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Yu, Iris K M, Tsang, Daniel C W, Chen, Season S et al. (7 more authors) (2017) Polar aprotic solvent-water mixture as the medium for catalytic production of hydroxymethylfurfural (HMF) from bread waste. BIORESOURCE TECHNOLOGY. pp. 456-462. ISSN 0960-8524

https://doi.org/10.1016/j.biortech.2017.08.170

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PII: S0960-8524(17)31484-0
DOI: http://dx.doi.org/10.1016/j.biortech.2017.08.170
Reference: BITE 18779

To appear in: *Bioresource Technology*

Received Date: 30 June 2017
Revised Date: 26 August 2017
Accepted Date: 29 August 2017

Please cite this article as: Yu, I.K.M., Tsang, D.C.W., Chen, S.S., Wang, L., Hunt, A.J., Sherwood, J., De Oliveira Vigier, K., Jérôme, F., Ok, Y.S., Poon, C.S., Polar Aprotic Solvent-Water Mixture as the Medium for Catalytic Production of Hydroxymethylfurfural (HMF) from Bread Waste, *Bioresource Technology* (2017), doi: http://dx.doi.org/10.1016/j.biortech.2017.08.170

Polar Aprotic Solvent-Water Mixture as the Medium for Catalytic Production of Hydroxymethylfurfural (HMF) from Bread Waste

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Abstract

Valorisation of bread waste for hydroxymethylfurfural (HMF) synthesis was examined in dimethyl sulfoxide (DMSO)-, tetrahydrofuran (THF)-, acetonitrile (ACN)-, and acetone-water (1:1 v/v), under heating at 140°C with $SnCl_4$ as the catalyst. The overall rate of the process was the fastest in ACN/H_2O and acetone/H_2O, followed by DMSO/H_2O and THF/H_2O due to the rate-limiting glucose isomerisation. However, the formation of levulinic acid (via rehydration) and humins (via polymerisation) was more significant in ACN/H_2O and acetone/H_2O. The constant HMF maxima (26-27 mol%) in ACN/H_2O, acetone/H_2O, and DMSO/H_2O indicated that the rates of desirable reactions (starch hydrolysis, glucose isomerisation, and fructose dehydration) relative to undesirable pathways (HMF rehydration and polymerisation) were comparable among these mediums. They also demonstrated higher selectivity towards HMF production over the side reactions than THF/H_2O. This study differentiated the effects of polar aprotic solvent-water mediums on simultaneous pathways during biomass conversion.

Keywords: food waste; 5-hydroxymethylfurfural; levulinic acid; biorefinery; waste valorisation.

1 Introduction

Global food waste of approximately 1.3 billion tonnes per year accounts for one-third of the total food production (Gustavsson et al., 2011). This implies the significant wastage of resources associated with substantial and unnecessary emissions, which may further worsen in case of improper downstream disposal (FAO, 2013). The generation of catering refuse is unavoidable, and thus, establishment of recycling and recovery technologies is highly important in the sustainable waste management agenda to ease the environmental burden. Technologically mature options, including anaerobic digestion, composting, and animal feed production, have been in place for food waste recycling across the world (Pham et al., 2015; Salemdeeb et al., 2017). Entering the bioeconomy era (Tuck et at., 2012; Mohan et al., 2016), researchers have reckoned food waste as low-cost raw materials for the production of chemicals and fuels with higher economic values, such as succinic acid and lactic acid via fermentation (Pleissner et al., 2016).

Previous studies demonstrated the feasible production of hydroxymethylfurfural (HMF) and levulinic acid from various pre-consumer food waste through the thermochemical process (Yu et al., 2016; Chen et al., 2017; Yu et al., 2017a, 2017b). The HMF is a versatile platform chemical that can be upgraded into a wide spectrum of commodity chemicals and products, i.e., medicines, polymers, resins, fungicides, and biofuels (Mukherjee et al., 2015). The high market potential of HMF is also reflected by the competitive economic value up to USD 300 (industrial-grade) and 5,916 (food-grade) per kilogram (Alibaba, 2017; Sigma Aldrich, 2017), in comparison to other chemicals, e.g., glucose (USD 0.39 per kilogram) and acetic acid (USD 1.14 per kilogram) (Koutinas et al., 2014a, 2014b). This encourages the development of cost-effective conversion system to valorise food waste for HMF synthesis.

The conversion of food waste to HMF involves three steps, which are typically catalysed by two types of acid, respectively: (1) hydrolysis of glucan (glucose-based polymer, e.g., cellulose and starch) to glucose catalysed by Brønsted acid, (2) isomerisation of glucose to fructose mediated by Lewis acid, and (3) dehydration of fructose to HMF facilitated by Brønsted acid (Yu and Tsang, 2017). In addition, side reactions that reduce the yield and selectivity of HMF occur simultaneously, including (5) rehydration of HMF to levulinic acid and formic acid, and (6) polymerisation among the intermediates and HMF to the heterogeneous humins. Brønsted and Lewis acid promote these undesirable side reactions to various extents depending on their strength and quantity (Li et al., 2016; Tsilomelekis et al., 2016; Tang et al., 2017). Therefore, the key to achieving high HMF production is to promote the desirable reactions and suppress the undesirable pathways by manipulating the system components (Yu and Tsang, 2017; Yu et al., 2017a).

While tailoring the active sites in catalysts presents as a possible way, engineering of the reaction medium shares equal importance for the selective promotion of the desirable reactions. The use of water and alcohols that are polar and protic allows HMF formation, but the yield and selectivity are usually low as the side reactions including rehydration and polymerisation occur significantly. In particular, the use of alcohols promotes the esterification of HMF (Yang et al., 2012a), which generates fuel chemicals instead of HMF as the major product. Ionic liquid is an effective medium for producing HMF with high yield and selectivity, however, its high cost may be prohibitive for large-scale application and its toxicity may raise critical safety concern.

As an economically viable and relatively safe alternative, polar aprotic solvents enable selective production of HMF with a promising yield. For example, the HMF yield from catalytic conversion of standard glucose over $CrCl_3$ increased significantly from <10 to 31.6% upon the addition of dimethyl sulfoxide (DMSO) at a molar fraction of 0.5 (at 130^{o}C for 3 h) (Jia et al., 2014). Another study reported that the HMF yield from glucose conversion improved from 22 to 52-61% when tetrahydrofuran (THF) was added as a co-solvent, in the presence of $AlCl_3$ as the catalyst (Yang et al., 2012b). It was demonstrated that THF could suppress humin formation and facilitate the desirable pathways for synthesis of small molecules such as HMF (Fu et al., 2017). These solvents competed with water to solvate the substrates and products at the immediate vicinity of the reactive functional groups, protecting them from the detrimental side reactions, according to the previous computational studies (Mushrif et al., 2012; Vasudevan and Mushrif, 2015).

Despite the well-recognized high performance, the potential environmental and health impact imposed by the use of these polar aprotic solvents may constrain their upscale application. For example, the high boiling point of DMSO (189^{o}C) demands energy-intensive downstream separation process, while THF is relatively hazardous to human health (Hammond et al., 2013; Prat et al., 2016). It is thereby important to seek or devise environmentally benign alternatives for food waste valorisation, with a better understanding of the favourable medium properties upfront. Although the solvation effect has been revealed for some particular solvents (Mushrif et al., 2012; Vasudevan and Mushrif, 2015), there is limited comparison of their performance in the literature. The critical properties of a selective reaction medium for HMF production remain uncertain.

Some knowledge on manipulating the medium properties by adjusting the type and proportion of the co-solvent has been in place. For instance, in the binary system of polar aprotic solvent and water, the extrema of the mixture properties (i.e., polarity, viscosity, and molar excess enthalpy that vary with the water-to-solvent ratio) showed a linear dependence on the electrostatic basicity of the organic solvent (Duereh et al., 2017). To apply such knowledge for developing a selective valorisation system, it is necessary to unravel the effects of solvents on the simultaneous reactions during the food waste-to-HMF process, enlightening the desirable physicochemical properties of the medium. Different reaction environments may show selectivity towards different pathways.

Herein, bread waste was used as a model of starch-rich food waste in the catalytic production of HMF, in several binary mixtures of polar aprotic solvent and water. This study aimed to differentiate the effects of selected mediums on the desirable reactions (i.e., hydrolysis, isomerisation, and dehydration) and undesirable pathways (rehydration and polymerisation). Four types of polar aprotic solvent, namely, DMSO, THF, acetone, and acetonitrile (ACN), were selected as the organic phase considering their satisfactory performance in HMF production based on the recent reviews (Mukherjee et al., 2015; Yu and Tsang, 2017).

2 Materials and Methods

2.1 Bread waste

Bread waste was selected as the substrate because it is a common stream of food waste across the world. More importantly, its high conversion feasibility as demonstrated in our earlier studies can yield HMF in promising amount (Yu et al., 2017a, 2017b), which allowed vivid comparison of the performance of solvent mixtures. The bread waste used in this study originated from the Hong Kong International Airport. Collected samples were subject to freeze-drying, grinding, and sieving through a 0.2-mm-mesh. Prepared samples were then stored in an airtight storage container at 4°C in the dark for the subsequent characterisation as well as conversion experiments.

Characterisation was conducted in terms of dietary fibre (including cellulose, hemicellulose, lignin, and pectin; AOAC 985.29), protein (N x 6.25, Kjeldahl Nitrogen Method, AOAC 928.08), total fat (acid hydrolysis and gravimetric method, AOAC 922.06), and ash (AOAC 923.03). Available carbohydrate was estimated on the basis of a mass balance (HK FEHD, 2008):

$$\text{Available carbohydrate} = 100 - \frac{(\text{Dietary fibre} + \text{Protein} + \text{Fat} + \text{Ash} + \text{Alcohol})\ \text{g}}{100\ \text{g Dried substrate}}, \qquad (1)$$

where alcohol was omitted in view of its negligible concentration shown in the USDA National Nutrient Database. Free sugars were quantified as the sum of disaccharides, glucose, and fructose dissolved in water using high-performance liquid chromatography (HPLC). Starch content was estimated by subtracting the content of available carbohydrates by free sugars (HK FEHD, 2008). Water content was calculated based on the change in sample mass before and after freeze-drying. The total organic carbon (TOC) content was measured using the TOC analyser (Shimadzu SSM-5000A).

2.2 Chemicals

The polar aprotic solvents including DMSO (≥99.9%) and THF (≥99.8%) from RCI Labscan, and ACN (99.9%) and acetone (99.5%) from Duksan Pure Chemicals, respectively, were used to prepare the solvent-water mixture as the reaction medium. The metal chloride catalyst, $SnCl_4 \cdot 5H_2O$ (98%), was purchased from Sigma Aldrich. The analytical equipment was calibrated using the model compounds: 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. All the chemicals were used as received.

2.3 Catalytic conversion

The conditions of catalytic bread waste conversion were determined with reference to previous studies (Yu et al., 2016; Yu et al., 2017a, 2017b). The dried bread waste (5 wt/v%) was added to a medium comprising polar aprotic solvent (DMSO, THF, ACN, or acetone) and water in a ratio of 1:1 (v/v) with a total volume of 20 ml. The solvent mediums were denoted as DMSO/H_2O, THF/H_2O, ACN/H_2O, and acetone/H_2O, respectively. The $SnCl_4$ (55.5 mM) was used as the catalyst in view of its good catalytic performance in the conversion of model compounds and starch-rich food waste (Yu et al., 2016; Yu et al., 2017b). Mixtures without the addition of $SnCl_4$ were also prepared as the control. For catalytic reaction, the mixture was placed in a closed vessel and heated to 140^{o}C within 5 min in an Ethos Up Microwave Reactor (Milestone, maximum power 1900 W). The reaction time ranged from 1 to 120 min to generate the comprehensive kinetic profiles. Magnetic stirring was maintained throughout the heating process for uniform heat distribution and mixture homogeneity. Upon completion of the reaction, the vessels cooled down in 40 min with the assistance of mechanical ventilation. All the trials were conducted in duplicate.

The reacted mixture was centrifuged to separate the liquid and solid phase. The liquid phase was diluted with deionized (DI) water (1:1 v/v), and then was filtered through the mixed cellulose esters filter (0.22 µm) before product analysis. The organic solvents and soluble compounds in the solid fraction were removed prior to freeze-drying and further characterisation. They were washed three times by vortexing with DI water, centrifugation, and decantation.

2.4 Sample analysis

Products in the solution phase were quantified by high-performance liquid chromatography (HPLC) using the Chromaster (Hitachi, Japan), which consisted of a 5110 pump, 5210 autosampler, 5310 column oven, and 5450 refractive index detector. The analysis was performed with an Aminex HPX-87H column (Bio-rad) at 50^{o}C, and the 0.01 M H_2SO_4 as the mobile phase at a flow rate of 0.5 ml min^{-1} (Ohara et al., 2010; Yu et al., 2016). Blank (i.e., DMSO/water in 1:1 v/v) and spiked samples (i.e., standard compounds with known concentrations) were included in every series of injection for quality assurance. The yield of products was calculated in terms of carbon content as shown in equation (2).

$$Product\ yield\ (Cmol\%) = \frac{Conc_p(mg\ ml^{-1}) \times Vol(ml)/MW_P \times Cn_p}{C_s(mol)} \times 100, \qquad (2)$$

where $Conc_p$ represented the concentration of product, i.e., disaccharide, glucose, fructose, HMF, levoglucosan, levulinic acid, formic acid, and furfural; MW_p and Cn_p were referred to molecular mass and number of carbon in the corresponding product, respectively; C_s represented the number of organic carbon in the bread waste substrate (TOC of 41.5 wt% equivalent to 34.6 mmol at the substrate loading of 5 wt/v%).

The pH of the resultant solution was measured using a pH meter (Shanghai Leici, Model E-201F). It described the Brønsted acidity qualitatively for comparing samples generated using the same solvent mixture only, as calibration protocols were not available for the organic solvent-water mediums selected in this study to our best knowledge.

Selected dried solid residues were subject to the thermogravimetric analysis (TGA; Rigaku Thermo plus EVO2) to reveal their thermal stability as the temperature increased from 100 to 500^{o}C at a rate of 10^{o}C min^{-1}.

3 Results and discussion

3.1 Bread waste characterisation

The bread waste used in this study contained 72.6% available carbohydrates that encompassed 67.6% starch and 5% free sugars, 4.2% total dietary fibre, 14.8% protein, 6.1% total fat, and 2.3% ash, while the TOC was 41.5% on a dry mass basis. The water content was 28.1% by mass.

3.2 Facile HMF production in ACN- and acetone-water systems

Using ACN/H_2O and acetone/H_2O as the medium, the maximum HMF yield of approximately 26 mol% was obtained from bread waste within 10 min over $SnCl_4$ as the catalyst (**Fig. 1a&b**). It was promising with reference to the recent studies, which reported, for example, 23-58 mol% HMF from lignocellulosic biomass waste after heating at 160-175^{o}C for 0.5-2 h (Wang et al., 2014; Zhang et al., 2017). Yet, it should be noted that direct comparison remains difficult due to the varying conditions (e.g., catalyst, medium, and total volume) in these studies.

Our results also showed that the maximum yield of products was attained within 3 min in both mediums (**Fig. 1a&b**). The short optimal reaction time for the solubilisation of bread waste and formation of HMF implied that the desirable tandem reactions, i.e., starch hydrolysis, glucose isomerisation, and fructose dehydration, were fast in these systems. Starch hydrolysis and fructose dehydration were probably promoted by protons (Brønsted acid) released upon the partial hydrolysis of Sn^{4+} in water as observed in our earlier studies (Yu et al., 2016; Yu et al., 2017a). The noticeable amount of fructose (6-9 mol%) at the early stage of conversion ($\leq$ 3 min) evidenced isomerisation as the intermediate step, where the critical hydride shift within glucose was catalysed by Sn^{4+} as the Lewis acid (Binder et al., 2010; Li et al., 2014; Delidovich and Palkovits, 2016).

The moderate accumulation of fructose in the product profiles ($\leq$ 3 min) suggested the faster glucose isomerisation compared to fructose dehydration in both ACN/H_2O and acetone/H_2O (**Fig. 1a&b**), given that the stoichiometric ratio of both glucose-to-fructose and fructose-to-HMF is 1:1. This led to the speculation that the presence of ACN and acetone facilitated the isomerisation step in particular, possibly by activating the substrate (glucose) or catalyst (Sn^{4+}). According to a previous study on molecular dynamics simulation, the former possibility may be low in view of the relatively minor interaction between ACN and glucose (Saielli and Bagno, 2010), because glucose was preferentially solvated by water in the ACN/H_2O mixture. The average number of ACN molecules bound to a hydroxyl group of glucose decreased significantly from 0.4 to 0.3 (i.e., by 25%) as the H_2O-to-ACN molar ratio increased from 1:1 to 2:1. In the current work, glucose was probably less solvated by ACN, where the H_2O-to-ACN molar ratio was close to 3:1. Therefore, the good performance of ACN in bread waste conversion to HMF may be associated with the activation of Sn catalyst instead of glucose. Yet, the literature contains little information on the solvation of glucose in the acetone-water mixture, which should be further addressed by future modelling studies.

3.3 Glucose conversion as the major hurdle in DMSO- and THF-water systems

In contrast with ACN/H_2O and acetone/H_2O, the HMF formation was much slower in DMSO/H_2O and THF/H_2O (comparing **Fig. 1** and **2**). The highest HMF yield of 27.4 mol% was achieved in DMSO/H_2O after 60-min reaction, while it was only 8 mol% at maximum in THF/H_2O after 120 min (the longest tested reaction time). It was noted that the THF/H_2O mixture in this work was less effective compared to those reported previously, e.g., up to 19 mol% HMF from biomass over $AlCl_3$ at 140°C (Yang et al., 2012c), in which THF at a high proportion served as an extractive layer in the presence of salt.

Our results indicated that glucose was the dominating substance in the product profile of both DMSO/H_2O and THF/H_2O, which was distinctive from the ACN/H_2O and acetone/H_2O. Such glucose accumulation was evident of the impeded isomerisation of glucose released from the starch hydrolysis, limiting the availability of fructose for HMF formation. This was substantiated by **Fig. 3**, in which less fructose was yielded from standard glucose in DMSO/H_2O and THF/H_2O (~4%) than in ACN/H_2O and acetone/H_2O (13-16%) after the 3-min heating.

The isomerisation efficiency may be related to the activity of metal ion and the distribution of glucose tautomers. Recent studies suggested that solvents could promote the formation of reactive tautomer of fructose and xylose for enhancing the dehydration reaction (Lin et al., 2017; Wang et al., 2017). Solvent characters may also play an important role. Among the studied systems, the glucose conversion to HMF was the lowest in THF/H_2O, in which heat transfer could be hindered because of the particularly low dielectric constant and low dipole moment of THF that disfavoured microwave absorption (**Table 1**). Nevertheless, the relative significance should be evaluated via future spectroscopic analysis and modelling work, to expand our understanding on the local environment of substrate and catalyst in different solvent mixtures.

In common with the ACN- and acetone-containing medium, the catalytic hydrolysis of bread starch was fast in both DMSO/H_2O and THF/H_2O because the total product yield reached the maximum within 10 min (~70 mol%) (**Fig. 2a&b**). The results showed a trace amount of fructose (< 3 mol%) throughout the conversion period, implying that fructose dehydration was highly efficient, or an alternative pathway (i.e., direct glucose dehydration to HMF bypassing fructose formation) was activated under the strong Brønsted acid derived from the hydrolysis of Sn (Yu et al., 2017a). The strong acidity may also pertain to the proton activity in association with its solvation status in these mediums (Mellmer et al., 2014). A recent simulation study proposed the complex of DMSO and proton as the active species, of which the catalytic performance was better than that of the discrete proton without coordination (Ren et al., 2017). Further computational investigations should be conducted to reveal the proton solvation in different mixtures of solvents.

3.4 Slow formation of side-products in the presence of DMSO and THF

In all the studied systems, the HMF production from bread waste became less appealing as the reaction time prolonged beyond the respective optimum, at which the highest HMF yield was achieved (**Fig. 1&2**). The HMF was partly lost via rehydration reaction, as evidenced by the significant generation of levulinic acid (e.g., 15.4 mol% in acetone/H_2O at 120 min). The decrease in the sum of detectable products was probably attributed to the formation of insoluble humins via polymerisation among HMF and intermediates. The occurrence of polymerisation was substantiated by TG and TDG analysis of the solid residues collected after the 120-min conversion in different mediums. The solid fractions exhibited high thermal stability as a feature of char-like substance (**Fig. 4a**), pointing to the formation of carbonaceous humins under long reaction time. None of them contained remaining starch, as the characteristic peak of starch at 240–340°C was absent (**Fig. 4b**). Both rehydration and polymerisation were frequently reported as the major hindrance to effective HMF production in the literature (Moreno-Recio et al., 2016; Qing et al., 2017; Zhang et al., 2017).

The degree of side reactions varied across the solvent mixtures. After the 120-min conversion, the HMF yield tended to increase further in THF/H_2O, whereas it dropped slightly by 6.1% in DMSO/H_2O (relative to the HMF maximum) (**Fig. 2a&b**). Comparatively, the reduction of HMF yield was more pronounced in acetone/H_2O (84%), followed by ACN/H_2O (25%) under the same conditions (**Fig. 1a&b**). Similarly, the decline in the total product yield at 120 min relative to the maximum was less significant in DMSO/H_2O (23%) and THF/H_2O (28%), compared to ACN/H_2O (42%) and acetone/H_2O (59%). These results demonstrated that the sugars, HMF, and other intermediates were more stable in the presence of DMSO and THF during the course of bread waste valorisation, which will be further addressed in **Section 3.5**.

The HMF yield was more stable in ACN/H_2O than acetone/H_2O (**Fig. 1**). It was observed that in ACN/H_2O, the final pH increased from the value of ~1 at 3 min to ~3.5 at 120 min, such that the decreasing acidity helped to suppress the acid-catalysed side reactions. The hydrolysis of ACN is found to develop alkalinity (Lei et al., 2016), because ammonium acetate forms as a buffer and counteracts the existing acidity in the medium. This was further supported by the detection of acetate/acetic acid in the current study, with the concentration ranging from 4 to 16 mg ml^{-1} depending on the reaction time. The solvent loss was insignificant, amounting to 3 mol% of the initial ACN loading only.

Interestingly, it was noted that the maximum HMF yield of 27.4 mol% in DMSO/H_2O was comparable to that in ACN/H_2O and acetone/H_2O (~26 mol%), despite the faster HMF production in the latter two systems (**Fig. 1&2**). The constant maximum HMF yield implied that the relative rates of HMF formation were comparable among the three mixtures. In other words, when changing the organic phase from DMSO to ACN or acetone, the desirable reactions (hydrolysis, isomerisation, and dehydration) were promoted to a similar extent as the undesirable pathways (rehydration and polymerisation), resulting in faster HMF formation but a negligible change in the maximum yield. These results highlighted the difference in considerations for achieving different goals – fast overall rate for rapid HMF production; and fast rate of the desirable reactions relative to the undesirable reactions for high yield and selectivity of HMF (Yu et al., 2017a; Yu and Tsang, 2017). The solvent effect on the system selectivity towards the desirable and undesirable pathways will be further discussed in the **Section 3.5**.

3.5 Qualitative selectivity towards desirable and undesirable reactions

The yield of HMF was correlated to its precursors (i.e., sugars) as well as its rehydration product (i.e., levulinic acid) in different mediums for comparison (**Fig. 5a&b**). This approach allowed direct experimental result-based examination on the selectivity towards particular reaction steps in a qualitative manner, without considering reaction time that masked the reaction preference.

In the HMF vs total sugars correlation, solid line (i) and (ii), which depicted the increase of HMF at the expense of the total sugars (disaccharides, glucose, and fructose), represented that sugars released from starch hydrolysis were converted to HMF during the early stage of bread waste conversion (Yu et al., 2017a) (**Fig. 5a**). The slope (i) for DMSO/H_2O was steeper than slope (ii) for THF/H_2O. Moreover, the band gap between solid and dotted line was smaller for DMSO/H_2O. The dotted line was the ideal trend of HMF evolution projected from the maximum total sugar yield detected in each system, assuming complete transformation of released sugars to HMF without any side reactions. Therefore, the steeper slope and smaller band gap can be interpreted as a smaller loss of HMF and sugars to rehydration and polymerisation products, i.e., the higher selectivity of sugar conversion to HMF, in DMSO/H_2O than in THF/H_2O. It can be deduced that ACN/H_2O and acetone/H_2O showed a similar selectivity towards HMF formation as DMSO/H_2O (i.e., similar slopes in **Fig. 5a**), reinforcing the observation that these three mediums generated nearly the same maximum HMF yield despite different optimal reaction times (**Fig. 1&2**).

The HMF vs levulinic acid profile added that HMF was less susceptible to rehydration in ACN/H_2O, acetone/H_2O, and DMSO/H_2O as their rising solid lines were steeper than that of THF/H_2O (**Fig. 5b**). These rising solid lines illustrated the positive correlation between the yield of HMF and levulinic acid, which appeared during the most productive stage of HMF formation with concurrent HMF rehydration to levulinic acid.

The selectivity towards desirable reactions may be attributed to the favourable coordination between the solvent molecules and sugars and HMF. Previous computational studies on solvent-water mixtures reported the favourable arrangement of DMSO molecules near the hydroxyl group of glucose and fructose, protecting the side reaction-susceptible sites without blocking water access to where the desirable reactions were initiated (Mushrif et al., 2012; Vasudevan and Mushrif, 2015). It was also revealed that DMSO preferentially coordinated with the carbonyl group of HMF, where off-path rehydration and polymerisation were triggered (Mushrif et al., 2012). In the current work, it was hypothesized that such solvent-sugar and solvent-HMF interactions also existed in

ACN/H_2O and acetone/H_2O, but were reduced in THF/H_2O, resulting in the lower selectivity towards HMF formation in the latter (**Fig. 5&b**). These interactions were possibly governed by the polarity, dipole moment, and dielectric constant of the organic solvent, because the values of these parameters are the lowest for THF (**Table 1**).

On the other hand, the HMF vs levulinic acid correlation provided insights into the dominating undesirable pathway that accounted for the majority of HMF loss. Similar to **Fig. 5a**, the solid line in **Fig. 5b** depicts the experimental evolution of levulinic acid, whereas the dotted line represents the projected evolution with the assumption of no HMF loss to polymerisation. It was observed that the solid line overlapped with the dotted line for the DMSO system, implying that HMF was lost to rehydration rather than polymerisation (**Fig. 5b**). Comparatively, polymerisation was suggested to be the major HMF consumption pathway in ACN/H_2O, where the solid line clearly diverted from the dotted line.

It was interesting to note that in acetone/H_2O, the levulinc acid production followed the projected dotted line but gradually became divergent at high levulinic acid yields, i.e., at long reaction times, denoting the changing selectivity towards rehydration and polymerisation (**Fig. 5b**). Such divergence possibly emerged in the case of DMSO/H_2O if the conversion duration extended beyond the studied range (120 min), which might complete the correlation profiles for DMSO/H_2O and THF/H_2O.

In summary, ACN/H_2O and acetone/H_2O allowed a higher rate of HMF production from bread waste than DMSO/H_2O and THF/H_2O, whereas the HMF selectivity, which depended on the relative rate of the desirable reactions, was similar among ACN/H_2O, acetone/H_2O, and DMSO/H_2O and was lower in THF/H_2O. Nevertheless, these solvents may incur moderate environmental or safety concerns according to the recent CHEM21 solvent selection guide (Prat et al., 2016). For instance, acetone, DMSO, and THF share the same environmental score of 5, whereas the safety and health score of ACN, acetone, and THF range from 3 to 7, compared to water that is rated at 1 in every aspect. Therefore, green alternatives, especially the bio-derived candidates such as Cyrene, γ-Valerolactone, and 2-methyltetrahydrofuran, should be examined as the reaction medium for HMF synthesis in future studies.

4 Conclusions

The overall rate of bread waste valorisation to HMF was the fastest in ACN/H_2O and acetone/H_2O, followed by DMSO/H_2O and THF/H_2O that were limited by glucose isomerisation. Yet, the nearly constant HMF maxima in ACN/H_2O, acetone/H_2O, and DMSO/H_2O suggested the similar selectivity towards HMF formation in these mediums. This was a result of the comparable rates of desirable reactions (hydrolysis, isomerisation, and dehydration) relative to undesirable pathways (rehydration and polymerisation). These mediums were more selective for HMF formation compared to THF/H_2O. This study expanded our understanding on the effects of solvent mixtures on individual desirable and undesirable reactions.

5 Acknowledgement

The authors appreciate the financial support from the Hong Kong International Airport Environmental Fund and the Environment and Conservation Fund, and the provision of food waste by South China Reborn Resources Co. Ltd.

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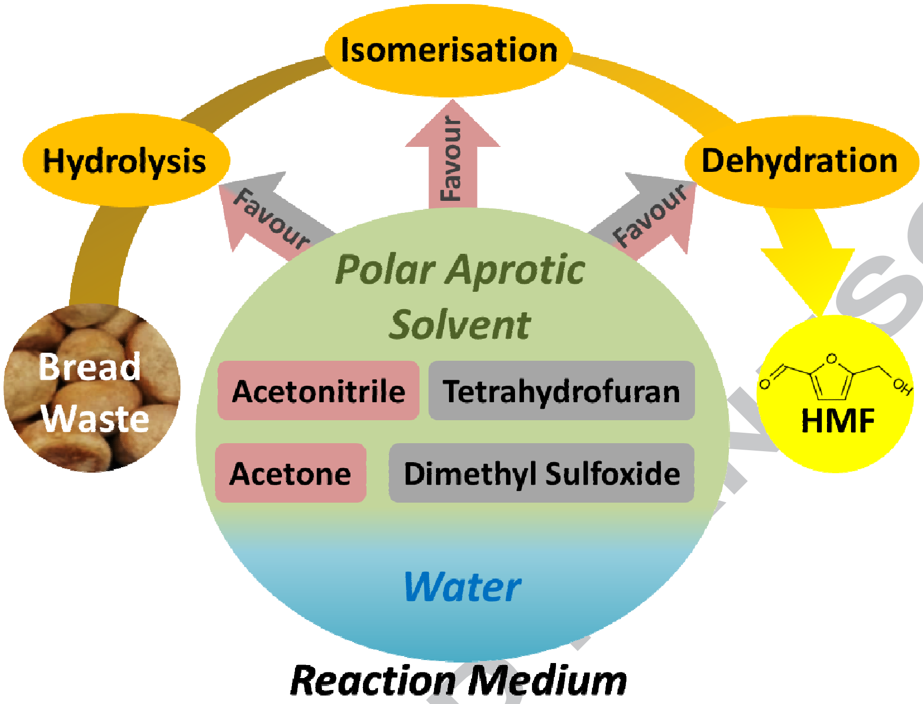
Highlights:

- Bread waste was valorised for the synthesis of HMF, with yields of 26-27 mol%.
- Fastest HMF production took place in ACN/H_2O and acetonitrile/H_2O systems.
- Slow glucose isomerization hindered HMF formation in DMSO/H_2O and THF/H_2O.
- Similar HMF selectivity was achieved in ACN/H_2O, acetonitrile/H_2O, and DMSO/H_2O.

Graphical Abstract:



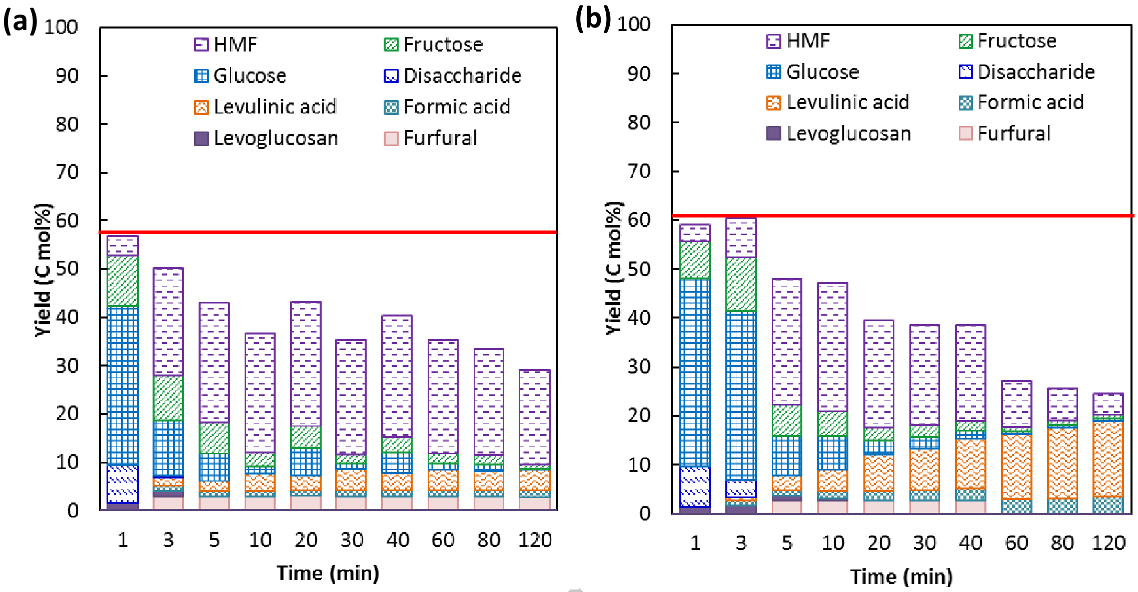


Figure 1. Product yields during the catalytic conversion of bread waste in (a) ACN/H_2O and (b) acetone/H_2O (conditions: 5 wt/v% substrate and 55.5 mM $SnCl_4$ in solvent mixture (1:1 v/v) at 140°C; yield = $\text{product}_{\text{Cmol}}/\text{substrate}_{\text{Cmol}} \times 100\%$; the red line represents the highest total product yield).

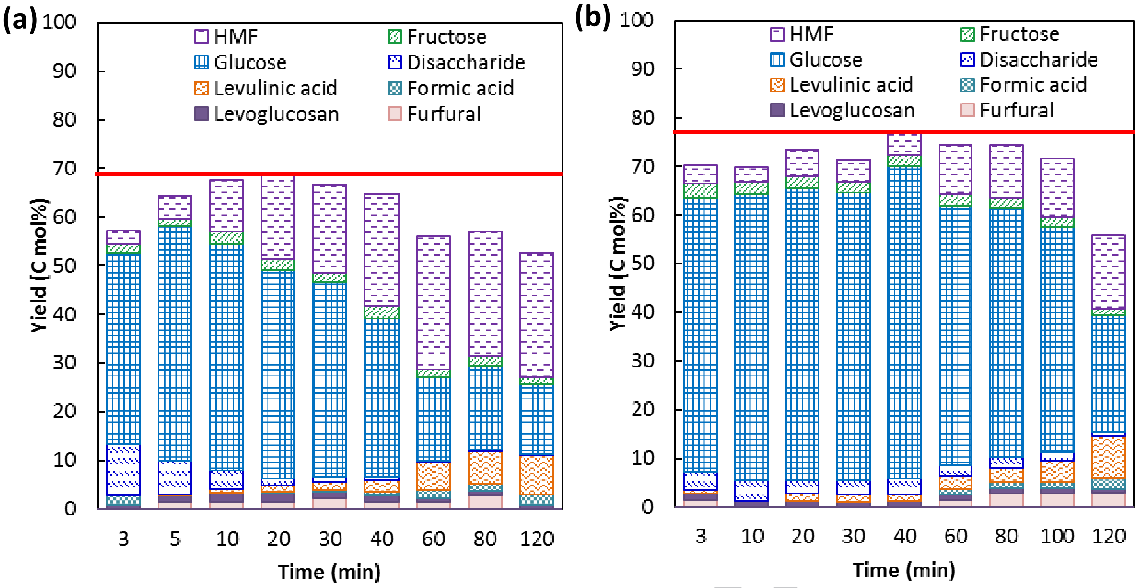


Figure 2. Product yields during the catalytic conversion of bread waste in (a) DMSO/H_2O and (b) THF/H_2O (conditions: 5 wt/v% substrate and 55.5 mM $SnCl_4$ in solvent mixture (1:1 v/v) at 140°C; yield = $\text{product}_{\text{Cmol}}/\text{substrate}_{\text{Cmol}} \times 100\%$; the red line represents the highest total product yield).

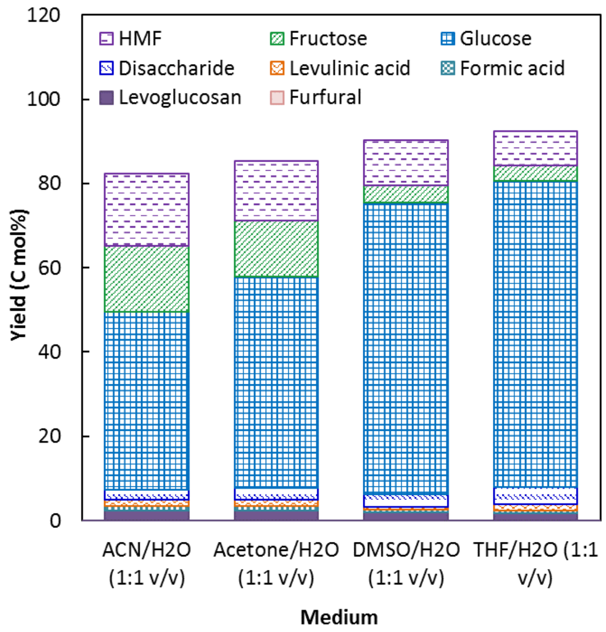


Figure 3. Product yields during the catalytic conversion of standard glucose in different solvent mixtures (1:1 v/v) (conditions: 5 wt/v% substrate and 55.5 mM $SnCl_4$ in solvent mixture (1:1 v/v) at 140°C for 3 min; yield = $product_{Cmol}/substrate_{Cmol} \times 100\%$).

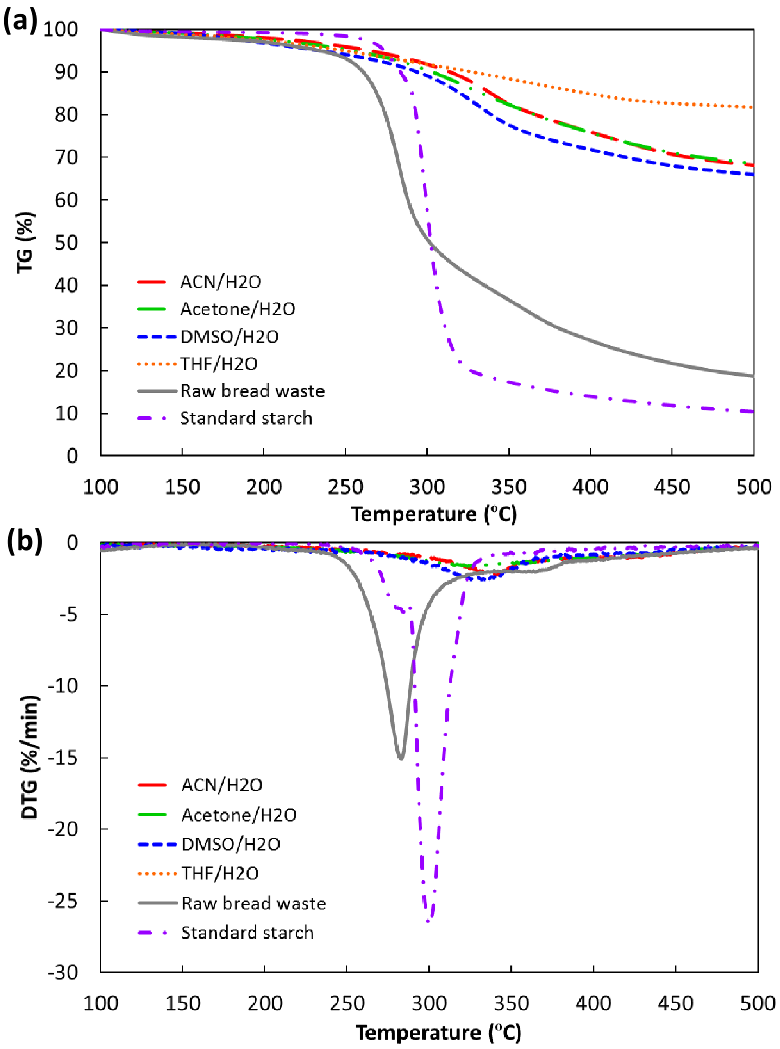


Figure 4. (a) TG and (b) DTG spectra of solid residues from catalytic conversions of bread waste in different solvent mixtures (1:1 v/v), raw bread waste, and standard starch (conditions: 5 wt/v% substrate and 55.5 mM $SnCl_4$ at 140°C for 120 min).

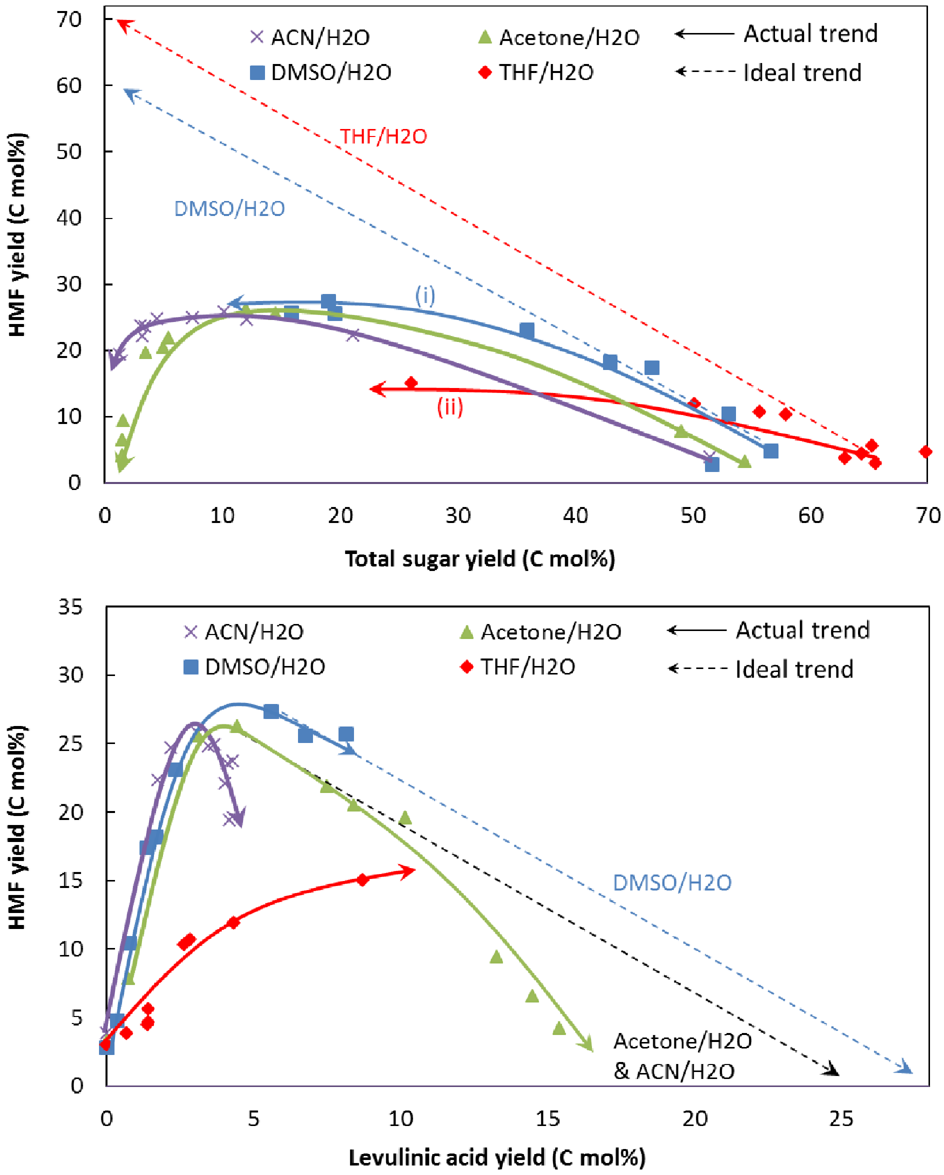


Figure 5. Yield of HMF as a function of (a) total sugar yield and (b) levulinic acid yield during the catalytic conversion of bread waste in different solvent mixtures (1:1 v/v) (conditions: 5 wt/v% substrate and 55.5 mM $SnCl_4$ at 140^{o}C; yield = product$_{Cmol}$/substrate$_{Cmol}$ × 100%) (remarks: the ideal trend was proposed assuming negligible HMF-consuming side reaction(s); projected maximum HMF [C mol%] = actual maximum total sugar [C mol%] + actual co-existing HMF [mol%] for (a); projected maximum levulinic acid [C mol%] = actual maximum HMF [C mol%] x 5/6 + actual co-existing levulinic acid [C mol%] for (b); arrows indicate the direction of temporal development of patterns; line (i) and (ii) represents the actual trend of HMF evolution in DMSO/H_2O and THF/H_2O in (a), respectively).

Table 1. Physicochemical properties[a] of different solvents and glucose.

	Density (g/ml)	DE[b]	DM[c]	Polarity
Acetone	0.78	20.7	2.91	5.1
ACN	0.78	37.5	3.44	5.8
DMSO	1.09	46.7	3.96	7.2
THF	0.88	7.6	1.63	4
Water	1	78.5	1.8	9
Glucose	1.54	-	8.6	-

[a] extracted from Gajula et al. (2017);

[b] dielectric constant (DE);

[c] dipole moment (DM) in D units.