PLANT GROWING, PLANT PROTECTION AND BIOTECHNOLOGY

Multiple Parameter Assessment of Grain Quality for Populations of Winter Rye with Various Viscosity of Water Extract

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Abstract—The results from the multiple parameter (based on 37 indicators) analysis of physicochemical, technological, rheological, and baking properties of two populations of winter rye, contrastingly different in the viscosity of the water extract (VWE) of grain meal, are presented. The initial material for comparison was the high-viscosity GK-494-HV population ($\eta = 12.0 \text{ cP}$) obtained as a result of tenfold selection for high VWE and relatively low-viscous Moscovskaya 15 variety ($\eta = 4.1$ cP), which was used as the standard. It is established that it is difficult to combine high VWE with high grain unit, large grain size, and a high content of starch, but it positively correlates with a high content of protein and grain hardness. The compared populations differed more in flour quality than in quality of grain. The GK-494-BB population was distinguished by a higher falling number (164.7% of the standard), large flour particle sizes (149.7%), high viscosity peak of starch paste (146.2%), a high temperature of starch gelatinization (119.7%), and stronger water-absorption capacity (123.1%). Dough made from high-viscosity grains was distinguished by a significant superiority in shape-retaining (200% of the standard), gas-forming (107.9%), and gas-retaining (107.4%) ability. Pan bread made from such a dough had the best structural and mechanical properties of the bread crumb. A characteristic feature of high-viscosity rye is a relatively low volume of pan bread (93.9% of the standard), low specific volume (93.4%), and crumb porosity (91.8%). Bread made from high-viscosity flour is characterized by relatively low oven loss (8.6 vs. 12.2%). As a result of selection, the maximum viscosity of the amylopectin fraction in comparison with the standard increased by 4.9% and the amylose fraction by 102.6%, i.e., by 20 times. Purposeful selection for high VWE correlatively affected many traits of winter rye grain quality. The peculiarity is that these changes were achieved not only as a result of an increase in the content of water-soluble pentosans in grain but also due to the influence of water-soluble amylose.

Keywords: winter rye (*Secale cereale* L.), population, variety, viscosity of water extract, quality of grain, flour, dough, bread, multiple parameter assessment

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INTRODUCTION

Winter rye differs from wheat by a relatively high content of nonstarch polysaccharides (pentosans) in the grain, which play an important role in the technology of baking rye bread [1]. These polysaccharides serve as the main substances that bind water during dough kneading, increase its viscosity, and improve its physical properties [2]. It has been established that their total content in rye grain varies from 7.0 to 13.0% [3]. In relation to water, they are divided into watersoluble and water-insoluble variants. Water-insoluble pentosans (WIP) are mostly contained in cell membranes, water-soluble (WSP) pentosans are mainly present inside the cells. It is believed that rye grain with a high content of total pentosans is more suitable for bread production since they, being adsorbed on the surface of starch and rye flour proteins, reduce the rate

belongs to WSP, which account for 20–38% in the structure of total pentosans [6]. Their valuable property is the ability to produce highly viscous water solutions at a relatively low content, which is very important in the preparation of rye dough [7, 8]. The noted features allow us to explain why almost

of the swelling process and also help to reduce their attack by enzymes [4, 5]. A special role in baking

all cultivated rye varieties belong to the bakery category and do not meet the requirements for fodder grain. The reason is that the tasks of rye breeding for baking and grain fodder suitability do not coincide and they should be solved according to different breeding programs [9]. Grain-fodder rye, in contrast to bakery rye, should have a high protein content and a relatively low content of pentosans, especially their water-soluble fraction [10]. Previously, rye breeding in this direction was not carried out, but the problem of pentosans in rye has recently begun to attract more attention of breeders. It was found [11] that the content of watersoluble pentosans in rye grain is directly dependent on the viscosity of the water extract (VWE) of grain meal $(r = 0.97)$. This was the basis for using the VWE as an indirect criterion in determining the content of pentosans in rye grain.

It also turned out that pentosans are heterogeneous in their molecular weight and, therefore, they can have different VWE with their equal concentration [12]. A comparison of two groups of pentosans contrasting in molecular weight showed [13] that biopolymers with a high substitution density of xylose residues correlate more closely with VWE than pentosans with a lower density of such substitution. This indicates a high informational value of the VWE in relation to the biochemical structure of pentosans. The quantitative content and internal structure of WSP to a certain extent determine the use of rye grain. On the one hand, with an increase in the content, they reduce the nutritional value of fodder grain, on the other hand, on the contrary, they improve the baking properties of rye flour [14]. From the point of view of breeding, it is important that the VWE level of grain meal can serve as a good indicator of the target suitability of winter rye grain.

Therefore, the comparison of winter rye varieties with contrasting VWE is of particular interest. For the first time, such varieties were created at the Federal Research Center Nemchinovka as a result of a longterm selection of winter rye for high and low VWE. For this purpose, we developed a methodology for evaluating the breeding material on the basis of VWE using a rotational viscometer and conducted ten cycles of divergent selection according to VWE on the basis of Alfa and Moskovskaya 12 rye varieties [15]. As a result, unique rye populations characterized by a contrasting VWE trait were obtained. High viscosity populations (designated as HV) exceeded the VWE of original form by 3.3–6.0 times, and low-viscosity (LV) were inferior to the original form by 2.6–3.5 times. The preliminary study showed that high-viscosity populations are characterized by higher yields and better grain quality than low-viscosity populations. The highest correlative effect was achieved by the grain unit, the falling number, the height of the amylogram, the shape retention of the bread, and the structural and mechanical properties of the crumb of the finished product. It was concluded that selection for high VWE can significantly improve many baking properties of rye grain.

The selection evaluation of populations divergent in viscosity revealed the need for their deeper study. Since high-viscosity populations contain a lot of WSP, while low-viscosity populations contain a relatively low amount, it is practically important to know how much various physicochemical characteristics of rye, including those that determine its baking properties,

will change against the background of a change in the VWE potential. The question of the correlative variability of various quality attributes in high-viscosity grains in the scientific literature is still open; thus, its consideration is of great scientific and practical interest. For a clearer differentiation of the initial breeding material, it is necessary, in addition to determining the content of WSP, to develop more advanced methods for the technological assessment of high-pentosan rye varieties.

The goal of the research is a multiple parameter assessment of the physicochemical characteristics of winter rye populations, contrasting by VWE trait. The task was to expand the number of indicators that control the important parts of the quality of rye grain for the more efficient use of the grain resources of this crop.

MATERIALS AND METHODS

The source material for the study was the high-viscosity population of GK-494-HV (η = 12.0 cP) and the relatively low-viscosity Moskovskaya 15 variety $(\eta = 4.1 \text{ cP})$, which was used as a standard for comparison. Moskovskaya 15 variety is included in the State Register of Breeding Achievements of the Russian Federation and has been approved since 2016 for use in the Northwestern, Central, and Volga-Vyatka regions. The high-viscosity population GK-494-HV was obtained by crossing two high-viscosity rye samples (Mos-12-HV and Alfa-HV), created by the method of multiple selection of plants with a high VWE of grain meal (ten cycles were carried out in 2004–2013) [16]. A comparative test of the GK-494- HV population and the Moskovskaya 15 variety for grain quality was carried out in 2017 on the experimental field of the Federal Research Center Nemchinovka on plots of 15 $m²$ in four repetitions. After harvesting, an average sample of grain with the weight of 15 kg was taken from each population to assess its physical-technological and flour-grinding-baking qualities according to various indicators (Table 1).

The relative VWE from whole grain flour and bread flour was measured in centipoise (cP) using a VT5L/R rotational viscometer (Germany) according to the method of A.S. Timoshchenko et al. [17].

The fundamental difference of this approach was that, in addition to the falling number, the following parameters were additionally used when evaluating the rheological behavior of a gelatinized suspension:

1. indicators of grain hardness, reflecting its structural and mechanical properties; they were determined using an information-measuring system (IMS) based on the Polyreotest PRT-1 device with a grinding device [18];

2. rheological indicators of rye dough, determined using Farinograph-E device allowed us to obtain an

Table 1. Indicators of grain, bread flour, dough, and bread, which were used for multiple parameter assessment of two rye populations

integral assessment of the state of all biopolymers of rye flour, which determine its baking properties.

Laboratory grinding of rye grain into bread flour was carried out using a Nagema mill. The duration of softening of each sample of rye was 4 h, the mass fraction of moisture in the grain before the first break system was 14.0%. The evaluation of the technological properties of rye flour included determining the average equivalent particle diameter (Granulometer GIU-1), then the falling number (Amylotest AT-97 (ChP)) and its whiteness index (Blik-R3) were measured confirming the grade of processed flour. The evaluation of the rheological behavior of the gelatinized water suspension was carried out according to the parameters of the amylogram and testogram using an Amylotest AT-97 (ChP-TA) [19]. The parameters reflecting the rheological behavior of the rye dough during its kneading were determined. These parameters included the characteristics of the gel-forming ability of rye flour biopolymers during the formation of the coagulation structure of the dough, taking into account the waterabsorption capacity of the flour. For the evaluation of the baking properties of rye flour, the effective viscosity of the kneaded dough was measured. The control of the rheological behavior of the rye dough during the

kneading process was carried out using the Farinograph E according to the farinogram parameters. During kneading, a certain amount of water was added, which ensured the production of rye dough with a consistency of 300 ± 15 FU.

An integral assessment of the technological properties of rye flour by organoleptic and physicochemical indicators of the quality of bread made as a result of trial laboratory baking was carried out according to the method of the Scientific Research Institute of the Baking Industry [19–21]. Baking was performed under the condition of optimizing the biotechnological operations of dough maturation and final proofing of dough pieces according to the parameters of the reofermentographic curve. Dough pieces weighing 1200 g each were baked in a laboratory oven at 230°C. The bread baking time was 65 min. Final products were stored at 20–23°C. The quality of the baked bread was assessed by organoleptic and physicochemical parameters after 16–18 h in accordance with existing methods. The shaping stability of the hearth bread was measured as the ratio of height (H) to the diameter (D), and the quality of the pan bread was assessed by measuring the volumetric yield of bread and sensory evaluation of crumb quality indicators (color, sticki-

| Material | Trait | GK-494-BB (VWE = 12.0 cP) (VWE = 4.1cP) | Moskovskaya 15 |
|--------------|--|--|----------------|
| Grain | grain unit, g/L | 718 | 741 |
| | 1000-grain weight, g | 32.4 | 35.4 |
| | starch content, % | 50.7 | 54.7 |
| | protein content, % | 13.2 | 12.6 |
| | amount of mechanical energy used for grinding a grain sample, kJ/kg | 875.4 | 795.6 |
| | grain hardness index, N m/% dry matter | 0.63 | 0.56 |
| Flour | average equivalent particle diameter, µm | 255 | 170 |
| | flour yield, % | 89.26 | 82.92 |
| | bran yield, % | 9.52 | 16.23 |
| | flour whiteness, units of R3-BPL | 38.1 | 41.8 |
| | falling number, s | 209 | 127 |
| | Maximum viscosity of starch paste (F_{max}) , u.a. | 0.76 | 0.52 |
| | starch gelatinization start temperature $(t_{\rm g,s.})$, °C | 63.5 | 61.0 |
| | temperature of the maximum viscosity of the paste (t_{max}) , °C | 73.0 | 68.5 |
| | water-absorption capacity, % | 53.3 | 43.3 |
| Dough | gas-generating capacity, $cm3$ | 1252 | 1160 |
| | gas-retention capacity, $cm3$ | 1096 | 1021 |
| | dough resistance, min | 3.5 | 4.9 |
| | time of dough development, min | 5.3 | 4.4 |
| | dough dilution, FU | 28 | 21 |
| | Energy consumption for dough structure formation during kneading, W, kJ/kg | 9.8 | 9.1 |
| | quality number according to farinograph QN | 110 | 153 |
| Bread | dimensional stability (ratio of height to diameter of hearth bread) | 0.46 | 0.23 |
| | volume of pan bread, cm ³ | 1240 | 1320 |
| | specific volume of bread, cm^3/g | 1.14 | 1.22 |
| | crumb porosity, % | 59.7 | 65.0 |
| | crumb moisture, % | 54.0 | 54.5 |
| | loss of moisture, % | 9.3 | 10.0 |
| | oven loss, % | 8.6 | 12.2 |

Table 2. Comparative assessment of grain quality in rye populations with different aqueous extract viscosities

ness, elasticity). The crumb porosity was determined as a percentage according to GOST 5669-96 using a Zhuravlev's probe [19].

RESULTS AND DISCUSSION

The compared rye populations differ significantly by many indicators (Table 2, Fig. 1). A distinctive feature of the high-viscosity GK-494-HV population in terms of grain, in comparison with the Moskovskaya 15 variety (see Fig. 1a), is the relatively low grain size (96.9% of the standard), the 1000-grain weight (91.5%), and starch content (92.7%). Only two traits demonstrated positive expression: protein content (104.8% relative to the standard) and grain hardness, which was expressed as the specific amount of energy for grinding a grain sample (110.0%) and strength index (112.5%). The results of the analysis indicate that the differences in the listed traits are due to their correlative dependence on the level of viscosity of the water extract, according to which the selection was carried out. Similar conclusions were made earlier based on the results of multiple divergent selection for the VWE trait [15]. In this comparison, this relationship was most pronounced for the 1000-grain weight, which implies that it is difficult to combine the high viscosity of the water extract with a large grain size. The grain hardness had a positive effect on other quality indicators.

Compared populations differed even more in flour quality than in grain (see Fig. 1b). First of all, the large particle size of the flour from the grain of the GK-494-

Fig. 1. Evaluation of quality traits in the high-viscosity GK-494-HV population in comparison with the low-viscosity Moskovskaya 15 variety (in %, the value of the trait in Moskovskaya 15 = 100%): (a) grain, (b) flour, (c) dough, (d) bread; \Box Moskovskaya 15; —GK-494-HV.

HV population (149.7% of the standard), the high falling number (164.7%), the high viscosity peak of the starch paste on the amylogram (146.2%), the temperature at which it is reached (119.7%), and the high water-absorption capacity (WAC) of flour (123.1%) should be noted. The relatively high yield of flour (107.7%) and the relatively low yield of bran (58.7%) also should be mentioned. These features are probably due to differences in the structural and mechanical properties of the grains of the compared populations, in particular, difference in hardness. The endosperm of high-viscosity rye during grinding is destroyed mainly along the boundaries of the cells, due to which larger flour particles are formed (in our experiment 255.2 vs. 170.5 μ m) and the flour is more granular, crumbly, and better sieved. It can be assumed that the grain of high-viscosity rye contains thinner bran covering, which determines the reduced yield of bran.

Water-soluble pentosans in rye flour, the high content of which can be indirectly assessed using the VWE index, have a significant effect on the falling number (209 vs. 127 s) and the starch gelatinization process. These mucous substances, surrounding starch grains and swollen protein granules, make it difficult for starch to be attacked by enzymes, thereby slowing down the entire gelatinization process. At the same time, as a result of the interaction of protein substances with mucus, the initial viscosity of the suspension significantly increases and the amylogram maximum increases [22].

An important property of high-viscosity flour is its high water-absorption capacity (53.3 vs. 43.3%). This is due to the high hydrophilicity of water-soluble pentosans, which increase the viscosity of rye dough and undoubtedly has a great influence on its rheological properties. Ultimately, the viscosity of the rye dough determines the yield and stability of the dough as well as the volume of the bread. As the viscosity of the dough increases, its yield increases due to the retention of more water. As a result, it has better stability, but the baked bread has smaller volume [23].

The compared populations also markedly differed in the rheological characteristics of the rye dough and the indicators of its kneading (see Fig. 1c). Attention is drawn to the increased gas-forming (107.9%) and gasretaining (107.4%) ability of the high-viscosity dough. This is due to the fact that the leading role in the gasforming ability of rye flour belongs to amylolytic enzymes and starch, while water-soluble pentosans determine the gas-retaining ability. The higher content of water-soluble pentosans in the flour, which increase the viscosity of the aqueous extract, the higher the gas-retaining ability of the dough. At the same time, dough based on high-viscosity grain flour is characterized by greater water-absorption capacity (123.1%) and formation time (120.5%) . At the same time, it is characterized by higher values of the dilution index and relatively low stability. Different estimates for these properties are explained by the different ratio of destroyed and undestroyed starch grains in flour as well as the presence of larger particles in bread flour, which determine the rate and strength of osmotic binding of water to free protein and pentosans surrounding individual starch grains.

The comparison of the studied populations in terms of the quality of baked bread is of particular interest (see Fig. 1d). First of all, the two-fold (200%) superiority of hearth bread from the grain of the highviscosity GK-494-HV population in terms of shape stability should be noted. In principle, this was expected since the flour obtained from this population has a high VWE, which is the reason why the dough almost "does not flow" during proofing and retains its shape better. The reason for such a high shape retention is the correlative effect due to intensive selection for high VWE. A characteristic feature of high-viscosity rye is the relatively low volume of pan bread (93.9%), specific volume (93.4%), and crumb poros-

ity (91.8%). From this it follows that the volumetric yield of bread directly depends on the viscosity of rye dough, provided by water-soluble pentosans. With a high viscosity, the dough is able to retain more water and has better dimensional stability, but the baked bread is characterized by a smaller volume, more elastic crumb, and less stickiness and porosity. In addition, it was noted that bread made from high-viscosity flour becomes stale slower and retains a soft texture longer. Thus, the VWE level is an important component of rye dough, which determines its water and gasretention capacity and these parameters significantly affect the quality of the final product.

The activity of amylolytic enzymes in flour has a great influence on the expression of quality traits. If the activity is low, then the baked bread is obtained with an elastic crumb and small thick-walled pores, with a flat upper crust, which is generally characteristic for products made from grain of the high-viscosity GK-494-HV population. On the other hand, pan bread made from low-viscosity flour of the Moskovskaya 15 variety, despite a larger volume, is distinguished by a concave upper crust, crumb separation from the crust, poor porosity structure, and a strongly creased, moist, and sticky crumb (Fig. 2).

An important feature of pan bread made from high-viscosity rye is a relatively low oven loss (70.5% of the standard). That is, the decrease in the weight of the dough piece during baking is 29.5% less than that of the Moskovskaya 15 standard. As a result, as the VWE of grain meal increases, the water-absorption capacity of the flour obtained from it and the yield of bread from such flour increase. This favorably distinguishes the high-viscosity GK-494-HV population from the low-viscosity Moskovskaya 15 variety.

As we mentioned earlier, water-soluble pentosans are the main contributor to the VWE potential. As for the role of starch, it has not been fully elucidated, although it is known [22] that all water-soluble polysaccharides provide viscous solutions due to the large size of their molecules. Taking into account the fact that the ability of starch to gelatinization is due to the presence of amylose and amylopectin in it, we conducted a comparative assessment of the studied rye populations according to four qualitative indicators of these components. The results of these studies indicate (Table 3) that the maximum viscosity of the amylose fraction of grain starch in both populations was lower than that of amylopectin fraction, which can be explained by the branched structure of the amylopectin molecule. Similar differences were also manifested in other traits: the temperature of maximum viscosity and the consumption of specific energy for destruction, in which the same amylopectin fraction had an advantage.

At the same time, the multiple selection of highviscosity genotypes caused noticeable qualitative changes in both amylose and amylopectin (Fig. 3).

Fig. 2. Cross section of pan bread made from the flour of populations: (a) GK-494-HV, (b) Moscow 15.

The high-viscosity GK-494-HV population, in comparison with the Moskovskaya 15 variety, was characterized by a slow rate of destruction of both polysaccharides (it was 59.3% of the standard for amylose, while it was 42.1% for amylopectin). Ultimately, this led to a sharp increase in the consumption of specific energy for the destruction of their structure (up to 391.3% for amylose and up to 254.6% for amylopectin).

However, according to the maximum viscosity, the reaction of the amylopectin and amylose fractions was ambiguous. As a result of intensive selection for high VWE, the viscosity level of the amylopectin fraction, compared to the standard, increased by only 4.9%, while the viscosity of the amylose fraction increased by 102.6%, i.e., it was 20 times higher. The implication is that the high potential of VWE achieved by the selection method was due not only to a higher content of water-soluble pentosans in the grain but also due to an additional contribution from amylose. In our opinion, this explains the higher water solubility of the amylase fraction compared to the amylopectin fraction, as a result of which repeated selection for high VWE affected this particular starch fraction.

Thus, a versatile assessment of the grain quality of rye populations with different VWE showed that the high-viscosity GK-494-HV form significantly differs from Moskovskaya 15 standard by number of physicochemical, technological, and baking properties. The positive correlative effect of high VWE selection was manifested by such traits as grain hardness; falling number; bran yield during grinding; average flour particle size; water-absorbing, gas-forming, and gasretention capacity of flour; and temperature of maximum viscosity of starch paste. A significant improvement in the rheological properties of high-viscosity rye dough was noted. Taken together, these differences contributed to the fact that bread made from high-viscosity rye flour was characterized by better dimensional stability, had better structural and mechanical properties of the crumb, and provided a higher bread yield due to low oven loss. The lower starch content, grain size, 1000-grain weight, the volume of pan bread, as well as a finer porosity of crumb should be noted as a negative effect of the selection.

The obtained results also allowed us to conclude that the method of targeted selection for high VWE can significantly influence the course of the process of

| Trait | GK-494-BB VWE $= 12.0$ cP | Moskovskaya 15 VWE = $4.1cP$ | | | |
|--|---------------------------|------------------------------|--|--|--|
| Amylose | | | | | |
| Maximum viscosity (f_2) , N | 0.316 | 0.156 | | | |
| Maximum viscosity temperature (t_2) , ^o C | 69.0 | 69.8 | | | |
| Destruction rate (λ_2) , s ⁻¹ | -0.048 | -0.081 | | | |
| Consumption of specific energy for destruction (e_2) , J/g | 0.587 | 0.150 | | | |
| Amylopectin | | | | | |
| Maximum viscosity (f_1) , N | 0.384 | 0.366 | | | |
| Maximum viscosity temperature (t_1) , ^o C | 77.4 | 72.1 | | | |
| Destruction rate (λ_1) , s ⁻¹ | -0.011 | -0.026 | | | |
| Consumption of specific energy for destruction (e_1) , J/g | 0.812 | 0.319 | | | |

Table 3. Comparative assessment of the quality of amylose and amylopectin in the GK-494-HV population and the Moskovskaya 15 variety

Fig. 3. Comparative assessment of the quality of amylopectin and amylose in two rye populations (in %, the value of the trait in Moskovskaya 15 was taken as 100%): \Box - Moskovskaya 15; \Box - GK-494-HV.

starch gelatinization and dough formation, changing the dynamics and kinetics of the rheological behavior of the gelatinized suspension in the right direction. Therefore, selection methods can improve such important parameters of the farinogram of rye flour as the time of formation of rye dough, the stability and degree of dough dilution, the amount of mechanical energy for the formation of the dough structure during kneading, etc. Taken together, this opens up great prospects for using the method of multiple parameter assessment of technological properties when creating winter rye varieties with the best grain quality.

COMPLIANCE WITH ETHICAL STANDARDS

This article does not contain any studies involving animals or human participants performed by any of the authors.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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