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Influence of selected treatment methods on the dry residue and sugars content extracted from wheat and rye bran

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Abstract: *Influence of selected treatment methods on the dry residue and sugars content extracted from wheat and rye bran*. In this paper 1% NaOH extraction and 1% NaOH extraction with α-amylase pre-treatment were conducted on wheat and rye bran. Different times of reaction (0.5, 1, 2 and 4 h) and different temperatures (40°C, 45°C, 50°C and 95°C) of process were applied during experiments. After the process, dry residue content was calculated. Additionally, monosaccharides content in liquid was determined after α-amylase pre-treatment and 1% NaOH extraction. Monosaccharides content (glucose, xylose and arabinose) after acid hydrolysis of obtained liquids was determined by the HPLC technique. Obtained results showed that there was a positive correlation between time, temperature and content of compounds extracted by 1% NaOH solution. The lowest dry residue content for wheat and rye bran after 1% NaOH extraction was obtained at 95 °C during 4 hours of conducting the process (24.7±0.1 and 18.4±2.8 respectively). Additional pre-treatment by α-amylase increased solubility of compounds included in bran, especially for wheat bran. α-amylase influenced not only starch solubility but also other compounds from bran. The next advantage of pre-treatment by α-amylase was easier access to remaining sugars inside the bran, which in the form of xylose and arabinose can be obtained.

Keywords: rye bran, wheat bran, 1% NaOH extraction, α-amylase, monosaccharides

INTRODUCTION

Bran is a byproduct of grain processing. They are the tough outer layers of mainly cereal grains (fruit and seed coat). The most popular bran in Poland are wheat, rye and oat. Bran accounts for approximately 15% of the weight of the whole corn (Prückler et al. 2014). Wheat and rye bran are byproducts of the milling of grain to obtain flour. They contain part of the starchy endosperm and are particularly rich in carbohydrate components (mainly starch), proteins and minerals. Other compounds of bran are lignin and fatty acids. The large variation in the content of the stated components depends mainly on the wheat and rye cultivars taken for analysis. The most important part of bran is the carbohydrate fraction - for wheat bran it is 56-57% (Apprich et al. 2014) including: starch 13.8-29.0% (Dornez et al. 2006), cellulose 5.6-12.0% (Hemery et al. 2010), hemicelluloses 20.8-33.0% (Dornez et al. 2006; Gebruers et al. 2008) in which arabinoxylan is 10.9-26.0% (Dornez et al. 2006; Gebruers et al. 2008). In rye bran carbohydrate components account 62.6-63.6% (Nilsson et al. 1996) including: starch 17.8-30.2% (Nilsson et al. 1996; Katina et al. 2007;), cellulose 4-6% (Rakha et al. 2010), hemicelluloses over 34% of which arabinoxylan is 18-25% (Van Craeyveld et al. 2009; Rakha et al. 2010). A particularly important compound found in bran is arabinoxylan, which is the main component of hemicelluloses.

Wheat and rye bran are an interesting lignocellulosic biomass in the context of further processing, including the extraction of starch for the production of ethanol, and protein for use in animal feed. A very important direction of bran utilisation are carbohydrates. Complex carbohydrates such as arabinoxylan can be utilised in the food industry (Pietiäinen et al. 2022). Polysaccharides are also an attractive source of monosaccharides, those made of five

carbon atoms (xylose and arabinose) and those made of six carbon atoms (glucose, mannose and galactose). Monosaccharides, using various processing methods, can be converted into many valuable compounds such as xylitol, ethanol, furfural or furfuryl alcohol.

The products of converting furan compounds into so-called furan fuels of the future are very widely used today (Malinowski and Wardzińska 2012). For the isolation of selected carbohydrates, biorefining processes are used (Wood et al. 2016, Pietiäinen et al. 2022). The isolation method mainly involves extracting the constituents of the bran. A direct alkali extraction method for carbohydrates has shown that higher temperatures and time of the process are more favourable for isolating sugars. An obstacle is the high viscosity of the resulting solutions due to, among other things, interactions between other bran components (Kaur et al. 2019). Hence, the mostly used extraction techniques are mainly chemical (removal of starch, lignin and protein), mechanical (grinding, extrusion or ultrasound), physico-chemical (steam explosion – SE, liquid hot water - LHW), involving pre-treatment of the raw material (Pietiäinen et al. 2022). The prepared material is subjected to further treatment steps consisting mainly of alkaline extraction or enzymatic hydrolysis. The use of suitable alkaline extraction conditions facilitates the hydrolysis of the ester bonds between arabinoxylan and ferulic acid (Ruthes et al. 2020) and increases the carbohydrate extraction efficiency dramatically.

The aim of the study was to examine how one-step and two-step alkaline treatment preceded by pre-treatment with α-amylase will affect the content of carbohydrates obtained from wheat and rye bran.

MATERIALS AND METHODS

Material

Rye (*Secale* L.) and wheat (*Triticum* L.) bran were used for the study. The bran were obtained from the mill POLSKIE MŁYNY sp. z o. o. (Teresin, Poland). The material was seasoned in the laboratory and then sorted using a laboratory shaker with a set of sieves. A bran fraction of 0.43-1.02 mm was used in the study.

A commercial enzyme blend of α-amylase Avantec®Rev FG from Novozymes was used for starch hydrolysis.

A sodium hydroxide (NaOH) (pure, Chempur), acetic acid 99.5% (pure, Chempur), disodium hydrogen phosphate (pure for analysis, Chempur), citric acid (pure for analysis, Chempur), sulphuric acid VI 72% (pure for analysis, Chempur), sodium carbonate (Na_2CO_3) (pure for analysis, Chempur) and sodium azide (NaN_3) (pure for analysis, Chempur) were used.

Extraction with sodium hydroxide

Extractions of rye and wheat bran were carried out with a 1% NaOH aqueous solution with the $1{:}100_{(w/v)}$ ratio of solid dry sample to liquid NaOH solution. The extraction times were 0.5, 1, 2, and 4 h. Temperatures 40, 50 and 95 °C were applied. The residues were removed by filtration.

Table 1. Variables of wheat and rye bran to 1% NaOH extraction

Material	Wheat bran								Rye bran							
Temperature/°C	40		50		95				40		45		95			
Process time/h	1	4	1	4	0.5	1	2	4	1	4	1	4	0.5	1	2	4

The remaining dry mass of solid residues after neutralization with 10% acetic acid was determined. The liquid containing alkaline wheat bran extract was collected for analysis of monosaccharides content and profile by HPLC (high-performance liquid chromatography)

method. A compilation of the performed experiments was shown in Table 1. Dry residue content was always calculated with reference to the mass of raw material.

Starch enzymatic hydrolysis

All experiments of starch hydrolysis were conducted in 20 cm^3 volumes. Solid loading was 20%$_{(w/v)}$. A citrate buffer was prepared from 0.1 M citric acid solution, 0.1 M disodium hydrogen phosphate solution, and distilled water. The solutions were combined in proportions of 14.8 cm^3:35.2 cm^3:50 cm^3, respectively. Adjusted to pH 5.5 by sodium hydroxide. Hydrolysis was performed using 0.5 µL of enzyme α-amylase Avantec®Rev FG per 1 g of dry mass of the bran. The process was carried out at 85 °C for 4 h. The solid fraction was separated from the liquid fraction by filtration and a dry mass of residues was determined. The liquid fraction was collected for HPLC analysis of profile and content of monosaccharides. Part of the solid fraction from wheat and rye bran after treatment with α-amylase was treated with an aqueous solution of 1% NaOH at 95 °C for 1 h. Then the content and profile of sugars were examined using the HPLC method. Dry residue content was always calculated with reference to the mass of raw material.

Saccharides acid hydrolysis

Liquid fractions obtained in the processes using 1% NaOH and α-amylase were used to hydrolyse sugars. For the hydrolysis of sugars, the method described by Sluiter et al. (2008) was used. The selected method was partially modified and adapted to the tested material. The use of this method allows for a more accurate determination of sugars content because this method (besides of free simple sugars) also takes into account sugars in the oligomeric form. First, approximately 25 cm^3 of the liquid fraction was taken and the pH of the solution was adjusted to the range of 3.15-4.99. Then, 20 cm^3 of sample was taken from the prepared solution and transferred to a 50 cm^3 heart flask. Then, 0.697 cm^3 of 72% sulfuric acid VI was added using an electronic pipette and the flask was closed with a stopper. Then, the sample was heated for 1 h in an oil bath at 120 °C under reflux. After heating was completed and cooled to room temperature, the sample was frozen and left until the next day. After thawing the sample, 1 cm^3 of 2% NaN_3 was added. Then, 15 cm^3 of the solution was taken and neutralized with Na_2CO_3 to pH=5-6. After obtaining the appropriate pH, 1 cm^3 of the sample was filtered through a 0.2 µm nylon syringe filter into vials. Chromatographic analysis was performed on an HPLC system (LC-20AD, Shimadzu, Kyoto, Japan) equipped with refractometer detector (RID-10A, Shimadzu, Kyoto, Japan). Monosaccharides (glucose, xylose and arabinose) separation was done using a RHM-Monosaccharide column (300 mm × 7.80 mm, Rezex, Torrance, USA) at 80 °C and demineralised water as a mobile phase flowing with 0.6 cm^3/min. All of the acid hydrolysis tests were done at least in triplicate and single standard deviations were calculated.

RESULTS AND DISCUSSION

Extraction study was conducted on wheat and rye bran. The investigation involved varying the temperature and extraction time to observe their effects on the extraction efficiency. The percentage of dry residue left after the extraction process was determined for this purpose. This indicates the amount of material that remains after extracting certain components. Table 2 provides information about how the dry residue percentage varies based on different extraction conditions for both wheat bran and rye bran. The standard deviation (SD) values indicate the variability or precision of the measurements.

The temperature effect on the dry residue content after 1% NaOH treatment was observed. As the temperature increased from 40 °C to 95 °C, the dry residue generally decreased. Dry residue content after treatment with 1% NaOH at 40 °C for 1 hour was almost

one and a half times higher than the dry residue after extraction at 95 °C for 1 hour. The temperature effect was similar to wheat and rye bran, there was a trend of decreasing of dry residue with increasing temperature, but the change was smaller for rye bran than for wheat bran.

Also, the time effect on the dry residue content after 1% NaOH treatment was noticeable. For both, rye and wheat bran, increasing extraction time generally led to a decrease a dry residue.

Table 2. Dry residue content after 1% NaOH extraction at different temperatures and extraction times

Material	Temperature/°C	Extraction time/h	Dry residue/%
Wheat bran	40	1	43.6 ± 0.3
	40	4	35.6 ± 0.2
	50	1	37.0 ± 0.3
	50	4	32.5 ± 0.4
	95	0.5	31.8 ± 0.3
	95	1	29.4 ± 1.0
	95	2	26.5 ± 0.8
	95	4	24.7 ± 0.1
Rye bran	40	1	25.1 ± 0.1
	40	4	21.5 ± 0.2
	45	1	25.4 ± 0.2
	45	4	21.5 ± 0.1
	95	0.5	21.9 ± 0.8
	95	1	19.9 ± 2.2
	95	2	20.6 ± 2.8
	95	4	18.4 ± 2.8

From the presented data, the conditions that resulted in the maximum dry residue percentages for both wheat and rye bran were 40 °C and 1 hour of extraction. For rye bran similar dry residue percentage was also obtained for 45 °C and 1 hour of extraction. The minimum dry residue content for both wheat and rye bran was for 95 °C and 4 hours of extraction. These conditions represented the extremes in terms of dry residue percentages for each material.

Table 3. Dry residue content after α-amylase and 1% NaOH treatment

Material	Treatment	Dry residue/%
Wheat bran	α-amylase	55.9 ± 0.4
	α-amylase followed by 1% NaOH 95 °C, 1 h	19.0 ± 0.1
Rye bran	α-amylase	44.2 ± 3.9
	α-amylase followed by 1% NaOH 95 °C, 1 h	20.5 ± 0.5

These trends provide valuable insights into how temperature and extraction time influence the dry residue content in both wheat bran and rye bran, which can be essential n optimizing extraction processes for specific applications. Also, valuable information is obtained after 1% NaOH treatment liquid composition in terms of the content of monosaccharides. Therefore, a further investigation was performed on liquid fraction.

The 1% NaOH extraction process was also carried out, preceded by a pre-treatment with α-amylase. For the most promising results of previous extraction, one set of conditions was chosen, that was, a 95 °C and a process time of 1 h. The dry residue content after hydrolysis with α-amylase and hydrolysis with α-amylase followed by 1% NaOH extraction was shown in Table 3. Obtained data suggest that the treatments, especially the combination of hydrolysis with α-amylase followed by 1% NaOH extraction at 95 °C for 1 hour, significantly decreased the dry residue in both wheat and rye bran compared to the one-step treatment with α-amylase alone. The lower percentage of dry residue may indicate the effectiveness of the combined treatment in breaking down and solubilizing the bran components. It also eases the extraction step after the 1% NaOH extraction process. The two-step process allows the bran components removed in each stage to be separated.

In Table 4 the monosaccharides contents in liquid fraction obtained from wheat and rye bran after 1% NaOH treatment at different temperature and time conditions were presented. Based on the results it can be observed that depending on the conditions of bran treatment in 1% NaOH, different glucose, xylose and arabinose contents were obtained. Hence, the following relationship was found: the higher temperature and processing time, the higher sugars content.

Table 4. Monosaccharides content in liquid fraction obtained from wheat and rye bran after 1% NaOH treatment

Sample	Monosaccharides after acid hydrolysis		
	Glucose/%	Xylose/%	Arabinose/%
Wheat bran after 1% NaOH treatment (40 °C, 1 h)	7.7 ± 0.3	6.2 ± 0.2	1.8 ± 0.2
Wheat bran after 1% NaOH treatment (40 °C, 4 h)	9.1 ± 0.1	7.1 ± 0.1	2.5 ± 0.2
Wheat bran after 1% NaOH treatment (50 °C, 1 h)	12.7 ± 0.2	7.4 ± 0.1	2.6 ± 0.3
Wheat bran after 1% NaOH treatment (50 °C, 4 h)	13.6 ± 0.1	8.7 ± 0.1	3.4 ± 0.2
Rye bran after 1% NaOH treatment (40 °C, 1 h)	22.1 ± 0.5	7.1 ± 0.2	1.2 ± 0.1
Rye bran after 1% NaOH treatment (40 °C, 4 h)	23.8 ± 0.4	8.3 ± 0.1	2.1 ± 0.2
Rye bran after 1% NaOH treatment (45 °C, 1 h)	23.5 ± 0.4	8.4 ± 0.2	2.3 ± 0.1
Rye bran after 1% NaOH treatment (45 °C, 4 h)	25.1 ± 0.5	8.9 ± 0.3	2.8 ± 0.3

Generally, the highest content was found for glucose (7.7-25.1%), lower for xylose (6.2-8.9%), and the lowest for arabinose (1.2-3.4%). Moreover, rye bran, due to its higher starch content, always had a higher glucose content than wheat bran. The contents of other sugars (xylose and arabinose) in the tested bran were at a similar level.

Additionally, in order to compare and increase the availability of five-carbon sugars, the effect of α-amylase was checked. The results were presented in Table 5.

If we compare the results presented in Table 5, it can be observed that the removal of starch from wheat and rye bran resulted in an increase in the content of five-carbon sugars, which were extracted in the next stage using 1% NaOH at 95 °C during 1 h.

Table 5. Monosaccharides content in liquid fraction obtained from wheat and rye bran after α-amylase and 1% NaOH treatments

Sample	Monosaccharides after acid hydrolysis		
	Glucose/%	Xylose/%	Arabinose/%
Wheat bran after α-amylase treatment	9.1 ± 0.2	3.6 ± 0.3	0.8 ± 0.1
Wheat bran after α-amylase and next 1% NaOH (95 °C, 1 h) treatments	1.5 ± 0.4	10.6 ± 0.8	8.8 ± 0.3
Rye bran after α-amylase treatment	19.6 ± 1.2	5.3 ± 0.3	1.1 ± 0.1
Rye bran after α-amylase and next 1% NaOH (95 °C, 1 h) treatments	2.1 ± 0.4	12.6 ± 0.7	8.0 ± 0.3

After this treatment from the bran, high contents of xylose (10.6-12.6%) and arabinose (8.0-8.8%) were obtained. Moreover, it should be noted that the process of removing starch at 85 °C for 4 hours also caused a partial loss of xylose (in the liquid fraction for wheat bran 3.6%, and for rye 5.3%) and arabinose (in the liquid fraction for wheat bran 0.8%, and for rye 1.1%).

CONCLUSIONS

On the basis of the studies performed, the following conclusions were drawn:

1. During 1% NaOH treatment, the decreasing trend of dry residue with increasing temperature and time of extraction was observed. This change was smaller for rye bran than for wheat bran.

2. The combination of hydrolysis with α-amylase followed by 1% NaOH treatment at 95 °C for 1 hour, significantly decreased the dry residue in both wheat and rye bran compared to the one-step treatment with α-amylase alone. The lower percentage of dry residue may indicate the effectiveness of the combined treatment in breaking down and solubilizing the bran components.

3. In case of the sugars content in liquid fraction, after 1% NaOH treatment, with increasing a temperature and processing time, so the higher sugars contents were achieved. Moreover, rye bran, due to its higher starch content, always had a higher glucose content than wheat bran. The contents of other sugars (xylose and arabinose) in the tested bran were at a similar level.

4. The removal of starch from wheat and rye bran resulted in an increase in the content of five-carbon sugars, which were extracted in the next stage using 1% NaOH at 95 °C during 1 h. After this treatment from the bran, high contents of xylose (up to 12.6%) and arabinose (up to 8.8%) were obtained.

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Streszczenie: *Wpływ wybranych metod obróbki na zawartość suchej pozostałości i cukrów pozyskanych z otrąb pszennych i żytnich*. W niniejszej pracy podjęto próbę pozyskania cukrów z otrąb pszennych i żytnich za pomocą obróbki roztworem 1% NaOH. Dodatkowo na części materiału wykonano obróbkę wstępną w postaci usunięcia skrobi za pomocą α-amylazy. Zastosowano różne czasy gotowania (0,5, 1, 2 i 4 h) oraz różne temperatury (40°C, 45°C, 50°C, 95°C) obróbki w roztworze 1% NaOH. Dla przeprowadzonych wariantów ustalony został udział suchej pozostałości po ekstrakcji oraz obróbce wstępnej. Dodatkowo oznaczono zawartość monosacharydów we frakcji ciekłej po wstępnej obróbce α-amylazą i ekstrakcji 1% NaOH. Zawartość monosacharydów (glukozy, ksylozy i arabinozy) po hydrolizie kwaśnej badano za pomocą techniki HPLC. Uzyskane wyniki wskazują, że występuje korelacja między czasem, temperaturą i ilością rozpuszczonych związków w roztworze 1% NaOH. Najniższą zawartość suchej pozostałości w otrębach pszennych i żytnich po ekstrakcji 1% NaOH uzyskano w 95°C w ciągu 4 godzin prowadzenia procesu (odpowiednio 24,7±0,1 i 18,4±2,8). Dodatkowa obróbka za pomocą α-amylazy zwiększa rozpuszczalność związków zawartych w otrębach, szczególnie w przypadku otrąb pszennych. Samo działanie α-amylazy powoduje przechodzenie do roztworu skrobi, a także innych związków zawartych w badanym materiale, zwiększając przy tym dostępność do cukrów zawartych w otrębach, które można pozyskać w postaci ksylozy i arabinozy.

Słowa kluczowe: otręby żytnie, otręby pszenne, ekstrakcja 1% NaOH, α-amylaza, cukry proste

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