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Wheat bran biorefinery: An investigation on the starch derived glucose extraction accompanied by pre- and post-treatment steps

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HIGHLIGHTS

- Glucose of starch fraction of wheat bran was extracted using a conventional method.
- The purity of free glucose in the extract was 44%.
- After a pre-separation of water-solubles the purity of free glucose was enhanced to 58%.
- Hydrothermal treatment of the residual bran did not generate hydroxymethylfurfural.
- Hydrothermal treatment of the residual bran induced an increased level of furfural.

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ABSTRACT

Wheat bran, a side product of the milling industry, can be considered as a feedstock for biorefineries. Unlike other lignocellulosic feedstock, wheat bran contains a reasonable amount of starch, which is not of recalcitrant nature. Therefore, it can be extracted without a costly pretreatment process. The present work evaluates the extraction of starch derived glucose in relation to a wheat bran biorefinery. The purity of free glucose extracted quantitatively was 44%. The extract was concentrated by threefold via nanofiltration, thereby reaching a glucose concentration of 49 g/L. Hydrothermal treatment (180 °C – 20 min) of the starch-free bran did not induce the formation of hydroxymethylfurfural and levulinic acid. Interestingly, the furfural level increased compared to the process, in which bran was treated hydrothermally without a preceding starch extraction. By separation of water-extractables prior to enzymatic hydrolysis, the free glucose purity was increased to 58%, however the yield of glucose decreased to 61%.

1. Introduction

While an incremental growth can be observed in the world demand for energy and commodity chemicals, the main resource that covers this demand is expected to be depleted within a foreseeable future. As a response to this, the interest shown in lignocellulosic biomass as a promising alternative to the fossil fuel for the production of energy and commodity chemicals is growing (Almeida et al., 2009; Liu et al., 2012). Up to date, several lignocellulosic feedstocks, e.g., wood, corn stover, wheat straw have been investigated for the utilization following future-oriented biorefinery concepts (Huijgen et al., 2012; Kadam et al., 2008; Liu et al., 2012). The wheat bran, constituting up to one fifth of the wheat kernel (Javed et al., 2012) and being generated in enormous quantities as the side product of white wheat flour production, was also considered as an alternative lignocellulosic raw material (Palmarola-Adrados et al., 2005; Reisinger et al., 2013).

The utilization of lignocellulose to fuel and chemicals most likely involves various fermentation routes of monosaccharides (Almeida et al., 2009). In this respect, one of the challenges lies in inherent recalcitrant fractions of plant material, which require so-called pretreatments to alter their macroscopic, microscopic as well as chemical structures in order to achieve an effective hydrolysis to their monomeric sugars (Mosier et al., 2005). Self-evidently, pretreatment processes increase the cost of end products not only by being technically demanding but also requiring costly downstream processes. Recently, Blanch et al. (2011) summarized the advantages and disadvantages of current pretreatment technologies and their impacts on overall process economics. It was also reported that in the conversion of biomass into fuels, pretreatment stands for one of the most expensive processing

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steps (Blanch et al., 2011; Mosier et al., 2005; Lynd et al., 1996). Furthermore, severe conditions of several pretreatment methods result in the formation of degradation products. Among these, 5-hydroxymethyfurfural (HMF) and furfural are generated from hexose and pentose degradation, which in turn are further degraded to formic and levulinic acid. The formation of those degradation products should be minimized not only to avert the inhibition of the microbial growth performance in subsequent fermentation processes but also to avoid the loss of sugars (Ask et al., 2013; Palmqvist and Hahn-Hägerdal, 2000a,b).

Referring to the abovementioned context, it should be noted that wheat bran as a raw material of a biorefinery exhibits some pronounced differences to typical lignocellulosic biomass feedstocks. While, e.g., wood, straw, corn stover as well as switchgrass are composed mainly of hemicellulose, cellulose and lignin (Lee et al., 2007), wheat bran contains lower amounts of cellulose and lignin, albeit relatively high amounts of protein, starch and minerals. Hence, considering wheat bran as a feedstock for a biorefinery, a pretreatment application as the first processing step introduces a highly complex slurry, which subsequently requires further treatment steps. Additionally, increased severities of the pretreatment parameters result in some loss of sugar and protein content (Reisinger et al., 2013). Thus, pre-fractionation steps appear to be reasonable not only to simplify the composition of the pretreated slurry, but also to recover valued components. In this respect, for several reasons starch is also one of the fractions of major interest. Firstly, unlike lignin, cellulose and hemicellulose, the starch fraction is not recalcitrant, thus does not require pretreatment for the monomerization. An enzymatic hydrolysis of starch can be easily performed by applying commercially available amylolytic enzymes. Secondly, it should be noted that based on the enormous quantities of wheat bran produced worldwide, correspondingly high amounts of starch are available. By roughly assuming that the whole wheat available worldwide is milled for human food consumption, the annual by-product stream would account for approximately 15 million tons of glucose originating from the wheat bran-based starch fraction (Prückler et al., 2013). This calculation suggests potential utilizations as food and also as substrate for building blocks (Apprich et al., 2014). Last but not least, it can be expected that the removal of starch prior to pretreatment will lead to reduced formation of degradation products originated from hexoses.

The work presented primarily aims at investigating the production of starch-derived glucose (SDG) from wheat bran by circumventing complex processing methods. Particular interest is shown in the yield and the purity of SDG, hereby to improve the purity a pre-extraction step preceding the SDG extraction is also investigated. A nanofiltration (NF) process for concentrating the SDG retaining extract is examined. Furthermore, the effect of SDG extraction on the further hydrothermal treatment of the residual bran regarding the inhibitors formation is evaluated. The findings of the present study should serve as a contribution to a development of a future biorefinery valorizing an agricultural side product.

2. Methods

2.1. Raw material

Wheat bran used in this study was provided by GoodMills (Schwechat, Austria) and stored at 4 °C till the use. The carbohydrate content of the wheat bran was 56.9% of the bran dry mass. Total carbohydrates comprised 25.4% of the total glucose, 20.3% of the total xylose, 9.3% of the total arabinose and 1.9% of the total galactose. Starch content of the wheat bran corresponded to 9.1% of the bran dry mass. The crude protein, crude fat, lignin and ash fractions of the bran dry mass were 13.2%, 4.3%, 8.0% and 7.0%, respectively. Additionally, 3.5% of the bran dry mass consisted of acetic acid.

2.2. Enzymatic hydrolysis

A sample of 160 g of wheat bran was weighed and mixed with deionized water (DW) at a ratio of 1:4. Starch degrading enzymes, α-Amylase from *Bacillus licheniformis* and Amyloglucosidase from *Aspergillus niger* (300 unit/mL) were purchased from Sigma–Aldrich, and 100 μL of each were added to the bran suspension, starting with α-Amylase at 85 °C and pH 6.5 for 3 h, followed by Amyloglucosidase, at 55 °C and pH 5.5 for 18 h. The pH values were adjusted with 37% HCl (Sigma–Aldrich).

2.3. Solid–liquid separation

The bran–water suspension was separated into its solid and liquid fractions (cake and extract, respectively) with a manually operated filter press. Double cheese cloth was employed for the press-filtration. After enzymatic hydrolyses as well as after pre-extraction, the cakes obtained were washed twice with water amounts equal to the water contents of the cakes. The dry mass content of solid fractions after pressing was in the range of 35(±4)%. In all cases, extracts were mixed with their washings and centrifuged for 30 min at an rcf of 7878*g* (Sorvall evolution RC, Rotor SLC 6000). Pellets were returned to corresponding cakes.

2.4. Membrane filtration

An acid/base stable flat sheet NF membrane (SelRO® MPF-34) with a molecular weight cut off (MWCO) of 200 Da was purchased from Koch Membrane Systems Inc. (Aachen, Germany). A stirred membrane filtration cell with 2 L hold-up volume and 0.017 m^2 filtration area was employed and the rotation frequency of the magnetic stirrer (Midi MR1 digital, Ika Labortechnik) was set at 500 rpm. The NF was initiated at a pressure of 2.5 MPa and increased to 3.5 MPa. Throughout the process the temperature was maintained at 60 °C using an external water circulating heat exchanger (Julabo-F12, -ED, Germany) jacketing the cell. In order to restore the flux after filtration process, the membrane was rinsed with NaOH (pH 13) for 3 h followed by flushing with HCl (pH 3) for 2 h. Prior and after the filtration as well as after the membrane cleaning process, the fluxes were measured with DW at 25 °C and at a pressure of 0.5 MPa.

Necessary calculations used in this study regarding the membrane filtration were carried out by adopting following equations:

$$Percent\ recovery = (1 - (cp \cdot Vp/cf \cdot Vf)) \cdot 100\ [\%]$$

$$Retention = 1 - (cp/cf) \cdot 100\ [\%]$$

where the *cp* and *cf* represent concentrations of the compound of interest in the permeate and in the feed and the *Vp*, *Vf* represent volume of permeate and of feed, respectively.

Flux reduction was calculated following the equation below;

$$Water\ flux\ reduction = ((Ji - Jii)/Ji) \cdot 100\ [\%]$$

where *Ji* and *Jii* stand for the water fluxes before and after the process, respectively.

2.5. Hydrothermal treatment

The hydrothermal treatment of the remaining bran fraction (cake) was performed in a 2 L double jacketed pressure-tight agitator vessel heated by thermal oil (Kiloclave type 3, Büchi Glas Uster, Switzerland). DW was added to the cake in an amount resulting in a solid-to-water ratio of 1:9. The reactor was sealed,