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RATIONALE OF TECHNOLOGY OF MASHING OAT MALT FOR THE PRODUCTION OF GLUTEN-FREE BEER

Abstract

The article is devoted to the substantiation of the technology of mashing oat malt for the production of gluten-free beer. Oats are a promising raw material for the production of products with functional properties due to their rich chemical composition and high nutritional and biological value, as well as their good acceptance by consumers, including those suffering from celiac disease. On the other hand, oats are a cereal crop with unrealized brewing potential. The use of oat malt for beer production can be innovative but also challenging. It has been found that oat malt is characterized by properties different from barley malt. The increased content of β-glucan in oat malt causes difficulty in filtering intermediate products and finished beer. Due to the low activity of α-amylase in oat malt, the duration of starch saccharification is prolonged, resulting in lower extract yield and lower degree of fermentation. The increased protein content in malt can cause a decrease in the stability of beer during storage. To eliminate the difficulties encountered in the processing of oat malt and to obtain wort with the required carbohydrate and nitrogen composition, it is proposed to use complex-action enzyme preparations Alphalase Sorghum, Alphalase AP3, Diazyme FA (Danisco, Denmark), which are optimized mixtures of α-amylase, β-glucanase, and protease. The complex enzyme preparation reduces the viscosity of the mash and facilitates its filtration, while increasing the wort yield and making it easier to filter finished beer when using the membrane method. When adding an enzyme preparation of complex action, the viscosity of wort decreases, since the preparation effectively breaks down β-glucan, starch and pentosans. The temperature regime for mashing oat malt by the infusion method using an enzyme preparation of complex action, developed taking into account the technological properties of oat malt, is recommended. The use of atypical malted raw materials in brewing - oat malt - can give beer completely new organoleptic properties, which is another advantage of gluten-free oat beer.

Key words: oats, oat malt, quality indicators, technological properties, mashing regime, gluten-free beer, celiac disease.

Introduction

The modern beer market is dominated by beer containing a wide range of starch additives. Using some of them helps to reduce production costs, while others lead to the formation of favourable organoleptic properties of beer: changes in colour (dark or pink beer) or aroma and taste (fruity aromas and more intense flavours). Wheat or rye malt is usually used for this purpose, while other additives, such as corn or rice, are mostly processed in an unmalted form. Non-traditional starch additives, such as black rice, buckwheat or sweet potato, contribute to increasing the polyphenol content of beer, and therefore its antioxidant capacity. However, not all starch additives have the properties necessary for use in brewing [1].

The growing demand for functional food products – products that have high nutritional and biological value, specific properties beneficial to human health and require minimal processing – opens up new opportunities for expanding the range of beer produced, improving the organoleptic properties and functionality of the beverage. Beer can be a good basis for creating products with functional properties by adding various substances or removing alcohol, gluten or carbohydrates from it. Some functional additives to beer have already been introduced into production, while others are the subject of scientific research. Recently, various types of food intolerance have become widespread among consumers, in particular gluten intolerance (celiac disease). Gluten is a protein fraction found in some cereals, in particular wheat, rye, barley. It is generally accepted that safe gluten-free food products should contain no more than 20 mg of gluten per 1 kg. In order for a product to meet this standard, gluten-free raw materials must be used in its production.

A gluten-free diet completely excludes the consumption of beer, since barley and barley malt contain gluten. Despite the fact that various protein fractions are removed during the brewing process (some precipitate during fermentation, and some are removed during colloidal stabilization and filtration of beer), a certain amount of gluten still remains in the finished product. In this regard, the processing of cultures that do not contain this protein to obtain gluten-free beer, which will not be inferior in its organoleptic characteristics to traditional beer, is relevant.

Literary review

Gluten-free raw materials for beer production

In brewing, rice, corn, millet, buckwheat, sorghum, oats, amaranth and other gluten-free crops can be used instead of barley and barley malt to produce gluten-free beer [2]. It is believed that the best results for gluten-free beer can be achieved by using buckwheat, rice and corn [3]. The physicochemical and physiological characteristics of domestic rice varieties were studied and compared in order to determine the best varieties for producing rice malt and gluten-free rice beer or kvass [4].

Oats are a promising gluten-free raw material [5], as consumer interest in food products derived from this cereal is constantly growing. This is due to its rich chemical composition and high nutritional and biological value. In addition, oats are characterized by a high content of non-starchy carbohydrates (dietary fibre) and, in particular, β-glucan [6, 7], which helps to lower blood cholesterol levels, reduce the risk of coronary heart disease [8] and has prebiotic properties [9].

The use of oats in brewing is expedient due to its availability, as well as the chemical composition of carbohydrate and protein complexes, the presence of B vitamins, macro- and microelements [10]. The introduction of oats into the wort is technologically justified both in terms of the nutritional needs of production strains of *Saccharomyces cerevisiae* yeast and in terms of regulating the nutritional and biological value of the finished product.

It should be noted that studies on the use of oats and oat malt in brewing are not numerous [5, 11-16]. In European countries, oats and oat malt have been used in brewing for a long time, but now it is used to a limited extent, only in certain types of beer [17]. This is likely due to the problems that arise when filtering wort and beer. In addition, husked oats have a high content of floral hulls, β-glucans, pentosans, proteins and fats, and therefore lower extractability compared to barley.

Nowadays, there is a tendency in the world to reorient the industrial use of husked oats to new high-yielding naked varieties [18]. In Ukraine, despite its availability, naked oats are not used for food production. This is due, in particular, to the fact that the existing recommendations for its use do not take into account the specific technological properties and chemical composition of naked oats [19]. Breeding work on new oat varieties is ongoing, and the market for oat grain concentrates and isolates is growing on, which will allow for wider use of oats and oat products in the production of functional foods [20].

Technological properties of oat malt

Beer is made from malt derived from almost all grains grown in a particular geographical area. Recently, even legume seeds have been malted [21]. To produce malt from gluten-free raw materials, the standard barley malt method can be adapted by changing the duration and temperature of soaking, as well as the moisture content during germination for each of these crops. For some of them, the optimal malt-growing parameters have been determined.

Among the oat varieties, Avena sativa is used for malt production, and Avena graminae is used as an unmalted raw material [22]. The oats are soaked at a temperature of 16 ℃ until the moisture content reaches 44-46 %. After soaking, the grain is germinated at a temperature of 14-18 ℃ for 5 days. Humidity is maintained at 44-46% throughout the entire period. The final stage of oat malt production is drying of freshly germinated malt. To maximize the retention of enzymes accumulated in the malt, it is dried in a gentle mode with preliminary drying. The maximum drying temperature is 80 ℃.

During the malt growing process, a number of biochemical processes take place that change the chemical composition and properties of the grain. During grain steeping, followed by germination and drying of malt, amylolytic, proteolytic and cytolytic enzymes are activated to hydrolyze starch, proteins and non-starch polysaccharides, the endosperm structure is loosened, and malt acquires appropriate sensory properties.

The quality of malt largely determines the course of the technological process in brewing and the quality of the finished product. A special importance for brewing is the content of extract and nitrogen in malt, as well as the degree of cytolytic malt modification. The results of studies have shown that during germination, oat starch is hydrolyzed slowly, so the starch content in ungerminated and germinated oats is approximately the same [22]. It was found that sprouted oats have an increased amount of essential amino acids, especially lysine and tryptophan, and a slightly lower amount of proline.

The technological properties and quality indicators of oat malt in comparison with the main raw material of beer production – barley malt – were investigated (Table 1) [5].

Table 1 – Characteristics of barley and oat malt [5]

Indicator	Value of the indicator for malt	
	oat	barley
Extract, % dm	62,1	83,7
pH value of congress wort	5,9	5,9
Viscosity, mPa·s	1,81	1,55
Degree of fermentation, % ASBC	80,9	85,0
Protein, % dm	9,3	8,8
FAN, mg/L	172	182
α-Amylase, DU	23	57
Colour of wort, EBC units	9	3
β-Glucan, % dm	0,21	0,30

The oat malt produced in the micro-malthouse showed lower values of extract content compared to barley malt. The pH values of the laboratory wort samples prepared from barley and oat malt did not differ. The viscosity of the oat wort was significantly higher (by about 17 %). The high viscosity of the oat wort may indicate possible problems during beer filtration due to the high β-glucan content. The protein content of oat malt was slightly higher than barley malt, and the degree of fermentation was slightly lower. The importance of free amino acids for yeast nutrition during fermentation has long been known. Although the oat malt contained more nitrogen, the wort prepared from it showed a slightly lower amount of free amine nitrogen than barley malt. The activity of α-amylase in oat malt was significantly lower (by half) than in barley malt, which will negatively affect the course of starch hydrolysis during mashing.

Depolymerization of malt components during mashing

Most of the dry matter of malt, which is valuable for brewing and is represented mainly by starch and protein, is insoluble. The water-soluble content is only 10-15%. During the mashing process, insoluble substances are subjected to enzymatic hydrolysis under the action of enzymes present in the malt to convert them into a soluble state and transfer them to the wort. The most important processes are the hydrolysis of starch and proteins.

The main enzymes in the mashing process are malt amylolytic enzymes. α-Amylases of different structures (isozymes) break down starch to form dextrins. Exogenous β-amylase promotes the formation of maltose disaccharide, in which the free hydroxyl group is characterized by a β-configuration. The process of starch depolymerization also involves boundary dextrinases, which have three forms: free active, bound inactive, and latent soluble. The release of glucose from the terminal non-reducing groups of oligodextrins and maltose occurs under the influence of another enzyme, α-glucosidase [23].

Most of the amino acids or free α-amine nitrogen of the wort is released during maltification rather than during mashing, but the breakdown of proteins during mashing continues and goes through two stages. In the first stage, they dissolve, after that they are hydrolyzed to peptides, which decrease in size during proteolysis. In the second stage, peptides are converted into amino acids (mainly by carboxypeptidase) [23]. Enzymes that hydrolyze peptide bonds of oligopeptide and polypeptide/protein chains can be divided into endo- and exopeptidases. It is noteworthy that some proteases have both exo- and endoenzymatic activity [24].

The mashing of malt produces wort with the appropriate composition of soluble substances. It has been established that the course of the mashing process of oat and barley malt and the indicators of the resulting wort differ (Table 2) [5].

Table 2 – Characteristics of wort produced from barley and oat malt [5]

Indicator	Value of the indicator for wort	
	oat	barley
Extract, % w/w	11,6	12,0
Apparent fermentation, % ASBC	72,2	78,5
pH	5,6	5,6
Colour, EBC units	14,5	12,0
Viscosity, mPa·s	1,9	1,8
FAN mg/L	225	206
TSN, mg/L	1082,4	845,6
β-Glucan, mg/L	182,4	143,7

Complete saccharification of barley mash starch at +72°C was achieved in 5 min, while oat starch was saccharified in 15 min. This could be due to the significantly lower α-amylase activity of oat malt (Table 1). Higher extract extraction was achieved in barley malt. This can be explained by the higher content of hulls, protein, and lipids in oats [10], which reduced the total weight of the malt extract. The pH value of the wort samples was the

same. It should be noted that the oat wort had a higher viscosity, more total soluble nitrogen, free amino acids, and β-glucan compared to barley wort. In addition, oat wort showed a darker color than barley wort. The level of β-glucan in oat wort was significantly higher than in barley wort. This may be due to the significantly lower activity of β-glucanase in oat malt. Because of this, not enough β-glucan is decomposed during the mashing, it remains in the wort, causing a higher viscosity.

Application of enzyme preparations in beer technology

The use of commercial enzymes in brewing can have various benefits: reducing the saccharification time, breaking down undesirable long-chain molecules (e.g., β-glucans), achieving a higher degree of beer fermentation and lower carbohydrate concentration in the finished beer, reducing gluten content, increasing colloidal stability, saving energy and water, etc. [24].

Enzymes can be used at different stages of production - during mashing, fermentation, and maturation. For example, during mashing, enzymes can be used to degrade proteins, starch, β-glucan, etc. Enzymes can be used to process lower-quality grain raw materials, produce beer wort of a given composition, and improve product quality. The activity of these enzyme preparations is several times higher than that of malt enzymes, and their use contributes to the intensification of technological processes and reduction of product material intensity [25].

The most important enzymes are amylases, proteases, and hemicellulases. Amylolytic preparations are used during mashing when the proportion of unmalted raw materials in the mash is significant or in case of low quality of the initial malt. They significantly increase the extract yield [26] and improve the quality of wort. In particular, to increase the yield of extractive substances from malt and unmalted materials, the use of the enzyme preparation Hytemphase, which is a source of thermostable α-amylase, is recommended [27]. Proteolytic enzyme preparations are used with increased amounts of unsalted raw materials and to improve the quality of wort from poor quality malt, as well as to eliminate colloidal turbidity in beer [28]. Cytolytic preparations increase the extract yield by hydrolyzing non-starch polysaccharides, mainly hemicellulose. At the same time, wort quality and beer stability are improved. To solve specific problems of improving beer quality, special enzymes with specific catalytic effects have been developed and used at the fermentation stage: α-acetolactate decarboxylase [29], amyloglucosidase, β-glucanase, maltogenic fungal α-amylase, and pullulanase.

It has been established that the enzyme preparation Viscoferm has the best effect on the stability of beer [30]. To accelerate the technological process and obtain finished products with high colloidal stability, it is recommended to use Brewers Clarex (at the fermentation and maturation stages) and Profix 6500 (before bottling) enzyme preparations [31]. The influence of Laminex MAX Flow 4G, Amylex 5T, Beerzym AMYL HT, Beerzym BG, EnerZyme P7 enzyme preparations on the wort filtration process was studied [32].

One of the flagships in the production of enzyme preparations for brewing is the Danish company Danisco. The characteristics of enzyme preparations of this company are given in Table 3 [33].

Table 3 – Characteristics of enzyme preparations [33]

Product	Enzyme	Usage levels	Optimal pH	Temperature, °C
Laminex MaxFlow 4G	β-glucanase, xylanase	0,05-0,4 kg/MT grist	4,5-6,5	35-75
Laminex 750	β-glucanase, xylanase	0,05-0,3 kg/MT grist	3,0-6,5	40-95
Diazyme TGA	glucoamylase, amyloglucosidase	1,5-7 kg/MT grist [1] 1,5-3 ml/barrel[2]	3,5-6,0	35-70
Diazyme P10	pullulanase	0,5-2 kg/MT grist [1] 0,03-0,12 ml/hectoliters[2]	3,8-5,5	40-60
Alphalase Sorghum	α-amylase, β-glucanase, protease	0,5-2 kg/MT grist	5,0-6,5	30-70
Alphalase AP3	α-amylase, β-glucanase, protease	0,1-0,5 kg/MT grist	4,5-7,5	30-90
Laminex C2K	cellulase, xylanase, β-glucanase	0,05-0,3 kg/MT grist	3,0-6,5	30-75
Amilex 5T	heat stable α-amylase	0,2-0,6 kg/MT grist	5,4-6,5	40-110
Alphalase NP	neutral protease	0,1-0,3 kg/MT grist	3,0-8,0	30-80
Diazyme FA	α-amylase, β-glucanase, protease	0,5-1,5 kg/MT grist	3,0-7,0	25-60

[1] Application at the mashing stage; [2] Application at the fermentation stage

For the breakdown of oat malt polymers, enzyme preparations can be used that are sources of the corresponding enzymes: thermostable α-amylase of bacterial origin, fungal α-amylase for starch dextrinization; xylanase for hydrolysis of xylans and hemicelluloses; pullulanase for starch saccharification; protease for protein breakdown. At the same time, the main criteria for choosing the best variant of the used enzyme preparation are the extract yield, wort viscosity and its organoleptic properties.

Development of oat malt mashing technology using enzyme preparations

When developing a mashing regime for oat malt, its technological properties should be taken into account. Oat malt, as well as unmalted oats, differs from other grain products used in brewing by a higher content of β-glucan. This causes increased viscosity of the mash, wort and beer and makes it difficult to filter them. The second characteristic property is the low activity of α-amylase, which results in a lower extract yield and a lower degree of fermentation (Table 2). Another feature of oat malt is its high protein content, which can cause a decrease in the stability of finished beer during storage.

To solve these problems, targeted enzyme preparations can be used, which are sources of the relevant enzymes. Among the above enzyme preparations (Table 3), the use of Laminex MaxFlow 4G, Laminex 750, Laminex C2K is aimed at reducing the content of non-starch polysaccharides in the wort, and therefore at reducing the viscosity of the mash. Enzyme preparations Diazyme TGA, Diazyme P10, Amilex 5T as an additional source of α-amylase is recommended due to insufficient amount of own amylolytic enzymes in oat malt. Alphalase NP enzyme preparation is an additional source of protease for protein breakdown.

When processing oat malt, it is advisable to use an enzyme preparation with a wide range of enzymatic activity. Enzyme preparations Alphalase Sorghum, Alphalase AP3, Diazyme FA are optimized mixtures containing α-amylase, β-glucanase, and protease. It is the use of such complex enzyme preparations that can eliminate the difficulties encountered in oat malt processing and can play a significant role in enriching the wort with soluble substances.

During mashing, the heating rate is important, which should be related to the degree of malt endosperm modification. For malt with a low degree of endosperm breakdown (modification), enzyme preparations of β-glucanase and protease are added before the mashing process to completely destroy the cell walls. Without their use, potential fermentable substances remain inside the starch grains and will be lost for fermentation [23]. Mashing produces a mixture of carbohydrates, minerals, salts, and potential sources of nitrogen needed for the synthesis of yeast biomass. The resulting wort is a solution of fermentable and non-fermentable sugars, dextrins with linear or branched structure, amino acids, peptides and proteins, fats, organic acids and phosphates. The specific composition of the wort can vary greatly and depends on the type of oats, additives, the degree of malt modification, the presence of enzymes (endogenous and exogenous), and the type of their action.

Despite the high viscosity of oat mash and its significant increase at mashing temperatures below 65 ℃, which is associated with the low temperature of gelatinization of oat starch (55-60 ℃) and insufficient activity of malt endo-β- and exo-β-glucanase [10], when using enzyme preparations, the ratio of raw materials to water (hydromodulus) can be in the range of 1:3-1:4, and the mashing process can be started at a lower temperature of 45 ℃. The temperature regime of mashing oat malt using an enzyme preparation of complex action, developed taking into account the technological properties of oat malt, is shown in Fig. 1.

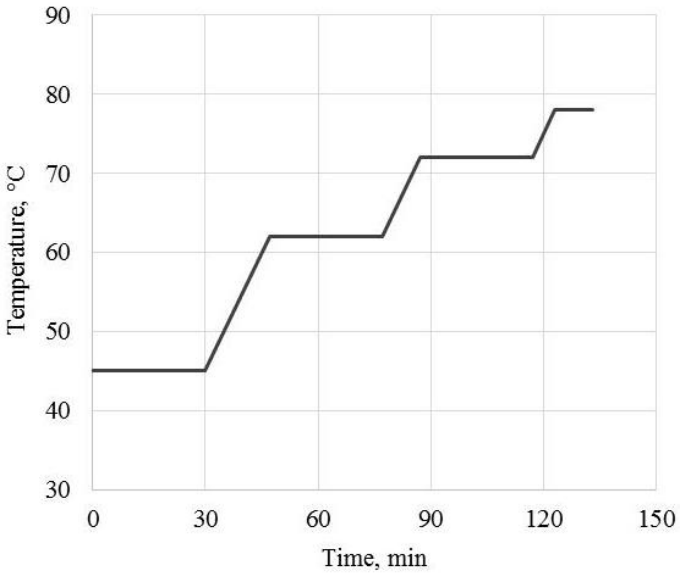

Fig. 1. Temperature regime of oat malt mashing using enzyme preparation

At the beginning of the mashing process, the crushed oat malt is mixed with water, an enzyme preparation of complex action is added in an amount corresponding to the dosage recommended by the manufacturer (Table 3) and, if necessary, the mash is acidified. The temperature regime provides for gradual heating of the mash at a rate of 1 ℃/min with pauses optimal for the action of hydrolytic enzymes of malt - amylolytic (α- and β-amylases), proteolytic and cytolytic. The mash is consistently kept in accordance with the regime (Fig. 1): at 45 ℃ for 30 min; 62 ℃ - 30 min; 72 ℃ - 30 min (until complete saccharification). Then, after heating to 78 ℃ and holding at this temperature for 10 min, the mash is transferred to filtration.

The complex enzyme preparation reduces the viscosity of the mash and facilitates its filtration, at the same time increasing the wort yield, and filtering of finished beer becomes easier when using the membrane method. When adding an enzyme preparation of complex action, the viscosity of wort decreases, as the preparation effectively breaks down β-glucan, starch and pentosans. It should be borne in mind that the mechanism of enzymes action of bacterial and fungal origin differs from the enzymes action of plant origin [10]. This primarily concerns the change in the ratio between fermentable wort sugars, which further affects the formation of the flavor profile of the beverage.

Conclusions

The development of new beer varieties with functional properties is a promising area for improving technology and expanding the range of the beverage. The main advantage of using oats for this purpose is the protein content, which has virtually no allergenic properties, unlike barley, wheat and rye proteins, which makes it possible to expand the range of products for people suffering from celiac disease. However, the use of oat malt in beer production due to its specific technological properties and chemical composition causes difficulties associated with longer starch saccharification and filtering of the mash and finished beer, lower wort extract, and therefore lower alcohol content in beer.

The temperature regime for mashing oat malt by infusion using an enzyme preparation of complex action is recommended. Enzyme preparations Alphalase Sorghum, Alphalase AP3, Diazyme FA (Danisco, Denmark) are optimized mixtures containing α-amylase, β-glucanase, and protease. Enzyme preparations with a wide spectrum of enzymatic activity catalyze during mashing the hydrolysis of oat malt biopolymers to obtain products that ensure the optimal composition of beer wort substances. Improvement of beer technology through the use of effective enzyme preparations will contribute not only to the successful processing of new types of raw materials in the preparation of beer wort, but also to the production of high-quality functional beverage that are stable during storage.

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ОБҐРУНТУВАННЯ ТЕХНОЛОГІЇ ЗАТИРАННЯ ВІВСЯНОГО СОЛОДУ ДЛЯ ВИРОБНИЦТВА БЕЗГЛЮТЕНОВОГО ПИВА

Анотація

Стаття присвячена обґрунтуванню технології затирання вівсяного солоду для виробництва безглютенового пива. Овес є перспективною сировиною для отримання продуктів з функціональними властивостями завдяки багатому хімічному складу й високій харчовій і біологічній цінності та добрим сприйняттям споживачами, зокрема тими, що страждають на целіакію. З іншого боку, овес є злаковою культурою з нереалізованим пивоварним потенціалом. Використання вівсяного солоду для отримання пива може бути інноваційним, але водночас складним. Було встановлено, що для солоду з вівса характерні властивості, відмінні від ячмінного солоду. Підвищений уміст β-глюкану в солоді з вівса спричиняє утруднене фільтрування напівпродуктів і готового пива. Через низьку активність α-амілази вівсяного солоду подовжується тривалість оцукрювання крохмалю, досягається менший вихід екстракту та нижчий ступінь зброджування. Підвищений уміст білка в солоді може стати причиною зниження стійкості пива під час зберігання. Для усунення труднощів, які виникають при переробленні вівсяного солоду, та отримання сусла з необхідним вуглеводним і азотистим складом запропоновано використання ферментних препаратів комплексної дії Alphalase Sorghum, Alphalase AP3, Diazyme FA (Danisco, Данія), що являють собою оптимізовані суміші α-амілази, β-глюканази та протеази. Ферментний препарат комплексної дії знижує в'язкість затору й полегшує його фільтрування, водночас збільшується вихід сусла, фільтрування готового пива при застосуванні мембранного способу стає легшим. При додаванні ферментного препарату комплексної дії в'язкість сусла зменшується, оскільки препарат ефективно розщеплює β-глюкан, крохмаль і пентозани. Рекомендовано режим затирання вівсяного солоду настійним способом із використанням ферментного препарату комплексної дії, розроблений з урахуванням технологічних властивостей вівсяного солоду. Використання у пивоварінні нетипової солодженої сировини – вівсяного солоду – може надати пиву абсолютно нових органолептичних властивостей, що є ще однією перевагою вівсяного безглютенового пива.

Ключові слова: овес, вівсяний солод, показники якості, технологічні властивості, режим затирання, безглютенове пиво, целіакія.

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