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Conversion of carbohydrates into 5-hydroxymethylfurfural in an advanced single-phase reaction system consisting of water and 1,2-dimethoxyethane

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5-Hydroxymethylfurfural (HMF) is a bio-based platform chemical that may be converted into various chemicals and fuels. In the present study, we developed an advanced low-boiling single-phase reaction system for producing HMF from glucose. It consists of water and 1,2-dimethoxyethane (DMOE) and uses $AlCl_3$ as catalyst. Our results show that introduction of DMOE can substantially enhance HMF production because of the polar aprotic solvent effect provided by DMOE. Under optimal conditions, a high HMF yield (58.56%) was obtained. GC-MS of the liquid-phase products revealed that HMF and furans comprised 80% and ~90% of the detected products. Formation of liquid-phase products, including furans, oxygenated aliphatics, cyclopenten-1-ones, and pyrans is discussed. Further study of the humins formed during glucose conversion showed the effective inhibition of humin formation by DMOE. The structure of humins was characterized by FTIR spectroscopy. Finally, HMF production from disaccharides (sucrose, maltose and cellobiose) and polysaccharide (cellulose) using the water–DMOE system resulted in good yields, demonstrating that our single-phase water–DMOE solvent system has good potential use in HMF production from glucose and complex carbohydrates.

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Introduction

Biomass, the only renewable carbon resource that can be converted to chemicals and liquid fuels, is a highly significant substitute for fossil resources.[1,2] 5-Hydroxymethylfurfural (HMF), a dehydration product of C_6 carbohydrates, is one of the 10 most value-added bio-based platform chemicals, as it can be used in the synthesis of chemicals and liquid fuels.[3,4] Therefore, the efficient and economical conversion of carbohydrates to HMF is crucial to biomass utilization. Production of HMF using fructose as feedstock has high yield, but the limited sources and high price of fructose restrict the large-scale application of this process.[5] Compared with fructose, glucose is the more abundant monosaccharide in nature and is inexpensive.[6]

HMF production from glucose mainly comprises two steps, namely, isomerization of glucose to fructose and dehydration of fructose to HMF.[7] Isomerization may be catalyzed by a Lewis acid, and dehydration is usually catalyzed by a Brønsted acid.[8] Thus, combining a Lewis acid and a Brønsted acid is an important strategy in the catalytic conversion of glucose to HMF.[8] Metal chlorides such as $CrCl_3$, $SnCl_4$, $CrCl_2$, and $AlCl_3$ have been proven to be high-performance catalysts for HMF production from glucose.[8,9] In aqueous medium, they dissociate to form metal-complex ions and hydrogen ions. Metal-complex ions behave as Lewis acids and promote the isomerization reaction, while hydrogen ions behave as a Brønsted acid, which catalyzes the dehydration reaction.[10] Among the metal chlorides, $AlCl_3$ holds promise in industrial applications because of its low cost and low toxicity.

The reaction medium is one of the main factors that affect HMF production. A good solvent favors not only a high HMF yield, but also facilitates product separation and solvent circulation.[11] Water, a green solvent, is cheap and readily available. However, HMF easily rehydrates into levulinic acid (LA) in aqueous systems, leading to a decrease in the HMF yield.[12] To overcome this problem, a single-phase system consisting of an aprotic polar organic solvent (such as *N*,*N*-dimethylacetamide (DMA), *N*,*N*-dimethylformamide (DMF), and dimethylsulfoxide (DMSO)) and a biphasic solvent system (such as water–methyl isobutyl ketone (MIBK), water–tetrahydrofuran (THF), and water–2-*sec*-butylphenol) was used as reaction media. Both media can markedly increase the HMF yield.[5] For example, Liu *et al.*[13] reported that the HMF yield from glucose in DMF and DMA in the presence of $CrCl_2$ catalyst reached 49.7% and 56.7%, respectively. When De *et al.*[14] performed microwave-assisted glucose dehydration in DMSO solvent and in

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a water–MIBK biphasic system using $AlCl_3$ catalyst, they obtained HMF yields of 52% and 43%, respectively. Yang *et al.*[15] obtained a HMF yield of 61% from glucose in a biphasic water–THF system using $AlCl_3$ as catalyst and NaCl as additive. Pagan-Torres *et al.*[9] achieved a HMF yield of 62% in glucose conversion in a water–2-*sec*-butylphenol biphasic system using $AlCl_3$ and HCl as catalysts. However, use of the aforementioned reaction media still has some disadvantages. DMA, DMF, and DMSO have high boiling points, which make product separation difficult.[2] Biphasic solvent systems require a large amount of organic solvent for extraction, and additional salt such as NaCl is usually necessary to increase extraction efficiency, making the reaction system complex and energy-intensive.[5] In 2007, Zhao *et al.*[16] obtained ~70% HMF yield in glucose conversion using the ionic liquid 1-ethyl-3-methyl-imidazolium chloride as solvent and $CrCl_2$ as catalyst. This high yield has drawn interest in the use of ionic liquids in HMF production and has led to its further improvement.[5] However, the high price of ionic liquids and the difficulty of HMF separation from ionic liquids due to their high viscosity and high boiling point prevent the extensive application of ionic liquids.[5] Recently, Liu *et al.*[17] obtained a HMF yield of 68% from fructose conversion in isopropanol using NH_4Cl as catalyst. When Gallo *et al.*[18] adopted a single-phase system consisting of water and THF (1 : 9 w/w) for glucose conversion, they achieved 50.4% HMF yield in the presence of $AlCl_3$ and HCl. These important results suggest that a single-phase reaction system based on a low-boiling-point green solvent has strong potential use in large-scale HMF production.[11]

In the present study, we developed a single-phase reaction system for HMF production. It is composed of water and 1,2-dimethoxyethane (DMOE) solvent and uses $AlCl_3$ as catalyst. DMOE is a polar aprotic organic solvent with low boiling point (84.6 °C) and has good solubility in water. Therefore, the water–DMOE solvent system can significantly decrease the cost of product separation. In addition, DMOE is recognized as a renewable solvent because it can be synthesized from bio-based ethylene glycol.[19] We first focused on the conversion of glucose to HMF in this reaction system. Specifically, we investigated the effects of the water/DMOE ratio, reaction temperature, reaction time, catalyst dosage and glucose load to optimize the reaction conditions for HMF production. We also analyzed the liquid-phase products and polymers formed under optimum conditions by gas chromatography-mass spectrometry (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR), respectively. Finally, the conversion of disaccharides and polysaccharide to HMF in the single-phase reaction system was analyzed.

Experimental

Materials

Glucose, sucrose, maltose, cellobiose, microcrystalline cellulose, DMOE, HMF, and LA were purchased from Aladdin Industrial Corporation. $AlCl_3 \cdot 6H_2O$ was purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and were used without further purification.

Procedure for conversion of carbohydrates into HMF

A Parr reactor (Parr Instrument, 100 mL) was charged with a mixture of 10 mmol sugar (glucose, sucrose, maltose, cellobiose, or cellulose) based on monosaccharide units, 50 mL H_2O–DMOE at a specified volume ratio (1 : 0, 1 : 1, 1 : 2, 1 : 4 and 0 : 1), and a specified amount of the catalyst $AlCl_3 \cdot 6H_2O$ (0.25 mmol to 2.5 mmol). The reactions were carried out under mechanical agitation in a N_2 atmosphere, and the stirring rate was maintained at 300 rpm. After the preset reaction temperature and time were reached, heating was stopped and the reactor was cooled by air flow. Samples were filtered through a 0.22 μm syringe filter prior to high performance liquid chromatography (HPLC) and GCMS analyses.

Analytical methods

The filtered samples were analyzed on a Dionex HPLC system equipped with a Bio-Rad Aminex HPX-87H column and an RI 2000 refractive index detector. A H_2SO_4 solution (pH 2.5) was used as the mobile phase. The flow rate and column temperature were kept at 0.6 mL min^{-1} and 60 °C, respectively. The concentrations of glucose, HMF, and LA were determined by comparison against standard calibration curves. The conversion of glucose, as well as the yields of HMF and LA were calculated as follows:

$$\text{Glucose conversion} = \frac{\text{moles of glucose reacted}}{\text{moles of starting glucose}} \times 100\%$$

$$\text{Fructose yield} = \frac{\text{moles of fructose produced}}{\text{moles of starting glucose}} \times 100\%$$

$$\text{HMF yield} = \frac{\text{moles of HMF produced}}{\text{moles of starting glucose or hexoses}} \times 100\%$$

$$\text{LA yield} = \frac{\text{moles of LA produced}}{\text{moles of starting glucose or hexoses}} \times 100\%$$

In order to understand the process of glucose decomposition, the filtered samples were also analyzed by GC-MS (Thermo Scientific, Trace DSQII) equipped with a DB-wax capillary column (30 m × 0.25 mm × 0.25 μm). Helium (99.999%) at a flow rate of 1 mL min^{-1} was used as carrier gas. The GC oven temperature was programmed to increase from 40 °C (1 min) to 240 °C (20 min) at 8 °C min^{-1} heating rate. The mass spectrometer was operated in electron ionization mode at 70 eV ion-source electron energy. The scanning m/z ratio ranged from 35 to 450. All detected chemicals were identified by comparison with the NIST (National Institute of Standards) MS library.

Humins isolation and analyses

Insoluble and soluble polymeric humins of the glucose conversion process were obtained as follows. After reaction, the samples were filtered through a 0.22 μm organic filter

membrane to obtain the insoluble residue. The remaining solid residue after washing with water and DMOE was considered as humin-insoluble. Filtrates were further evaporated under vacuum to remove DMOE, and the precipitate was collected and then washed with deionized water. The obtained solid was considered as humin-soluble. Both humins were dried at 105 °C for 2 h prior to further analyses. The elemental composition of the humins was determined on a Vario Micro elemental analyzer (Elenemtar Analysensysteme GmbH, Germany). FTIR spectra of the humins were recorded from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} on a Nicolet 5700 FTIR spectrometer by averaging 36 scans.

Results and discussion

Conversion of glucose into HMF

Effect of solvent system composition. The effect of solvent system composition on glucose conversion at the reaction temperature of 150 °C in the presence of $AlCl_3$ is depicted in Fig. 1. At a water–DMOE ratio of 1 : 0, the HMF yield was only 16.35% at a glucose conversion of 78.73%. And the yield of fructose was up to 27%, indicating the good efficiency in glucose isomerization catalyzed by $AlCl_3$ in aqueous phase. With the increase in the proportion of DMOE, the glucose conversion and the HMF yield increased markedly, while the yield of fructose decreased drastically. At a water–DMOE ratio of 1 : 4, the glucose conversion was 94.30%, and the HMF and fructose yield reached 48.55% and 0.28%, respectively, suggesting that DMOE favored the isomerization of glucose and subsequent dehydration of fructose to HMF. This increase may be due to the polar aprotic solvent effect provided by DMOE. As the presence of polar aprotic organic solvent can change the sugar tautomerism equilibrium to form more reactive tautomer, thus enhancing the conversion of sugar;[8,20] moreover, dilution effect from DMOE solvent, together with hydrogen-bond interaction between DMOE and HMF, can also prevent HMF from reacting with intermediates to form polymers, or from reacting with water to form LA.[8,21] While in pure DMOE solvent, the HMF yield decreased to 9.13% sharply with a glucose conversion of 92.99% without fructose formation, indicating that the absence of water might alter glucose decomposition route. Similarly, Cao *et al.*[22] performed the glucose dehydration in THF and also found that the HMF yields were 4% and 19% in pure THF and THF with 2.7 wt% water, respectively, proposing that glucose was mainly dehydrated to produce anhydrosugars in pure polar aprotic solvent. Therefore, DMOE with a small amount of water may be more beneficial for selective conversion of glucose to HMF. LA, an important byproducts of hexose decomposition, was easily formed *via* rehydration of HMF catalyzed by Brønsted acid. Zhang *et al.* reported that the methyl carbon of LA was derived from the hydroxymethyl carbon of HMF.[23] As shown in Fig. 1, the LA yield increased slightly with addition of DMOE into water, staying at a low level with a maximum yield of 6.5% at the water–DMOE ratio of 1 : 4.

Effect of reaction temperature. Fig. 2 shows the effect of reaction temperatures of 130 to 170 °C on the dehydration of glucose to HMF. At 130 °C, both the HMF and fructose yield were low (24.29% and 2.88%, respectively), indicating that low temperature hindered the isomerization of glucose to fructose. With the increase in temperature to 150 °C, glucose conversion increased gradually to 93.97%, while the HMF yield increased to a maximum of 48.55%, which then decreased to 39.96% at 170 °C. LA production had the same trend as glucose conversion, reaching 8.34% at 170 °C. These observations indicate that high temperature promoted the conversion of HMF to LA. In their kinetic analysis of LA formation from glucose decomposition in aqueous medium, Weingarten *et al.*[24] found that low temperature favored the rehydration of HMF to LA, in contrast to the results of our study. This difference may be ascribed to the different reaction medium used in glucose decomposition. In the water–DMOE solvent system, high temperature can accelerate water to contact more easily with the formed HMF to

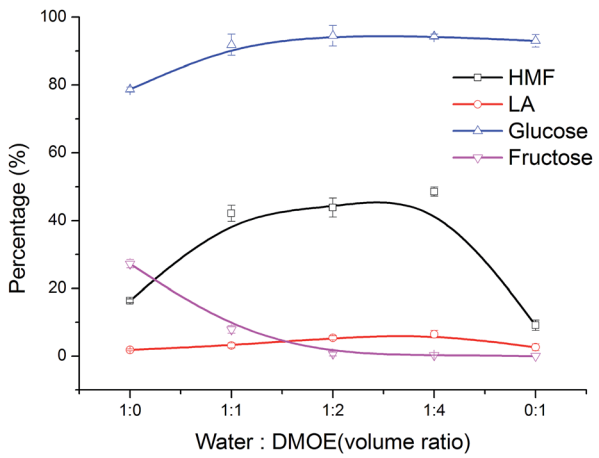

Fig. 1 Effect of water/DMOE ratio on glucose conversion and products formation (reaction condition: 10 mmol glucose, 2.5 mmol $AlCl_3 \cdot 6H_2O$, 50 mL water–DMOE, reaction temperature 150 °C, reaction time 15 min).

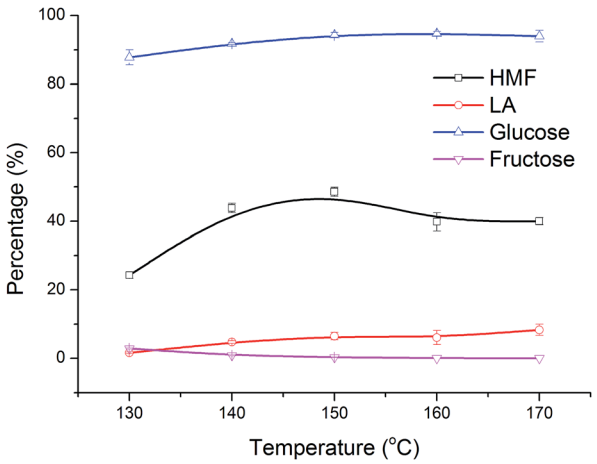

Fig. 2 Effect of reaction temperature on glucose conversion and products formation (reaction condition: 10 mmol glucose, 2.5 mmol $AlCl_3 \cdot 6H_2O$, 50 mL water–DMOE (volume ratio = 1 : 4), reaction time 15 min).

form LA. Therefore, mild reaction conditions are more suitable for HMF production.

Effect of catalyst dosage. In the water–DMOE solvent system, $AlCl_3$ hydrolysis forms the metal-complex ion $[Al(OH)(H_2O)_5]^{2+}$, which behaves as a Lewis acid, and the Brønsted acid hydrogen ion.[14] The $AlCl_3$ dosage may affect hydrolysis equilibrium and may alter levels of active species, thereby influencing product formation.[10] As shown in Fig. 3(a), glucose conversion apparently increased when the $AlCl_3$ dosage increased from 0.25 to 1 mmol; further addition of $AlCl_3$ had negligible impact on the increase in glucose conversion. Notably, extending the reaction time improved glucose conversion to 95% at a reaction time of 60 min. The fructose yield decreased obviously with the adding of $AlCl_3$, inferring that higher catalyst dosage accelerated the conversion of fructose. Fig. 3(b) presents the effect of $AlCl_3$ dosage on HMF and LA production. The HMF yield increased first and then decreased with the addition of $AlCl_3$; maximum yields of HMF corresponding to $AlCl_3$ dosages of 0.25, 0.5, 1, and 2.5 mmol were 48.96%, 58.56%, 57.07%, and 48.55%, respectively. The reaction time needed to reach the maximum yield shortened from 45 to 15 min. Higher $AlCl_3$ dosage (2.5 mmol) enhanced the yield of LA to >6.5%. The reason for the opposing trends in HMF and LA formation at high catalyst dosage is the increase in H^+ concentration due to $AlCl_3$ hydrolysis, which promoted the condensation of HMF and intermediates to polymers and the rehydration of HMF to LA.[25]

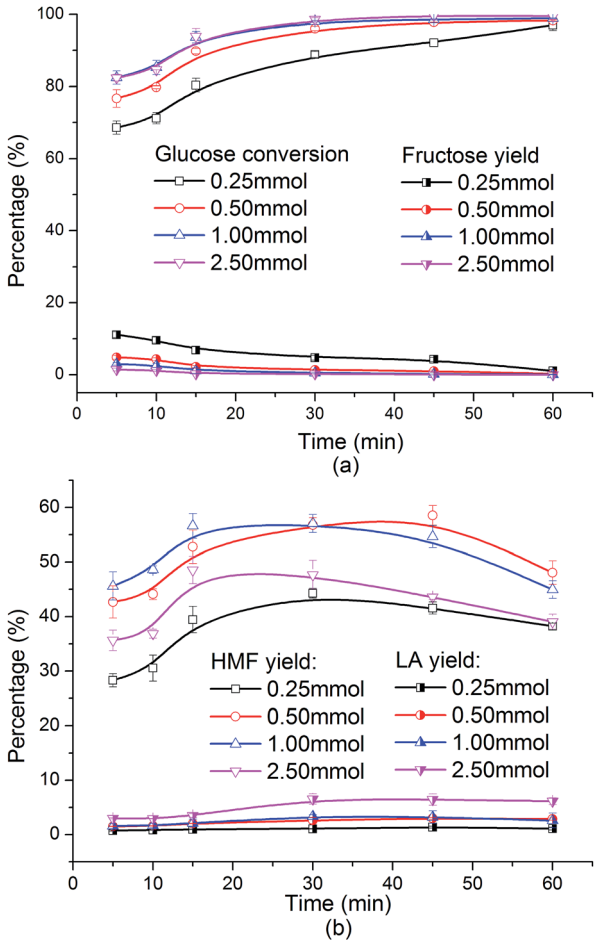

Fig. 3 Effect of $AlCl_3 \cdot 6H_2O$ catalyst dosage on glucose conversion (a) and products formation (b) (reaction condition: 10 mmol glucose, 50 mL water–DMOE (volume ratio = 1 : 4), reaction temperature 150 °C).

Effect of glucose load. As shown in Table 1, with the increase of glucose load, the HMF yields decreased gradually. The HMF yields corresponding to glucose load of 10, 20 and 50 mmol were 58.55%, 50.55% and 39.57%, respectively. This decrease may be due to the side reactions at high glucose concentration. Nevertheless, the HMF yield maintained at a medium level when the glucose load was up 50 mmol, indicating the potential use of this single-phase water–DMOE solvent system for HMF production from glucose.

Glucose decomposition products analyses

Liquid-phase products analysis. To further our understanding of glucose decomposition in the water–DMOE solvent system, we performed GC-MS to analyze the evolution of typical products under optimal conditions for HMF production. As shown in Fig. 4, the decomposition products may be classified into four categories, namely, furans, oxygenated aliphatics, cyclopenten-1-ones, and pyrans. HMF (**1**) was the dominant furan product, comprising >80%, which increased gradually with extended reaction time. Other furans mainly included furfural (**2**), 2-furanmethanol (**3**), 2-(2-hydroxyacetyl)furan (**4**), 5-methylfurfural (**5**), 2-methylfuran (**6**), 5-methyl-2(3*H*)-furanone (**7**), and 2,5-dicarboxaldehydefuran (**8**). Together with HMF, the furans comprised ~90% of the products detected by GC-MS, indicating that the water–DMOE solvent system could promote the formation of furans. In addition to LA (**9**) and formic acid (**10**) formed from the rehydration of HMF, other oxygenated aliphatics composed of glycolaldehyde (**11**), dihydroxyacetone (**12**), acetic acid (**13**), 1,3-propanediol (**14**), and 1,2-propanediol-3-methoxy (**15**) were mainly formed by retro-aldolization of the intermediates.[26–28] Levels of oxygenated aliphatics had low values varied in range of 3–4.5% with prolonged reaction time. Cyclopenten-1-ones mainly consisted of 2-cyclopenten-1-one (**16**), 2-hydroxy-2-cyclopenten-1-one (**17**), and 2-methyl-2-cyclopenten-1-one (**18**). These five-carbon-ring products might have been produced by cyclization of chain intermediates containing multifunctional groups. Their proportion increased from 0.76% to 1.16% with extended reaction time. GC-MS detected two pyrans, namely, levoglucosan (**19**) and 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-

Table 1 Effect of glucose load on HMF yield (reaction conditions: 50 mL water–DMOE (volume ratio = 1 : 4), reaction temperature 150 °C, reaction time 45 min)

Entry	Glucose load (mmol)	Catalyst dosage (mmol)	Glucose conversion (%)	HMF yield (%)	LA yield (%)
1	10	0.5	97.80	58.56	2.99
2	20	0.5	96.60	50.59	2.23
3	50	0.5	96.67	39.57	2.07

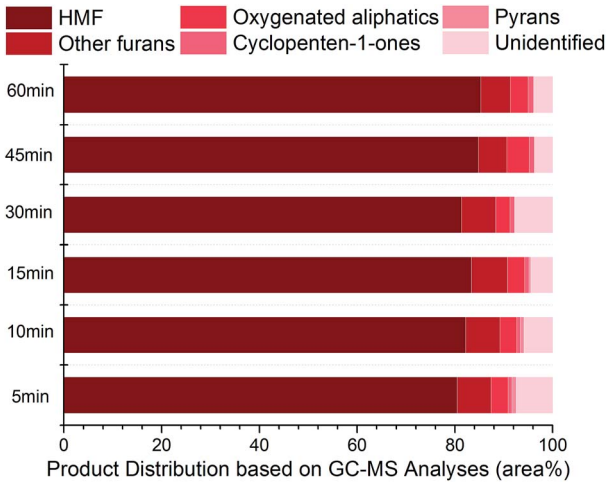

Fig. 4 Products distribution from glucose conversion in water–DMOE solvent system based on GC-MS analysis (reaction condition: 10 mmol glucose, 0.25 mmol $AlCl_3 \cdot 6H_2O$, 50 mL water–DMOE (volume ratio = 1 : 4), reaction temperature 150 °C).

one (DDMP) (**20**). Levoglucosan is a dehydration product of glucose, while DDMP forms from the dehydration and cyclization of enediol intermediates.[27] The proportion of levoglucosan and DDMP decreased to zero at 30 and 60 min, respectively, implying that they could further convert to other products. Levoglucosan can be dehydrated to HMF *via* acid catalysis.[29] Fig. 5 depicts the simplified reaction pathways for products formed from glucose. However, the mechanism related to formation of various products is very complex; much work is still required to reveal them.

Polymeric humins analysis. In the acid-catalyzed conversion of carbohydrates to HMF by liquid-phase reaction, solid polymer humin is the main byproduct. Humin has been reported to have a furanic polymer structure formed by condensation of sugars, HMF, and intermediates.[30] As they are carbonaceous materials, humins have to be structurally characterized for their value-added utilization. For example, humins can be used as feedstock for production of synthesis gas or liquid-fuels through thermal–chemical conversion, which may further improve the market competitiveness of HMF production from carbohydrates.[31,32]

In aqueous medium, acid-catalyzed conversion of glucose can produce >30 wt% insoluble humins;[31] whereas pure organic solvent or a biphasic system may suppress formation of humins or may cause them to dissolve, thereby reducing the effect of insoluble solids on reactor operation.[5] In our water–DMOE solvent system, the amounts of humin-insoluble and humin-soluble byproducts formed under optimal conditions for HMF production were 0.67 and 4.17 wt% (Table 2), suggesting that the water–DMOE solvent system was capable of inhibiting humin formation. Moreover, most of the formed humins (86.16%) could dissolve, implying that our water–DMOE system may be used as an alternative to large-scale production of HMF from glucose.

Elemental compositions of the two humins are presented in Table 2. The carbon content of humin-insoluble and humin-soluble was 52.37 and 58.13 wt%, respectively, which are lower than that of humin (65 wt%)[33] formed in aqueous medium *via* catalysis by H_2SO_4. These results reveal that the dehydration and condensation catalyzed by $AlCl_3$ was much milder than mineral acids (H_2SO_4, HCl, *etc.*). In particular, the carbon and hydrogen content of humin-insoluble was lower than that of humin-soluble, suggesting that formation of humin-insoluble might not have resulted from aggregation and particle growth of humin-soluble. The van Krevelen diagram (Fig. 6) reveals the reactions for the formation of two humins. Humin-insoluble is located in the dehydration line and between

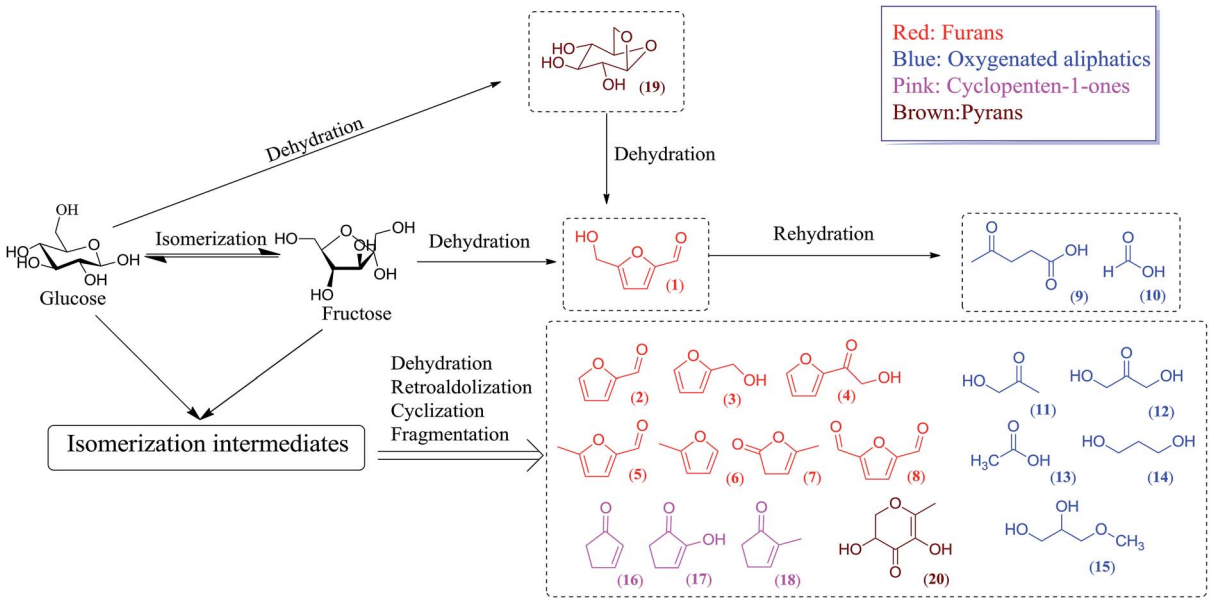

Fig. 5 Liquid-phase products formation pathways for glucose conversion in water–DMOE solvent reaction system.

Table 2 Yields and elemental compositions of the humins formed under optimal conditions (10 mmol glucose, 0.5 mmol $AlCl_3 \cdot 6H_2O$, 50 mL water–DMOE (volume ratio = 1 : 4), reaction temperature 150 °C, reaction time 45 min)

Humin	Yield (wt%)	C (wt%)	H (wt%)	O (wt%)	O/C	H/C
Humin-insoluble	0.67	52.37	5.28	42.35	0.61	1.21
Humin-soluble	4.17	58.13	5.39	36.48	0.47	1.11

glucose and HMF, implying that the humin-insoluble formed by condensation of glucose, HMF, and intermediates, along with formation of water.[30] Humin-soluble is located below the dehydration line and on the right side of HMF, indicating that its formation might involve alkylation or alkyl-chain elongation.[34]

To further illuminate the structural properties of the two humins, we carried out FTIR spectroscopy. As shown in Fig. 7, the two spectra are similar, differing only in absorbance intensity. The broad peaks at 3600–3200 cm^{-1} correspond to O–H strong stretching, thus indicating the existence of hydroxyl groups.[35] Absorptions at 2960–2850 cm^{-1} were due to stretching of methyl and methylene groups,[36] and humin-soluble showed sharper absorptions, indicating the higher content of alkyl group in humin-soluble, which was in line with the above conclusion that formation of humin-soluble may involve alkylation or alkyl-chain elongation. The peak at 1703 cm^{-1} may be attributed to C=O stretching in acids, aldehydes, and ketones.[33] Peaks derived for the substituted furanic rings could be observed in the spectra of the two humins. For example, peaks at 1619 and 1518 cm^{-1} correspond to C=C stretching in furan rings. Peaks at 1395 cm^{-1} and bands at 798 cm^{-1} are respectively ascribed to C–O–C stretching and C–H out-of-plane deformation in furan rings.[30,31] Absorptions at 1022 cm^{-1} and at 1164–1072 cm^{-1} correspond to primary and secondary alcohols, respectively. Humin-soluble showed notable absorption at 1022 cm^{-1}, while humin-insoluble showed sharp absorptions at 1164–1072 cm^{-1}. Considering that HMF contains only primary alcohol while sugars contain both primary and secondary alcohols, we can conclude that the formation of humin-insoluble may incorporate with HMF and glucose, while the formation of humin-soluble may incorporate with HMF. This may be confirmed by the elemental compositions of both humins, which were close to those of glucose and HMF, respectively. In particular, the absence of absorption at 1665 cm^{-1} for the two humins, which corresponds to the aldehyde group in HMF, indicates that humin formation involves aldol addition or condensation reactions that destroy carbonyl groups.[37]

Conversion of disaccharides and polysaccharide into HMF

The conversion of disaccharides (sucrose, maltose, and cellobiose) and polysaccharide (cellulose) to HMF in the single-phase water–DMOE solvent system was examined (Table 3). Under the optimal conditions for HMF production from glucose, the disaccharides sucrose, maltose, and cellobiose had modest HMF yields (36.81%, 35.24%, and 33.51%, respectively). Cellulose had a very low HMF yield (7.15%), which was much lower than that from glucose (58.56%). This difference may be due to the insufficient acidity of the Brønsted acid from $AlCl_3$ leading to inefficient breakage of glucosidic bonds. Cellulose has a stable crystalline structure with strong intramolecular and intermolecular hydrogen bonds, which makes its depolymerization very difficult.[38,39] This stability is confirmed by the large amount of unreacted cellulose remaining after the reaction. To promote the cleavage of glucosidic bonds, the $AlCl_3$ dosage was increased from 0.5 to 2.5 mmol. This increase improved the HMF yields from sucrose, maltose, cellobiose, and cellulose to 44.86%, 40.74%, 41.98%, and 18.89%, respectively, suggesting the positive effect of breaking glucosidic bonds efficiently on the conversion of polysaccharides to HMF. Although the HMF yield from cellulose distinctly increased, it was still low. Therefore, we performed cellulose conversion under more

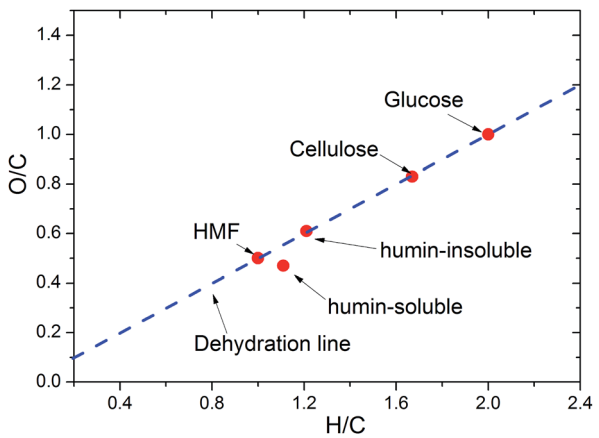

Fig. 6 van Krevelen diagram of humins, HMF, glucose and cellulose.

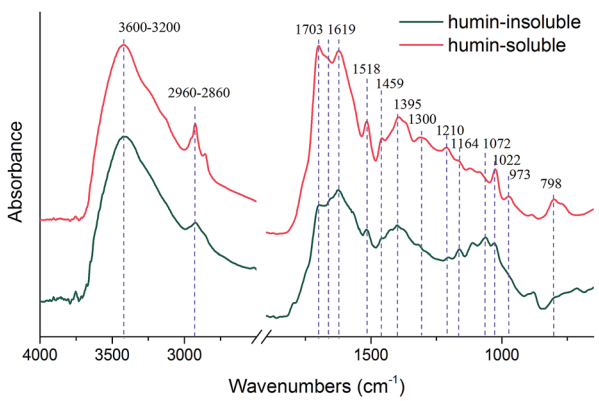

Fig. 7 FTIR spectra of humin-insoluble and humin-soluble.

Table 3 HMF yield from various carbohydrates in water–DMOE solvent reaction system[a]

Entry	Feed	Catalyst/mol%	HMF yield/%
1	Glucose	5	58.56
2	Sucrose	5	36.81
3	Sucrose[b]	25	44.86
4	Maltose	5	35.24
5	Maltose[b]	25	40.74
6	Cellobiose	5	33.51
7	Cellobiose[b]	25	41.98
8	Cellulose	5	7.15
9	Cellulose[b]	25	18.89
10	Cellulose[c]	25	37.73

[a] Reaction conditions: feed load 10 mmol, 50 mL water–DMOE (volume ratio = 1 : 4), reaction temperature 150 °C, reaction time 45 min. [b] Reaction time 15 min. [c] Reaction temperature 170 °C, reaction time 80 min.

severe conditions of increased reaction temperature and extended reaction time (170 °C and 80 min) using 2.5 mmol $AlCl_3$. We thus obtained a satisfactory HMF yield (37.73%). This is comparable to the results for the biphasic reaction system. Yang *et al.*[15] reported a HMF yield of 37% from cellulose in a biphasic water–THF medium using $AlCl_3$ as catalyst and NaCl as additive. Similarly, Shen *et al.*[40] observed a HMF yield of 39.7% when they applied a biphasic water–THF system for cellulose conversion using $InCl_3$ as catalyst and NaCl as additive. Therefore, our single-phase water–DMOE system also has potential use in production of HMF from complex polysaccharides.

Conclusions

We investigated the application of DMOE, a low-boiling polar aprotic organic solvent, in HMF production from carbohydrates. The results show that the HMF yield of a single-phase reaction system of water and DMOE using $AlCl_3$ catalyst increased substantially relative to that of pure water reaction medium with the increase in DMOE proportion because of the polar aprotic solvent effect of DMOE. Under optimal conditions (1 : 4 water–DMOE volume ratio, 5 mol% $AlCl_3 \cdot 6H_2O$ dosage, 150 °C reaction temperature, 45 min reaction time), a significant HMF yield (58.56%) from glucose was obtained. GC-MS of the liquid-phase products showed that the total proportion of HMF and furans respectively comprised 80% and up to 90% of the products detected. In addition to furans, oxygenated aliphatics, cyclopenten-1-ones, and pyrans, were present. Formation of these various products involved many complex reactions, including dehydration, retroaldolization, cyclization, and fragmentation. Analyses of the polymer humins revealed that DMOE inhibited the formation of humins, with yields of 0.67 and 4.17 wt% for humin-insoluble and -soluble byproducts, respectively. On the basis of results for glucose conversion, the reaction system was further optimized for the conversion of disaccharides (sucrose, maltose, and cellobiose) and polysaccharides (cellulose) to achieve a satisfactory HMF yield. The results suggest that our simple single-phase water–DMOE solvent system could be used efficiently and economically in HMF production from carbohydrates.

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