Catalytic Ethanolysis of Fructan-rich and Starchy Expired Food into Biofuel 5-Ethoxymethylfurfural

Luxin Zhang,[a,]* Yuting Liu,[a] Chang Liu,[b] Simin Yi,[a] Wen Sun,[a] and Jianfeng He [a]

Catalytic systems were investigated for the ethanolysis of expired food into 5-ethoxymethylfurfural (5-EMF). Fructan-rich expired food (expired probiotics beverage powder, onion powder, garlic powder, and burdock tea), and starchy expired food (expired steamed buns and egg yolk battercake) were tested as starting substrates. Optimization of the reaction conditions included varying the catalyst type, temperature, catalyst loading, and reaction time to maximize 5-EMF yield. Several co-solvents were added to evaluate their impact on the generation of 5-EMF. The selected expired foods produced 5-EMF yields ranging from 0.2 mol% to 68 mol%. The 5-EMF yield from fructan-rich expired food was more noticeably affected by the content of the non-carbohydrate part than that from starchy expired food. The effect of co-solvents on conversion efficiency was closely related to the catalyst type but was not strongly correlated with the feedstock used. This study provides a facile way to produce biofuel chemicals from carbohydrate-rich expired food.

Keywords: Biorefinery; Biofuel; 5-EMF; Catalysis; Fructan-rich expired food; Starchy expired food

Contact information: a: College of Environmental and Municipal Engineering, Key Laboratory of Northwest Water Resources, Environment, and Ecology, MOE, Key Laboratory of Environmental Engineering, Shaanxi Province, Xi'an University of Architecture and Technology, Xi'an, 710055, P.R. China; b: Department of Civil and Environmental Engineering, College of Engineering and Mellon College of Science, Carnegie Mellon University, 5000 Forbes Ave, Pittsburgh, PA 15213, USA;
** Corresponding author: zhangluxinxx@126.com*

INTRODUCTION

Approximately one third of the food produced globally for human consumption is lost or wasted in food supply chains (FAO 2011; Abeliotis *et al.* 2015); therefore the valorization of food waste biomass, both pre-consumer and post-consumer food waste, has been of increased interest recently (Pfaltzgraff *et al.* 2013; Chen *et al.* 2017; Zhai *et al.* 2018). Conventional food supply chain waste (FSCW) recycling strategies (first generation food waste treatment and recycling) include anaerobic digestion for biogas generation, composting, bioethanol generation, and animal feed production (Pham *et al.* 2015). These microbiological treatments have several disadvantages, which include long production times and the underutilization or loss of chemical functionalities. The need to avoid the production of waste and find new renewable resources has led to second generation FSCW valorization approaches, which use FSCW as an alternative to "virgin biomass" to produce bio-derived marketable chemicals, materials, and fuels (Pfaltzgraff *et al.* 2013; Karmee and Lin 2014; Xiong *et al.* 2019; Mak *et al.* 2020). Among these value-added chemicals that are produced using a biorefinery process, furan-derived compounds, such as 5-hydroxymethylfurfural (5-HMF), have recently received increased attention (Galaverna *et al.* 2018; Tyagi *et al.* 2018). 5-Hydroxymethylfurfural is an important platform molecule that provides an efficient route from waste or biomass derived-carbohydrates to chemicals and fuel precursors. Furthermore, 5-HMF derivatives have been utilized for various applications, several of which are in major growth industries (Yu and Tsang 2017). The production of 5-HMF from post-consumer carbohydrate-rich food waste, such as cellulosic food, starchy food, sugary food, and beverage waste, has been investigated (Yu *et al.* 2016, 2017, and 2018). Appreciable yields of 5-HMF can be obtained from these post-consumer food wastes by the sequential reaction steps of hydrolysis-isomerization-dehydration of carbohydrates in food waste (Parshetti *et al.* 2015).

Despite the versatile application potential of 5-HMF as an intermediate in the synthesis of liquid transportation fuels, fine chemicals, polymers, solvents, or pharmaceuticals, it has not yet been produced on an industrial scale, which is largely due to high production costs. Although satisfactory 5-HMF yields can be obtained from polar organic solvents (*i.e.*, dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF)), it is prohibitively difficult to separate the target compound from these polar aprotic solvents because their boiling points are relatively high (this is energy intensive and cost-ineffective), and substantial product loss occurs due to the inherent reactivity of 5-HMF at high temperatures. Furthermore, the hydroxyl group of 5-HMF has a strong affinity for polar organic solvents; thus, isolating 5-HMF by extraction is challenging.

In alcoholic solvents, the conversion of carbohydrates to 5-HMF occurs under acidic conditions in parallel with 5-HMF etherification reaction with alcohol to produce alkoxymethyl furfurals. 5-HMF is a crucial intermediate product in the conversion of carbohydrates to alkoxymethyl furfurals (Zhu *et al.* 2017; Guo *et al.* 2018). Therefore, for the multistep reaction of hydrolysis-isomerization-dehydration to produce 5-HMF from food waste-derived carbohydrates, alcohol is a suitable reaction solvent to permit the etherification reaction (Sun *et al.* 2018). The selective etherification of the hydroxylmethyl group in 5-HMF to an alkoxymethyl substituent can enable the facile isolation because ethers are more stable. "Extraction + distillation" was found to be feasible for the separation of EMF from the polar organic solvents/ethanol solvent system (Yu *et al.* 2018; Wang *et al.* 2013). Alkoxymethyl furfurals have not been explored until recently as fuel chemicals, despite much earlier reports of their synthesis.

Among the alkoxymethyl furfurals, 5-ethoxymethylfurfural (5-EMF) has received notable attention due to its superior physical and chemical properties as a promising liquid biofuel (liquid at room temperature, high volumetric energy density, high cetane number, and good oxidation stability) (Zhang *et al.* 2018). In addition, 5-EMF has been widely used for flavor adjustment in beers and wines. For 5-EMF production, broad ranges of feedstock from commercial carbohydrates to raw lignocellulosic biomass have been used, and their performances have been evaluated (Alipour *et al.* 2017). However, the current approaches for producing 5-EMF in appreciable yields are primarily dependent on the conversion of simple monosaccharides, such as fructose and glucose (Chen *et al.* 2018; Gawade and Yadav 2018; Xu *et al.* 2020), and the continued use of these edible saccharides may have a negative impact on global food supplies. Although lignocellulosic biomass is a more economically attractive feedstock than commercial carbohydrates, the conversion of lignocellulosic materials to 5-EMF requires harsh reaction conditions and results in low yields of 5-EMF due to their complex, highly polymerized molecular structures.

Therefore, this study considered FSCW that contained large amounts of carbohydrates as an alternative feedstock for 5-EMF production. Past biorefinery of food waste biomass to produce products with high economic value has largely focused on food waste streams produced from the manufacturing stage or post-consumer stage (Arancon *et al.* 2013; di Bitonto *et al.* 2018). However, pre-consumer expired food is also an important component of food waste and is generated in a more concentrated and homogeneous manner, but it has not been well explored. Currently, there are three main modes of recycling and processing pre-consumer expired food in China, which include using specialized incinerators to destroy the pre-consumer expired food, directly disposing the pre-consumer expired food with municipal solid waste, and selling the pre-consumer expired food to fertilizer and feed manufacturers at low prices. All these options for disposing pre-consumer expired food do not achieve the goal of maximizing the value-added reclamation.

This study evaluated the viability of expired starchy and fructan-rich food as substrates for the catalytic production of 5-EMF *via* ethanolysis reaction. The expired food included probiotic beverage powder, garlic powder, onion powder, burdock tea, steamed buns, and egg yolk battercake that had exceeded their shelf life. For comparison, the activity of these catalytic systems was further studied with the addition of a co-solvent. Further, this study assessed the production of 5-HMF and ethyl levulinate (EL) formation, as they are the main by-products in these reactions and represent important platform chemicals and fuel additives (Démolis *et al.* 2014; Ahmad *et al.* 2016; Unlu *et al.* 2016; Huang *et al.* 2018). A new catalytic valorization approach for carbohydrate-rich expired food was established, and the conclusions from this study can provide a new approach to pre-consumer food waste reclamation.

EXPERIMENTAL

Materials and Methods

Dimethylsulfoxide (99%) was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). The $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and Amberlyst-15 used were purchased from Acros (Geel, Belgium). The H-β, H-Y, H-USY zeolites were purchased from Nankai University Catalyst Co., Ltd. (Tianjin, China). All other reagents were supplied by Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). The expired food in this study contained expired probiotics beverage powder, garlic powder, onion powder, burdock tea, steamed buns, and egg yolk battercake. These fructan-rich and starchy expired foods were obtained from local residents in Xi'an (Shaanxi, China).

Probiotic beverage powder is a fructan-rich health food. In addition to *acidophilus*, *bifidobacteria*, *Bifidobacterium longum*, *Streptococcus thermophilus*, and other beneficial bacteria, water soluble dietary fiber and oligofructose were added to the beverage powder to provide nutrition for the probiotics. Burdock tea is a natural tea product made from burdock (*Arctium lappa* L.) root. It is made by washing fresh burdock root with water followed by slicing and drying the burdock root. A 100 g sample of fresh burdock root contains 90.1 g of water, 4.1 g of protein, 0.1 g of fat, 5 g of carbohydrate and crude fiber, 0.7 g of ash, 0.03 mg of thiamine, 0.5 mg of ribochrome, 2 mg of calcium, 2 mg of iron, and 116 mg of phosphorus. The determination methods for the contents of fructan (or starch) in these tested expired foods are shown in supporting information in the Appendix. On this basis, the contents of fructan (or starch) in expired probiotics beverage powder, onion powder, garlic powder, burdock tea, steamed buns and egg yolk battercake were 79.6%, 76.2%, 73.7%, 34%, 67.9%, and 37.7% (based on dry weight), respectively.

Experimental Procedure for the Production of 5-EMF from Diverse Feedstocks

In each batch run, catalyst (0.02 to 10 mmol), anhydrous ethanol (2 to 80 mL), expired food feedstock (20 to 1600 mg), and co-solvent (0 to 1 mL) were added and then mixed in a pressure vessel (no need for inert atmosphere). The pressure vessel was sealed through screw threads on the bottle cap. The pressure vessel was then immersed in a preheated and thermally controlled oil bath with magnetic stirring. Each pressure vessel was used for one residence time. The pressure vessel was not opened until the allocated time had elapsed. The reaction conditions were chosen based on our preliminary experiments. After the allocated time had elapsed, the vessel was removed from the oil bath and cooled in an ice bath. The sample was then immediately analyzed after dilution and filtration.

HMF and EMF were quantified by HPLC (Shimadzu LC-2010AHT, ultraviolet detector, XDB-C18 column, column oven temperature of 30 °C). Acetonitrile/0.1 wt% acetic acid aqueous solution with a volume ratio of 15:85 at a flow rate of 1.0 mL min^{-1} was used as the mobile phase. The yields of EL was determined by gas chromatography (GC-PE680) equipped with flame ionization detector (FID), and a HP-5MS capillary column. The inlet temperature of the GC was set at 270 °C, and the detector temperature was kept at 280 °C. The column temperature was maintained at 120 °C for 3.3 min, and then increased to 200 °C at a ramp rate of 80 °C/min.

RESULTS AND DISCUSSION

5-EMF Production from Starchy Expired Food in Pure Ethanol

The conversion of expired starchy food into 5-EMF consisted of the following steps (Flannelly *et al.* 2015; Ma *et al.* 2017; Sun *et al.* 2018): hydrolysis of starch to glucose, glucose isomerization to fructose (or the reaction of glucose with ethanol to furnish ethyl glucoside), fructose dehydration to 5-HMF (or ethyl glucoside isomerization to ethyl fructoside), and etherification of 5-HMF into 5-EMF (or dehydration of ethyl fructoside to 5-EMF), as shown in Figs. 1 and 2. A time-course study on the ethanolysis of egg yolk battercake was conducted using $CrCl_3·6H_2O$ and $SnCl_4·5H_2O$ as catalysts to examine the activity to furnish 5-EMF. The catalysts of $CrCl_3·6H_2O$ and $SnCl_4·5H_2O$ were selected because they contain Lewis acid sites, and the important and decisive isomerization step for 5-EMF formation is predominantly catalyzed by a Lewis acid. Figure 3 shows that up to 22.3% of 5-EMF was generated in the presence of $CrCl_3·6H_2O$, after 30 min at 130 °C. Formation of ethyl levulinate (EL) was observed when both $CrCl_3·6H_2O$ and $SnCl_4·5H_2O$ were employed. The EL yields obtained at 130 °C were slightly higher than those obtained at 110 °C, which was likely because the high temperature facilitated 5-EMF rehydration to EL. Trifluoromethyl sulfonic acid and p-toluenesulfonic acid achieved 5-EMF yields (12 mol% to 26 mol%) comparable to those achieved with metal chlorides when starchy expired food was used as the substrate (Table 1). This may have occurred because trifluoromethyl sulfonic acid and p-toluenesulfonic acid possess strong Bronsted acid sites, and Bronsted acids are more active than Lewis acids in other reaction steps of 5-EMF synthesis, excluding isomerization (Dai *et al.* 2018). In addition, the yield of EL was consistently below 3%, which indicated that the EL formation reaction was not remarkable under the typical reaction conditions.

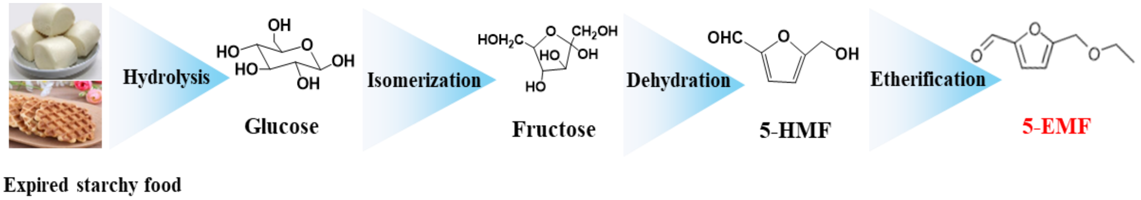

Fig. 1. The reaction pathway for 5-EMF formation from expired starchy food with 5-HMF as the intermediate

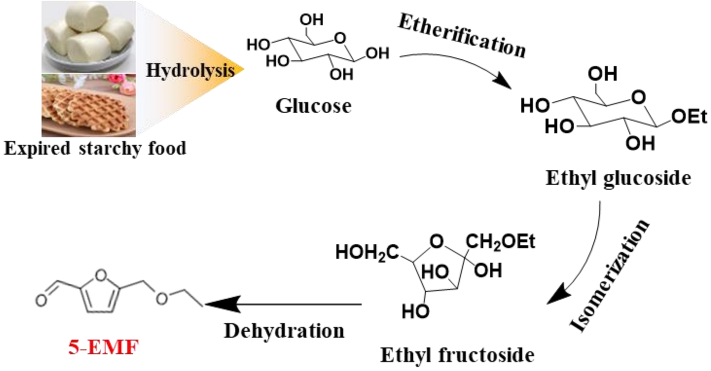

Fig. 2. The reaction pathway for 5-EMF formation from expired starchy food without 5-HMF as the intermediate

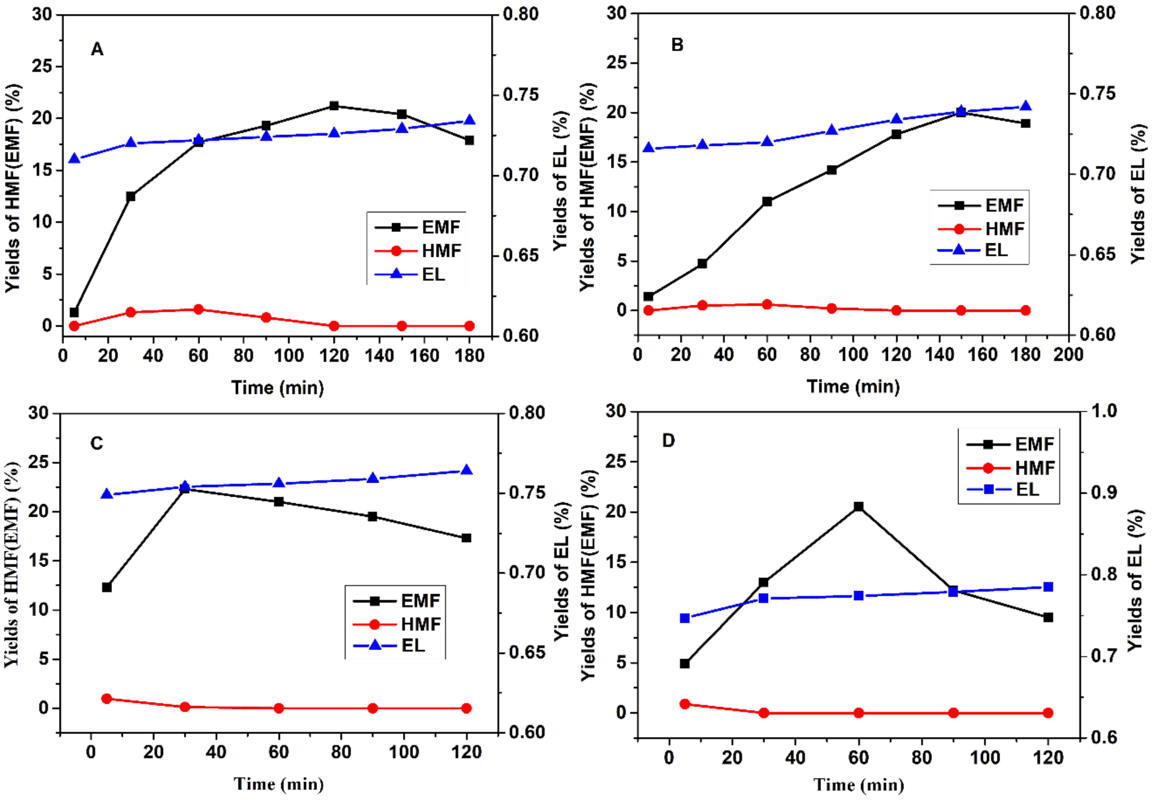

Fig. 3. The catalytic performances of metal chlorides in the conversion of expired egg yolk battercake into 5-EMF. Reaction conditions: 2 mL of ethanol, 20 mg of expired egg yolk battercake, (A) 0.02 mmol $CrCl_3 \cdot 6H_2O$, 110 °C; (B) 0.02 mmol $SnCl_4 \cdot 5H_2O$, 110 °C; (C) 0.02 mmol $CrCl_3 \cdot 6H_2O$, 130 °C; (D) 0.02 mmol $SnCl_4 \cdot 5H_2O$, 130 °C

Table 1. Starchy Expired Food Conversion to 5-EMF in Pure Ethanol Catalyzed by Homogeneous Acids[a]

Entry	Substrate	5-HMF Yields (%)	5-EMF Yields (%)	EL Yields (%)
1	Expired egg yolk battercake	/	21.7	2.2
2[b]	Expired egg yolk battercake	/	23.4	2.6
3[c]	Expired egg yolk battercake	/	12.6	1.4
4[b]	Expired steamed bun	0.81	26.8	2.8
5[c]	Expired steamed bun	/	12.9	1.4
6[d]	Expired steamed bun	/	11.2	1.1

[a] Reaction conditions: 2 mL of ethanol, 20 mg of expired food, and 100 μL of p-toluenesulfonic acid at 110 °C for 10 min; [b] 100 μL of p-toluenesulfonic acid at 130 °C for 10 min; [c] 5 μL of trifluoromethyl sulfonic acid at 120 °C for 30 min; [d] 1.6 g expired steamed bun, 80 mL ethanol, 10 mmol H_2SO_4 at 130 °C for 30 min

Although the starch contents of the expired steamed buns and expired egg yolk battercake differed substantially (67.9% and 37.7%, respectively), there was little difference in the 5-EMF yields on a molar basis. The copresence of more "non-starch" content in the expired egg yolk battercake did not have a notable negative influence on the overall reactivity. Further, 5-EMF production from expired steamed buns and expired egg yolk battercake only occurs in moderate yields because there are considerable challenges with obtaining 5-EMF from aldose-based polysaccharides (Alipour *et al.* 2017). The reaction route is long, and many by-products and intermediates are present in the reaction system. For example, the desired etherification of glucose units in starchy expired food is suppressed by several side reactions, such as acetalization and polymerization. These result in the production of recalcitrant humic substances and limit the yield of 5-EMF (Hu *et al.* 2011; Démolis *et al.* 2014; Filiciotto *et al.* 2018).

Fructan-rich Expired Food Conversion into 5-EMF in the Presence of $CrCl_3·6H_2O$ or Trifluoromethyl Sulfonic Acid in Pure Ethanol

Given the difficulty with the production of 5-EMF from glucose units, fructan-rich expired food was used to avoid the isomerization step in the ethanolysis reactions and was investigated as the feedstock for 5-EMF production. Table 2 shows that considerable yields of 5-EMF were achieved in ethanol from three kinds of fructan-rich expired foods, which included probiotic beverage powder, onion powder, and garlic powder catalyzed by $CrCl_3·6H_2O$ (Table 2, entries 1 to 3). Expired probiotic beverage powder achieved yields of 7.2%, 31.5%, and 7.0% of 5-HMF, 5-EMF, and EL, respectively, after 50 min at 130 °C. When the reaction time was extended to 70 min, the intermediate product (5-HMF) was converted to downstream products, and the yield of 5-HMF decreased, whereas both the yield of 5-EMF and that of EL increased (Table 2, entry 4). For comparison, expired onion powder and expired garlic powder were treated under the same reaction conditions, and a similar decreasing trend for the 5-HMF yield was observed as the reaction times increased. However, contrary to the 5-EMF yield trend when expired probiotics beverage powder was used as a feedstock, the yield for 5-EMF decreased as the reaction times increased from 50 min to 70 min when expired onion powder and garlic powder were used as substrates (Table 2, entries 5 and 6). Although the contents of fructosyl moieties in the expired probiotic beverage powder, onion powder, and garlic powder were similar, expired garlic powder achieved lower 5-EF yield for all of the catalytic systems. Generally, the 5-

EMF yields obtained from expired onion powder and garlic powder were lower than those obtained from expired probiotic beverage powder, which likely occurred because the impurities present in expired onion powder and garlic powder had adverse effects on the reaction process. Further, the varying degrees to which fructosyl moiety was polymerized in the starting materials may have influenced the product yield.

Table 2. 5-EMF Production from Expired Probiotic Beverage Powder, Onion Powder, and Garlic Powder

Entry	Substrate	5-HMF Yields (%)	5-EMF Yields (%)	EL Yields (%)
1[a]	EPBP	7.2	31.5	7.0
2[a]	EOP	10.2	26.1	4.6
3[a]	EGP	3.4	23.9	4.3
4[b]	EPBP	4.4	33.0	7.8
5[b]	EOP	7.6	25.2	4.9
6[b]	EGP	1.9	22.5	5.3
7[c]	EPBP	/	35.1	30.5
8[c]	EOP	/	35.4	30.4
9[c]	EGP	/	18.2	15.9

Reaction conditions: [a]20 mg of substrate, 0.02 mmol of $CrCl_3{\cdot}6H_2O$, and 2mL of ethanol at 130 °C for 50 min; [b] 20 mg of substrate, 0.02 mmol of $CrCl_3{\cdot}6H_2O$, and 2mL of ethanol at 130 °C for 70 min; [c] 20 mg of substrate, 2mL of ethanol, 5 μL of trifluoromethyl sulfonic acid for 15 min at 130 °C; EPBP: Expired probiotics beverage powder; EOP: Expired onion powder; EGP: Expired garlic powder.

The ethanolysis of fructan-rich expired food follows a multistep approach of fructan–fructose–5-HMF–5-EMF (or fructan–fructose–ethyl fructoside–5-EMF); the process involves sequential hydrolysis–dehydration–etherification (or hydrolysis–etherification–dehydration) reaction steps (Unlu and Hilmioglu 2016; García-Bosch *et al.* 2018). Moderate total yields of "5-HMF+5-EMF+EL" (29.7 mol% to 45.7 mol%) were observed from the three raw materials in the presence of $CrCl_3{\cdot}6H_2O$. This was because $CrCl_3{\cdot}6H_2O$ is a Lewis acid and is not active enough to catalyze efficient hydrolysis, dehydration, and etherification. Therefore, trifluoromethyl sulfonic acid was selected for the following experiments. After heating for 15 min at 130 °C (Table 2 entries 7 to 9), no 5-HMF was detected, but the amounts of EL increased for all of the tested substrates. The total "5-EMF+EL" yields reached 65.8 mol%, which was accomplished with expired onion powder when the reaction was conducted in ethanol at 130 °C for 15 min. The 5-HMF, 5-EMF, and EL yields with different feedstocks in Table 2 show that the reaction rate catalyzed by trifluoromethyl sulfonic acid was faster than that catalyzed by $CrCl_3{\cdot}6H_2O$ because no 5-HMF was detected. However, a noticeable amount of the end product (EL) was obtained within 15 min. The fast reaction rate in the presence of trifluoromethyl sulfonic acid may have been due to the strong acidic site and the homogeneous property, which are favorable for fructan depolymerization, fructose/ethyl fructoside dehydration, and 5-HMF etherification to 5-EMF in the ethanol solvent. The accumulation of EL mainly comes from the rehydration of 5-EMF and the esterification of LA (levulinic acid produced by the rehydration of 5-HMF) with ethanol in the acidic reaction environment (Rao *et al.* 2017; Liu *et al.* 2018; Zhou *et al.* 2018).

Production of 5-EMF from Expired Burdock Tea Catalyzed by Various Catalysts in Pure Ethanol

The expired garlic powder, onion powder, and probiotic beverage powder all contained more than 70 wt% fructosyl moieties. For comparison, expired burdock tea with 34 wt% fructan was selected as a feedstock for the experiments. Figure 4 shows the conversion of expired burdock tea in ethanol at 130 °C. The activity of the catalysts, trifluoromethyl sulfonic acid, benzenesulfonic, acid and p-toluenesulfonic acid, were compared. Initially, 5-HMF was observed along with 5-EMF. However, as time progressed, 5-HMF decreased below the detection limit for each of the three tested organic acids. In the presence of benzenesulfonic acid, the 5-EMF yield reached a maximum of 32.3% after 40 min, whereas a 30.2% 5-EMF yield was achieved in the presence of trifluoromethyl sulfonic acid after 20 min. In addition, p-toluenesulfonic acid had higher catalytic activity than both benzenesulfonic acid and trifluoromethyl sulfonic acid, as a 5-EMF yield of 40.7% was observed.

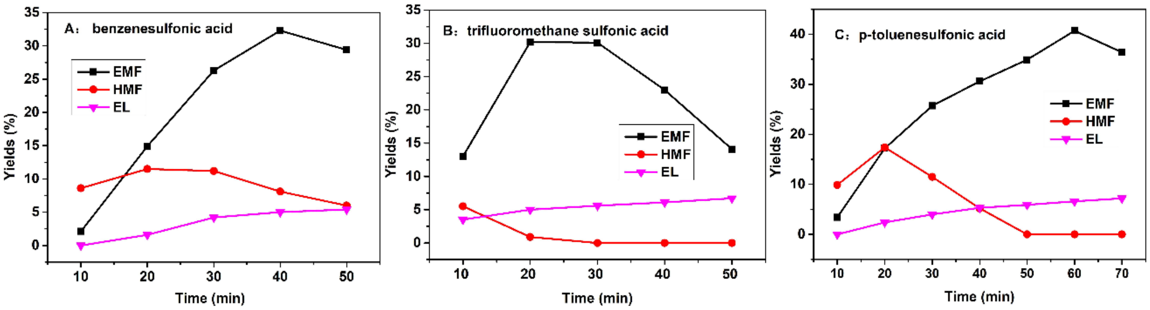

Fig. 4. Effect of reaction time on expired burdock tea conversion into 5-EMF catalyzed by organic acids; reaction conditions: 60 mg of expired burdock tea and 0.1 mmol of catalyst at 110 °C

Further, a series of experiments were carried out to evaluate the catalytic activity of several mineral acids, heteropolyacids, and solid acids for the conversion of expired burdock tea into 5-EMF, and the results are shown in Table 3. The obtained 5-EMF yields were between 0.2% and 40.4% with these catalysts. The formation of EL was also observed with all catalysts, and the values ranged from 0.2% to 9.6%. The H_2SO_4 gave a comparable yield of 5-EMF to that of p-toluenesulfonic acid (Fig. 4C). Among the tested chlorides, the 5-EMF yields are arranged in descending order from entry 2 to entry 5 (Table 3). The $AlCl_3$ exhibited the best performance with a 32.9% 5-EMF yield achieved. Among the solid acids employed, Amberlyst-15 was the most efficient catalyst for the conversion of expired burdock tea to 5-EMF, as it yielded 14.4% 5-EMF and 0.9% EL. It was noteworthy that a small amount of furfural was also detected in these reactions. The produced furfural mainly originated from the C_5 carbohydrates in the expired burdock tea.

The content of fructosyl moieties in expired burdock tea and that in fructan-rich substrates (expired probiotic beverage powder, onion powder, garlic powder) differed substantially (34% and 73.7-79.6%, respectively), and there were large differences in the total “5-HMF+5-EMF+EL” yields regardless of the reaction conditions, which indicated that increases in the non-fructan proportion of expired burdock tea had a notable negative influence on the reaction process.

Table 3. Ethanolysis of Expired Burdock Tea in the Presence of Various Catalysts [a]

Entry	Catalyst	*T* (°C)	*t* (min)	Catalyst Dosage	5-HMF Yield (mol%)	5-EMF Yield (mol%)	EL Yield (mol%)
1	H_2SO_4	130	15	0.1 mmol	5	40.4	5.4
2	$AlCl_3$	130	30	0.2 mmol	0	32.9	4.3
3	$SnCl_4$	130	30	0.2 mmol	3.1	15.4	2.6
4	$FeCl_3$	130	30	0.2 mmol	/	5.9	0.5
5	$CrCl_3·6H_2O$	130	30	0.2 mmol	/	1.5	0.4
6	$H_3PW_{12}O_{40}$	138	130	34.5 mg	2.2	19.1	2.8
7	$H_3PMo_{12}O_{40}$	138	130	22.1 mg	6	12.2	2.7
8	$H_4SiW_{12}O_{40}$	138	130	34.5 mg	0.8	17.9	2.8
9	Sulfamic acid	138	130	0.1 mmol	8.2	0.2	2.7
10	p-aminobenzene sulfonic acid	138	130	0.05 mmol	22.7	1.3	2.7
11[b]	H-beta	150	12h	40 mg	2.7	1.8	1.5
12[b]	H-Y	150	12h	40 mg	0	6.7	2.7
13[b]	H-USY	150	12h	40 mg	0	7.4	3.2
14[b]	Amberlyst-15	150	12h	40 mg	/	14.4	0.9
15[c]	Trifluoromethyl sulfonic acid	130	15	5 µL	/	11	9.6
16[c]	$CrCl_3·6H_2O$	130	70	0.02 mmol	0	1.2	0.2

[a] Reaction conditions: 60 mg of expired burdock tea and 2 mL of ethanol; [b] 60 mg of expired burdock tea and 3 mL of ethanol; [c] 20 mg of expired burdock tea and 2 mL of ethanol

Table 4. Effect of Co-solvent on 5-EMF Production from Fructan-rich Expired Food

Entry	Substrate	Catalyst	Solvent	Co-solvent	5-HMF Yield (%)	5-EMF Yield (%)	EL Yield (%)
1[a]	EPBP	$CrCl_3·6H_2O$	1.9 mL ethanol	0.1 mL H_2O	25.2	8.6	2.2
2[a]	EPBP	$CrCl_3·6H_2O$	1.9 mL ethanol	0.1 mL DMSO	43.4	12.4	4.1
3[a]	EPBP	$CrCl_3·6H_2O$	1.9 mL ethanol	0.1 mL THF	16.2	30.3	4.2
4[b]	EPBP	TSA	1.8 mL ethanol	0.2 mL DMSO	8.7	68.3	19.3
5[b]	EOP	TSA	1.8 mL ethanol	0.2 mL DMSO	10.1	64.9	17.2
6[b]	EGP	TSA	1.8 mL ethanol	0.2 mL DMSO	2.4	31.3	11.7
7[c]	EPBP	TSA	1.8 mL ethanol	0.2 mL DMSO	ND	57.7	31.7
8[c]	EOP	TSA	1.8 mL ethanol	0.2 mL DMSO	0.8	64.0	21.9
9[c]	EGP	TSA	1.8 mL ethanol	0.2 mL DMSO	ND	30.1	17.9
10[d]	EBT	H-Y	2 mL ethanol	1 mL DMSO	17.8	4.4	2.4
11[d]	EBT	H-USY	2 mL ethanol	1 mL DMSO	47.4	1	1.3
12[d]	EBT	Amberlyst-15	2 mL ethanol	1 mL DMSO	19.3	28.1	8.8

[a] Reaction conditions: 20 mg of substrate, 0.02 mmol $CrCl_3·6H_2O$ at 130 °C for 70 min; [b] 0.05 mmol trifluoromethyl sulfonic acid at 130 °C for 15 min; [c] 0.05 mmol trifluoromethyl sulfonic acid at 130 °C for 20 min; [d] the other conditions were the same as entries 12, 13, and 16 in Table 3; EPBP: Expired probiotics beverage powder; EOP: Expired onion powder; EGP: Expired garlic powder; EBT: Expired burdock tea; TSA: trifluoromethyl sulfonic acid

Effect of Co-solvent on 5-EMF Yields

In addition to the effects of temperature and time, a co-solvent may also affect the conversion of expired food to 5-EMF because adding specific solvents can change the characteristics of the reaction solvent, which could lead to unique solvent effects (Yuriy *et al.* 2006). Thus, DMSO, THF, and water were selected as co-solvents, and the results are summarized in Table 4.

Compared with the results in Table 2, entry 1, when $CrCl_3 \cdot 6H_2O$ was used as the catalyst for expired probiotic beverage powder conversion, the introduction of DMSO caused side effects, and the yield of 5-EMF decreased remarkably (Table 4, entry 2). Although THF has been reported to improve 5-EMF yields when Amberlyst-15 or $H_3PW_{12}O_{40}$ are used as catalysts (Zhu *et al.* 2011; Yang *et al.* 2012), the introduction of a small amount of THF reduced the yield of 5-EMF (Table 4, entry 3). Further, the addition of small amounts of H_2O also caused a noticeable decrease in the yield of 5-EMF (Table 4, entry 1), and similar results were reported previously (Di *et al.* 2018).

However, compared with the results in Table 2, entries 7 to 9, when trifluoromethyl sulfonic acid was employed as the catalyst, the introduction of 10 vol% DMSO greatly improved the 5-EMF yield and decreased the EL yield over the 15 min reaction time. The yield of 5-EMF increased sharply from 35.1% to 68.3%, and the yield of EL decreased from 30.5% to 19.3% when the expired probiotic beverage powder was tested (Table 4, entry 4). Expired onion powder and garlic powder showed a similar trend for product yields when DMSO was added as the co-solvent in the presence of trifluoromethyl sulfonic acid. When the expired onion powder was used as the raw material, the 5-EMF yield increased from 35.4 % to 64.9%, and the EL yield decreased from 30.4% to 17.2% (Table 4, entry 5). Using expired garlic powder resulted in a 5-EMF yield increase from 18.2% to 31.3%, and the EL yield decreased from 15.9% to 11.7% (Table 4, entry 6). Prolonging the reaction time to 20 min decreased the yield of 5-EMF for all three substrates, but the yield of EL increased notably (entries 7 to 9 in Table 4). Controlling the formation of 5-EMF was challenging, as it is rapidly rehydrated to form EL in the presence of strong acid catalysts.

To explore the effect of adding a second organic solvent on the production of 5-EMF in the presence of solid acids, the introduction of DMSO to the reaction systems for expired burdock tea ethanolysis was investigated. As demonstrated in Table 4 (entries 10 to 12), for H-Y and H-USY, the addition of DMSO lowered the yield of 5-EMF, but greatly increased the 5-HMF yields. However, both the yield of 5-EMF and that of 5-HMF increased when Ambelyst-15 was used as a catalyst.

The results above indicated that the effect of a co-solvent depended largely on the catalyst type, whereas it was not closely related to the properties of the feedstock.

CONCLUSIONS

1. Several fructan-rich and starchy expired food (expired probiotic beverage powder, onion powder, garlic powder, burdock tea, steamed buns, and egg yolk battercake) were tested as raw substrates for 5-EMF production. The catalytic performances of different homogeneous and heterogeneous catalysts were evaluated. The conversion of expired food to 5-EMF depended on factors of substrate properties, catalyst type and loading, reaction time, temperature, and the presence of a co-solvent.

2. Expired steamed buns resulted in a 26.8% 5-EMF yield when p-toluenesulfonic acid was used as a catalyst. Fructan-rich expired food was better than starchy expired food for 5-EMF production, and peak yields of 68% 5-EMF were achieved from expired probiotic beverage powder. For the four tested fructan-rich expired food, increased “non-fructan” content negatively influenced the 5-EMF yield. However, for the two tested starchy expired foods, although the starch contents were remarkably different, the 5-EMF molar yields from expired egg yolk battercake were close to that obtained from expired steamed buns, which indicated that the increased amounts of “non-starch” components in the expired egg yolk battercake did not negatively affect the overall reaction noticeably.
3. Compared to the ketose-based fructan-rich expired food, aldose based starchy expired food was more difficult to convert into 5-EMF. The effect of co-solvents on 5-EMF yield was not strongly related to substrate properties but was related to catalyst type.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the National Natural Science Foundation of China (Grant No. 21607119), the Key Research and Development Plan of Shaanxi Province-Industrial Innovation Chain Project (Grant No. 2020ZDLNY06-08), the Special Funds of the Education Department of Shaanxi Province (Grant No. 19JK0475), the Young Talents Support Program of Colleges and Universities Association for Science and Technology of Shaanxi Province (Grant No. 20190420), the Innovative Talents Promotion Plan-Science and Technology Innovation Group of Shaanxi Province (Grant No. 2019TD-025), the Special Program in Natural Science of Xi’an University of Architecture and Technology (Grant No. ZR19020) and the 15th SSRT Program of Xi’an University of Architecture and Technology (Grant No. 1595).

REFERENCES CITED

Abeliotis, K., Lasaridi, K., Costarelli, V., and Chroni, C. (2015). “The implications of food waste generation on climate change: The case of Greece,” *Sustainable Production and Consumption* 3, 8-14. DOI: 10.1016/j.spc.2015.06.006

Ahmad, E., Alam, M. I., Pant, K. K., and Haider, M. A. (2016). “Catalytic and mechanistic insights into the production of ethyl levulinate from biorenewable feedstocks,” *Green Chemistry* 18, 4804-4823. DOI: 10.1039/c6gc01523a

Alipour, S., Omidvarborna, H., and Kim, D.-S. (2017). “A review on synthesis of alkoxymethyl furfural, a biofuel candidate,” *Renewable and Sustainable Energy Reviews* 71, 908-926. DOI: 10.1016/j.rser.2016.12.118

Arancon, R. A. D., Lin, C. S. K., Chan, K. M., Kwan, T. H., and Luque, R. (2013). “Advances on waste valorization: New horizons for a more sustainable society,” *Energy Science & Engineering* 1(2), 53-71. DOI: 10.1002/ese3.9

Chen, S. S., Yu, I. K. M., Tsang, D. C. W., Yip, A. C. K., Khan, E., Wang, L., Ok, Y. S., and Poon, C. S. (2017). “Valorization of cellulosic food waste into levulinic acid catalyzed by heterogeneous Brønsted acids: Temperature and solvent effects,” *Chemical Engineering Journal* 327, 328-335. DOI: 10.1016/j.cej.2017.06.108

Chen, T., Peng, L., Yu, X., and He, L. (2018). "Magnetically recyclable cellulose-derived carbonaceous solid acid catalyzed the biofuel 5-ethoxymethylfurfural synthesis from renewable carbohydrates," *Fuel* 219, 344-352. DOI: 10.1016/j.fuel.2018.01.129

Dai, J., Peng, L., and Li, H. (2018). "Intensified ethyl levulinate production from cellulose using a combination of low loading H_2SO_4 and $Al(OTf)_3$," *Catalysis Communications* 103, 116-119. DOI: 10.1016/j.catcom.2017.10.007

Démolis, A., Essayem, N., and Rataboul, F. (2014). "Synthesis and applications of alkyl levulinates," *ACS Sustainable Chemistry & Engineering* 2(6), 1338-1352. DOI: 10.1021/sc500082n

Di Bitonto, Antonopoulou, G., Braguglia, C., Campanale, C., Gallipoli, A., Lyberatos, G., Ntaikou, I., and Pastore, C. (2018). "Lewis-Brønsted acid catalysed ethanolysis of the organic fraction of municipal solid waste for efficient production of biofuels," *Bioresource Technology* 266, 297-305. DOI: 10.1016/j.biortech.2018.06.110

Food and Agriculture Organization of the United Nations. (2011). *Global Food Losses and Food Waste. Extent, Causes and Prevention*, FAO, Rome, Italy.

Filiciotto, L., Balu, A. M., Van der Waal, J. C., and Luque, R. (2018). "Catalytic insights into the production of biomass-derived side products methyl levulinate, furfural and humins," *Catalysis Today* 302, 2-15. DOI: 10.1016/j.cattod.2017.03.008

Flannelly, T., Dooley, S., and Leahy, J. J. (2015). "Reaction pathway analysis of ethyl levulinate and 5-ethoxymethylfurfural from d-fructose acid hydrolysis in ethanol," *Energy & Fuels* 29(11), 7554-7565. DOI: 10.1021/acs.energyfuels.5b01481

Galaverna, R., Breitkreitz, M. C., and Pastre, J. C. (2018). "Conversion of D-fructose to 5-(hydroxymethyl)furfural: Evaluating batch and continuous flow conditions by design of experiments and in-line FTIR monitoring," *ACS Sustainable Chemistry & Engineering* 6(3), 4220-4230. DOI: 10.1021/acssuschemeng.7b04643

García-Bosch, N., Bachiller-Baeza, B., Rodríguez-Ramos, I., and Guerrero-Ruiz, A. (2018). "Fructose transformations in ethanol using carbon supported polyoxometalate acidic solids for 5-ethoxymethylfurfural production," *ChemCatChem* 10(17), 3746-3753. DOI: 10.1002/cctc.201800657

Gawade, A. B., and Yadav, G. D. (2018). "Microwave assisted synthesis of 5-ethoxymethylfurfural in one pot from D-fructose by using deep eutectic solvent as catalyst under mild condition," *Biomass and Bioenergy* 117, 38-43. DOI: 10.1016/j.biombioe.2018.07.008

Guo, H., Duereh, A., Hiraga, Y., Qi, X., and Smith, R. L. (2018). "Mechanism of glucose conversion into 5-ethoxymethylfurfural in ethanol with hydrogen sulfate ionic liquid additives and a Lewis acid catalyst," *Energy & Fuels* 32(8), 8411-8419. DOI: 10.1021/acs.energyfuels.8b00717

Hu, X., Lievens, C., Larcher, A., and Li, C. Z. (2011). "Reaction pathways of glucose during esterification: Effects of reaction parameters on the formation of humin type polymers," *Bioresource Technology* 102(21), 10104-10113. DOI: 10.1016/j.biortech.2011.08.040

Huang, Y.-B., Yang, T., Lin, Y.-T., Zhu, Y.-Z., Li, L.-C., and Pan, H. (2018). "Facile and high-yield synthesis of methyl levulinate from cellulose," *Green Chemistry* 20(6), 1323-1334. DOI: 10.1039/c7gc02883k

Karmee, S. K., and Lin, C. S. K. (2014). "Valorisation of food waste to biofuel: Current trends and technological challenges," *Sustainable Chemical Processes* 2, Article Number 22. DOI: 10.1186/s40508-014-0022-1

Liu, C., Feng, Q., Yang, J., and Qi, X. (2018). “Catalytic production of levulinic acid and ethyl levulinate from uniconazole-induced duckweed (*Lemna minor*),” *Bioresource Technology* 255, 50-57. DOI: 10.1016/j.biortech.2018.01.087

Ma, Y., Tan, W., Wang, K., Wang, J., Jiang, J., and Xu, J. (2017). “An insight into the selective conversion of bamboo biomass to ethyl glycosides,” *ACS Sustainable Chemistry & Engineering* 5(7), 5880-5886. DOI: 10.1021/acssuschemeng.7b00618

Mak, T. M. W., Xiong, X., Tsang, D. C. W., Yu, I. K. M., and Poon, C. S. (2020). “Sustainable food waste management towards circular bioeconomy: Policy review, limitations and opportunities,” *Bioresource Technology* 297, article ID 122497. DOI: 10.1016/j.biortech.2019.122497

Parshetti, G. K., Suryadharma, M. S., Pham, T. P. T., Mahmood, R., and Balasubramanian, R. (2015). “Heterogeneous catalyst-assisted thermochemical conversion of food waste biomass into 5-hydroxymethylfurfural,” *Bioresource Technology* 178, 19-27. DOI: 10.1016/j.biortech.2014.10.066

Pfaltzgraff, L. A., Bruyn, M. D., Cooper, E. C., Budarin, V., and Clark, J. H. (2013). “Food waste biomass: A resource for high-value chemicals,” *Green Chemistry* 15(2), 307-314. DOI: 10.1039/c2gc36978h

Pham, T. P. T., Kaushik, R., Parshetti, G. K., Mahmood, R., and Balasubramanian, R. (2015). “Food waste-to-energy conversion technologies: Current status and future directions,” *Waste Management* 38, 399-408. DOI: 10.1016/j.wasman.2014.12.004

Rao, B. S., Kumari, K. P., Lakshmi, D. D., and Nakka, L. (2017). “One pot selective transformation of biomass derived chemicals towards alkyl levulinates over titanium exchanged heteropoly tungstate catalysts,” *Catalysis Today* 309, 269-275. DOI: 10.1016/j.cattod.2017.05.040

Sun, Y., Zhang, Q., Zhang, P., Song, D., and Guo, Y. (2018). “Nitrogen-doped carbon-based acidic ionic liquid hollow nanospheres for efficient and selective conversion of fructose to 5-ethoxymethylfurfural and ethyl levulinate,” *ACS Sustainable Chemistry & Engineering* 6(5), 6771-6782. DOI: 10.1021/acssuschemeng.8b00570

Tyagi, U., Anand, N., and Kumar, D. (2018). “Synergistic effect of modified activated carbon and ionic liquid in the conversion of microcrystalline cellulose to 5-hydroxymethyl furfural,” *Bioresource Technology* 267, 326-332. DOI: 10.1016/j.biortech.2018.07.035

Unlu, D., and Hilmioglu, N. D. (2016). “Synthesis of ethyl levulinate as a fuel bioadditive by a novel catalytically active pervaporation membrane,” *Energy & Fuels* 30(4), 2997-3003. DOI: 10.1021/acs.energyfuels.5b02911

Unlu, D., Ilgen, O., and Hilmioglu, N. D. (2016). “Biodiesel additive ethyl levulinate synthesis by catalytic membrane: SO_4^{-2}/ZrO_2 loaded hydroxyethyl cellulose,” *Chemical Engineering Journal* 302, 260-268. DOI: 10.1016/j.cej.2016.05.047

Wang, H., Deng, T., Wang, Y., Qi, Y., Hou, X., and Zhu, Y. (2013). “Efficient catalytic system for the conversion of fructose into 5-ethoxymethylfurfural,” *Bioresource Technology* 136, 394-400. DOI: 10.1016/j.biortech.2013.02.110

Xiong, X., Yu, I. K. M., Tsang, D. C. W., Bolan, N. S., Sik Ok, Y., Igalavithana, A. D., Kirkham, M. B., Kim, K.-H., and Vikrant, K. (2019). “Value-added chemicals from food supply chain wastes: State-of-the-art review and future prospects,” *Chemical Engineering Journal* 375, article ID 121983. DOI: 10.1016/j.cej.2019.121983

Xu, G., Zhang, S., Zheng, Z., Wang, C., Wang, S., and Tao, H. (2020). “Direct conversion of fructose to 5-ethoxymethylfurfural catalyzed by ultra stable Y zeolite,” *BioResources* 15(2), 3621-3635. DOI: 10.15376/biores.15.2.3621-3635

Yang, Y., Abu-Omar, M. M., and Hu, C. (2012). "Heteropolyacid catalyzed conversion of fructose, sucrose, and inulin to 5-ethoxymethylfurfural, a liquid biofuel candidate," *Applied Energy* 99, 80-84. DOI: 10.1016/j.apenergy.2012.04.049

Yu, I. K. M., Tsang, D. C. W., Yip, A. C. K., Chen, S. S., Ok, Y. S., and Poon, C. S. (2016). "Valorization of food waste into hydroxymethylfurfural: Dual role of metal ions in successive conversion steps," *Bioresource Technology* 219, 338-347. DOI: 10.1016/j.biortech.2016.08.002

Yu, I. K. M., Tsang, D. C. W., Yip, A. C. K., Chen, S. S., Ok, Y. S., and Poon, C. S. (2017). "Valorization of starchy, cellulosic, and sugary food waste into hydroxymethylfurfural by one-pot catalysis," *Chemosphere* 184, 1099-1107. DOI: 10.1016/j.chemosphere.2017.06.095

Yu, I. K. M., and Tsang, D. C. W. (2017). "Conversion of biomass to hydroxymethyl-furfural: A review of catalytic systems and underlying mechanisms," *Bioresource Technology* 238, 716-732. DOI: 10.1016/j.biortech.2017.04.026

Yu, X., Gao, X., Peng, L., He, L., and Zhang, J. (2018). "Intensified 5-ethoxymethyl-furfural production from biomass components over aluminum-based mixed-acid catalyst in co-solvent medium," *ChemistrySelect* 3(47), 13391-13399. DOI: 10.1002/slct.201803059

Yu, I. K. M., Ong, K. L., Tsang, D. C. W., Haque, M. A., Kwan, T. H., Chen, S. S., Uisan, K., Kulkarni, S., and Lin, C. S. K. (2018). "Chemical transformation of food and beverage waste-derived fructose to hydroxymethylfurfural as a value-added product," *Catalysis Today* 314, 70-77. DOI: 10.1016/j.cattod.2018.01.011

Yuriy, R. L., Chheda, J. N., and Dumesic, J. A. (2006). "Phase modifiers promote efficient production of hydroxymethylfurfural from fructose," *Science* 312, 1933-1937. DOI: 10.1126/science.1126337

Zhai, Y., Wang, T., Zhu, Y., Peng, C., Wang, B., Li, X., Li, C., and Zeng, G. (2018). "Production of fuel pellets *via* hydrothermal carbonization of food waste using molasses as a binder," *Waste Management* 77, 185-194. DOI: 10.1016/j.wasman.2018.05.022

Zhang, J., Dong, K., Luo, W., and Guan, H. (2018). "Catalytic upgrading of carbohydrates into 5-ethoxymethylfurfural using SO_3H functionalized hyper-cross-linked polymer based carbonaceous materials," *Fuel* 234, 664-673. DOI: 10.1016/j.fuel.2018.07.060

Zhou, L., He, Y., Ma, L., Jiang, Y., Huang, Z., Yin, L., and Gao, J. (2018). "Conversion of levulinic acid into alkyl levulinates: Using lipase immobilized on meso-molding three-dimensional macroporous organosilica as catalyst," *Bioresource Technology* 247, 568-575. DOI: 10.1016/j.biortech.2017.08.134

Zhu, H., Cao, Q., Li, C., and Mu, W. (2011). "Acidic resin-catalysed conversion of fructose into furan derivatives in low boiling point solvents," *Carbohydrate Research* 346(13), 2016-2018. DOI: 10.1016/j.carres.2011.05.026

Zhu, S., Guo, J., Wang, X., Wang, J., and Fan, W. (2017). "Alcoholysis: A promising technology for conversion of lignocellulose and platform chemicals," *ChemSusChem* 10(12), 2547-2559. DOI: 10.1002/cssc.201700597

Article submitted: April 9, 2021; Peer review completed: June 7, 2021; Revised version received and accepted: July 20, 2021; Published: July 23, 2021.
DOI: 10.15376/biores.16.3.6186-6200

APPENDIX

Supplementary Information

Determination of Fructan Content and Starch Content

Fructan content of expired probiotics beverage powder, onion powder, garlic powder, and burdock tea were measured based on the Chinese national standards for food safety: “Determination of fructan in food” (GB 5009.255-2016). The starch content in expired steamed buns and egg yolk battercake were measured based on the Chinese national standards for food safety: “Determination of starch in food” (GB 5009.9-2016).

Calculation of Products Yields

For fructan-rich expired food, product yields were calculated on a molar basis as follows:

$$\text{HMF yield (mol\%)} = \frac{moles\ of\ HMF\ produced}{moles\ of\ fructosyl\ moiety\ \text{in expired food}} \times 100$$

$$\text{EMF yield (mol\%)} = \frac{moles\ of\ EMF\ produced}{moles\ of\ fructosyl\ moiety\ \text{in expired food}} \times 100$$

$$\text{EL yield (mol\%)} = \frac{moles\ of\ EL\ produced}{moles\ of\ fructosyl\ moiety\ \text{in expired food}} \times 100$$

For expired steamed buns and egg yolk battercake, all the products were calculated in a similar method as mentioned above but based on the content of glucosyl moieties.

LC-MS Profile of the Products

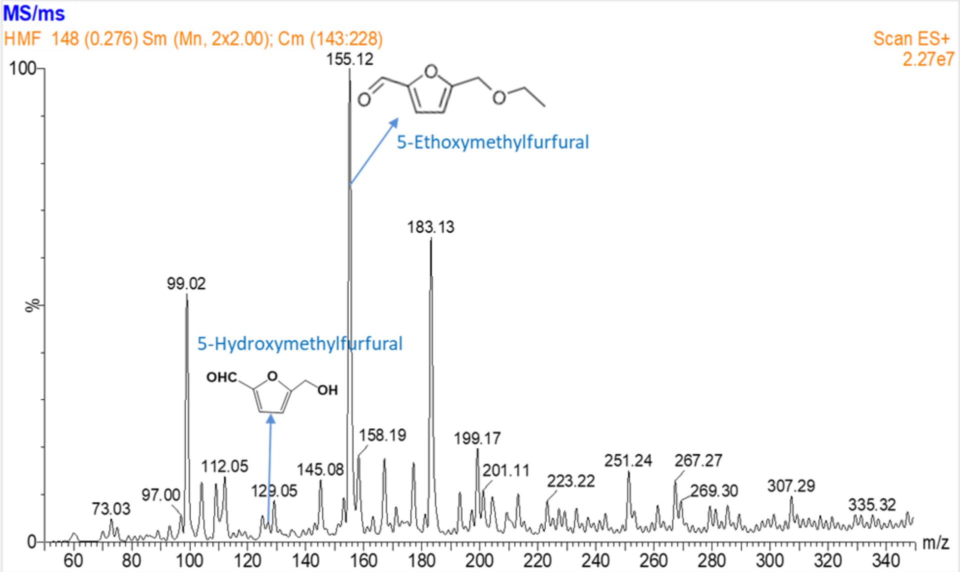

Fig. S1. LC-MS profile of the products