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REVIEW PAPER

TRENDS IN THE DEVELOPMENT OF GLUTEN-FREE BAKERY PRODUCTS

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Food intolerance became an important public health concern, and identification of effective strategies for prevention is required. There is an increasing incidence of coeliac disease or other allergic reactions/intolerances to gluten, so the coeliac disease became one of the most common food intolerances. This intolerance can be present at any age, from early childhood to elderly.

The present paper presents an overview of the results/approaches of the latest scientific investigations on gluten-free products based on (i) the use of different gluten-free base flours (rice, maize, sorghum, oat, buckwheat, amaranth, quinoa, teff); (ii) the use of different ingredients/additives (starches, dairy products, egg proteins, dietary fibre, gum and hydrocolloids) for improving nutritional quality and consumer acceptability; (iii) developing alternative technologies such as enzymatic or sourdough technology and high hydrostatic pressure processing.

Keywords: coeliac disease, gluten-free base flours, alternative technologies

Introduction

Identifying dietary solutions and innovations leading to improvements in health and well-being is a permanent concern of the food scientists. Enhancing the health benefits of the cereal foods represent one the most important research direction developed in the last years.

The complexity of diet-health relationship requires constant development of cereal foods tailored on the consumers' specific needs, involving the need for new ingredients and new processing tools.

Among food intolerances which present public health concern, for which preventive strategies are required, the coeliac disease and other allergic reactions/intolerances to gluten are the most common ones (Catassi and Fasano, 2008) and affect people from early childhood to elderly.

Gluten was defined by WHO/FAO as the protein fraction found in wheat, rye, barley, oats or their crossbred varieties (e.g. Triticale) and derivatives thereof, that is insoluble in water and 0.5M NaCl (Arendt *et al.*, 2008). Prolamins are defined as the protein fraction that can be extracted by 40–70% aqueous ethanol.

According to the Romanian Ministry of Health, the number of people affected by coeliac disease is 1,300, out of whom 1,000 are children. Dobru *et al.* (2003) evaluated the prevalence and the clinical features of coeliac disease in Romanian adults and they report a total prevalence of 2.22%, being fairly equally distributed among genders. The age distribution includes two peaks, at 30-40 and 50-60 years of age, and predominate patients from urban areas. In 2005, the Romanian Ministry of Health organized four regional centers in Cluj, Iasi, Timisoara and Bucuresti counties, for managing coeliac disease. Nevertheless, in Romania there is few data about the prevalence of coeliac disease in general population or in high risk population (Cev *et al.*, 2010).

According to Gallagher *et al*. (2004) coeliac disease is an autoimmune disorder of the small intestine that leads to the malabsorption of several important nutrients such as iron, folic acid, calcium and fat-soluble vitamins. Anaemia, mouth ulcers, diarrhoea or constipation, abdominal pain, bloating, fatigue, osteoporosis, infertility, cancer, anxiety and depression are the most important symptoms associated with coeliac diseases (Gallagher *et al.*, 2004). Moreover, Garcia-Manzanares *et al*. (2011) reported an association between coeliac disease and metabolic syndrome. The coeliac disease is a global phenomenon and its prevalence is largely increasing due to improved diagnostic procedures and changes in dietary habits (Arendt *et al.*, 2010). According to Mustalahti *et al.* (2010) the mass screening based studies have shown that coeliac disease affects 1% of the population.

Coeliac disease is a life-long intolerance to the prolamins fraction of wheat (gliadins) rye (secalins) and barley (hordeins) (*Gallagher et al*, 2004). The only effective treatment for coeliac disease is the gluten-free diet throughout the patients' lifetime. The prolamins are rich in proline and glutamine amino acids. Gliadins have high proline content and are resistant to proteolysis within the gastrointestinal tract because of the lack of post-proline cleaving activity of gastric and pancreatic enzymes (Catassi and Fasano, 2008). Furthermore, the high glutamine content makes prolamins good substrates for the enzyme tissue transglutaminase. Intestinal transglutaminase acts on glutamine residues of gliadins, catalyzes their specific deamidation, generating a negatively charged complex that fits into HLA-DQ2 or HLA-DQ8 and activates T cells. The inflammatory reaction in the upper small intestine is due to the antibodies acting against transglutaminase and gliadin, causing villous atrophy, crypt hyperplasia and intraepithelial lymphocytocis (Minarro, 2013).

Bread, mostly made from wheat, is an important part of a normal diet. According to Lopez *et al.* (2001) and Dewettinck *et al.* (2008), the ideal bread should have a lower glycemic index, be an important source of proteins and contain tolerated dietary fibers, vitamins, magnesium, trace elements and antioxidants. Gluten play key role in the overall quality and structure of breads and is responsible for extensibility and elasticity of the dough. During breadmaking the gluten proteins form a continuous protein network which confers viscoelasticity to dough. In order to obtain dough and then bread with optimal properties, the gluten network must retain the carbon dioxide produced by the yeast. In these conditions the replacement of gluten represents a major technological challenge, and the production of high quality gluten-free bread is difficult (Gallagher *et al.*, 2004). Only few gluten-free products can be found on the Romanian market, having prices by 50% to 300% higher compared to the conventional products. On the other hand, the demand for gluten-free products is also affected by the low palatability and nutritional (vitamins, minerals and fibers) deficiencies, caused by their consumption. Therefore, the production of low-priced high quality gluten-free products became an important socio-economical issue.

According to Arendt *et al.* (2008) most of the gluten-free products currently available on the market are of very poor quality. Successful development of gluten-free bread and other bakery products requires (i) incorporation of different functional ingredients into the gluten-free base flour, that allow obtaining viscoelastic properties similar to the gluten, meant to improve bread quality (texture, mouth-feel, acceptability, and shelf-life), and (ii) the use of novel processing approaches (Arendt *et al.*, 2008; Huttner and Arendt, 2010).

In the last years several approaches have been investigated to develop high quality gluten-free bread: the use of different gluten-free base flours (rice, maize, sorghum, oat, buckwheat, amaranth, quinoa, teff); the use different ingredients/additives (starches, dairy products, egg proteins, dietary fibre, gum and hydrocolloids) to improve de nutritional quality and consumer acceptability; developement the alternative technologies such as enzymatic or sourdough technology and high hydrostatic pressure processing (Huttner and Arendt, 2010; Zannini *et al.*, 2012).

Gluten-free flours

The cereals and pseudocereals base flour allowed in the development of gluten-free bread are rice, sorghum, maize, millets and teff, and buckwheat, amaranth and quinoa, respectively.

Rice flour is the most suitable cereal flour for the production of gluten-free breads. There are many attributes that make rice the best cereal grain for patients suffering from allergies. Rice flour has low levels of prolamins and easily digested carbohydrates. In addition to good digestibility and hypoallergenic properties, rice proteins bring additional sensorial advantages such as bland taste and white colour. Anyway, rice proteins have rather poor functional properties relevant for food production (Rosell and Marco, 2008). The baking products made of rice flour have low specific volume and very compact crumb, because of the low content of prolamins fractions required for developing the specific dough's' protein network.

Most of the gluten-free bread formulas are based of flour blends of rice with other cereal or pseudocereal and starch of different sources.

The amylose content varies within flours from different rice varieties, highly influencing the pasting behaviour and viscoelastic properties of the dough. In addition to the rice variety, the grinding method influence the functional properties of the flour. According to Rosell and Marco (2008) the long rice varieties with higher contents of amylose, have higher gelatinization temperatures, and a greater tendency to retrograde with respect to the medium or short rice varieties. The milling method and type of mill determine the particle size distribution and the amount of starch damage. In particular the roller mills allow obtaining rice flours with medium particle size, and good baking performance (Rosell and Marco, 2008).

In order to achieve dough consistency suitable for breadmaking the rice flour dough requires higher hydration with respect to wheat flour (Marco and Rosell, 2008). Mixing at constant temperature of 30°C, during the Mixolab test, a more hydrated rice dough leads to the improvement of dough behaviour, whereas during heating-cooling the peak torque (related to the starch gelatinisation) and final torque at the end of cooling, due to starch dilution effect, are lower. Moreover, the setback (related to amylose tendency to retrograde) is lower, while the rate of starch retrogradation and enzymatic degradation speed increase because of the large amount of water availability (Rosell *et al.*, 2007).

Sorghum and maize have similar properties and several researchers have reported the production of gluten-free bread from sorghum flour (Schober *et al.*, 2005; Taylor *et al.*, 2006) and blend of sorghum flour and maize starch (Olatunji *et al.*, 1992). According to Schober *et al.* (2008) sorghum presents easy adaptability to wide range of growing conditions due to its drought and heat tolerance, while maize is a major cereal grain that is grown worldwide.

The grain quality characteristics, hybrid selection and flour quality influence the end use application. Grain hardness plays an important role in particle size distribution of the flour and in starch damage. Olatunji *et al.* (1992) reported the production of bread using a simple formulation with maize and sorghum, and identified the amount of mechanically damaged starch in the flour as the most important factor that can explain the differences in the crumb and texture of bread. They noted that the higher starch damage determines a coarser crumb structure. Liu *et al.* (2012) suggested that by controlling the starch damage and flour particle size, it is possible to manufacture noodles with good physical attributes. Moreover, in the last years the sourdough technology was used for manufacturing bread based on the maize and sourdough flour (Schober and Bean, 2008), but the specific volume of the obtained products was rather low. Schober *et al.* (2008) obtained a significantly improved quality in case of a gluten-free formulation with commercial zein and maize starch hydroxypropyl methylcellulose (HPMC).

Anyway, there is limited knowledge about the possibility of modifying the properties of proteins and/or starches in sorghum and maize flour in order to improve their functionality in gluten-free bread.

Pearl millet have high protein contents (11.8%) compared with other millets (e.g. Proso millet 10%, Teff 9.6% or Finger millet 7.3%), but the prolamins content is lower than that in other millet (Taylor and Emmambux, 2008). The nutritional benefits brought by pearl millet include also significant amounts of essential amino acids (lysine and methionine), as well as significant amounts of calcium, phosphorus, potassium, iron, zinc and pro-vitamin A (Kamara *et al.*, 2009; Kamara *et al.*, 2010). Sorghum and millet grains contain substantial levels of a wide range of phenolic compounds and can be used as sources of nutraceutical and functional food ingredients in health promotion (Taylor *et al.*, 2006). The gluten-free bread formulation with millet requires hydrocolloids, starch or gum (Taylor and Emmambux, 2008).

Recent studies have shown that ***oat*** can be tolerated by most people suffering from coeliac disease. Moreover, oat is a cereal with important nutritional properties due to the high contents in β-glucan, essential amino acids, unsaturated fatty acids, vitamins, minerals and antioxidants (Huttner and Arendt, 2010).

Amaranth, quinoa and buckwheat do not contain prolamins and can be therefore integrated into gluten-free bread formula. Amaranth and quinoa have excellent protein quality, while buckwheat is characterized by a high content of phythochemicals. The protein content of amaranth is higher than wheat and contains acceptable levels of essential aminoacids, which are found in low concentrations in cereals. The fat of amaranth has high contents of unsaturated fatty acids, with high levels of linoleic acid (Mariotti *et al.*, 2009). Amaranth contains also significant amounts of calcium, iron, potassium, phosphorous, vitamins, and dietary fibers. Buckwheat has been reported to possess higher antioxidant activity compared to oat and barley, mainly due to the high contents of phenolic compounds (3-flavanols, rutin, phenolic acids and their derivatives) (Holasova *et al*., 2002). Moreover, buckwheat protein is of high nutritional quality due to the relatively high level of lysine (Sedej *et al.*, 2011).

Marco and Rosell (2008) obtained gluten-free bread with good sensory attributes using blends of buckwheat and rice flours in the presence of hydrogenated vegetable fat. Torbica *et al.* (2010) noted that the gluten-free bread formulation prepared with the blend of rice and buckwheat flour does not require the addition of the hydrocolloids for the dough structure effect. The increase of the amount of buckwheat flour from 10 to 30% leads to the increase of dough development time and to the weakening of the protein network, and also to the decrease of starch retrogradation degree.

Ingredients/additives for gluten free bakery products

In order to improve the structure, mouth-feel, acceptability and self-life of the gluten-free bread, different ingredients were used in the last years to replace the gluten (Gallagher *et al.*, 2004). It was shown that dairy ingredients and/or hydrocolloids could mimic the viscoelastic properties of gluten in bread dough (BeMiller, 2008).

Dairy ingredients

The gluten-free formulations can include the *dairy ingredients* such as: low lactose powders, sodium caseinate, milk protein isolate, whey protein isolate and whey protein concentrate (Nunes *et al.*, 2009; Riemsdijk *et al.*, 2011; Storck *et al.*, 2013) that are known for both nutritional and functional benefits. Different scientific studies showed the ability of the dairy ingredients to form a network similar to gluten in the bread containing these ingredients. The most important aspect that significantly influences the quality of the gluten-free bread is the type of dairy ingredient used. It is highly important to use lactose free or dairy ingredients with low levels of lactose for getting gluten-free bread of good quality (Gallagher *et al.*, 2004). Nunes *et al.* (2009) demonstrated that whey proteins have the ability to increase significantly the specific volume of the bread. On the other hand, sodium caseinate had a negative impact on the specific volume, which led to an increase in crumb hardness (Nunes *et al.*, 2009).

Hydrocolloids

The *hydrocolloids* are hydrophilic polymers that commonly contain many hydroxyl groups, and may be polyelectrolytes. They are usually added to food systems that contain starch. The most important effects of hydrocolloids addition on food system properties, are summarized by the BeMiller (2008): improve food texture and organoleptic properties, improve viscoelastic characteristics, slow down the retrogradation of starch, act as water binders, extend the overall quality of products during, act as fat replacers having good properties as substitutes for fats in different products, and as gluten substitutes in the formation of gluten-free breads. In breadmaking and bread quality the most important effects associated with hydrocolloids are: improve the dough stability during proofing by addition of sodium alginate, κ-carrageenan, xanthan gum, hydroxypropylmethylcellulose (HPMC) (Rosell *et al.*, 2001); increase the specific volume by addition of κ-carrageenan, xanthan gum, HPMC (Guarda *et al.*, 2004; Rosell *et al.*, 2001); softening and retardation of firmness during storage by addition of κ-carrageenan, alginate, guar gum, pectin, xanthan, HPMC (Davidou *et al*., 1996; Rojas *et al.*, 1999; Collar *et al.*, 2001).

The effect of hydrocolloids on gluten-free bread depends on the source and obtaining/extraction method, chemical structure and eventual chemical modification, the dosage and specific interactions with other ingredients of the gluten-free bread formulas. Chemical modification is an important tool that allows improving functional properties of hydrocolloids such as water retention, interfacial activity within the system during proofing, and gel networks forming during breadmaking process, mainly because of the hydrophilic groups (Guarda *et al.*, 2004; BeMiller, 2008).

The role of cellulose derivatives on gluten-free bread structure formation is ensured by the behavior of their chains bundles which unfold in a similar manner to starch gelatinisation, exposing non-polar groups to the aqueous environment and therefore participating to specific hydrophobic association. Cellulose modification induces the formation of water-soluble polymers with affinity for the non-polar phase of the dough, therefore supporting the homogeneity and stability of the dough emulsion. In addition, the increase of interfacial activity on the surface of expanding gas cells has been reported, providing stability during proofing and generating firmer doughs and breads with increased loaf volume (Bell, 1990; BeMiller, 2008; Lazaridou *et al.*, 2007).The antistaling effect of the hydrocolloids can be explained by inhibition of amylopectin retrogradation in case of HPMC and guar gum, since these hydrocolloids preferentially binds to starch. According to Rojas *et al.* (1999) κ-carrageenan, alginate, and pectin favor the formation of amylose-lipid complexes, while the xanthan and HPMC slightly affect these complexes.

Onyango *et al.* (2009) investigated the effect of selected hydrocolloids and emulsifiers (glycerol monostarate, sodium stearoyl-2-lactylate, diacetyl tartaric acid esters of mono- and diglycerides, and calcium stearoyl-2-lactylate) commonly used in wheat bread production to strengthen the dough or soften the crumb, on creep and creep-recovery properties of gluten-free dough prepared from gelatinised cassava starch and sorghum. Among hydrocolloids, cellulose derivatives, such as microcrystalline cellulose, carboxymethylcellulose sodium salt, methyl cellulose, HPMC and hydroxypropylcellulose were selected since their production through chemical modification of cellulose ensure that they have uniform properties. Unlike most of cellulose derivatives which are non-ionic and do not dissociate in water due to their covalent bonds, carboxymethylcellulose is anionic. Onyango *et al.* (2009) observed that the effect of cellulose derivatives on dough strength was influenced by the type, concentration and ionic character. Compared with control formulations, cellulose derivatives did not decrease crumb firmness and staling rate of gluten-free breads. They also showed that emulsifier concentrations of 0.4 to 2.4% cause an improvement of the crumb structure of the gluten-free bread prepared from pregelatinised cassava starch and sorghum. The gluten-free bread treated with cellulose derivatives obtained by substituting the hydrogen atoms on some hydroxyl groups of cellulose by methylether, carboxymethylether or hydroxypropyl groups under alkaline conditions were firmer than the control and firmness increased with increasing the concentration of cellulose derivatives. On the other hand the cellulose derivative (microcrystalline cellulose) produce by acid hydrolysis of cellulose had an opposite effect, probably due to failing in strengthening the boundaries of expanding gas cells.

One of the most important study regarding the effect of hydrocolloids on dough rheology (performed by farinography and rheometry) and bread quality parameters in gluten-free formulations was performed by Lazaridou *et al.* (2007). They used in their study pectin, carboxymethylcellulose (CMC), agarose, xanthan and oat β-glucan, which were added to the rice flour. The results showed that xanthan addition yielded doughs' strengthening and highly influenced the viscoelastic properties. The oscillatory and creep measurements revealed that the elasticity and resistance to deformation of dough decreased as follows: xanthan > CMC > pectin > agarose > β-glucan. The addition of hydrocolloids, except for xanthan, resulted in breads with increased volume. Breads made of flour supplemented with 1% CMC and β-glucans aand 2% pectin had good porosity, whereas flour supplemented with CMC, pectin and xanthan at 2% allowed obtaining products with high crumb elasticity. The addition of pectin, CMC, agarose, and β-glucan did not significantly influence the crumb firmness.

Lorenzo *et al.* (2009) studied the effect of different hydocolloids mixtures, such as xanthan/guar, and xathan/HPMC gums on textural and rheological behavior of non-fermented gluten-free doughs. Regardless of guar or HPMC presence, the products made of mixtures including xanthan gum exhibited the best elasticity and resistance to puncture. Different kinds of lipid phase, sunflower oil or low and high solid content margarine at two different levels (20–30%), were also studied. The highest resistance to puncture was observed when margarine was used to increase the fat content, while the opposite effect was found using sunflower oil. Lorenzo *et al*. (2009) concluded that the margarine with higher solids content provided greater elasticity to the dough, rendering it more ductile. When referring to the commercial acceptability, the mixture xanthan/HPMC was preferred.

Gluten-free formulations are often supplemented with proteins. Addition of soybean based derivatives improves the protein biological value of the product. Moreover, the consumption of soy protein causes the reduction in total low density lipoprotein cholesterol and also in triacylglycerols (Marco and Rosell, 2008). Crockett *et al.* (2011) analyzed the effects of soy protein isolate and dried egg white solids on the hydrocolloids (HPMC) treated gluten-free dough system. Addition of soy protein to gluten free bread formulation including HPMC and cassava altered dough stability by suppressing HPMC functionality, affecting the water distribution within dough matrix, weakening the starch - HPMC interactions and reducing foam stability. The dried egg white solids are considered the most important protein scaffold in the gluten-free dough, because negative interactions with HPMC are avoided and the interconnected honeycomb matrix is formed, leading to improved loaf volume and crumb regularity.

The Crockett *et al.* (2011) considered that these gluten free formulations need further optimisation in terms of flavour and perceived moistness in a future study.

Pulses are important sources of proteins with high contents of lysine, aspartic acid and arginine, being therefore suitable for enhancing the biological value of cereal based products. In addition, because of the good functional properties are recommended for improving the technological behavior of the gluten free doughs. The chickpea and pea protein derivatives have a positive effect on physical-chemical and sensory properties of gluten free breads, being therefore considered an alternative for soy proteins (Minarro *et al.*, 2012).

Dietary fibers

The enrichment of gluten free bread with dietary fibers has been the concern of various researchers. Coeliac patients generally have a low intake of fiber due their gluten free diet (Sabanis *et al.*, 2009; Thompson, 2000). It has been shown that the addition of high fiber ingredients can give texture, gelling, thickening, emulsifying and stabilizing properties to gluten free products (Taylor and Emmambux, 2008).

Psyllium is an excellent source of natural soluble fiber that has been recognized for its cholesterol-lowering effect and insulin sensitivity improvement capacity (Zandonadi *et al.*, 2009; Mariotti *et al.*, 2009). The addition of *Psyllium* fiber to the gluten free formulations containing corn starch, amaranth flour (for nutritional benefits) and pea isolate (to increase the protein content) increased the physical properties of dough, due to the ability to form a film-like structure. The association of HPMC (2%) with *Psyllium* fiber (1%) in the formulation of gluten free bread that includes as base the rice flour, allowed improving the loaf volume as a consequence of forming a weak gel network with ability of trapping the CO_2. This achievement was due to the good abilities of *Psyllium* fiber of gelling and retaining water, and of HPMC to form heat-induced gels (Haque and Morris, 1994; Mariotti *et al*., 2009).

Inulin is an important ingredient that can be used to increase the fiber content of the gluten free bread. It was reported that inulin and hydrocolloids have synergistic effect, increasing the viscosity of the food systems (Silva, 1996). Korus *et al*. (2006) studied the influence of different prebiotics on the quality of gluten free bread. They found that the addition of 5% inulin leads to increased loaf volume, reduces the rate of crumb hardening, and improves the sensory quality.

Alternative technologies

Enzymatic processing

The researches published in the last years have shown that the enzymatic processing is a powerful tool to improve bread making performance of gluten free flours and for the development of new gluten free formulation. The enzymatic processing is used in order to enhance protein functionality, improve dough handling and bread quality (Buchert *et al*., 2010; Huttner and Arendt, 2010).

The most important enzymes that have been successfully used in gluten free baking are transglutaminase (TG), proteases, glucose oxidase and laccase. The protein source is a key element determining the impact of the enzyme (Renzetti *et al*., 2008).

Transglutaminases (EC2.3.2.13) mainly catalyze protein cross-linking reactions, through acyl-transfer between the γ-carboxyamine group of a glutamyl residue and the ε-amino group of lysine or lysyl residues from proteins or peptides (Buchert *et al*., 2010). TGs have high substrate specificity for glutamine as acyl donor, but wide specificity for substrates acting as acyl acceptors. TGs can be obtained from different sources of vegetal, animal or microbial origin, and their properties vary significantly with the source. The most widely used are TGs from *Streptomyces mobaraense*, S. *ladakanum*, *S. cinnamoneum*, and *Bacillus subtilis*. The activity of some TGs, such as those of mammalian origin, is dependent on the presence of Ca^{2+}, while *Streptomyces* TGs, with food applications, are independent of Ca^{2+} as cofactor.

Marco and Rosell (2008) studied the effect of TG on rice based gluten free bread enriched with soybean and having HPMC as structuring agent. Individual additions or combinations of 4% HPMC, 13% soybean and 1% TG produced significant changes in the physical properties of the rice-based gluten-free bread.

Renzetti *et al*. (2008) investigated the TG potential of network forming on flours from gluten-free cereals/pseudocereals: brown rice, buckwheat, corn, oat, sorghum and teff. Regarding buckwheat and brown rice the fundamental rheological tests showed a significant increase in the pseudoplastic behaviour when 10U of TG were used. The enzyme addition led to the significant improvement of the specific volume crumb hardness and chewiness. On the other hand, Renzetti *et al*. (2008)

noted that no effects of TGase could be observed on bread made of oat, sorghum or teff.

In another study, Gujral and Rosell (2004) studied the possibility of modifying the protein functionality from rice by cross-linking. They noted that the addition of TG improved the dynamic rheological properties of rice flour doughs. According to Gujral and Rosell (2004), due the improvement in rice protein functionality was possible to obtain rice bread with an increased specific volume and softer crumb at 1% TG level in the presence of 2% HPMC. The TG catalyzed cross-linking ensured the protein network suitable for the efficient retention of the gas produced during fermentation.

The effects of TG on the rheological and thermal properties of oat dough were evaluated by Huang *et al.* (2010). They showed that TG catalyzed cross-linking influence the dough water absorption, alters the viscoelastic behaviour, and enhances the thermal stability. During breadmaking the number of free amino groups decreased due to protein crosslinking catalysed by TG. Huang *et al.* (2010) demonstrated that both globulin and avenin from oat are good substrates for TG.

Recently Renzetti *et al.* (2010) have showed that *proteases* (EC 3.4.24.28) addition to oat flour improves its breadmaking behaviour. In another study, Renzetti and Arendt (2009) reported that protein degradation improves the breadmaking performance of brown rice flour by increasing batter deformability and paste stability during proofing and in the early stages of baking. On the other hand, controlled proteolysis has no influence on the breadmaking properties of the gluten free dough formulations based on sorghum and buckwheat.

Laccases (EC 1.10.3.2) are copper ion-containing enzymes that oxidize a wide range of phenolic compounds which result in the formation of free radicals with concomitant reduction of molecular oxygen to water (Buchert *et al.*, 2010; Joye *et al.*, 2009). Suitable substrates for lacasses are tyrosine containing proteins and ferulic acid esters linked to arabinoxylans. There is little available data on the efficiency of the laccase-catalyzed crosslinking on functionality of proteins.

Renzetti *et al.* (2010) showed that breadmaking performances of oat bread formulation can be significantly improved by addition of laccase and protease. The specific volume was increased and crumb hardness and chewiness was reduced. Laccase and protease increased the softness, deformability and elasticity of oat batters. Renzetti *et al.* (2010) explained that, in case of laccase, the effect is due to prevalence of β-glucan depolymerisation over protein polymerization, while in case of protease, the effect is due to the combined effect of protein and β-glucan degradation. Moreover, they considered that extensive protein hydrolysis during baking may have increased the functionality of the soluble protein fraction.

Glucose oxidase (EC 1.1.3.4) is considered an alternative to chemical oxidizing agents in the breadmaking. In the presence of molecular oxygen, the enzyme catalyses the oxidation of β-D-glucose to D-gluconic acid and hydrogen peroxide (Joye *et al.*, 2009).

Gujral and Rosell (2004) and Renzetti and Arendt (2009) reported the positive effect of glucose oxidase on the quality of gluten free bread based on white rice flour and with sorghum and corn flours, respectively. The increase of loaf volume and decreased of crumb hardness were noted.

In contrast, Renzetti *et al.* (2010) and Renzetti and Arendt (2009) observed that glucose oxidase did not affect bread quality in case of gluten free formulations that include buckwheat, teff and oat.

Sourdough technology

The sourdough is a stage in the breadmaking process, consisting of a mixture of flour and water fermented by lactic acid bacteria (LAB) and yeasts. In addition to the nutritional benefits, the use of sourdough in the breadmaking process ensures dough leavening, improvement of dough properties, of bread flavour, texture and taste, as well as shelf life extension (Banu and Aprodu, 2012; Hansen, 2006). The enzymatic equipments of LAB used for sourdough fermentation facilitate the macromolecules hydrolysis, therefore improving the bread digestibility (Katina *et al.*, 2005). Sourdough technology has a long tradition in rye and wheat bread making (Huttner and Arendth, 2010).

Recently sourdough technology was used for the production of gluten free bread. The suitability of a great variety of lactic acid bacteria and yeasts, as starters for wheat and rye sourdough was investigated (Vogelmann *et al.*, 2009). The main findings were that, there is a need for development and designing starter mixtures and fermentation conditions specific for sourdoughs prepared with gluten free flours (Huttner and Arendth, 2010). In this respect the work of Cagno *et al.* (2004) should be mentioned. They showed that selected sourdough strains are able to minimize the risks associated to gluten ingestion.

High hydrostatic pressure processing

High hydrostatic pressure is considered a technology that can enhance gluten free bread quality (Huttner and Arendt, 2010). Recent studies indicated that the high hydrostatic pressure can improve the functionality of protein and starch, by creating new structures and textures that compensates for the absence of gluten network (Ahmed *et al.*, 2007). Ahmed *et al.* (2007) and Huttner *et al.* (2010) investigated the effect of the high hydrostatic pressure on gluten free flours such as rice and oat, and reported the possibility to reduce the rate of stailing.

Conclusions

Because of their high incidence, the coeliac disease and other allergic reactions/intolerances to gluten are considered important public health concerns. It is therefore necessary to increase the efforts for developing high quality gluten-free products. In addition to efficient by exploiting the gluten free flours (rice, maize, sorghum, oat, buckwheat, amaranth, quinoa, teff) and specific ingredients/additives (starches, dairy products, egg proteins, dietary fibre, gum and hydrocolloids) for nutritional benefits and specific texture development of the bakery products, the latest researches have been focused on developing alternative technologies based on the use of enzymes (transglutaminase, glucose oxidase, laccases and proteases) sourdough technology and high hydrostatic pressure processing.

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