



Valorization of food waste into hydroxymethylfurfural: Dual role of metal ions in successive conversion steps

Iris K.M. Yu^a, Daniel C.W. Tsang^{a,*}, Alex C.K. Yip^b, Season S. Chen^a, Yong Sik Ok^c, Chi Sun Poon^a

^aDepartment of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

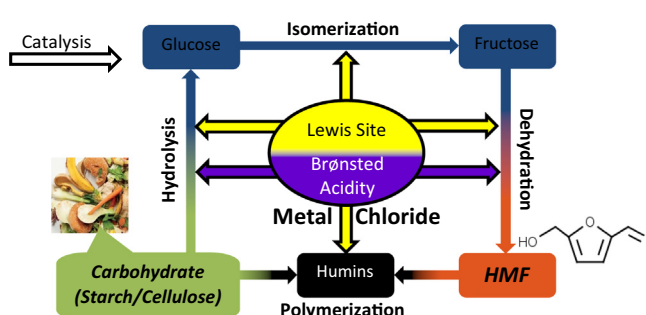
^bEnergy and Environmental Catalysis Group, Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand

^cSchool of Natural Resources and Environmental Science & Korea Biochar Research Center, Kangwon National University, Chuncheon 24341, Republic of Korea

HIGHLIGHTS

- Brønsted acidity was developed via metal hydrolysis and by-product formation.
- Lewis acid sites of metal ions catalyzed hydrolysis and dehydration.
- Catalytic performance was primarily determined by electrochemical properties.
- HMF and glucose (~54–73%) could be yielded from cooked rice and bread crust.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 21 June 2016

Received in revised form 31 July 2016

Accepted 1 August 2016

Available online 3 August 2016

Keywords:

Biomass conversion

Bread/rice

Homogeneous catalysis

Lewis acid

Metal chloride

ABSTRACT

This study aimed to transform food waste into a value-added chemical, hydroxymethylfurfural (HMF), and unravel the tangled effects induced by the metal catalysts on each single step of the successive conversion pathway. The results showed that using cooked rice and bread crust as surrogates of starch-rich food waste, yields of 8.1–9.5% HMF and 44.2–64.8% glucose were achieved over SnCl_4 catalyst. Protons released from metal hydrolysis and acidic by-products rendered Brønsted acidity to catalyze fructose dehydration and hydrolysis of glycosidic bond. Lewis acid site of metals could facilitate both fructose dehydration and glucose isomerization via promoting the rate-limiting internal hydride shift, with the catalytic activity determined by its electronegativity, electron configuration, and charge density. Lewis acid site of a higher valence also enhanced hydrolysis of polysaccharide. However, the metals also catalyzed undesirable polymerization possibly by polarizing the carbonyl groups of sugars and derivatives, which should be minimized by process optimization.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Food waste has been a global environmental problem that around one-third of food production goes to wastage (Gustavsson et al., 2011), particularly in well-developed countries. For example, the United States discards 32 million tonnes of catering waste at

* Corresponding author.

E-mail address: dan.tsang@polyu.edu.hk (D.C.W. Tsang).

landfills daily, accounting for approximately 15% of the total disposed waste (Thyberg et al., 2015); and Hong Kong also has a high dumping rate of 3640 tonnes of food waste per day (HK EPD, 2015). Massive landfilling of organics has been recognized as unsustainable due to the significant greenhouse gas emission (Levis and Barlaz, 2011). Recycling biodegradable wastes through composting and anaerobic digestion represents an environmentally benign and widely adopted option today (Arsova, 2010; Levis and Barlaz, 2011). However, these traditional biological processes take a few

weeks to complete. The market need for fertilizers is also diminishing in densely populated regions where agricultural activities are limited. Therefore, efficient valorization of food waste into products with high market potential should be developed to diversify and boost the recycling industry. More importantly, the recovery of valuable compounds from waste introduces the concept of bio-refinery and circular economy to organic waste management (Pleissner et al., 2016), driving our community towards sustainable development.

Hydroxymethylfurfural (HMF) has been considered as one of the top value-added biomass-derived chemicals (Bozell and Petersen, 2010). It is a versatile building block that serves as a substitute for fossil fuel derived chemicals, such as dimethylfuran, 2,5-furandicarboxylic acid and 5-ethoxymethylfurfural (Zhou and Zhang, 2016). These chemicals are precursor materials for the synthesis of polymers, pharmaceuticals, and fuel, enabling the establishment of downstream sustainable chemical industry. However, the common practice of HMF production that requires edible monosaccharides as substrate arouses concerns of its adverse impact on world food supply (Yin et al., 2011). Therefore, this research considers food waste as an inexpensive renewable feedstock, which presents a huge sugar reservoir containing 47–74% carbohydrates on a dry basis (Pleissner et al., 2014). A recent study has achieved a maximum HMF yield of 4.3% from catering waste and articulated the associated economic benefit (Parshetti et al., 2015), illustrating the significance and need for technology development. To improve the conversion efficiency, our work scrutinized the fundamental roles of catalysts in order to master the underlying principles for selection of favourable conditions.

The conversion of cellulose and starch involves three major chemical reactions in series: (a) hydrolysis of glycosidic bonds in the polymeric carbohydrate to release glucose units, followed by (b) isomerization to transform glucose into fructose, and (c) dehydration process to convert fructose to HMF (Fig. S1a–c) (Dutta et al., 2012). High temperature is often employed for the non-catalytic HMF production from polysaccharides. Previous studies found that under heating at 270–300 °C pure cellulose produced 10–20% HMF in water without the use of catalyst (Jin et al., 2005; Yin et al., 2011), while a temperature of 270 °C derived 3% HMF from sugarcane bagasse (Iryani et al., 2013). The high energy consumption during the heating process would significantly dampen the environmental compatibility of the technology with reference to the life cycle analysis of cellulose extraction from food waste (Piccinno et al., 2015). The use of catalyst could significantly reduce energy demand and enhance conversion efficiency. For instance, a study on catalytic conversion of cellulose achieved 54.9% of HMF under a moderate temperature of 150 °C (Xiao et al., 2014).

The formation of HMF from food waste is acid-catalyzed and can be achieved over Brønsted and/or Lewis acids. While the Brønsted acid accelerates hydrolysis of cellulose via attacking the C–O–C glycosidic bond between glucose units and facilitating breakdown of linkage (Tao et al., 2011; Zhou et al., 2013), it also initiates dehydration of fructose to produce HMF through protonation of the sugar hydroxyl group (de Souza et al., 2012; Wrigstedt et al., 2015). Excessive acidity given by Brønsted acid may incur undesirable side reactions such as polymerization between sugars and derivatives (Hu et al., 2015) as well as rehydration of HMF (de Souza et al., 2012), which decrease the yield of HMF. On the other hand, Lewis acid, which is exemplified by metal ions, has been shown to increase the rate of glucose isomerization by accepting electron pairs from glucose to form a transitional complex with a lower energy barrier, which favours intramolecular hydride shift during the aldose-ketose transformation (Binder et al., 2010; Román-Leshkov et al., 2010).

Although recent investigations have evaluated the catalytic roles of Lewis acid property of metal ion on the isomerization step, Brønsted acidity derived from metal ions that potentially extends its functionality are seldom considered. We postulated that protons (Brønsted acid) released from partial hydrolysis of metal ions in the aqueous medium could facilitate hydrolysis and dehydration, as well as off-path reactions such as the abovementioned polymerization and rehydration. In addition, despite a broad spectrum of metal ions investigated in individual studies, it is difficult to compare their performance in different publications due to varying conditions such as temperature, time, and loading, etc. Only a few studies examined a series of metal ions under the same conditions (Zhao et al., 2007; Dutta et al., 2012; Pagán-Torres et al., 2012; Rasrendra et al., 2012), but the factors leading to the discrepancy in their catalytic activity remained uncertain. It is necessary to fill this critical knowledge gap in order to develop robust and sustainable options for the catalytic systems.

In this research, we intended to assess the significance of the electrochemical characteristics of the inorganic metal chloride catalysts, which determine their ability to coordinate with the reactant to facilitate hydride shift, for the catalytic conversions of carbohydrates and food waste to HMF. A range of Lewis acids were scrutinized of the effects of their indirectly derived Brønsted acidity and electrochemical properties on each reaction step during the HMF production from carbohydrates. Food waste was then used as a feedstock to demonstrate the applicability of the catalytic HMF production process in the real-life application.

2. Materials and methods

2.1. Chemicals

Standard compounds were used in this study: glucose (99%), cellobiose ($\geq 98\%$), levulinic acid (98%) and formic acid (98%) from Alfa Aesar; maltose monohydrate ($\geq 98\%$) from Wako; HMF ($\geq 99\%$) and rice starch from Sigma Aldrich; and levoglucosan from Fluorochem, respectively. Their molecular structures were provided in Fig. S2. The catalysts were purchased from Sigma Aldrich, including $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ($\geq 98\%$), FeCl_3 (97%), CuCl_2 (99%), ZnCl_2 ($\geq 98\%$), InCl_3 (98%), $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (98%), $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%) as well as H_3PO_4 ($\geq 85\%$ in water), whereas $\text{Zr}(\text{O})\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ (99.0+%) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (ACS grade) were from Wako and Anaqua, respectively. Dimethyl sulfoxide (DMSO) ($\geq 99.9\%$) from Sigma Aldrich was used to make the solvent mixture in all tested reactions. All the chemicals were used as received. Pre-consumer food waste, i.e., cooked rice and bread crust, from the Hong Kong International Airport (HKIA) were then used as the food waste substrates in this study. The cooked rice and bread crust samples were freeze-dried, sieved through a 0.2-mm-mesh, and stored in air-tight storage containers at -4 °C in the dark.

2.2. Catalytic conversion

The carbohydrate was added to a DMSO/water (1:1 v/v) mixture because it gave a higher yield of HMF than using water alone according to our preliminary results (Fig. S3a and b). This enabled distinct performance of each tested metal chloride for comparison in this fundamental research, while the associated environmental considerations will be evaluated and addressed in our future work. A substrate loading of 5 wt/v% was adopted with reference to a previous study (Jia et al., 2014). Maltose and cellobiose were loaded based on the available quantity of glucose. The metal chlorides of 20 mol% with respect to monosaccharide (Dutta et al., 2012), i.e., 55.5 mM, were used, instead of 5 mol% (i.e., 13.9 mM) as reported by Jia et al. (2014) that produced less HMF in our pre-

Download English Version:

<https://daneshyari.com/en/article/7070041>

Download Persian Version:

<https://daneshyari.com/article/7070041>

[Daneshyari.com](https://daneshyari.com)