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Maximization of monomeric C5 sugars from wheat bran by using mesoporous ordered silica catalysts

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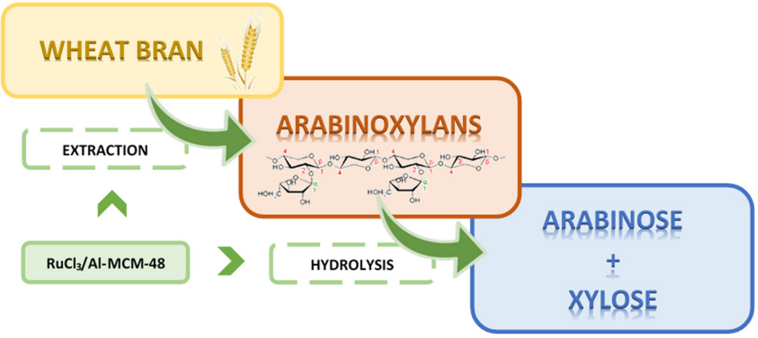
HIGHLIGHTS

- $RuCl_3$/Al-MCM-48 is an active catalyst for arabinoxylan hydrolysis.
- $RuCl_3$/Al-MCM-48 accelerates conversion of arabinoxylans into arabinose and xylose.
- $RuCl_3$/Al-MCM-48 catalysts inhibit further dehydration into furfural.
- Significant reduction in hydrolysis time from several hours to 15 min is achieved.
- A two-step process using $RuCl_3$/Al-MCM-48 maximizes C5 sugars from wheat bran.

GRAPHICAL ABSTRACT



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ABSTRACT

The hydrolysis process of a real fraction of arabinoxylans derived from wheat bran was studied. The influence of catalyst type and loading, reaction time and different metal cations were discussed in terms of the hydrolysis yield of arabinose and xylose oligomers as well as the formation of furfural as degradation product. A high yield of arabinoxylans into the corresponding monomeric sugars (96 and 94% from arabino- and xylo-oligosaccharides, respectively) was obtained at relatively high temperatures (180 °C) and short reaction times (15 min) with a catalyst loading of 4.8 g of $RuCl_3$/Al-MCM-48 per g of initial carbon in hemicelluloses.

1. Introduction

The current depletion of fossil resources is forcing society to seek renewable alternatives for energy and chemicals production. Biomass is considered a sustainable and renewable feedstock to substitute fossil-based fuels (Negahdar et al., 2016; Oh et al., 2015; Putro et al., 2016; Singhvi et al., 2014). Biomass accrues in large amounts all over the world as forestry and agricultural waste. Moreover, around 95% of this biomass consists of lignocellulosic material not edible for humans. Thus, its application to biofuels or chemicals synthesis does not compete with food production (Negahdar et al., 2016; Sahu and Dhepe, 2012).

Agricultural residues like straw, corn stover or wheat bran appear as interesting feedstocks to obtain high added-value products (Apprich et al., 2014). Wheat bran is a by-product of the wheat grain milling. About 150 million tons are produced per year worldwide and its main use is as a low value component in animal food (Prückler et al., 2014). The general composition of wheat bran is as follows: water (12.1%), proteins (13.2–18.4%), fats (3.5–3.9%), starch (13.8–24.9%), cellulose (11.0%), arabinoxylans (10.9–26.0%), β-glucans (2.1–2.5%), phenolic acids (0.02–1.5%) and ash

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(3.4–8.1%) (Apprich et al., 2014). Arabinoxylans (AXs) are a major component contained in the cell walls of wheat bran. AXs belong to the hemicellulosic part of biomass and are composed of a backbone of β-1,4 linked D-xylopyranosyl residues (Izydorczyk and Biliaderis, 2007). The abundance of arabinoxylans in wheat bran makes them susceptible to be extracted and converted into different intermediate or final chemicals with high added-values such as furfural, succinic acid, xylitol, arabitol, among others (Apprich et al., 2014).

In general, hemicelluloses are partly solubilized and hydrolyzed during biomass fractionation, resulting in an aqueous fraction enriched in hemicellulosic poly/oligosaccharides and in a solid fraction with a high content in cellulose and lignin. Although hemicellulosic poly/oligosaccharides have important applications in pharmaceutical and food industries, the potential as platform molecules is larger for monomeric sugars. Several interesting routes of pentoses valorization use monomers (xylose and arabinose) as platform molecules, such as hydrogenation to sugar alcohols or fermentation to biofuels. In such cases, hydrolysis of oligosaccharides into pentoses without further dehydration into furfural is critical to increase the global efficiency of the process (Vilcocq et al., 2014). Arabitol and xylitol, for example, obtained from the hydrogenation of C5 sugars are found among the top 12 value-added products derived from biomass included in the report published by the US Department of Energy (DOE).

Therefore, the fractionation and the complete hydrolysis of hemicellulosic poly/oligosaccharides into monomers are critical for an integrated biorefinery. Fractionation implies the selectively release of hemicelluloses from the biomass structure to the liquid medium and it involves the partial hydrolysis of the hemicellulosic fraction and their solubilization as poly/oligosaccharides. Hydrolysis of hemicelluloses is historically carried out by two different methods: using mineral acids (hydrolysis yield: 50–89%) (Hilpmann et al., 2016; Kim et al., 2013; Kusema et al., 2013; Li et al., 2016; Nakasu et al., 2016) or enzymes (hydrolysis yield: 6–84%) (Jia et al., 2016; Lee et al., 2013; Li, Wang et al., 2016; Li, Xue et al., 2016; Lou et al., 2016; Moreira and Filho, 2016). Chemical hydrolysis using mineral acids is not a selective process and it presents environmental drawbacks. Moreover, acids removal requires the addition of cations with the formation of salts as side products, and capital costs are increased due to corrosion (Negahdar et al., 2016). Although enzymes are very selective, they are currently not commercial. The long time required (several hours and even days), the nonexistence of recovery methods, the extremely high prize of enzymes and the critical control of reactions make necessary to look for other alternatives (Aden et al., 2002; Cará et al., 2013; Hendriks and Zeeman, 2009; Ormsby et al., 2012). Hydrolysis of oligosaccharides using heterogeneous acid catalysts appears as a green alternative to these methods. Heterogeneous catalysts can easily be separated, recovered and reused and they are safe and non-corrosive. Therefore, they represent an opportunity to develop more efficient and greener hydrolysis processes for soluble poly/oligosaccharides. Vilcocq et al. (2014) reviewed the advantages and limitations of the use of heterogeneous catalysis for the main groups of solid acid catalysts (zeolites, resins, carbon materials, clays, silicas and other oxides) and identified desirable characteristics in the design of future solid acid catalysts. Hydrolysis of polysaccharides over solid acid catalysts is a sequence of three first order reactions: 1) hydrolysis of polysaccharides into oligosaccharides, 2) hydrolysis of oligosaccharides into monosaccharides, 3) depending on the reaction conditions, dehydration of monosaccharides into products such as furfural. According to kinetic and mechanistic considerations, it is important to take into account the water effect on Brønsted acid sites and the diffusion limitations due to the size of the biggest poly/oligosaccharides. Acid strength, time and temperature should be chosen carefully to permit hydrolysis reactions and limit degradation reactions (Vilcocq et al., 2014; Mäki-Arvela et al., 2011). Carbon and silica have been modified by treatments involving sulfonic groups ($-SO_3H$), however their reutilization is limited due to the leaching of these acid groups.

In the recent years, the development of solid acid catalysts applied to hydrolysis processes of hemicelluloses has attracted the interest of several authors (Cará et al., 2013; Dhepe and Sahu, 2010; Kusema et al., 2011; Sahu and Dhepe, 2012; Salmi et al., 2014; Vilcocq et al., 2014; Zhang et al., 2017; Zhou et al., 2013; Zhong et al., 2015). Cará et al. (2013) reported a maximum hydrolysis yield of xylose + arabinose of 80% using Amberlyst 35 as solid catalyst and commercial beechwood xylan as raw material (120 °C, 10 bar argon, 4 h). Dhepe and Sahu (2010) achieved a hydrolysis yield (xylose + arabinose) equal to 54% from oat spelt using zeolite HUSY (Si/Al = 15) (170 °C, 2 h, 50 bar nitrogen). Kusema et al. (2011) used two different sulfonated resins to study the hydrolysis of commercial arabinogalactan. The highest yield they reported was 95% (monomeric arabinose) with Smopex-101 (pH = 2) at 90 °C after 3 h. Sahu and Dhepe (2012) studied the effect of different solid acid catalysts on the oat spelt hydrolysis. They got a hydrolysis yield (xylose + arabinose) of 41% using zeolite HUSY (Si/Al = 15) (170 °C, 3 h, 50 bar nitrogen). Although the use of zeolites in these works have reported good saccharification yields, the kinetics is controlled by the microstructure that hinders the diffusion of poly/oligosaccharides due to their size. Moreover, all these studies use commercial hemicelluloses and only few studies focused on the hydrolysis of hemicelluloses extracted directly from raw biomass (Vilcocq et al., 2014). When hemicelluloses are extracted from real biomass, the purity of the extracts is limited. Other compounds such as extractives, sugars, proteins and lignin or degradation products are also co-extracted with the hemicelluloses. All these compounds can diminish the efficiency of the hydrolysis process by poisoning the catalyst or occupying acid sites. Optimizing the hydrolysis step of a real fraction of hemicelluloses is an issue of utmost importance for a concept of a biorefinery.

In this work, we study the heterogeneous catalytic hydrolysis of hemicellulosic poly/oligosaccharides that are present in a real extract obtained from wheat bran. Different experimental conditions, such as type and amount of catalyst and reaction time, have been tested to maximize the production of pentoses avoiding further degradation to furfural. The use of MCM-48 as mesoporous support to improve mass-transfer limitations induced by the dimensions of poly/oligosaccharides, and the incorporation of aluminium to the support (Al-MCM-48) and/or metals (Ru and Fe) have been studied. The final aim of this work is to validate a two-step method consisting on a hydrothermal fractionation of arabinoxylans from destarched wheat bran that uses $RuCl_3$/Al-MCM-48 as catalyst at 180 °C and 10 min (Sánchez-Bastardo et al., 2017), followed by a second heterogeneous catalytic hydrolysis step developed in the present work.

2. Materials and methods

2.1. Support and catalyst preparation

Synthesis of two mesoporous silica supports, MCM-48 and Al-MCM-48, was carried out using the procedure described by Romero et al. in a previous work (Romero et al., 2016). 2.0 g of *n*-hexadecyltrimethylammonium bromide (for molecular biology, ≥99%; Sigma-Aldrich) were dissolved in 42 mL of distilled water, 18 mL of absolute ethanol (Panreac AppliChem) and 13 mL of an aqueous ammonia solution (20% w w^{-1}) (Panreac AppliChem). After 15 min stirring, 0.077 g of sodium aluminate (technical,