Heterogeneous catalysis for the extraction of arabinoxylans from wheat bran

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Introduction

Nowadays, wheat bran is gaining interest as raw material for biorefineries due to its high content in polysaccharides. In this sense, arabinoxylans (AX), which are the most abundant valuable components in wheat bran, are seen as 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 AX and 2) hydrogenation of these hemicelluloses into polyols (Figure 1).

![Scheme of the complete process of hydrogenation of arabinoxylans from wheat bran](image)

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

To make a single-step process possible, the AX extraction and hydrolysis must be also studied using the same heterogeneous catalysts required for the hydrogenation, usually ruthenium supported catalysts.

The aim of this work is to study the extraction-hydrolysis process of AX from wheat bran using heterogeneous ruthenium supported catalysts. This will let not only to develop a single-pot process for polyol synthesis but also take advantage of the heterogeneous catalysis itself in the extraction step or in different subsequent steps. Dissolution and hydrolysis of the AX into sugars were performed by pressurized hot water (PHW) and the acid sites of the ruthenium catalyst. The extent of the hydrolysis of AX is a key parameter to be studied, and AX molecular weight and the content of monomeric sugars must be determined. The effects of time (10-30 minutes), temperature (140-180 °C) and the presence of ruthenium catalysts were studied in the extraction-hydrolysis process of AX from wheat bran in terms of (1) matter
solubilization, (2) content in total and free monosaccharides and (3) degradation products.

Results
Table 1 shows the main results obtained in the different extraction experiments carried out from destarched wheat bran.

- **Influence of catalyst** was studied at 160 °C and 10 min (exp. #1, 2, 3). When MCM-48 support was used (exp. #2), the total AX extraction yield was much higher than that in the blank experiment (exp. #1). However, this yield could be also significantly improved using Ru(4%)/MCM-48 (exp. #3).

- **Influence of temperature** was investigated at 10 min using Ru(4%)/MCM-48 (exp. #3, 4, 5). At 140 °C, the total AX yield was really low, about 12% (exp. #4). Increasing temperature up to 160 °C and 180 °C (exp. #3, 5), the effect on the yield was very remarkable (32.2% and 71.1% respectively).

- **Influence of time** was considered at 180 °C using Ru(4%)/MCM-48 (exp. # 5, 6). After 10 minutes of extraction time (exp. #5), best results in terms of AX yield were obtained than after 20 minutes (exp. #6). This is due to the more degradation products formed.

- **Influence of support** was analyzed at 180 °C and 10 minutes. Two catalysts with different supports (MCM-48 and Al-MCM-48) were used (exp. #5, 7). Ruthenium catalyst supported on Al-MCM-48 (exp. #7) gave a higher AX yield than the one supported on MCM-48 (exp. #5). This could be explained as a consequence of the higher acidity of Ru(4%)/Al-MCM-48.

**Table 1.** Main results obtained in the extraction of AX from destarched wheat bran

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>t (min)</th>
<th>T (°C)</th>
<th>Catalyst (mg)</th>
<th>Mon. AX yield&lt;sup&gt;a&lt;/sup&gt; (Arab. + Xyl.) (%)</th>
<th>Tot. AX yield&lt;sup&gt;b&lt;/sup&gt; (Arab. + Xyl. + AX) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>160</td>
<td>-</td>
<td>4.2</td>
<td>13.2</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>160</td>
<td>MCM-48 (480)</td>
<td>3.7</td>
<td>24.4</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>160</td>
<td>Ru(4%)/MCM-48 (500)</td>
<td>7.2</td>
<td>32.3</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>140</td>
<td>Ru(4%)/MCM-48 (500)</td>
<td>2.2</td>
<td>12.2</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>180</td>
<td>Ru(4%)/MCM-48 (500)</td>
<td>13.3</td>
<td>71.1</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>180</td>
<td>Ru(4%)/MCM-48 (500)</td>
<td>15.2</td>
<td>67.5</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>180</td>
<td>Ru(4%)/Al-MCM-48 (500)</td>
<td>15.1</td>
<td>78.3</td>
</tr>
</tbody>
</table>

<sup>a</sup>Mon. AX yield (%) = (Arabinose + Xylose extracted as monomeric sugars)/(Arabinose + Xylose in raw material)·100

<sup>b</sup>Tot. AX yield (%) = (Arabinose + Xylose extracted as monomeric and oligomeric sugars)/(Arabinose + Xylose in raw material)·100
Conclusions
Ruthenium catalysts developed in this work improved the AX extraction yield in more than twice when only water was used. Best results were obtained at 180 °C after 10 minutes and using Ru(4%)/Al-MCM-48, achieving a total AX yield of 78.3%.

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