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RESEARCH OF POLYSACCHARIDE AND PROTEIN SUPPLEMENTS INFLUENCE ON VISCOUS PROPERTIES OF GLUTEN-FREE DOUGH

Досліджено процес клейстеризації крохмалю в безглютеновій борошняній сировині в присутності гідроколоїдів та різних видів рідкої фази. Підтверджено обґрунтованість і доцільність застосування в рецептурі безглютенового бездріжджового хлібного тіста водних розчинів карбоксиметилцелюлози як потенційного розпушувача структури тіста. Встановлено суттєве зростанням в'язкості тіста в присутності цього рецептурного компоненту. Доведено ефективність застосування борошняних сумішей.

Ключові слова: *клейстеризація крохмалю, число падіння, борошняні суміші, безглютеновий хліб, карбоксиметилцелюлоза, рідка фаза тіста.*

1. Introduction

It is generally accepted that quality of grain and bread depends on both, quantity and quality of gluten and degree of damage of starch granules, and condition of grain amylase complex. Amylase complex is usually defined as a «falling number» (*FN*). *FN* of wheat flour can vary widely depending on flour quality. But the State Standard for wheat flour sets the lowest limit of it in the range of 160–185 sec. Optimal bread quality can be obtained with *FN* in the range of 200–400 sec.

FN indicator is crucial in assessment of baking properties of rye flour, because quality of rye bread depends on the state of starch in flour and activity of α-amylase. In case of wheat flour, if amylase activity is increased, the activity of proteolytic enzymes that cause the destruction of gluten is also high.

All the above is relevant primarily for bread that contains gluten, duration of dough making is long-term process, activity of enzyme complex is a very important factor.

Bakery products, which belong to gluten-free group, as the main raw materials include corn, rice, soybean and buckwheat flour. The major component of gluten-free dough is starch with the appropriate botanical origin. Due to the absence of gluten as a determining factor of structure forming substance in dough and finished product, the role of functional and technological behavior of starch is significantly increased. Under circumstances of microbiological fermentation being absent in dough formation, value of attacking index of starch grains due to the action of amylase enzymes is markedly reduced in contrast.

While heating, i.e., the initial stage of baking, one of the most important tasks is to ensure a certain level of dough viscosity and maintaining of dough loosening degree provided by mechanical method. This is a strong reason for research of colloidal status of starch grains, their ability to gelatinize, viscosity level of flour suspensions and dough in general, and the impact of structure-forming additives on these characteristics.

Thus, for gluten-free bread the dough making process, particularly with use of rice and/or corn flour, is characterized by significant differences. In a condition of gluten absence it is necessary to solve specific technological task – to provide certain rheological properties of dough and to get the desired degree of bread porosity.

If a yeast loosening method is used it is necessary to keep the carbon dioxide during short fermentation process and the first stage of baking of gluten-free dough. In the case of mechanical loosening of gluten-free non-yeast dough it is important to provide foamy structure during dough kneading and to keep this structure at the initial stage of baking.

Taking into account the increased viscosity of corn and rice flour, correction of rheological properties of dough while different ways of dough loosening, should be differently directed. We consider that it is appropriate to reduce *FN* index of flour for gluten-free dough to improve the viscoelastic properties of dough and bring them closer to wheat dough characteristics. *FN* index of gluten-free non-yeast dough can be slightly increased to provide good foaming ability and foam stability.

2. The object of research and its technological audit

The objects of research were different kinds of flour:
– rice (Fl_{rc}), corn (Fl_{cn}), buckwheat (Fl_{bt}) sorghum (Fl_{sm}), millet (Fl_{mt}), oat (Fl_{ot}) according to current reference documentation;
– flour mixture (Fl_{rc}:Fl_{cn} respectively 70 %:30 %);
– flour mixture (Fl_{sm}:Fl_{cn} respectively 5, 10, 20 %:95, 90, 80 %);
– flour mixture (Fl_{sm}:Fl_{rc} respectively 5, 10, 20 %:95, 90, 80 %);
– flour-water suspensions.

As research materials the following types of liquid phase were used:
– distilled water;
– milk whey TM «Zarechye»;

– yogurt with 1 % of fat content TM «Zarechye»;
– distilled water, milk whey, yogurt with 1 % of fat content with adding of 0.5 % of carboxymethyl cellulose.

Hydrothermal properties of water-flour suspensions were determined on the «Falling Number» instrument «FN 1700» (Sweden) and Brabender Amilograph (Germany).

We believe that in the production of gluten-free non-yeast dough technological concept lies first of all in providing of maximum foam forming ability of recipe mixture; secondly – in the maximum resistance of such foams during dough treatment (placing in shapes) and the first stage of baking.

Currently, there is no clear explanation of the reasons of the foam structures stability. Researchers involved in this issue [1] have taken various factors as the main reason:

– stability of foam films is explained via increasing of surface tension at the place of extension;
– stability of foam films is explained due to the formation of a special structure;
– foam stability is associated with disjoining pressure in thin liquid layers;
– viscosity of liquid is very high in foam films and it slows their thinning a lot.

Aggregate stability of foams is connected with their ability to maintain a constant disperse composition. Kinetic stability is related to liquid leakage from foam films and Plato-Gibbs channels. It is recognized that surface viscosity can't become a determining factor in foams stability, although correlation between these properties was established. The viscosity of adsorbed layer and film in general rises sharply when a solution of small amounts of surfactants (thousandths parts of a percent) is added. Implementation of surfactants must increase the ability of liquid to foam forming. Increasing of liquid viscosity, reduction of its volatility, as well as mechanical strength of foam, which depends on the phenomenon of surface orientation of the molecules contribute to formation of stable foams as well.

In summary, it can be claimed that to improve the porous structure of gluten-free non-yeast bread it is necessary to research influence of hydrocolloids on rheological properties of model water-flour suspensions.

3. The aim and objectives of research

The aim of research at this stage of the work was to determine the effect of different types of gluten-free flour and carboxymethyl cellulose on rheological properties of model water-flour suspensions with use of various liquid phases.

To reach the specified goal it is necessary to accomplish the following tasks:

1. To determine Falling Number index (*FN*) for different kinds of flour and flour mixture ($Fl_{rc}:Fl_{cn}$ respectively 70 % : 30 %).

2. To establish the dependence of this index on use of different liquid phases with adding of 0.5 % of CMC and without it.

3. To determine the viscosity of water-flour suspensions on the basis of corn and rice flour separately and in conditions of particular replacement of its quantity by sorghum flour in amount of 5, 10, 20 % respectively.

4. Research of existing solutions of the problem

It is known that gluten-free bread recipes involve different types of flour, such as rice, corn, sorghum, quinoa, amaranth, buckwheat and soybean [2]. These types of flour differ by the number of flour protein, starch characteristics (amylose and amylopectin ratio) particle size distribution. It is found that a variety of corn or grinding process affect on the physicochemical and sensory properties of bread [3]. Regarding rice flour, low amylose content leads to improvement of bread structure, but wax varieties (about 0 % of amylose) are not suitable itself for gluten-free bread [4].

Two groups of additives that fulfill the need of formation of viscoelastic properties of dough for gas retention during the dough making process and during the bread rise are hydrocolloids and proteins [5].

They are able to control the rheology of aqueous phase and stabilize the structure of emulsions, foams, suspensions, and multiphase systems [6]. Hydrocolloids are water-soluble polysaccharides with different chemical structure, which depends on the type of carbohydrate and provides a wide range of technical and functional properties. They are widely used as structuring agents to simulate the viscoelastic properties of gluten.

Hydrocolloids and proteins are able to increase dough volume, stabilize its foamy structure by increasing the viscosity, flocculation and coalescence, prevent influence of aqueous phase and, thus improve the stability of the film liquid that surrounds gas bubbles [7].

Typically, neutral hydrocolloids are less soluble, while polyelectrolytes have a greater solubility. However, the dynamics of hydration depends on many other factors. Carboxymethyl cellulose (CMC), guar and xanthan gums have the ability to be dissolved in cold water. Carrageenan, carob gum and alginates require a significant amount of hot water for an effective hydration. Water is held in intermolecular and intramolecular cavities and through the formation of hydrogen bonds. Since this interaction is caused by hydrogen bonds and, therefore, depends on the temperature and pressure, as well as the formation of water clusters. This interaction is determined by hydrogen bonds, that is why it depends on temperature and pressure as well as water clusters formation [8].

Hydrocolloids and thickeners are mainly used in gluten-free bread for various reasons, including gelatinization, thickening and structure development [9]. They remain in a form of polysaccharides and/or proteins from various sources of seeds and fruits. These are herbal extracts, algae and microorganisms [10]. Among starches, the most traditionally used substances for gluten replacement are, first of all, corn and potato starch because of their functional characteristics, price and availability, as well as corn starch, rice and sorghum [5].

The effective influence of xanthan, gum, carob gum, agar, methyl cellulose (MC), carboxymethyl cellulose (CMC), hydroxypropylmethyl cellulose (HPMC) and mixtures (gum and xanthan, xanthan and carob gum) on porosity of gluten-free bread was established [11]. By impact effectiveness on the elasticity and resistance to deformation of gluten-free dough recipes hydrocolloids form an order «xanthan > CMC > pectin > agarose» [12]. The interaction between HPMC (2–4 g/100 g of flour) and rice flour, which has a positive effect on the rheological properties of gluten-free bread, was proven [13]. But while rising of dough hydration level, effect of hydrocolloids on dough rheology was reduced. The combination of CMC and HPMC demonstrated a good compatible effect on the viscoelastic properties of gluten-free dough [14].

Overall, in recent years the number of publications in scientific journals on the production of gluten-free baking products is growing rapidly:

– from 10 papers a year in 2000–2006;
– from 50 to 70 papers per year in 2010–2014;
– to 100 papers a year in 2015 [15].

Researchers suggest various approaches to solve this task:

– use of different types of gluten-free flour (rice, corn, sorghum, soybean, buckwheat);
– starches (corn, potato, cassava, rice, beans);
– milk ingredients (caseinate, skimmed milk, milk powder, whey);
– hydrocolloids (guar and xanthan, alginate, carrageenan, HPMC, CMC);
– emulsifiers and others.

Actually hydrocolloids are used as structuring agents that are able to imitate gluten and viscoelastic properties of gluten-free bread.

However, scientific data connected with effect of hydrocolloids on quality forming of gluten-free non-yeast bread in general and on rheological properties of dough masses were not found in current information resources.

Most of these papers are devoted to current issues of gluten-free bread production with use of yeast as baking loosening agents. In other words, the rheological properties of dough masses should provide maximum preservation of gas bubbles in a long fermentation, and the first stage of baking.

5. Methods of research

«Falling number» indicator was determined by Hagberg-Perten method according to GOST 30498-97. The main point of method is to determine the total time (from the moment of viscometric tube immersing in boiling water) that is required for mixing the suspension by rod stirrer, and for its free fall through this suspension from the liquid phase and flour.

Viscosity indicator for aqueous suspensions of mixtures from rice or corn flour with sorghum flour was determined by the ISO 4235:2003. The method is based on viscosity assessment of suspension during its gelatinization by heating using Brabender Amilograph to reveal influence of amylase enzyme and starch properties on gelatinization process.

The processing of experimental data was performed using the application package MS Office Excel (USA).

6. Research results

At the first stage of experiment, *FN* research of different types of flour, and dependence of this index on a liquid phase and CMC content were conducted. It was shown that use of different types of flour has a significant impact on the studied index (Fig. 1, 2). The lowest values of FN were observed for sorghum flour (within 60–65 eq. un. – Fig. 1, *c*) regardless of the liquid phase and the presence of CMC.

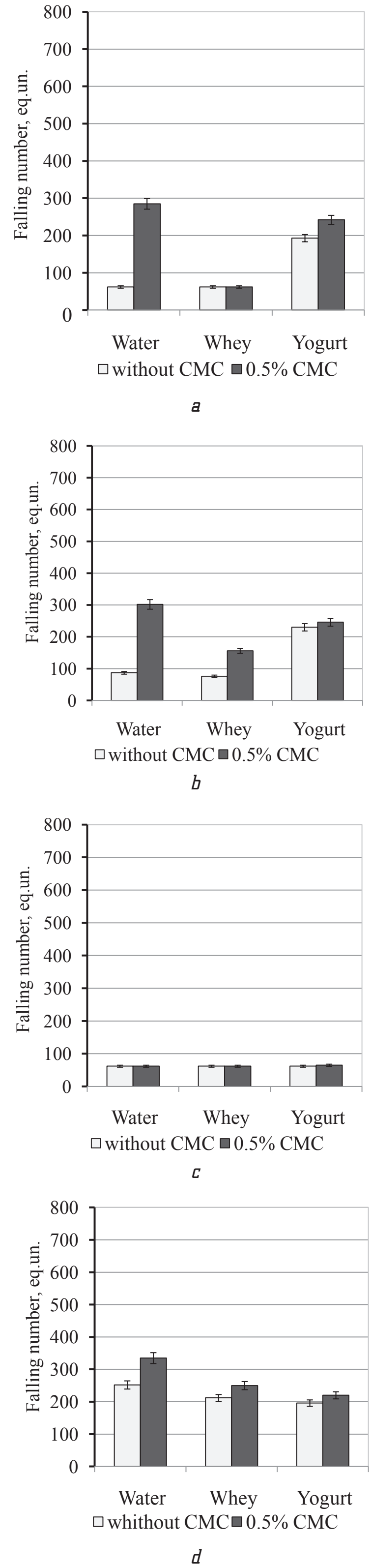
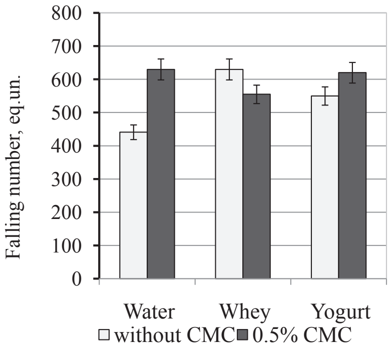


Fig. 1. «Falling number» index of water-flour suspensions on the basis of different types of flour: *a* – buckwheat flour; *b* – oat flour; *c* – sorghum flour; *d* – millet flour and liquid phases: water, whey, yogurt with adding of 0.5 % CMC

As for buckwheat and oat flour, the use of yogurt caused a significant increase of *FN* index – in the rate from 60–85 eq. un. to 200–230 eq. un. (Fig. 1, *a*, *b*). It can be assumed that a significant increase of viscosity in this particular system is connected with protein-protein interaction between animal and plant proteins. Such interactions prevailed since hydrocolloids adding (CMC) did not dramatically increase *FN* index.



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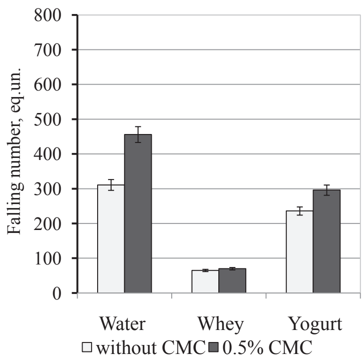

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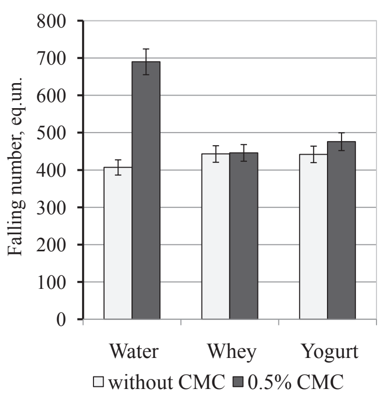

c

Fig. 2. «Falling number» index of water-flour suspensions prepared from different types of flour: *a* – rice flour; *b* – corn flour; *c* – flour mixture «$Fl_{rc}:Fl_{cn}$ that corresponds to 70 % : 30 %» and liquid phases: water, whey, yogurt with adding of 0.5 % CMC

Adding of CMC aqueous solutions to these types of flour, apparently led to increase of hydration degree of macromolecular substances; *FN* index has risen nearly in 5 times – up to 300 eq. un. But the presence of protein-polysaccharide interaction also can't be excluded, although it requires a more detailed research.

Water-flour suspensions prepared from a millet flour and various liquid phases are characterized by *FN* index within 200–250 eq. un. CMC addition slightly increased it – mostly in that case when we used water as a liquid phase, i.e. in the absence of animal protein.

In case of rice flour usage, systems viscosity has grown rapidly – from 440 eq. un. in the control sample (water) to 550–630 eq. un. (for yogurt and whey) (Fig. 2, *a*). It corresponds to the assessment of rice flour as highly effective raw materials for gluten-free bread with consideration for quality of the finished product. Adding CMC has contributed to the further improvement of the studied parameter.

Values of the sample based on corn flour (Fig. 2, *b*) were lower in a comparison with rice flour. *FN* index of the sample of mixture «$Fl_{rc}:Fl_{cn}$ that corresponds to 70 % : 30 %» (Fig. 2, *c*) has had a middle values in comparison with mentioned flours. However, particularly significant increase of *FN* index was established for sample based on flour mixture with adding of 0.5 % water solution of CMC – almost up to 700 eq. un. These data perfectly correspond to results of the laboratory baking. Good results have been found for bread from different flours in the presence of 0.5 % of CMC, including the best options – based on rice and corn flour mixture.

On the next stage of research, effect of sorghum flour on viscosity of water-flour suspensions from rice and corn flour was determined. As it is known, sorghum flour is widely used in the production of healthy food because of the high content of essential amino acids. However, its use as a part of the flour mixture for gluten-free bread production to regulate structural and mechanical properties of the final product needs to be studied in details.

Research of viscosity of water-flour suspension were conducted with addition of sorghum flour in the amount of 5, 10 and 20 % by weight of corn or rice flour, and as a control sample rice flour and corn without additives were used. The experimental data are presented in Tables 1, 2.

Amylogram analysis is shown that implementation of sorghum flour in mixture with corn flour in amount of 5.0...20.0 % increases time of starch gelatinization beginning by 7.4...14.8 %, and reduces time of starch gelatinization completion by 2.2...6.6 %.

Maximum viscosity of the suspension was reduced due to adding of sorghum flour by 5.5...8.3 %, which can be explained by a decreased amount of starch in the samples with additives by partly replacement of corn flour. Temperature of suspension with maximum viscosity level was also reduced from 1.1 to 5.3 %.

Similar research has been conducted for water flour suspensions on the basis of rice flour (Table 2).

Table 1

Influence of sorghum flour on the properties of the corn starch

Sample	Amount of additives, %	Indexes			
		Time of starch gelatinization beginning, min	Time of starch gelatinization completion, min	Maximum suspension viscosity, am. un	Temperature of suspension with maximum viscosity level, °C
Fl_{cn}		27.0	45.0	720.0	95.0
Fl_{sm}	5.0	29.0	44.0	680.0	94.0
	10.0	30.0	40.0	660.0	93.0
	20.0	31.0	42.0	660.0	90.0

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Table 2

Influence of sorghum flour on the properties of the rice starch

Sample	Amount of additives, %	Indexes			
		Time of starch gelatinization beginning, min	Time of starch gelatinization completion, min	Maximum suspension viscosity, am. un	Temperature of suspension with maximum viscosity level, °C
Fl_{rc}		32.0	47.0	760.0	93.0
Fl_{sm}	5.0	30.0	45.0	500.0	92.0
	10.0	30.0	43.0	480.0	91.0
	20.0	31.0	39.0	400.0	89.0

Research results of rice and sorghum flour mixtures have shown a similar trend. Addition of sorghum flour in the amount of 5.0 to 20.0 % also increased time of starch gelatinization beginning by 3.1...6.25 %, and reduced time of starch gelatinization completion by 4.25...17.0 %.

Maximum viscosity of the suspension was reduced more significantly, namely by 34.2...47.3 % while adding of 5.0 to 20.0 % of sorghum flour, respectively. Perhaps this trend is caused by the fact that significant part of sorghum flour consists of dietary fiber that can absorb formidably less amount of moisture.

In addition, it should be noted that the temperature decrease of suspension with maximum viscosity level may be a prerequisite to slow down the process of bread firming because it is believed that lowering of this index can slow the process of starch retrogradation [16].

7. SWOT analysis of research results

Strengths. Among the strengths of this research it should be noted that the findings point to the positive impact of hydrocolloids and flour additives on carbohydrate-amylase complex of gluten-free dough. Adding of CMC increases FN index of water-flour suspensions, indicating the formation of more stable systems for improvement of porous structure of gluten-free non-yeast bread. In addition, implementation of flour additives (sorghum flour) can adjust beginning and completion of starch gelatinization in aqueous suspensions of flour for gluten-free bread yeast dough that leads to lengthening the shelf life of the product.

Weaknesses. Weaknesses of this research are related to the simultaneous use of several components and providing of continuous whipping of dough for obtaining of gluten-free bread with porous structure. This can lead to a slight increase in production costs as manufacturing of gluten-free products requires implementation of additional equipment.

Opportunities. It is known that in the process of moisture binding in dough not only polysaccharides are involved but also proteins. Therefore, further research should be aimed at establishing of polysaccharide-protein interactions between proteins and hydrocolloids of flour.

In the development of this research direction it is necessary to determine the effect of CMC and liquid phase on hydrothermal properties of starches from different flour raw materials and dough viscosity. Understanding of protein-polysaccharide interactions behavior contributes to stabilization of the quality of gluten-free bread, reducing time of production process and expanding the product assortment.

Threats. Difficulties in implementation of obtained results may be related to the fact that manufactures are mainly focused on the production of bakery products for mass consumption that is made from wheat flour containing gluten. The presence of gluten and its residues in gluten-free bread is not allowed. Therefore producers for the production of gluten-free products should use separate manufacturing equipment (lines), which entails additional economic costs.

8. Conclusions

1. It was determined that use of different types of flour and flour mixes significantly affects on *FN* index. Thus, the lowest values of *FN* index were observed for sorghum flour (within 60–65 eq. un.) regardless of the liquid phase, the highest – for rice (in the range of 440 eq. un. in control sample based on water to 550–630 units eq. un. in samples based on yogurt and whey).

2. It was established that the addition of CMC solutions to different types of flour except of sorghum flour, led to increase of the degree of hydration of macromolecular substances. FN index increased in comparison with control samples. Particularly significant growth of FN index was established for sample based flour mixture ($Fl_{rc}:Fl_{cn}$ respectively 70 %:30 %) by adding 0.5 % of aqueous CMC – almost up to 700 eq. un.

3. It was proved that the index of maximum viscosity of suspension while adding of 5...20 % of sorghum flour to corn flour decreased by 5,5...8,3 % in comparison with control sample. The maximum viscosity of suspension while adding of 5...20 % of sorghum flour to rice flour reduced more significantly, i.e. by 34.2...47.3 % in comparison with control sample. Perhaps this trend is caused by the fact that part sorghum flour is occupied by dietary fiber that can absorb significantly less amount of moisture.

Thus, experimental studies confirmed the justification and feasibility of aqueous solutions of CMC as a potential dough loosening agent in a non-yeast bread recipe of gluten-free dough. It is connected, in particular, with a significant increase of dough viscosity in the case of presence of the recipe component.

Moreover, it is advisable to use flour mixture based on rice and corn flour with sorghum flour for the production of gluten-free bread, which positively affects the process of starch gelatinization and slow down the process of bread firming.

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ИССЛЕДОВАНИЕ ВЛИЯНИЯ ПОЛИСАХАРИДНЫХ И БЕЛКОВЫХ ДОБАВОК НА ВЯЗКОСТНЫЕ СВОЙСТВА БЕЗГЛЮТЕНОВОГО ТЕСТА

Исследован процесс клейстеризации крахмала в безгллютеновом мучном сырье в присутствии гидроколлоидов и разных видов жидкой фазы. Подтверждены целесообразность и обоснованность использования в рецептуре безглютенового бездрожжевого хлебного теста водных растворов карбоксиметилцеллюлозы как потенциального разрыхлителя структуры теста. Установлено существенное увеличение вязкости теста в присутствии этого рецептурного компонента. Доказана эффективность использования мучных смесей.

Ключевые слова: клейстеризация крахмала, число падения, мучные смеси, безглютеновый хлеб, карбоксиметилцеллюлоза, жидкая фаза теста.

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