Chapter 22

Cereal-Derived Gluten-Free Foods

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Doi: http://dx.doi.org/10.3926/oms.221

How to cite this chapter

Rosell C.M. *Cereal-Derived Gluten-Free Foods.* In Rodrigo L and Peña AS, editors. *Celiac Disease and Non-Celiac Gluten Sensitivity.* Barcelona, Spain: OmniaScience; 2014. p.447-461.

Abstract

During the last decades, the demand for gluten-free products has escalated due to the increased number of diagnosed celiac patients. The celiac patient population seeks gluten-free products resembling gluten-containing products, even with similar nutritional quality.

The present chapter aims to provide information about the design and development of cereal-based gluten-free products as well as on their technological, nutritional and sensory characteristics. During the last decade there has been an exponential increase in the number of gluten-free products in the market. Initially, the development of these products focused on making economically viable and palatable products. However the current awareness of a healthy diet also applies to gluten-free foods.

Gluten-free foods derived from grains are rich in carbohydrates and fats but deficient regarding some macronutrients and micronutrients. It is for this reason that gluten-free diets can generate unbalanced, long-term diets deficient in some nutrients. The addition of other ingredients/nutrients like omega-3 oils, specific proteins, fibers, probiotics and prebiotics is seen as an option to improve the nutritional composition of gluten-free foods.

1. Introduction

Cereals are the staple food for most of the world's population and occupy an undisputed place at the base of the various recommended food pyramid nutritional guidelines. However, despite the benefits of eating these grains, they are able to cause allergies and food intolerances, gluten intolerance, celiac disease being of special interest. The term "gluten" designates a protein fraction from wheat, rye, barley, oats or their crossbred varieties and derivatives thereof, to which some persons are intolerant and which is insoluble in water and in 0.5 M NaCl.[1]

Gluten is present in cereal grains such as wheat *(Triticum aestivum),* rye *(Secale cereale),* spelt *(Triticum spelta), kamut (Triticum turgidum),* triticale *(Triticum spp x Secale cereale)* and some oat varieties *(Avena sativa)*.[2]

Currently the celiac patients' community has, as sole treatment, a nutritional therapy that restricts their food to gluten-free products; therefore, the consumption of cereals such as wheat, rye, barley and foods containing these grains is excluded. Specifically, the CD N 41/2009[1] Regulation defines "food products for gluten intolerant people" as those foodstuffs intended for particular diet which are processed, treated or specially prepared to meet the special dietary needs of gluten-intolerant people.

The limits on the composition and labeling of gluten-free foods set by CD Regulation No. 41/2009[1] are:

- Foodstuffs for gluten-intolerant people, consisting of one or more ingredients from wheat, rye, barley, oats or their crossbred varieties, which have been especially processed to reduce gluten, must not contain a gluten level exceeding 100 mg/kg in the food as sold to the final consumer. The labeling, advertising and presentation of the abovementioned products will bear the term "very low gluten content". They may bear the term "gluten-free" if their gluten content does not exceed 20 mg/kg in the food as sold to the final consumer.
- Oats contained in foodstuffs for gluten-intolerant people must be produced, prepared or treated specially to avoid contamination by wheat, rye, barley or their crossbred varieties and the gluten content must not exceed 20 mg/kg.
- Foodstuffs for gluten-intolerant people, consisting of one or more ingredients which substitute wheat, rye, barley, oats or their crossbred varieties shall not contain a level of gluten exceeding 20 mg/kg in the food as sold to the final consumer. The labeling, presentation and advertising of these products must be labeled as "gluten-free".

The food categories most affected by this limitation are wheat-based bread and bakery products. Therefore, this chapter focuses primarily on this type of food and on the various technological alternatives that have been developed to mimic the function of gluten in baked goods. Other foods may contain "invisible gluten", namely wheat or gluten derivatives that may be included among the ingredients used as thickener or protective film. Hamburgers, sauces, powdered soups, processed cheese, etc., are included in this group.

In general, gluten-free products are of lower quality than their gluten-bearing counterparts since their structure disintegrates easily and they have a very dry texture.

2. Ingredients for Manufacturing Food Derived from Gluten-Free Cereals

Gluten accounts for nearly 80% of the proteins found in wheat, it confers its elastic properties to flour and provides bread with consistency and viscoelastic crumb. The composition of gluten, composed mostly by proteins formed by glutenin and gliadin, explains its cohesiveness and viscoelastic properties. The gliadin fraction contributes to the viscous properties and extensibility of the bread dough while glutenin confers elasticity and strength. The relative proportions between gliadins and glutenins affect the functional properties of bread dough.

The elimination of gluten, especially in bread recipes, results in liquid batters which generate breads with crumbly texture and other quality defects associated with color and flavor. Therefore, the manufacture of gluten-free bread requires the use of polymeric ingredients that mimic the function of gluten during the baking process.

2.1. Cereals and Other Grains Gluten-free

Gluten-free grains available for gluten-free bread production are rice, maize, buckwheat, teff and kamut®. There has been a notable increase in the use of rice flour in the formula of gluten-free products due to its organoleptic characteristics and hypoallergenicity,[3] although the use of a hydrocolloid emulsifier, enzyme or protein is necessary to give it viscoelastic properties.[4] Several studies have focused on gluten-free bread-like products made with rice flour, in which the impact of wholemeal rice flour has been analized,[5] as have the effects of hydrocolloids[6] and of mixtures with other flours and starches[7-10] or with other proteins.[11-12] These studies confirm the importance of flour characteristics, of the other ingredients and of the process in the instrumental and sensory characteristics of the end products.

Brites et al.[13] described the bread baking process based on *broa* (traditional Portuguese bread) production technology. The production of sorghum bread has also been described.[14-15] Grain flours, including rice and other grains such as unconventional legumes, musaceans, roots and tubers are perceived as potential ingredients in the development of numerous products worldwide; there are even many traditional products in several countries which could be used for this end.

Pseudocereals such as sorghum, millet, quinoa, amaranth and buckwheat are also being introduced as ingredients in the formula of gluten-free products. In North America, several breads based on amaranth can be found, with which it is possible to improve nutritional composition since it has a larger amount of protein, fiber and minerals.[16] Flour obtained from buckwheat and millet are richer in protein and minerals and, therefore, have been proposed for the development of nutritionally richer alternative products.

2.2. Other Ingredients, Additives and Processing Aids

Other ingredients typically present in the manufacture of gluten-free breads are starch, dairy, eggs, soy protein and hydrocolloids. The presence of a certain amount of starch significantly improves the quality of gluten-free breads. Rice, potato or tapioca starches are preferable for this purpose.

Hydrocolloids

Hydrocolloids are essential additives in gluten-free bread production since they mimic, to some extent, the function of gluten through the granting of viscosity or viscoelastic properties. In the baking industry these compounds contribute to improving the food's texture, water holding capacity, aging delay and increase overall product quality during storage.[17]

Hydrocolloids, such as locust bean gum, guar gum, xanthan gum and agar are used as substitutes for gluten in the development of rice flour breads targeting the celiac or gluten-intolerant population.[6,18-19] The specific volume of these breads increased in the presence of hydrocolloids, excepting xanthan gum. However, Gambus et al.[20] obtained the largest volume in gluten-free bread using xanthan, which also decreased the crumb hardness of fresh bread fresh and 72-hour storage. Furthermore, these authors concluded that the combination of xanthan gum, pectin and guar gum allowed for products of a better quality.

The crumb characteristics are also modified by the presence of hydrocolloids, in particular, greater porosity has been obtained in the presence of 1% carboxymethylcellulose (CMC) and β-glucans or 2% pectin. Among the cellulose derivatives, hydroxypropylmethylcellulose (HPMC) is a suitable structuring agent and thus a gluten substitute, with good ability to retain gas.[21] Xanthan gum and HPMC have been highlighted as good gluten replacements that improve quality[22] (Figure 1). Regarding the effective mechanism, it has been described that the addition of HPMC to rice flour significantly increases the viscoelastic properties of dough, the overall effect being a strengthening of the rice dough mass.[21]

Combinations of additives and/or technological processing aids to obtain palatable gluten-free products are generally sought.

Figure 1. Effect of HPMC on rice bread volume (Photo: C. Marco).

Proteins

Gluten-free breads are generally protein-deficient when compared with their wheat flour counterparts. Several strategies have been proposed to increase the protein content of breads and other gluten-free cereal products. The enrichment of rice flour crackers with soy flour (25%) increases protein with reduced cost and also improves palatability.[23] Marco and Rosell[24] described that the resulting mixture of rice flour mix with 13 g/100 g of soy protein isolate and 4 g/100 g of HPMC results in gluten-free bread with an energy intake of 220.31 kcal/100 g whose composition (42.38% carbohydrates, 10.56% protein and 0.95% fat) is similar to that of gluten-bearing bread products. The addition of milk solids, inulin and fish surimi has been proposed as an alternative to increase dietary fiber content and protein in gluten-free breads.[25] The use of leguminous flours in the composition of gluten-free products is increasing due to their high protein content. With this objective in mind pea, lentil, bean and chickpea flours have been used.[26]

Dietary Fiber

The enrichment of gluten-free bakery products with dietary fiber confers texture, gelling capacity, thickening, emulsifying and stabilizing their properties. Among the fibers that have been proposed for the enrichment of gluten-free breads are wheat, maize, oats and barley.[27] The addition of these fibers to 6 g/100 g improves the product's nutritional profile without significantly altering its palatability. When amounts of 9 g/100 g are added, products with a 218% higher fiber content than that of the reference bread are achieved, but with significantly impaired palatability.

Stojceska et al.[28] increased the total dietary fiber content in gluten-free products using extrusion and incorporating different fruits and vegetables such as apples, beets, carrots, cranberries and teff flour. These authors incorporated up to 30% to a gluten-free formula consisting of rice flour, potato starch, maize starch, powdered milk and soy flour. By optimizing the extrusion conditions it was possible to obtain gluten-free products enriched in dietary fiber.

Enzymes

Another option for improving the quality of gluten-free breads is to use enzymes or technological aids.[29] Enzymes like amylase, protease, hemicellulase, lipase, oxidase, transglutaminase and oxidase have been used to improve the quality of bakery products. Some of these enzymes have been used as technological adjuvants to improve the quality of gluten-free breads. Among the various available enzymes, transglutaminase and glucose oxidase have allowed improvements in the texture of gluten-free bread, although the effect depends greatly on the flour used in the formula.[30-31] Both enzymes form intra- and intermolecular bonds between rice proteins generating a protein network. However, the protein network generated by these enzymes does not completely mimic gluten functions and the presence of a hydrocolloid is necessary.[30-31] The action of transglutaminase can also be enhanced by the addition of other proteins that increase the number of lysine residues which limit the enzyme crosslinking action. Moore et al.[32] studied transglutaminase impact on gluten-free breads containing soy protein, milk or egg. The most striking effect was a reduction in bread volume of due to protein polymerization.

Sourdoughs

Sourdoughs are a very attractive alternative to improve the quality of gluten-free breads. Sourdough is a natural fermentation starter which has been used to ferment numerous types of food. These doughs are obtained by mixing flour, water and other ingredients and allowing them to be fermented by naturally present lactic acid bacteria and yeasts. These microorganisms proceed mainly from the flour and the environment, but the microbiota specific to each sourdough depends on exogenous factors such as temperature and fermentation time. The use of sourdough in bread making is a widespread practice due to its positive effects on the quality of bakery products. Among them, improved texture, aroma and flavor, increased nutritional value and longer half-life should be emphasized. Therefore, its use has spread to gluten-free baked goods. There is little information on the use of sourdough in the formulas for baked gluten-free products. Crowley et al.[33] conducted a comparative study on the sourdough influence of various lactic acid bacteria on the texture of gluten-free products. In recent years, several patents have been published which are focused on the use of various lactic acid bacteria for gluten-free bakery products manufacture aimed at improving quality and reducing any potential residual toxicity.[34-35]

3. Preparation Processes of Gluten-Free Cereal Products

Food production of gluten-free grain-derived food faces many technological difficulties associated with the absence of the functionality of gluten. This absence has forced to adapt the formulas or recipes and manufacturing processes for the production of bread, cakes, cakes, pizzas, pastas and other grain products with sensory characteristics as similar as possible to those of their gluten counterparts.

3.1. Manufacturing Process of Gluten-Free Breads

The production of gluten-free breads differ significantly from traditional wheat bread making, in which the solid ingredients are kneaded with water, followed by bulk fermentation, division, rounding, fermentation and baking. These formulas are generally very complex and consist of mixtures of the aforementioned ingredients and of various additives (Table 1). Most gluten-free breads are made with high water content and the dough masses they generate are very fluid. Furthermore, they require very short kneading and fermentation times. Regarding the formulas, in numerous occasions the response surface methodology has been used to optimize the concentration of each ingredient.[21] The search for parameters characteristic of each one of the gluten-free doughs, which will allow to predict the quality of gluten-free baked products, is an important issue.

Matos and Rosell[36] described statistically significant correlations between dough consistency when subjected to heating and cooling and crumb hardness, so that these parameters could be used to predict final product quality.

Bread type	Qualitative Composition
Pan Bread	Maize starch, water, sugar, eggs, vegetable margarine, acidifier, preservative, yeast, thickener, salt, leavening agents, antioxidants
Rustic Bread	Maize starch, water, vegetable margarine, acidifier, preservative, antioxidants, aromas, colorants, eggs, sugar, yeast, emulsifier, dextrose, humectants, stabilizers, salt
Carré Bread	Maize starch, water, vegetable margarine, acidifier, preservative, antioxidants, aromas, colorants, eggs, sugar, yeast, emulsifier, dextrose, humectant, stabilizer, salt
Round Bread buns	Potato starch, Maize starch, water, caseinates, sugar, vegetable oil, maize flour, yeast, soy protein, stabilizers, salt, preservatives
Brioches	Maize starch, water, sugar, eggs, vegetable margarine, acidifier, preservative, aromas, colorant, thickener, yeast, emulsifier, salt, leavening agents, aniseed, cinnamon, antioxidants
Carré Bread	Maize starch, rice starch, water, vegetable oil, sugar, thickener, lupin protein, yeast, salt, vegetable fiber, aromas, emulsifier
Pan Bread	Maize starch, water, sugar, eggs, vegetable margarine, acidifier, preservative, aromas, colorant, yeast, thickener, emulsifier, salt, leavening agents, antioxidant
Precooked Baguette	Maize starch, water, sugar, yeast, thickeners, salt, leavening agents, acidifier, preservative, aroma, colorant
Precooked Baguette	Maize starch, water, sugar, thickener, emulsifier, salt, yeast, preservative, leavening agents, antioxidant
Bread loaf	Maize starch, vegetable margarine, salt, sugar, emulsifier, leavening agents, antioxidant, thickener, preservative and yeast
Pan Bread	Maize starch, vegetable margarine, salt, sugar, emulsifier, leavening agents, antioxidant, thickener, preservative and yeast

Table 1. Ingredients and additives in the commercial gluten-free breads formulas

3.2. Manufacturing Process of Gluten-Free Cookies

The manufacture of gluten-free cookies involves no such problems since their gluten network develops minimally and the essential ingredients this type of products are starch and sugar. The manufacture of gluten-free cookies uses maize, millet, buckwheat, rice and potato starches combined with fat (palm oil, microencapsulated fat, low-fat content milk solids). Combinations of rice, maize, potato and soybean with microencapsulated fat originates gluten-free cookies of a quality comparable to those obtained with wheat flour.[37] Cookies also have been obtained by substituting wheat flour by rice flour. An optimized formula for these products includes rice flour (70%), soybean meal (10%), maize starch (10%) and potato starch (10%).[37]

3.3. Manufacturing Process of Gluten-Free Cakes

Cake is obtained by mixing and cooking from masses prepared with flour starches. In cakes, the gluten network is not required and starch is the most important constituent, which determines cake structure. Numerous formulas have been proposed for the manufacture of gluten-free cookies. Gularte and Pallarés[38] compared the characteristics of gluten-free cakes (made with rice flour) with those of gluten-bearing cakes. Both cakes exhibited no significant differences in color, texture and chewiness. Protein-enriched gluten-free cakes have even been made enriched adding leguminous flours[26] or else fibers diverse dietary fibers.[39]

3.4. Gluten-Free Pasta and Extruded Products

Pasta production includes the preparation of dough obtained by mixing hard wheat flour (semolina) with water and then extruding it to obtain the desired shape and size. In gluten-free pasta, the absence of gluten can be countered with the mixture of pregelatinized starch and maize flour before adding water or else pregelatinizing the starch during the mixing or extrusion. The use of high or ultra-high temperature during the pasta drying process to denature proteins and maintain its integrity during cooking is another option. Pseudo-cereals have also been used in gluten-free pasta formula. The combination of buckwheat, amaranth and quinoa with egg albumin, emulsifiers and enzymes has yielded gluten-free noodles with adequate quality features.[40] Buckwheat produces better quality noodles with adequate firmness. Maize and quinoa mixtures, or else quinoa and rice flour mixtures have also been used to obtain gluten-free spaghetti.[41]

4. Gluten-Free Bakery Products

4.1. Baking Gluten-Free Quality Products

Traditionally, products aimed at celiac patients were designed solely focusing on the absence of allergens, using polymer mixtures that could generate products with similar sensory characteristics gluten than those of their gluten-bearing counterparts. In recent years, the celiac community has attracted the attention of food companies and food technologists and a wide variety of gluten-free products has been developed. In the case of baked goods, the variety of commercial products is mainly due to the introduction of numerous formats and presentations rather than to the design of new products with different sensory and/or nutritional properties. Available gluten-free bakery products are characterized by being composed of starch and gluten-free cereal flour mixtures. The quality and characteristics of gluten-free breads depend mainly on the ingredients used to make them (Figure 2). Thus, maize breads have an intense aroma and flavor. In 2002, Arendt et al.[42] reviewed commercial gluten-free bread quality, detecting low quality due to their rapid aging, dry, crumbly texture and intense, unpleasant aroma. Gluten-free breads tend to age rapidly, due to the high amount of starch in the formulas. Furthermore, due to the absence of gluten there is more water available which originates soft crusts rapid crumb hardening. In recent years there have been many studies which seek to improve the quality of these products adding sourdoughs, hydrocolloids, enzymes, emulsifiers and proteins.

Since quality is a completely subjective term, there have been some researches which seek to establish relationships between sensory attributes and certain technological parameters determined by means of analytical instrumentation. Matos and Rosell[36] have established some correlations between the gluten-free bread crumb hydration properties and crumb cohesiveness and resilience.

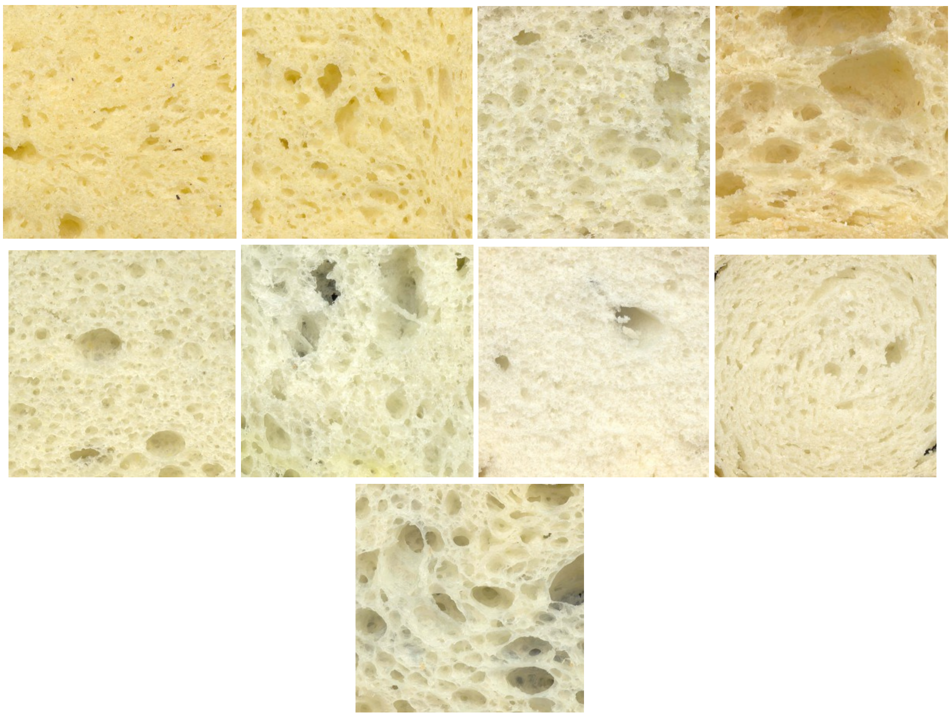

Figure 2. Digital images of different commercial gluten-free breadcrumbs (30x30 mm) (Photo: ME Matos).

4.2. Nutritional Aspects of Gluten-Free Products

Gluten-free products are generally not enriched or fortified and are often obtained from refined flours or starches. Consequently these products do not have the same amount of nutrients as their gluten-bearing counterparts. In a study by Matos and Rosell[43], 11 different types of gluten-free bread commercial available in Spanish supermarkets were evaluated in nutritional terms. The nutritional composition of commercial gluten-free breads had variations of 40-62% in carbohydrates, 0-8% in proteins, 1-11% in fat and highly variable fiber contents (0-6%) (Table 2). This profile differs significantly from the gluten-bearing bakery products which, in spite of their various existing formats, share a very similar nutritional composition which varies between 41-56% for carbohydrates, 8.0-13.0% for protein and 2.0-4.0% for fat, among its major constituents. These data indicate that nutritional differences in continuous gluten-free bread ingestion may arise if the ingestion of other types of food is not modified.

These differences in the nutritional profile of gluten-free products and their gluten counterparts have led to reformulate gluten-free products seeking to obtain nutritionally balanced products which will provide the necessary nutrients for people who are forced to follow these treatment guidelines. Thus, gluten-free breads enriched with calcium and inulin have been designed to combat calcium deficiency and provide a greater fiber intake.[44]

Product	Moisture content (%)	Protein (%)	Fat (%)	Minerals (%)	Total carbohydrates (%)
1	29.63	3.16	8.51	2.12	86.21
2	31.63	6.94	16.91	1.10	75.05
3	29.50	7.31	16.56	1.66	74.47
4	27.17	15.05	7.33	1.85	75.76
5	26.27	5.13	10.64	2.01	82.22
6	41.66	4.92	4.86	2.03	88.18
7	33.60	3.96	8.28	4.53	83.22
8	21.10	1.01	2.00	4.03	92.96
9	31.33	0.91	2.03	5.43	91.63
10	36.13	1.91	26.10	3.57	68.42
11	42.03	2.80	18.32	3.98	74.91
Average	31.82	4.83	11.05	2.94	81.18

Table 2. Chemical composition, expressed in dry g/100 g of 11 commercial types of gluten-free breads.[43]

Acknowledgements

We gratefully acknowledge the funding received from the Higher Council for Scientific Research (CSIC) and the Generalitat Valenciana to Scientific Excellence Groups (Prometeo Project 2012/064), as well as the Celiac Association of Madrid (Spain).

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