



Original Article

Production of non-digestible oligosaccharides as value-added by-products from rice straw

Supaporn Sophonputtanaphoca,^{*} Chanoknun Pridam, Jiraporn Chinnak, Mintita Nathong, Preeyaporn Juntipwong

Faculty of Agricultural Product Innovation and Technology, Srinakharinwirot University, Ongkharak Campus, Nakhon Nayok, 26120, Thailand

ARTICLE INFO

Article history:

Received 27 April 2017

Accepted 1 September 2017

Available online 17 July 2018

Keywords:

Cellooligosaccharides (COS)

Fructooligosaccharides (FOS)

Galactooligosaccharides (GOS)

Rice straw

Xylooligosaccharides (XOS)

ABSTRACT

The efficacy of rice straw as a raw material for the production of non-digestible oligosaccharides (NDOs) was evaluated using water and acid extraction. Fructooligosaccharides (FOS) were extracted with water at different times and temperatures. Other NDOs, consisting of xylooligosaccharides (XOS), cellooligosaccharides (COS), galactooligosaccharides (GOS) and arabinooligosaccharides plus mannoooligosaccharides (AOS + MOS), were investigated with different sulfuric acid concentrations, residence times and temperatures. FOS was found only when the straw was treated at 60 °C and 70 °C for all extraction periods (2 h, 3 h, and 5 h). The FOS production (1.55–1.61% weight per weight (w/w) dry biomass at 60 °C and 1.44–1.67% w/w dry biomass at 70 °C) did not differ with either temperature or extraction period. All the other NDOs were detected, with XOS being the predominant one found in the acidic extracts. The highest yield of XOS was 6.53% w/w dry biomass (equivalent to 27.82% by weight of xylan in the rice straw). The optimum conditions for XOS production were: 2% (w/w) sulfuric acid, 100 °C and 0.5 h. Extraction time, temperature and acid concentration had effects on the production of XOS, COS, GOS, AOS, and MOS. These factors determined whether the products were oligosaccharides or the monosaccharide constituents.

Copyright © 2018, Kasetsart University. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Introduction

Research interest in the conversion of lignocellulosic biomass to value-added products has been increasing in the past decade to correspond with the concepts of a bio-based economy and bio-refineries (FitzPatrick et al., 2010). The bio-based economy concept stems from the progress in farming and research for the development of bio-sourced chemical products from agricultural and forestry residues as raw materials (Huttner, 2004; FitzPatrick et al., 2010). A number of bio-sourced materials have been produced from extraction and from the recovery or synthesis or both of lignocellulosic materials derived from agricultural wastes (FitzPatrick et al., 2010). A wide range of lignocellulosic materials represents promising raw materials because of their low cost, abundance, ready availability and renewability (FitzPatrick et al., 2010), for example, rice straw, wheat straw, sugarcane bagasse, corn stover and corn cob (Mäki-Arvela et al., 2011). Among these agricultural residues, rice straw has received substantial interest

in worldwide research regarding the conversion of its structural lignocellulosic composition.

Asia is the leading rice production region, with production exceeding 90% of worldwide production (Kim and Dale, 2004). In 2007, the estimate of rice straw left after grain harvesting was 628–785 million dry tonnes (Cheng et al., 2010). The major structural polymeric compounds of rice straw are glucan (34%), xylan (15%), arabinan (2.2%) (Lau et al., 2012), lignin (17%) and ash (11%) (Roberto et al., 2003). These components can serve as raw materials for the production of value-added compounds such as fermentable sugars (Cheng et al., 2010; Hiden et al., 2012).

Non-digestible oligosaccharides (NDOs) are another group of high-value bioproducts that can be generated from processing lignocellulosic biomass (Moure et al., 2006; Garrote et al., 2007; Otieno and Ahiring, 2012). NDOs are water-soluble and most of them are composed of 3–10 different monosaccharides (Voragen, 1998). Some NDOs, such as inulin from chicory, have a degree of polymerization of up to 60 (Swennen et al., 2006). From a functional food aspect, NDOs are defined as oligosaccharides that are not hydrolyzed by the human digestive system (saliva, gastric juice, enzymes in the small intestine) and thus are susceptible to hydrolytic enzymes of colon bacteria (Swennen et al., 2006).

^{*} Corresponding author.

E-mail address: supapornsp@gs.wu.ac.th (S. Sophonputtanaphoca).

Consequently, these types of oligosaccharides are not absorbed in the upper gastrointestinal tract. They possess prebiotic properties as NDOs and also promote growth or activity or both of one or a limited number of beneficial intestinal bacteria (Gibson and Roberfroid, 1995). The inability of humans to digest NDOs is probably due to the fact that the sugar moieties are linked by glycosidic bonds and with a β -configuration in most NDOs. It is uncommon for the human gastrointestinal digestive enzymes to hydrolyze the β -configuration of a glycosidic bond because they are specific for α -configuration glycosidic bonds (Campbell et al., 1997; Swennen et al., 2006) such as those found in starch.

Some common β -configuration NDOs that have received research attention for their production and investigation of their health and other beneficial properties are fructooligosaccharides (FOS; β -2,1 for inulin type, β -2,6 for levan type, β -2,1 and β -2,6 for graminan type), cellooligosaccharides (COS) and hemicellulose-derived oligosaccharides, that is, xylooligosaccharides (XOS), galactooligosaccharides (GOS), arabinooligosaccharides (AOS) and mannoooligosaccharides (MOS) (Ritsem and Smeekens, 2003; Casci et al., 2006; Moure et al., 2006; Harrison et al., 2011; Otieno and Ahring, 2012). Some research has investigated the production of XOS or COS or both, GOS, AOS and MOS from agricultural residues, including rice husks (Garrote et al., 2007; Nabarlatz et al., 2007), wheat straw (Nabarlatz et al., 2007; Duarte et al., 2009; Sophonputtanaphoca, 2012), barley straw (Nabarlatz et al., 2007), sugar cane bagasse (Yang et al., 2007; Otieno and Ahring, 2012), olive stone (Nabarlatz et al., 2007), almond shells (Nabarlatz et al., 2007), corn cobs (Vázquez et al., 2006; Garrote et al., 2007; Samanta et al., 2012), peanut shells (Yang et al., 2007) and from grasses such as switchgrass, morning light (*Miscanthus sinensis*) and Karl forester feather reed (Otieno and Ahring, 2012). Most FOSs are extracted from food-based plants such as chicory, Jerusalem artichoke, other underground storage bulbs or roots and food-based sources (Campbell et al., 1997; Goio et al., 2009; Judprasong et al., 2011; Moongngarm et al., 2011). Nevertheless, there is little information on the extraction and quantification of fructooligosaccharides in lignocellulosic biomass. Nguyen et al. (2009) developed a novel hydrolysis method using dilute sulfuric acid for the quantification of fructose equivalents in lignocellulosic biomass (tall fescue grass). The results revealed that the tall fescue contained a significant amount of FOS (approximately 8%, weight per weight; w/w). Sophonputtanaphoca (2012) determined the amount of FOS, XOS, COS, GOS, AOS and MOS in wheat straw water extract and alkaline extract at 50 °C. The total oligosaccharides content from the water extract of wheat straw was 0.8% (w/w) with FOS as the predominant oligosaccharide while the oligosaccharides contents in the alkaline extract were as high as approximately 19%. However, neutralization of the alkaline extract in that study generated soluble salt (sodium chloride) that requires a complicated step to remove the salt from the extract. On the contrary, the production of oligosaccharides using dilute sulfuric acid as described by Nguyen et al. (2009) generates soluble salt (calcium sulfate) sparingly so that it is more convenient to remove the salt from the extract. Consequently, this method was chosen for the present study.

In Thailand, rice is a major crop widely cultivated throughout the country and varieties of rice cultivars can be rotated throughout the year (Bureau of Rice Research and Development, 2018). Consequently, a vast amount of straw is left as agricultural waste after harvesting rice grains. Practical utilization of rice straw, however, is still limited. Most rice straw is burnt or integrated into the field to prepare the soil for the next crop cultivation (Mäki-Arvela et al., 2011). In the present study, rice straw was chosen as the raw material for the production of NDOs, as there was no previous research attempting to extract complete profiles of NDOs

from rice straw. First, this work aimed to optimize the conditions for the production of NDOs using water extraction and dilute acid extraction. Second, it investigated the effect of residence time, temperature and acid concentration on the yields of FOS, XOS, COS, GOS, AOS, and MOS.

Materials and methods

Feedstock

Mature above-ground rice straw biomass (*Oryza sativa* RD 41) was harvested from a local farm in Nakhon Pathom province, Thailand. The vegetative parts of the straw (stems and leaves) were collected and air-dried before cutting into lengths of approximately 2.5 cm and milling using a blender. The milled straw was sieved to pass through a 20-mesh sieve and was kept in a glass jar with a screw cap lid at room temperature for all experiments.

Reagents

All chemicals used in this study were reagent grade purchased from Sigma-Aldrich (Sigma Chemical Co.; St. Louis, MO, USA), Mallinckrodt (Mallinckrodt Baker, Inc.; Hampton, NJ, USA) and EMD (Rockland, MA, USA).

The chemical composition of rice straw

All analysis for the determination of rice straw composition followed the Laboratory Analytical Procedures prepared by the National Renewable Energy Laboratory (NREL, Golden, CO, USA). The moisture content and total solids content were determined in triplicate following the NREL protocol (Sluiter et al., 2008a) by drying approximately 0.5 g (weighed to the nearest 0.1 mg) of straw at 105 °C until a constant weight was reached (5 h). The total solids content refers to oven-dry weight measurements. After cooling the sample in a desiccator to room temperature, the sample was weighed in an aluminum container to the nearest 0.1 mg. For determination of the structural carbohydrates and lignin in the rice straw, the rice straw biomass needed to be extractives-free. Extractives-free rice straw was prepared by extraction of the original rice straw using a Soxhlet apparatus with water extraction for 24 h, followed by 95% ethanol for 24 h (Sluiter et al., 2005a). The air-dried extractives-free solid was subjected to compositional analysis using two-step acid hydrolysis (Sluiter et al., 2008b). The neutral sugars of the hydrolyzate were measured using high-performance liquid chromatography (HPLC). The water and ethanol extractives in the liquid phase were dried and quantitatively determined using gravimetric analysis. Determination of ash was done by ashing the native rice straw in a furnace at 575 °C for 24 h (Sluiter et al., 2005b). All experiments were done in triplicate.

Determination of fructooligosaccharides

The extraction method used was adapted from Nguyen et al. (2009) and Sophonputtanaphoca (2012). The milled rice straw was extracted with deionized water at a solid loading of 6% (w/w). Three grams (dry weight) of rice straw (weighed to the nearest 0.1 mg) was mixed with pre-heated deionized water (water temperature was at the same extraction temperature) to attain a 50 g straw suspension in a 100 mL screw-cap bottle. Thirty-three total reaction mixtures were maintained in the water baths at 50 °C, 60 °C, and 70 °C each for 2 h, 3 h and 5 h and at 100 °C for 0.5 h and 1 h with 15 min intervals of manual agitation. Following the water extraction, the reaction mixture was filtered through Whatman No.1 filter paper to separate the solid residue and the liquid extract.

The extract was then filtered through a Gooch crucible (pore size = 10–15 μm) to obtain a clear filtrate. One portion of the filtrate was subjected to fructose and sucrose determinations using HPLC. The fructose determined in this step was referred to as “free fructose”.

The other portion of the filtrate was used for FOS determination using dilute acid hydrolysis as described by Sophonputtanaphoca (2012). First, a 10 mL aliquot of the clear water extract was diluted with deionized water and 20% (w/w) H_2SO_4 to yield a final acid concentration of 1% (w/w) in a total volume of 25 mL. The mixture was then transferred to an autoclavable screw-capped bottle and was incubated at 100 °C for 1 h. The mixture was quickly cooled down to room temperature in an ice bath and was neutralized by adding solid CaCO_3 to raise the pH to about 6. The pH of the neutralized hydrolyzate was checked using pH paper. The neutralized hydrolyzate was set aside for 1 h to allow the precipitate to develop at room temperature. The clear liquid above the precipitate was filtered through a 0.45 μm syringe filter and the supernatant was collected for fructose determination using HPLC. The sugar recovery standard (SRS) of 1 mg/mL fructose was carried out in the same manner as the acid hydrolysis of the water extract in order to compensate for the amount of fructose lost during the hydrolysis before quantifying the amount of FOS.

Quantification of FOS was achieved by subtracting the amount of the total fructose equivalents after the acid hydrolysis by the amount of fructose in the water extract. The fructose derived from sucrose was taken into account by subtracting half the weight of the sucrose found in the water extract from the fructose equivalent after the acid hydrolysis. A correction factor of 0.9 for converting the C6 monomeric sugar to the polymeric sugar was applied. All experiments were done in triplicate.

Determination of other non-digestible oligosaccharides

Xylooligosaccharides (XOS), cellooligosaccharides (COS), galactooligosaccharides (GOS), arabinooligosaccharide (AOS) and mannooligosaccharides (MOS) were produced using acid hydrolysis with different concentrations of sulfuric acid, residence times and temperatures, as shown in Table 1. A water bath and an autoclave were used to control the temperatures at 100 °C and 121 °C, respectively.

The production was carried out in the same manner as that of FOS. A solid loading of 6% (w/w) was mixed with the desired acid concentration to obtain a 50 g straw suspension. The sulfuric acid solution was at room temperature upon mixing. The production started when the screw-capped bottle containing the straw suspension was placed in the water bath. Regarding the autoclave method, the reaction time started once the temperature reached 121 °C. Following acid hydrolysis, the straw suspension was cooled in an ice bath to room temperature. The acid hydrolyzate was divided into two portions for determination of free monosaccharides and oligosaccharides. The first portion was subjected to neutralization to determine the monosaccharides content. Neutralization with solid CaCO_3 and

neutralized supernatant collection were performed as described previously. Monomeric sugars in the neutralized extract and SRS were determined using HPLC.

To quantify the oligomeric sugars content, 10 mL of the acid hydrolyzate was transferred to an autoclavable screw-capped bottle and was raised to 4% (w/w) sulfuric acid by adding 72% (w/w) sulfuric acid. The amount of 72% (w/w) sulfuric acid added depended on the initial pH of the acid hydrolyzate (Sluiter et al., 2006). The hydrolyzate and SRS were subjected to the autoclave conditions (121 °C, 1 h). Neutralization and neutralized supernatant collection were performed as described previously. Note that the SRS for this determination contained a 1 mg/mL solution of glucose, xylose, galactose, arabinose, and mannose. The monomeric sugars content in the neutralized extract and SRS were determined using HPLC.

Quantification of XOS, COS, GOS, AOS, and MOS was achieved by subtracting the amount of the individual monosaccharide after the 4% acid hydrolysis by the amount of total individual monosaccharide in the acid extract. Correction factors of 0.9 and 0.88 were applied to the polymeric sugars for converting the C6 monomeric sugars and the C5 monomeric sugars, respectively. All experiments were done in triplicate.

High-performance liquid chromatography analysis

All water extract and hydrolyzate samples were filtered through 0.2 μm syringe filters prior to HPLC analysis. An Alltech (Rockland, ON, Canada) HPLC system was equipped with an evaporative light scattering detector (Alltech, Model 200ES), a column heater (Alltech, Model 630) and a pump (Alltech, Model 626). A Rezex RPM-Monosaccharide Pb^{2+} column (300 \times 7.8 mm, Phenomenex; Torrance, CA, USA) equipped with a guard column (Phenomenex; Torrance, CA, USA) was used to separate the monosaccharides and the sucrose in the samples. The separation conditions were: 50 μL sample injection, HPLC-grade water as the mobile phase, 0.6 mL/min flow rate, 60 °C column temperature and 25–30 min retention time.

Statistical analysis

Statistical analysis of the data including averages and standard deviations (SD) were performed using Excel (Microsoft; Redmond, WA, USA). Data comparison used SPSS version 11.5 statistical package (IBM; Chicago, IL, USA) with a one-way ANOVA test (95% confidence).

Results and discussion

The chemical composition of rice straw

The chemical composition of the rice straw (RD41) is presented in Table 2. Because the column heater could not reach the desired

Table 1
Production conditions for quantifying XOS, COS, GOS, AOS and MOS.

Sulfuric acid (weight per weight)	Temperature (°C)	Residence time (hr)
2.0	100	0.5
		1.0
		1.0
3.0	100	0.5
		1.0
		1.0
0.1	121	0.5
		1.0
		1.0
0.2	121	0.5
		1.0
		1.0

Table 2
Chemical composition of rice straw RD41. Data represented as average \pm SD.

Component	% weight per weight of dry biomass
Cellulose	36.72 \pm 0.13
Xylan	23.47 \pm 1.47
Galactan	7.15 \pm 0.42
Arabinan + Mannan	3.92 \pm 0.04
Acid-soluble lignin	0.40 \pm 0.00
Acid-insoluble lignin	11.07 \pm 0.01
Water extractives	15.49 \pm 0.58
Ethanol extractives	3.75 \pm 0.73
Ash	11.16 \pm 0.13

temperature (75 °C), all sugars were properly separated, except arabinose and mannose; therefore, they were reported as a combination (arabinose plus mannose). The correction factor used for converting both sugars into their polymeric forms was 0.88 because arabinose is generally more predominant than mannose in cereal straws and grasses (Otieno and Ahring, 2012).

Determination of fructooligosaccharides

Fig. 1A,B show the amount of free fructose and FOS, respectively, found in the water extract of the rice straw under the conditions tested. Free fructose (0.15–0.17%, w/w dry biomass) was found in the water extract at all the extraction temperatures regardless of the residence time. The amount of fructose extracted at 50 °C for 5 h was lower than the free fructose (1.19%, w/w) found in the water extract of wheat straw extracted under the same conditions (Sophonputtanaphoca, 2012). The temperature had an effect on FOS extraction. No FOS was detected in the extract when a low temperature (50 °C) and a high temperature (100 °C) were applied. The stability of FOS in a neutral pH solution at an elevated temperature and prolonged incubation time has been reported, with one work revealing that FOS decomposed after 30 min of incubation in water at 100 °C (Courtin et al., 2009); however, the FOS extracted from wheat straw with water extraction at 50 °C for 5 h amounted to 0.15% (w/w dry biomass) (Sophonputtanaphoca, 2012). In the present study, FOS was found when the straw was extracted with water at 60 °C and 70 °C for 2–5 h. At 60 °C, the amount of FOS (approximately 1.55–1.61%, w/w dry biomass) was not significantly different with regard to extraction time. Likewise, the amount of

FOS (1.44–1.67%) found in the water extract incubated at 70 °C did not differ significantly with extraction time. This suggests that the optimum temperature for FOS extraction was either 60 °C or 70 °C and the optimum extraction time was 2 h. Sucrose was detected (approximately 0.08%) only at 70 °C regardless of the extraction period.

Determination of other non-digestible oligosaccharides

Xylooligosaccharides

The amounts of quantified xylose and XOS are presented in Fig. 2A,B, respectively. In terms of free xylose, the incubation temperature and concentration of sulfuric acid had an effect on xylose extraction. No xylose was detected when the higher temperature (121 °C) was applied, regardless of the acid concentration. At the lower temperature (100 °C) a xylose content of up to 17.44% (w/w dry biomass) was found in the extract with 2% (w/w) sulfuric acid for 1 h. In contrast to free xylose, XOS production with 2% (w/w) sulfuric acid was only detected for the 0.5 h incubation period and not for the 1 h incubation period. This suggests that the longer production time favored xylose extraction when 2% (w/w) sulfuric acid was used for the extraction for 0.5 h and 1 h. This result corresponds to findings reported by Akpinar et al. (2009) who found that a reaction time greater than 30 min resulted in the hydrolysis of XOS derived from lignocellulosic materials to mostly monosaccharides when 0.25 M sulfuric acid was applied.

The acid concentration also had an effect on XOS production. No XOS was found when 3% (w/w) sulfuric acid was used for the production compared to 2% (w/w) sulfuric acid. This result was

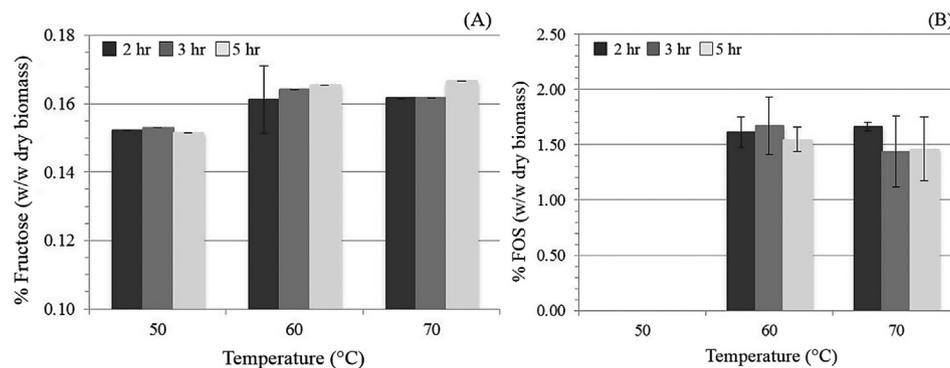


Fig. 1. Comparison of the amounts (weight for weight; w/w) in the water extract of rice straw RD41 at different extraction times and temperatures of (A) free fructose; (B) fructooligosaccharides (FOS), where error bars represent \pm SD.

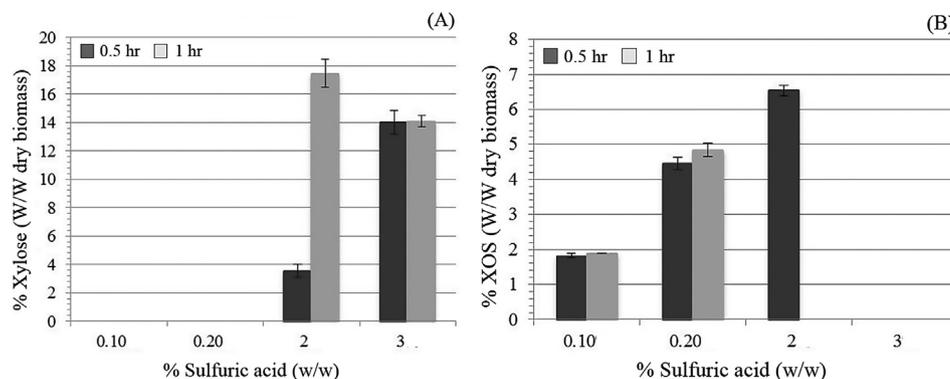


Fig. 2. Comparison of the amounts in the water extract of rice straw RD41 at different extraction times and acid concentrations of: (A) free xylose; (B) xylooligosaccharides (XOS), where temperature for extraction with 0.10% (w/w) and 0.20% (w/w) sulfuric acid = 121 °C, temperature for the extraction with 2% (w/w) and 3% (w/w) sulfuric acid = 100 °C and error bars represent \pm SD.

comparable to the findings of Courtin et al. (2009) who reported that a lower acidic pH had more effect on the decomposition of XOS at the same temperature. In addition, in this present study, XOS levels ranging from 1.82 to 4.84% were detected at a higher temperature (121 °C) only at lower acid concentrations—0.10% (w/w) and 0.20% (w/w)—were used for the production. Different concentrations of sulfuric acid and times for the production of other NDOs were investigated since it has been reported that concentrations and time courses affected the number of fructose equivalents produced from dilute sulfuric acid extract of tall fescue (Nguyen et al., 2009). These factors showed significant impact on amount and type of the products to determine whether they are XOS or its constituent (Fig. 2).

The optimum conditions for the production of free xylose were 2% (w/w) sulfuric acid, 100 °C, and 1 h. These conditions yielded 17.44% xylose by weight of dry biomass or 65.39% by weight of xylan in the rice straw. The optimum conditions for the production of XOS were 2% (w/w) sulfuric acid, 100 °C, and 0.5 h, yielding 6.53% XOS by weight of dry biomass or 27.82% by weight of xylan in the rice straw.

Cellooligosaccharides

The amounts of quantitated glucose and COS are presented in Fig. 3A,B. At 100 °C, the treatment time and acid concentration had different effects on glucose and COS production. The source of additional glucose and glucooligosaccharides was possibly from the depolymerization of cellulose in the presence of an acid catalyst at elevated temperature (Vancov and McIntosh, 2012). Thus, the glucooligosaccharides were then

referred to as cellooligosaccharides. At the same acid concentration (2% (w/w) sulfuric acid), a longer treatment period favored glucose production over COS production. Glucose (5.32% by weight of dry biomass) was treated using a 1 h incubation period but no COS was detected at this condition. At a higher acid concentration (3% (w/w) sulfuric acid), glucose was only found in the extract at 0.5 h (4.81% by weight of dry biomass or 14.49% by weight of cellulose) whereas no COS was found at this condition. Similar to XOS production, at 121 °C, the low acid concentrations (0.10% (w/w) and 0.20% (w/w) sulfuric acid) were more suitable for COS production than glucose production. The highest COS production was under conditions of 0.20% (w/w) sulfuric acid and a 0.5 h extraction period, accounting for 4.16% by weight of the cellulose in the rice straw.

Galactooligosaccharides

Fig. 4A,B present the amount of quantitated galactose and GOS in the acidic extract of the rice straw. The profiles of both the galactose and GOS production were in agreement with those of the glucose and COS production. At 100 °C and a lower acid concentration (2% (w/w) sulfuric acid), a longer treatment period favored galactose production. The highest galactose content (4.4% by weight of dry biomass or 61.54% by weight of galactan) was found in the extract with 2% (w/w) sulfuric acid for 1 h whereas under the same conditions no GOS was detected. The highest GOS content (0.69% by weight of dry biomass or 9.64% by weight of galactan) was found in the extract with 2% (w/w) sulfuric acid for 0.5 h. A lower acid concentration (0.20% (w/w) sulfuric acid) at the higher temperature (121 °C) favored GOS production over monosaccharide production.

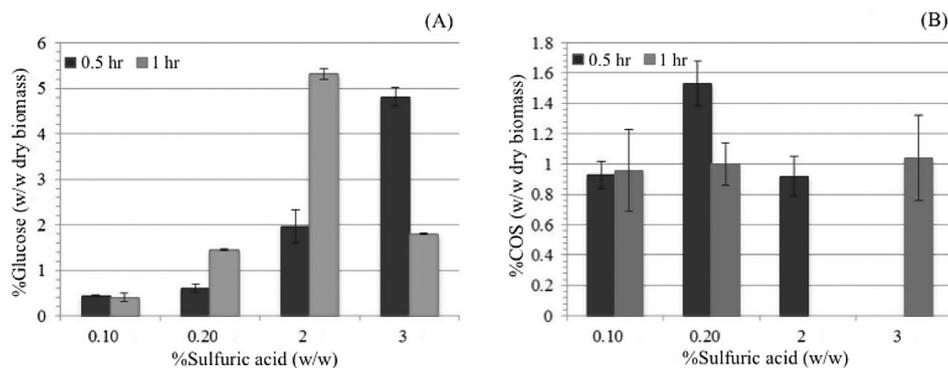


Fig. 3. Comparison of the amounts in the water extract of rice straw RD41 at different extraction times and acid concentrations of: (A) free glucose; (B) cellooligosaccharides (COS) where temperature for the extraction with 0.10% (w/w) and 0.20% (w/w) sulfuric acid = 121 °C, temperature for the extraction with 2% (w/w) and 3% (w/w) sulfuric acid = 100 °C and error bars represent \pm SD.

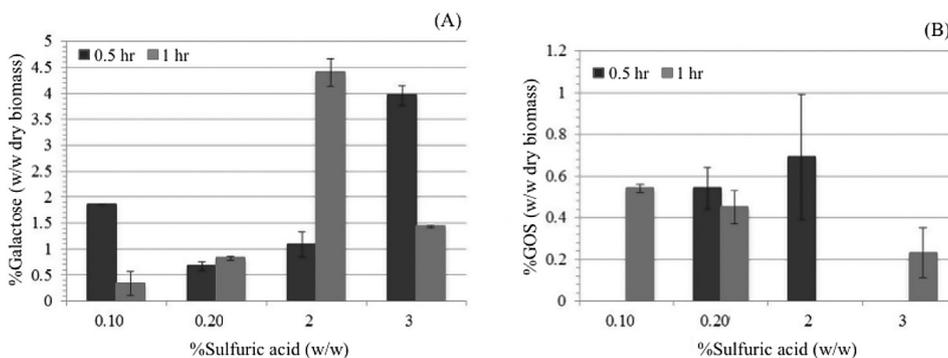


Fig. 4. Comparison of the amounts in the water extract of rice straw RD41 at different extraction times and acid concentrations of: (A) free galactose; (B) galactooligosaccharides (GOS) where temperature for the extraction with 0.10% (w/w) and 0.20% (w/w) sulfuric acid = 121 °C, temperature for the extraction with 2% (w/w) and 3% (w/w) sulfuric acid = 100 °C and error bars represent \pm SD.

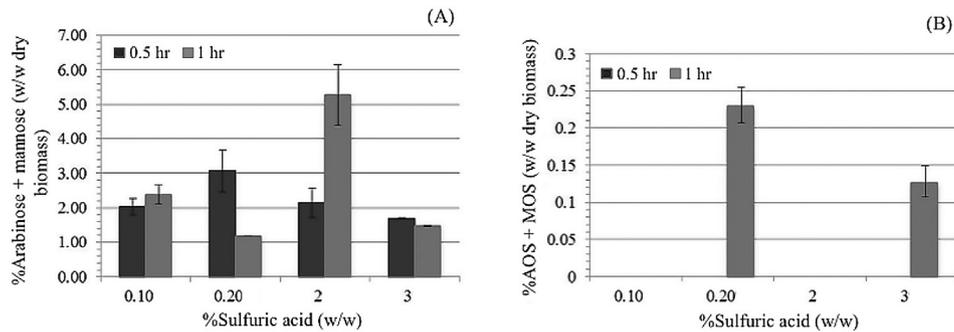


Fig. 5. Comparison of the amounts in the water extract of rice straw RD41 at different extraction times and acid concentrations of: (A) free arabinose plus mannose; (B) arabiooligosaccharides (AOS) plus mannoooligosaccharides (MOS), where temperature for the extraction with 0.10% (w/w) and 0.20% (w/w) sulfuric acid = 121 °C, temperature for the extraction with 2% (w/w) and 3% (w/w) sulfuric acid = 100 °C and error bars represent ± SD.

Arabinoooligosaccharides plus mannoooligosaccharides

In this study, the amounts of AOS and MOS were reported as AOS plus MOS jointly as well as the amount of arabinose and mannose due to the inability to separate arabinose and mannose using the HPLC column under the operating conditions described above. The highest arabinose plus mannose production (5.28% by weight of dry biomass) was detected in the extract with 2% (w/w) sulfuric acid at 100 °C for 1 h (Fig. 5A). Only two treatment conditions yielded AOS plus MOS: 0.20% (w/w) sulfuric acid at 121 °C for 1 h and 3% (w/w) sulfuric acid at 100 °C for 1 h (Fig. 5B). The first set of conditions had the highest AOS plus MOS yield (0.23% by weight of dry biomass or 5.89% by weight of arabinan plus mannan).

In conclusion, rice straw was chosen for NDO production in this study because of its availability in vast amounts, its low cost and it is an important agricultural waste in Thailand. Treatment conditions (acid concentration, residence extraction time and temperature) had an effect on oligosaccharides production. These factors determined whether the products are oligosaccharides or their monosaccharide constituents. Mostly, NDOs were produced under a shorter extraction period and lower acid concentration compared to NDO production at the same temperature. Among all NDOs, XOS was the predominant oligosaccharide produced from rice straw RD41 while xylose was the major monosaccharide produced from the rice straw. The abundant amounts of other NDOs were: FOS, COS > GOS > AOS + MOS. The NDOs produced in this study was limited to hot water-soluble and acid-soluble NDOs, with other high molecular weight and water-insoluble NDOs not being quantified. However, determination of the molecular weight of NDOs produced in this study may be considered in future research since it is a key factor for the utilization of NDOs as prebiotics.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

This research was funded by Srinakharinwirot University, Thailand (grant number 031/2557). The authors also would like to thank Dr. Michael Penner, Department of Food Science and Technology, Oregon State University for generously providing the sugar standards used in this study.

References

Akpınar, O., Erdogan, K., Bostancı, S., 2009. Production of xylooligosaccharides by controlled acid hydrolysis of lignocellulosic materials. *Carbohydr. Res.* 344, 660–666.

- Bureau of Rice Research and Development, Rice Department, 2018. Rice Knowledge Bank, 31 January 2018. <http://www.ricethailand.go.th/Rkb/varieties/index.php.htm>.
- Campbell, J.M., Fahey, G.C., Wolf, B.W., 1997. Selected indigestible oligosaccharides affect large bowel mass, cecal and fecal short-chain fatty acids, pH and disease: focus on prebiotics. *J. Nutr.* 127, 130–136.
- Casici, T., Rastall, R.A., Gibson, G.R., 2006. Human gut microflora in health and disease: focus on prebiotics. *Food Sci. Technol.* 148, 1133–1166.
- Cheng, Y.-S., Zheng, Y., Yu, C.W., Dooley, T.M., Jenkins, B.M., VanderGheynst, J.S., 2010. Evaluation of high solids alkaline pretreatment of rice straw. *Appl. Biochem. Biotechnol.* 162, 1768–1784.
- Courtin, C.M., Swennen, K., Vergans, S., Delcour, J.A., 2009. Heat and pH stability of prebiotic arabinoxyloligosaccharides, xylooligosaccharides and fructooligosaccharides. *Food Chem.* 112, 831–837.
- Duarte, L.C., Silva-Fernandes, T., Carvalho, F., Gírio, F.M., 2009. Dilute acid hydrolysis of wheat straw oligosaccharides. *Appl. Biochem. Biotechnol.* 153, 116–126.
- FitzPatrick, M., Champagne, P., Cunningham, M.F., Whitney, R.A., 2010. A biorefinery processing perspective: treatment of lignocellulosic materials for the production of value-added products. *Bioresour. Technol.* 101, 8915–8922.
- Garrote, G., Falqué, E., Domínguez, H., Parajó, J.C., 2007. Autohydrolysis of agricultural residues: study of reaction byproducts. *Bioresour. Technol.* 98, 1951–1957.
- Gibson, G.R., Roberfroid, M.B., 1995. Dietary modulation of the human colonic microbiota: introducing the concept of prebiotics. *J. Nutr.* 125, 1401–1412.
- Goio, F., Rodríguez, M.A., Alméciga-Díaz, C.J., Sánchez, O.F., 2009. Recent trends in fructooligosaccharides production. *Recent Pat. Food, Nutr. Agric.* 1, 221–230.
- Harrison, S., Fraser, K., Lane, G., Hughes, D., Villas-Boas, S., Rasmussen, S., 2011. Analysis of high-molecular-weight fructan polymers in crude plant extracts by high-resolution LC-MS. *Anal. Bioanal. Chem.* 401, 2955–2963.
- Hideno, A., Inoue, H., Yanagida, T., Tsukahara, K., Endo, T., Sawayama, S., 2012. Combination of hot compressed water treatment and wet disk milling for high sugar recovery yield in enzymatic hydrolysis of rice straw. *Bioresour. Technol.* 104, 743–748.
- Huttner, J., 2004. Genencor and the Biobased Economy of the Future: an International Biotechnology Company's Perspective on Biomass and Agriculture. *Biomass and Agriculture: Sustainability, Markets and Policies*. OECD Publishing, Paris, France.
- Judprasong, K., Tanjor, S., Puwastien, P., Sungpuag, P., 2011. Investigation of Thai plants for potential sources of inulin-type fructans. *J. Food Compos. Anal.* 24, 642–649.
- Kim, S., Dale, B.E., 2004. Global potential bioethanol production from wasted crops and crop residues. *Biomass Bioenergy* 26, 361–375.
- Lau, M.W., Bals, B.D., Chundawat, S.P.S., Jin, M., Gunawan, C., Balan, V., Jones, A.D., Dale, B.E., 2012. An integrated paradigm for cellulose biorefineries: utilization of lignocellulosic biomass as self-sufficient feedstocks for fuel, food precursors and saccharolytic enzyme production. *Energy Environ. Sci.* 5, 7100–7110.
- Mäki-Arvela, P., Salmi, T., Holmbom, B., Willför, S., Murzin, D.Y., 2011. Synthesis of sugars by hydrolysis of hemicelluloses – a review. *Chem. Rev.* 111, 5638–5666.
- Moongarm, A., Trachoo, N., Sirigungwan, N., 2011. Low molecular weight carbohydrates, prebiotic content and prebiotic activity of selected food plants in Thailand. *Adv. J. Food Sci. Technol.* 3, 269–274.
- Moure, A., Gullón, P., Domínguez, H., Parajó, J.C., 2006. Review: advances in the manufacture, purification and applications of xylo-oligosaccharides as food additives and nutraceuticals. *Process Biochem.* 41, 1913–1923.
- Nabarlatz, D., Ebringerová, A., Montané, D., 2007. Autohydrolysis of agricultural by-products for the production of xylo-oligosaccharides. *Carbohydr. Polym.* 69, 20–28.
- Nguyen, S.K., Sophonputtanaphoca, S., Kim, E., Penner, M.H., 2009. Hydrolytic methods for the quantification of fructose equivalents in herbaceous biomass. *Appl. Biochem. Biotechnol.* 158, 352–361.
- Otieno, D.O., Ahring, B.K., 2012. A thermochemical pretreatment process to produce xylooligosaccharides (XOS), arabiooligosaccharides (AOS) and mannoooligosaccharides (MOS) from lignocellulosic biomasses. *Bioresour. Technol.* 112, 285–292.

- Ritsema, T., Smeeckens, S., 2003. Fructans: beneficial for plants and humans. *Curr. Opin. Plant Biol.* 6, 223–230.
- Roberto, I.C., Mussatto, S.I., Rodrigues, R.C.L.B., 2003. Dilute-acid hydrolysis for optimization of xylose recovery from rice straw in a semi-Pilot reactor. *Ind. Crop. Prod.* 17, 171–176.
- Samanta, A.K., Senai, S., Kolte, A.P., Sridhar, M., Sampath, K.T., Jayapal, N., Devi, A., 2012. Production and in vitro evaluation of xylooligosaccharides generated from corn cobs. *Food Bioprod. Process.* 90, 466–474.
- Sluiter, A., Hames, B., Hyman, D., Payne, C., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Wolfe, J., 2008a. Determination of Total Solids in Biomass and Total Dissolved Solids in Liquid Process Samples - Laboratory Analytical Procedure (LAP). Technical Report NREL/TP-510-42621. National Renewable Energy Laboratory (NREL), Golden, CO, USA.
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., 2006. Determination of Sugars, Byproducts and Degradation Products in Liquid Fraction Process Samples- Laboratory Analytical Procedure (LAP). Technical Report NREL/TP-510-42623. National Renewable Energy Laboratory (NREL), Golden, CO, USA.
- Sluiter, A., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., 2005a. Determination of Extractives in Biomass - Laboratory Analytical Procedure (LAP). Technical Report NREL/TP-510-42619. National Renewable Energy Laboratory (NREL), Golden, CO, USA.
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., 2005b. Determination of Ash in Biomass - Laboratory Analytical Procedure (LAP). Technical Report NREL/TP-510-42622. National Renewable Energy Laboratory (NREL), Golden, CO, USA.
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Crocker, D., 2008b. Determination of Structural Carbohydrates and Lignin in Biomass - Laboratory Analytical Procedure (LAP). Technical Report NREL/TP-510-42618. National Renewable Energy Laboratory (NREL), Golden, CO, USA.
- Sophonputtanaphoca, S., 2012. Science and Efficacy of Mild Sodium Hydroxide Treatments in Enzyme-based Wheat Straw-to-glucose Processing. PhD Dissertation. Oregon State University, Corvallis, OR, USA.
- Swennen, K., Courtin, C.M., Delcour, J.A., 2006. Non-digestible oligosaccharides with prebiotic properties. *Crit. Rev. Food Sci. Nutr.* 46, 459–471.
- Vancov, T., McIntosh, S., 2012. Mild acid pretreatment and enzyme saccharification of *Sorghum bicolor* straw. *Appl. Energy* 92, 421–428.
- Vázquez, M.J., Alonso, J.L., Domínguez, H., Parajó, J.C., 2006. Enhancing the potential of oligosaccharides from corncob autohydrolysis as prebiotic food ingredients. *Ind. Crop. Prod.* 24, 152–159.
- Voragen, A.G.J., 1998. Technological aspects of functional food-related carbohydrates. *Trends Food Sci. Technol.* 9, 328–335.
- Yang, C.-H., Yang, S.-F., Lui, W.-H., 2007. Production of xylooligosaccharides from xylans by extracellular xylanases from *Thermobifida fusca*. *J. Agric. Food Chem.* 55, 3955–3959.