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## INFLUENCE OF ION-OZONE EXPLOSIVE-CAVITATION ON THE PROTEIN AND STARCH CONTENT IN BREWING BARLEY

**Abstract.** The article studies the influence of ion-ozone explosive-cavitation process on the protein and starch content in brewing barley. At the present time, in most cases, brewing enterprises receive low quality brewing barley. The use of barley grain, which fails to meet the standard requirements, results in reduction in the quality of beer. The results of the experiments performed represent the fact that the use of the ion-ozone explosive-cavitation allows to increase the biological value of the product, improving these barley grain quality indicators: the protein to +0.65 % and starch to –4.19 % in relation to the control.

**Keywords:** ion, ozone, explosive-cavitation, barley, malt, protein, starch.

**Introduction.** Barley is the main raw material used in the malt and beer production throughout the entire world [1]. The pace and volume of world trade in brewing barley and malt keep growing. The demand for brewing barley is on the rise. In recent times, beer production has increased by 19 % [2].

Grain farming is the key industry of agriculture in Kazakhstan. 1.32-1.6 million tons of barley are required for domestic consumption [3].

One of the quality indicators of malt raw materials is the protein content in the grain [4]. The protein content in barley can range from 8 to 11 and to 16 %. Only a third from this amount of proteins come out to be in the finished beer, and although the content of protein substances in beer is comparatively small, they can significantly affect its quality. Thuswise, the protein substances affect the appearance of turbidity to some extent [5].

Proteins are of great importance at all stages of making beer and especially when malting. They are nutrition for yeast, involved in foaming, the formation of beer taste, increase its biological stability [6].

The best beer is produced from grain with a protein content of 9.5-11 %. In addition, protein quality is of major importance in the composition of essential amino acids and other biochemical elements [4].

Starch is the most important carbohydrate in terms of quantitative content and significance [7]. The bulk of organic compounds that do not contain nitrogen are carbohydrates and, primarily, starch, the content of which is 60-65 % (calculated with reference to dried substance). It accumulates in the grain during the assimilation of CO<sub>2</sub> and H<sub>2</sub>O under the action of solar radiation with the aid of chlorophyll and with the involvement of oxygen [8].

The accumulation of starch in the grain is designed to provide the germ with nutrients when germinating (during the initial development). Starch accumulates in the form of starch grains, which vary in shape [8]. The larger starch granules in barley grain, the better its technological properties [9].

In brewing, high protein content in barley is undesirable, as it is accompanied by a reduction in the starch content, which adversely affects the malt extractivity, resulting in a reduction in the profitability of its processing for beer [10].

The customer-related positive characteristics and storage stability of beer significantly depend on the quality and composition of barley [4].

It should be noted that the use of innovative germination technologies allows achieving the improvement of the quality of brewing malt. As such technology, we used ion-ozone explosive-cavitation under specific parameters of which we processed barley grain [11].

**Objects and methods of research.** The objects of research at the planned stages of work were:

- 1) brewing barley as per 5060-86 State standard «Brewing barley. Technical specifications» [12];
- 2) ion-ozone explosive-cavitation installation (ozone concentration 2, 4, 6 mg/m<sup>3</sup>, ion concentration – 500±20, 50250±250, 100000±25 units/cm<sup>3</sup>, explosive-cavitation – 2, 4, 6 at);

The weight ratio of protein substances was determined in accordance with 10846-91 State standard «Grain and products after its processing. Method for the determination of protein» by using the Kjeldahl method [13]. The essence of the method was a decomposition of the organic matter of the sample in boiling concentrated sulfuric acid resulting in the formation of ammonium salts. Ammonium sulphate, in turn, decomposed under the action of alkali, while the ammonia released during this process was being titrated by sulfuric acid. By the consumption of sulfuric acid during the titration, the nitrogen content in the sample taken was calculated according to the formula [14]:

$$N = T * 14 / W * (100 - M),$$

where  $T$  is the amount of the standard acid solution, required to neutralize the ammonium, after deduction of the blank experiment, cm<sup>3</sup>;  $W$  is the weight of the sample taken, g;  $M$  is the mass moisture content in the grain, %.

To convert nitrogen to protein, the result was multiplied by 6.25 [15].

The starch content was determined in accordance with 10845-98 State standard «Grain and products after its processing. Method for the starch determination» by a polarimetric method using a universal saccharimeter US-5 [16]. The basis of the method is the starch hydrolysis resulting in sugars by boiling it in a solution of hydrochloric acid (concurrently dextrans are being formed as well as a partial transition into a solution of optically active substances, such as pentosans and proteins). Then, the proteins are precipitated, and the solution of the sugars is polarized [17, 18].

Mathematical treatment of the obtained data was carried out using the computer program Mathcad 140, which allowed to estimate the sampling characteristics and to perform a comparative analysis.

**Results and their discussion.** When determining the quality assessment criteria for the barley protein ( $y_1$ ) and barley starch ( $y_2$ ) using Mathcad 140 and in accordance with the experimental studies, depending on the parameters of the ion-ozone mixture ( $x$ ), cavitation treatment ( $y$ ) and time exposure ( $z$ ), the parameters were introduced in accordance with the experimental data of barley protein ( $u$ ) and barley starch ( $v$ ).

We calculate the elements of the matrix ( $s$ ) of the solution of linear algebraic equations. The solutions of this system function as the coefficients of the desired polynomials:

$$\begin{aligned}
 s_{0,0} &:= 12 & s_{0,1} &:= \sum_{i=0}^{11} x_i & s_{0,2} &:= \sum_{i=0}^{11} (x_i)^2 & s_{0,3} &:= \sum_{i=0}^{11} (x_i)^3 & s_{0,4} &:= \sum_{i=0}^{11} (x_i)^4 \\
 s_{1,0} &:= s_{0,1} & s_{1,1} &:= s_{0,2} & s_{1,2} &:= s_{0,3} & s_{1,3} &:= \sum_{i=0}^{11} (x_i)^4 & s_{1,4} &:= \sum_{i=0}^{11} (x_i)^5 \\
 s_{2,0} &:= s_{1,1} & s_{2,1} &:= s_{1,2} & s_{2,2} &:= s_{1,3} & s_{2,3} &:= \sum_{i=0}^{11} (x_i)^5 & s_{2,4} &:= \sum_{i=0}^{11} (x_i)^6 \\
 s_{3,0} &:= s_{2,1} & s_{3,1} &:= s_{2,2} & s_{3,2} &:= s_{2,3} & s_{3,3} &:= \sum_{i=0}^{11} (x_i)^6 & s_{3,4} &:= \sum_{i=0}^{11} (x_i)^7 \\
 s_{4,0} &:= s_{3,1} & s_{4,1} &:= s_{3,2} & s_{4,2} &:= s_{3,3} & s_{4,3} &:= s_{3,4} & s_{4,4} &:= \sum_{i=0}^{11} (x_i)^8
 \end{aligned}$$

We calculate the right side, i.e. the free terms of the above-mentioned system of linear algebraic equations for all the cases under investigation:

$$\begin{aligned}
 f_{00} &:= \sum_{i=0}^{11} y_i & fz_0 &:= \sum_{i=0}^{11} z_i & fu_0 &:= \sum_{i=0}^{11} u_i \\
 f_{10} &:= \sum_{i=0}^{11} (y_i x_i) & fz_1 &:= \sum_{i=0}^{11} (z_i x_i) & fu_1 &:= \sum_{i=0}^{11} (u_i x_i) \\
 f_{20} &:= \sum_{i=0}^{11} [y_i (x_i)^2] & fz_2 &:= \sum_{i=0}^{11} [z_i (x_i)^2] & fu_2 &:= \sum_{i=0}^{11} [u_i (x_i)^2] \\
 f_{30} &:= \sum_{i=0}^{11} [y_i (x_i)^3] & fz_3 &:= \sum_{i=0}^{11} [z_i (x_i)^3] & fu_3 &:= \sum_{i=0}^{11} [u_i (x_i)^3] \\
 f_{40} &:= \sum_{i=0}^{11} [y_i (x_i)^4] & fz_4 &:= \sum_{i=0}^{11} [z_i (x_i)^4] & fu_4 &:= \sum_{i=0}^{11} [u_i (x_i)^4] \\
 fv_{00} &:= \sum_{i=0}^{11} v_i & fv_1 &:= \sum_{i=0}^{11} (v_i x_i) & fv_2 &:= \sum_{i=0}^{11} [v_i (x_i)^2] \\
 fv_3 &:= \sum_{i=0}^{11} [v_i (x_i)^3] & fv_4 &:= \sum_{i=0}^{11} [v_i (x_i)^4]
 \end{aligned}$$

The system of linear algebraic equations for determining the coefficients of the desired polynomials appear as follows:  $a$  – the unknowns,  $s$  – matrix of algebraic equations,  $f$  – matrix of free terms of the system.

To solve the said system by the matrix method for the first case, as well as for other cases of experimental data, we find the inverse matrix of the matrix  $s$ , i.e.:  $s^{-1} := s^{-1}$ . Next, we determine the coefficients of the desired polynomials for all the considered options of the experimental data, that is,  $a := s^{-1} f$ .

$$\begin{aligned}
 a &= \begin{pmatrix} 3.028 \times 10^{11} \\ 4.963 \times 10^{12} \\ 8.171 \times 10^{13} \\ 1.35 \times 10^{15} \\ 2.236 \times 10^{16} \end{pmatrix} & b := s^{-1} fz & b = \begin{pmatrix} 1.892 \times 10^9 \\ 3.102 \times 10^{10} \\ 5.107 \times 10^{11} \\ 8.436 \times 10^{12} \\ 1.397 \times 10^{14} \end{pmatrix} \\
 c := s^{-1} fu & c = \begin{pmatrix} 1.314 \times 10^{11} \\ 2.154 \times 10^{12} \\ 3.546 \times 10^{13} \\ 5.858 \times 10^{14} \\ 9.702 \times 10^{15} \end{pmatrix} & d := s^{-1} fv & d = \begin{pmatrix} 8.221 \times 10^{11} \\ 1.348 \times 10^{13} \\ 2.219 \times 10^{14} \\ 3.665 \times 10^{15} \\ 6.07 \times 10^{16} \end{pmatrix}
 \end{aligned}$$

Now we write down 5 polynomials of the seventh degree, which correspond to the five experimental cases under investigation:

$$\begin{aligned} \text{ff}_y(w) &:= a_0 + a_1 \cdot w + a_2 \cdot w^2 + a_3 \cdot w^3 + a_4 \cdot w^4 \\ \text{ff}_z(w) &:= b_0 + b_1 \cdot w + b_2 \cdot w^2 + b_3 \cdot w^3 + b_4 \cdot w^4 \\ \text{ff}_u(w) &:= c_0 + c_1 \cdot w + c_2 \cdot w^2 + c_3 \cdot w^3 + c_4 \cdot w^4 \\ \text{ff}_v(w) &:= d_0 + d_1 \cdot w + d_2 \cdot w^2 + d_3 \cdot w^3 + d_4 \cdot w^4 \end{aligned}$$

For comparison, we construct graphs in two ways: according to the polynomials and directly from the experimental points of processing the barley protein and barley starch according to the experimental data, depending on the values of the ion-ozone mixture (x), cavitation treatment (y), and time exposure (z) [19].

Graphs, constructed according to the polynomials and according to the experimental points using the Mathcad 140 program, characterize the result of the experimental studies to determine the criteria for assessing the quality of barley protein and barley starch, depending on the ratio of the ion-ozone mixture under ozone concentrations in the range of 2, 4, 6 mg/m<sup>3</sup> and the number of molecular ions within the limits of 500±20 and 100000±25 units/cm<sup>3</sup>, excessive pressure under cavitation within the limits of 2, 4 and 6 at with time exposure of 5, 10 and 15 minutes.

As a result, we obtained figures of graphs, constructed according to the found polynomials (figure 1) and experimental points (figure 2) to determine the criteria for assessing the quality of barley protein (y<sub>1</sub>) and barley starch (y<sub>2</sub>): i:=0...14.

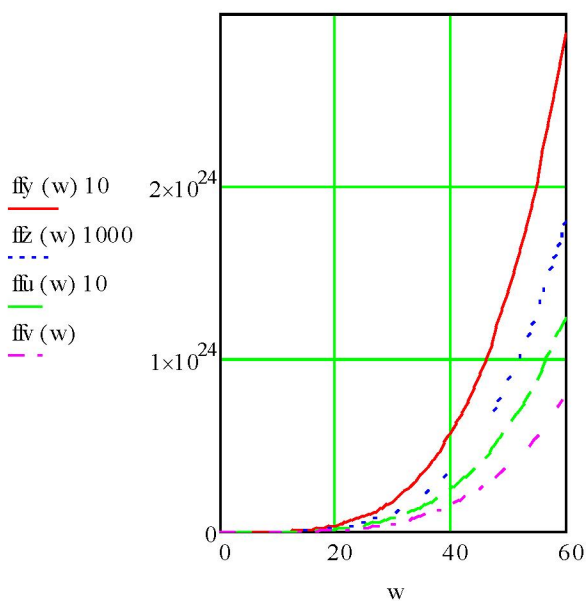


Figure 1 – Graph, constructed according to the found polynomials

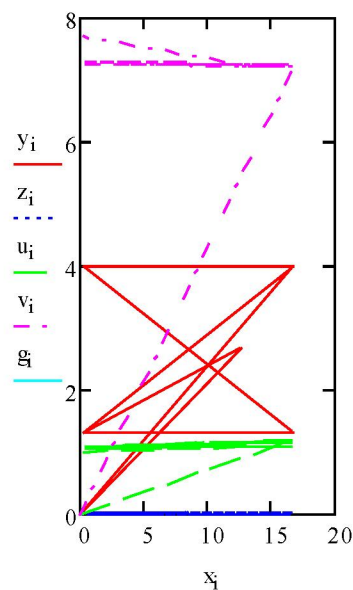


Figure 2 – Graph, constructed according to the experimental points

On the graphs of figures 1 and 2, constructed according to the found polynomials and experimental points, we determined the criteria for assessing the quality of barley protein (y<sub>1</sub>) and barley starch (y<sub>2</sub>).

The best result of the experiments was the value of 1.066 for the barley protein and 7.296 for the barley starch, determined by the Mathcad 140 program. The minimum protein content and the maximum starch content, which correspond to the requirements applicable to brewing barley, were noted in the barley sample, treated under an ozone concentration of 2 mg/m<sup>3</sup>, molecular ions of 500±20 units/cm<sup>3</sup>, an excessive pressure of 2 at, and an exposure time of 5 minutes.

**Conclusion.** This study found that the high starch content and the low protein content are the main characteristics that have changed under the influence of ion-ozone explosive-cavitation [20].

As is well known, the bulk of carbohydrates is represented by starch, the content of which depends on the conditions of cultivation and genotype. In the breeds, cultivated within the territory of Kazakhstan, the starch content in the grain varies from 44 to 77 %, calculated with reference to dried substance.

The high concentration of starch, found in our study, increases the brewing value of barley, since two thirds of the malt extractives consist of the sugars, formed from starch under the action of amylolytic enzymes, and one third of the malt extractives consist of other sugars [21].

The fact that grain is a living biological system is of no small importance [22]. Proteins and starch are essential to the construction of living matter and to all aspects of life [23].

The theoretical justification of the experimental studies shows that ozone and molecular ions increase the biological value of the product. Cavitation makes an increase in the pores of the product, thereby improving the penetration of the ion-ozone mixture into biological cells. The best time exposure of 5 minutes gives evidence of the completion of biological processes, occurring when processing barley grain.

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### СЫРА АШЫТУҒА АРНАЛҒАН АРПАНЫҢ ҚҰРАМЫНДАҒЫ АҚУЫЗ БЕН КРАХМАЛҒА ИОНОЗОНДЫҚ ЖАРЫЛЫС КАВИТАЦИЯСЫНЫҢ ЫҚПАЛЫ

**Аннотация.** Мақалада сыра қайнатуға арналған арпаның құрамындағы ақуызға және крахмалға ионозондық жарылыс кавитациясы үдерісінің ықпалы зерттелді. Қазіргі уақытта көпшілік жағдайда сыра қайнату кәсіпорындарына сапасы төмен сыра ашытуға арналған арпа түседі. Стандарт талаптарына сәйкес келмейтін арпа дәнін пайдалану сыраның сапасының төмендеуіне әкеп соқтырады. Жүргізілген эксперименттердің нәтижесі ионозондық жарылыс кавитациясын пайдалану өнімнің биологиялық құндылығын көтеруге, арпа дәнінің сапа көрсеткіштерін жақсартуға, бақылауға қатысты ақуызды – +0,65 % дейін және крахмалды – –4,19 % дейін көтеруге мүмкіндік беретінін көрсетеді.

**Түйін сөздер:** ион, озон, жарылыс кавитациясы, арпа, уыт, ақуыз, крахмал.

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### ВЛИЯНИЕ ИОНОЗОННОЙ ВЗРЫВОКАВИТАЦИИ НА СОДЕРЖАНИЕ БЕЛКА И КРАХМАЛА В ПИВОВАРЕННОМ ЯЧМЕНЕ

**Аннотация.** В статье исследовано влияние ионозонных взрывокавитационных процессов на содержание белка и крахмала в пивоваренном ячмене. В настоящее время в большинстве случаев на пивоваренные предприятия поступает пивоваренный ячмень низкого качества. Использование зерна ячменя, не удовлетворяющего требованиям стандарта, приводит к снижению качества пива. Результаты проведенных экспериментов указывают на то, что использование ионозонной взрывокавитации позволяет повысить биологическую ценность продукта, улучшая данные показатели качества зерна ячменя, белок – до +0,65 % и крахмал – до –4,19 % по отношению к контролю.

**Ключевые слова:** ион, озон, взрывокавитация, ячмень, солод, белок, крахмал.

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