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# EFFECT OF THE ADDITION OF SELECTED UNMALTED RAW MATERIALS TO BARLEY MALT ON SELECTED PARAMETERS OF MALT EXTRACTS

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ARTICLE INFO	ABSTRACT
Article history: Received: December 2023 Received in the revised form: April 2024 Accepted: May 2024 Keywords: barley malt, unmalted grain, malt extract	The paper presents the results of research on the problem of the influ- ence of various types of unmalted grain and its quantitative share on important parameters of the malt extract. The aim of the work was to control what precentage of unmalted grain can be added to malt, so that their starch is saccharified only thanks to the action of endogenous malt enzymes. The grains of millet, oats, buckwheat and spelt were used as unmalted raw materials. The basis of the mixture subjected to extraction
	was Pilsner type barley malt. The percentages of the additives ranged from 5 to 50%. Both the unmalted grain and the malt were crushed. The extract was prepared with the use of two methods: congress and infu- sion. Saccharification time, pH and extract content were tested. The re- sults were analyzed statistically. It was found that the amount and type of unmalted raw material influenced the saccharification time of starch and the content of the extract and had no effect on the pH of the extract. Millet grain starch was saccharified if its amount was about 40% of the tested mixtures. In other variants of the experiment, endogenous malt enzymes were able to break down the starch when the amount of addi- tive was as high as 50%.

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### Introduction

The increase in the export of Polish food products in recent years has been dynamic. This applies to goods sold to Asia. Purchases of Polish food in the first half of 2019 by China increased by 76% y/y. Japan also bought more by 73% of Polish food products. Malt extract and its hopped and attenuated form, beer, are the export commodities whose growth was high. Despite the COVID pandemic, the export of the extract to China increased by 63% in 2019 and continues to grow. The production of malt extract can additionally compensate for the progressive decline in beer consumption in Europe. The value of beer exports to China is also increasing, reaching PLN 5 million in the first five months of 2019, i.e. 50% more than in the previous year. One of the Polish beer producers is successful in selling its products in South Korea. The value of beer exports to this country in 2018 amounted to PLN 67 million, while in the previous year it was only PLN 17 million. By May 2019, the value of beer sales to this country had already reached PLN 29 million, which is why its forecast value this year may be higher than in 2018 (www.money.pl, 2017).

The decline of the beer purchase has made the beer market highly competitive. Therefore, breweries are trying to expand their offer by introducing new, innovative products to stop this downward trend. Among these products are malt extracts (Carvalho et al., 2009; Hager et al., 2014; Harasym and Podeszwa, 2015; Yeo and Liu, 2014).

One of the solutions to this problem is the use of various additives in manufacturing beer and malt extracts. Almost 80% of beer and malt extracts produced globally contains such additives. Breweries try to replace the more expensive barley malt with other cheaper additives. In Europe, the share of this type of unmalted additives in the production of beer reaches up to 30% (Annemüller and Manger, 2013). Even a small amount of unmalted raw material added to the grist changes the flavor and aroma of the product (Brányik et al., 2008; Piddocke et al., 2009).

Unmalted additives sometimes pose production problems. This is related to the fact that starch contained therein is pasted at temperatures higher than the optimal temperatures for the activity of amylolytic enzymes (Glatthar et al., 2005; Meussdoerffer and Zarnkow, 2009; Poreda et al., 2014).

The use of additives has another advantage. Dimethyl sulfide (DMS) in high concentrations gives the beer a cooked sweet corn flavor. Therefore, a reduction in the DMS content of the wort and malt extract can result from a low percentage of malt in the mixture (Gresser, 2009).

Reducing malt, or eliminating it from the recipe completely in favour of additives, changes the characteristics of the final product, the beer. It then becomes lighter. This allows the brewing industry to produce new products with unusual sensory characteristics. The disadvantage, on the other hand, is a possible reduction in foaming properties and content. The absence of hulls in many additives may be another problem that limits their applicability (Poreda et al., 2014). This problem is irrelevant in the production of malt extracts, since after extraction they undergo a concentration process in which they lose their flavors (Kunze, 2014).

The aim of this study is to investigate the impact of the use of different amounts of various unmalted raw materials on the most important parameters of malt extract, i.e. saccharification time, extract content, and pH.

### Materials and methods

The research material consisted of mixtures of light Pils malt and unmalted ingredients: buckwheat, oats, millet and spelt.

Pilsner type light malt and selected unmalted raw materials were crushed on a Mockmill 200 laboratory mill (Wolfgang Mock GmbH, Groß-Umstadt, Germany). Thereafter, mixtures of malt and unmalted raw materials were made. The percentage of these unmalted raw materials was increased from 5% to 50% every 5%. The range of unmalted components in the mixture was assumed after preliminary tests, assuming a maximum acceptable extraction time of 90 min. The control sample consisted of extract made of malt only. The mixtures prepared in this way were subjected to extraction by the congress and infusion methods in a laboratory water bath with adjustable extraction parameters (MLL 547, AJL Electronic, Krakow, Poland).

In the case of congress extraction, malt samples were transferred to specially labelled beakers. Distilled water was heated in a bath to 45°C. 200 ml of distilled water at about 46°C was added to the malt beakers. The mixture was blended using a glass spatula so as to avoid the formation of malt clumps, known as 'balling'. Over the next 30 minutes the temperature of the mixture inside the beakers was maintained at 45°C. The temperature of the mixture was then started to rise, which took 25 minutes and the temperature was raised by 1°C per minute (Analytica EBC, 2019).

When the mixture reached a temperature of 70°C, 100 ml of distilled water at the same temperature as the mixture was added to the beakers. Measurement of the starch saccharification rate was started by performing iodine tests every 1 minute. The tests were performed by taking a drop of the suspension from the beaker to a Petri dish and then adding a drop of iodine. Saccharification occurs when the colour of the liquid changes to a clear yellow after the addition of iodine. Iodine tests were performed for a maximum of 1 hour. In samples where saccharification did not occur, this fact was noted. The saccharification test result was expressed in minutes counted from the start of extraction. The mixture temperature (70°C) was maintained for 1 hour only. The beakers were then removed from the bath and allowed to cool at room temperature (Analytica EBC, 2019).

Infusion extraction was started at 50°C and maintained at this level for 20 minutes. After 20 minutes, the mixture was heated to 62°C (within 5 minutes). This temperature was maintained for 30 minutes. After this time, iodine tests were started, which were performed every 1 minute. Then, the temperature of the mixture was raised to 75°C and was maintained for 1 hour, after which the extraction and iodine tests were ended. The mixture was then allowed to cool under room conditions. After cooling, both mixture (congress and infusion) were filtered using filter paper.

Laboratory analyses were performed according to Analytica EBC (2019) standards. Determination of extract content in the extract was made on a PAL1 digital refractometer (ATAGO CO. LTD., Japan). An Elmetron CP-411 pH meter (ELMETRON, Poland) with an accuracy of 0.01 was used for extract pH analysis.

All measurements and tests were carried out in triplicate.

Statistical analysis was performed in three stages. By performing the Shapiro-Wilk test, normality of distribution was confirmed. Next, the results were subjected to a multivariate

analysis of variance (ANOVA). At the final stage, the results were subjected to significance analysis using Tukey's test (HSD), significance level  $\alpha$ =0.05.

## **Results and Discussion**

Fig. 1 presents the dependence of the saccharification time on the amount of addition of the tested unmalted raw materials. Fig. 2 presents the dependence of the extract pH on the percentage share of the additive in the mixtures subjected to extraction. Fig. 3 shows the dependence of the extract content in the obtained extract on the quantitative percentage of the tested unmalted grain additives.



Figure 1. The dependence of the saccharification time on the amount of addition of the tested unmalted raw materials

The research confirmed that with the increase of the amount of the additive, the saccharification time of the starch from the unsweetened grain was extended. For oats it was from 64 minutes with a 5% share to 78 minutes with a 50% share and was the shortest. In the case of buckwheat, it was the longest and ranged from 72 min with a 5% share to 120 minutes with a 50% share. In the case of millet, the endogenous malt enzymes were not able to break down their starch if its addition was above 30%.



Figure 2. The dependence of the extract pH on the percentage share of the additive in the mixtures subjected to mashing

The pH of the tested extracts decreased slightly as the percentage of unmalted ingredients in the mixture increased. However, statistical analysis showed no significant differences.

The relationship between the extract content of the extract and the proportion of additives used was confirmed.

Table 1 summarizes the results of statistical analysis of the relationship between basic extract parameters and a series of variables. The type of additive and its percentage had a significant effect on changes in saccharification time and extract content. In contrast, there were no changes according to the chosen extraction method. In addition, the acidity of the extract did not change significantly.



Figure 3. The dependence of the extract content in the obtained extract on the quantitative percentage of the tested unmalted grain additives

Analysis of the influence of different proportions of tritordeum malt in the blend (from 0 to 100%) on the course of successive stages of wort production showed that saccharification times did not variate significantly (Zdaniewicz et al., 2020).

The literature shows that the extract content of the wort decreases with the introduction of additives into the mixture composition, or the replacement of malt with them. In addition, such modifications to the mixture composition result in a decrease in the amount of enzymes that are involved in the hydrolysis of malt starch, proteins or cell wall components (Yano et al. 2008; Kordialik-Bogacka et al. 2014; Donkelaar et al., 2015). Because of this, the use of such modifications to the composition of the mixture requires the use of additional preparations in the production process. For example, the addition of buckwheat, oats or raw barley in excess of 20% without the use of exogenous enzymes will cause a decrease in the extract content of the wort. Subsequently, this is also related to a decrease in the alcohol content of the beer (Depraetere et al., 2004; Lowe et al., 2004; Kordialik-Bogacka et al., 2014; Schnitzenbaumer and Arendt, 2014).

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#### Table 1.

The analysis of the significance of the influence of the examined factors on the extracts parameters

Factor	Value	Saccharification time	pН	Extract content
		(min.)		(°Bx)
Type of add-on	Spelt	79.5a	5.6a	9.0a
	Millet	80.6a	5.0ab	10.6b
	Buckwheat	76.2ab	5.6bc	10.5b
	Oat	70.7b	5.6c	9.4c
Mashing method	Infusion	80.0a	5.5a	10.3a
	Congress	77.6a	5.5b	10.3a
Percentage of the allowance (%)	0	59.0a	5.5a	10.8a
	5	63.3ab	5.5a	10.7ab
	10	68.9bc	5.5a	10.4bc
	15	74.3c	5.5a	10.3c
	20	79.4cd	5.5a	10.3cd
	25	85.3de	5.5a	10.3d
	30	91.3e	5.5a	10.3de
	35	90.1e	5.5a	9.8e
	40	86.0de	5.6a	9.8ef
	45	89.0e	5.5a	9.6f
	50	92.1e	5.5a	9.7f

A means followed by the same letter in the columns are not statistically different at 5% probability

However, the use of enzyme preparations in the recipe can also solve the problem of lowering the extract content of the wort. The use of raw materials with a high starch content also improves the extract parameter. For example, 73% corn or 75% rice in a blend will improve the extract content of the wort (Annemüller and Manger, 2013; Poreda et al., 2014).

The malting process is accompanied by synthesis and activation of enzymes that degrade cell wall components (including b-glucan and arabinoxylans). In the absence of these enzymes, non-decomposed b-glucan is contained in unmalted cereals; hence, it is present in the wort in greater amounts than when malt is used alone (Lu et al., 2005; Lu and Li, 2006). b-Glucan may cause production problems, e.g. high viscosity of the wort, slower filtration of the wort, low extract content, the risk of beer haziness (Steiner et al., 2012; Tügel et al., 2015).

According to the literature, such effects have been reported in brewing with the use of additives such as triticale or oats (Glatthar et al, 2005; Kordialik-Bogacka et al, 2014; Kunz et al, 2011; Schnitzenbaumer and Arendt, 2014). The use of malt with high b-glucanase or b-glucanase/cellulase activity in the mashing process can be to minimize the undesirable effects of b-glucan, malt should be used during the mashing process (Schnitzenbaumer and Arendt, 2013).

Additives, that have a lower content of b-glucan than barley malt (e.g. rice, wheat, corn) do not increase the viscosity of wort or beer (Blazewicz and Zembold-Guła, 2007; Meussdoerffer and Zarnkow, 2009; Lyu et al., 2013). In a mash with additives (triticale, rye or wheat), pentosans make the production process much more difficult than b-glucan (Glatthar et al., 2005). A beneficial method is to change the acidity of wort to the level of 5.4-5.5. Then a lower viscosity is obtained, the color improves during brewing and the phosphatase activity improves. Due to this, the buffer capacity of wort is increased. Then the beer is characterized by pleasant bitterness, unstable proteins are precipitated.

A significant decrease in acidity during the fermentation process leads to a change in the color of beer (to green) and generally lowers its pH value. Low pH promotes the degradation of diacetyl below its taste thresholds. This is a prerequisite for the beer maturation process to proceed properly. The reports on the effect of supplementation with unmalted raw materials on wort pH are ambiguous. Raw barley was found to both increase and reduce the pH value (Lowe et al., 2004; Annemüller and Manger, 2013). In turn, the use of oats or sorghum resulted in an increase in wort pH (Schnitzenbaumer et al., 2012; Schnitzenbaumer and Arendt, 2013; Schnitzenbaumer et al., 2013; Kordialik-Bogacka et al., 2014, Gorzelany et al., 2019).

#### Conclusions

The starch saccharification time increased with the higher percentage of the tested additives in the mixtures. Only when millet was added in amounts above 35% no starch saccharification was observed. Additives used in mixtures are characterized by reduced buffer capacity and significantly affect the acidity of the extracts. The extract content is closely related to the pH value. In addition, acidity is also an important determinant of enzymatic activity. The addition of all tested raw materials had no effect on the pH of the extracts. In none of the examined cases fluctuations in this parameter were observed, but no trend was observed. The tests and statistical analysis of the obtained results confirmed the decrease in the extract content along with the increase in the percentage of unmalted grain in the mixture subjected to extraction. For buckwheat, the extract contents were the highest. Generally, this parameter decreased with the increase of unmalted material amount in the mixture. In the case of oats, the decrease in extract content was the lowest.

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# WPŁYW DODATKU WYBRANYCH SUROWCÓW NIESŁODOWANYCH DO SŁODU JĘCZMIENNEGO NA WYBRANE PARAMETRY EKSTRAKTÓW SŁODOWYCH

**Streszczenie.** W artykule przedstawiono wyniki badań nad problematyką wpływu różnych rodzajów niesłodowanego ziarna i ich udziału ilościowego na istotne parametry ekstraktów słodowych. Celem pracy było sprawdzenie, jaką ilość niesłodowanych ziaren można dodać do słodu, aby ich skrobia była scukrzana tylko dzięki działaniu endogennych enzymów słodowych. Jako surowce niesłodowane wykorzystano nasiona prosa, owsa, gryki i orkiszu. Podstawą mieszanki poddanej zacieraniu był słód jęczmienny typu pilzneńskiego. Udział procentowy dodatków wahał się od 5 do 50%. Zarówno niesłodowane ziarno, jak i słód zostały rozdrobnione. Ekstrakty przygotowywano dwiema metodami: kongresową i infuzyjną. Badano czas scukrzania, pH i zawartość ekstraktu. Wyniki poddano analizie statystycznej. Stwierdzono, że ilość i rodzaj niesłodowanego surowca wpływa na czas scukrzania skrobi i zawartość ekstraktu, natomiast nie ma wpływu na pH ekstraktu. Skrobia z ziaren prosa była scukrzana, jeśli jej ilość w badanych mieszankach była mniejsza niż 30%. W innych wariantach eksperymentu endogenne enzymy słodu były w stanie rozłożyć skrobię, gdy ilość dodatku wynosiła nawet 50%.

Słowa kluczowe: słód jęczmienny, ziarno niesłodowane, ekstrakt słodowy