Synthesis of a 5-(Hydroxymethyl)furfural-based resin and its use as heterogeneous catalyst.

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Abstract
The synthesis and characterization of a new 5-(Hydroxymethyl)furfural-based resin was evaluated. The product obtained, a dark brownish solid and insoluble in several organic solvents and water, presents acidic properties (-COOH). The characterization was performed by using FTIR, solid carbon NMR, TGA, DSC analyses and the results showed an amorphous material. Its acidity was explored in an organic reaction under continuous flow conditions.

Key words:
Flow chemistry, Green chemistry, Heterogenous catalysis

Introduction
The use of renewable raw materials, such as biomass-derived compounds, to the production of chemicals and materials has gained considerable attention aiming at the substitution of fossil-based compounds.

In this study, a polymeric material was obtained after an unsuccessful attempt to do a Diels-Alder reaction between 2,5-di(hydroxymethyl)furan (DHMF) and maleic anhydride. In view of the acidity presented by the synthesized compound, it was investigated as a heterogeneous catalyst for a known transformation, allowing its comparison to an acid sulphonic acid resin reported in the literature.1

Results and Discussion
Firstly, the diene (DHMF, 2) was prepared from 5-HMF and was used in the Diels-Alder reaction with maleic anhydride (3).

The desired Diels-Alder adduct could not be isolated using several conditions (solvent and temperature screening). At 140 ºC, a dark brownish solid was formed after a few seconds of mixing and several analyses were performed in order to characterize this material. Scheme 2 shows part of the solid state 13C NMR spectrum obtained and the carbon assignment.

After the structure was elucidated, the ionic change capacity was measured and defined as 1.7 mmol.g−1. Then, this acidic resin was evaluated as a heterogeneous catalyst in the dehydration of fructose.

Table 1. Acid catalyzed dehydration of D-Fructose to 5-HMF in continuous flow regime.

<table>
<thead>
<tr>
<th>Entry</th>
<th>T (ºC)</th>
<th>Flow rate (mL.min−1)</th>
<th>P (bar)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1[a]</td>
<td>120</td>
<td>0.25</td>
<td>6</td>
<td>62</td>
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<tr>
<td>2</td>
<td>120</td>
<td>0.25</td>
<td>6</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>0.25</td>
<td>6</td>
<td>40</td>
</tr>
<tr>
<td>4[b]</td>
<td>120</td>
<td>0.25</td>
<td>6</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
<td>0.25</td>
<td>6</td>
<td>40</td>
</tr>
<tr>
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<td>40</td>
</tr>
<tr>
<td>7</td>
<td>120</td>
<td>0.25</td>
<td>6</td>
<td>40</td>
</tr>
</tbody>
</table>

[a] Fructose in DMSO/iPrOH (15% v/v) and only iPrOH as solvent.[b] Yield was determined by using 1,3,5-trimethoxybenzene as internal standard for 1H NMR. [c] First run after activation using HCl 1M in the 1 mL loop.[d] First run after a second reactivation using HCl 1M.

Conclusions
The strategy adopted here allowed the characterization of the unexpected polymeric product. Its physicochemical properties were determined and an application for this material was presented. Although it leads to lower yields than those reported in the literature, the resin showed potential application as a heterogeneous catalyst.

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Scheme 1: DHMF synthesis and Diels-Alder reaction using maleic anhydride as dienophile.

Scheme 2: Solid state 13C NMR for the HMF-based resin.

According to the pattern observed, the mechanism that follows was proposed to explain the structure and the acidity of the synthesized solid.

Scheme 3: Proposed mechanism for the resin formation.