

Quality of beer with added pseudocereals

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Abstract

This study dealt with the addition of pseudocereals in the production of beer without the use of exogenous enzymes. The effect of added pseudocereals (quinoa, amaranth, and buckwheat) on characteristics of beer was studied on beer samples prepared from barley malt, pseudocereals, water, hops, and brewer's yeasts. Pseudocereals were used as a partial malt substitute (0%, 10%, 20%, 30%). The colour of laboratory prepared beers was measured using a Konica Minolta CM 3500d. Basic parameters of beers (alcohol content, real extract and original extract of the wort) were measured using a FermentoFlash. The amount of fructose, glucose, maltose and maltotriose in the wort and in the beers was determined using an Agilent Technologies HPLC. A sensory evaluation was also performed. The results of the different variants of beer samples did not vary in terms of alcohol content. Beer lightness did not differ much between the pseudocereals variants. However, control beer was darker than beers with added pseudocereals. It is evident from the results of the determination of carbohydrates, that even the addition of pseudocereals in sprinkles can guarantee a sufficient amount of fermentable carbohydrates. From the results of the sensory analysis, it can be concluded that the addition of buckwheat to the work proved to be very acceptable. We can therefore evaluate that the addition of pseudocereals up to 30% in the pouring can be used in the production of beers.

Keywords: beer; pseudocereals; malt; colour; sugar content; sensory quality

1 Introduction

Beer is the most widely consumed alcoholic beverage in the world. It can be described as a colloidal system. It contains over a thousand compounds, including proteins, nucleic acids, carbohydrates and lipids (Škoda et al., 2016; Lorencová et al., 2019).

The basic raw materials used in the production of beer are water, barley malt, hops and brewer's yeasts (Lorencová et al., 2019; Basařová et al., 2010). The barley malt may be replaced by other cereal malts or suitable substitutes containing sufficient quantities of fermentable sugars (Estevão et al., 2021). Brewers are under considerable pressure to reduce production costs. As a result, malt is being replaced by a variety of cheaper carbohydrate substitutes (Bogdan and KordialikBogacka, 2017). The applicability of pseudocereals is being explored to broaden the range to meet consumer demand. Pseudocereals (quinoa, amaranth and buckwheat) can be used to replace a certain portion of the barley malt in beer formula.

Buckwheat is rich in antioxidants, minerals, polyunsaturated fatty acids, protein and fibre (Cela et al., 2020). Buckwheat can be used as a partial substitute for malt. The amylolytic activity is lower than that of barley malt (Giménez-Bastida et al., 2015).

Quinoa can be classified as a raw material for the production of functional foods, especially because of its high content of phenolics, antioxidants, vitamins and minerals. It contains proteins with a wide range of amino

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acids (Cela et al., 2020; Dakhili et al., 2019). Quinoa can be used in the brewing process as a partial substitute for barley malt. However, it can completely replace barley malt only when exogenous hydrolytic enzymes are added. The presence of outer layers may cause bitter taste of beer (Kordialik-Bogacka et al., 2018).

Amaranth is a rich source of protein, fibre, essential micronutrients and antioxidants. It is distinguished by its low antinutrient content (Cela et al, 2020; Zapotoczny et al., 2016). Its enzymatic activity is significantly weaker than that of buckwheat, resulting in a reduced yield of the extract and a corresponding decrease in the final product volume (Buiatti et al., 2018).

The greatest proportion of beer extractable substances is derived from malts (Cejpek, 2014). The fundamental component of cereal malt extract is starch, which is subjected to enzymatic hydrolysis during the mashing process, whereby the starch is broken down into simple sugars (Yu et al., 2020). The quality of beer is impacted by the composition and properties of its individual components, which are the result of enzymatic activity (Bettenhausen et al., 2018).

The production of beer with the addition of pseudocereals is a multistage process. The initial stage of beer production involves the crushing of barley malt and pseudocereal grains, followed by mashing, wherein The aim of this paper is to study the effect of partial substitution of barley malt by buckwheat, quinoa and amaranth (10%, 20%, 30%) on the characteristics of laboratory-produced beer.

2 Materials and methods

The beer samples were prepared using water that met the requirements for drinking water. The Pilsner type malt, made from barley grains of the Malz variety, was purchased from the BERNARD, a.s. malting plant in Rajhrad (Bernard, Czech Republic). Two varieties of hops were used: Žatecký poloraný červeňák and Sládek in the form of granules (Svoboda-Fraňková, Czech Republic). Both varieties were grown in the Czech Republic. A bottom-fermenting yeasts (strain RIBM95) from the the Research Institute of Brewing and Malting (Czech republic) was used for the fermentation process. Non-traditional raw materials such as amaranth pseudocereals (purchased from COUNTRY LIFE s.r.o., Czech Republic), quinoa (purchased from COUNTRY LIFE s.r.o., Czech Republic) and buckwheat (purchased from PROBIO obch. spol. s.r.o., Czech Republic) were used as partial substitutes for malted barley. Altogether 10 beers were produced (Table 1).

Beer variant	Quinoa [g]	Amaranth [g]	Buckwheat [g]	Malt [g]	Pseudocereal/ /Malt
Q10	60	-	-	540	10/90
Q20	120	-	-	480	20/80
Q30	180	-	-	420	30/70
A10	-	60	-	540	10/90
A20	-	120	-	480	20/80
A30	-	180	-	420	30/70
B10	-	-	60	540	10/90
B20	-	-	120	480	20/80
B30	-	-	180	420	30/70
С	_	_	_	600	0/100

 Table 1
 Amount of added pseudocereals (quinoa, amaranth, buckwheat) and ratio of pseudocereals to malted barley in formula

Q10: quinoa 10%, Q20: quinoa 20%, Q: quinoa 30%, A10: amaranth 10%, A20: amaranth 20%, A30: amaranth 30%, B10: buckwheat 10%, 20: buckwheat 20%, B30: buckwheat 30%, C: beer without added pseudocereals

pseudocereals serve as a partial substitute for barley malt. This is then followed by saccharification (Basařová et al., 2010, Kosař and Procházka, 2000). Subsequently, the wort is subjected to boiling with three doses of hops. Thereafter, the wort is filtered and cooled. Once cooled, bottom-fermenting brewer's yeasts is introduced into the process, after which fermentation, finishing, filtration and stabilization of the beer is performed (Basařová et al., 2010). Barley malt was milled on a Romill MS 100 (Design by Romill Czech Republic). Pseudo cereals were ground on a KM 10 mill (Laboratorní přístroje Praha, Czech Republic). Beer samples were produced with the addition of quinoa (variants 1–3), amaranth (variants 4–6) and buckwheat (variants 7–9). A control beer without the addition of pseudocereals (variant 10) was also prepared. The wort was prepared in mash tanks. Ground malt and pseudocereals were mixed with 2.5 litres of water (37 °C). Mashing was carried out with constant stirring. The temperature of the mixture was gradually increased as summarised in Table 2.

At the end of the mashing, the mixture was pumped into a sedimentation tank where it was left to sediment for 20 minutes. After this time, the spent grains were separated with water at 80 °C (Table 3). The volume of sweet wort obtained was 4 litres.

The wort was boiled and then the first batch of Sládek hops (3.8 g) was added, after another 45 minutes the second batch of Sládek hops (2.5 g) was added, after another 30 minutes Žatecký poloraný červeňák hops (7.2 g) was added, after another 15 minutes the wort was finished. The prepared wort was pumped into fermenters where it was cooled to a fermentation temperature of 10 °C. Bottom fermentation yeasts were added to the wort in an amount of 3 g. The main fermentation followed, which lasted 5 days at 10 °C. The beer was then cooled to 4 °C and, after the yeasts had settled to the bottom of the vats, was pumped into the maturation vats for 21 days.

2.1 Determination of the basic parameters of the beer

The basic parameters of the final beer product were determined using the FermentoFlash instrument (Funke Gerber, Germany). This allowed the assessment of the alcohol content in volume percent, the original extract of the wort and the real residual extract in beer. The instrument was calibrated with distilled water. Before determination, all beers were plain filtered and all beers were decarboxylated on a shaker.

2.2 Colour determination

The colour of all beers was measured using a Konica Minolta CM-3500d spectrophotometer. The spectrophotometer was connected to a computer with the CMs-100w Spectramagic NX program. This program can measure L* (lightness) values in the range 0 (black) – 100 (white). Colour coordinates a* and b*, where the a* value defines the colour green (-a*) to red (+a*) and the b* value defines the colour blue (-b*) to yellow (+b*). Negative and positive values depend on the position of the values in the three-dimensional CIELAB system. Transmittance was measured for all beer variants. A cuvette was used to measure all variants and distilled water was used as a blank.

Table 2 Temperatures and time lags applied during wort preparation

Temperature [°C]	Time lag [min]
37	10
45	10
52	15
62	30
72	30
83	5

 Table 3
 The amount of water used to separate spent grains

Beer variant	Amount of water [I]
Q10	2.5
Q20	2.2
Q30	2.6
A10	2.2
A20	2.2
A30	2.7
B10	2.6
B20	2.6
B30	2.8
С	2.6

Q10: quinoa 10%, Q20: quinoa 20%, Q: quinoa 30%, A10: amaranth 10%, A20: amaranth 20%, A30: amaranth 30%, B10: buckwheat 10%, 20: buckwheat 20%, B30: buckwheat 30%, C: beer without added pseudocereals

2.3 Determination of carbohydrates

Carbohydrates (fructose, maltose, maltotriose and glucose) were determined chromatographically in sweet wort, wort and beer using an Agilent Technologies instrument (Agilent Technologies, USA). The pre-column used was ARION® 5 mm cartridges for Guard System, NH2 5.0 μ m, ID 4.0 mm. The analytical column was an ARION® NH2 HPLC column, 5.0 μ m, 250 mm × 4.6 mm, with a flow rate of 1.5 ml/min. Acetonitrile (30 °C) was used as the mobile phase and the column was heated with water in a 75:25 ratio. The injection rate for each sample was 10 μ L A refractometric detector was used for the determination.

2.4 Sensory evaluation

All beers were sensory evaluated. A total of 10 evaluators took part in the evaluation. The sensory profile method according to the ČSN EN ISO 13 299 standard was used. An unstructured graphic scale was used with a verbal description of 100 mm endpoints, with 1 mm corresponding to a rating of 1 point. The endpoints of the scale were described verbally. 0 was marked as an extremely bad impression and 100 as an extremely good impression. The raters were not provided with any information about the beer samples. The beer was cooled to 8 °C before tasting. Drinking water was used as a neutralizer.

2.5 Statistical evaluation

The measured data were statistically evaluated using Statistica 13 software (StatSoft, USA). The Shapiro-Wilk test was used to calculate normality and the Levene's test was used to calculate homogeneity. Data were further evaluated using analysis of variance (one-way ANOVA) and Scheffe's multiple comparison method at a significance level of p < 0.05. Tables were generated in Microsoft Excel 2013.

3 Results and discussion

3.1 Basic parameters of beer

The addition of pseudocereals decreased the alcohol content (Table 4). The highest alcohol content (4.10% V/V) was observed in variant 10, prepared without added pseudocereals. However, the highest extract in the original wort was found in variant 8, which was the variant where buckwheat was used in the mash at 20%. Buckwheat grains contain 10-14% protein, 55-70% starch, 1.5-3.7% fat and 3.4-5.2% fibre (Tůmová et al., 2007). From the results, it is evident that the addition of pseudocereals had some effect on the composition of the wort and it was less fermentable, which was negatively reflected in the % alcohol content (V/V). The wort fermented the worst in variants where amaranth was used in the mashing process (var. 4, 5, 6). The use of pseudocereals in brewing is a very demanding process. The substitution of barley malt increases the viscosity of the mash. Higher viscosity worsens wort separation. This can lead to a lower extract yield, which can cause a lower alcohol content in the final product (Cela et al, 2023). Quinoa contains proteins that provide high stability of beer foam (Vidaurre-Ruiz et al., 2023). The physiological aspects of pseudocereals, such as grain size and amount of husk, are very important for their processability in brewing. The hulls can act as a filtering layer, but they are also a protective layer of the kernel, which leads to insufficient milling of the grain and consequently lower extract content (Bailliére et al., 2022).

3.2 Evaluation of beer colour

The lightness (L*) of the beers with added pseudocereals was significantly (p>0.95) higher than that of the control beers (Figure 1). However, the effect of the amount of pseudocereal addition was small. The lightest beers were produced by adding buckwheat. Conversely, beer brewed with 30% amaranth was significantly (p>0.95) darker. It is evident that the presence of pseudocereals had a significant effect (p>0.95) on the lightness of the beer colour. The colour of beer is mainly influenced by the characteristics of the malt. Melanoidins, as end products of Maillard reactions, are also known to contribute to the physical, chemical, organoleptic and colour properties of beer (Pieczonka et al., 2021). The presence of betaline pigments, which are abundant in pseudocereals, may also be responsible for the observed change in beer lightness (Thakur et al., 2021).

Figure 2 shows that the beers with the addition of pseudocereals were characterised by a moderate amount of green colour, as all beers had a* values in the negative range. The highest percentage of green colour was observed in variant 3 (-2.14) where 30%

Table 4 Effect of added pseudoceredi on content of alconol, the real residual extract and original extract of the wort						
Variant	Content of alcohol % (V/V)	Real residual extract %	Original extract of the wort $\mathfrak L$			
Q10	4.05	6.19	10.61			
Q20	3.95	5.48	10.91			
Q30	3.9	4.94	10.44			
A10	3.73	5.37	10.46			
A20	3.72	5.97	10.88			
A30	3.43	5.80	10.26			
B10	3.93	5.72	11.06			
B20	3.93	6.08	11.33			
B30	3.5	5.33	10.53			
С	4.10	4.56	10.80			

 Table 4
 Effect of added pseudocereal on content of alcohol, the real residual extract and original extract of the wort

Q10: quinoa 10%, Q20: quinoa 20%, Q: quinoa 30%, A10: amaranth 10%, A20: amaranth 20%, A30: amaranth 30%, B10: buckwheat 10%, 20: buckwheat 20%, B30: buckwheat 30%, C: beer without added pseudocereals

quinoa was used, indicating that the strongest green colour was observed after the addition of quinoa (-2.12). The differences, although significant, were not obvious when comparing the effect of quinoa with that of amaranth (-1.73) and buckwheat (-1.97). In the control, where no pseudo cereals were used, a shift towards becoming more red was observed (2.02). We can assume that the products of Maillard reactions (melanoidins) played a significant role here. Melanoids are coloured, high-molecular substances characterized by a light yellow to brown colour. Melanoidins, which are formed in the Maillard reaction, inhibit the growth of bacteria that promote the chelation of metal ions such as magnesium. The latter is an important ion in the brewing process, as it is a necessary cofactor for a number of catalytic reactions and plays a major role in the protection of yeast cells (Dack et al., 2017). Colour is one of the most important quality indicators of beer, especially for consumers. Each beer has its own typical colour, according to which we can further divide it into groups (light, semi-dark, dark) (Fengxia et al., 2004).

The coordinates of the parameter b* are shown in Figure 3. The highest (p>0.95) proportion of yellow colour was found when using barley malt without the addition of pseudocereals 30.18 (variant 10). Conversely, the lowest value of b* was found in variant 8 (19.96), in which 20% buckwheat was used. The addition of quinoa increased the b* value most (24.04) in the average of all variants (variants 1–3) compared to amaranth (22.34) and buckwheat (21.50).

The dose of pseudocereals did not significantly affect the lightness of the beer (93.9–94.9) (Figure 4). However, the control variant was significantly (p>0.95) darker (70.9) than the other variants.

When the effect of pseudocereal dose on colour was evaluated for parameters a* and b* (Figure 5), similar trends were observed as for lightness. It can be noted that the difference between the variants regarding a* where pseudocereals were added was minimal (-2.0 to -1.96) and all the variants were characterised by the presence of a green colour, which was observed in the control variant. The colour of the control beer was more characterised by red hues (2.02). The control beer (30.18) also had the highest b* values. The results of the beer colour analysis can be used to differentiate beers on the basis of their colour (Koren et al., 2020).



Figure 1 Effect of pseudocereal addition on lightness of beers L*(D65)



Figure 2 Effect of pseudocereal addition on red-green components of beer colour a*



Figure 3 Effect of pseudocereal addition on blue-yellow components of beer colour b*

Legend to the Figures 1-3:

Q10: quinoa 10%, Q20: quinoa 20%, Q: quinoa 30%, A10: amaranth 10%, A20: amaranth 20%, A30: amaranth 30%, B10: buckwheat 10%, 20: buckwheat 20%, B30: buckwheat 30%, C: beer without added pseudocereals



Figure 4 Effect of the amount of added pseudocereal (10%, 20%, 30%, 0%) on lightness of beer L*(D65)



Figure 5 Effect of the amount of added pseudocereal (10%, 20%, 30%, 0%) on red-green a* and blue-yellow b* components of beer colour



Figure 6 Overall evaluation of beers

Q10: quinoa 10%, Q20: quinoa 20%, Q: quinoa 30%, A10: amaranth 10%, A20: amaranth 20%, A30: amaranth 30%, B10: buckwheat 10%, 20: buckwheat 20%, B30: buckwheat 30%, C: beer without added pseudocereals

3.3 Evaluation of the organoleptic characteristics of the beer

Nevertheless, the overall evaluation is decisive in assessing the quality of the beer (Figure 6). The best rated beer was variant 9 (78.4). This variant contained 30% buckwheat in the mash. Figure 6 shows that all variants with buckwheat in the mash scored higher than variants with other pseudo grains. Quinoa was the lowest rated substitute in the mash and the lowest rated variant was variant 3 (65.6). Pseudocereals provide different sensory characteristics to those commonly found in beers made from barley malt (Cela et al., 2020). While buckwheat was well accepted, quinoa was not.

3.4 Carbohydrate content in sweet wort

The carbohydrate composition of the sweet wort for each variant is shown in Figure 7. For variants 1-3, which were quinoa variants, it can be observed that the proportion of maltose decreased as the quinoa dosage increased, while the proportion of glucose increased, as is the case for variants 4-6, which were amaranth variants. This observation can be explained by the lower content of carbohydrates in the grains of quinoa and amaranth than in the grains of barley. Amaranth grains contain 59.2% carbohydrate, quinoa grains 69% and barley 80.7% carbohydrate, but this did not show up much in the finished beer (Kocková and Valík, 2011). The highest (p>0.95) maltose content was found in variant 1 with 10% quinoa (54.43 mg/ml). On the other hand, the lowest (p>0.95) maltose content was found in the sweet wort with the addition of 20% buckwheat (31.57 mg/ml). The addition of starchy raw materials in the form of pseudocereals altered the activity of the enzymes added in the form of barley malt. For this reason, the mashing process may produce different degradation products from those found in beers made from barley malt alone. Pseudocereals have little or no β-amylase activity and are therefore unable to add sufficient enzymatic power to the mash (Baillére et al., 2022).

3.5 Carbohydrate content in wort

High quality wort is essential for the production of high-quality beer, so the preparation of wort from suitable raw materials and proper management of the brewing process are important (Pahl et al., 2016). In beer production, malting barley is commonly used as a source of carbohydrates and any change in the recipe will affect the composition of the wort (Sterczyńka et al., 2021). This is illustrated in Figure 8, which shows that the addition of pseudocereals can significantly affect the composition of the wort. Carbohydrates are the main constituents of pseudocereals, accounting for 60-80% of the dry matter. The most common carbohydrate is starch. Buckwheat starch has the highest proportion of amylose (18.3-47% of total starch) compared to quinoa (11-12% of total starch) and amaranth (7.8-34.3% of total starch) (Martínez-Villaluenga et al., 2020). The highest level of maltose was found in variant 4 (49.09 mg/ml), where amaranth was added at 10%. In the variants where amaranth was used. it can also be observed that the amount of maltose decreased as the amount of pseudocereals increased, while the amount of glucose increased. The highest percentage of glucose was then measured for variant 3 with the addition of 30% quinoa (52.56 mg/ml). However, it should be noted that the proportion of carbohydrates in the wort of all the variants with the addition of pseudocereals did not differ significantly from the control variant.

The amount of carbohydrates in the residual unfermented extract is shown in Figure 9. During fermentation the carbohydrates are broken down into ethanol and carbon dioxide (Alves et al., 2020). The figure shows that only maltose remains unfermented. Maltotriose, fructose and glucose were no longer detected in the finished beers. Therefore, the wort can be considered well fermented. The figure also shows that the higher the dose of pseudocereals increased the amount of unfermented maltose. Variant 9 with 30% buckwheat (1.66 mg/ml) had the highest values. The lowest levels of maltose were found in variant 4, where amaranth was used at 10% (0.60 mg/ml).

4 Conclusion

The addition of pseudocereals affected the composition of the wort. Less alcohol by volume was produced during fermentation than in the control. But it should be noted that this was not significant. The results of the different variants did not vary in terms of alcohol content. Beer lightness did not differ much between the pseudocereals variants. However, the control variant was significantly darker. This is a positive result, as Czech consumers prefer beers with a lighter colour. The beers with pseudocereals were characterised by a low proportion of green colour. The beer with 30% added buckwheat had the best sensory evaluation. Ac-

cording to the evaluation, buckwheat had a positive effect on the overall evaluation, as all variants with buckwheat scored higher than variants with other pseudocereals. The



Figure 7 Effect of added pseudocereal on the content of fructose, glucose, maltose and maltotriose in sweet wort



Figure 8 Contents of fructose, glucose, maltose and maltotriose in wort



Figure 9 Maltose content in beers with added pseudocereals

Legend to the Figures 1-3:

Q10: quinoa 10%, Q20: quinoa 20%, Q: quinoa 30%, A10: amaranth 10%, A20: amaranth 20%, A30: amaranth 30%, B10: buckwheat 10%, 20: buckwheat 20%, B30: buckwheat 30%, C: beer without added pseudocereals

glucose content of the wort was also increased, but the maltose content decreased, by increasing the dose of quinoa and amaranth. The wort was sufficiently fermented, as indicated by the results showing that maltotriose, glucose and fructose were no longer present in the finished beer and that maltose was present only at low levels. According to the results obtained, the beers with pseudocereals did not differ much from the beers without pseudocereals.

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