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## Eco-friendly preparation of 5-hydroxymethylfurfural from sucrose using ion-exchange resins

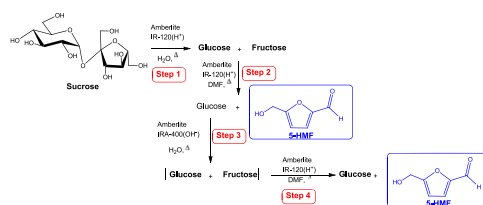
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## HIGHLIGHTS

- Conversion of sucrose into 5-HMF was achieved in 4 steps using ion exchange resins.
- Unprecedented dehydration of fructose took place with Amberlite IR120 (H<sup>+</sup>) resin.
- Glucose/fructose isomerization was analyzed using Amberlite IRA-400 (OH<sup>-</sup>) resin.
- Catalysts were reused for the hydrolysis, dehydration and isomerization steps.
- Chromatographic purification is avoided in the isolation of pure 5-HMF.

## GRAPHICAL ABSTRACT



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## ABSTRACT

An efficient preparation of 5-hydroxymethylfurfural from sucrose, a renewable resource, is reported herein, following a sequence of four steps catalyzed by reusable cation- and anion-exchange resins: hydrolysis, dehydration, glucose/fructose isomerisation and dehydration. The title compound, a key building block in current industrial chemistry, was isolated in its pure form without chromatographic purification in an overall yield of 50%.

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## 1. Introduction

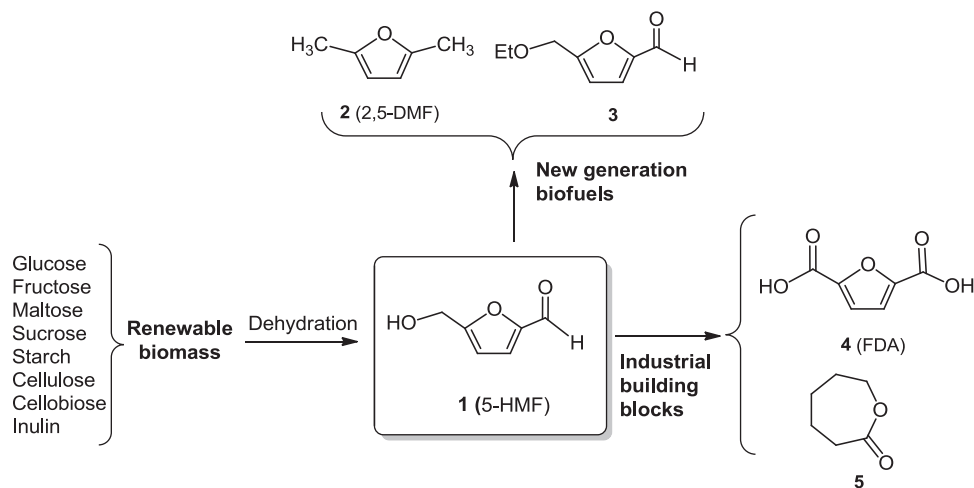
A change in the world concept of energy resources is necessary because of the increasing energy demand of modern society, together with environmental concern on the use of classical fuels, and fear of gradual exhaustion of the natural resources (Panwar

et al., 2011). Furthermore, fossil-fuels are not only widely required for providing energy supply, but are also a pivotal source of building blocks and raw materials in the chemical industry. For all these reasons, new environmentally-benign and sustainable chemical energy resources are highly demanded nowadays.

In this context, the first generation of biofuels (Naik et al., 2010), comprised of bioethanol and biodiesel, emerged as promising candidates for replacing oil; nevertheless, their production directly competes with food production, an important drawback (Corma et al., 2011). A second generation of biofuels was developed from non-edible plant material based on carbohydrates (Naik et al., 2010),

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Scheme 1. Synthetic applications of 5-HMF.

the most abundant organic molecules in nature (Taufiqurrhami and Bhatia, 2011). One of these recently-introduced approaches make use of 5-hydroxymethylfurfural (5-HMF) **1** (Tong et al., 2010), a versatile building block that can be obtained mainly by dehydration of carbohydrate-based biomass (Scheme 1); 5-HMF is readily-available (Rosatella et al., 2011) starting from monosaccharides (e.g. glucose, fructose), disaccharides (maltose, sucrose, cellobiose), polysaccharides (starch, cellulose, inulin), or from lignocellulosic biomass. The selective formation of 5-HMF from its precursors was found to be strongly dependent on the reaction conditions including not only the catalyst, but also temperature, solvent (traditional solvents or ionic liquids (Ryu et al., 2012); the latter also acting as catalysts), and reaction times; a major drawback is the frequent formation of levulinic acid, or humins as by-products (Tong et al., 2010), especially when starting from glucose, or glucose-containing products.

Numerous catalysts have been reported so far for the effective dehydration of carbohydrates, giving access to 5-HMF: mineral and organic acids (Tuercke et al., 2009), zeolites (Jadhav et al., 2012), metal-containing catalysts (Yang et al., 2012), and others (Rosatella et al., 2011).

The importance of 5-HMF lies on the fact that it can be converted into numerous derivatives with high added value (Rosatella et al., 2011). Thus, reduction (Hansen et al., 2012) of both ring substituents, or alkylation leads to compounds **2** (Thananathanachon and Rauchfuss, 2010) and **3** (Che et al., 2012), respectively, which are currently being investigated as efficient new generation fuels, or more likely, as fuel additives; in fact, **3** is already being commercialized. Furthermore, 5-HMF is currently considered as a promising bio-based chemical platform for further transformations into chemicals for industry (Rosatella et al., 2011). Thus, many derivatives, like monomers  $\epsilon$ -caprolactone **5** (Buntara et al., 2011), or hexane-1,6-diol (Buntara et al., 2012), can be obtained from 5-HMF (Scheme 1). Chemical modification of 5-HMF can also give access to building blocks for polymeric materials (Gandini, 2010). In this context, compound **4** has been used in the preparation of novel polyesters with the aim of mimicking the properties of PET (Gandini, 2008); vinyl polymers have also been reported from 5-HMF (Yoshida et al., 2008). All these examples prove the sustainability of the industrial processes based on 5-HMF.

## 2. Materials and methods

### 2.1. General procedures

$^1\text{H}$  NMR (300 MHz) spectra were recorded on Bruker Avance-300 spectrometer using  $\text{D}_2\text{O}$  as solvent. Chemical shifts are reported in  $\delta$

units (ppm) relative to the solvent peak (4.76 ppm). TLCs to follow the evolution of the reactions were performed on aluminum pre-coated sheets (E. Merck Silica Gel 60  $\text{F}_{254}$ ); spots were visualized by UV light, by charring with 10%  $\text{H}_2\text{SO}_4$  in EtOH or with vanillin (1.5% in EtOH in the presence of 1%  $\text{H}_2\text{SO}_4$ ).

Technical specifications of the resins (<http://www.sigmaaldrich.com/chemistry/chemical-synthesis/learning-center/technical-bulletins/al-142/amberlite-amberlyst.html>. (Accessed: 8th December 2013): Amberlite IR-120( $\text{H}^+$ ): apparent density 0.85 g/mL; true density 1.26 g/mL; effective size 0.50 mm; surface area 0.78  $\text{mm}^2$ ; and total exchange capacity 1.9 meq/mL. Amberlite IRA-400( $\text{OH}^-$ ): apparent density 0.71 g/mL; true density 1.11 g/mL; effective size 0.45 mm; surface area 0.64  $\text{mm}^2$ ; and total exchange capacity 1.4 meq/mL.

### 2.2. Preparation of 5-hydroxymethylfurfural

To a solution of sucrose (500 mg, 1.46 mmol) in  $\text{H}_2\text{O}$  (40 mL) was added Amberlite IR-120( $\text{H}^+$ ) resin (256 mg), and the corresponding mixture was refluxed for 16 h (step 1, sucrose hydrolysis). After that, the resin was filtered off, and the filtrate was concentrated to dryness; the residue was dissolved in DMF (10 mL), Amberlite IR-120( $\text{H}^+$ ) resin (303 mg) was added, and the mixture was heated at 100  $^\circ\text{C}$  with vigorous stirring for 10 h (step 2, fructose dehydration). Removal of the resin and the solvent, followed by partitioning of the residue between EtOAc ( $5 \times 20$  mL) and  $\text{H}_2\text{O}$  (35 mL) afforded a fraction of 105 mg of pure 5-HMF (29% yield) from the organic fraction. Amberlite IRA-400( $\text{OH}^-$ ) (1.74 g) was added to the previous aqueous fraction (35 mL), and the mixture was refluxed at 100  $^\circ\text{C}$  for 24 h (step 3, glucose/fructose isomerization). After that, removal of the resin, concentration to dryness and subsequent treatment with Amberlite IR-120( $\text{H}^+$ ) (163 mg) in DMF (10 mL) at 100  $^\circ\text{C}$  for 15 h allowed another dehydration step (step 4, fructose dehydration). Work-up as described above afforded a second fraction of pure 5-HMF (78 mg, 21% yield). Total yield: 183 mg (50%).

## 3. Results and discussion

Despite the numerous literature reporting the synthesis of 5-HMF, in many occasions, lack of selectivity, difficulties involving isolation, together with expensive and/or hazardous reagents are the main drawbacks associated to this synthesis. Herein we present a green and good-yielding procedure for the preparation of 5-HMF based on inexpensive starting materials (sucrose) and heterogeneous catalysts, (cation- and anion-exchange resins), together with

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