Thermal technologies to enhance starch performance and starchy products

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ABSTRACT

Starch and starchy products can be modified by different technologies in order to improve its properties and expand the applications. Among the different technologies, thermal techniques are interesting as no chemical pollution is involved and are generally recognized as simple and safe. In this opinion paper, we discuss about selected thermal technologies which are drum drying, extrusion, spray drying, autoclaving, instantaneous controlled pressure drop (DIC®) process, and dry heating treatment. A brief description is proposed for each technology, followed by the major findings described in the literature, and the most relevant developments in the field over the last five years. Thermal technologies present different parameters to be evaluated and optimized. In this way, each technology interacts with starch involving particular mechanisms. This results in different modifications of the starch structures and consequently in diversified functionalities.

Keywords: starch, functionality, drum drying, extrusion, spray drying, autoclaving, dry heating, and instantaneous controlled pressure drop (DIC®) process.

1. Introduction

Starch is a natural polymer stored in plants as an energy source. It is present as semicrystalline granules that, according to their botanical origin, have different compositions, sizes, and shapes [1]. The versatile nature of starches makes it useful in food as well as non-food applications. On the other hand, native starches have some limiting, as they are not soluble at room temperature and require heating for processing, which results in higher energy and infrastructure costs. Different technologies have overcome these barriers resulting in modified starches with improved properties [2].

Structural modification of starch through processing can confer functional properties not found in native starches, widening its the application in several industries. Among the different techniques, physical methods have gain attention since most of them are cheap, safe and simple to use. Moreover they require no chemicals or biological agents, therefore they don't contain chemical reagents by-products [3]. Within the physical methods, thermal technologies are consisting in starch heating to improve its functional properties or bring new ones to a particular ingredient. The hydration level plays a major role on the final functionality, as the presence of water will control the degree of starch gelatinization during the process.

The use of thermal technologies regarding the modification of flour properties have been first reported in 1934 by Mangels. Then, patents emerged from 1960 and is now very much considered from an academic and an industrial point of view [1,4]. The most common use of thermal treatment is related to starch gelatinization. Thermal technologies can also be used to modify proteins, increase the availability of nutrients and inactivation of toxic thermolabile compounds and other enzyme inhibitors; which can result in a new sensory and nutritional profile for starchy products [5].

In this opinion article, we bring a brief description, discussion and the main findings of a selection of thermal technologies such as drum drying, extrusion, spray drying, autoclaving, instant controlled pressure drop process (DIC®), and dry heating treatment, each having different level of novelty.

2. Process and Technology

Thermal technologies are able to produce either pregelatinized starches or non pregelatinzed starches when the process is carried in low water content conditions. Pregelatinized starches, also called instant starches, belong to the class of modified starches that have the ability to hydrate without heating and when dissolved in cold water. Thus pregelatinized starches allow instant viscosity and smooth texture to make starchy products more suitable for various food and non-food applications [6,7]. This modified starch has been used mainly in the production of products that are sensitive to heat. Its application allows to simplify and shorten the production processes. Also, it can be useful as a thickening agent in food that does not require a thermal process such as creams, sauces, puddings, or dairy products [8]. In addition, pregelatinized starches can be divided into fully gelatinized and partially gelatinized. On the one hand, fully gelatinized starches have been mainly used as thickening agents, bulking agents in food products and in pharmaceutical formulations. On the other hand, partially gelatinized starches show a mix of native and fully gelatinized starches properties [9].

In the literature, it was observed that the pregelatinized starch show better water absorption, solubility in cold water, higher viscosity at 25 °C, and swelling power when compared to its native counterparts [7]. However, pregelatinized starch are characterized by a loss of crystallinity, disruption of granule structure, molecular depolymerization, and formation of porous structure [6,10].

Besides, thermal technologies could also affect the other flour components such as lipids, proteins, nutrients and active compounds. For example, thermal technologies are able to promote protein denaturation and lipid saponification, making these compounds soluble. Thus, heat-treated flours may have a reduced content of proteins and lipids [11]. Moreover, thermal technologies may increase the availability of nutrients. They also play a major role in the inactivation of toxic thermolabile compounds and other enzyme inhibitors, degradation of active compounds [5].

Finally, in this section, we will discuss selected thermal techniques that can be applied for the production of pregelatinized starch or to modify the starch performance. The selected thermal technologies are drum drying, extrusion, spray drying, autoclaving, dry heating treatment, and instantaneous controlled pressure drop.

2.1 Drum drying to produce pregelatinized starches

Drum drying, amongst the methods available, is the easiest and the most economical method. For these reasons, it has been widely used in pregelatinized starch production industries [10]. This technology refers to specific physical-chemical modifications of the starch granules and involves two stages: gelatinization and drying. This method can be performed using single or double drum dryers. However, double drum dryers are preferred over single drum dryers due to their ability to be applied to a wide range of products. They are also more economical, more efficient, presenting higher production rates and lower operational labor requirements [6].

The processing conditions of drum drying such as "cooking" and drying can significantly affect the internal and external structure of the starch granules, and consequently, their functional properties [10]. In this way, the process variables: steam pressure, drum speed, drum dryer interval, feed concentration, and residence time are crucial for the implementation of the technique.

Drying in the drum is relatively slow, therefore macromolecules have the possibility of re-associating. Starches can undergo retrogradation during this process, being the result of a new reorganization carried out using numerous hydrogen bonds in their structure. This effect is more evident in starches with a high amylose content due to their more linear polymeric structure [10].

Drum drying can promote an increase of water absorption index and swelling power values, reduction of the peak viscosity, partial depolymerization of starch components, degree of crystallinity, alteration of the crystallinity pattern. It also impact the granule structure through the formation of a porous structure, reduction of particle size, formation of irregular surfaces, and color darkening of the starchy products [5–7]. In relation to the application, one example is the work of Li et al. [12], in which they considered pre-gelatinized corn starch produced by drum drying which was added to noodles; it allowed an improvement in the quality of the processing and ingestion of the noodles when compared to addiction of the native starch.

Finally, drum drying is recommended when compared to other thermal technologies, because it has the advantage of high drying rates and economical use of heat.

2.2 Extrusion

The extrusion process involves a continuous method where there is a combination of shear stress, high temperature and pressure capable of altering the physical characteristics of starchy products [13]. The extrusion process forces the material to pass through a die so that sudden pressure drops cause some of the water to vaporize and with reduction of the moisture content, the starchy material suffers expansion [14]. Among the techniques presented, extrusion technology is recommended because it is a relatively fast and very flexible when compared to other processes.

For the pregelatinized starch production process, single screw or double screw extruders can be used. The process parameters that play an important role in the final product are the starch feed moisture, screw speed, cylinder temperature, compression, and extruder die sections [6].

The extrusion can cause loss of integrity of the starch granules and even partial depolymerization of its polymers, since it is capable of causing breakage of covalent bonds between the components of the starch [15]. These structural changes are reflected in the modification of the functional properties of starch or starchy products. The extrusion process can result in starchy materials with lower percentage and rate of retrogradation, improved the freeze-thaw stability of starch, reduction of syneresis and retarding changes of the honeycomb structure. It also affects proteins through denaturation and cleavage. Finally, formation of particles uneven and more porous, reduction of particle size, and increase of the water holding capacity [13,14,16,17]

An emerging extrusion technology called "Improved Extrusion Cooking Technology" (IECT) has been highlighted. The IECT technique corresponds to a new gelatinization technology, which consists of a single screw extruder with a longer screw (ca. 2 m), lower processing temperature (50-150 °C), longer residence time (18-90 s), and lower screw speed (15-75 rpm) than conventional extrusion [13]. The technique IECT results in pregelatinized starches with a lower percentage and rate of retrogradation, and it also improves the freeze-thaw stability of starch [16].

In relation to the application, Giraldo-Gómez et al. [14] observed that banana flour modified by extrusion process resulted in a starchy material with higher water solubility with adequate characteristics for instant drink preparation. Also, according to Hayes et al. [18], the single screw extrusion process applied to normal and waxy rice starches allowed fragmentation of amylopectin and resulted in modified starches with the capacity to promote a lessened extent of staling in breads and cakes.

2.3 Spray drying

The spray drying process consists in pumping a solution into an atomizer, which sprays the liquid feed in the form of fine droplets inside the drying chamber. Hot air is simultaneously injected in the latter leading to moisture evaporation and eventually the formation of dry particles. Then the dried particles are collected in a tank [15]. The process can be described in a simplified manner by three main phases: atomization, drop-to-particle conversion and particle collection [19]. In this type of process, the feed flow rate, inlet temperature, sludge concentration and the air flow rate are parameters to be investigated and optimized, since they affect the nature or the free flow properties of dry matter [15].

Spray drying has been commonly used for the production of pregelatinized starch, as it efficiently converts liquid droplets into amorphous particles without interfering with their granular integrity [20]. Moreover, this technique has the advantage of being relatively low-cost, fast, and having available equipment when compared to other processes which involves drying. Another fact is that the scalability and cost-effectiveness of this manufacturing process in obtaining dry particles going from a submicron-to-micron scale allows this technique to be efficient for a variety of applications involving from the food industry, polymers and pharmaceuticals [21]. We can cite as a disadvantage of this technique the fact that it presents a high content of material losses during the processing, and the process parameters are very complex and interrelated, difficult to optimize [22].

When using drum drying or extrusion methods to prepare pregelatinized starches, the starch has a structure similar to a hard stone, usually in millimeters, which is then ground in sophisticated and high-performance mills. Thus, the spray dryer method is more effective than drum drying and extrusion, once that does not lead to loss of the granular integrity [20]. In addition, it was reported that the spray drying process promotes the formation of spherical aggregates of starch granules, interesting for the production of wall material for microencapsulation in the pharmaceutical sector [23,24].

Spray drying can promote reduction in the molecular weight of amylopectin and reduction on crystallinity, partial depolymerization of starch components, alteration in surface granules as folds and wrinkles, an increase of coating efficiency value [15,23,24].

2.4 Autoclaving

Autoclaving is extensively applied in food industries for food safety; however, it can also be applied for starch pregelatinized production. The principle relies on maintaining the material at high temperature, through contact with water vapor, for a specific period of time. The process includes compression and decompression cycles to facilitate the contact of the vapor with the materials. The usual pressure values are in the range of 3 to 3.5 bar and the temperature reaches 135 ºC [25]. This technology has the advantage of being relatively simple, and can be used for different types of products. On the other hand, this technique has the disadvantage of presenting a relatively high cost due to the volume of water needed to carry out the process cycle and also the electrical energy needed to heat the water. The production of pregelatinized starches from autoclaving has been studied (REF) but is still not as common at an industrial scale as the other methods mentioned in this work, mainly due its limitations [26].

The autoclave process promotes hydration of the amorphous zone in the starch granules under the action of a pressure field. The amorphous layer of the crystallization zone of the starch granule swells in the presence of water with increasing pressure, which causes the rearrangement of the double helix of amylopectin [25]. Also, the process parameters of autoclaving duration and paste concentration have a profound impact on the morphological and physicochemical properties of pregelatinized starches [6]. According to Patindol et al. [27], greater paste concentration and autoclaving duration resulted in starches with higher average particle size and lower bulk density. Also, these authors observed that the impact of these parameters is more evident for starches than for flours properties.

Autoclaving process can result in partial depolymerization of starch components, disruption of crystalline network, increase of the granule area of native starch, increase of resistant starch content, reduction of the dietary fiber content, an increase of the retrogradation process, increase of the water holding capacity, reduction of the water solubility, reduction of molecular weight, and alterations in granule size distribution patterns [8,25,28,29].

In relation to application, according to Soler et al. [29], autoclaved corn starches had repercussions on the formation of resistant starch, which expands the processing and nutraceutical properties of starch.

2.5 Instantaneous Controlled Pressure Drop (DIC®) process

The Instantaneous Controlled Pressure Drop (DIC®) process is a process that was patented by the French Laboratory Maîtrise des Technologies Agro-Industrielles at the Université de La Rochelle-Pole Sciences (La Rochelle, France). This technique is based on an abrupt transition from a high vapor pressure level to a vacuum, thus having a hydro-thermo-mechanical effect. The DIC® process involves specific treatment involving high pressure (up to 0.7 MPa), high temperature (up to 160 °C), for a short time (ranging from seconds to tens of seconds) and then an abrupt fall pressure towards the vacuum (~5 kPa with a rate greater than 0.5 $MPa.s^{-1}$) [30]. The DIC process begins with the formation of a vacuum before the injection of the saturated steam. This allows to reduce the air resistance and to intensify the saturated steam diffusion into the starchy materials resulting in an optimized the time to reach the equilibrium steam temperature [31].

The DIC® process final stage is an abrupt decompression, as the pressure suddenly decreases and promotes self-evaporation. Self-evaporation occurs due to the adiabatic transition, so that the water evaporates and rapid cooling occurs. The value of temperature stabilizes at the equilibrium temperature of the final pressure [31]. This final process in which both mechanical and intense shearing occurs in the granules contributes to the modification of the starch's crystalline structure.

Mounir et al. [30] explained that treatment with DIC® leads to the fusion of low cohesion crystals, as they require less energy. And after the process, residual structure remains, crystals with greater cohesion.

The DIC® process can cause structural and functional modifications. Considering the structural modifications, it has been highlighted that DIC leads to an increase in gelatinization temperature, an increase in oil retention capacity and melting the low cohesion crystals. From the functional side, DIC causes a reduction of enthalpy, a loss of birefringence of starch granules, an alteration of the crystalline structure revealing the formation of amylose-lipid complexes and weakens the starch granules. [30–32]. In addition, DIC® process can enhance the color of the treated materials, and also the availability of antioxidant nutritional molecules [33]. Also, according to Mazen Hamoud-Agha and Allaf (2020) [32], DIC® can the texture quality and the aroma content of several food products.

Finally, DIC® reactors are operating worldwide (Spain, United States, France, Malaysia, Mexico, Italy and China) on a laboratory and industrial scale [32]. However, compared to other techniques mentioned here, the DIC® process is relatively slow and expensive, which limits its use at an industrial scale for the production of high value-added starchy materials, such as for pharmaceutical applications [34].

2.6 Dry heating treatment (DHT)

DHT is considered as a green technology to be applied on flour and starchy products with the aim of increasing water absorption capacity and swelling properties of the starch granules. It has been studied as an alternative to flour chlorination – forbidden in many countries as Australia and Europe – to produce ingredients with similar functionalities [35,36]. Most of the time, the process is applied to wheat flour but it can also be applied on other flours.

The general procedure for dry heating treatment consisting in two main steps: a drying process followed by a thermal treatment aiming at functionalizing the four. The first step allows the flour to reach a suitable moisture content that prevents caking, possible starch gelatinization, undesirable denaturation of the glutenin and sensory defects. In terms of processing, it could also affect the heat transfer. The second is based on a thermal treatment for a given treatment time (0-30 min) and temperature (120-140 ºC) to achieved the aimed characteristics [37]. For starch modifications, high temperatures (~130-140 ºC) and treatment time (from ~1 up to 20 h) are commonly applied [1]. The final product is cooled by the moisture content adjustments, which may lead to the formation of agglomerates [37].

Regarding the starch granules, the DHT can affect the overall structure like their shape and surface. It is also thought to modify their physicochemical properties such as pasting and thermal properties, the firmness of the starchy gels which is altered, the improvement of solubility and swelling capacity, the increase of oil-binding ability, the improvement of Maillard reaction and the modification of protein functionality. Those modifications may be linked to structure evolutions observed in the meantime such as the crystallinity pattern, relative crystallinity, the enthalpy, increase of hydrophobicity, and the expansion of the Maltese cross center [1,38–43]. Lastly, some researches have shown a loss of the digestibility degrees, and higher glycation concomitant to a decrease in the anti-tryptic activity [1,44,45].

Improvements in flours treated by dry heating are also attributed to modifications in the proteins and lipid fractions. The proteins and lipids located onto the starch granules surface usually act as a barrier against water absorption, impairing the starch swelling during the flour processing [40]. After DHT, the structure of the protein fraction is affected by means of denaturation and oxidation of the soluble sulfhydryl groups [46]. The folded structure of albumen-type proteins is then disrupted, exposing the entrapped lipid core by the hydrophobic aminoacids. The exposed lipids contribute to the flour functionality more intensively by their interaction with the modified proteins and starch instead by its chemical modifications [41]. In the meantime, the water migrates more easily towards the starch granule surface during gelatinization. Moreover, a more hydrophobic surface improves the contact between starch and air bubbles by the Pickering method [47]. This effect is particularly interesting to improve air incorporation in baking products and to make them more resistant against collapse [38].

In relation to the application, DHT flour is used as a baking improver in bread baking with partial substitution of wheat flour (2-5%), whereas application in cake making consider substitution by 50 to 100% of wheat flour. Keppler et al. [36] observed that DHT improved swelling starch properties at elevated temperatures and increasing effects on the gluten network and enhanced the interactions between flour polymers in high-ratio cakes (i.e. sponge cake). Dudu et al. [39] observed that the incorporation of dry heat-treated cassava flour in wheat flour could slightly increase the water absorption capacity of the flour, dough development time and softening degree. Breads formulated with heat treated cassava flour had slightly higher specific volume with increased anti-staling properties. Maniglia et al. [42,43] observed that cassava and wheat starches treated by DHT resulted in modified starches capable to form stronger gels with lower syneresis and higher potential for 3D printing applications as “inks”.

Emerging technologies has been applied with minor adjustments in the processing conditions to perform DHT process. Hassan et al. [48]investigated the radio frequency heating on maize grains for improving flour functionalities. Microwave irradiation was used to thermally treat rice flour– which showed great effect on the resulting functionality

[49]. Le-Bail et al. [50] also observed a faster heat up and higher damage on flour proteins when treating wheat flour with microwave instead of conventional process.

Finally, in order to achieve different applications, additional technologies have can be performed in combination with DHT to confer distinct functionalities to starch, from weaker to stronger gels. It includes methods as ozonation [51], repeated or continuous DHT [52] or even the combination of mechanical and thermal treatments [53].

Although DHT is conventionally performed in rotary drums, screw conveyors, agitated beds or even during milling processes, developing methods for continuous DHT of flours are still challenging and studied [36].

In Table 1, we approached the evaluated parameters, the major findings described in the literature, and selected references involving the application of these techniques.

3. Conclusion and future perspectives

In general, we can conclude that there is indeed great potential for thermal technologies to modify and improve the functional properties of starch and starchy products. Each technique offers in general a large number of process parameters resulting in the access to a large panel of functionalities. The composition and the botanical source of each starch/flour is also a determining factor, resulting in a particular behavior about each applied method.

The optimization of the presented technologies can be based on functional properties but also on process performance, energy consumption and eventually sustainability. The optimization of the parameters must also accommodate the nutritional value of the treated product. In this way, we suggest that there should be an assessment of how interesting the modification is in relation to the nutritional loss of food; in particular, pregelatinized starches may exhibit high glycaemic index. However, they are used most of the time as a minor ingredient providing gelling properties.

In future perspectives, the combination approach between methods would be an interesting way to enhance or even bring new properties for these materials. Also, we noted that it is still necessary to understand more about the exact mechanisms behind these modification techniques, as they are inconclusive because of, many factors that mainly affect the processing parameters, type of source, and composition of starch and flours.

Finally, we can conclude that together with a careful design of the application and processing conditions, the thermal technologies can be industrially applicable (and are effectively applied) as a clean technique to improve functionality of flours and starchy products – mainly those made of alternative and non-gluten sources.

Conflict of interest statement

The authors declare that they have no conflict of interest.

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Table 1. Current researches about starch/flour modification involving selected thermal technologies.

Thermal technology	*Evaluated parameters*	*Major findings*	*Selected references*
Drum drying	- Steam pressure; - Drum speed; - Drum dryer interval; - Feed concentration; - Residence time.	- Partial depolymerization of starch components; - Increase of water absorption index and swelling power values; - Reduction of the peak viscosity and the relative crystallinity; - Alteration of the crystallinity pattern; - Formation of porous structure; - Reduction of particle size and formation of irregular surfaces; - Color darkening of the starchy product.	[5–7]
Extrusion	- Starch feed moisture; - Screw speed; - Cylinder temperature; Compression and extruder die sections.	- Partial depolymerization of starch components; - Lower percentage and rate of retrogradation; - Improved the freeze-thaw stability of starch; - Reduction of the syneresis; - Retarding changes of honeycomb structure; - Denaturation and cleavage of the protein; - Formation of particles uneven and more porous; - Alteration in the pasting properties; - Reduction of particle size; - Increase of the water holding capacity;	[13,14,16,17]

Spray drying	- Feed flow rate; - Inlet temperature; - Sludge concentration; Airflow rate.	- Partial depolymerization of starch components; - Reduction on the molecular weight of amylopectin and reduction on crystallinity; - Reduction of the crystallinity relative; - Alteration in the pasting properties and in the surface granules as folds and wrinkles; - Formation of spherical aggregates; - Increase of coating efficiency value.	[15,23,24]
Autoclaving	- Autoclaving duration; - Paste concentration.	- Disruption of the crystalline network; - Increase of granule area and resistant starch content; - Partial depolymerization of starch components; - Reduction of the dietary fiber content; - Increase of the retrogradation process; - Increase of the water holding capacity and in the water solubility; - Reduction of molecular weight; - Changes in granule size distribution patterns; - - Alteration in the pasting properties.	[8,25,28,29]
DIC®	- Temperature; - Pressure; - Process time.	- Increase of gelatinization temperature, reduction of the enthalpy, and loss of granules birefringence; - Alteration of the crystalline structure, revealing formation of amylose-lipid complexes;	[30–32]

		- Weakening of the starch granules; - Partial depolymerization of starch components; - Increase of the oil holding capacity; - Alteration in the pasting properties; - Melting of crystallites of low cohesion Formation of open porous structure.	
Dry heating treatment	- Time; - Temperature; - Moisture content.	- Alteration in the pasting, thermal properties, crystallinity pattern, relative crystallinity, and in the enthalpy; - Increase of hydrophobicity and in the oil-binding ability; - Improved Maillard reaction and modified protein functionality; - Alteration in the firmness of the starchy gels; - Expansion of the Maltese cross center; - Improved solubility and swelling capacity; - Alteration in the digestibility degrees; - Increase of glycation together with a reduction in the anti-tryptic activity; - Reduction of the syneresis; - Depolymerization in the middle size molecules; - Increase of water absorption capacity and swelling properties; - Denaturation and oxidation of the soluble sulfhydryl groups; Increase of effects on the gluten network;	[1,38–45]