HETEROGENEOUS CATALYSIS FOR THE EXTRACTION OF ARABINOXYLANS FROM WHEAT BRAN

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Introduction

The conversion of biomass within biorefineries into chemicals and energy is seen as a real possibility for the substitution of fossil resources. Raw materials of high lignocellulosic content are an interesting option. Besides wood and non-food crops, agricultural residues like straw and corn stover as well as other by-products of various origins are of high interest as feedstocks. Wheat bran represents such a by-product, which accrues in enormous quantities during the production of white wheat flour. It is estimated that 150 million tons are produced per year worldwide [1]. Currently wheat bran is mainly used as a low value ingredient in animal feed. Arabinoxylans are the most abundant structural polysaccharides in wheat bran, and they can be suitable compounds for the production of sugar alcohols. In general terms, the conversion of these hemicellulosic components from biomass into sugar alcohols is a two-step reaction: 1) extraction and hydrolysis of arabinoxylans and 2) hydrogenation of these hemicelluloses into polyols (Figure 1).

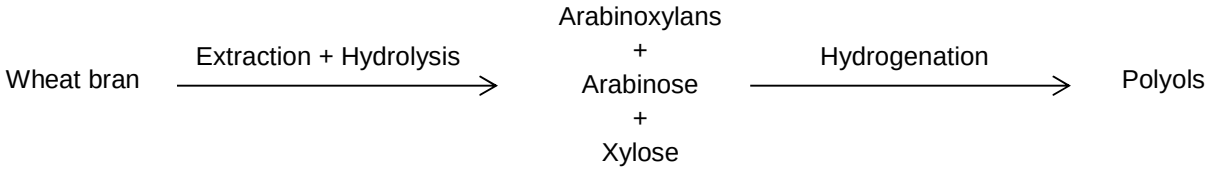

Fig 1. Scheme of the complete process of hydrogenation of arabinoxylans from wheat bran

Hydrogenation of hemicellulosic compounds as monomeric sugars, such as xylose and arabinose, using heterogeneous catalysts has been already deeply studied [2-6]. However, only few researchers have studied the hydrogenation of commercial hemicelluloses, such as arabinogalactans [7-9], and there are not too many works focused on the hydrogenation of arabinoxylans from real biomass. What is more, only one work has been found in which the extraction-hydrolysis-hydrogenation process in one pot using real biomass is investigated [10]. The extraction-hydrolysis process is the limiting step of the polyol synthesis and its rate, efficiency and selectivity must be improved. In order to perform the whole process in one-single pot, the strategy of the present work is to use the same heterogeneous catalysts required for the hydrogenation, such as ruthenium supported catalysts [8, 9], for the extraction-hydrolysis process. From previous works, it is known that arabinoxylans can be extracted from different cereal sources using water [11-13], chemical solvents [14-17], enzymes [14, 16, 18-21] or mechanical-chemical processes [22-25]. Some of the disadvantages of these methods can be seen in Table 1.

Table 1. Disadvantages of the classical methods for arabinoxylans extraction from cereals

Extraction treatment	Cereal source	Disadvantages	References
Water extraction	Barley, rye flour, wheat flour	Low AXs extraction yields	[11-13]
Chemical extraction	Wheat bran, corn bran, barley husks, wheat straws	Homogeneous solvents	[14-17]
Enzymatic extraction	Wheat bran, barley husk, corn husk, rye flour	High enzyme price	[14, 16, 18-21]
Mechanical extraction	Wheat bran, wheat straw, corn bran, corn hull, corn cobs, corn pericarp, barley	Uncontrolled degradation of molecules of AXs	[22-25]

Therefore, the aim of this work is to study the extraction-hydrolysis process of arabinoxylans from wheat bran using heterogeneous ruthenium supported catalysts. This will let not only make the whole process of

hydrogenation in one-pot in the future but also take advantage of the heterogeneous catalysis itself, as they can be easily separated from the extract liquid by filtration. Dissolution and hydrolysis of the arabinoxylans into sugars are performed by pressurized hot water (PHW) and the acid sites of the ruthenium catalyst. Hydrolysis of arabinoxylans into monomeric sugars is an important parameter to be studied: the smaller of molecular weight of the arabinoxylans, the easier to be hydrogenated. The effects of time (10-30 minutes), temperature (140-180 ºC) and the presence of ruthenium catalysts were studied in the extraction-hydrolysis process of arabinoxylans from wheat bran in terms of (1) matter solubilization, (2) content in total and free monosaccharides, (3) degradation products and (4) A/X of the released polymers.

Materials and methods

Destarched wheat bran (DWB) contained 36.3% hemicellulose, with an arabinose/xylose ratio (A/X) equal to 0.54, has been used as raw material. The complete composition was determined using a Laboratory Analytical Procedure (LAP) from NREL [26] and it can be seen in Table 2.

Table 2. Chemical composition of wheat bran (% dry basis)

Component	Cellulose	Hemicellulose	Soluble lignin	Insoluble lignin	Protein	Ash
g/100 g DWB	15.1 ± 0.6	36.3 ± 1.6	21.5 ± 0.4	4.9 ± 1.3	14.5 ± 0.5	3.2 ± 0.1

Support and catalysts preparation

Synthesis of mesoporous silica MCM-48 and Al-MCM-48 was carried out using the hydrothermal procedure described by Alberto Romero et al. [27]. First, n-hexadecyltrimethylammonium bromide was dissolved in a solution formed by 42 mL of distilled water, 18 mL of absolute ethanol and 13 mL of aqueous ammonia (20%) by stirring for 15 minutes; then 4 mL of tetraethyl orthosilicate were added dropwise. This solution was further stirred for 18 h. A white precipitate was then collected by filtration and washed with distilled water. This precipitate was dried at 60 ºC overnight. Dried samples were calcined from 80 to 550 ºC with a heating rate of 2 ºC/min and maintained at 550 ºC overnight.

Ruthenium catalyst was synthesized by the wetness impregnation (WI) method using the so prepared MCM-48 or Al/MCM-48 as supports. The ruthenium precursor (ruthenium (III) chloride anhydrous) and the corresponding support were suspended in water and sonicated for 10 minutes. The suspension containing the ruthenium precursor and the support were mixed and heated up with a rate of 1 ºC/min from 30 ºC to 80 ºC. The impregnation finished when the water was completely evaporated. The catalyst was then dried overnight at 105 ºC.

Products analysis

The identification and quantification of sugars, alcohols and degradation products were done by High Performance Liquid Chromatography (HPLC). Three different columns were used for these analyses: 1) Supelcogel Pb for sugars (milliQ water as mobile phase, 0.5 mL/min as flow rate and 85 ºC as temperature); 2) Sugar Shodex SH-1011 for degradation products (sulfuric acid 0.01 N as mobile phase, 0.8 mL/min as flow rate and 50 ºC as temperature). All the sugars, alcohols and acids were identified using a Waters IR detector 2414. 5-hidroxymethylfurfural (5-HMF) was determined with an UV-Vis detector at a wavelength of 254 nm. The standards employed for this analysis were: cellobiose (98%), glucose (99%), glycolaldehyde (99%), fructose (99%), acetic acid (99%), 5-hydroxymethilfurfural (99%), glyceraldehyde (95%), lactic acid (85%), pyruvaldehyde (40%), formic acid (98%), mannose (99%), galactose (99%), xylose (99%), arabinose (99%), acrylic acid (99%), levulinic acid (98%) and erythrose (75%). All these chemicals were purchased from Sigma Aldrich (Spain).

Total Organic Carbon (TOC) of the extracted sample was measured to get an idea of how much matter was solubilized.

The monomeric AX yield (%), the total AX yield and the AX purity (%) were calculated as follows:

$$\% \text{ Monomeric AX yield} = \frac{\text{(arabinose + xylose) as monomeric sugars in liquid extract (g)}}{\text{(arabinose + xylose) in raw material (g)}} \times 100 \quad (1)$$

$$\% \text{ Total AX yield} = \frac{\text{(arabinose + xylose) total in liquid extract (g)}}{\text{(arabinose + xylose) in raw material (g)}} \text{ x } 100 \quad (2)$$

$$\% \text{ AX purity} = \frac{\text{g of C in (arabinose + xylose) total extracted}}{\text{g of C in the liquid extract}} \text{ x } 100 \quad (3)$$

Experimental set-up

All the experiments were carried out in an AISI 304 stainless steel vessel (170 mL). The extractor was heated by an electric heater (275 W) placed around the wall and the temperature was controlled by a PID controller (ICP, TC21). A pressure gauge 0-25 bar was used to measure the autogeneous pressure inside the reactor. The solution was stirred continuously during the process with a magnetic stirrer at a constant rotational speed of 300 rpm. The typical reaction procedure was carried out introducing 160 mL of the wheat bran suspension in the reactor. When required, a ruthenium catalyst was added and the reactor. This mixture was stirred at 600 rpm for 5 minutes before the reactor was closed and the temperature set. Initial time (0 min) was considered when the desired temperature was reached. At the end of the experiments, the reactor was cooled down with a dry ice bath. A scheme of the experimental set-up is shown in Figure 2.

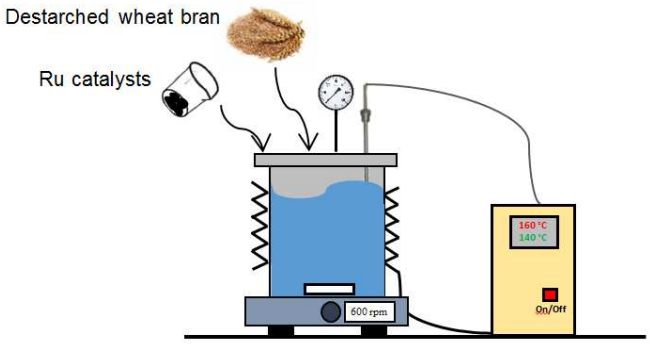

Fig 2. Scheme of the experimental set-up

Results

The effects of time, temperature and the presence of ruthenium catalysts were studied in the arabinoxylans extraction process.

Influence of catalyst

In order to compare the influence of the catalyst in the extraction of arabinoxylans from wheat bran, several experiments were carried out at 160 ºC and 10 minutes of extraction. The best results in terms of total arabinoxylans extracted were obtained when Ru/MCM-48 was used as catalyst. Using the corresponding amount of support MCM-48, the extraction was improved regarding the blank experiment, but not as much as the one with ruthenium catalyst (Figure 3). Although the purity of the liquid is higher using only the support than the catalyst, Ru/MCM-48 was chosen for further investigation as this catalyst will be required for the second hydrogenation step. On the other hand, the amount of sugars extracted as monomers was also higher in the experiment with Ru/MCM-48.

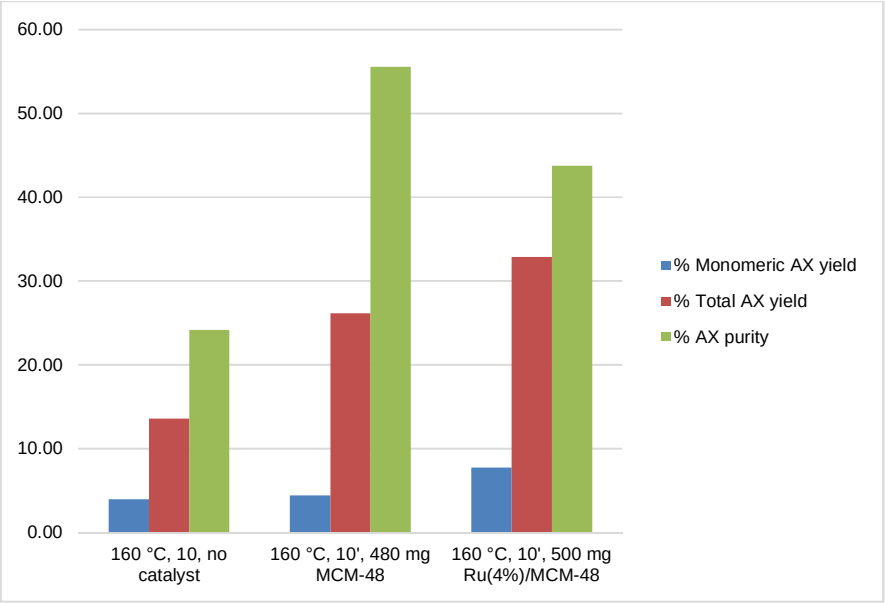

Fig 3. Influence of the catalyst on the arabinoxylans extraction

Influence of temperature

The influence of temperature was studied from 140 ºC to 180 ºC at 10 minutes and using Ru/MCM-48. The purity of the extracted liquid at 140 ºC was quite high (62%). However, the arabinoxylans extraction yield obtained at this temperature was very low (12%). The yield was increased up to 33% and 73% at 160 ºC and 180 ºC, respectively. 180 ºC was chosen as optimum temperature in the studied range because of the high extraction yield and the relatively high puritity of the extract. Moreover, the higher the temperature, the higher the monomeric sugars (xylose + arabinose) extracted. This is important because they will be more suitable for further processing, that is hydrogenation. These results are presented in Figure 4.

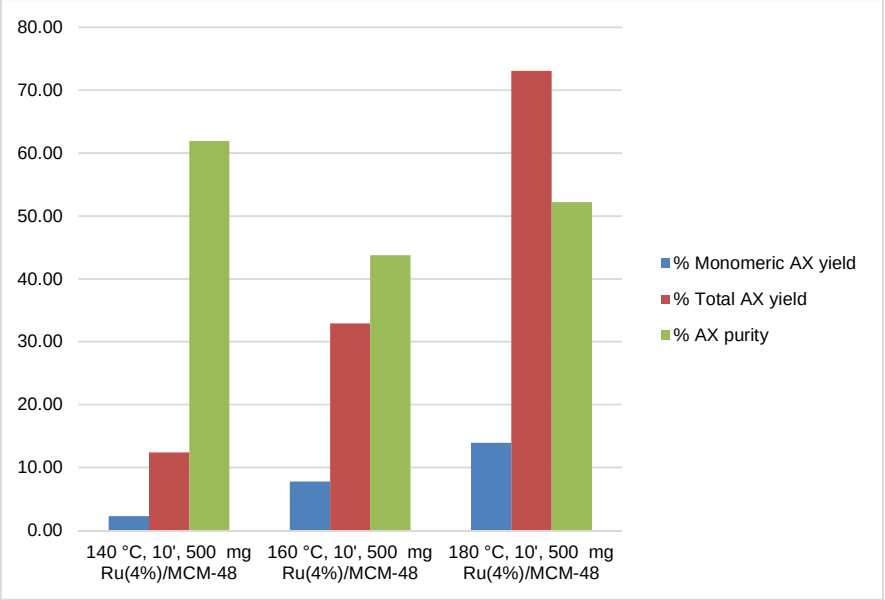

Fig 4. Influence of temperature on the arabinoxylans extraction

Influence of time

The effect of time was studied at 180 ºC and using Ru/MCM-48. Different experiments were carried out at 10 and 20 minutes. Both purity and extraction yield were higher at 10 minutes. At 20 minutes, the purity is lower due to many degradation products, such as acetic acid, 5-HMF, glycolaldehyde and formic acid that start to appear in the extracted liquid. The amount of monomeric sugars (xylose and arabinose) is quite similar for these two extraction times (Figure 5).

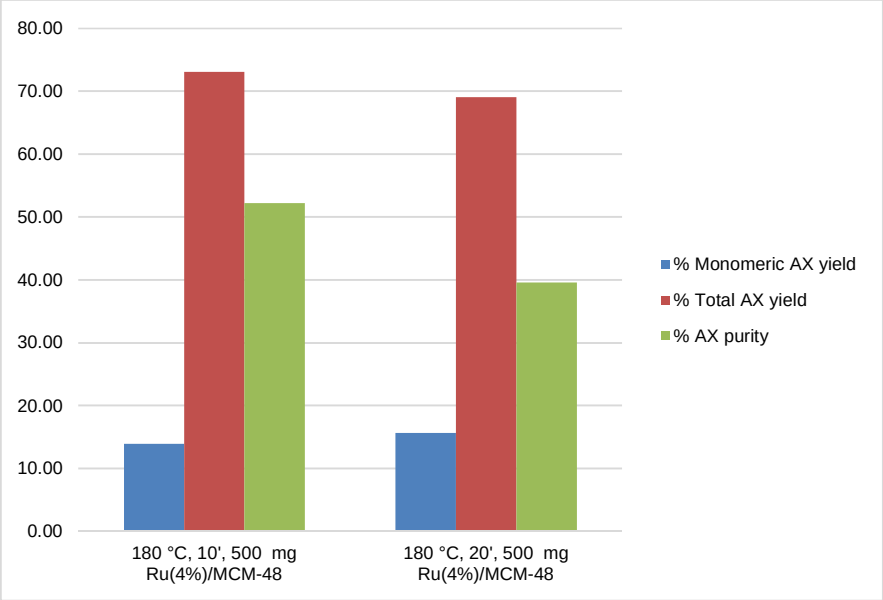

Fig 5. Influence of time on the arabinoxylans extraction

Influence of the support

Two different catalysts with the same metal and the same amount of it (ruthenium, 4%) but with different supports (MCM-48 and Al-MCM-48) were used in this work. From the previous experiments, it is known that Ru/MCM-48 improved the extraction process of AX from wheat bran. The influence of these two supports were tested at 180 ºC and 10 min with 500 mg of catalyst. The results are presented in Figure 6. As it can be seen, both catalysts have shown a great efficiency in the AX extraction process: the arabinose and xylose extraction yield as monomers and as total AX, as well as the purity of the liquid extract are higher when the ruthenium catalyst is used. Regarding the effect of the support, Ru/Al-MCM-48 works slightly better than Ru/MCM-48. At 180 ºC, after 10 min of extraction and using 500 mg of Ru/Al-MCM-48, the total AX yield is 79% and the purity of the liquid extract is equal to 54%.

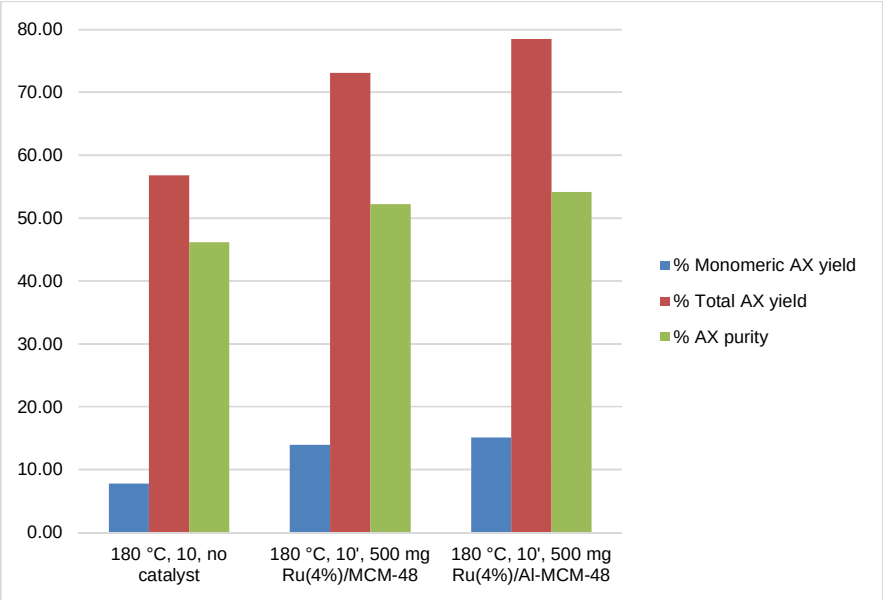

Fig 6. Influence of the support catalyst on the arabinoxylans extraction

Conclusions

A deep study of the influence of different parameters, as the use of ruthenium catalysts, temperature, time and catalyst support, on the arabinoxylans extraction process from wheat bran was carried out. Heterogeneous ruthenium catalysts developed in this work have demonstrated to have a great activity in the extraction process. Better results than those reported in literature using another extraction techniques are achieved and they present many advantages over chemical or enzymatic methods. Best results were obtained at 180 ºC and 10 min of extraction time using 500 mg of Ru/Al-MCM-48. At these operating conditions the total AX yield was 79% and the purity of the liquid extract was equal to 54%.

Acknowledgements

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