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Chapter 17

Gluten-Free Bakery Products and Pasta

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Abstract

Wheat-based bakery products are basic components in the diet of most countries all over the world. Intuitively, obtaining gluten-free bakery products of similar characteristics to wheat-based products is a difficult task and because of this, over the last decades extensive research has been done to get gluten-free bread with the adequate crumb structure and texture. Based on this research, this chapter will focus on the strategies for the development of gluten-free bakery products of good technological, sensory and nutritional properties. In gluten-free products, wheat flour has to be replaced by a mixture of flour and starch from different sources. Nevertheless, for products like bread, pasta and some cookies, gluten network development is required; in this case, a gluten substitute –usually hydrocolloids– must be added in the formulation. Some other products, such as cakes, wafers and crepes, do not need this continuous network and, thus, their gluten-free counterparts are more easily obtained. Gluten-free products are usually very rich in starch and contain few proteins and fibers. To overcome this problem, proteins and fibers are common ingredients in these products. Additives and enzymes are being increasingly added to gluten-free products, as well; but their functionality has to be explored since some discrepancies with their function in wheat-based and gluten-free products are observed.

Keywords

Gluten-free flours, gluten replacement, gluten-free bread, gluten-free cakes, gluten-free cookies, gluten-free pasta.

1. Introduction

Among cereals, wheat has specific proteins that make it ideal for certain applications. Thus, wheat gliadins and glutenins, in the presence of water and mechanical work, form a continuous phase named *gluten network*. It is responsible of the extensible and cohesive properties of the dough while reducing its stickiness. Wheat dough is characterized for its tenacity (dough resistance to stretching) and elasticity (dough ability of regaining its original shape after being stretched). These characteristics allow the retention of gas produced during proofing, resulting in a volume increment and the development of an alveolar structure responsible for a sponge-like product after baking. It is still unclear why this network develops in wheat based dough, and why it is absent in dough prepared with other cereals, but a number of variables are known to influence its development, such as the type and ratio of aminoacids that influence the tertiary and quaternary structure of proteins. In this network, the occurrence of many types of bonds among proteins has been suggested, like hydrogen bonds, hydrophobic interactions and, particularly, disulfide bonds among sulfur residues. The strength of gluten network will depend on glutenin and gliadin quantity –and ratio–, their molecular weight and, more generally, of overall quality of wheat proteins. The characteristics of these proteins will determine the strength, elasticity and extensibility of dough. The way in which specific products need specific gluten characteristics will also be addressed in the chapter.

It is important to clarify the concept of *gluten*, since this word is used in different areas and within each area it has different meanings. In the bakery industry, *gluten* is usually related to the protein that makes the dough both cohesive and extensible, easily sheeted and shaped, as well as capable of retaining the gases produced during fermentation and proofing. According to bakers, the only cereal that possesses gluten is wheat. Under certain circumstances, *gluten* makes reference to the network formed by wheat proteins under wet conditions and after the application of mechanical work (during mixing). Using this concept, wheat would not contain any gluten, but dough and bread or pasta would. Finally, in the food industry, *gluten* is usually used to refer to corn proteins obtained after wet milling. This particular corn gluten can be consumed by celiac patients, unless it is contaminated with other toxic cereals. This gluten does not form a continuous network for bakery processes. In this chapter, *gluten* will be used to refer to wheat protein network.

Another important issue that must be considered is the need for establishing a gluten network in certain processes. Products where the gluten network plays a key role should contain a “gluten substitute” in their formulation; hydrocolloids usually play this role. However, if gluten does not have a basic function or its formation is even undesirable, the production of their gluten-free counterparts will be easier. As a general rule, gluten plays a basic role in doughs needing a minimal consistency, for example to be sheeted and/or in doughs which should retain fermentation gases, such as bread, pizza, croissants, puff pastries and Marie-like cookies, among other products. Gluten network is also needed in pasta production, while, in liquid dough –batter– it does not develop. Examples of this type of batters are layer and sponge cakes, wafers, crepes and waffles. During the processing of some cookies, mixing time is much reduced to avoid gluten formation, since gluten network is not desirable in these products. Finally, in certain products, such as scalded doughs and *churros* –not addressed in this chapter–, processing includes the addition of hot water. In these cases, the incorporation of hot water increases dough temperature inducing partial gelatinization of starch and protein denaturation, thus, avoiding the development of gluten network.

In the first part of this chapter, the production of bakery products where the gluten network is required is analyzed. Then, in section 3, it is discussed the development of pastry products considering that in certain processes gluten network is not required. Finally, in section 4, gluten-free pasta production is explored.

2. Development of Gluten-free Bakery Products

2.1. Raw Materials: Flours and Starches

When wheat flour is removed from any bakery formulation, a large amount of starch is eliminated and has to be replaced by some other ingredient. Among gluten-free raw materials that can be used for this purpose, the most important ones are cereal flours without gluten, as well as native starches. Flours present a more complex composition including starch, a variable amount of proteins, a low quantity of lipids and some minor components, such as fiber, vitamins and minerals. Rice flour is one of the most suitable raw materials due to its hypoallergenic properties, low sodium content, bland taste and light color[1], and its easy availability in the market. Although less frequently, corn flours[2], mainly those from white varieties, and sorghum and millets[3] are also used. Cereal flours have a variable particle size, usually between 0-200 µm, whereas starches have, on average, smaller particles than flours and a simpler composition (almost 100% of dry matter are carbohydrates). Among the starches most traditionally used for the elaboration of gluten-free products, corn and potato starches are found, due to their functional characteristics, price and availability, but also cassava and cereal starches, such as rice and sorghum. Some years ago, gluten-free breads were based on wheat starch, as it had the advantage of presenting a similar taste to wheat flour; but since it contained trace amounts of allergic protein, it was discarded as a possible raw material for gluten free products. However, in recent years, starch isolation procedures have been significantly improved and, since 2008, a gluten-free wheat starch with gluten content lower than 20 mg kg^{-1} –the limit set by the *Codex alimentarius*– is available on the market; this product does not have harmful effects on most celiac patients[4]. Nevertheless, celiac people are still reluctant to consume products with wheat-based ingredients.

Traditionally, oats have been considered harmful for celiac patients. Recent research, though, considers it safe for celiac population, as long as cross contamination with some toxic cereals is avoided[5,6]. A small percentage of celiac people, however, do not tolerate avenins (proteins present in oat). A variation in oat addition in gluten-free formulations can be observed from one country to another: while its consumption is allowed and extended in Finland, in other countries celiac people are encouraged to seek medical advice before eating it, while in some others there is still a great reluctance towards its consumption by celiac population. Dough prepared with oat flour does not develop a continuous protein network and some "gluten substitute" has to be added. Breads obtained using oat flour have higher protein and beta-glucan contents, and better sensorial score than those obtained with flours from other gluten-free cereals[7], therefore its incorporation is an alternative to be considered in gluten-free bread production.

For wheat-based products, it is known that every particular case requires a particular type of flour, and thus optimum flours for cookie production will not be appropriate for pan bread and vice versa. However, for gluten-free product development, information about flour requirements is scarce. These flours differ mainly in protein quantity, starch characteristic (e.g. amylose and amylopectin ratio) and particle size distribution. It has been established that corn variety or milling process affect bread physicochemical and sensory properties[2]. In the case of rice, low amylose flours lead to breads with better texture, but waxy varieties (ca. 0% amylose) are not appropriate on their own for gluten-free bread production[8]. Ylimaki et al.[9] have also found that medium-length grain varieties are preferred to long grain varieties for obtaining breads with better sensorial properties. The particle size of the rice flour is also known to have an effect on gluten-free bread-making[10,11]. Consistently, studies carried out with rice and corn flours have shown that particle size is the most important variable affecting bread quality[12,13]. Bigger particle size is preferred, while fractions below 80-100 µm should be discarded for the production of gluten-free bread with high volume and soft crumb. However, using flours with extremely large particles may lead to breads with sandy texture, therefore 200 µm should not be exceeded. Flours with larger particles have been shown to reduce the gas retention capacity of the dough and the batter, as well as final bread volume, and this effect was attributed to differences in internal dough structure.

When starches are added in gluten-free formulations, breads with higher volume and more closed crumb structure are obtained, although crust is lighter because Maillard reactions are largely reduced due to the lack of proteins. The addition of starch lead to softer, more cohesive and resilient crumbs. These conclusions apply to breads based on rice flour[14,15] and other cereal flours[16]. The type of starch also influences bread quality but the conclusions drawn in different studies are sometimes contradictory. Thus, while Sanchez et al.[15] obtained an optimum formulation using higher contents of corn than cassava starch, Onyango et al.[16] found that breads based on cassava and rice starches have better crumb texture compared to corn or potato starch. Consequently, different kinds of flour and starch mixtures should be optimized according to the specific basic formulation.

During the last years, research has focused on the study of novel raw materials, such as pseudocereals (Andean crops –such as quinoa and amaranth– and buckwheat) and minor cereals, like teff. Usually, these flours are nutritionally more balanced than corn or rice flours or starches, especially if they are whole-grain flours. Moreover, they have higher protein, fiber, vitamin and mineral contents[17-19], but their availability on the market is rather limited and their price, higher than most current flours and starches. Because of this, their commercial use is restricted to supplement recipes based on rice flour and starches. Among the flours used for this purpose are buckwheat, as a main ingredient or combined with starch[20], rice flour[21,22] or as a supplement[23]. Amaranth and quinoa –both from South America– have also attracted attention, and so has teff, a minor cereal grown in Ethiopia. Generally, the incorporation of these flours affects baking[24] and sensorial properties[7], color and taste.

Soy flour has also been considered for gluten-free breads, either as a supplement[25] or as a main ingredient[26], as well as other pulse flours, such as chickpea flour[27]. Soy flour contains higher amounts of isoflavonoids and proteins than cereal flours. Usually, these flours modify the internal structure and rheological properties of the dough, affecting the texture and volume of loaves, and bread sensory properties. However, the effect will depend on the formulation that is used. When used as a main component, soy flour with a thermal pretreatment and, as a consequence lower lipoxygenase activity, is preferred since the typical beany flavor of pulse flours is much reduced; however, bread quality, is reduced and appearance is negatively affected, when compared to non-treated soy flour. Nonetheless, the specific volume of bread made of soy flour as a main ingredient is usually lower than bread made with rice flour and/or starches. Other raw material that may be interesting is chestnut flour[28], but it is also used as a supplement for starches or other gluten-free flours; besides, it should not exceed 30%, since higher levels may affect bread quality negatively. In addition, chestnut flour has a characteristic flavor and thus its addition may dramatically change sensory properties and consumer acceptance of the final product.

2.2. Gluten Substitutes

In wheat dough, the gluten network formed during mixing is placed among starch granules and gives cohesion to the system, making gas retention during proofing possible. During the development of gluten-free bread, proteins present in non-wheat flours are not able to form this network, therefore other products must be added so that the dough/batter can retain gases and expand. Thus, Jongh[29], in one of the first studies on gluten-free dough, already suggested that any agent joining together starch granules may favor these processes and with this purpose glycerol monoestereate was used. At present, this function is performed by hydrocolloids. Hydrocolloids, nutritionally classified as soluble fibers, show high water absorption capacity; during mixing, they combine with water and form a continuous phase surrounding flour particles; this phase results in an increased cohesiveness. However, not all hydrocolloids behave in the same way, as they have various effects on bread characteristics. The use of hydroxypropylmethylcellulose (HPMC) has been proposed to obtain gluten-free breads with appropriate physical characteristics[9,30]. This hydrocolloid, which can form thermoreversible gels when heated, is preferred to other hydrocolloids due to the higher specific volumes of resulting breads, and their improved sensory scores[31-34]. The use of xanthan gum (XG) is also very widespread among gluten-free technologists. Acs et al.[35,36] studied the effect of different hydrocolloids on corn-starch bread properties and found higher volumes when using XG, compared to guar gum, locust bean gum and tragacanth. At present, most commercial gluten-free breads, as well as formulations used in different research works, contain one of these two hydrocolloids. However, the results of their incorporation are usually contradictory in the literature. While XG increases specific volume in some works[35-37], in others, it does not modify this parameter[31]. These differences may arise from the addition of different amounts of hydrocolloids[34,38] or from the type of flour used[33], as well as from differences in the formulation and baking procedures employed in each particular research. Another important effect of hydrocolloids is that they modify the alveolar structure of breads, XG, HPMC and carboxymethylcellulose (CMC) being the ones producing a finer structure and a higher cell number, when compared to agar or MC (methylcellulose)[39]; these changes in crumb structure also modify crumb texture.

Since hydrocolloids usually increase dough/batter consistency, high quantities of water should be added during bread-making. Actually, most researchers do this correction, but the way it is done is very variable and it is not always well explained; this may be one reason for the differences of hydrocolloids effect observed in the literature. Among the most common hydrocolloids, XG induces the greatest dough/batter consistency[31,37,38], and thus higher water amounts should be added. In order to optimize gluten-free bread formulations, and in particular hydrocolloid level and water amount, the use of response surface designs could be useful[9,40,41]. Sometimes, other hydrocolloids such as CMC, guar gum, locust bean gum or psyllium are added, along with XG or HPMC, to improve bread texture or shelf life (not to increase bread specific volume), since they retain high amounts of water, affect starch retrogradation and delay staling. In this regard, psyllium is an interesting alternative because it is a natural product obtained from the milling of *Plantago ovata* seed hulls; it improves bread sensory properties and shows anti-constipation properties[42] as well as a complementary effect with HPMC[43].

2.3. Proteins and Fibers

The use of starch or flours with low protein and fiber contents for obtaining gluten-free bakery goods leads to a poor nutritional quality of these products compared to their wheat counterparts. As a consequence, research on proteins and fiber incorporation in gluten-free breads has significantly increased in the last years. Both fibers and proteins, not only enhance nutritional properties of bread, but also have an important functional role.

Among proteins proposed for gluten-free bread-making, particularly noteworthy are dairy proteins –both whey proteins and caseins–[44-48], egg proteins[45,46,49-51] and soy proteins[46-51]. Proteins from other sources, such as collagen or lupine[49], pea[48,49,51], yeast[52], or even structured corn proteins[53] or whey[54-56] have also been studied. These studies present contradictory results either because they use different formulations or different levels of protein incorporation. In general, it can be said that the addition of proteins reduces crust lightness[44] because Maillard reactions produced during baking, reduce cell density[49] and modify dough rheology. It has also been observed that using animal proteins, especially egg proteins, leads to breads with higher specific volume compared to vegetable proteins, such as soy proteins[46,49,50]. Moreover, most studies dealing with the incorporation of animal proteins report an increase in loaf volume, while vegetable proteins do not affect this parameter, or even reduce it. This result could be related to the effect of these proteins on dough/batter rheology, since animal proteins –egg proteins– reduce batter consistency, but vegetable proteins –soy proteins– increase it[49-51]; this effect on batter consistency may, in turn, be explained in terms of changes in dough structure. The relationship between dough consistency and bread volume has been reported in other studies[57].

The effect of fiber, as well as proteins, addition will depend on the type of fiber used. Studies on fiber addition into gluten-free breads have mainly focused on the effect of a single type of fiber and fructooligosaccharides[49,58,59], resistant starch[60] or cereal fibers[61,62]. Results are, once again, contradictory and while in some cases fiber enrichment reduces bread volume, in others the contrary effect is observed. Nevertheless, no direct comparison can be made due to the different formulations, the bread-making procedure, the correction of water amount and the amount of fiber addition used in each case. Hager et al.[63] did compare the effect of inulin and oat β-glucans, but both fibers were added in different amounts. In general, the addition of soluble fibers, such as inulin, polydextrose or nutriose, improves bread quality by enhancing volume and produces darker crust, whereas insoluble fibers, such as celluloses, usually reduce bread volume. However, works carried out by Gómez (unpublished) show that, among celluloses, those with lower particle size and elongated shape lead to the production of loaves with higher volume and lower firmness. The overall effect of insoluble fibers can be related to the fact that they remain intact during mixing and interrupt dough structure; this interruption is less important when small, elongated fibers are used. Soluble fibers, on the other hand, interact with water, hydrocolloid and soluble ingredients in the continuous phase, enhancing its cohesiveness and, as a consequence, gas retention capacity. These studies show that the effect of fibers on dough/batter structure affects its rheology, while those fibers that reduce consistency increase specific volume. Additionally, in the case of fibers like polydextrose and inulin, a partial hydrolysis is produced during bread-making, and the resulting simple sugars, through Maillard reactions, increase crust darkness.

2.4. Additives and Enzymes

Additives and enzymes used in wheat-bread production usually act either on starch fraction or on proteins and gluten network. Those acting on starch fraction will also be appropriate for gluten-free bread production, since their functionality will be similar. Thus, alpha-amylases producing fermentable sugars from starch, enzymes slowing starch retrogradation (anti-staling effect) such as certain amylases, or emulsifiers interacting with starch to reduce retrogradation –such as monoglycerides–, are also suitable for gluten-free bread-making.

On the other hand, additives acting on gluten network will not necessarily have a positive effect on gluten-free breads. Therefore, it has been shown that

DATEM or SSL (emulsifiers used to strengthen gluten doughs) do not have the same effect on gluten-free systems, do not modify loaf volume, or even decrease bread overall quality with firmer crumbs, coarser crumb structure[64], or very slight volume increments[65]. However, other emulsifiers with better air-stabilizing properties, such as monoglycerides or lecithins lead to higher volumes[65].

Unlike wheat breads, the use of proteases with good results in gluten-free systems has been reported[66]. But these results may vary according to the type and the reactivity of protease employed[67], as well as the type of flour used[68]. In this last study, the effect of protease is even negative. It seems that the level of enzyme application also affects bread quality.

The use of transglutaminase has also been explored in gluten-free dough[69,70], sometimes combined with exogenous proteins[45-48,51,71]. Although results are variable and depend on the substrate, the transglutaminase level and the formulation used, it has been proved that transglutaminase acts on proteins increasing their molecular weight[45] and modifying rheological properties of doughs[48,51,69]. In spite of these findings, quality enhancement of gluten-free breads is negligible, and overall quality can even be reduced. This shows that it is not only the presence of a protein continuous network responsible for the volume increment produced during proofing of gluten-free doughs, but its properties are highly relevant as well. The use of glucose oxidase –enzyme capable of enhancing disulphide bonds among protein molecules– has been proposed to increase rice bread volume[72], but once again, the effect of this enzyme depends on the flour used[68] and in some cases it does not significantly influence loaf volume[64].

Starches or flours with a hydrothermal pretreatment –process during which starch is gelatinized– show high water absorption and high thickening properties even at room temperature. Their effect is thus comparable to that of hydrocolloids, and their use has also been suggested to improve the quality of gluten-free breads, increasing their volume and extending their shelf life[73,74], although results are still quite variable and it is important to adjust dough moisture to achieve the optimal rheological properties.

Some enzymes that are not employed in the wheat bread-making process have been proposed as gluten-free breads improvers. Such is the case of cyclodextrin glycosyl transferase (CGTase)[75]; its positive effect on specific volume could be related to the consistency decrease produced after starch hydrolysis. This enzyme, as well as amylases, has been employed to reduce staling in gluten-free breads[76], probably one of the most important problems of these products. Both enzymes hydrolyze starch and reduce its retrogradation. Similarly, the use of lipases –which produce emulsifiers *in situ*– reduces this phenomenon[73], since emulsifiers also present anti-staling properties.

2.5. Processing

As already mentioned, the incorporation of hydrocolloids increases dough/batter consistency, and the water amount needed. Thus, the moisture level in gluten-free bread formulations is higher than 80%, and in most cases, even higher than 100%, whereas the usual water level in wheat dough is lower than 60%. It is generally assumed that higher water amounts lead to breads with higher specific volumes[11-13,30], but large holes are found between crust and crumb when water incorporation is too high or proofing is extended. In addition, breads with excessive hydration present a weak final structure which becomes difficult to cut without breaking. The higher water amount also requires a modification in the baking process. Thus, for gluten-free bread production, baking is longer and usually at lower temperatures than conventional wheat breads.

The existence of an inverse relationship between dough/batter consistency and gluten-free bread volume is widely accepted[57]. A lower consistency can be obtained by adding higher water amounts, but also by using oil in the formulation. The incorporation of oil produces breads with higher volume, but also more cohesive and moister crumbs. This effect is worth highlighting, since a typical defect of gluten-free breads is lack of cohesiveness and very dry texture.

During wheat bread-making, mixing is essential for gluten network development because it is at this point when the energy necessary for this process is generated. So, mixing time is defined as a function of gluten development. In gluten-free bread-making, the mixing process is different for two main reasons. Firstly, gluten-free formulations present lower consistency than wheat formulations and are considered batter rather than dough, and thus mixing accessories are also different. Secondly, mixing ingredients together takes shorter than in conventional systems. However, a very short mixing may lead to lower volumes[77], either because yeast does not adapt to the medium or because the incorporation and distribution of air into the dough is insufficient. After mixing, dough is placed into molds and fermented. Fermentation is critical in gluten-free bread production, since dough structure is usually weaker than in wheat dough, and a long fermentation may produce a collapse and reduction of dough volume, especially in doughs with high water contents[12,13]. This results in flat breads or breads presenting a depression in the central region, with low volume and coarse crumb structure. Therefore, fermentation time should be defined for each particular formulation and bread-making procedure, considering amount of yeast and fermentation temperature. Usually, fermentation time for gluten-free systems is shorter than for conventional wheat formulations. The behavior of dough during proofing can be studied with a rheofermentometer, an instrument used for the study of gluten systems, avoiding the use of overweight on doughs, considering the weakness of gluten free doughs.

2.6. Sourdough

This process consists in fermenting a mixture of flour and water for a relatively long period of time at a moderate temperature. This technique, employed as such almost since the beginning of bread history, allows naturally occurring microorganisms (lactic acid bacteria and yeasts) in the flour to leaven. To facilitate continuous production, bakers started to save a portion of ripe sourdough to seed subsequent doughs; this procedure continued until the nineteenth century. During fermentation, cereal-associated lactic acid bacteria

(LAB) produce lactic and acetic acids, typically lowering pH below 5, and yeast produces CO_2 and ethanol. These conditions favor the activation of enzymes that are beneficial for bread-making. In wheat and barley breads, it is known that this technique improves loaf volume, texture, taste, nutritional value and shelf-life since it delays staling and protects bread from mold spoilage[78,79].

Although sourdough application was replaced in the nineteenth century for other technologies that reduced production time –and thus, overall costs–, its use has become popular again in the last decade, due to the nutritional and technological benefits obtained with this procedure.

In gluten-free breads, incorporating sourdough into the formulation has also resulted in breads with better technological and nutritional properties. The lower pH activates amylolytic and proteolytic enzymes. Moore et al.[80] have shown a decrease in the size of both protein particles and starch granules after 24 h of fermentation of the sourdough, as well as softer breads with a lower firming rate. For oat-based breads, a higher specific volume has been observed when using sourdough[81]. This effect was attributed to a decrease in dough consistency produced by a change in the viscosity profile of the starch, probably caused by acid and enzymatic hydrolysis. As a result of the change in starch behavior, a stronger gel is produced during heating, increasing dough stability and allowing to obtain breads with a better texture[82].

Another effect of the change in pH is the activation of phytases that degrade the phytic acid normally present in most cereal flours, as reported for sorghum-based breads[83]. Phytic acid forms complexes with the minerals present in the dough, reducing their bioavailability. Sourdough also carries nutritional benefits, since it favors mineral availability. Another beneficial effect of sourdough in gluten-free breads that is being a subject of intense research is the *in situ* production of exopolysaccharides[84,85] which will act as hydrocolloids. The importance of hydrocolloids in gluten-free bread production has been discussed earlier in this chapter. Also, by applying sourdough technology, a decrease in mold spoilage rate has been observed, thus enhancing breads' shelf-life[86].

Most studies performed so far have focused on working with autochthonous flora present in the system, with the obvious advantage of being already adapted to the medium. Thus, they show a clear competitive advantage over any other strain. However, in the industry, sourdough is preferentially obtained by using commercial starters which favor the production of breads with constant quality. The selection of strains of LABs and yeast to be used as starters is a condition to ensure the constant quality of end-products; in particular, such selection must be oriented to find those microorganisms that are adapted to the substrate and are able to dominate the fermentation process inhibiting the development of contaminants or autochthonous strains[87].

3. Gluten-Free Pastry

3.1. Cake-Making

Cake production consists in mixing the ingredients together to make a batter that will be finally baked. During the baking process, an increase in batter volume is observed, partly due to the expansion of gas bubbles contained in the batter as a consequence of temperature rise, and partly to the effect of leavening agents, in case they are present in the formulation. This volume increase is produced during the first stages of baking until starch gelatinization, which renders the structure more rigid and makes further expansion more difficult, if not impossible.

The batter is an emulsion composed of air (discontinuous phase) in a mixture of ingredients (continuous phase). In this system, not only is air incorporation of fundamental importance, but its distribution and the viscosity of the continuous phase surrounding gas bubbles are so too. Consequently, the smaller the gas bubbles, the higher their stability in the batter, and the higher the final volume of the cake. In addition, the viscosity of the continuous phase should be high enough to avoid bubbles coalescence and at the same time allow volume increase during baking. There is an enormous variety of cake formulations leading to quite different products.

But, in general, they can be divided in two groups. The first one includes those formulations with no added fat and usually with no leavening agent, in which the cake is obtained by incorporating a huge amount of tiny gas bubbles. In this group we can find *sponge cakes* or *chiffon cakes*, where the performance of egg-albumin as foaming agent is of key importance. The second group is composed of *layer* or *pound cakes*, where the presence of oil or fat is fundamental. In these cases, the use of a leavening agent to enhance the volume increment during baking is very frequent.

It is worth highlighting that gluten does not have a key role in cake production, and in most cases a gluten network is not developed at all. In liquid batters, mixing accessories do not apply enough mechanical work as to develop the network. On the other hand, the starch present in the batter does have a basic function, since it confers viscosity; this, in turn, stabilizes the emulsion and, after gelatinization, confers structure, preventing the dough from flattening. Thus, gluten-free cake-making is, in most cases, rather simple; it is only a matter of changing wheat flour for other gluten-free flour, such as rice or corn, or for a starch. Nevertheless, some factors should be taken into account when making this substitution. First, the proteins present in wheat flour, although they have no functional properties, act on Maillard reactions producing the brown color of the cake surface. Hence, if wheat flour is substituted for a starch, the color of the product will probably not be satisfactory, and the viscosity of the batter will be modified, and thus its capacity to obtain a good air-emulsion will change as well. When starch content in the batter is increased –and as a consequence, protein content is decreased–, the viscosity of the system changes as well as the capacity of producing an appropriate emulsions[88]. Another aspect to consider is starch gelatinization temperature, since this parameter varies according to the botanical source of starch. The end of dough/batter expansion in the oven depends on gelatinization temperature; the latter will also depend on other factors, such as type or quantity of sugar in the formulation.

Usually, the formulation of different cakes is optimized for the use of wheat flour, therefore its substitution for a starch should be accompanied with the addition of some kind of protein (vegetal or animal) or the complete reformulation of the recipe. The final result will depend on the type and quantity of the starch and protein employed[88]. Proteins usually absorb more water than starch, and this should be taken into account when replacing wheat starch: the water present in the system will be in a more free state and because of this the final batter will be wetter. Adding proteins is a useful strategy when using flours such as rice flour where the protein content is lower than wheat[89]. These authors have shown that the amount of the protein added is important, and so is the type of protein. In this regard, they obtained better results when incorporating animal proteins (caseins and egg proteins) than vegetal proteins (soy and pea).

When wheat flour is substituted for a gluten-free flour, an important aspect to take into consideration is the sensorial effect that this substitution may have, since different flours have quite different color and flavor. Rice flour usually has a neutral flavor and a pale color, which makes it similar to wheat flour; corn flour has a stronger flavor and its color is rather yellowish, which will influence the characteristics of the final product. In Western countries, the use of rice flour to substitute wheat flour is usually preferred. Nonetheless, consumers' preferences may be different from one country to another based on cultural and traditional aspects, and the use of different flours (corn or sorghum) is not only possible but sometimes also advisable. The selection of the leavening agent is also critical, since it should produce gases when the dough has the necessary structure to retain them and be able to expand; this critical point depends on starch gelatinization temperature. As a general rule, the differences in gelatinization temperature for wheat starch and gluten-free cereal flours is not very important, but any problem arise during the development of these products should be solved by changing the leavening agent or the amount of sugar in the formulation.

One of the most important issues when choosing gluten-free flour for cake-making is probably particle size. *Flour* particle size is usually considered to be smaller than 200 µm, but in the case of corn and rice –which are harder grains requiring higher energy input for milling–, particle size is larger. The *japonica* variety of rice grains is usually softer than *indica* and produces finer flours. When wheat flour is used for cake-making, finer flours are preferred because a more stable emulsion with larger amounts of smaller bubbles is obtained. When coarse flours, such as rice and corn, are used the emulsions are unstable, and better results are obtained if bigger particles (bigger than 100-140 µm) are removed. Optimum particle size will depend on the type of cake that is produced. Thus, finer flours are preferred for sponge-cakes and coarser flours for layer-cakes[90]. It is possible to re-mill this flour fraction, but at the expense of a higher content of damaged starch that may affect the quality of the final product.

Once wheat flour is substituted for an adequate gluten-free flour, the same additives used for wheat-based cakes can be used with satisfactory results in stabilizing the emulsion[91], reducing mold spoilage or improve batter viscosity (hydrocolloids and modified starches). The use of extruded flours, with a high thickening ability has also been proposed[92]. By using a small amount of hydrocolloids, such as XG, cake quality may improve[91-94], however, they are not indispensable and their addition does not exceed 0.5-1%.

The recommendations made in this section are also applicable to muffin and Madeleine production because these products are very similar to cakes, even though they are baked in smaller cups (cupcakes). Nevertheless, in products where batter viscosity is higher, the mechanical force applied during mixing may develop gluten network (in wheat based products), and for their gluten-free counterparts it may be useful to follow the recommendations made for gluten-free breads, including the addition of hydrocolloid in the formulation.

3.2. Other Products Obtained from Batters

There is a huge amount of products made from a batter that is poured into molds and then baked, such as tea pasta, or put between two hot metal sheeting, such as wafers and waffles, or even heated in a metallic surface, such as crepes. In these products, as well as in cakes, gluten network is not developed and gluten-free counterparts are easy to obtain. Wheat flour is replaced by gluten-free flour, taking into account the aspects mentioned for cake-making. For this type of products the differences in gelatinization temperature are not important. Nonetheless, it is important to select the gluten-free flour according to its particle size, since this parameter has a great influence on product quality and sensory properties such as taste, flavor and color. It is not possible to make general recommendations due to differences among products and regional preferences and different flours may be used in each case. It is essential, however, to use flour with regular characteristics, like particle size, color and starch properties, to obtain homogeneous products with a regular quality.

3.3. Cookie-Making

Considering that most cookies are made of dough in which the gluten network is not developed, gluten-free cookie-making should not represent a difficult task. In this group of cookies where gluten network is not important, we find batter cookies, such as tea-cookies (extruded) or wafers (discussed in section 3.2 above), and those in which mixing is reduced to avoid gluten network formation, such as wire-cut or molded short-dough cookies. Once again, it is important to carefully select the gluten-free flour or starch to be used. As in the case of bread- and cake-making, several authors have suggested the use of different gluten-free flours, like rice flour[1,95], buckwheat[1,96], amaranth[97], teff[98] or chick peas[99], in addition to corn and potato flours and starches[100]. Sensory characteristics and particle size are aspects to be considered. Finer flours facilitate particles hydration, but also affect the final texture of cookies since batter/dough emulsion properties are also modified.

In addition, there are cookies where a continuous gluten network is formed, such as crackers or Marie-type cookies. In these cases, dough must be sheeted and then cut, and crackers proofed. Due to the gluten network, these cookies present a less brittle texture.

Usually, gluten-free Marie-type cookies do not include any gluten substitute, like hydrocolloids, in their formulation and are made in the same way as conventional cookies, without gluten development, shaped or sheeted into a circle or rectangle, similar to their wheat counterparts, but with a slightly different texture. If hydrocolloids are added, water amount should be corrected; since cookies are products with low water contents –typically less than 5% and particularly less than 2% for the Marie type–, adding high amounts of water may have a negative effect during the drying process (baking). And thus, adding hydrocolloids makes it more difficult to reduce moisture and achieve the typical crispy texture in this product.

3.4. Puff-Pastry Making

Puff-pastry making is based on the formation of multiple interspersed layers of dough and fat, in such a way that when water is evaporated during baking, a laminar structure is obtained. The first step in puff-pastry making is to prepare the dough –similar to bread dough–, place a piece of fat with it and bring together. The product is then sheeted and folded several times to increase the number of layers. On the one hand, fat should present a high melting point to prevent it from melting during sheeting, as it would mix with dough, which is undesirable. On the other hand, dough should be cohesive, extensible (easy to sheet) and have low stickiness. This type of dough usually requires a gluten network able to confer cohesion and allow the dough to be stretched without breaking. In this way, for the formulation of gluten-free puff-pastry, a gluten substitute should be incorporated. The same hydrocolloids used for gluten-free bread-making, such as xanthan gum, guar gum, locust bean gum or cellulose derivatives, may be used for puff-pastry. However, after hydrocolloid addition, this type of dough tends to be too sticky. To reduce stickiness, it is important to limit water incorporation. Sometimes it is also important for the dough not to be too consistent so that it can be easily sheeted. A possible alternative is to use oil in the formulation. Also, some extra flour added onto the dough surface or letting air flow can be used to dry out dough surface and thus reduce its stickiness. However, in spite of these alternative techniques, it is not possible to sheet gluten-free puff pastry to the same extent as wheat puff-pastry; final products present a different texture, are less crunchy and have thicker and coarser layers.

Some puff-pastries include yeast in their formulation, and are fermented after sheeting. During fermentation, an increment in the volume of the pieces is registered. Examples of these products are croissants, where the recommendations for gluten-free bread-making apply to flour/starch selection, gluten substitutes and additives. Stickiness should be reduced to a minimum and extensibility should be enhanced, making the sheeting process easier.

4. Pasta-Making

Pasta is probably the simplest cereal-based product. From the formulation point of view, it consists of a mix of flour or semolina with water and it may also contain egg. Regarding processing, pasta is prepared by following a hydration step, mixing, shaping/cutting and drying. Pasta can be classified according to some of the following parameters: water content, processing type and/or shaping. According to water content of the final product, it can be fresh or dried. Looking at the technology employed to shape it, pasta can be extruded or sheeted. It can also be short, long or filled. This section will be focused on dry extruded pasta, widely consumed all over the world.

High protein content, as well as a strong gluten network, is required for obtaining pasta with a proper cooking performance. During pasta cooking, two main phenomena take place: on the one hand, gluten network –developed during mixing– hydrates and, as temperature rises, coagulates and becomes insoluble, thus creating a strong network that entraps starch granules. On the other hand, water diffusion inside pasta and temperature rise lead to starch gelatinization. During gelatinization, part of the amylose leaches out of the granule and diffuses to pasta surface and –if pasta structure is inadequate– to cooking water as well. Once on the pasta surface, amylose is responsible for the increase in stickiness, with a detrimental effect on its sensory quality.

Starch gelatinization and protein coagulation are competitive phenomena, since they occur at the same temperature range and are both influenced by water availability[101]. The faster the protein coagulation, the more limited starch swelling, and the lower the amylose quantity that leaches out from the granules, ensuring a firmer texture and a lower stickiness of the final product. Pasta with good technological properties shows high resistance to overcooking, a firm texture, low stickiness and reduced organic matter loss into cooking water. These parameters are of vital importance when pasta is chosen by consumers.

In gluten-free pasta –which lacks the protein network– the structural role may be assumed by starch. The retrogradation of amylose solubilized during gelatinization implies a double-helix formation, stabilized through hydrogen bonding and thus forming a continuous phase surrounding swelled and deformed starch granules. This retrograded amylose is thermally stable and can only be dissociated at temperatures higher than 100°C. The empiric knowledge of this phenomenon has been used in Asia for many years, where the traditional process to obtain rice-based noodles include several –and complex– heating and cooling steps of rice flour that lead to starch pregelatinization –and later retrogradation–, and this flour is then mixed with the rest of flour and water to complete noodle-making. In this way, a tridimensional network with viscoelastic properties is obtained[102]. So, ideal starch for gluten-free pasta production should present high tendency to retrograde, such as high amylose starches or pulse starches. In this last part of the chapter, the main raw materials employed for gluten-free pasta will be covered.

Traditionally, gluten-free pasta is made of rice flour. Pasta of good technological properties has been obtained by using this flour[103,104]. Usually, flour obtained from long grains is preferred since it presents high amylose content. Moreover, parboiled grains have good performance for pasta making, since during parboiling starch gelatinizes and the amylose-lipid complex is formed. These changes in starch structure limit starch swelling and amylose loss during pasta cooking.

Considering corn flour, Dexter and Matsuo[105] have shown that the lower the amylose content, the lower the noodles quality. However, there is a compromise between amylose content and flour performance, since corn with more than 40% amylose does not completely gelatinize during heating and this limits later retrogradation[106].

In addition to amylose content, it has been found that flour particle size, as well as the pretreatment of flour/water mixture (microwave heating), have a considerable influence on noodle quality[107]. The presence of big particles delays protein and starch dispersion during heating in water (pretreatment). Higher temperatures and moisture during pretreatment favor, on the one hand, gelatinization and retrogradation and, on the other, protein interaction, once glass transition temperature has been reached. However, corn proteins provide a weak and transitory structure unable to stabilize the final product. Therefore, the structural role lies, again, with starch[107].

As already mentioned, pseudocereals have received important attention essentially because of their high nutritional value. A rapid literature search suggests that buckwheat is the favorite pseudocereal for gluten-free pasta-making. It has been shown that these grains have a lower detrimental effect on pasta quality compared to quinoa and amaranth[108], in terms of firmness, cooking time and cooking loss. When using quinoa, and particularly amaranth, pasta firmness is substantially reduced, as well as its tolerance to overcooking. Nevertheless, it has also been reported that buckwheat is susceptible to undergoing Maillard reactions during the drying process because of its high lysine and reducing sugars content, which yields a product of unpleasant brown color[109]. The performance of these flours will also depend on the pretreatment they are subjected to before pasta-making. Thus, extrusion-cooking of a mix of rice and amaranth flours produces pasta with good quality parameters, whereas the same mix of flours without pretreatment shows a low performance for pasta production[110].

Sorghum presents some interesting characteristics, such as being a source of antioxidant and cholesterol lowering compounds[3]. It has been proposed that the main factor determining the high performance of this cereal is grain hardness[111], which determines flour particle size and quantity of damaged starch. In general, pasta with a higher firmness and tensile strength is obtained when using flours from grains with hard endosperm, subjected to a more extensive milling process; thus flours present lower particle size and higher quantity of damaged starch[112,113]. Liu et al.[112] have corroborated that pasta quality is not related to protein quantity. Moreover, it has been shown that flour pretreatment, such as microwave heating, has a positive effect on the final quality of pasta. Waxy sorghum flour has also been studied, but cooking loss is too high and the resulting pasta presents high stickiness due to a limited starch retrogradation after pretreatment[113].

The most widely used additives for pasta production are undoubtedly hydrocolloids and emulsifiers. With hydrocolloids addition higher consistency is obtained, as well as higher firmness and more pleasant mouth-feel[114,115]. Therefore, the negative effect of adding functional ingredients to the gluten-free flours (corn and rice) traditionally used can be offset by adding hydrocolloids, which confer cohesion to the system. For example, the nutritional quality of corn-based pasta can be enhanced by adding oat flour, and its negative effect counteracted with hydrocolloids, best results being obtained by adding CMC and chitosan[115].

Emulsifiers lubricate the system during the extrusion process, increasing consistency and decreasing stickiness[116]. Furthermore, when the emulsifier is added, starch swelling and amylose leaching are reduced when heated[117] and thus, cooking loss is reduced[118].

Nevertheless, despite the positive effect of emulsifiers and hydrocolloids addition, some researchers[119] suggest that consumers usually associate their presence in gluten-free pasta with an artificial food. In this context, looking for alternatives when selecting raw materials and/or processing conditions seems a viable option for good quality pasta.

As already mentioned, the pretreatment of raw materials has an important effect on pasta quality. Treatments inducing starch gelatinization –and subsequent retrogradation–, such as parboiling[120], pregelatinization[121], annealing and heat moisture treatment[122] among the most important ones, favor the structural development of pasta, increasing the firmness of the final product and decreasing cooking loss.

Regarding pasta-making process itself, extrusion-cooking probably represents the most suitable alternative for gluten-free pasta, since it unifies two different processes: pregelatinization and shaping. Wang et al. produced pea flour-[123] and starch-[124] based pasta employing two extrusion methods: the classic method, consisting in shaping pasta dough at room temperature and atmospheric pressure, and extrusion-cooking (twin-screw), in which dough is subjected to high temperatures for a short period of time; using this method, starch is partially gelatinized and proteins are partially denatured, and thus a restructuration takes place in the extruded dough. These authors found a decrease in cooking time, a lower weight of cooked pasta, a notable decrease in cooking loss and a more pleasant texture for pasta produced with extrusion-cooking, when compared to room temperature extrusion. Extrusion-cooking has been successfully employed in mixtures of corn and broad bean flours[125], rice flour[103], and in mixtures of rice and amaranth flours[110], among other raw materials.

5. Concluding Remarks

Some wheat-based products, such as bread, puff-pastry and pasta, are obtained from a dough where a continuous gluten network has been developed; whereas other products, like cakes, pastries and cookies are obtained from a dough without a developed gluten network –with gluten development being even negative. Thus, in the first case, obtaining gluten-free counterparts is more difficult than in the second. However, there are some alternatives to overcome this problem. Regarding formulation, for products where a gluten network is required, a gluten 'substitute' is usually added in the gluten-free formulation, and this substitute is usually a hydrocolloid. In pasta making, the role of gluten is usually played by pregelatinized starch. It is also important to analyze processing parameters (e.g. mixing, proofing, baking) adapting them to the new needs. Various gluten free flours and starches from different sources have been studied for their use in gluten-free formulations. The huge amount of raw materials and their combinations that can be used for the elaboration of gluten-free products make it impossible to generalize about their behavior in a gluten-free dough/batter. Moreover, the availability in the market of flours obtained from sources different from wheat is non-continuous; and, moreover, flours from a single botanical origin but commercialized by different suppliers may also present different properties, such as particle size, pasting properties, fiber and protein contents, leading to products of varying quality. It is therefore important to work on understanding, first, the functional properties of the most appropriate flour/starch mixtures for each gluten-free product and, second, the most suitable conditions for continuous processing.

Many additives and enzymes are also analyzed in the literature for improving the technological quality of end products. It is important to note that the functionality of these additives may be different in a gluten-free system compared to a traditional –wheat containing– one, particularly when additives interact with gluten network; in this case, additives effect should be studied for each particular product.

Regarding processing, some alternatives to improve end product quality are also possible, like sourdough for bread-making or extrusion-cooking for pasta-making.

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