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Co-production of HMF and gluconic acid from sucrose by chemo-enzymatic method

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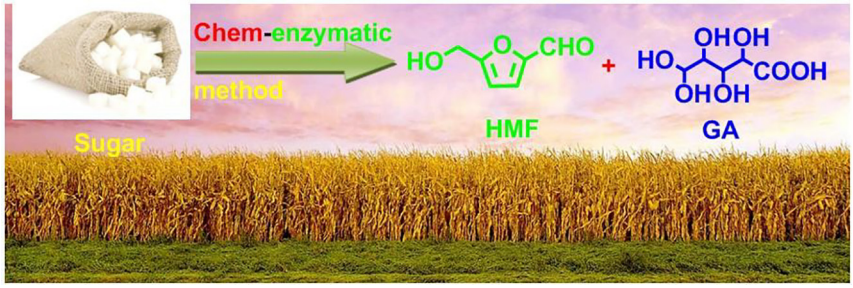
HIGHLIGHTS

- Co-production of gluconic acid and HMF from sucrose was presented.
- The yields of HMF and gluconic acid reached 42.5% and 48%, respectively.
- Gluconic acid and HMF were easily separated because they were in different phases.

GRAPHICAL ABSTRACT

The co-production of HMF with 42.5% yield and gluconic acid with 48% yield from sucrose by chem-enzymatic method was explored.



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ABSTRACT

Co-production of multi-products is one of the core principles of chemical industry, and it is also an important way to improve the atom economy. Herein, we proposed an approach to co-producing two valuable platform compounds, gluconic acid (GA) and 5-hydroxymethyl furfural (HMF), from sucrose by successive hydrolysis, oxidation and dehydration. In the enzymatic oxidation step, only glucose was oxidized to GA, meanwhile fructose was 100% retained. In the further biphasic dehydration system, only fructose was converted into HMF, whereas GA was maintained with over 95% recovery. After three reactions, the yields of HMF and GA were respectively 42.5% and 48% when the initial feedstock of sucrose was 200 g/L. Two products were easily separated because GA was completely existed in aqueous phase, and HMF was mainly in organic phase. In the whole process, only commercial enzymes and mineral acid were used instead of self-made catalysts.

1. Introduction

HMF, one of the most important bio-based platform compounds, is used to produce a variety of biopolymers, biofuels, commodity chemicals, pharmaceuticals, and can be synthesized from all types of monomeric or polymeric glucose and fructose, such as glucose, fructose, sucrose, starch, inulin, cellulose and so on [1–4]. Fructose is the best raw material for HMF preparation because of its natural furanose structure which is beneficial to the formation of HMF. However, its price is too high to be applied in the large-scale HMF production. This conclusion was also demonstrated by Torres [5] and Kabir Kazi [6] in their studies about the techno-economic evaluation of HMF production. Hence, lots of cheaper materials like glucose, sucrose and cellulose were chosen to manufacture HMF.

Abbreviations: HMF, 5-hydroxylmathyl furfural; GA, gluconic acid; NaGlc, sodium gluconate; 2-MeTHF, 2-methyl tetrahydrofuran; GOD, glucose oxidase; INV, invertase; CAT, catalase.

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Compared to fructose, glucose is a more abundant and less expensive hexose (its price was shown in Table S1) and can be obtained from cheaper raw materials like cellulose or starch. However, due to the stable nature of its pyranose ring structure, harsh reaction conditions are required to offset side-reactions and increase HMF yield. Based on this, lots of progresses have recently been made in integrating the glucose isomerization (by solid bases [7–9], enzymes [10,11], or Lewis acids [12–16]) and fructose dehydration to produce HMF in a "one-pot" configuration. Nonetheless, several limitations were revealed in recent publications [17,18]. For example, high HMF yields (70–90%) are reported from glucose in ionic liquid with the Lewis acid catalyst, but ionic liquids are not yet suitable for large scale applications due to the difficulty of HMF's separation, deactivation by small amounts of water and their high cost [19]. Another choice is separating fructose after the isomerization of glucose. Alipour [20] recently explored a novel enzyme-based Simultaneous-Isomerization-and-Reactive-Extraction (SIRE) process to extract fructose into a water-immiscible organic phase (octanol). Then the fructose transferred from the organic phase by Back-Extraction (BE) into an acidic IL ([EMIM]HSO_4) reaction medium was dehydrated into HMF. Finally, HMF was re-extracted into the low boiling point organic solvent. The whole process has undergone three extractions, which consumed amounts of solvent and was difficult to be operated. Sucrose, another one of the most widely-traded commodities in the world with a low price (see also Table S1), is easily hydrolyzed into one molecular glucose and fructose. For the adequate use of these two carbohydrates, the Brφnsted-Lewis composite catalytic system was commonly applied to produce HMF. However, those approaches have the same limitations as the process of HMF preparation from glucose. Inedible cellulose has been recognized as most promising renewable resource for the production of HMF. Commonly, the synthesis of HMF from cellulose is also considered through the pathway of glucose isomerization and will face the same difficulty like glucose as raw material. We had explored a different route from cellulose to HMF in polar aprotic solvents and its yield reached 44%, however, its reaction conditions are very harsh [21]. Therefore, we need a new process of HMF to change this status.

Co-production of multi-products is an important method for chemical engineering processes and the revenue of the co-products will reduce the overall cost. Gluconic acid (GA), an oxidation production of glucose, is a valuable platform chemical and widely used in the pharmaceutical, food, detergent, textile, leather, and concrete industries with its salts [22]. Different from other glucose oxidation methods including catalytic oxidation [23–26], electrochemical oxidation [27], fermentation [28,29], enzymatic oxidation, especially glucose oxidase (GOD, β-D-glucose: oxygen 1-oxidoreductase, E. C.: 1.1.3.4), merely oxidized glucose into GA without affecting other carbohydrates because of its high substrate specificity [30]. Based on this character, GOD was often applied to remove the residue glucose and improve the purity of the other sugars or polysaccharides [31,32]. GA production form sucrose through the multi-enzyme reaction has also been reported in the literatures [33–35]. In these processes, a mixture solution of GA and fructose was formed. Consequently, HMF will be co-produced with GA from GA and fructose mixtures if GA is stable, does not affect the dehydration of fructose under acidic reaction condition and is easily separated in the subsequent separation process. Meanwhile, the overall revenues of HMF preparation will be greatly improved and the restrictions of raw materials and catalysts will be reduced.

Herein, we reported an approach to co-producing GA and HMF from sucrose by a chemo-enzymatic method (Scheme 1). A glucose and fructose mixture was obtained from sucrose hydrolysis, and then was converted into GA and fructose using GOD and catalase (CAT, E. C.:1.11.1.6). This mixture solution was further converted into HMF by dilute sulfuric acid in a water/2-methyl tetrahydrofuran biphasic system (H_2O/2-MeTHF). The presence of GA did not affect the fructose dehydration and GA was reserved in the aqueous phase. While the HMF went into the organic phase and therefore it was easy to separate from the GA. Base on the conditions of batch reaction, a continuous co-production of GA and HMF in a micro-flow reactor was also explored.

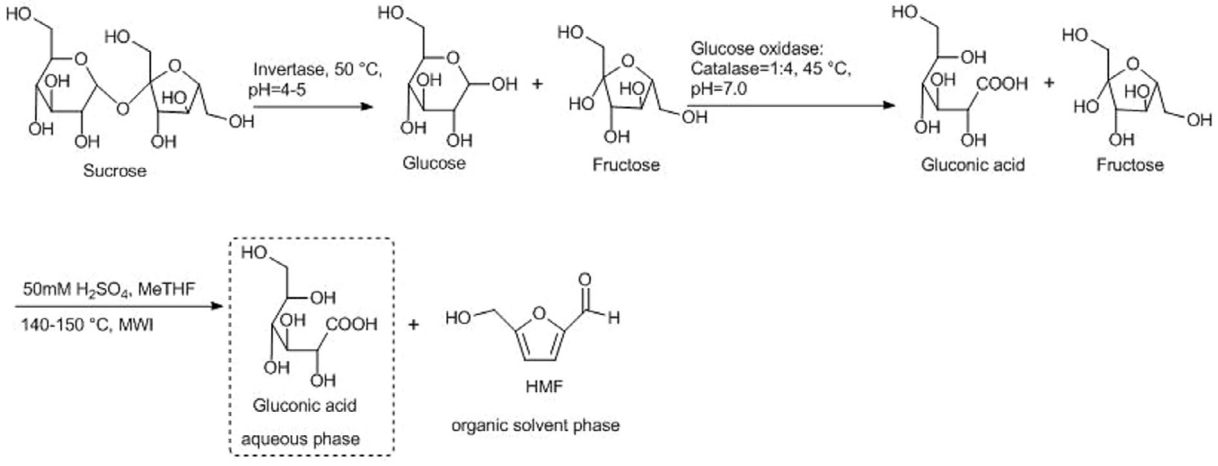
2. Experimental

2.1. Chemicals

Sucrose, sodium gluconate, glucono-δ-lactone, 2-methyltetrahydro-furan, sulphuric acid were purchased from Sigma–Aldrich. Invertase (INV, E. C.: 3.2.1.26), glucose oxidase and catalase were supplied by Shanghai Baoman Biotech. Co. Other regents were provided from Aladdin.

2.2. Sucrose enzymatic hydrolysis

Solution of sucrose (200 g/L) were prepared in water (pH was adjusted to 4.5) and putted into a 50 mL conical flask. Immobilized



Scheme 1. The co-production of HMF and GA from sucrose.