

EFFECTS OF HUMIDITY AND THE CONTENT OF SPROUTED AND SPOILED BUCKWHEAT GRAINS ON THE CHANGES OF ACID NUMBER OF FAT AND GRAIN ACIDITY

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Abstract: The connection between buckwheat grain quality and the changes of the acid number of fat (AN) and grain acidity after eight months of storage has been investigated. Parameters of buckwheat with different content of moisture, germinated grains, and spoiled grains were determined. The studies performed have shown that oxidative damage to buckwheat grain increases concomitantly to the increase of humidity and content of germinated and spoiled seeds. All three defects of grain (increased humidity and increased content of germinated and spoiled seeds) accelerate the hydrolysis of grain lipids, and this leads to an increase of the acid number of fat. AN can be considered an indicator of grain freshness and should be introduced as an indicator of buckwheat quality for inward inspection of grain.

Keywords: Acidity, acid number of fat, spoiled grain, sprouted grains, humidity, buckwheat

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INTRODUCTION

Buckwheat is the second most popular grain (after rice) on the Russian market. It accounts for over 20% of total consumption. All buckwheat on the Russian market is produced domestically.

Buckwheat (*Fagopyrum esculentum Moench.*) is the most common cereal crop in the Altai region: in 2012, buckwheat cultivation area occupied more than 420 thousand hectares in this region, this amounting to almost half of the total cultivation area of buckwheat in Russia. Altai region ranks first in the production of buckwheat in Russia. Grain from this region is supplied to all regions of Russia, and the volume of production amounted to 119 thousand tons in 2012 [1].

However, deterioration of the quality of incoming grain was observed during the recent years. Operational experience at OAO "Biiskii elevator" showed that the harvested buckwheat grain often remained in floor storage for several months prior to the post-harvest treatment and contained large amounts of moisture, spoiled, and sprouted grains upon submission for processing [2].

This is due to the deterioration of farming conditions and standards and the lack of post-harvest processing resulting in spoilage of grain and changes in its technological properties [3, 4].

Quality of the raw grain has a considerable effect on the storage ability of buckwheat. Deterioration of grain quality due to adverse environmental influences resulting in germination, spoilage, or frost damage, decreases the storage ability of the grain and makes the cereals produced from this grain more prone to spoilage upon storage.

In contrast to grain, which is alive and therefore

capable of active resistance to various adverse influences, cereal is more vulnerable to microorganisms, moisture and heat, and therefore it becomes spoiled much easier and faster than grain. Biochemical processes occurring during storage of cereals are primarily manifested as lipid changes.

The content of lipids in buckwheat reportedly varies from 1.5 to 4.0 % [5], being maximal in the embryo (7–14 %) and minimal in the shell (0.4–0.9 %) [6]. Analysis of the neutral lipid fraction revealed the predomination of palmitic (16:0), oleic (18:1), and linolenic acid (18:2) residues in the triglycerides (16, 42, and 32%, respectively) [7]. The rate of oxidation for linolenic acid is twice higher than that for oleic acid, and 20 times higher than that for palmitic acid [8]. Lipid oxidation impairs the organoleptic characteristics of grain.

Rancidification is caused by the hydrolysis of lipids; the extent of this process depends on such parameters as grain humidity and the content of sprouted and spoiled grains, in which the process of hydrolysis had already started. Organoleptic detection of the beginning of cereal spoilage is impossible, since distinctive and easily identifiable changes in appearance and odor do not occur during the initial stage. Measurements of the acid number of fat (AN) reported by L.G. Priezzheva included the investigation of rice groats, millet, peeled rye flour, and top grade wheat flour; changes in the AN during the guaranteed shelf life of Hercules oat flakes were reported in [9].

The aim of the present work was to investigate the effect of humidity and the proportion of sprouted and spoiled buckwheat grains on the changes of acid number (AN) of the fat and grain acidity.

OBJECTS AND METHODS OF STUDY

Buckwheat batches (moisture content up to 20% by mass, sprouted grain content up to 4.0%, spoiled grain content up to 1.6%) stored at the manufacturer's facilities without post-harvest handling were the objects of the present study.

Batches of buckwheat grain of Dialog variety harvested in the foothill area of Altai region were selected for the study. Samples were collected from batches of buckwheat harvested in 2012 and stored at the manufacturer's facilities for eight months. Samples from batches of grain harvested in 2013, stored for one month or less, and lacking spoiled and sprouted grains were used for comparison. Samples were collected at the grain handling center, and a representative sample was formed and used for the study. The analysis of acidity and AN in grain samples differing with regard to humidity and the content of spoiled and sprouted grains was of especial interest for the present study. The quality parameters were assessed using conventional methods.

The method of acidity assessment was based on the ability of grain components to neutralize alkali and involved titration of an aqueous slurry of ground grain.

Fifty grams of grain were selected from the composite sample and ground until the fragments passed through a sieve with openings of 0.8 mm in diameter. Ground grain was transferred onto a glass plate; a smooth layer was formed and pressed down by another glass plate to obtain a 3–4 mm thick layer. A 5-g sample of ground grain was transferred into a flask, mixed with 100 cm³ of distilled water, and stirred until all clumps disappeared. Phenolphthalein (5 drops of a 3% solution) was added to the suspension; the mixture was stirred and titrated with 0.1 M sodium hydroxide.

Acidity (X) was expressed in degrees of acidity as the volume of 1 mole/dm³ sodium hydroxide solution required to neutralize the acid in 100 g of the product and calculated according to formula 1 of the conventional procedure.

$$X = V \times 100 / m \times 10, \quad (1)$$

where V is the volume of exactly 0.1 M alkali solution required for titration, cm³; m is the mass of the ground grain sample, g; 1/10 is the factor used to convert the volume of 0.1 M sodium hydroxide solution to moles/dm³.

The acid number of fat was determined according to a procedure involving the extraction of fat from ground grain by hexane, solvent removal, drying of the fat, and titration of the fatty acids extracted by a 0.1 M KOH solution.

For this, 2 g of phenolphthalein were dissolved in 40 cm³ of ethanol in a 100 cm³ volumetric flask.

Potassium hydroxide (5.6 g) was dissolved in 500 cm³ of distilled water in a 1000 cm³ volumetric flask, and the solution was cooled to room temperature.

The solution containing alcohol and ether was prepared by mixing the required amount of ethyl alcohol and diethyl ether at a ratio of 1:1, adding five drops of phenolphthalein, and titrating with 0.1 M KOH until a weak pink coloration appeared.

Fifty grams of grain were taken from the composite sample and ground in a laboratory mill until the fragments passed through a sieve with openings of 0.8 mm in diameter. Ten grams of the ground product were mixed with 50 cm³ of hexane and stirred with a magnetic stirrer for 10 minutes. The mixture was allowed to stand for 10 minutes to separate the precipitate and the solvent.

The top (hexane) layer of the supernatant was decanted through a paper filter into a flask containing calcium chloride. Hexane was completely removed from the flask using a rotary evaporator at 70 °C, and afterwards the flask was placed into an oven, dried at 70 °C for one hour, cooled to room temperature for 30 minutes in a desiccator over calcium chloride, and weighed on a laboratory balance. The weight of the fat was calculated as the difference in the weight of the flask kept in a desiccator and the weight of the flask containing the extracted fat. All the extracted fat was dissolved in 10 cm³ of ethanol-ether mixture, five drops of phenolphthalein solution (concentration 2 g/cm³) were added, and the mixture was titrated with potassium hydroxide until a weak pink coloration appeared and persisted for 30 s.

Acid number of the fat in the sample under investigation, mg KOH/g fat, was calculated according to formula 2 of the conventional procedure.

$$AN = 5.611 AK/m, \quad (2)$$

where 5.611 is a constant calculated as the weight of KOH contained in 1 cm³ of 0.1 mole/dm³ solution; A is the volume of 0.1 M KOH used for titration, cm³; K is the correction coefficient for the titer of 0.1 M KOH; m is the mass of the extracted fat after drying, g.

Since the hydrolysis of fat occurring during the decay of reserve substances in grain begins earlier than that of proteins and carbohydrates, the AN assay is a more sensitive indicator of acceptable grain quality [10]. Analyses performed in the laboratory showed that the organoleptic parameters of the grain batches investigated complied to the existing requirements.

Batches of buckwheat grain received from the growers were divided into three groups:

- 1 - with moisture content ranging from 11.0 to 20.0%;
- 2 - with the content of germinated seeds ranging from 0 to 4.0 %;
- 3 - with the content of damaged grains ranging from 0 to 1.6 %.

All other parameters of the samples conformed to the existing requirements. Germinated seeds were not detected and the content of spoiled grains did not exceed 0.2% in samples of the first group; moisture content in the samples of the second and third groups did not exceed 14.5 %.

RESULTS AND DISCUSSION

The level of unground buckwheat consumption is fairly stable, and the demand for it is expected to grow in the near future. Increasing production volumes in Russia provide for the domestic market demand for buckwheat; domestic production of buckwheat is sufficient to satisfy the demand completely.

The quality of cereal products is an important factor for competition on the market. Wholesale consumers of unground buckwheat have recently come up with a number of critical remarks concerning the significant deterioration of cereal quality within the guaranteed period of shelf life. Organoleptic parameters of the cereal deteriorate, uncharacteristic odors appear, taste changes occur, and the cereal eventually becomes moldy and unfit for consumption. Moisture content in the grain is one of the main factors affecting the storage ability of the grain. High humidity is the main cause of poor conservation of wet and humid grain, as well as the products of processing of such grain.

Grain humidity is an important indicator of its quality. Grain can easily absorb and release moisture, since it has a capillary porous structure. Moist grain breathes intensively, and the concomitant enzymatic processes lead to adverse changes of the quality of the original grain. Such grain can easily germinate and is vulnerable to microorganisms.

The quality of cereals is directly dependent on the quality of grain from which the cereals were produced. However, the existing requirements are not sufficient for the assessment of grain freshness, especially in the initial period of grain deterioration when the changes of the organoleptic characteristics are slight. Buckwheat freshness is characterized by the maximal value of buckwheat AN, at which the product still retains its characteristic organoleptic parameters. At higher AN values, the product acquires an unusual odor, taste and color. Therefore, the AN value, which characterizes the degree of lipid hydrolysis resulting in the formation of free fatty acids, can be used to characterize the freshness of grain and predict changes in the quality parameters during grain storage. Accumulation of free fatty acids in grains reduces the quality of cereals.

Research conducted at Biisk Institute of Technology during the last few years showed that the AN of buckwheat grain supplied for the production of unground buckwheat ranges from 4.2 to 16.5 mg KOH/g; such grain meets the existing requirements and is accepted for processing and buckwheat grain production. Results of the measurements of fat AN and grain acidity for buckwheat grain of varying quality are reported in the present article.

All the measurements were conducted in 10 replicates and processed statistically. The effect of the content of moisture, germinated grains, and spoiled grains on the acidity and AN was investigated for buckwheat grain. The average values are reported in the present article.

The effect of moisture content (by mass) on indicators of oxidative damage in grain stored for one month is illustrated by Fig. 1. This grain was analyzed as it was received by the processing facility; no sprouted or spoiled grains were detected in the batches.

Grain acidity decreases with increasing moisture content, and increases as the content of spoiled and sprouted grains increases; this can be attributed to different mechanisms of the biochemical processes. Increasing humidity results in the dilution of acids,

while spoilage processes result in an increase of acid concentration.

The results show that an increase in humidity in the fresh grain leads to a 1.3-fold increase in AN and a 1.5-fold decrease in acidity. The currently existing requirements allow unground buckwheat production from grain with a moisture content below 16 % (at groats mills equipped with dryers), and this corresponds to a threshold AN of 9 mg KOH/g.

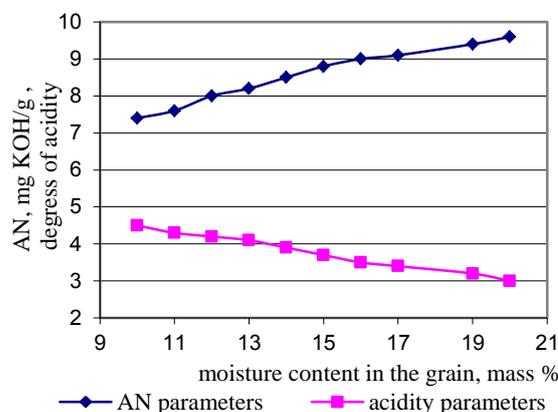


Fig. 1. Effect of moisture content on acidity and AN.

The effect of moisture content on AN parameters after 8 months of storage is illustrated by Fig. 2.

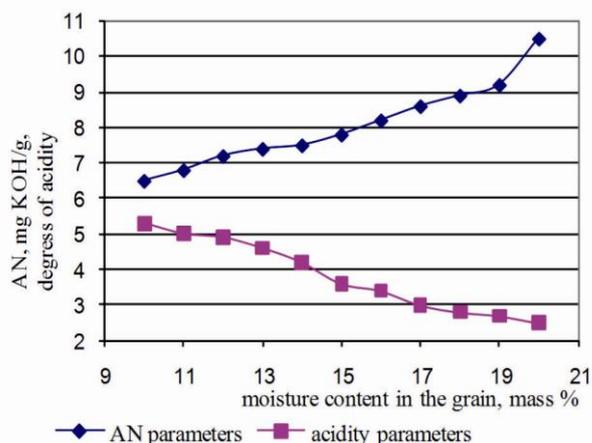


Fig. 2. Effect of moisture content on acidity and AN.

The data show that a 2.1-fold increase in humidity of the stored grain leads to a 1.6-fold increase in AN and a 2.1-fold decrease in acidity. The currently existing requirements allow unground buckwheat production from grain with a moisture content below 16 % (at groats mills equipped with dryers), and this corresponds to a threshold AN of 8.2 mg KOH/g.

Comparison of the results illustrated by Figures 1 and 2 reveals the identical character of processes in samples stored for 1 and 8 months, with an increase of AN and a decrease of acidity that can be attributed to protein hydrolysis processes resulting in the formation of amino acids.

The effect of the content of sprouted grains on oxidative spoilage of buckwheat grain is illustrated by Fig. 3.

The data shows that a 4.0-fold increase in the content of sprouted grains results in a 1.3-fold increase of AN and a 1.1-fold increase in acidity. The currently existing requirements allow cereal production from grain with a content of germinated seeds below 3% (by mass), and this corresponds to a threshold AN of 8 mg KOH/g.

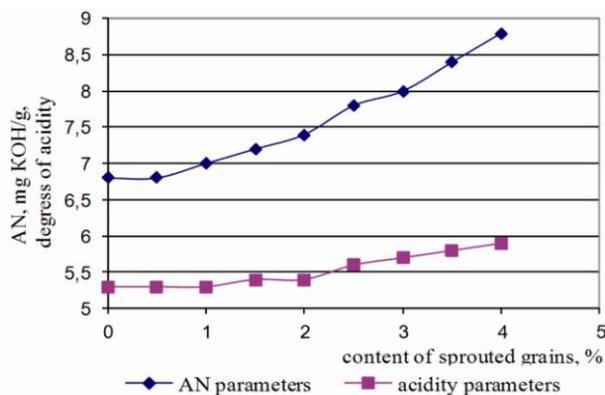


Fig. 3. Effect of the content of sprouted grains on oxidative deterioration of buckwheat.

The effect of the content of spoiled grains on oxidative deterioration of buckwheat grain is illustrated by Fig. 4.

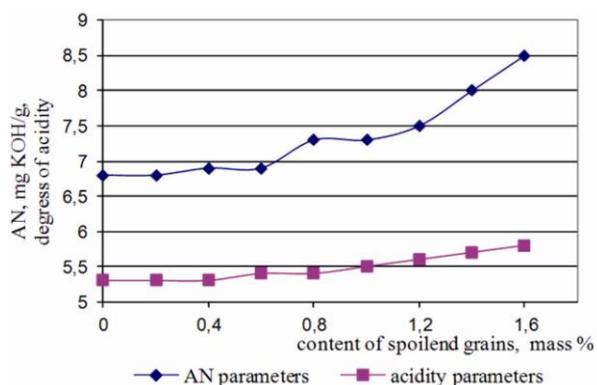


Fig. 4. Effect of the content of damaged grains on oxidative deterioration of buckwheat.

The data presented shows that a 1.6-fold increase in the content of damaged grains results in a 1.3-fold increase of the AN and a 1.1-fold increase in acidity. The currently existing requirements allow the production of third-grade unground buckwheat from grain containing 1.2 mass. % of damaged seeds at the highest, this being equivalent to a threshold AN value of 7.5 mg KOH/g.

The direction of changes related to the content of sprouted and spoiled grains is the same for acidity and AN, in contrast to the previous case. This change in the shape of the curves can be explained by the replacement of chemical hydrolysis processes by biochemical processes occurring during germination and spoilage of buckwheat and resulting in increases of grain acidity and AN.

Notably, the acidity of the grain cannot objectively characterize buckwheat quality due to opposite changes concomitant to quality deterioration. Grain acidity reportedly increases after drying of moist and wet grain.

All three factors (increased humidity or a high content of germinated or damaged grains) accelerate lipid hydrolysis in the grains, and this leads to an increase of the acid number of fat. AN can be regarded as an indicator of grain freshness, and it must be included into the range of buckwheat quality parameters assessed during input control. The data obtained suggest that AN is related to the history of grain storage and general quality of the grain.

Use of AN as an indicator will eliminate the need to control such parameters as humidity, the content of sprouted grains, and the content of damaged grains, and will allow for the use of one parameter in the monitoring of the proper storage conditions that ultimately determine organoleptic characteristics of buckwheat grain processing products; at the same time, the amount of work required for input control will be reduced.

The experiments performed yielded four threshold values of AN for the assessment of buckwheat quality, namely, 9.0, 8.2, 8.0, and 7.5. The minimal value, i.e. 7.5 mg KOH/g, should serve as a unified threshold value.

Thus, buckwheat grain with an AN higher than 7.5 mg KOH/g should not be accepted for processing for the production of unground buckwheat cereal.

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