application as ingredient for GF products. Therefore, much more efforts must be done to elucidate the suitability of the new starches for GF food production.

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