

Application of Extruded Maize Flour in Gluten-free Bread Formulations

Laila Ozola, Evita Straumite, Ruta Galoburda and Dace Klava

Abstract—Celiac disease is an immune-mediated disease, triggered in genetically susceptible individuals by ingested gluten from wheat, rye, barley and other closely related cereal grains. The only effective treatment is a strict gluten free diet for life. Latvian producers do not offer gluten-free products. In this research, use of extruded maize flour was tested for substituting rice, maize or buckwheat flour in gluten-free bread formulations at different ratios. Also the influence of extruded maize flour on the quality parameters of gluten-free bread was investigated.

The aim of research was to study the influence of extruded maize flour on gluten-free bread quality. Addition of extruded maize flour affect gluten-free bread crumb color, structure of crumb, weight loss and dry off of bread.

Keywords—extruded maize flour, gluten-free bread, quality

I. INTRODUCTION

CEREALS and cereal products are one of the major sources for human nutrition (carbohydrates, proteins, dietary fiber, many vitamins and non-nutrients) worldwide [1], [2].

Celiac disease (also known as non-tropical spure, gluten-sensitive enteropathy, celiac spure, idiopathic steatorrhea, primary malabsorption, Gee-Herter disease, gluten-induced enteropathy and adult celiac disease) is common complex disease caused by a dietary intolerance to gluten proteins found in all wheat types and closely related cereals such as barley and rye [1], [3]-[4]. The only effective treatment is a strict gluten-free diet throughout the life [5]. The term “gluten-free” does not refer to the total absence of gluten. In definition of gluten-free, some residual amount of gluten is allowed; this amount is strictly regulated [2]. Celiac disease is not only recognized as the most common food disease throughout Europe, but also in Middle East, Asia, Australia, America, and North Africa. Celiac disease occurs in adults and children with rates approaching 1% of the population [2]. Celiac disease is one of the most frequent genetically based diseases occurring in 1 of 130–300 in European population and 1 of 111 of the US population [6].

Gluten is composed of alcohol-soluble prolamins, which consist of gliadin fraction, and alcohol-insoluble glutelins,

which consist of glutenin fraction, portions that trigger the disease. The prolamin fractions are the most toxic for celiac patients and are known as gliadin in wheat, secalin in rye, and hordein in barley [2]. The gluten proteins in wheat have unique properties, such as good water absorption capacity, cohesiveness, viscosity and elastic properties. In a dough system, gliadin contributes to the viscous properties, while glutelin contribute to elastic properties. A proper mixture of both fractions is essential to impart the viscoelastic properties of dough. The adequate mixture of these fractions is only found in wheat, making this cereal the most valuable of all the food grains [2]. Maize, rice, tapioca, sorghum, amaranth, buckwheat and potato flour, which are allowed in a gluten-free diet, are not able to supply the same technological characteristics as gluten [7]. Replacement of gluten is one of the major challenges for gluten-free product development. The main task to food producers is production of high quality, tasty, inexpensive and easily available gluten-free products.

Nowadays, the number of people intolerable to grain albumen increase in Latvia, but Latvian producers do not offer gluten-free products. Usually, the gluten-free products are imported into Latvia from foreign countries and these are very expensive.

Many researchers has tried improving gluten-free bread quality using gluten-free flour mixtures [8], [9], additives such as hydrocolloids, gums, enzymes, emulsifiers [10], [11]. Researchers from Brazil produced gluten-free bread using extruded rice flour as a gluten replacement. Results showed that the gelatinization of starch by extrusion could make the gluten-free bread production process viable and improve the colour of the crust and texture characteristics, which were similar to those of wheat bread, despite presenting a low specific volume [12].

II. MATERIALS AND METHODS

Experiments were carried out at the laboratories of the Faculty of Food Technology, Latvia University of Agriculture in 2010 and 2011.

A. Ingredients

White rice (moisture $9.09 \pm 0.10\%$), yellow maize (moisture $10.97 \pm 0.10\%$), buckwheat (moisture $9.53 \pm 0.10\%$) flour, and extruded maize flour (moisture $6.69 \pm 0.10\%$) from *Joint Stock Company “Ustukių Malūnas”* (Lithuania), eggs, sugar, salt, apple vinegar, dry yeast and vegetable oil from local market were the materials used in study.

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B. Bread Making Process

The general technological scheme used to make the gluten-free bread is presented in Figure 1. All ingredients were mixed for 10 ± 3 min at minimum speed using a dough mixer BEAR Varimixer (A/S Wodschow & Co., Denmark). Dough was incorporated in the greased stainless rectangular moulds $7 \times 14 \times 7$ cm and fermented for 25 ± 3 min at 37 ± 2 °C temperature. Bread samples were baked at 200 ± 5 °C for 25 ± 3 min in convective oven and then cooled at 22 ± 2 °C for 40 ± 5 min.

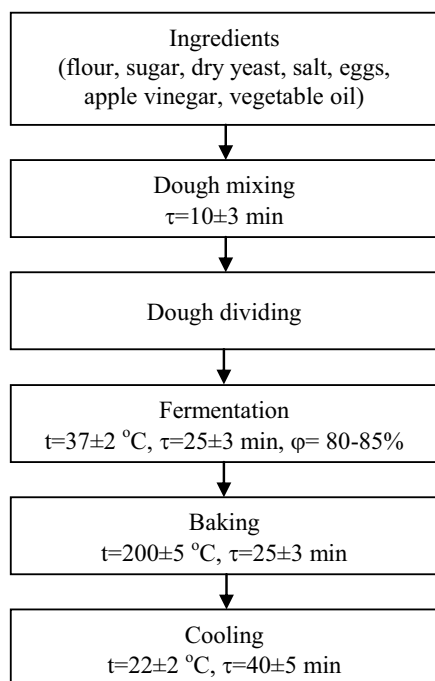


Fig. 1 The general technological scheme for gluten-free bread making

Six samples were prepared, and following abbreviations of the samples in the article are used:

- MB – maize bread;
- MBE – maize bread with extruded maize flour;
- RB – rice bread;
- RBE – rice bread with extruded maize flour;
- BB – buckwheat-rice bread;
- BBE – buckwheat-rice bread with extruded maize flour.

C. Microstructure Analysis

Structure of the bread crumb pores was analysed under the triocular microscope *Axioskop 40*. Pictures were taken by a digital compact camera *Canon PowerShot A620* via 16x40 magnification of the microscope. Size and area of cells and starch granules was measured using the software *Axioskop 4.7*. Equivalent diameter of bread pores was defined by the equation (1):

$$D = \sqrt{\frac{S \times 4}{\pi}} \quad (1)$$

where, D - equivalent diameter, μm ;

S – area, μm^2 ;

π - mathematical constant, 3.14159.

D. Color Analysis

Crumb color of the bread samples was measured in CIE $L^*a^*b^*$ color system using a *ColorTec-PCM/PSM* (Accuracy Inc., USA). Before measuring, the colorimeter was calibrated using a white reference tile and a light trap (black tile). For crumb color measurement, bread was sliced and the color was measured at five different points within the crumb region through the plastic pockets and mean values (total 10 readings/sample) were reported for each type of product. In color measurement, CIE $L^*a^*b^*$ coordinates show the degree of brightness (L), the degree of redness (+a), or greenness (-a), and the degree of yellowness (+b), or blueness (-b), respectively. An important factor characterizing the variation of color in the test sample is the total color difference or TCD [13]. The total color difference (ΔE) was defined by the Minolta equation (2):

$$\Delta L = (L - L_0), \Delta a = (a - a_0), \Delta b = (b - b_0)$$

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}, \quad (2)$$

where L, a, and b are the measured values of bread samples, L_0 , a_0 , and b_0 are the values of the respective bread samples without extruded maize flour additive (Table 2) or rice bread which was selected as reference point.

E. Moisture Content

Moisture content was analyzed by *Precisa XM 120* (Precisa Gravimetrics AG, Switzerland) at temperature 110 ± 1 °C in duplicate.

F. Bread Analysis

The percentage weight loss of bread (WL%) during the baking was calculated by measuring the weight of the bread samples before and after the baking process [14], [15]. The weight loss as the percentage was defined by the equation (3):

$$\text{WL}(\%) = \left[\frac{W_{\text{dough}} - W_{\text{bread}}}{W_{\text{bread}}} \right] \times 100, \quad (3)$$

where, WL (%) – weight loss of bread, %, (W_{dough}) – weight of the bread samples (dough) before baking, g, (W_{bread}) – weight of the bread samples after the baking process, g.

The measurements were done in triplicate for each sample.

The dry off percentages for bread (DO%) during the storage was calculated by measuring the weight of the bread immediately after baking process and after the cooling. The bread dry off as the percentage was defined by the equation (4):

$$DO(\%) = \left[\frac{W_{\text{bread}} - W_{\text{cool bread}}}{W_{\text{cool bread}}} \right] \times 100, \quad (4)$$

where, DO (%) – bread dry off, W_{bread} – weight of the bread after baking process, $W_{\text{cool bread}}$ – weight of the bread after the cooling process.

The measurements were done in triplicate for each sample.

G. Statistical Analysis

Statistical analysis was carried out using the SPSS Statistics software version 17.0. Significance of differences between gluten-free bread with and without extruded maize flour for each bread type was assessed using one-way analyses of variance (ANOVA) followed by Bonferroni's multiple comparisons test, significance was defined at $p < 0.05$.

III. RESULTS AND DISCUSSION

The quality of bread depends on quality of flour, so it is important to choose high-quality flour. Table 1 shows parameters of gluten-free flour.

One of the most important characteristics of the flour quality is moisture content. Flour moisture depends on the grain milling technology and flour storage conditions. Wheat flour moisture must not exceed 15%; otherwise the flour contains free water, which contributes to the development of microorganisms and effect positively enzyme activity. The process of nutrient degradation begins as a result of enzyme activity and causes adverse changes in quality of flour [16].

Gluten-free flour moisture ranges from $6.69 \pm 0.1\%$ (extruded maize flour) to $10.97 \pm 0.1\%$ (maize flour) (Tab. 1). Moisture content of gluten-free flour is relatively low; a small moisture content of extruded flour is the optimal for storage, which is experimentally proved. If the moisture content of extruded flour exceeds to optimum, it can cause adverse changes in quality of flour.

Starch granules differ in structure, size and shape depending on their botanical sources, which affect starch physicochemical properties. Size of starch granules affects the gelatinization temperature. Starches are widely used as food ingredients in gluten-free products to impart appearance and textural properties. These properties include gelling, texturizing, thickening, adhesion, moisture retention, stabilizing and anti-staling [17], [18].

The smallest starch granules were detected in rice flour $5.77 \pm 0.2 \mu\text{m}$, while starch granules of maize and buckwheat flour are nearly two times larger being $10.07 \pm 0.2 \mu\text{m}$ and $9.76 \pm 0.2 \mu\text{m}$, respectively (Tab. 1). The largest starch grains

TABLE II
GLUTEN-FREE BREAD FORMULATION

Ingredients (g)	MB	MBE	RB	RBE	BB	BBE
Maize flour	640	606	-	-	-	-
Rice flour	350	314	1000	860	510	460
Buckwheat flour	-	-	-	-	490	450
Extruded maize flour	-	80	-	140	-	90
Dry yeast	16	16	19	19	18	18
Sugar	82	82	76	76	100	100
Salt	16	16	16	16	6	6
Vegetable oil	130	130	56	56	280	280
Apple vinegar	20	20	8	8	-	-
Eggs	320	240	240	160	160	160
Water	760	800	500	780	1220	1220

MB – maize bread; MBE – maize bread with extruded maize flour; RB – rice bread; RBE – rice bread with extruded maize flour; BB – buckwheat-rice bread; BBE – buckwheat-rice bread with extruded maize flour.

were in extruded maize flour $17.98 \pm 0.2 \mu\text{m}$, due to the fact that flour properties changes during the extrusion process. In the extrusion process, pressure and temperature impact the size of starch granules, it increases, changes a structure, as a result increase flour ability bind water and swell [19].

Three types of gluten-free breads were made in the first series of experiment, where as the bases were used maize, rice and buckwheat flour. Samples were with unsatisfactory porosity and specific volume, crumb was dense and short. In order to improve the quality of bread, flour blends were prepared from maize and rice, buckwheat and rice flour. For each type of bread extruded maize flour was added in 5-25% from the total quantity of flour, as an alternative to food additives, to improve the texture and the quality of bread. The results show that the optimal ratio of extruded maize flour to maize bread is 8%, rice - 14%, buckwheat-and-rice – 9% of the total amount of flour. In the next set of dough recipe development experiments a ratio of the ingredients was defined – reduced amount of added water, eggs and vegetable oil. Thus the final gluten-free formulation was acquired (Tab. 2), which was found to be the best and was used in the further research.

Extruded maize flour affects stabilization and retention of gas cells; it helps to develop regular porosity in gluten-free bread crumb. Extruded maize flour affects the specific volume and the porosity of gluten-free bread. According to study of Ozola et al. the samples with extruded maize flour are softer than the samples without extruded flour, namely, buckwheat-rice bread with extruded maize flour by 8.4%, maize bread with extruded maize flour by 14.5% and rice bread with

TABLE I
PARAMETERS OF GLUTEN-FREE FLOUR

Flour type	Moisture, %	Size of starch granules, μm	Color values		
			L*	a*	b*
Rice	9.09 ± 0.1	5.77 ± 0.2	93.26 ± 0.79	-1.21 ± 0.87	9.65 ± 1.53
Maize	10.97 ± 0.1	10.07 ± 0.2	90.13 ± 0.29	-3.00 ± 0.32	31.64 ± 0.58
Buckwheat	9.53 ± 0.1	9.76 ± 0.2	71.22 ± 0.57	0.84 ± 0.52	22.17 ± 1.54
Extruded maize	6.69 ± 0.1	17.98 ± 0.2	82.87 ± 1.05	-2.22 ± 0.70	22.60 ± 1.22

extruded maize flour by 40.9% [20].

Digital images of the gluten-free maize bread (MB) and maize bread with extruded maize flour (MBE) are presented in Figure 2.

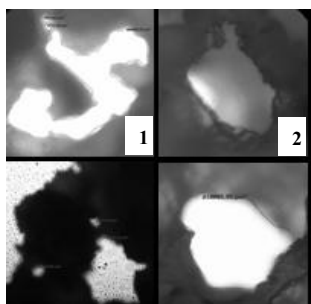


Fig. 2 Digital images of gluten-free maize bread (1) and maize bread with extruded maize flour (2) crumb pores (16x40)

Both maize bread samples have a homogeneous pore structure. Pores of maize bread are characterized by thin walls and so close to each other that coalescence in one network (Fig. 2). Equivalent diameter of MBE pores decreased from 578.9 μm to 434.5 μm . Crumb porosity of the maize bread samples with extruded maize flour (MBE) is homogeneous, because maize flour baking properties are similar to those of wheat.

Digital images of the gluten-free rice bread (RB) and rice bread with extruded maize flour (MBE) are presented in Figure 3.

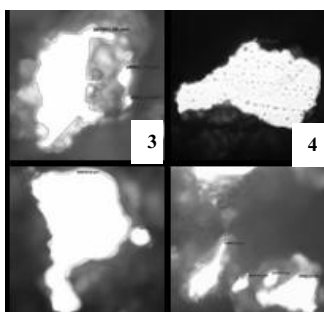


Fig. 3 Digital images of gluten-free rice bread (3) and rice bread with extruded maize flour (4) crumb pores (16x40)

Pores of rice bread are large with irregular structure, equivalent diameter 752.7 μm , added extruded maize flour improves porosity, equivalent diameter decreases to 620.1 μm (Fig. 3).

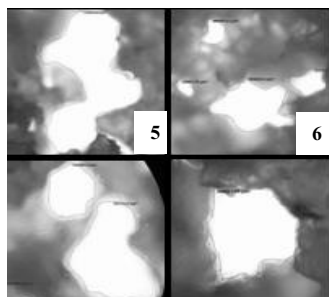


Fig. 4 Digital images of gluten-free buckwheat-rice bread (5) and buckwheat-rice bread with extruded maize flour (6) crumb pore

TABLE III
COLOR VALUES OF GLUTEN-FREE BREAD

Samples	Color values ^a			ΔE
	L*	a*	b*	
RB	65.09 \pm 1.21	-1.98 \pm 0.48	21.34 \pm 1.13c	-
RBE	65.67 \pm 1.40	-2.18 \pm 0.96	15.70 \pm 1.32c	5.67
MB	66.67 \pm 1.41	-3.16 \pm 0.65	33.72 \pm 1.49	-
MBE	66.44 \pm 1.99	-3.51 \pm 0.56	33.72 \pm 1.72	0.41
BB	54.79 \pm 1.14a	1.31 \pm 0.76b	18.99 \pm 1.15	-
BBE	52.79 \pm 1.64a	2.21 \pm 0.86b	18.76 \pm 0.94	2.20

Samples with same letters in the same column indicate significant differences between certain types of gluten-free bread with or without extruded maize flour ($p < 0.05$)

^a Average values and standard deviations

Digital images of the gluten-free buckwheat-rice bread (BB) and buckwheat-rice bread with extruded maize flour (BBE) are presented in Figure 4. The buckwheat bread samples has irregular pores, which are small and dense, more located along the crust (Fig. 4), equivalent diameter 587.8 μm . Added extruded maize flour decreased equivalent diameter to 420.9 μm , porosity of buckwheat bread with extruded maize flour is homogeneous with small and dense pores located all over the crumb.

Extruded maize flour has better water absorption capacity; it is associated with changes in starch granules during extrusion. Moisture content in maize and rice bread samples with extruded flour was higher by approximately 3.25% (maize bread with extruded maize flour) and 6.99% (rice bread with extruded maize flour) comparing to bread without extruded maize flour [20].

Color is variable measurement, depends on used materials, temperature, storage conditions and time, and spot of the measurement [21]. Table 3 shows the effect of extruded maize flour on color of bread crumb.

According to one-way analysis of variance extruded maize flour significantly affected some values of each bread type. The total color differences between the bread samples with or without extruded maize flour are expressed by ΔE . Extruded maize flour did not significantly affect crumb color of maize bread samples $\Delta E = 0.41$, but it significantly affected crumb color of rice bread $\Delta E = 5.67$, increased a* value (from -1.98 \pm 0.48 to -2.18 \pm 0.96), but b* value decreased (from 21.34 \pm 1.13 to 15.70 \pm 1.32) and crumb color lost pale shades and became more yellow, because extruded maize flour is darker comparing with rice flour, and has more typical yellow color (b* = 22.60 \pm 1.22). Crumb color of buckwheat-rice bread had impact of extruded maize flour $\Delta E = 2.20$, crumb became darker. Crumb of buckwheat-rice bread with extruded maize flour was the darkest (L* = 52.79 \pm 1.64) comparing with the other bread types.

ΔE values of crumb of gluten-free bread increased comparing with rice bread (Fig. 5). This may be due to the fact that different amount of sugar is used in different types of bread formulations that may promote the formation of brown pigment through Maillard type reaction or caramelization [17]. Another possible reason might be the naturally light color of

rice ($L^* = 93.26 \pm 0.79$) flour, in other gluten-free bread formulations was used relatively darker flour (maize flour $L^* = 90.13 \pm 0.29$, extruded maize $L^* = 82.87 \pm 1.05$, and buckwheat $L^* = 71.22 \pm 0.57$).

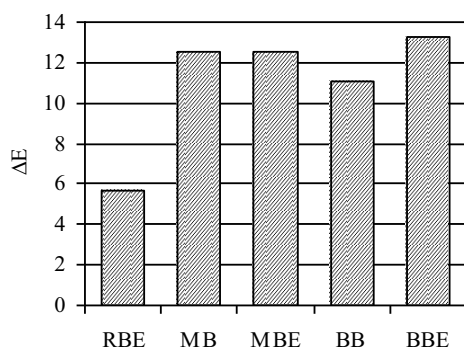


Fig. 5 The total color differences (ΔE) of gluten-free bread comparing to rice bread

RBE – rice bread with extruded maize flour, MB – maize bread, MBE – maize bread with extruded maize flour, BB – buckwheat bread, BBE – buckwheat-rice bread with extruded maize flour.

The major losses in bread making process are weight loss of bread. Changes in the values of weight loss of bread samples are calculated using the equation 3 and shown in Figure 6.

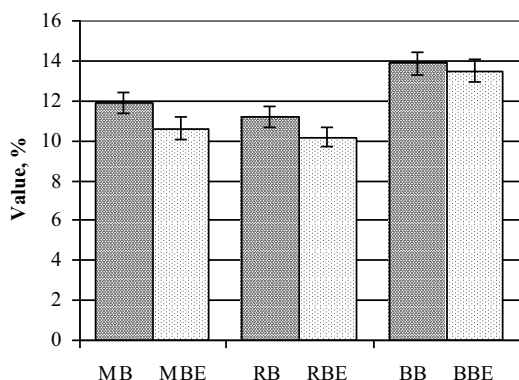


Fig. 6 Changes in the values of weight loss of bread samples

MB – maize bread, MBE – maize bread with extruded maize flour, RB – rice bread, RBE – rice bread with extruded maize flour, BB – buckwheat-rice bread, BBE – buckwheat-rice bread with extruded maize flour.

Addition of extruded maize flour decreased the weight loss of bread by 1.28% in the maize bread sample (MBE), 1.05% – rice (RBE) and 0.37% buckwheat-rice (BBE), which can be explained by changes in the starch granules during the extrusion; extruded maize flour has better water absorption capacity. Buckwheat-rice bread samples have the biggest weight loss of bread, but the smallest had the rice bread samples, comparing with other types of gluten-free breads. Rice bread with extruded maize flour had the smallest weight

loss of bread comparing with other types of breads, due to a fact that the added amount of extruded maize flour in rice bread is the largest comparing to other types of bread. Reference [16] shows weight loss of bread is 9 to 12%, according with that both maize and rice bread weight loss is within the limits, but buckwheat-rice bread samples exceed the above mentioned value.

The bread weight loss during storage was expressed as the bread dry off. Changes in the values of dry off of the bread samples were calculated using the equation 4 and are shown in Figure 7.

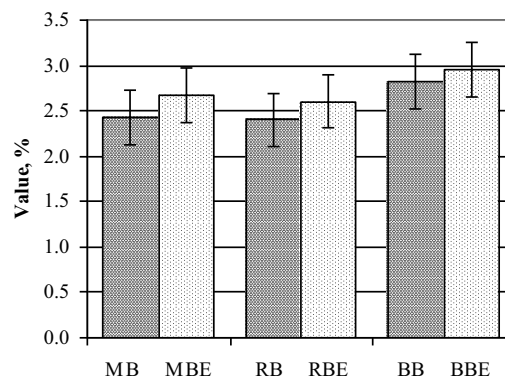


Fig. 7 Changes in the values of dry off of bread samples

MB – maize bread, MBE – maize bread with extruded maize flour, RB – rice bread, RBE – rice bread with extruded maize flour, BB – buckwheat-rice bread, BBE – buckwheat-rice bread with extruded maize flour.

The results show that gluten-free breads with extruded maize flour have a slightly higher dry off. Maize bread dry off is by about 0.25% lower than for bread with extruded maize flour, rice bread by 0.20%, buckwheat-rice bread by 0.13%. Comparing to the results presented in reference [16], which shows dry off of bread in the range from 1.5 to 2%, all gluten-free bread samples in this study have higher values of bread dry off.

IV. CONCLUSIONS

1. Porosity of gluten-free bread with extruded maize flour crumb was more homogeneous, equivalent diameter of pores decreased on average from 639.8 μm to 491.9 μm comparing to gluten-free bread without extruded maize flour.

2. Extruded maize flour affects gluten-free bread crumb color; color difference for maize bread with extruded maize flour comparing to maize bread was $\Delta E=0.41$, for buckwheat-rice bread with extruded maize flour $\Delta E=2.20$, and for rice bread with extruded maize flour $\Delta E=5.67$.

3. Addition of extruded maize flour decreased the weight loss of bread by 1.28% for maize bread with extruded maize flour, 1.05% – rice with extruded maize flour, and 0.37% buckwheat-rice with extruded maize flour.

4. Gluten-free breads with extruded maize flour has a slightly higher dry off, maize bread dry off is about by 0.25% lower than for bread with extruded maize flour, rice bread by 0.20%, buckwheat-rice bread by 0.13%.

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