Gluten-Free Bread and Bakery Products Technology

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Gluten intolerance is becoming more common in the population, and patients with this intolerance must follow a gluten-free diet. Bread and other bakery products are staple foods and pose a problem in a gluten-free diet due to their short shelf life and the need to replace gluten. Naturally gluten-free cereals and pseudocereals, but also milled legumes, seeds and nuts, are being increasingly used for the preparation of gluten-free baked goods.

Gluten-Free Technologies Bread Bakery products

1. Proteins in Gluten-Free Dough and Products

Proteins improve the nutritional value of gluten-free products. The choice of flour and possibly another source of protein affects the rheological properties of the dough and the water binding in the dough. Proteins interact with starch and lipids and together contribute to the stability of the dough and the structure of the product. They also give the impression of full product flavour. Proteins can be of plant origin (legumes, soya, gluten-free cereals, rapeseed, canola, sunflower, potato), animal origin (whey, egg, casein, caseinate) or microorganism-, algae-, seaweed- and insect-based [1].

Conventional proteins represent egg and milk proteins. Eggs are very useful in forming the structural network, but they are not usually used in bread. Milk proteins, including caseinates and whey protein concentrates, are sources of calcium and can bind moisture satisfactorily. They have a positive effect on the colour and volume of bread and bakery products. For example, protein-rich gluten-free bread with the addition of 15% whey protein concentrate and 3% of HPMC were prepared by Rustagi et al. (2018) [2]. However, many celiacs do not tolerate lactose and must omit milk from their diets [3].

The source of proteins are naturally gluten-free cereals—rice, corn, teff, sorghum, Job's tears. These cereals contain prolamins too (an ethanol-soluble protein fraction), but the molecules of these proteins do not contain amino acid sequences that are toxic to people with celiac disease. Rice is often used as the basis for gluten-free bread formulations. Gluten-free oats have also very good properties [4]. The zein protein, a prolamin from corn, behaves similar to gluten when heated to 35–40 °C. Both corn zein and sorghum kafirin increase the plasticity of the dough [5][6].

Cereal flours are combined in gluten-free bread and bakery products formulations with flour from other crops and with starches. A combination of cereals with legumes is nutritionally advantageous. Pseudocereals also contain proteins with a preferred amino acid composition [7]. This category includes buckwheat, amaranth and quinoa. For example, Föste et al. (2013) [8] used various buckwheat milling fractions, rice and corn flour and fermented buckwheat brans for gluten-free bread preparation. The specific bread volume, porosity and crumb texture can be improved by using buckwheat flour. Soya is a traditional gluten-free ingredient. Soy protein has a very advantageous amino acid composition, participates in interactions with other substances, binds water well and slows down the staling of bread. Legume flours from pea, chickpea, lupine, lentil and bean are rich in proteins with a high lysine content. They significantly affect the dough quality. Lupine and soya flour show emulsifying properties because of the lecithin content. Legumes reduce the glycemic index of food products. The disadvantage of legumes is their typical taste [9][10]. Recently, other flours, such as from nuts and seeds, have appeared in the range of bakery products. Typically, walnut flour and peanut flour are relatively expensive, but very suitable for some formulations. Fat in walnut flour or other nuts flours (except for coconut) contains polyunsaturated fatty acids, and nut proteins are also of very high quality due to their composition. Coconut flour binds water very well, too [11][12].

An alternative solution is the use of insect proteins, e.g., cricket flour which improves the texture of gluten-free bread [5].

The use of proteins in the form of protein concentrates or isolates from different sources in gluten-free baked goods leads to the quality and nutritional profile improvement [1]. Through the comparison of plant- and animal-based proteins, Gorissen et al. [13] reported lower content of essential amino acids in plant-based protein isolates than in animal-based proteins. Differences in the composition of the amino acid spectrum of gluten-free raw materials are known, especially in the composition of essential amino acids. Cereal proteins are deficient in lysine, and some cereals also in threonine and tryptophan. Therefore, from this point of view, it is recommended to combine different types of plant proteins and thus optimize the ratio of amino acids. The combination of different ingredients makes easier to ensure the presence of other nutrients, such as vitamins or minerals.

2. Starch in Gluten-Free Dough and Products

Starch, together with flours from gluten-free crops, is one of basic ingredients in gluten-free bread and bakery products. It is involved in the formation of the crumb structure, responsible for the volume and colour of the product. It is also used as a thickening, gelling, stabilizing, moisture retention and anti-staling agent [14]. According to Abdel-Aal (2009) [15], starch influences gluten-free products in three ways: it enhances crumb softness, ensures dough consistency and affects starch gelatinization. Starch is stored in starch grains of various sizes and shapes according to its plant source. Individual starches differ in their composition, size and shape depending on the plant species and the interactions between genes and environment [14]. The amylose starch fraction forms single chains, whereas amylopectin is branched with a significantly larger molecule. When heated in suspension/dough, the starch grains swell, are partially solubilized, and gradually lose their cohesiveness. Starch gelatinization occurs at a temperature of 50–70 ° C, when their chains are released, and a viscous solution is formed from the suspension. Upon cooling, the viscosity increases, new bonds are formed between the molecules and a gel is formed. During storage, the gel further changes, loses water and eventually retrogrades. Amylose retrogradation proceeds faster than the same process for amylopectin. It follows that by choosing the type of starch, it is possible to partially influence the staling of the bread [14]. Starch behavior may be affected by bound lipids.

Native starches are the most commonly used in gluten-free products, e.g., potato, corn, rice and tapioca, and pea starch has also appeared. Specially prepared gluten-free wheat starch is also used for its properties ensuring an optimal bread texture. Modified starches are produced for food purposes have a wide range of physical properties according to the purpose they are used. Starches can be modified by heating of the starch solution or by heating in the dry state; the heating can be performed by drying or extrusion. Chemical modification of starch is also possible [16]. For gluten-free products, starches with good water absorption and slow retrogradation are selected. Specially modified starches are suitable for frozen products. A new modification is the so-called superheated starch, prepared by heating the starch suspension to high temperatures until dissolved and then cooling to form a spreadable gel with a creamy consistency [17][18]. Additionally, various types of banana flour can be applied as well as the direct use of bananas in the dough [19].

There are significant differences in granular structure among various types of starches, which affect their ability to produce high quality gluten-free baked goods. When the baked goods are based on starch, they show higher volume, lower hardness and a lighter crust since Maillard reactions are reduced. The starch addition results in softer, and resilient crumbs. The type of starch also influences the quality of the baked goods. For the specific gluten-free formulations different mixtures of flours and starches must be optimized [20][21].

Preventing the retrogradation of starch and thus prolonging the shelf life of gluten-free bread and bakery products can be achieved in several ways:

(a) Using enzyme preparations.
(b) Application of hydrocolloids.
(c) Using sourdough fermentation.
(d) Suitable packaging method.

2.1. Use of Enzyme Preparations

The most common enzyme preparations use amylases, which improve the colour of crumbs and support the production of flavors. Amylases partially degrade amylopectin and thus modify the starch recrystallization process [22][23][24]. Transglutaminase improves the dough viscoelasticity and decrease crumb hardness, and cyclodextrinase also enhances dough viscoelasticity, leading to improvement in shape index and crumb firmness [25].

Cyclodextrin glycosyltransferases form cyclic structures from starch with different affinities for water outside and inside the ring. Lactase and tyrosinase create crosslinks of non-starch polysaccharides with proteins with the use of phenolic substances. Oxidases such as lipoxygenase, sulfhydryl oxidase, glucose oxidase and peroxidase stabilize the dough; for example, glucose oxidase added to rice bread improved volume and reduced stiffness. Proteases and peptidases improve the interaction between protein molecules and starch and reduce the viscosity of the dough [5][26]. Microbial transglutaminase, which forms covalent bonds between the free epsilon-amino group of lysine and the amide group of glutamine, is used to promote the formation of a spatial network of gas bubble trapping molecules. Transglutaminase supports the rheological and viscoelastic properties of the dough [27][28][29][30][31]. Silva et al. (2020) [32] tested gluten-free bread from red rice flour and cassava flour, with the addition of transglutaminase and chitosan at concentrations of 0%, 1% and 2%. Bread with chitosan and transglutaminase showed lighter brown coloration because of incomplete Maillard reaction and low specific volumes, probably related to chitosan interference with yeast fermentation. With the use of chitosan, viscosity increased. Bread containing chitosan had a lower rate of staling due to water retention.

The use of enzymes influences the quality of the gluten-free baked goods, and the effect depends on the type of the flour used. Some enzymes have positive effects on product volume and delay staling [20].

2.2. Use of Hydrocolloids

The application of hydrocolloids is crucial for the quality of gluten-free bread. Hydrocolloids swell and form a gel. This heated gel thickens the mass of dough forming the walls of gas bubbles, preventing the loss of gas released during whipping, leavening or from raising agents. After baking, hydrocolloids stabilize the crumb structure, bind water, and prevent rapid starch retrogradation. They stabilize the product during freezing. Due to the higher water binding, the recipes with the addition of hydrocolloids contain higher doses of water [33][34].

Vegetable gums (guar gum, locust bean gum, arabic gum, tara gum, carob, konjac gum), beta-glucans, pentosans and arabinoxylans, cellulose derivatives (methyl cellulose MC, carboxymethyl cellulose CMC, hydroxypropylmethyl cellulose HPMC), microbial exopolysaccharides (xanthan, dextrins) and seaweed polysaccharides (agar, carrageenans) are used to produce gluten-free bread and bakery products [2][35][36][37]. Flax flour or ground chia seeds are sometimes used to increase viscosity.

Cellulose derivatives, especially CMC and HPMC, are among the most used hydrocolloids in gluten-free dough. They can interact with other raw materials in the matrix. They are most often combined with other types of thickeners, proteins, and emulsifiers [26]. For example, Liu et al. (2018) [38] compared the effect of HPMC, CMC, xanthan gum and pectin on the behavior of steamed potato dough. The addition of 2% HPMC increased mostly the specific volume of bread and porosity and reduced the stiffness of the crumb by almost 29%. The addition of hydrocolloids significantly reduced the content of both readily available and slowly available starch and, conversely, increased the content of resistant starch. Model experiments with HPMC and rice flour on Mixolab examined the effect of HPMC dose (1–3%) and water dose (90–110%) on the rheological properties of gluten-free dough and crumb quality. The optimal dose is 2.2% HPMC and 110% water) [39]. Lazaridou et al. (2007) [40] showed that 1% CMC and 2% pectin led to breads with improved breads volume, porosity and crumb elasticity. With the use of HPMC, Hager et al. (2013) [41] observed an increased volume in corn and teff breads, a decreased size of rice breads and a positive effect on the crumb hardness of each bread.

Salehi (2019) [21] dealt with the application of HPMC, CMC and other hydrocolloids in rice flour dough. HPMC in combination with carrageenan forms a softer crumb. To slow down the aging of bread, the addition of CMC or HPMC 0.1–0.5% is recommended. Kaur and Chopra (2018) [19] tested 74% corn starch bread with tapioca, rice flour and 2.2% HPMC. Belorio and Gómez (2020) [42] tested the use of different types of hydrocolloids (HPMC, xanthan and psyllium) in rice and corn bread and the effect of water levels. The water dose has been optimized to form a thermoreversible gel that provides a sufficient volume of bread. For corn bread with added HPMC, the optimal hydration was 80%; for rice bread with HPMC, the hydration was higher—100%.

Fruit and vegetable pomace containing fiber and antioxidants can also be used [43][21]. Djeghim et al. (2021) [43] observed the addition of various by-products with gluten-free bread formulations based on corn and chickpea flours (2/1 *w*/*w*)—orange and apple pomace, tomato peel, pepper peel, prickly pear peel and prickly pear seed peel on the dough rheology and properties of gluten-free breads. They found out that the addition of the above-mentioned by-products significantly improved the specific volume of gluten-free bread, with values increasing from 1.48 to 2.50 cm^3/g, and increased the maximum dough height, the total CO_2 production and CO_2 retention coefficient.

The effect of apple, orange and carrot pomace powders, on dough rheology and quality characteristics of the rice sweet bakery were studied by Kirbas et al. (2019) [44]. With an increase in the content of pomace powders, the dough elasticity, specific gravity and apparent viscosity increased. The addition of pomace powder increased crumb hardness and decreased the specific volume of the rice-based sweet bakery products. The addition of 5% of orange pomace powder had the highest acceptance scores with respect to the colour, flavour, texture, appearance and acceptability of the products.

The comparison of breads and bakery products prepared from gluten-free flour alone and with various hydrocolloids (gums) showed that the incorporation of hydrocolloids led to a significant improvement in the texture, volume, color, appearance, flavor and overall acceptability. Different hydrocolloids have slightly different effects on rheology, texture and other properties, thus affecting the resulting quality of various types of gluten-free breads and bakery products. For example, xanthan gum is able to maintain unchanged texture parameters during storage; the addition of xanthan, carrageenan and guar gums decrease dough extensibility, whereas arabic gum and HPMC lead to increased extensibility [21]. HPMC is preferred to other hydrocolloids since it provides gluten-free products with appropriate physical characteristics, higher specific volumes of products and better sensory properties [20]. Moreover, the use of hydrocolloids is the easiest way to raise the content of dietary fiber in gluten-free baked goods [7].

2.3. Microbial Fermentation in Gluten-Free Bread Production

The use of sourdough is a traditional procedure in conventional baking technology. In the preparation of gluten-free bread, starter cultures began to be applied later, because gluten-free raw materials have a specific composition different from rye flour; therefore, the classical culture of rye sourdough bacteria and yeasts may not grow sufficiently in gluten-free substrates. Although it is possible to gradually “dilute” rye flour with gluten-free raw material during repeated fermentation so that the proportion of rye is reduced to a minimum value, such a process would take a long time, and there would still be the danger of the presence of gluten traces [45]. Therefore, suitable strains of microorganisms capable of fermenting rice, buckwheat, sorghum or corn flour are sought. The choice of a suitable starting culture will significantly affect the resulting properties of the dough and the product. Additionally, the oilseed, chia and flaxseed sourdoughs can be used [46]. During fermentation, the dough is acidified. At the same time, the enzymes naturally contained in the flour are also activated and break down high molecular weight substances, and thus make them more accessible. The activity of the cereal grain's own enzymes is combined with the action of microbial enzymes. Substances affecting the taste and smell of the products are formed. Fermentation increases the swelling of carbohydrates and improves the viscoelastic properties of the dough. The fermentation products include organic acids with a predominance of lactic and acetic acids, but some strains also produce propionic acid. These acids significantly increase the shelf life of the bakery products. For example, Kaur and Chopra (2018) [19] deal with the use of teff flour and rice sourdough as a possible combination. Bacterial strains of sourdough microflora, for example *Lactobacillus reuterii* or *Weisella cibaria*, are able to produce the exopolysaccharides fructan, levan, dextran or reuteran. These polysaccharides naturally increase the viscosity of the dough and thus contribute to the formation of the product texture. The presence of these polysaccharides reduces the hardness of the crumb, improves its porosity, and slows down the staling of the bread [47][5]. Additions of dried sourdough are also being applied. The advantage of dried sourdough is its standardized quality, the disadvantage is the possible inactivation of living microbial strains during the drying process [48]. A non-traditional sourdough using *Lactobacillus sanfranciscensis* for fermentation of chia, quinoa and hemp flour to produce gluten-free corn/rice bread was tested by Jagelaviciute and Cizeikiene (2021) [49]. This sourdough showed a decreased pH, specific volume and rate of bread staling and, on the other hand, increased bread porosity compared with bread made only with chia, quinoa or hemp seed flour. The use of non-fermented chia and hemp flour increased the firmness and the rate of bread staling, whereas use of non-traditional hemp and quinoa sourdough reduced the rate of bread staling.

The use of sourdough in gluten-free baked goods leads to products with improved technological and nutritional properties [50], which are softer, tend to stale more slowly and have a delayed mould spoilage rate and thus a prolonged shelf life. Sourdough also brings nutritional benefits because it makes minerals more available and its presence leads to the production of exopolysaccharides, which function as hydrocolloids [20].

3. New Technologies in Gluten-Free Dough and Bread Preparation

Recently, several technological processes have been tested to influence the properties of gluten-free dough and improve baking. Treatment of the dough with a high pressure (pascalization) of 100–1000 MPa reduces the temperature of starch gelatinization and change the properties of proteins, including crosslinking. Starch swells and gelatinizes without granules degradation; the extent of swelling depends on the intensity and length of pascalization. This changes the viscoelastic properties of the dough, increases its flexibility, but sometimes also its viscosity [47][5]. The experiments were also performed using ultrasound and micromilling to reduce flour particles. However, no positive effects on bread volume and porosity have been found [5][6].

The properties of gluten-free dough can also be influenced by heating of dry ingredients before dough preparation. Protein denaturation and partial gelatinization of the starch occurs, which increases the flexibility of the dough and the ability to retain gas. The dough viscosity, resistance and stiffness increase, as well as the dough volume [5][51]. Microwave heating was used to heat the rice flour with a moisture content of 20–30%. Proteins denatured after opening their three-dimensional structure. The specific volume and elasticity of bread has significantly improved, and the staling of bread has slowed down [52]. The “Instant controlled pressure drop” technology based on the heating of gluten-free flour for a short time under reduced pressure was tested on a mixture of rice and bean flour. The temperature was in the range of 100–165 °C, and the pressure of 5 kPa and the heating time of 20–60 s were used. The appropriate heating conditions of gluten-free raw materials were determined so that the bread baked from the heat-treated mixture resembled the control wheat bread [53].

Microwave and infrared technologies are also tested in the gluten-free bread baking process. Microwave heating would be cost effective and fast, but the resulting product had low volume, a solid crumb and was rapidly subject to the staling process. The poorer energy penetration into the bread mass is the disadvantage of infrared heating technology, but the resulting product was better sensory evaluated. The so-called “jet-impingement” using hot air convection heating on the surface of the bread was also tested. Homogeneous heat transfer occurred, but the process was energy consuming. The disadvantage was the formation of a solid crumb and dense texture, loss of water and aroma. The starch gelatinization was not complete and starch digestibility was thus decreased. The combination of both methods was recommended for this reason.

Ohmic heating was the other tested technology. The food material was heated up by its resistance during the electric current passage. The advantage of this process would be the homogeneity of the heating [26]. Another possibility of heating is the partial baking under the reduced pressure. In the first stage, bread was baked at a normal pressure at 180 °C, and after the formation of a solid crust preventing the bread collapsing, it was baked at a pressure reduced to 60 kPa. No changes in bread volume or stiffness were observed, but product moisture was lost and the crust colour was affected. After vacuum baking, other types of starch crystals were formed in the bread and the bread tended to grow stale more slowly [54].

The new technologies improving the gluten-free dough and products quality and shelf life have been still evolving. Some of them have proven to be appropriate. It has been shown that some promising methods do not give completely satisfactory results. Other technologies need to be combined. Research in this area will certainly continue. In practice, however, the economic side of the process would be crucial. Gluten-free bakery products should be not only of high quality, but also be affordable for customers.

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