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Chemical transformation of food and beverage waste-derived fructose to hydroxymethylfurfural as a value-added product

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ABSTRACT

A novel alternative bioconversion and chemical transformation method for valorisation of food and beverage (F&B) waste to hydroxymethylfurfural (HMF) is reported. Solid-to-liquid ratio of 70% was applied to hydrolyse F&B waste by glucoamylase and sucrase to yield a hydrolysate consisted of glucose and fructose. After impurity removal using chromatography columns, the purified hydrolysate was processed by glucose isomerase to produce syrup with a fructose-to-glucose ratio of 1:1. After removal of the residual impurities using ion exchange columns, Simulated Moving Bed system was applied to separate sugars in fructose-glucose syrup. The resultant high-fructose syrup contained 89.0 g/L fructose, which was demonstrated as an ideal feedstock for the synthesis of HMF. By employing a commercial solid acid catalyst (Amberlyst 36), 71 mol% HMF with a high selectivity of 77 mol% was generated from this high-fructose syrup under mild microwave heating at 140 °C within 40 min. The increase in catalyst loading accelerated both HMF formation and HMF-consuming side reactions, underscoring the trade-off between the conversion rate and product selectivity. The solid catalyst can be recovered and successfully reused for four runs with the HMF yield at 70 mol%. An overall conversion yield of 30 g HMF/kg F&B waste was achieved. This work emphasises a novel integration of chemical and biological technologies for selective production of HMF from mixed F&B waste.

1. Introduction

The generation of commercial and industrial food waste shows a growing trend globally. For example, in Hong Kong, disposal of food waste from the food industries, hotels, restaurants, etc. increased from 400 t daily in 2002 to 1033 t daily in 2014 [1]. In order to meet the sustainability metrics towards the deployment of circular bioeconomy, it is desirable to turn waste streams into valuable and tradable chemicals and materials with market competitiveness through innovative recycling approaches [2,3]. The great amount of carbohydrates in the industrial food waste [4,5] becomes an untapped opportunity, making the waste a potential feedstock for the production of sugar-based value-added products to substitute petro-chemicals [6,7]. In addition, the homogenous nature of the waste presents an advantage in production of high-purity products via biological or chemical methods.

Beverage waste is a significant category of industrial food waste, for instance, 4500 million litres of beverage waste were generated from the soft drink industries per annum in Argentina [8]. This waste stream is rich in simple sugars including glucose, fructose, and sucrose [9]. These are highly feasible starting materials for conversion processes and superior to glucans (e.g., cellulose and starch) in terms of energy demand for breaking down the macrostructure. Our recent study has successfully demonstrated the use of beverage waste to generate high-fructose syrup via enzymatic hydrolysis followed by chromatographic separation [9]. More investigations should be conducted to validate the integrated operation for production of high-quality fructose syrup and subsequent upgrading to value-added products (Fig. 1).

Hydroxymethylfurfural (HMF) is one of the attractive fructose derivatives. It is a versatile platform chemical for the synthesis of a wide spectrum of commodities including pharmaceuticals, polymers, resins, solvents, and biofuels [10]. The market value of HMF ranges from USD 2 to 300 per kilogram depending on the quality [11], which is more competitive than other products such as glucose (USD 0.39 per kilogram) and acetic acid (USD 1.14 per kilogram) [4,12]. Nevertheless, the

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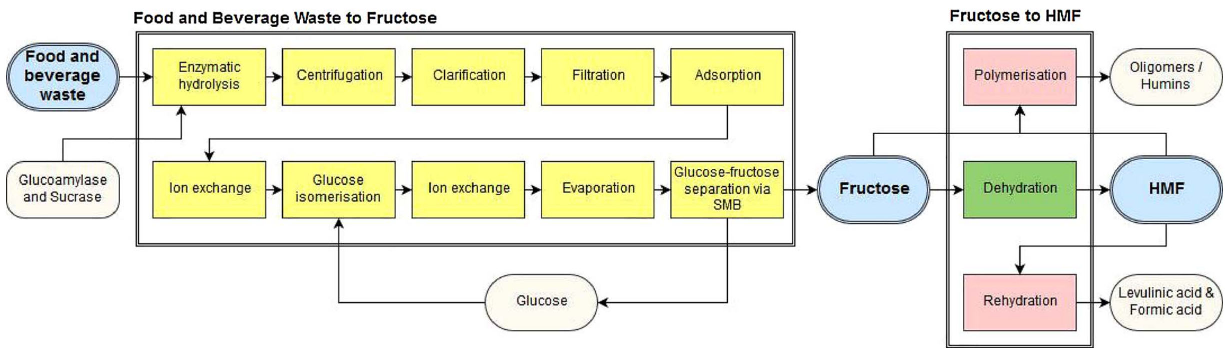

Fig. 1. Process flow diagram for bioconversion of food and beverage waste to fructose, and the chemical transformation of fructose to hydroxymethylfurfural.

current industrial HMF production mainly relies on fructose extracted from energy crops as the major feedstock [13]. As the market price of HMF is highly sensitive to the feedstock cost [14], replacing the virgin fructose by a waste-derived alternative would improve the economic merit.

The high-fructose syrup produced from food and beverage waste could be a potential renewable feedstock, in which fructose can be converted to HMF via dehydration over Brønsted acid (i.e., protons) as the catalyst. As compared to lignocellulosic feedstock, the high purity and simple structure of the high-fructose syrup make it more feasible for chemical transformation. The complex and recalcitrant structure in lignocellulosic feedstock requires intensive pretreatment and the subsequent transformation processes normally involve high operating temperature or toxic ionic liquids [7,15]. In addition, significant side reactions in chemical conversion of biomass as the conventional approach disfavour high-yield HMF production [15]. Therefore, this study aims to enhance HMF synthesis by integrating bioconversion and chemical transformation, in high selectivity and efficiency, respectively, as the complementary advantages for synergistic improvement of the system performance.

This study targets the production of high-quality fructose syrup from industrial food and beverage waste using a 10-L paddle mixer for enzymatic hydrolysis, adsorption and ion exchange columns for purification, and Simulated Moving Bed (SMB) for high-fructose syrup separation. The next-stage upgrade into the value-added HMF was also demonstrated via facile thermochemical conversion over a recyclable commercial solid catalyst. Significance of operating parameters (e.g., reaction time and catalyst dosage) in governing conversion rate and HMF selectivity were also scrutinised. This study presents an innovative and high-performance integrated upcycling technology for sustainable management of mixed F&B waste.

2. Materials and methods

2.1. Raw materials

The industrial food and beverage waste used in this study contained potato chips, oatmeal products, fruit juice, sport drink, and soft drink. Glucoamylase and sucrase were the enzymes employed for the hydrolysis of food and beverage waste, while glucose isomerase was used in the isomerisation process, all of which were obtained from Novozyme®, Denmark. Purification of hydrolysate was performed using columns filled with different types of resins: Lewatit VP OC 1064 MD pH resin from Lanxess, Netherlands, in adsorption chromatography column; DOWEX MONOSPHERE™ 88 and DOWEX MONOSPHERE™ 66 resin from The Dow Chemical Company, USA, in cation and anion exchange chromatography columns, respectively. Separation of fructose for producing high-fructose syrup was conducted using the SMB system containing DOWEX MONOSPHERE™ 99 Ca separation resins. For comparison to the food and beverage waste-derived syrup, defined medium was also used as feedstock in the SMB unit, including standard sugars consisting of glucose and fructose, which were obtained from Daesang, South Korea and Xiwang, China, respectively.

For the catalytic valorisation of high-fructose syrup, Amberlyst 36 (polystyrene-*co*-divinylbenzene sulfonic acid resin) from Sigma Aldrich was used as the commercial solid catalyst, with the cation exchange capacity of 5.4 mmol/g, surface area of 10.4 m^2/g, pore volume of 0.06 cm^3/g, and average pore size of 27.6 nm [16]. It was selected in view of its favourable acid site density for efficient catalytic reactions [15] and high thermal stability, and it possesses a high degree of durability for real-life application. Dimethyl sulfoxide (DMSO; ≥99.9%, RCI Labscan) served as a co-solvent in the aqueous reaction medium. For the quantification of HMF and by-products, the high performance liquid chromatography (HPLC, Waters, USA) was calibrated by model compounds, including cellobiose (≥98%), levulinic acid (98%), and formic acid (98%) from Alfa Aesar; fructose (≥99%) and maltose monohydrate (≥98%) from Wako; glucose (≥99.5%), HMF (≥99%), and furfural (99%) from Sigma Aldrich; and levoglucosan from Fluorochem, respectively. Amberlyst 36 was dried at 105 °C overnight before use, while other chemicals were used as received.

2.2. Upscale enzyme hydrolysis of food and beverage waste

Five different solid-to-liquid ratios (30–70%) of food and beverage waste were tested in enzymatic hydrolysis, which was conducted in a 10-L paddle mixer. The temperature was maintained at 50 °C and the agitation speed of paddle mixer was set at 50 rpm. When the temperature reached 50 °C, 1% (v/w) of glucoamylase and 0.025% (w/v) of sucrase were added into the hydrolysis broth. The samples were taken every 30 min and centrifuged at 10,000 rpm for 5 min. The supernatant was filtered using 0.22 mm membrane filter for quantification of sugars using HPLC. After 24 h, the hydrolysis broth was collected and centrifuged at 10,000 rpm for 15 min for the separation of supernatant from the remaining solids and lipid. Afterwards, the supernatant was subjected to clarification and filtration to obtain clean hydrolysate, namely glucose syrup (Fig. 1), which was stored at −20 °C prior to the downstream processes. Glucose yield was calculated according to Eq. (1).

$$\text{Glucose yield} = \frac{\text{Weight of glucose produced in hydrolysis (g)}}{\text{Amount of starch} \times 1.11 + \text{Amount of sucrose} \times 0.56 + \text{Amount of free glucose in F\&B waste (g)}} \times 100\% \quad (1)$$

2.3. Isomerisation of glucose syrup and purification of glucose-fructose syrup

Purification of the glucose syrup was conducted prior to isomerisation to remove the impurities and colourants. The glucose syrup first passed through the adsorption chromatography column at the