

## Biological Value Changes in Wheat, Rye and Hull-less Barley Grain During Biological Activation Time

### Kviešu, kailgraudu miežu un rudzu graudu bioloģiskās vērtības izmaiņas bioloģiskās aktivēšanās laikā

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**Abstract.** Cereal products are the main part of human diet, as they contain high amount of proteins, carbohydrates, vitamins, and dietary fibre. Germinated seeds, grain and grain germs have already been used in food since ancient times. Biologically activated grain application is a new direction in white bread technology. The aim of the investigation was to determine the optimal wheat grain activation parameters and study the changes of biological composition in wheat, hull-less barley, and rye grain during activation process. Wheat, rye and hull-less barley grain were biologically activated with the purpose of adding such grain to wheat dough and of increasing biological value of wheat bread. It was found that the optimal grain biological activation parameters were: relative air humidity –  $80\pm 1\%$ , temperature –  $+34\pm 1^\circ\text{C}$ , and time –  $24\pm 1$  h. The quality of gluten in wheat grain became unsatisfactory during the grain activation of up to 36 h due to the occurrence of intense dissimilation processes during activation time. Gluten was found neither in activated nor in inactivated rye and hull-less barley grain. The content of dietary fibre, vitamins B<sub>2</sub>, E and niacin increased and vitamin C synthesized during the grain activation time. Compared to inactivated grain samples, activated hull-less barley grain showed an increase in glycosamin content, i.e., by 4.7 times, while in rye and wheat grain the content of glycosamin increased only 1.7 times. The developed mathematical model demonstrates that the change in the falling number value during grain activation depends on the grain activation time.

**Key words:** biological activation, hull-less barley grain, gluten, dietary fibre, air humidity.

### Introduction

Cereal products are the main part of human diet, as they contain high amount of proteins, carbohydrates, vitamins of group B, and dietary fibre. Germinated seeds, grain and grain germs have already been used in food since ancient times. Vitamin C was found in soybean's germ in 1782, as a result such grains were used for the treatment of scurvy (Nöcker, 1995).

The literature provides a description of some examples on the use of germinated wheat grain in bread and confectionary industry (Хоперская, 1995, 1998; Djačenko, 2002; Хоперская, 2004).

The results of researches show that germinated grain is a healthy product and, if such grain is used in conventional food, it would intensify metabolism, strengthen immunity, compensate deficiency of vitamins and mineral substances, and normalize acid and alkali balance.\*

The activity of enzymes increases during germination: endohydrolase enzymes

( $\alpha$ - and  $\beta$ -amylases), proteolytic enzymes, diphenoloxsydase, and catalyse are activated. Stability of gluten depends on the amount of formed disulfide bonds (-S-S-) and on disulfide bonds correlation with the sulfhydryl groups (-SH-) (Казаков, Кретович, 1989; Hugh et al., 1998).

Protein content in wheat grain varies between 7–20% from the total dry matter content (Kulp et al., 2000). Whereas composition of amino acids is a very important aspect for wheat grain. The amount of amino acids is higher in the central part of a grain compared to periphery. The aleurone protein has a higher food value compared to protein of endosperm (Казаков, Кретович, 1989; Johansson, 1995; MacRitchie, 1999; Tanacs et al., 1994). Gluten content is the most important part of wheat albumen.

In rye grain, the protein content (9–20% from total dry matter) is lower, whereas that of essential amino acids – by 1.5 times higher (lysine and threonine)

\* Иванов, С.Г., Шаскольская, Н.Д., Харламова, А.Н. (2005) *Оздоровительные свойства пророщенных семян и эффективность лечения пациентов, страдающих хроническим гепатитом «С», пророщенными семенами расторопши*. Доказательная медицина: <http://newmedt.ru/atat12.php> – accessed on 27.09.2005.

compared to wheat grain (Казаков, Карпиленко, 2005; Lásztity, 1996).

Rye grain starch gelatinization temperature is lower (+52 – +55 °C) compared to wheat grain. The amount of riboflavin and vitamin E in rye grain is higher. Physical properties of rye grain gluten are similar to those of wheat grain – it is with lower elasticity and stability. Gluten content in rye grain makes up 40% from the total amount of protein. The biggest part of rye grain albumen dissolves in water and low-concentration salt dilutions. The increase in glutenin amount promotes strengthening of gluten (Казаков, Кретович, 1989).

In food industry, hull-less barley is considered as more valuable and more economical compared to flaky barley. The hull-less barley flour has a little darker colour because, compared to flour from soft wheat, it has a higher ash value and a higher protein and  $\beta$ -glucans content. Soluble dietary fiber, mainly  $\beta$ -glucans, provides a promoted viscosity. As a result, digestion, cholesterol and fat absorption are decreased (Bhatty, 1999; Bengtsson et al., 1990; Newman, Newman, 1991; Belicka, Bleidere, 2005; Legzdina, 2003). Compared to wheat and rye grain, the highest content of natural antioxidants (copherol and tocotrienols) and vitamin E is established in barley grain. Protein content in hull-less barley grain is from 9 to 20% from total dry matter (Shewry, 1993). The properties of barley gluten, similarly to rye grain gluten, are similar to those of wheat grain gluten with poor quality. The proteolytic enzyme papain activity deteriorates the quality of gluten (Казаков, Кретович, 1989).

Total sugar content is approximately  $\frac{3}{4}$  from total dry matter in wheat, rye, and hull-less barley grain.

Information can be found in the literature that the biological value of grain is increased during the grain germination time. No data was found on the changes in physical and chemical composition of rye and hull-less barley grain, especially during the activation time in various activation stages, therefore it is necessary to determine the optimum grain biological activation time when grain has the highest biological value but its structure has not considerably changed.

The purpose of this research was to study the changes in physical-chemical and biological properties in rye, wheat, and hull-less barley grain during the biological activation process.

The objectives were:

- to determine experimentally the optimal parameters for grain activation – temperature, relative air humidity, and activation time;
- to investigate the qualitative changes in grain during the biological activation process.

## Materials and Methods

For the research the following materials were used: wheat grain (variety 'Kontrast'), rye grain (variety 'Voshod') harvested in 2003 by the limited liability company „Zelta vārpa 5”, and hull-less barley grain cultivated at Priekuļi Plant Breeding Station in Latvia and harvested in 2004, as well as drinking water for grain rinsing and steeping in compliance with Regulations No. 235 of the Cabinet of the Republic of Latvia „Compulsory Requirements for Harmlessness of Drinking Water”, 2003\*.

Grain was washed ( $H_2O$  t = +20±1 °C) and wetted ( $H_2O$  t = +20±1 °C,  $\tau$  = 24±1 h). Grain biological activation was performed in the climatic chamber at temperatures (t) +25±1, +30±1, and +35±1 °C at constant relative air humidity ( $\varphi$ ) of 80±1% for up to 36 hours (h).

For determination of the quality of raw materials, standard methods were used.

**Grain moisture** was determined by the standard method LVS 272.

**The content of gluten** was determined by the standard Perten method LVS 275 and using the equipment „Glutomatic”.

Changes in the **falling number** in grain were determined by the standard Hagberg-Perten method LVS 274.

**Fat content** was determined by the standard method ISO 6492 using the equipment „Büchi Extraction System B-811”.

**Dietary fibre** content was determined by the standard method ISO 5498 using the equipment „Fibertec system 1010 Heat Extractor”.

**Total protein content** was determined by the standard method AACC 46-20 by means of a Kjeldahl method.

**Total sugar content** was determined by the standard Bertran method. The combustion of keton group boiling solution with Felling reagent forms the base of this method.

**The content of amino acids** was determined by the chromatographic method using the amino acid analyser „Mikrotechna AAA 831” (Козаренко и др., 1981).

**Vitamin C content** was determined by the Tillman's method. The method is based on the extraction of L-ascorbic acid from the analysing material by means of the oxalic acid and conversion of 2,6-dichlorophenolindophenol into dehydroascorbic acid (Matiseks, Šnēpels, 1998).

**Niacin content** was determined by the method of Stepanova using a photoelectrocolorimeter (Нестерова, 1967).

**Vitamin B<sub>1</sub>** content was determined by means of the fluorometer „Specol 11” in compliance with the

\* Dzeramā ūdens obligātās nekaitīguma un kvalitātes prasības, monitoringa un kontroles kārtība (2006): <http://www.likumi.lv/doc.php?id=75442> – accessed on 18.12.2006.

Table 1

## Characterisation of grain activation parameters

Type of grain	$\varphi = 80 \pm 1\%$ $\tau = 24 \pm 1 \text{ h}$ $t = +25 \pm 1 \text{ }^\circ\text{C}$		$\varphi = 80 \pm 1\%$ $\tau = 24 \pm 1 \text{ h}$ $t = +30 \pm 1 \text{ }^\circ\text{C}$		$\varphi = 80 \pm 1\%$ $\tau = 24 \pm 1 \text{ h}$ $t = +34 \pm 1 \text{ }^\circ\text{C}$	
	Sprouted, %	Unsprouted, %	Sprouted, %	Unsprouted, %	Sprouted, %	Unsprouted, %
Rye	75	25	85	15	88	12
Hull-less barley	70	30	75	25	80	20
Wheat	69	31	88	12	91	8

Jansen's method by the modification of Jelesjeva (Matiseks, Šnēpels, 1998).

**Vitamin B<sub>2</sub>** was determined by means of the fluorometer „Specol 11” according to the method of Povolocka and Skorobogatova (Нестерова, 1967).

Determination of the amount of **vitamin E** is based on the ability of tocopherol to oxidise. Vitamin E was oxidized with FeCl<sub>3</sub>, while iron – with  $\alpha$ - and  $\alpha^1$ -dipiridil (Вальдман и др., 1993).

**Glycosamin content** was determined by means of the amino acid analyser „Mikrotechna AAA 831”. A new determination method was developed: N-acetylglucosamin at the ratio of 1 : 1 was added to grain extract, as a result of which the subsequent peak between amino acid tyrosine and histidine was assumed as glycosamin.

## Results and Discussion

The research proved that optimal **grain biological activation parameters** in the climatic chamber were:  $\varphi = 80 \pm 1\%$ ,  $t = +34 \pm 1 \text{ }^\circ\text{C}$ , and activation time – up to 36 hours. The characterisation of grain activation parameters is shown in Table 1.

Prior to the experiments, **the value of grain falling number** was 493 s for hull-less barley, 460 s for wheat, and 173 s for rye grain. The falling number for all kinds of grain was 62 s after grain activation for 36 hours. Such changes can be explained by biochemical reactions occurring in grain during activation as a high activity of  $\alpha$ - and  $\beta$ -amylase enzymes are observed (Ruža, 2001), as a result of which starch is split.

**Qualitative and quantitative changes in gluten.** Inactivated wheat grain and grain activated for 12, 24, and 36 hours were tested. Qualitative gluten was not found in the rye and hull-less barley grain. It was observed that the amount of dry gluten in wheat grain activated for 24 hours decreased 6.7 times, gluten index – 2.5 times, and gluten hydration

properties – 1.2 times. After wheat grain activation for 36 hours, gluten was not detected. This can be explained by the dissimilation processes during grain activation time and by the decrease in protein content. Therefore in order to obtain good quality gluten, grain activation time should not exceed 24 h. This can be mainly explained by the increased amount of gliadin, as well as by the decreased correlation between disulphide bonds and -SH- groups in activated rye grain and by enzyme paphain activity in hull-less barley grain (Казаков, Кретович, 1989; Hugh et al., 1998).

**Changes in fat content during grain activation.** Changes in fat content were not considerable during the biological activation time. The activity of 3-acetylglucercolliphase and lipoxigenesis enzymes increased during the grain activation time for up to 24 hours, compared to the inactivated grain samples.

**Changes in total protein content.** Proteins were split by proteolytic enzymes, as a result of which the total protein content decreased during the grain activation time. During the grain activation time for up to 24 hours, the total protein content decreased more intensively in rye grain (9.4 times), but in wheat and hull-less barley grain these changes were not so significant (from 13.18 to 12.89% and from 17.35 to 12.16% accordingly) (Fig. 1).

**Changes in dietary fibre content in grain during the activation time.** Dietary fibre content increased from 2.59 to 2.83% in rye grain, from 1.64 to 2.18% in hull-less barley grain, and from 3.22 to 3.34% in wheat grain (Fig. 2) during activation for up to 24 hours. Such changes can be explained by the activity of amylolytic enzymes and splitting of cellulose and maltose.

**Changes in total sugar content.** The highest total sugar content (6.00%) was determined in inactivated rye grain which was 2.4 times higher compared to hull-less barley grain and 1.8 times higher compared to wheat grain.

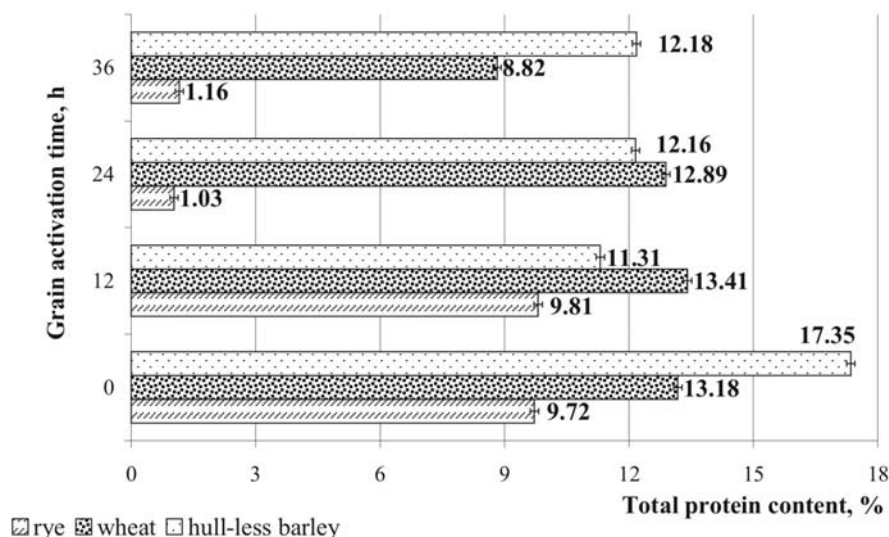


Fig. 1. Decrease in total protein content in grain during grain activation time.

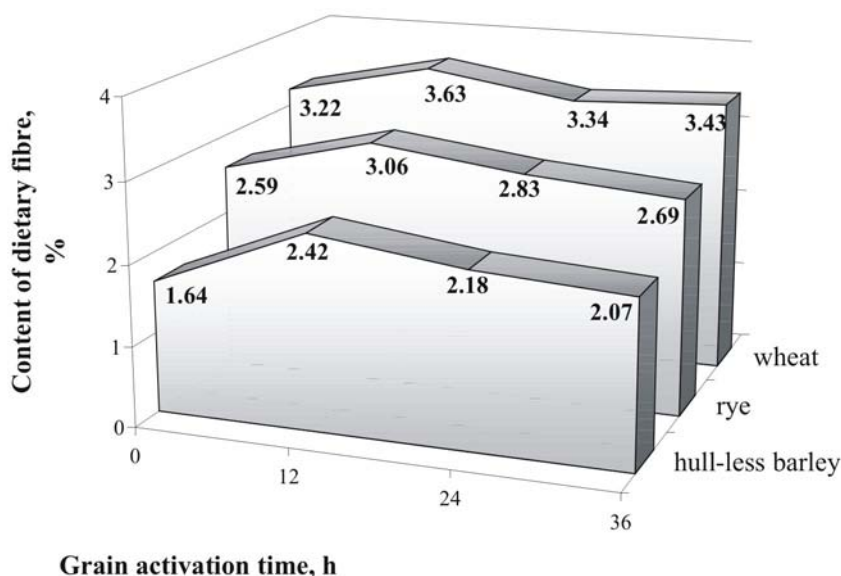


Fig. 2. Dynamics of dietary fibre content in grain during grain activation time.

The amount of total sugar content increased 1.3 times in hull-less barley grain, 1.2 times in rye grain, and 2.0 times in wheat grain during the grain activation time for up to 24 hours (Fig. 3) which can be explained by the synthesis of carbohydrates in cell walls of grain for grain sprout development.

**Changes in vitamin content in grain during the activation time.** The amount of **vitamin B<sub>1</sub>** in the activation process of wheat, rye and hull-less barley grain considerably decreased (Fig. 4).

The decrease in vitamin B<sub>1</sub> content can be explained by the possible metabolism and biochemical reactions occurring during the activation time and the availability of vitamin B<sub>1</sub> in enzyme phyrovatdecarboxylasis which participates in the growth and splitting reactions of

carbohydrates occurring in grain (Казиков, Кретович, 1989). During the activation for up to 24 hours, the content of vitamin B<sub>1</sub> decreased by 32.10% in wheat grain, by 57.78% in rye grain, and by 17.39% in hull-less barley grain.

Contrary results were observed for the content of **vitamin B<sub>2</sub>** (Fig. 5). The amount of vitamin B<sub>2</sub> increased by 45.5% in rye grain, by 54.5% in wheat grain, and by 88.9% in hull-less barley grain during the activation time for up to 24 hours. The increase of B<sub>2</sub> content in hull-less barley and wheat grain was very similar. As inactivated rye grain is richer in the content of vitamin B<sub>2</sub> compared to inactivated wheat and hull-less barley grain, the increase in vitamin B<sub>2</sub> amount was more pronounced which can be explained

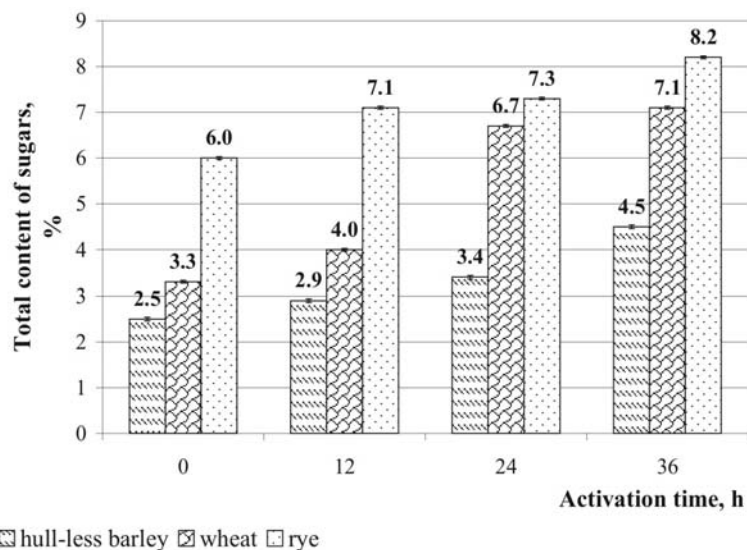


Fig. 3. Changes in total sugars in grain during grain activation time.

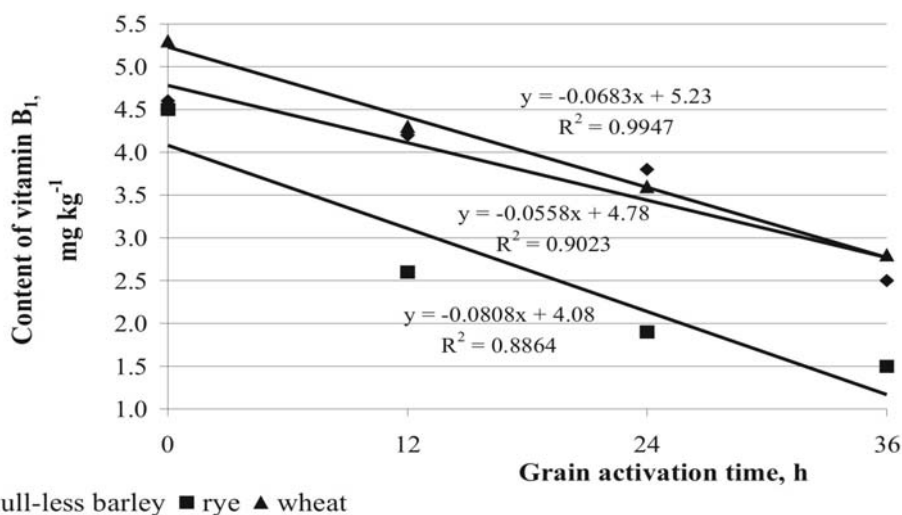


Fig. 4. Decrease in vitamin B<sub>1</sub> content in grain during grain activation time.

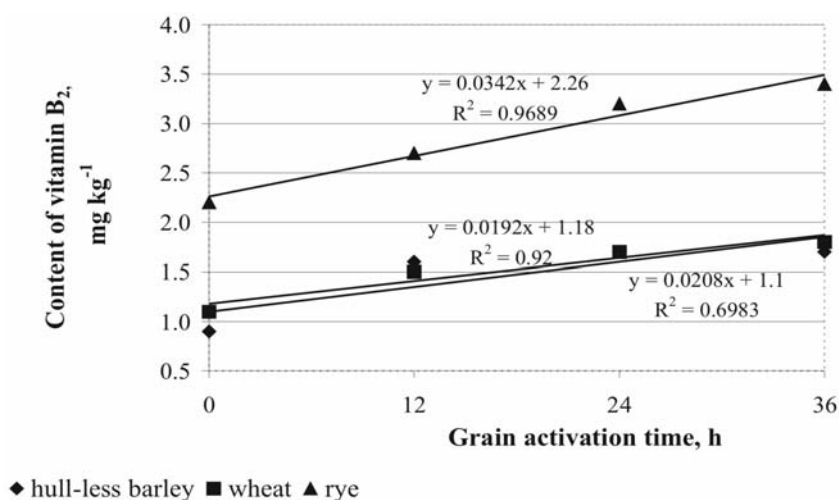


Fig. 5. Changes in vitamin B<sub>2</sub> content in grain during grain activation time.

by the short rest period and intensive process of metabolism occurring in rye grain.

Inactivated wheat grain was richer in the content of **niacin** by 70.10% compared to rye grain and by 57.23% compared to hull-less barley grain. The research proved that the increase in niacin content was more marked in hull-less barley and rye grain. Compared to inactivated grain samples, the content of niacin increased 1.3 times in wheat grain, 2.6 times in rye grain, and 2.1 times in hull-less barley grain activated for up to 24 hours.

**Vitamin C** was not found in inactivated grain samples. By means of biochemical reactions, during the activation process for up to 24 hours vitamin C was synthesized to 71.0 mg kg<sup>-1</sup> in wheat grain, to 69.4 mg kg<sup>-1</sup> in rye grain, and to 26.9 mg kg<sup>-1</sup> in hull-less barley grain.

The increase of the amount of **vitamin E** in wheat and rye grain during the activation process was similar.

Vitamin E content increased 6.5 times in wheat grain and 6.2 times in rye grain. The increase of vitamin E amount in hull-less barley grain during the activation time was not so intensive – only 1.7 times compared to inactivated grain samples.

**Changes in the content of total irreplaceable amino acids in grain during the activation time.** A comparatively higher content of irreplaceable amino acids was found in inactivated hull-less barley grain (Fig. 6). The total content of amino acids decreased by 18.8% in hull-less barley grain, by 17.4% in wheat grain, and by 47.4% in rye grain during grain activation time for up to 24 hours. The application of amino acids in grain metabolism explains the decline.

**Changes in the content of glycosamin.** The highest content of glycosamin was obtained in inactivated wheat (0.23 g kg<sup>-1</sup>) and rye (0.24 g kg<sup>-1</sup>) grain (Fig. 7) whereas in inactivated hull-less barley grain – only 0.10 g kg<sup>-1</sup>.

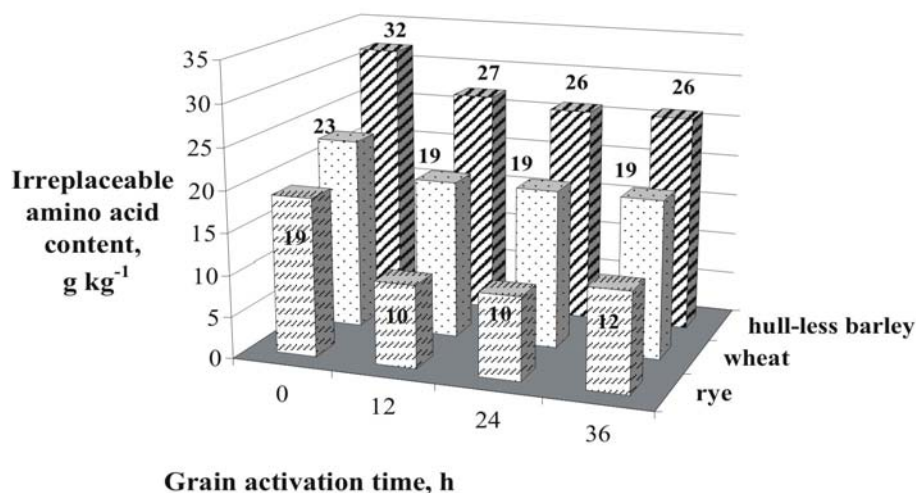


Fig. 6. Changes in the content of total irreplaceable amino acids in grain during grain activation time.

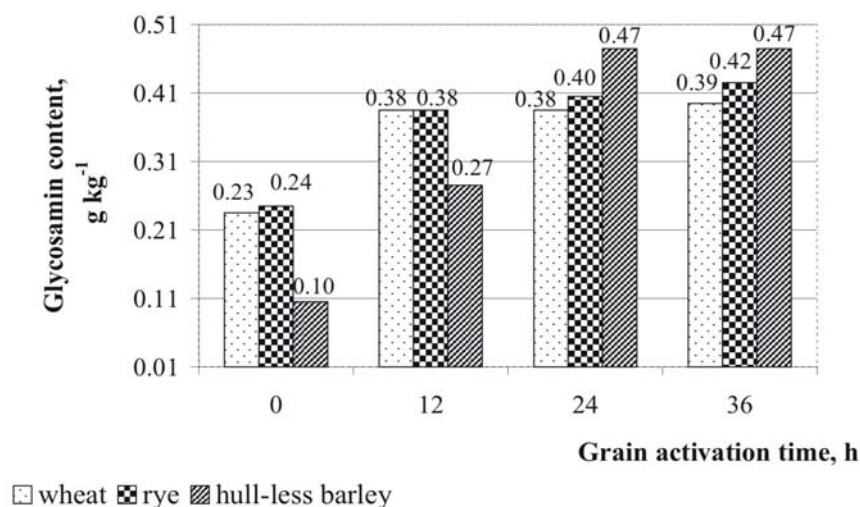


Fig. 7. Changes in glycosamin content in grain during grain activation time.

A comparatively higher increase of glycosamin was observed in hull-less barley (4.7 times) grain during activation for up to 24 hours, while in rye and wheat grain the amount of glycosamin increased only 1.7 times.

Glycosamin as a biologically active compound forms a part of glycopeptides and thus acts as a mediator of the human immunity system. Therefore addition of glycosamin-containing grain to dough increases the biological value of bread.

**Development of the mathematical model.** The mathematical model was developed on the basis of experimental data taking into account the changes in the value of wheat falling number during grain activation. Duration of wheat grain activation time was up to 36 hours. If grain activation time exceeds 36 hours, the active components (carbohydrates, protein, and lipids) regenerate in the process of synthesis to ensure the growth of grain therefore it can be supposed that the speed of active component splitting is proportional to the amount of active components.

It is not possible to determine the speed of biological processes depending on grain variety and activation parameters, but the speed of such processes can be assumed as a **constant V** (as there is no information on the kinds of processes occurring in grain). The decrease of the grain falling number value is possible due to the synthesis of active components.

As a result, a differential equation was obtained (1):

$$\frac{dK}{dt} + \frac{K}{\tau} = V \tag{1}$$

where  $\frac{dK}{dt}$  – speed of changes in the falling number value during the activation time, s;  
 K – falling number, s;  
 $\tau$  – time constant of the process;

V – speed of active component synthesis calculated through the speed changes in the falling number.

Initial term of the differential equation is:

$$K|_{t=0} = K_0, \tag{2}$$

where  $K_0$  – initial value of the falling number, s.

The differential equation is the linear preferential ordinal, non-homogeneous differential equation with constant coefficients, which may be solved by means of Euler’s method. The solution of problems (1 and 2) is shown in formula 3:

$$K(t) = (K_0 - \tau \cdot V) \cdot e^{-\frac{t}{\tau}} + \tau \cdot V \tag{3}$$

where K(t) – dependence of the falling number on the activation time;

t – time, h;

e – base of the natural logarithm.

To determine coefficients V and  $\tau$  in equation 3, the least square method of equation 3 is applied to the equation developed further. Using the experimental data, the sum is completed (4):

$$S = \sum_i [K_{exp}(t)_i - K_t(t)_i]^2 = \sum_i [K_{exp}(t)_i - ((K_0 - \tau \cdot V) \cdot e^{-\frac{t}{\tau}} + \tau \cdot V)]^2 \tag{4}$$

where S – sum of squares;

$K_{exp}(t)_i$  – experimental value of the falling number depending on the activation time;

$K_t(t)_i$  – theoretical value of the falling number depending on the activation time.

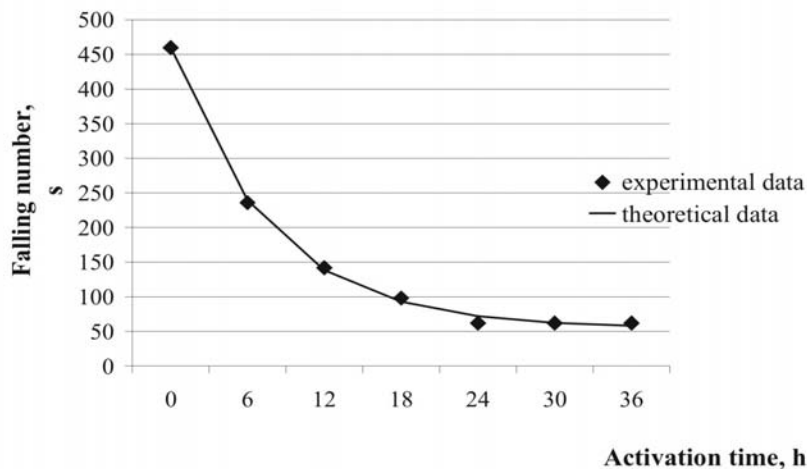


Fig. 8. The curve for the changes in theoretical and practical falling number value in wheat grain during grain activation time.

The Solver software was used for the sum (4) minimalization.

The coefficients  $V$  (7.13) and  $\tau$  (7.63) were determined by means of experimentally ascertained data and sum 4.

As a result, the changes in the theoretical falling number value in wheat grain during the activation time were calculated and a theoretical curve was obtained (Fig. 8). The designed mathematical model is suitable to predict the falling number value not only of wheat but of other grain too.

## Conclusions

1. The research proved that optimal grain biological activation parameters are:  $\varphi = 80 \pm 1\%$ ,  $t = +34 \pm 1^\circ\text{C}$ , and  $\tau = 24 \pm 1$  h.
2. The quality of gluten in wheat grain becomes unsatisfactory during grain activation for up to 36 h due to the occurrence of intensive dissimilation processes during the activation time. As a result, the content of total protein decreases. Gluten is found neither in activated nor in inactivated rye and hull-less barley grain.
3. Intensive biochemical processes occur during grain activation time, as a result of which grain biological value increases – the content of vitamins B<sub>2</sub>, E and niacin, of total sugars, dietary fibre and of glycosamin increases, vitamin C is synthesized, and the content of irreplaceable amino acids decreases.
4. The designed mathematical model is suitable to predict the falling number value not only of wheat but of other grain too.

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### **Anotācija**

Graudaugu produkti ir cilvēku uztura pamats, jo ar ogļhidrātiem un olbaltumvielām, ko tie satur, tiek uzņemtas gandrīz divas trešdaļas dienā nepieciešamo kaloriju, turklāt tie ir svarīgs vitamīnu un šķiedrvielu avots. Diedzētas sēklas, graudi un graudu dīglīši uzturā tiek izmantoti jau kopš seniem laikiem. Bioloģiski aktivētu graudu piedeva kviešu mīklai paaugstina tās kvalitāti un tādējādi iespējams iegūt bioloģiski augstvērtīgu produktu. Darba mērķis bija izpētīt rudzu, kviešu un kailgraudu miežu graudu izmaiņas bioloģiskās aktivēšanas laikā un noteikt graudu aktivēšanas optimālos apstākļus. Pētījumos tika noteikts, ka graudu optimālie bioloģiskās aktivēšanas apstākļi ir: relatīvais gaisa mitrums –  $80 \pm 1\%$ , temperatūra –  $+34 \pm 1$  °C, laiks –  $24 \pm 1$  h. Turpinot graudu aktivēšanu līdz 36 h, kviešiem lipekļa kvalitāte intensīvi notiekošo disimilācijas procesu dēļ pasliktinājās. No rudziem un kailgraudu miežiem lipekli iegūt neizdevās. Bioloģiskās aktivēšanās laikā graudos palielinājās šķiedrvielu, vitamīnu B<sub>2</sub>, E un niacīna daudzums, un sintezējās C vitamīns. Salīdzinot ar neaktivētiem graudiem, glikozamīna saturs visstraujāk, t.i., 4.7 reizes, palielinājās aktivētos kailgraudu miežos, bet rudzos un kviešos – tikai 1.7 reizes. Izstrādātais matemātiskais modelis raksturo krišanas skaitļa vērtības izmaiņas graudu bioloģiskās aktivēšanas laikā atkarībā no aktivēšanas ilguma.