

An Acid-free Conversion of Cellulose to 5-hydroxymethyl-furfural Catalyzed by Hot Seawater

Xiangcheng Li, Yayun Zhang, Qineng Xia, Xiaohui Liu, Kaihao Peng, Sihai Yang, and Yanqin Wang

Ind. Eng. Chem. Res., **Just Accepted Manuscript** • DOI: 10.1021/acs.iecr.8b00443 • Publication Date (Web): 28 Feb 2018

Downloaded from <http://pubs.acs.org> on March 1, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



An Acid-free Conversion of Cellulose to 5-hydroxymethylfurfural Catalyzed by Hot Seawater

Xiangcheng Li,[†] Yayun Zhang,^{‡§} Qineng Xia,[†] Xiaohui Liu,[†] Kaihao Peng,[†] Sihai Yang,^{*⊥} Yanqin Wang^{*‡}

[†] Shanghai Key Laboratory of Functional Materials Chemistry, Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, P. R. China.

[‡] Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Ministry of Education, College of Power Engineering, Chongqing University, Chongqing 400030, China.

[§] Bioproducts, Sciences and Engineering Laboratory, Department of Biological Systems Engineering, Washington State University, Richland, WA 99354-1671, USA.

[⊥] School of Chemistry, University of Manchester, Manchester, M13 9PL, UK.

Corresponding authors emails: Sihai.Yang@manchester.ac.uk (Sihai Yang);
wangyanqin@ecust.edu.cn (Yanqin Wang)

KEYWORDS: biomass, 5-hydroxymethylfurfural, acid-free, chloridions, seawater

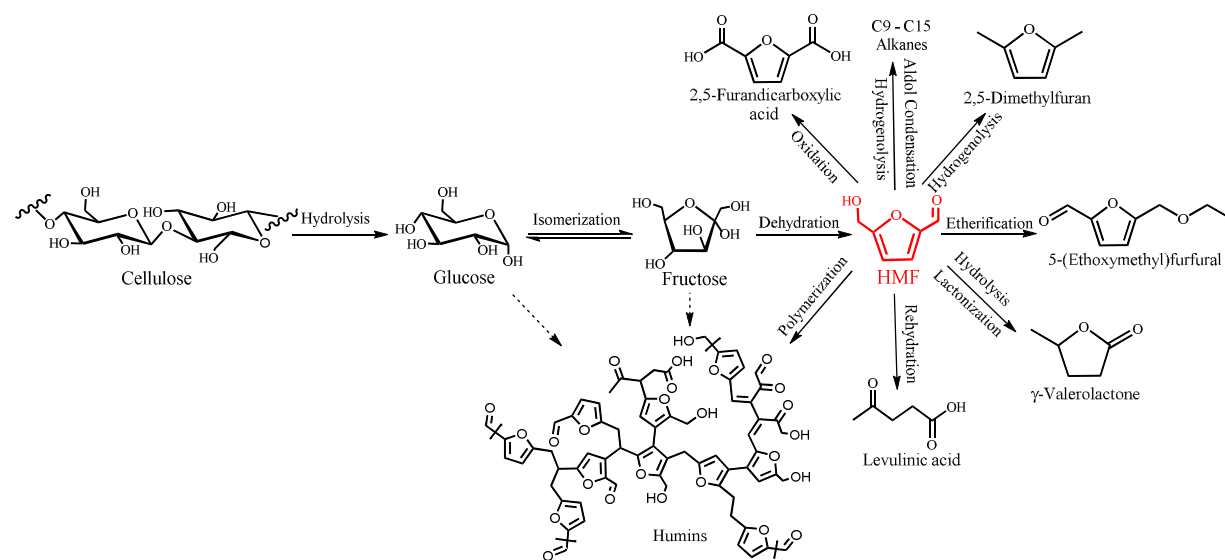
ABSTRACT

The conversion of cellulose from renewable biomass into the key platform chemical, 5-hydroxymethylfurfural (HMF), is of fundamental importance to the production of numerous bio-products and biofuels. Various acidic catalysts have been developed for this process; however, most systems suffer from low efficiency and poor sustainability. Here we report an acid-free conversion of cellulose into HMF in a biphasic system of tetrahydrofuran/concentrated seawater. The yield of HMF reached 48.6%, and this system has excellent reusability and sustainability. We found that the chloridions (Cl^-) can promote the isomerization of glucose *via* a 1,2-hydride shift path and accelerate the dehydration of fructose, thus driving the selective formation of HMF. This simple system is capable of converting raw biomass to furfural and HMF with the lignin residues transformed into useful alkanes via a sequential catalytic upgrading, paving a new economic-viable pathway for the full valorization of lignocellulosic biomass.

INTRODUCTION

The potential of utilizing HMF as a platform chemical for the production of a wide spectrum of sustainable bio-products, biofuels and polyesters is increasingly recognised.¹⁻³ HMF can be obtained from the conversion of cellulose, which is the most abundant bio-polymer comprising glucose units linked by β -1,4-glycosidic bonds and accounts for 35~45 wt% of renewable lignocellulosic biomass.^{4,5} Generally, the conversion of cellulose to HMF undergoes three tandem steps: (i) hydrolysis of cellulose to glucose; (ii) isomerization of glucose to fructose; and (iii) dehydration of fructose to HMF (Scheme 1).⁶ Lewis and Brønsted acids can promote (ii) and (iii), respectively.⁷ Therefore, state-of-the-art catalysts for this conversion have to combine Lewis and Brønsted acids and various homogeneous and heterogeneous acidic catalysts have been developed for this process.⁷⁻¹⁷ However, most existing systems suffer from low efficiency and poor sustainability. Additionally, expensive and harmful Lewis acids (*e.g.*, Cr, Zr and Al salts) employed for this conversion can lead to serious environmental impacts. Considering the astronomical production of biomass worldwide, development of new functional

catalysts with great abundance, easy recovery and, most importantly, reduced acidity to enhance the efficiency, reusability and sustainability, is the key to improve the HMF production.



Scheme 1. The reaction pathway for the conversion of cellulose to HMF and the potential application of HMF as a platform chemical.

Seawater is the most abundant natural resource in the world and there is an increasing need to improve its utilization. For example, seawater can be readily concentrated by sunlight to extract salts. Herein, we describe the conversion of cellulose to HMF with a high yield of 48.6% catalyzed by concentrated seawater (*ca.* 30 wt% salts) in a THF/seawater biphasic system in the absence of any external-added acid catalysts. An investigation combining control experiments, DFT calculations and D2-glucose isotopic labeling reveal that the halogen ions, chloridions in this case, play a key role in the cellulose hydrolysis, glucose isomerization and fructose dehydration, resulting in the selective HMF formation. This new process is overall extremely simple, inexpensive, and efficient for the mass production of HMF from renewable woody biomass. Importantly, transformative insight is uncovered to remove the current reliance on the use of dual acids (*i.e.*, Lewis and Brønsted acid) for the conversion of cellulose to HMF.

EXPERIMENTAL SETION

Chemicals

Microcrystalline cellulose powder (PH-101) was purchased from Fluka Analytical Co. Ltd. D-Glucose (>99.5%), sodium chloride (>99.5%), tetrahydrofuran (THF, >99.9%) were obtained from Sigma Aldrich and used without further purification. 5-Hydroxymethylfurfural (HMF, >98%) was purchased from Alfa Aesar Chemical Reagent Company. D2-glucose was purchased from Cambridge Isotope Corp. All other chemicals were chemically pure and purchased from Shanghai Chemicals Company. The ball-milled cellulose and lignocellulosic biomass samples were prepared by using a laboratory ball mill (QM-3SP04). To obtain desired samples, about 2 g microcrystalline cellulose or lignocellulosic biomass was charged in a grinding cell and the ball milling was operated at a frequency of 50 Hz with 6 mm agate balls for 12 h. The concentrated seawater was obtained from as-received seawater by natural volatilization. The components of seawater were analyzed by ion chromatography (Table S1).

Characterization

The powder XRD patterns were recorded with a Rigaku D/max-2550VB/PC diffractometer by using CuK ($\lambda=0.15406$ nm) radiation.

TGA was performed with PerkinElmer Pyris Diamond TG/DTA using air as the purge gas and a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The flow rate of purge gas was always 100 mL min^{-1} .

Catalyst preparation

NbOPO₄ was synthesized by a hydrothermal method at pH=2 according to literature.¹⁸ 5%Pt/NbOPO₄ was prepared by incipient wetness impregnation of NbOPO₄ with aqueous solutions of Pt(NO₃)₂, after impregnation, the catalyst was dried at $100\text{ }^{\circ}\text{C}$ for 12 h, followed by calcination in air at $500\text{ }^{\circ}\text{C}$ for 3 h and reduced in a 10% H₂/Ar flow at $400\text{ }^{\circ}\text{C}$ for 3 h.

Catalytic reaction

Catalytic test for cellulose and lignocellulosic biomass conversion in THF/seawater biphases. Catalytic experiments were conducted in a Teflon-lined stainless steel autoclave (25 mL, Anhui Kemi Machinery Technology Co. Ltd; with Teflon liner) equipped with a temperature-controlled heating-jacket and magnetic stirring. In a typical procedure, 50 mg of ball-milled cellulose (5wt%), 6 mL THF

and 1 mL concentrated seawater (*ca.* 30wt% salts) were charged in the sealed autoclave, and the mixture was stirred at 700 rpm. 0.5 MPa N₂ gas was used for purging air out of the reactor and retaining all solvent in liquid phase. When the reactor was heated to the targeted temperature, zero time was recorded. The reactor was then held at this temperature for a given period of time. After the reaction, the mixtures were cooled down quickly, and the reaction liquid was taken for analysis. During recycles, the upper organic phase was separated after reaction and the aqueous phase (concentrated seawater, *ca.* 30wt% salts) was directly used in the next run without further modification. For the cellulose conversion, the unreacted cellulose was washed with methanol *via* ultrasonic treatment to remove humins,¹⁹ then centrifuged and dried under vacuum (50 °C, 12 hours). Based upon this result, the conversion of cellulose was calculated. The influence of salt concentration in seawater on the product distribution of cellulose conversion and cyclic usage of concentrated seawater (*ca.* 30wt% salts) for the conversion of cellulose to HMF were repeated 3 times and all errors were found to be less than 2%.

Catalytic test for cellulose conversion in solvent/NaCl+H₂O biphas. Catalytic experiments were also conducted in a Teflon-lined stainless steel autoclave equipped with a temperature-controlled heating-jacket and magnetic stirring. In a typical procedure, 50 mg of ball-milled cellulose (5wt%), 0.30 g of NaCl (30 wt%), 6 mL THF and 1 mL deionized water were charged in the sealed autoclave (25 mL), and the mixture was stirred at 700 rpm. 0.5 MPa N₂ gas was used for purging air out of the reactor and retaining all solvent in liquid phase. When the reactor was heated to the targeted temperature, zero time was recorded. The reactor was then held at this temperature for a given period of time. After the reaction, the mixtures were cooled down quickly, and the reaction liquid was taken for analysis. The calculation of cellulose conversion is shown above.

Catalytic test for cellulose, glucose and fructose conversion in aqueous phase. Catalytic experiments were also conducted in a Teflon-lined stainless steel autoclave equipped with a temperature-controlled heating-jacket and magnetic stirring. In a typical procedure, 0.5 g of ball-milled cellulose (5wt%), 3.0 g of NaCl (30 wt%) and 10 mL deionized water were charged in the sealed autoclave (25 mL), and the mixture was stirred at 700 rpm. 0.5 MPa N₂ gas was used for purging air out

of the reactor and retaining all solvent in liquid phase. When the reactor was heated to the chosen temperature, zero time was recorded. The reactor was then held at this temperature for a given period of time. After the reaction, the mixtures were cooled down quickly, and the reaction liquid was taken for analysis. The calculation of cellulose conversion is shown above.

Collections of lignin residue and humins (cellulose). Lignin residue was collected after the conversion of cellulose and hemicellulose portions in raw biomass with concentrated seawater (*ca.* 30wt% salts). Typically, in a Teflon-lined stainless steel autoclave (500 mL) equipped with a temperature-controlled heating-jacket and magnetic stirring, 2 g of ball-milled lignocellulosic biomass, 40 mL concentrated seawater (*ca.* 30wt% salts) and 240 mL THF were combined and stirred at 700 rpm. 0.5 MPa N₂ gas was used for purging air out of the reactor and then the reactor was held at 200 °C for 5 hours. After the reaction, the mixtures were cooled down quickly and the organic phase was separated, and then THF was removed for recycling by rotary evaporation. Finally, the obtained lignin-enriched residue was poured into 200 mL water for full extraction of HMF and furfural, and lignin was collected by filtration, washed with a small portion of water and dried under vacuum. The yield of the representative birch lignin was 0.55 g (27.5 wt%). Lignin hydrodeoxygenation and details of alkylcyclohexanes analysis are shown in Supporting information.

Humins (cellulose) was collected as follows: the upper organic phase was separated after the reaction of cellulose conversion in THF/concentrated seawater (*ca.* 30wt% salts). Then THF was removed for recycling by rotary evaporation, the obtained residue was poured into 100 mL water for full extraction of HMF, and humins was collected by filtration and dried under vacuum.

Isotopic labelling experiments. The isotopic labelling experiments were conducted in a Teflon-lined stainless steel autoclave (25 mL, Anhui Kemi Machinery Technology Co. Ltd) equipped with a temperature-controlled heating-jacket and magnetic stirring. Reactions were conducted at 150 °C using 1 wt% unlabelled glucose or glucose labelled with ²H at C2 position (D2-glucose) in aqueous phase, and 30 wt% NaCl. After the reaction, the sugar fraction was collected and evaporated in a vacuum oven at 30 °C, and then dissolved in methanol. NaCl was removed after centrifugal separation and the filtrate

was evaporated in a vacuum oven at 30 °C once again, and then the collected samples were dissolved in D₂O for nuclear magnetic resonance (NMR) measurements. ¹H NMR was recorded using a Bruker 400 MHz NMR spectrometer.

Product analysis

The analysis of HMF and furfural were carried out by means of an HPLC apparatus (Agilent 1200 Series) equipped with an XDB-C18 column (Eclipse USA) and quantified with an ultraviolet detector (Agilent G1314B). The maximum absorption wavelengths for furfural and HMF were 274 and 282 nm, respectively. In order to quantify the content of furfural and HMF together, 254 nm was selected in this work and the values of linearity coefficient were 0.997 and 0.999, respectively. The eluent with a flow rate of 0.6 mL min⁻¹ was a mixture of methanol and water with volumetric ratio of 20:80. An auto-sampler (Agilent G1329A) was used to enhance the reproducibility. Glucose, fructose and levulinic acid (LA) were analysed on the same HPLC apparatus (Agilent 1200 Series), but with a refractive index detector (Agilent G1362A) and using a Biorad Aminex HPX-87H sugar column at 55 °C. The mobile phase was 0.004 M H₂SO₄ with a flow rate of 0.45 mL min⁻¹. The quantification of products was performed using an external standard method. The residual solid was dried under vacuum. The conversion of cellulose was determined based on the weight difference of cellulose before and after each reaction. Humins could not be observed by HPLC or GC-MS, and therefore the amount of humins produced was estimated from the carbon balance.²⁰ The details of alkylcyclohexanes and lignin monomers analysis is shown in Supplemental Experimental Procedures.

For the lignocellulosic biomass, the yields of HMF and furfural were defined as below:

$$\text{HMF yield} = \frac{\text{moles of HMF produced}}{\text{moles of hexose units in lignocellulosic biomass}}$$
$$\text{Fur yield} = \frac{\text{moles of furfural produced}}{\text{moles of pentose units in lignocellulosic biomass}}$$

Conversion of cellulose and yields of glucose (fructose) and HMF were defined as follows:

$$\text{Cellulose conversion} = \frac{\text{mass of cellulose reacted}}{\text{mass of starting cellulose}}$$

$$\text{Glucose (fructose) yield} = \frac{\text{moles of glucose (fructose) produced}}{\text{moles of hexose units in starting cellulose}}$$

$$\text{HMF yield} = \frac{\text{moles of HMF produced}}{\text{moles of hexose units in starting cellulose}}$$

In the glucose (fructose) conversion, the conversion of glucose (fructose) and the yield of HMF were defined as follows:

$$\text{Glucose (fructose) conversion} = \frac{\text{moles of glucose (fructose) reacted}}{\text{moles of starting glucose (fructose)}}$$

$$\text{HMF yield} = \frac{\text{moles of HMF produced}}{\text{moles of starting glucose (fructose)}}$$

DFT calculations. Quantum chemical calculations based on Density Function Theory (DFT) method was employed to study the molecular pictures of glucose conversion to HMF under the aqueous condition and to illuminate the effect of chlorine ion on the investigated reactions by theory. The equilibrium geometries of all reactants, intermediates and products involved in every chemical reaction were performed with the B3LYP method with AUG-cc-pVDZ basis set,²¹ which were embedded in Gaussian 09W suite of programs.²² No symmetry restrictions were used in any calculations. The water solvent effect was considered in all calculations by using SMD solvent model.²³ The transition states were located by the synchronoustransit-guided quasi-Newton method according to the structures of reactants and products and confirmed by frequency analysis and intrinsic reaction coordinate (IRC) calculations with the same basis set. All energies of structures were obtained after zero-point energy (ZPE) correction. The correctness of all the optimized structures were confirmed through frequency analysis in which reactants, intermediates and products had no imaginary frequencies while transition states had exactly one imaginary frequencies. Zero point, finite temperature, and entropic energy contributions were computed by normal-mode analysis within the SMD water solvent approximation at a temperature 473 K. The reaction (ΔG) and activation free energies (ΔG) were calculated throughout the reaction pathways.

The selection of departure configuration of glucose was based on results of previous studies²⁴ and was additionally validated by analysis of their stability by using the methods in present work. The throughout thermodynamic analysis was conducted in every elemental reactions and some kinetic analysis also performed in the reactions with transition states to compare pathways in different conditions. The Brønsted acid was modelled as H_3O^+ as an approximation for a proton in a water. Our calculation results indicated that choosing Zundel complex H_5O_2^+ model has same trends in differences of corresponding reactions. The processes of HMF formation from glucose can be divided into two tandem steps that glucose firstly reacts to fructose and followed with conversion of fructose to HMF. The most favourite reaction route stands out after conducting thermodynamic and kinetic analysis. Different conditions in the presence and absence of chloride ion are compared and theoretical results reveal that adding chloride ion can effectively promote the whole converting reactions, which consists with our experimental outcomes.

RESULTS AND DISCUSSION

Catalytic performance of seawater for cellulose conversion. Ball-milled cellulose (structure change of cellulose after ball milling is shown in Figure S1) in 5 wt% aqueous solution was used as feedstock to test its conversion into HMF in a THF/seawater (v:v = 6/1) biphasic by using raw or concentrated seawater (Table S1) as the catalyst at 200 °C for 6 hours. Surprisingly, high HMF yields of 32.7, 46.2 and 48.6% were achieved with full cellulose conversion by using raw or concentrated seawater (*ca.* 3wt%, 15wt% and 30wt% salts, respectively) as the sole catalyst (Figure 1A). These yields are higher than those over acid-catalysts in THF/ H_2O and comparable to those obtained over the acid-catalysts in ionic liquids (Table 1, entries 3, 7 and 8); the latter is the most prevalent homogeneous route for this conversion.^{25,26} The yields obtained here are however lower than those obtained with microwave heating or pretreated cellulose (mechanocatalytic depolymerized cellulose) as substrate (Table 1, entries 2, 5 and 6). The microwave irradiation can enhance the effective collision among reactant molecules owing to the highly localized heating.⁹ While, the pretreated cellulose contains soluble oligomers and is notably

more readily to be converted. The latter is evidenced by using microcrystalline cellulose as substrate under the same reaction conditions, and a much lower HMF yield of 33% with 56.7% cellulose conversion was obtained.¹⁶ A direct comparison between this work and all current leading systems is shown in Table 1, where homogeneous or heterogeneous acidic catalysts are essential except in this work. Meanwhile, this THF/seawater system is also efficient for the full conversion of microcrystalline cellulose under the same condition (43.5% HMF yield, Table S2). A blank test was carried out with THF/H₂O under the same conditions and a low cellulose conversion (65%) and HMF yield (14.8%) obtained with humins as the main product (Figure 1A), demonstrating the critical role of salts in seawater for this reaction. Moreover, this THF/seawater system has excellent reusability. After five successive reaction cycles in concentrated seawater (*ca.* 30wt% salts), the cellulose conversion and the HMF yield remain >99% and >47.5%, respectively (Figure 1B). Notably, the pH values of the aqueous solution were recorded as 7.78 and 7.72 before and post the reaction, respectively. Thus, this new reaction system not only avoids the use of external acid catalysts, but also reduces the pollution caused by the waste water through its cyclic use. This reaction system is also capable of converting cellulose with increased concentration (*e.g.*, 10 wt%, 20 wt%; the corresponding water/cellulose ratio is 10 and 5, respectively) to HMF (Figure S2). For example, cellulose at 20 wt% concentration with its water/cellulose ratio of 5 can be completely converted after reaction for 6 h with a high HMF yield of 42.8%, accompanied with 4.5% glucose and 2.7% fructose, implying this THF/seawater reaction system is efficient for cellulose conversion.

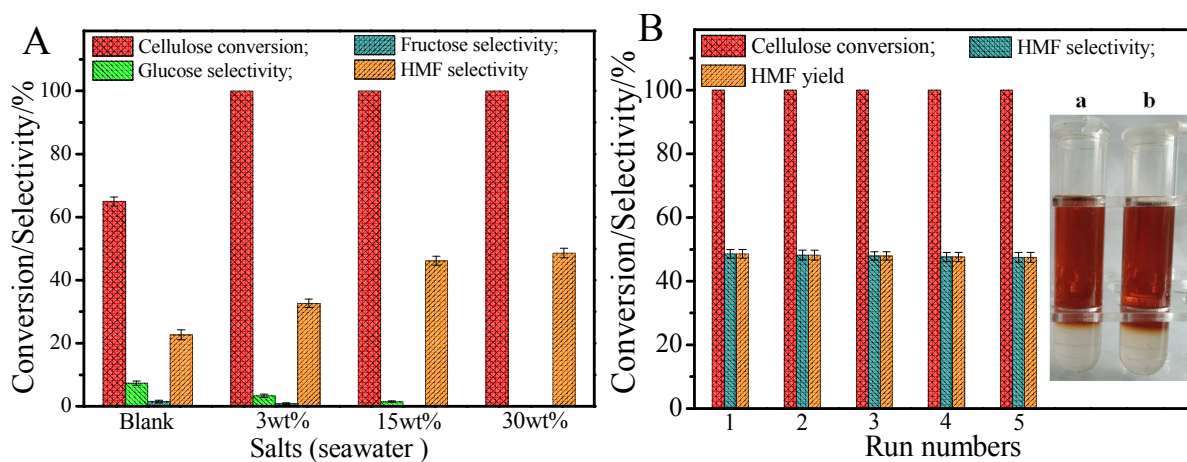


Figure 1. (A) Influence of salts concentration in seawater on the product distribution from cellulose conversion. (Reaction condition: 5wt% cellulose, 0.5 M N₂, 1mL seawater or pure water, 6mL THF, 200 °C, 6 h); (B) Cycling use of concentrated seawater for the conversion of cellulose to HMF. (Reaction condition: 5wt% cellulose, 0.5 M N₂, 1mL concentrated seawater (*ca.* 30wt% salts), 6mL THF, 200 °C, 6 h); inset photographs showing the post-reaction system: (a) the first and (b) fifth run.

Conversion of raw lignocellulosic biomass. We also attempted the direct conversion of raw lignocellulosic biomass (*i.e.*, cornstalk, pine, birch and poplar) from this new biphasic system. Interestingly, the cellulose and hemicellulose fractions of the raw biomass were found efficiently converted at 200 °C after 5 h and the molar yields of HMF/furfural from cornstalk, pine, birch and poplar were recorded as 55.4/47.8%, 54.1/44.6%, 42.9/40.5% and 40.5/41.5%, respectively (Table S2). Significantly, these yields are comparable to the state-of-the-art systems based upon heterogeneous and homogenous catalysts (Table 1, entries 11 and 12).^{27,28} Interestingly, the lignin residues in raw biomass can be readily collected by conventional extractions (lignin fraction accounts for *ca.* 36 wt% of lignin residue as determined by TGA, Figure S3) and further upgraded *via* a hydrodeoxygenation reaction over the Pt/NbOPO₄ catalyst, an excellent hydrodeoxygenation catalyst²⁹ to afford 16.5wt% alkylcyclohexanes as liquid fuels (Tables S3, S4). Importantly, the corresponding carbon yield of C₇~C₉ hydrocarbons is *ca.* 89.3%, as evidenced from an established lignin monomer analysis based upon the nitrobenzene oxidation method (Figure S4).³⁰ Thus, this seawater-based system enables a full valorization of the raw lignocellulosic biomass (Figure 2).

Table 1. Overview of HMF yields from the conversion of cellulose and lignocellulosic biomass in the best-behaving catalytic system.

Entry	Substrate	Solvent	Catalyst	T^a (°C)	t^a	C^a (%)	Y^a (%)	Ref.
1	Cellulose (4 wt%)	DMA- LiCl/[EMIM]Cl (10 wt%)	CrCl ₂ (25 mol%), HCl (6 mol%)	140	2 h	>99	54	8
2	Cellulose (4 wt%)	DMA- LiCl/[EMIM]Cl (10 wt%)	Zr(O)Cl ₂ /CrCl ₃ (20 mol%, 3:1 mol ratio)	120 (Microwave)	20 min	>99	62	9
3	Cellulose (40 mg)	THF (3mL)- H ₂ O (1mL)	AlCl ₃ •6H ₂ O (0.1 mmol)	180 (Microwave)	30 min	>99	37	10
4	Cellulose (0.25 g)	water (10 ml)	Bimodal-HZ-5 (0.50 g)	190	4 h	67	46	11
5	Pretreated cellulose (H ₂ SO ₄ -Ball- milled, 5g)	water/THF+ NMP= 1:4 v/v (100 mL)	P-TiO ₂ (1.25g)	180	105min	>99	86.2	16
6	Pretreated cellulose (H ₂ SO ₄ -Ball- milled, 10g)	water–MeTHF /NMP=3 : 7 v/v (100 mL)	P-TiO ₂ (1.25g)	180	80min	>99	74.7	17
7	Cellulose (50 mg)	[BMIM]Cl (1 g)	CrCl ₃ •3H ₂ O (15 mg)	150 (Microwave)	10 min	>99	54	25
8	Cellulose (50 mg)	[EMIM]Cl (0.5 g)	CuCl ₂ /CrCl ₂ (37 μmol/g, XCuCl ₂ = 0.17)	120	8 h	>99	57.5	26
9	Cellulose (50 mg)	THF (6mL)- seawater (1 mL)	Concentrated seawater (ca. 30wt% salts)	200	6 h	>99	48.6	this work
10	Cellulose (50 mg)	THF (6mL)- H ₂ O (1 mL)	NaCl (30 wt%)	200	6 h 8 h	>99	56.1 58.9	this work
11 ^b	Cornstalk (0.2 g)	THF (5mL)- H ₂ O (1mL)	Sn-Mont (0.1 g) + NbOPO ₄ (0.1 g)	160	2 h	>99	44.1	27

12	Cornstalk (5 wt%)	THF -H ₂ O (3/1, v/v)	FeCl ₃ (1 wt%)	170	80 min	>99	42	28
13	Cornstalk (50 mg)	THF (6mL)- Seawater (1 mL)	Concentrated seawater (ca. 30wt% salts)	200	5 h	>99	55.4	this work

^a T = temperature; t = time; C = conversion; Y = HMF yield; ^b Water saturated with NaCl.

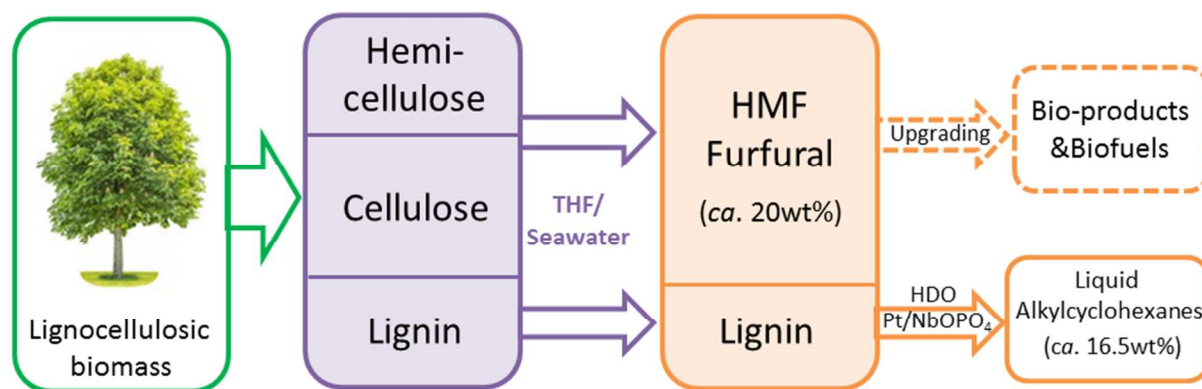


Figure 2. Schematic representation of the full valorization of lignocellulosic biomass into furfural, HMF catalyzed by the new THF/seawater biphasic system and cycloalkanes by the hydrodeoxygenation of lignin residues over Pt/NbOPO₄ catalyst.

Catalytic function of chloride ions. Although the influence of metallic chlorides on biomass conversion have been extensively investigated, the majority of research focused on the partition effect or the role of cations (*e.g.*, Cr²⁺, Zn²⁺, Sn⁴⁺ and Al³⁺) as Lewis acid on carbohydrate conversion,^{8-10,25,26,31-33} whereas the catalytic function of chloride ions has been rarely explored.^{34,35} NaCl is the main salt component of seawater (Table S1),³⁶ and therefore its catalytic activity is investigated here. Firstly NaCl was tested for cellulose conversion and an exceptionally high HMF yield of 56.1% was realized with full conversion of cellulose in 6h (Figure S5). The HMF yield was further increased to 58.9% with full conversion of the intermediates (glucose and fructose) at t = 8 h. Other chlorides in seawater, including KCl, MgCl₂, CaCl₂, were also tested and the selectivity to HMF was all over 46.2% at the similar cellulose conversion (*ca.* 50%) (Table S5). Interestingly, the conversion of cellulose in equally-

concentrated MgCl_2 and CaCl_2 systems was much faster (full conversion within 2 h) than that in NaCl (6 h), confirming the promotion effect of chlorides and cationic ions, leading to cellulose faster conversion in concentrated seawater (*ca.* 30wt% salts; 6h as optimal reaction time) than in NaCl solution (30wt%; 8 h as optimal reaction time). Tests with sulfates (*e.g.*, Na_2SO_4), another key component of seawater, were also carried out and a much lower HMF selectivity of 12.1% at 48.0% cellulose conversion obtained (Table S5, entry 9). Interestingly, this is even lower than that in the blank test (Table S5, entry 2), indicating that SO_4^{2-} ions have a detrimental effect on HMF formation. This is consistent with the slight decrease in the HMF yield from the concentrated seawater (*ca.* 30wt% salts with 1.71 wt% of SO_4^{2-}) when comparing with the NaCl (30wt%) system (Table 1, 48.6% and 56.1%, respectively).

To rule out the promotion effect of organic solvent, the product-profile of cellulose conversion in the aqueous phase was recorded in the absence and presence of NaCl (Figure 3A,B). Without NaCl , the conversion of cellulose is only 79% even after 12 h, while it reached 100% when reacted for 6 h with NaCl , indicating the promotion effect of NaCl on cellulose depolymerisation, which is consistent with the study reported by Hu *et al.*³⁷ Moreover, the conversion of glucose and formation of HMF are much faster in NaCl solution than in pure water, indicating that NaCl can also enhance the isomerization of glucose and the dehydration of fructose (Figure 3A,B). The presence of THF has little impact on the reaction rate, suggesting that the partitioning effect of organic solvent on accelerating this reaction is negligible (Figure 3B and Figure S5), while the extraction effect exists and prevents the further hydration of HMF to levulinic acid (LA) and the formation of additional humins. The latter is evidenced by a test without THF, where severe hydration of HMF to LA was found in the aqueous solution, consistent with high LA yield of 29.4% in the aqueous solution (*verse* <0.1% in the THF/ H_2O biphasic).

Based on the experimental results above, it is clear that Cl^- plays an important role in the conversion of cellulose to HMF. Therefore, glucose, a key intermediate in cellulose conversion was used as a model compound to explore the reaction mechanism. Figure 3C and D clearly shows that the conversion of

glucose and the formation of HMF become faster with NaCl addition, indicating that NaCl is capable of accelerating the isomerization of glucose to fructose and the dehydration of fructose to HMF, which was further confirmed by the modeling study of fructose dehydration to HMF (Figure 3E,F).

To verify the universality of chlorides, the catalytic performances of various chloride and bromide salts for cellulose conversion were investigated in the THF/H₂O biphase, namely LiCl, NaCl, KCl, NH₄Cl, HCl, LiBr, NaBr and KBr (Table S6). All neutral chlorides and bromides show similar promotion effect with HMF yields ranging from 40.7% to 58.9%, which are significantly higher than those obtained from tests in the blank (16.5%) and acidic NH₄Cl (11.4%), HCl (2.4%) systems (Table S6). In the latter two systems, the main products were unsurprisingly humins (85% and 95%, respectively) as a direct result of the presence of medium-to-strong acid catalysts.

The promotion effect of chloridions on the conversion of cellulose to HMF can be generally achieved at temperatures between 160 and 220 °C (Table S7). Moreover, a positive effect on cellulose conversion and HMF selectivity was observed by increasing NaCl concentration (0-30wt%, Figure S6). The cellulose conversion and HMF yield steadily enhanced from 76 and 16.5% to 99.9 and 58.9%, respectively, with the increase of NaCl concentration from 0 to 30 wt%.

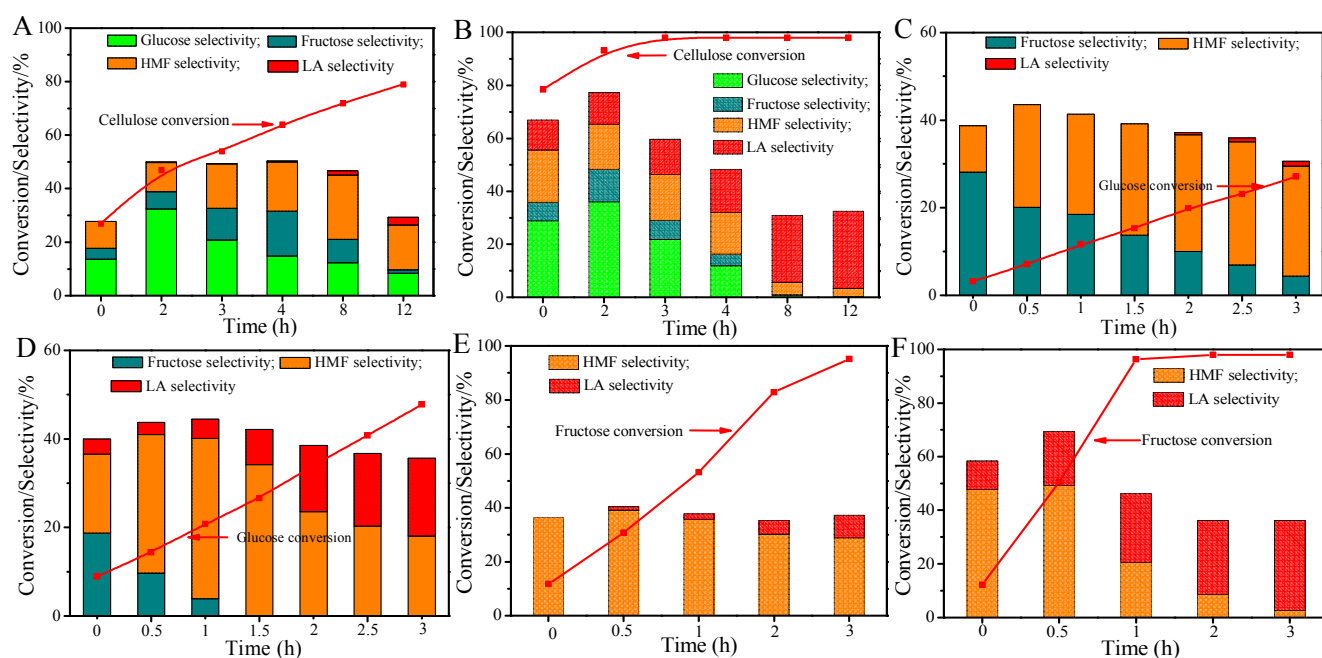


Figure 3. Conversion of cellulose, glucose and fructose in the absence and presence of NaCl. (A)

Cellulose conversion in the absence of NaCl and (B) Cellulose conversion in the presence of NaCl. Reaction condition: 30 wt% NaCl, 5wt% cellulose, 0.5 M N₂, 10 mL H₂O, 200 °C; (C) Glucose conversion in the absence of NaCl and (D) Glucose conversion in the presence of NaCl. Reaction condition: 30 wt% NaCl, 10wt% glucose, 0.5 M N₂, 10 mL H₂O, 180 °C; (E) Fructose conversion in the absence of NaCl and (F) Fructose conversion in the presence of NaCl. Reaction condition: 30 wt% NaCl, 10wt% glucose, 0.5 M N₂, 10 mL H₂O, 180 °C.

To rule out the presence of unique activity of THF, three other biphases [*i.e.*, methyl isobutyl ketone (MIBK)/H₂O, γ -valerolactone (GVL)/H₂O and 2-*sec*-butylphenol (SBP)/H₂O] were tested for this reaction (Figure 4). Without NaCl, reactions in all three systems gave poor yields of HMF (<16.5%) with excessive production of humins. Upon adding NaCl, the HMF yield increased significantly (over 43.5%) in all systems, confirming the absence of unique activity of THF and the general applicability of the promotion effect of NaCl. Indeed, the THF/H₂O and GVL/H₂O systems show HMF yields of 58.9% and 50.4%, respectively, owing to the enhanced partitioning effect of THF and GVL to HMF in the biphases.^{28,38,39}

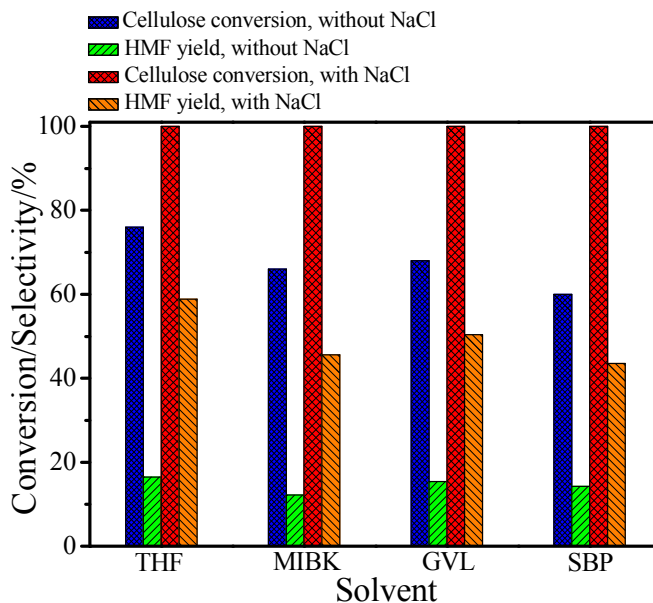


Figure 4. Promotion effects of NaCl for the conversion of cellulose to HMF in various solvents.

Reaction condition: 5wt% cellulose, 30wt% NaCl, 0.5M N₂, 1mL H₂O, 6mL solvents, 200 °C, 8 h.

Reaction mechanism and theoretical studies. It is likely that a small amount of H_3O^+ ions formed *in situ* in hot water (200 °C) act as weak Brønsted acids to promote the hydrolysis of cellulose to glucose.⁴⁰ We sought to understand the molecular details of the subsequent two-step conversion of glucose to HMF (*i.e.*, glucose isomerization to fructose and fructose dehydration to HMF) catalyzed by the chloridions by DFT calculations. Three possible pathways (**I**, **II** and **III**) for glucose isomerization were examined, and **I** was preferred both thermodynamically and kinetically (Figure 5 and Scheme S1), and therefore was used for the following in-depth analysis. Firstly, the protonation of glucose molecules at the O5 position is thermodynamically favored to give **I1** with an energy reduction of $-11.3 \text{ kJ mol}^{-1}$ (Table S8). Then **I1** undergoes a ring-opening reaction to give the most stable intermediate **I2**. **I3** is generated *via* intramolecular hydrogen transfer from C2 to C1, which is the rate-determining step with an activation energy (E_a) of 56.4 kJ in the absence of Cl^- ions (Figure 5). In contrast, upon adding Cl^- to the system, a unique chelation between chloride ions and carbohydrate is formed (Scheme S2), inducing a series of conformational changes to minimize the system energy of the corresponding structures (see supporting information for details). As a result, reactions of ring-opening and H transfer are both promoted significantly, leading to a much decreased E_a for H transfer of 45.6 kJ mol^{-1} . Sequential conformational transitions and deprotonations give rise to the formation of fructose.

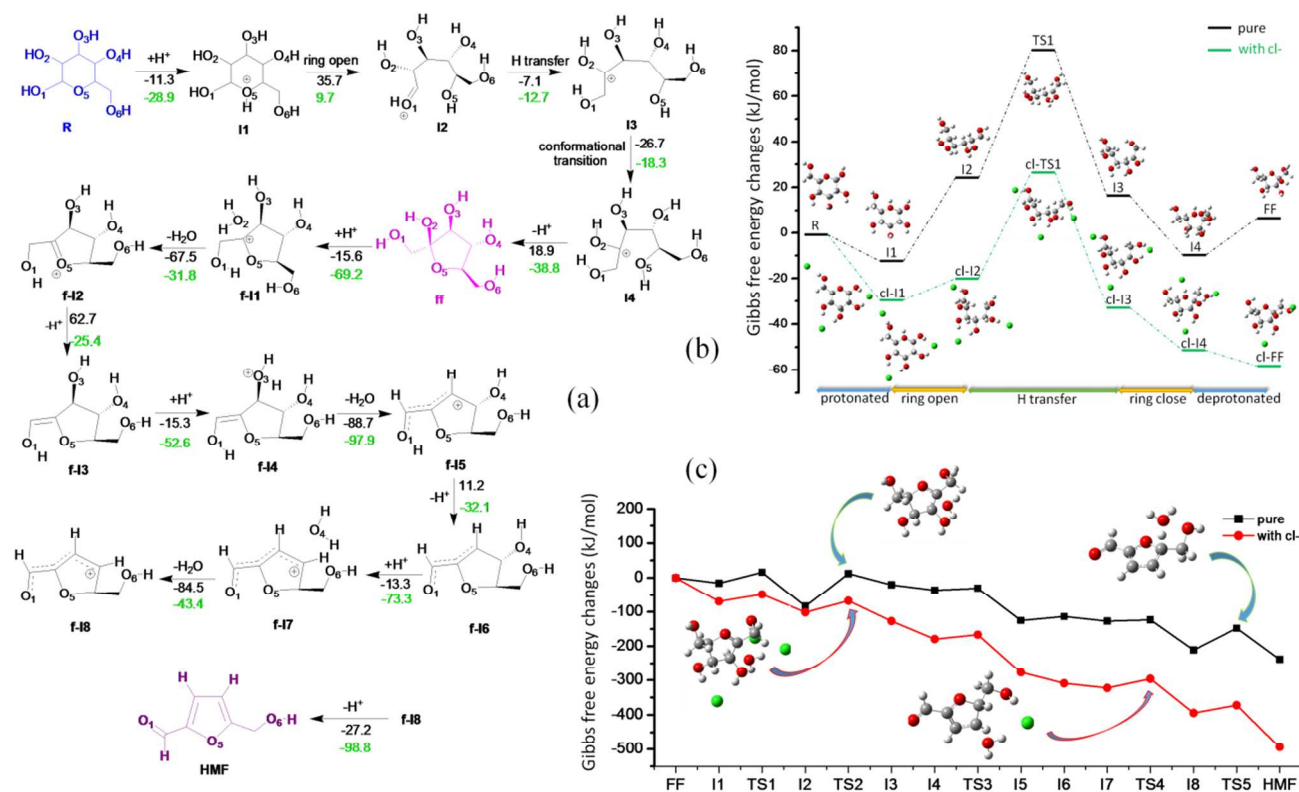


Figure 5. (a) The reaction pathway of the conversion of glucose to HMF. Changes of the free energy along the conversion of glucose to fructose (b) and reaction of fructose to HMF (c) with the corresponding molecular configurations.

An isotope labelling method by ^1H NMR has been used to monitor the transfer of the deuterium atom located at the C2 position of glucose-D2 during the reaction, and importantly, it confirms the above hypothesis of that the isomerization of glucose into fructose primarily proceeds *via* the 1,2-hydride shift mechanism in the presence of the chloridions. As shown in Figure 6, compared to the similar ratio of 1.3:1 and 1.4:1 observed for peaks at $\delta = 3.57$ and 3.45 ppm (both corresponding to the proton bonded to C1 of fructose) from unlabeled fructose and fructose from unlabeled glucose,⁴¹ the ^1H NMR spectrum of fructose from D2-glucose shows a much higher ratio of 5.8:1 for peaks at $\delta = 3.57$ and 3.45 ppm. This observation suggests that the majority of D-atoms located at the C2 position of D2-glucose have transferred to the C1 position upon the reaction in the presence of NaCl, thus confirming that the isomerization of glucose to fructose primarily proceeds *via* the 1,2-hydride shift mechanism in the

presence of Cl^- , instead via a proton-transfer mechanism. Interestingly, a considerable kinetic isotopic effect was observed: an approximate two-fold decrease in the initial reaction rate ($k_{\text{H}}/k_{\text{D}} = 1.87$, Figure S7) occurred owing to the deuteration at the C2 position, consistent with the nature of this rate-determining step.

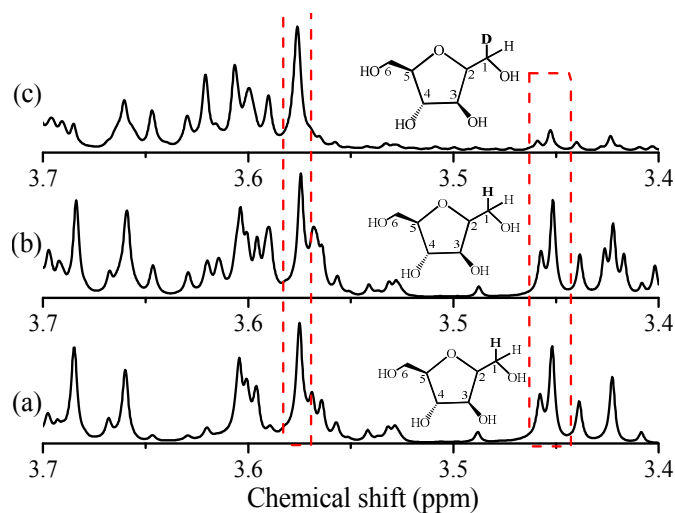


Figure 6. ^1H NMR spectra for fructose from (a) a mixture of D2-glucose and unlabeled fructose, (b) the sugar fraction after reaction in NaCl solution from unlabeled glucose and from D2-glucose (c).

The product HMF is subsequently generated through protonation, dehydration and deprotonation of fructose (Figure 5a).^{8,42} Introducing Cl^- enables the chelation with carbohydrates during these processes, thus accelerating associated protonation steps, but slightly raising the Gibbs free energy on dehydration. Nevertheless, ΔG for each dehydration step remains markedly negative and therefore the entire pathway is not altered fundamentally comparing to that without NaCl. More importantly, the deprotonation is vastly promoted *via* releasing hydrogen with the assistance of chloride ions. Therefore, the overall conversion of fructose to HMF is notably accelerated in the presence of chloride ions, highly consistent with the experimental observations.

CONCLUSIONS

State-of-the-art conversions of cellulose to HMF mostly adopt strong reliance on the use of dual-acid catalysts, which not only catalyze the formation of undesired humins but also bring potential

environmental impacts for the mass production. The present study revises the conventional reliance on acid catalysts and reports a simple, efficient and economically-attractive catalytic system based upon seawater without externally-added acids for the conversion of cellulose to HMF with both high HMF yields and system durability. The role of NaCl in seawater is two-fold: driving the phase separation and more importantly, promoting the hydrolysis of cellulose, isomerization of glucose and dehydration of fructose in a highly selective manner. We also demonstrate that this new system is capable of converting raw lignocellulosic biomass to furfural and HMF and provides a highly industrially-promising pathway for the direct production of valuable platform chemicals from renewable biomass.

ASSOCIATED CONTENT

Supporting Information

7 Figures, 2 schemes and 7 tables are available as supporting information on the web.

AUTHOR INFORMATION

Corresponding Author

Sihai.Yang@manchester.ac.uk; wangyanqin@ecust.edu.cn

AUTHOR CONTRIBUTIONS

X.C.L., K.H.P., X.H.L. and Q.N.X. conducted the experiments. Y.Y.Z. used DFT calculations. Y.Q.W. conceived the overall direction of the project. X.C.L., S.H.Y. and Y.Q.W. designed the experiments and wrote the paper.

ACKNOWLEDGMENT

This work was supported financially by the NSFC of China (No. 91545103, 21603072 and 21403065), the Science and Technology Commission of Shanghai Municipality (10dz2220500), EPSRC (EP/P011632/1) and the University of Manchester for funding.

REFERENCES

- (1) Zhao, H. B.; Holladay, J.; Brown, E. H.; Zhang, Z. C. Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural. *Science* 2007, 316, 1597-1600. (DOI: 10.1126/science.1141199)
- (2) Van Putten, R. J.; van der Waal, J. C.; de Jong, E.; Rasendra, C. B.; Heeres, H. J.; de Vries, J. G. Hydroxymethylfurfural, a versatile platform chemical made from renewable resources. *Chem. Rev.* **2013**, 113, 1499-1597. (DOI: 10.1021/cr300182k)
- (3) Rosatella, A. A.; Simeonov, S. P.; Frade, R. F. M.; Afonso, C. A. M. 5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications. *Green Chem.* **2011**, 13, 754-793. (DOI: 10.1039/C0GC00401D)
- (4) Klemm, D.; Heublein, B.; Fink, H. P.; Bohn, A. Cellulose: fascinating biopolymer and sustainable raw material. *Angew. Chem. Int. Ed.* **2005**, 44, 3358-3393. (DOI: 10.1002/anie.200460587)
- (5) Zhang, Z. R.; Song, J. L.; Han, B. X. Catalytic Transformation of lignocellulose into chemicals and fuel products in ionic liquids. *Chem. Rev.* **2017**, 117, 6834-6880. (DOI: 10.1021/acs.chemrev.6b00457)
- (6) Wang, T. F.; Nolte, M. W.; Shanks, B. H. Catalytic dehydration of C6 carbohydrates for the production of hydroxymethylfurfural (HMF) as a versatile platform chemical. *Green Chem.* **2014**, 16, 548-572. (DOI: 10.1039/C3GC41365A)
- (7) Xue, Z. M.; Ma, M. G.; Li, Z. H.; Mu, T. C. Advances in the conversion of glucose and cellulose to 5-hydroxymethylfurfural over heterogeneous catalysts. *RSC Adv.* **2016**, 6, 98874-98892. (DOI: 10.1039/C6RA20547J)

- (8) Binder, J. B.; Raines, R. T. Simple chemical transformation of lignocellulosic biomass into furans for fuels and chemicals. *J. Am. Chem. Soc.* **2009**, *131*, 1979-1985. (DOI: 10.1021/ja808537j)
- (9) Dutta, S.; De, S.; Imteyaz Alam, M.; Abu-Omar, M. M.; Saha, B. Direct conversion of cellulose and lignocellulosic biomass into chemicals and biofuel with metal chloride catalysts. *J. Catal.* **2012**, *288*, 8-15. (DOI: 10.1016/j.jcat.2011.12.017)
- (10) Yang, Y.; Hu, C. W.; Abu-Omar, M. M. Conversion of carbohydrates and lignocellulosic biomass into 5-hydroxymethylfurfural using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ catalyst in a biphasic solvent system. *Green Chem.* **2012**, *14*, 509-513. (DOI: 10.1039/C1GC15972K)
- (11) Nandiwale, K. Y.; Galande, N. D.; Thakur, P.; Sawant, S. D.; Zambre, V. P.; Bokade, V. V. One-pot synthesis of 5-Hydroxymethylfurfural by cellulose hydrolysis over highly active bimodal micro/mesoporous H-ZSM-5 catalyst. *ACS Sustainable Chem. Eng.* **2014**, *2*, 1928-1932. (DOI: 10.1021/sc500270z)
- (12) Choudhary, V.; Mushrif, S. H.; Ho, C.; Anderko, A.; Nikolakis, V.; Marinkovic, N. S.; Frenkel, A. I.; Sandler, S. I.; Vlachos, D. G. Insights into the interplay of Lewis and Brønsted acid catalysts in glucose and fructose conversion to 5-(hydroxymethyl)furfural and levulinic acid in aqueous media. *J. Am. Chem. Soc.* **2013**, *135*, 3997-4006. (DOI: 10.1021/ja3122763)
- (13) Ordonsky, V. V.; Sushkevich, V. L.; Schouten, J. C.; van der Schaaf, J.; Nijhuis, T. A. Glucose dehydration to 5-hydroxymethylfurfural over phosphate catalysts. *J. Catal.* **2013**, *300*, 37-46. (DOI: 10.1016/j.jcat.2012.12.028)
- (14) Zhang, Y.; Wang, J. J.; Li, X. C.; Liu, X. H.; Xia, Y. J.; Hu, B. C.; Lu, G. Z.; Wang, Y. Q. Direct conversion of biomass-derived carbohydrates to 5-hydroxymethylfurfural over water-tolerant niobium-based catalysts. *Fuel*. **2015**, *139*, 301-307. (DOI: 10.1016/j.fuel.2014.08.047)

- (15) Li, X. C.; Peng, K. H.; Liu, X. H.; Xia, Q. N.; Wang, Y. Q. Comprehensive understanding of the role of Brønsted and Lewis acid sites in glucose conversion into 5-hydroxymethylfurfural. *ChemCatchem*. **2017**, *9*, 2739-2746. (DOI: 10.1002/cctc.201601203)
- (16) Atanda, L.; Shrotri, A.; Mukundan, S.; Ma, Q.; Konarova, M.; Beltramini, J. Direct production of 5-hydroxymethylfurfural via catalytic conversion of simple and complex Sugars over phosphated TiO₂. *ChemSusChem* **2015**, *8*, 2907-2916. (DOI: 10.1002/cssc.201500395)
- (17) Atanda, L.; Konarova, M.; Ma, Q.; Mukundan, S.; Shrotri, A.; Beltramini, J. High yield conversion of cellulosic biomass into 5-hydroxymethylfurfural and a study of the reaction kinetics of cellulose to HMF conversion in a biphasic system. *Catal. Sci. Technol.*, **2016**, *6*, 6257-6266. (DOI: 10.1039/C6CY00820H)
- (18) Zhang, Y.; Wang, J.; Ren, J.; Liu, X.; Li, X.; Xia, Y.; Lu, G.; Wang, Y. Mesoporous niobium phosphate: an excellent solid acid for the dehydration of fructose to 5-hydroxymethylfurfural in water. *Catal. Sci. Technol.* **2012**, *2*, 2485-2491. (DOI: 10.1039/C2CY20204B)
- (19) Ding, D. Q.; Wang, J. J.; Xu, J. X.; Liu, X. H.; Lu, G. Z.; Wang, Y. Q. High-yield production of levulinic acid from cellulose and its upgrading to γ -valerolactone. *Green Chem.* **2014**, *16*, 3864-3853. (DOI: 10.1039/c4gc00737a)
- (20) Ordonsky, V. V.; Sushkevich, V. L.; Schouten, J. C.; van der Schaaf, J.; Nijhuis, T. A. Glucose dehydration to 5-hydroxymethylfurfural over phosphate catalysts. *J. Catal.* **2013**, *300*, 37-46. (DOI: 10.1016/j.jcat.2012.12.028)
- (21) Becke, A. D. A new mixing of Hartree-Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98*, 1372-1377. (DOI: 10.1063/1.464304)
- (22) Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M. Li, X., Hratchian,

H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, Vreven, Jr, H. T., Montgomery, J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A. Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C. Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, Ö., Foresman, J. B., Ortiz, J. V., Cioslowski, J., Fox, D. J. G. Gaussian 09 (Gaussian Inc: Wallingford CT, 2009).

(23) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B.* **2009**, *113*, 6378-6396. (DOI: 10.1021/jp810292n)

(24) Yang, G.; Pidko, E. A.; Hensen, E. J. M. Mechanism of Brønsted acid-catalyzed conversion of carbohydrates. *J. Catal.* **2012**, *295*, 122-132. (DOI: 10.1016/j.jcat.2012.08.002)

(25) Qi, X. H.; Watanabe, M.; Aida, T. M.; Smith, Jr, R. L. Fast transformation of glucose and di-/polysaccharides into 5-hydroxymethylfurfural by microwave heating in an ionic liquid/catalyst system. *ChemSusChem.* **2010**, *3*, 1071-1077. (DOI: 10.1002/cssc.201000124)

(26) Su, Y.; Brown, H. M.; Huang, X. W.; Zhou, X. D.; Amonette, J. E.; Zhang, Z. C. Zhang. Single step conversion of cellulose to 5-hydroxymethylfurfural (HMF), a versatile platform chemical. *Appl. Catal. A.* **2009**, *361*, 117-122. (DOI: 10.1016/j.apcata.2009.04.002)

(27) Wang, J. J.; Liu, X. H.; Hu, B. C.; Lu, G. Z.; Wang, Y. Q. Efficient catalytic conversion of lignocellulosic biomass into renewable liquid biofuels via furan derivatives. *RSC Adv.* **2014**, *4*, 31101-31107. (DOI: 10.1039/C4RA04900D)

- (28) Cai, C. M.; Nagane, N.; Kumar, R.; Wyman, C. E. Coupling metal halides with a co-solvent to produce furfural and 5-HMF at high yields directly from lignocellulosic biomass as an integrated biofuels strategy. *Green Chem.* **2014**, *16*, 3819-3829. (DOI: 10.1039/C4GC00747F)
- (29) Xia, Q. N.; Chen, Z. J.; Shao, Y.; Gong, X. Q.; Wang, H. F. Liu, X. H. Parker, S. F.; Han, X.; Yang, S. H.; Wang, Y. Q. Direct hydrodeoxygenation of raw woody biomass into liquid alkanes. *Nat. Commun.* **2016**, *7*, 11162. (DOI: 10.1038/ncomms11162)
- (30) Shuai, L.; Amiri, M. T.; Questell-Santiago, Y. M.; Héroguel, F.; Li, Y. D.; Kim, H.; Meilan, R.; Chapple, C.; Ralph, J.; Luterbacher, J. S. Formaldehyde stabilization facilitates lignin monomer production during biomass depolymerization. *Science* **2016**, *354*, 329-333. (DOI: 10.1126/science.aaf7810)
- (31) Rasrendra, C. B.; Makertihartha, I. G. B. N.; Adisasmito, S.; Heeres, H. J. Green chemicals from d-glucose: systematic studies on catalytic effects of inorganic salts on the chemo-selectivity and yield in aqueous solutions. *Top Catal.* **2010**, *53*, 1241-1247. (DOI: 10.1007/s11244-010-9570-0)
- (32) Pagán-Torres, Y. J.; Wang, T. F.; Gallo, J. M. R.; Shanks, B. H.; Demesic, J. A. Production of 5-hydroxymethylfurfural from glucose using a combination of Lewis and Brønsted acid catalysts in water in a biphasic reactor with an alkylphenol solvent. *ACS Catal.* **2012**, *2*, 930-934. (DOI: 10.1021/cs300192z)
- (33) Hu, S. Q.; Zhang, Z. F.; Song, J. L.; Zhou, Y. X.; Han, B. Xing. Efficient conversion of glucose into 5-hydroxymethylfurfural catalyzed by a common Lewis acid SnCl₄ in an ionic liquid. *Green Chem.* **2009**, *11*, 1746-1749. (DOI: 10.1039/B914601F)
- (34) Marcotullio, G.; De Jong, W. Chloride ions enhance furfural formation from D-xylose in dilute aqueous acidic solutions. *Green Chem.* **2010**, *12*, 1739-1746. (DOI: 10.1039/B927424C)

- (35) Tang, J. Q.; Zhu, L. F.; Dai, J. H.; Guo, X. W.; Hu, C. W. Insights into the kinetics and reaction network of Aluminum Chloride-catalyzed conversion of glucose in NaCl-H₂O/THF biphasic system. *ACS Catal.* **2017**, *7*, 256-266. (DOI: 10.1021/acscatal.6b02515)
- (36) Chave, K. E. Chemical reactions and the composition of sea water. *J. Chem. Edu.* **1971**, *48*, 148-151. (DOI: 10.1021/ed048p148)
- (37) Jiang, Z. C.; Yi, J.; Li, J. M.; He, T.; Hu, C. W. Promoting effect of sodium chloride on the solubilization and depolymerization of cellulose from raw biomass materials in water. *ChemSusChem* **2015**, *8*, 1901-1907. (DOI: 10.1002/cssc.201500158)
- (38) Gallo, J. M. R.; Alonso, D. M.; Mellmer, M. A.; Dumesic, J. A. Production and upgrading of 5-hydroxymethylfurfural using heterogeneous catalysts and biomass-derived solvents. *Green Chem.* **2013**, *15*, 85-90. (DOI: 10.1039/C2GC36536G)
- (39) Weingarten, R.; Rodriguez-Beuerman, A.; Cao, F.; Luterbacher, J. S.; Alonso, D. M.; Dumesic, J. A.; Huber, G. W. Selective conversion of cellulose to hydroxymethylfurfural in polar aprotic solvents. *ChemCatChem* **2014**, *6*, 2229-2234. (DOI: 10.1002/cctc.201402299)
- (40) Luo, C.; Wang, S.; Liu, H. C. Cellulose Conversion into polyols catalyzed by reversibly formed acids and supported ruthenium clusters in hot water. *Angew. Chem. Int. Ed.* **2007**, *46*, 7636-7639. (DOI: 10.1002/anie.200702661)
- (41) Barclay, T.; Ginic-Markovic, M.; Johnston, M. R.; Cooper, P.; Petrovsky, N. Observation of the keto tautomer of d-fructose in D₂O using ¹H NMR spectroscopy. *Carbohydr. Res.* **2012**, *347*, 136-141. (DOI: 10.1016/j.carres.2011.11.003)
- (42) Akien, G. R.; Qi, L.; Horváth, I. T. Molecular mapping of the acid catalysed dehydration of fructose. *Chem. Commun.* **2012**, *48*, 5850-5852. (DOI: 10.1039/C2CC31689G)

TABLE OF CONTENTS GRAPHICS (TOC)

Synopsis: This work demonstrates an acid-free conversion of cellulose into HMF in a biphasic system of tetrahydrofuran/concentrated seawater. Chloride ions not only catalyses the hydrolysis of cellulose, as well as the isomerization of glucose and dehydration of fructose.

