Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides†

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Furan derivatives, such as 5-hydroxymethylfurfural (HMF) and furfural, obtained from renewable biomass-derived carbohydrates have potential to be sustainable substitutes for petroleum-based building blocks used in production of fine chemicals and plastics. We have studied the production of HMF and furfural by dehydration of fructose, glucose and xylose using a biphasic reactor system, comprised of reactive aqueous phase modified with DMSO, combined with an organic extracting phase consisting of a 7 : 3 (w/w) MIBK–2-butanol mixture or dichloromethane (DCM). Experiments with the MIBK–2-butanol mixture were conducted at a temperature of 443 K using mineral acid catalysts (HCl, H_2SO_4 and H_3PO_4) at a pH from 1.0 to 2.0, whereas experiments with DCM as the extracting solvent were conducted at 413 K and did not require the use of an acid catalyst. The modifiable nature of the biphasic system allowed us to identify preferred DMSO and pH levels for each sugar to maximize the HMF selectivity at high sugar conversions, leading to selectivities of 89%, 91%, and 53% for dehydration of fructose, xylose, and glucose, respectively. Using these reaction conditions for each monosaccharide unit, we can process the corresponding polysaccharides, such as sucrose (a disaccharide of glucose and fructose), inulin (a polyfructan), starch (a polyglucan), cellobiose (a glucose dimer) and xylan (a xylose polysaccharide), with equally good selectivities at high conversions. In addition, we show that the biphasic reactor system can process high feed concentrations (10 to 30 wt%) along with excellent recycling ability. By processing these highly functionalized polysaccharides, that are inexpensive and abundantly available, we eliminate the need to obtain simple carbohydrate molecules by acid hydrolysis as a separate processing step.

1. Introduction

Renewable biomass resources have the potential to serve as a sustainable supply of fuels and chemical intermediates (*e.g.* alcohols, aldehydes, acids).[1] The challenge for the effective utilization of these sustainable resources is to develop cost-effective processing methods to transform highly function-alized carbohydrate moieties into value-added chemicals. In this respect, furan derivatives, such as furfural and 5-hydro-xymethylfurfural (HMF), can be produced from renewable biomass resources by acid-catalyzed dehydration of pentoses and hexoses, respectively. These compounds have the potential to be sustainable substitutes for building blocks derived from petrochemicals in the production of plastics and fine chemi-cals.[2] In the present work, we have identified preferred reaction conditions for the production of HMF and furfural in a biphasic reactor system for glucose, fructose and xylose monosaccharide units. Subsequently, we employed these reac-tion conditions to process the corresponding polysaccharides such as sucrose (a disaccharide of glucose and fructose), inulin (a polyfructan), starch (a polyglucan), cellobiose (a glucose dimer), and xylan (a xylose polysaccharide), with equally good

selectivities at high conversions. By processing polysaccharides that are inexpensive and abundantly available, we eliminate the need to obtain monosaccharides in a separate process, thereby moving the technology further toward practical application.

Following the production of HMF, this compound can be converted to 2,5-furandicarboxylic acid (FDCA) by selective oxidation, which can be used as a replacement for terephthalic acid in the production of polyesters (*e.g.* PET and PBT).[3] Because HMF is not yet a high-volume chemical (in view of the current difficulties regarding its cost-effective produc-tion),[4–6] the potential uses of HMF-derived compounds to produce polymers have not been studied in detail. Importantly, however, various research groups have, in fact, reported promising results in this direction.[6,7] For example, reports have shown that polyesters formed from the combination of furanic diacid derivatives and aromatic moieties exhibit excellent thermal stability and resistance to atmospheric oxidation.[7,8] Similarly, it has been suggested that thermally and mechanically stable polyesters can be obtained from the polymerization of 5-furanacrylic esters and also from furanic acid chlorides.[7,9] Furanic polyamides prepared using furan dicarboxylic acid and aromatic diamines show decomposition and glass temperature profiles analogous to those of Kevlar®.[7] Thermoplastic elastomers and foams based on furanic poly-urethanes are already used industrially in multiple applica-tions. It has been reported that furanic polyesters, polyamides,

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and polyurethanes show no difference in degradation when compared to that of the best aliphatic and aromatic counterparts.[7] In addition, disubstituted furan derivatives obtained from HMF serve as an important component of pharmacologically active compounds associated with a wide spectrum of biological activities.[6]

Furfural is a key chemical for the commercial production of furan (through catalytic decarbonylation) and tetrahydrofuran (through hydrogenation), thereby providing a biomass-based alternative to petrochemical production of these compounds by dehydration of 1,4-butanediol.[10] Furfural is primarily used in refining of lubricating oil, and in condensations with formaldehyde, phenol, acetone or urea to yield resins with excellent thermosetting properties and extreme physical strength.[10] Methyl tetrahydrofuran (MeTHF) serves as a principal component for P-series fuel,[11] which is developed primarily from renewable resources. In addition, we have recently shown that HMF and furfural can serve as precursors for production of liquid alkanes (C_7–C_{15}) that serve as diesel fuel components.[12] Indeed, furan derivatives, such as HMF and furfural, obtained from renewable sources have been described in the literature as key compounds that bridge the gap between carbohydrate chemistry and petroleum-based industrial chemistry[13] because of the wide range of chemical intermediates and end-products that can be produced from these compounds for use in the polymer, fuel, and pharmaceutical industries.

2. State of the art

The dehydration of hexoses to form HMF has been conducted in water,[14] aprotic organic solvents (dimethylsulfoxide (DMSO)),[15] and biphasic systems (water/methylisobutylketone (MIBK)),[16,17] using catalysts such as organic acids (oxalic, maleic),[18] inorganic acids (sulfuric, hydrochloric),[18] salts ($MgCl_2$),[19] organocatalysts ($LaCl_3$),[20] and solid acids (ion-exchange resin,[16] VPO_4,[21] zeolites[17]). However, all of these catalytic systems exhibit limitations. First, in pure water, dehydration of fructose is generally non-selective, leading to many byproducts besides HMF.[14] Carlini et al. obtained high HMF selectivities (>80%) from fructose in water using various heterogeneous catalysts at low temperatures (e.g., <370 K), but at low conversion (25–50%).[21,22] Next, biphasic systems used for fructose dehydration, where a water-immiscible organic solvent is added to extract continuously the HMF from the aqueous phase, have shown poor partitioning of HMF into the organic phase, necessitating large amounts of solvent and hence large energy expenditures.[16,17,23] Finally, as various researchers have shown, HMF can be produced in high yields (>90%) from fructose using pure high-boiling organic solvents, such as dimethylsulfoxide (DMSO), and mixtures of polyethyleneglycol (PEG) with water; however, this approach necessitates energy intensive isolation procedures.[15,24–27]

Compared to fructose, glucose is the preferred feed source for the production of HMF, as it is more abundant and readily available. Previous work by various researchers has focused on fructose dehydration to HMF, because fructose dehydration to HMF has higher reaction rates and better selectivity when compared to using glucose as a feed molecule.[4] In pure water,

glucose dehydration to HMF is non-selective (about 6%), leading to formation of insoluble humins.[28] Importantly, while it is possible to achieve high yields of HMF from fructose in DMSO, the yields of HMF from 3 wt% glucose solution are low (about 42%) in this high boiling-point solvent.[26] Recent advances by Bicker et al. in glucose dehydration have shown improved results (~48% HMF selectivity) in water-miscible solvent systems (e.g., acetone–water),[2] but only using low initial carbohydrate concentrations (<3 wt%), which inevitably generate low HMF concentrations. Acid–base mixtures (e.g., H_3PO_4–pyridinium) have been investigated with the purpose of increasing the HMF yields from glucose in a water–dioxane mixture; however, this system led to complicated product mixtures containing furans, pyrroles, and pyridines.[4] Limited work on HMF production using polysaccharides such as inulin (a polyfructan) and sucrose (a dimer of glucose and fructose molecule) has been reported, and only the fructose part of the sucrose molecule is processed leaving behind unconverted glucose.[22]

In addition to the use of glucose and fructose to make HMF, researchers have studied xylose as a feedstock for the production of furfural. The production of furfural requires raw materials rich in pentosan, such as corncobs, oat hulls, bagasse, and certain woods (like beech).[29] Most furfural production processes employ batch reactors using the Quaker Oats technology with yields less than 50%, requiring large amounts of steam (30 to 50 times the amount of furfural produced) and long reaction times.[29] Various researchers have studied the dehydration of xylose to furfural using acid catalysts, including mineral acids,[30] zeolites,[31] acid-functionalized MCM materials,[32] and heteropolyacids.[33] High yields of furfural, up to 75%, have been obtained with an MCM-41 catalyst modified with sulfonic acid groups in DMSO and water–toluene solvents, however at low initial concentrations of xylose (~3 wt%).[32] Moreau, et al. conducted the dehydration reaction in a batch mode using H-faujasite and H-mordenite catalysts at 443 K and in a solvent mixture of water and MIBK or toluene (1 : 3 by vol.), and they achieved selectivities ranging from 70–96% (in toluene) and 50–60% (in MIBK), but at low xylose conversions.[31]

Although a wide variety of systems exist that use various combinations of solvents and catalysts to produce HMF and furfural from one of the multiple feedstocks, a single system capable of efficiently processing glucose, fructose, and xylose into HMF and furfural is still lacking. We recently developed a biphasic catalytic process for the selective dehydration of fructose to 5-hydroxymethylfurfural (HMF) using aqueous and organic phase modifiers that delivers HMF in a separation-friendly solvent.[34] Unfortunately, the specific reaction conditions that generate good HMF yields (>80%) from fructose achieve low yields from glucose (e.g., 28%), providing further support for the well known behavior that keto-hexoses produce higher yields of HMF compared to aldo-hexoses.[4] However, a strong incentive exists for the development of processes that utilize cheap and abundantly available glucose directly without requiring an additional step of glucose isomerization to fructose. Besides, isomerization of glucose to fructose also necessitates an additional acid hydrolysis step to obtain simple sugars from polysaccharide molecules. In this

work, we have improved the HMF selectivity from glucose dehydration using a biphasic system containing a reactive aqueous phase modified with DMSO. We further show that by fine-tuning the processing parameters for monosaccharides such as glucose, fructose and xylose, we can process various inexpensive and abundantly available polysaccharides such as inulin, starch, cellobiose, sucrose and xylan, in the same reactor system with equally good selectivities, thereby eliminating an additional acid hydrolysis step.

3. Experimental

3.1. Materials and experimental methods

All dehydration reactions were carried out in a two-phase batch reactor system containing a reactive aqueous layer (mixture of water–DMSO) and an extracting organic layer (mixture of MIBK–2-butanol or dichloromethane(DCM)). Aqueous- and organic-phase components including glucose, fructose, xylose, cellobiose, starch, xylan, sucrose, inulin, DMSO, MIBK, 2-butanol, DCM, and HCl were obtained from Sigma–Aldrich Corp. Dehydration experiments using 7 : 3 (w/w) MIBK : 2-butanol as the extracting phase were carried out in 10 ml (Alltech), thick-walled glass reactors heated in a temperature controlled oil bath placed on a magnetic stirrer (Table 2, runs 1–20). The temperature in the oil bath was measured by a K-type thermocouple (OMEGA), and series 16A temperature controller (Dwyer Instruments) coupled with a 150 W heating cartridge (McMaster Carr) controlled the temperature. In a typical experiment, 1.5 g of aqueous phase solution adjusted to a pH value using HCl acid catalyst and 3.0 g of organic phase solution were poured into the reactor. The reactor was placed in an oil bath at 443 K for the time specified in Table 2. The reaction was stopped by rapidly cooling the reactor in an ethylene glycol bath at 298 K. In a typical run with DCM as the extracting solvent (Table 2, runs 21–29), a Parr reactor (Model # 4749, size 23 ml) was filled with 7 g of the sugar aqueous solution and 7 g of DCM. The Parr reactor was then immersed in an oil bath at 413 K for time indicated in Table 2 (Runs 21–29). After reaction, the reactor was cooled to room temperature by flowing air.

3.2. Analysis

After each dehydration run (Table 2, runs 1–29), portions of the aqueous and organic phases were pipetted out and analyzed using HPLC analysis in a Waters 2690 system equipped with PDA 960 UV and RI 410 refractive index detectors. Sugar disappearance was monitored with an Aminex HPX-87H column (Bio-Rad), using MilliQ water (pH = 2) as the mobile phase at a flow rate of 0.6 ml min^{-1} and a column temperature of 303 K. HMF was quantified in the aqueous and organic phases with a Zorbax SB-C18 reverse phase column (Agilent), using a 2 : 8 v/v methanol : water (pH = 2) gradient at a flow rate of 0.7 ml min^{-1} and a column temperature of 303 K using a UV detector (320 nm).

Sugar conversion and HMF selectivity were calculated from the aqueous and organic phase concentrations obtained from HPLC and the corresponding volume of each phase, as indicated in Table 1. Because the density of aqueous phase changes after addition of sugar, the volume occupied by the feed aqueous solution (V_{feed}) was measured using standard feedstock solutions (Table 1). In addition, after mixing the aqueous phase with the organic phase, some fraction of DMSO transfers to the organic phase, thereby changing the volumes of each phases to the values listed as V_{org} and V_{aq}. Thus, the volumes of the two phases were determined for each system using standard solutions. It was assumed that after the dehydration reaction the volume changes are negligible for the 10 wt% initial sugar concentration. The fraction of DMSO carried over to the organic phase was measured using HPLC analysis (Table 1).

3.3. Calculations

Sugar conversion and HMF selectivity were calculated as given below. Sugar concentration (micromoles per cm^3) refers to the aqueous phase concentration because no sugar was present in the organic phase.

$$\text{Conversion} = \frac{[\text{Sugar}]_{feed} \times V_{feed} - [\text{Sugar}]_{final} \times V_{aq}}{[\text{Sugar}]_{feed} \times V_{feed}}$$

$$\text{Selectivity} = \frac{[\text{HMF}]_{org} \times V_{org} + [\text{HMF}]_{aq} \times V_{aq}}{[\text{Sugar}]_{feed} \times V_{feed} - [\text{Sugar}]_{final} \times V_{aq}}$$

4. Results and discussion

4.1. Reaction scheme

Fig. 1 depicts a generalized reaction scheme for production of HMF from polysaccharides containing hexose monomer units, involving a series of consecutive and parallel reactions starting with acid hydrolysis of polysaccharides to form monosaccharides. Glucose or fructose thus formed can be dehydrated in the presence of an acid catalyst to produce HMF via an open-chain or the cyclic furanose intermediate pathways.[17,35] The reaction intermediates and the HMF product can further react

Table 1 Volumes (cm^3) occupied by different reaction systems using standard glucose (G) feed solutions with HCl

	Standard System	Volume of feed, V_{feed}	Volume of aqueous layer, V_{aq}	Volume of organic layer, V_{org}	DMSO in organic layer (wt%)
1	10% G 5:5 W:DMSO; 7:3 MIBK:2-butanol pH 1.0	4.5	3.9	12.9	5.1
2	10% G 5:5 W:DMSO; 7:3 MIBK:2-butanol pH 1.5	4.5	3.8	13.3	5.9
3	10% G 5:5 W:DMSO; 7:3 MIBK:2-butanol pH 2.0	4.5	3.8	13.3	5.9
4	10% G 4:6 W:DMSO; 7:3 MIBK:2-butanol pH 1.0	4.5	3.6	13.1	8.7
5	10% G 3:7 W:DMSO; DCM	4.4	3.6	4.6	20.0

^{a} V_{feed} corresponds to volume occupied by 5 g of feedstock solution. V_{aq} and V_{org} correspond to volume occupied by each phase after mixing 5 g of aqueous phase with 10 g of 7 : 3 (w/w) MIBK : 2-butanol organic solution (entries 1–4) and 5 g of DCM (entry 5).
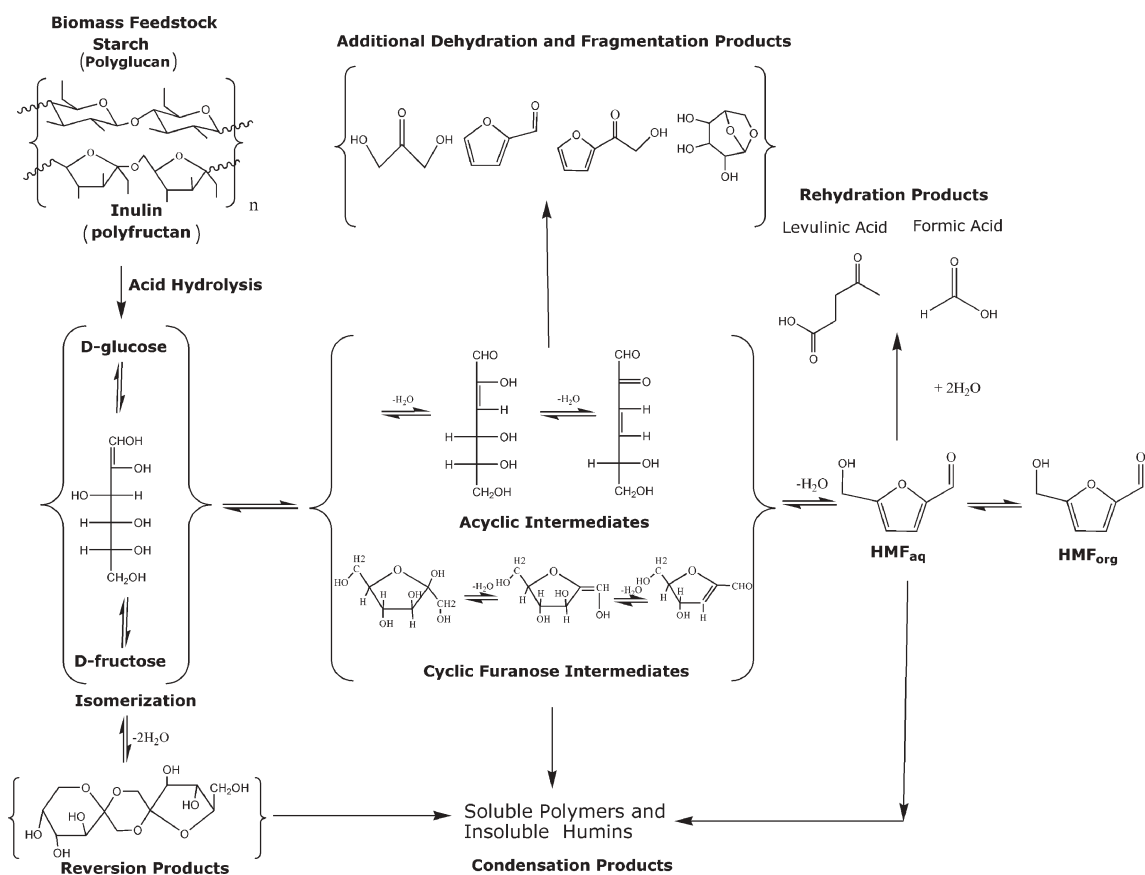
Fig. 1 Schematic representation of reaction pathways for acid-catalyzed hydrolysis and dehydration of polysaccharides (containing hexose monomer units) to 5-hydroxymethylfurfural (HMF) in a biphasic system. Structures in brackets correspond to representative species.

or degrade by processes such as isomerization, condensation, rehydration, reversion, fragmentation and/or additional dehydration reactions. Similarly, formation of furfural from xylose can proceed through two 1,2-eliminations and one 1,4-elimination of water or through a cyclic 2,5 anhydride intermediate.[29,36]

4.2. Effect of extracting and aprotic organic solvent

We conducted dehydration experiments with glucose, the least reactive but most abundant monosaccharide, in the presence of HCl (pH 1.0) as catalyst, with the goal of maximizing HMF selectivity at 443 K under autonomous pressure. Fig. 2 shows the effects on the HMF selectivity of adding DMSO (60 wt%) and an extracting organic phase containing 7 : 3 (w/w) MIBK : 2-butanol. In pure water, the HMF selectivity from glucose (Table 2, run 1) was low (11%), and the reaction resulted in formation of insoluble byproducts. Adding an extracting solvent improves the selectivity to 28% (Table 2, run 3). The extracting solvent not only improves the selectivity by minimizing degradation reactions arising from extended HMF residence in the reactive aqueous phase, but it also achieves efficient recovery by extracting 82% of HMF in the organic layer for subsequent isolation. In parallel, adding DMSO to the aqueous reactive phase with no extracting solvent results in improved dehydration rates (about nine times) along with an increase in the selectivity to 26% (Table 2,

run 2). Importantly, adding DMSO along with an extracting solvent improves the rate of dehydration and increases the selectivity to 53% (Table 2, run 4). Thus, it can be seen that adding DMSO to water and using an efficient extracting phase not only improves the dehydration rates and HMF selectivity, but it also provides a system that allows simpler product purification.
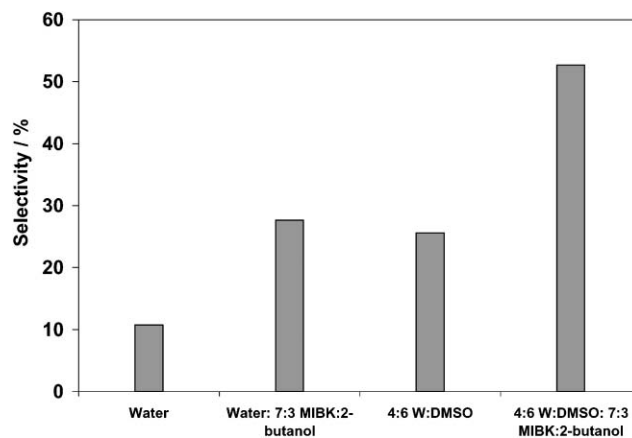
Fig. 2 Effect on HMF selectivity of adding an extracting organic solvent 7 : 3 (w/w) MIBK : 2-butanol and DMSO (60 wt%) to the aqueous phase for 10 wt% glucose dehydration at 443 K using HCl as catalyst at pH 1.0.

Table 2 Results for dehydration of various carbohydrates feedstock compounds. Runs 1–18 were carried out with 10 wt% initial concentration of carbohydrates using HCl as catalyst at 443 K. Runs 3–20 used 7 : 3 (w/w) MIBK : 2-butanol organic solvent in twice the amount by weight with respect to aqueous phase. Runs 21–29, except 22, were carried out with 10 wt% initial concentration of carbohydrates without catalyst at 413 K using equal amount by weight of dichloromethane (DCM) as organic solvent. R = [HMF or Fur]$_{org}$/[HMF or Fur]$_{aq}$

Run #	Sugar	Aqueous phase composition	pH	Time/ h:min	Conversion (%)	Selectivity (%)	HMF or Fur Organic Phase (%)	[HMF or Fur]$_{org}$/ mg cc^{-1}	[HMF or Fur]$_{aq}$/ mg cc^{-1}	R
No organic solvent										
1	Glucose	Water	1.0	0:45	20	11	—	—	1.5	—
2	Glucose	4:6 W:DMSO	1.0	0:10	41	26	—	—	8.3	—
Organic solvent: 7:3 (w/w) MIBK:2-butanol										
3	Glucose	Water	1.0	0:50	17	28	82	1.0	0.6	1.6
4	Glucose	4:6 W:DMSO	1.0	0:10	43	53	74	4.3	5.5	0.8
5	Fructose	5:5 W:DMSO	1.0	0:04	95	89	74	16.7	19.0	0.9
6	Fructose	5:5 W:DMSO	1.5	0:06	94	88	76	16.2	18.0	0.9
7	Fructose	5:5 W:DMSO	2.0	0:08	95	86	77	16.2	16.9	1.0
8	Glucose	5:5 W:DMSO	1.0	0:17	50	47	76	4.7	5.0	0.9
9	Glucose	5:5 W:DMSO	1.5	0:42	47	41	76	3.8	4.2	0.9
10	Glucose	5:5 W:DMSO	2.0	1:40	48	40	76	3.7	4.2	0.9
11	Xylose[a]	5:5 W:DMSO	1.0	0:12	71	91	91	14.1	4.7	3.0
12	Xylose[a]	5:5 W:DMSO	1.5	0:27	82	68	92	12.0	3.6	3.4
13	Xylose[a]	5:5 W:DMSO	2.0	0:55	53	54	92	6.2	2.0	3.1
14	Inulin	5:5 W:DMSO	1.5	0:05	98	77	76	16.3	18.0	0.9
15	Sucrose	4:6 W:DMSO	1.0	0:05	65	77	75	10.1	12.4	0.8
16	Starch	4:6 W:DMSO	1.0	0:11	61	43	74	5.5	6.9	0.8
17	Cellobiose	4:6 W:DMSO	1.0	0:10	52	52	74	5.6	7.0	0.8
18	Xylan[a]	5:5 W:DMSO	1.0	0:25	100	66	91	12.3	4.1	3.0
19	Glucose[b]	5:5 W:DMSO	1.5	1:00	48	34	77	3.2	3.5	0.9
20	Glucose[b]	5:5 W:DMSO	1.5	1:00	36	48	75	3.5	3.7	0.9
Organic solvent: dichloromethane (DCM)										
21	Fructose	3:7 W:DMSO	—	2:00	100	87	61	38.3	31.4	1.2
22	Fructose[c]	3:7 W:DMSO		4:30	100	78	62	105.0	81.1	1.3
23	Inulin	3:7 W:DMSO	—	2:30	100	70	62	34.4	27.4	1.3
24	Glucose	3:7 W:DMSO	—	4:30	62	48	63	13.6	10.0	1.3
25	Sucrose	3:7 W:DMSO	—	4:30	82	62	64	24.4	17.6	1.4
26	Starch	3:7 W:DMSO	—	11:00	91	40	65	18.9	12.9	1.4
27	Cellobiose	3:7 W:DMSO	—	9:30	85	45	68	20.6	12.5	1.6
28	Xylose[a]	3:7 W:DMSO	—	3:00	72	79	87	32.7	6.3	5.2
29	Xylan[a]	3:7 W:DMSO	—	3:00	100	76	85	36.2	8.4	4.3

[a] Furfural selectivity from xylose or xylan feed. [b] Runs were carried out using H$_2$SO$_4$ (run 19) and H$_3$PO$_4$ (run 20) as catalyst. [c] Run 22 has initial concentration of 30 wt% fructose using equal amount by weight of dichloromethane (DCM) as organic solvent.

4.3. Effect of acidity (pH)

Fig. 3 shows the effect of pH on the selectivity for dehydration of fructose, glucose and xylose using HCl as the acid catalyst. These experiments were conducted in a 5 : 5 (w/w) W : DMSO mixture at 443 K using 7 : 3 (w/w) MIBK : 2-butanol as an extracting solvent. Fructose dehydration to HMF had the highest rates among the three sugars, with selectivities higher than 85% at high conversion (>90%) for all levels of acidity (Table 2, runs 5–7). Previous studies have shown that the reaction rates are first order with respect to fructose concentration.[27,37] The highest selectivity achieved from glucose was 47% (pH 1.0), thus indicating the inherent difference in dehydration rates and selectivity of keto-hexoses and aldo-hexoses in a similar reacting environment (Table 2, runs 5 and 8). The low yields of HMF from glucose can be attributed to stable ring structures, thereby leading to a lower fraction of open chain forms in solution, and consequently lower rates of enolization, which determines the rate of HMF formation.[4] In addition, glucose forms oligosaccharides, which contain reactive hydroxyl groups leading to higher rates of cross-polymerizations with reactive intermediates and HMF.[4] For xylose dehydration to furfural, a significant increase in the

selectivity to a value of 91% is achieved by decreasing the pH to 1.0, with a 6-fold improvement in dehydration rate (Table 2,
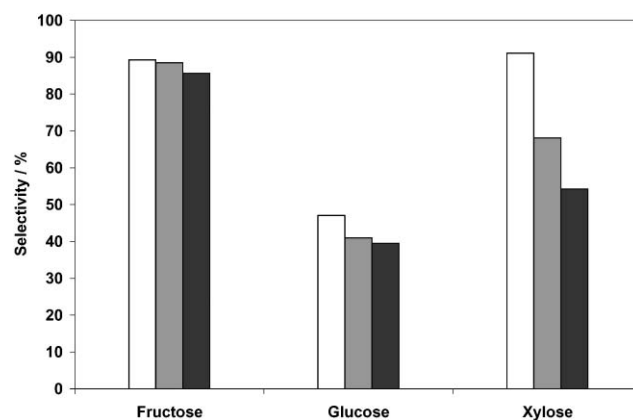

Fig. 3 Effect of pH on HMF selectivity from fructose and glucose, and furfural selectivity from xylose for dehydration of 10 wt% feed concentration of monosaccharides in 5 : 5 (w/w) W : DMSO aqueous mixture and 7 : 3 (w/w) MIBK : 2-butanol as organic phase at 443 K. White, grey, and black bars represent pH of 1.0, 1.5, and 2.0, respectively.

runs 11–13). Since furfural is less soluble in water, as compared to HMF, 91% of furfural is extracted into the organic phase, compared to a value of 75% for HMF (Table 2, runs 5, 8 and 11), thereby having higher efficiency for furfural production from xylose feedstock.

4.4. Effect of DMSO

The improved selectivities and dehydration rates observed in the presence of DMSO led us to study the effects of varying the DMSO level in the aqueous phase. Glucose dehydration was conducted at a constant pH, equal to 1.0, and 443 K in the presence of 7 : 3 (w/w) MIBK : 2-butanol as an extracting solvent. As seen in Fig. 4, adding DMSO to a level of 50 wt% improves the selectivity from 28% to 47%, with a further increase in selectivity to 53% for 60 wt% DMSO (Table 2, runs 3, 4 and 8). Earlier work has suggested that DMSO suppresses both the formation of condensation byproducts and the HMF rehydration by lowering the overall water concentration.[4,27] Whereas the predominant form of hexoses in water is the β-pyranose structure, the furanose form is stabilized in DMSO and is favored at higher temperatures.[38] We suggest that this shift toward the furanose form upon adding DMSO or increasing the temperature is reflected in higher reactivities and selectivities toward production of HMF (see Fig. 1). However, it should be noted that increasing the DMSO content decreases the extracting power of solvent, as indicated by a decrease in the value of R (defined as ratio of HMF concentration in organic phase to HMF concentration in aqueous phase) from 1.58 to 0.78. In addition, in the case of 4 : 6 (w/w) W : DMSO a larger portion of DMSO is carried-over into the extracting solvent (8.7 wt% DMSO as detected by HPLC), compared to the case of 5 : 5 (w/w) W : DMSO (5 wt% DMSO as detected by HPLC), leading to a balance between selectivity improvement and added energy in further recovery of HMF upon addition of DMSO (see Table 1 and section 4.8).
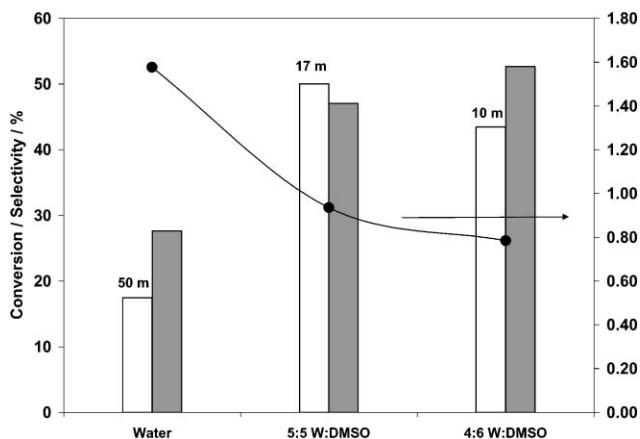
4.5. Processing of polysaccharide feed molecules

We subsequently studied the dehydration of various polysaccharide compounds at conditions optimized by adjusting pH and DMSO content for their monomer units. As seen in Fig. 5, dehydration of inulin, a fructose precursor obtained from chicory, gives a selectivity of 77% at high conversions in 5 : 5 (w/w) W : DMSO at pH 1.5, and this selectivity is consistent with the results obtained from fructose, assuming that some losses occur during the hydrolysis of the polyfructan to fructose. Similarly, reacting sucrose, a disaccharide having a unit of one fructose and one glucose monomer found in sugarcane or sugar beet, in 4 : 6 (w/w) W : DMSO at pH 1.0 achieves 77% selectivity at 65% sucrose conversion (Table 2, run 15). At these processing conditions, fructose would be completely converted and, assuming a glucose conversion of 30%, the expected selectivity to HMF from sucrose should be 81%. Thus, the conversion of sucrose follows the selectivity trends set by its monomer units, *i.e.*, fructose (89%) and glucose (53%). The conversion of cellobiose, a glucose dimer connected by β-1,4 glycosidic linkages obtained from partial hydrolysis of cellulose, gives similar selectivity for HMF (52%) as that of its monomer glucose unit. The conversion of soluble starch, a precursor for glucose containing α-1,4 glycosidic linkages and readily obtained from corn, rice *etc.*, gives a selectivity of 43% when processed at similar conditions. This value is lower than the value of 53% for glucose, suggesting that some loss of selectivity occurs during hydrolysis of the multiple glycosidic linkages in this polymer. Xylan (obtained from oat hulls), is a xylose polymer representative of
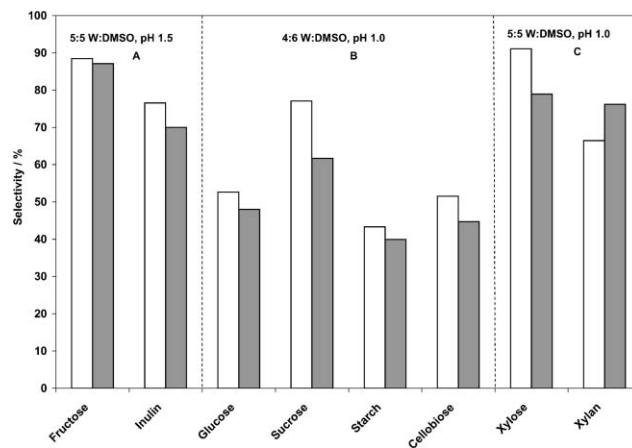
Fig. 5 HMF and furfural selectivities for processing biomass feedstocks at different conditions as separated by partitioning dotted lines. White bars represent the selectivity for dehydration in water–DMSO aqueous mixtures using HCl as catalyst and 7 : 3 (w/w) MIBK : 2-butanol as an extracting solvent at 443 K. First section (section A) represents HMF selectivity from fructose and inulin dehydration, in 5 : 5 (w/w) W : DMSO mixture at pH 1.5. Second section (section B) represents HMF selectivity from glucose, sucrose, starch and cellobiose dehydration, in 4 : 6 (w/w) W : DMSO mixture at pH 1.0. Third section (section C) represents furfural selectivity from xylose and xylan dehydration, in 5 : 5 (w/w) W : DMSO mixture at pH 1.0. Grey bars represent the selectivities in 3 : 7 (w/w) W : DMSO mixture and dichloromethane (DCM) as an extracting solvent at 413 K without catalyst.

Fig. 4 Effect of DMSO content in (w/w) W : DMSO mixture on glucose conversion and HMF selectivity (left axis), and effect on extraction ratio R (right axis). $R = [\text{HMF or Fur}]_{\text{org}}/[\text{HMF or Fur}]_{\text{aq}}$. White and grey bars represent glucose conversion and HMF selectivity respectively. Reaction time (in minutes) is indicated above the conversion bars.

hemi-cellulose, and the dehydration of this compound gave a selectivity of 66% at high conversions when subjected to the 5 : 5 (w/w) W : DMSO system and pH 1.0.

Even though fructose dehydration can be conducted with 20% DMSO to achieve 75% selectivity, as shown in our previous work,[34] under similar reaction conditions only the fructose fraction of sucrose would be converted, leaving the glucose molecules unreacted. However, in this system both monomers that constitute the sucrose molecule are converted to HMF by increasing the pH to 1.0 and DMSO content to 60%. In addition, this reaction system effectively processes polysaccharides such as starch or xylan, which have limited solubility in the aqueous phase. Indeed, solid biomass feeds (such as lignocelluloses) that are not completely soluble in any solvent, along with water-soluble carbohydrates, can be processed with further advances in this technology. Moreover, feed solutions consisting of mixed fractions such as hemi-cellulose and cellulose can be effectively handled without component separation. These results demonstrate the capability of the modifiable biphasic system to fine-tune the reaction conditions to process diverse biomass-derived feedstock molecules, which are inexpensive and abundantly available, to valuable furanic compounds by dehydration reactions.

4.6. Effect of mineral acids

We conducted experiments to study whether HCl could be replaced by less-corrosive mineral acids such as H_2SO_4 and H_3PO_4 and still achieve high HMF selectivity. These experiments were conducted using glucose as the feed molecule, at constant acidity (pH 1.5) with 5 : 5 (w/w) W : DMSO as the reacting mixture and MIBK : 2-butanol as the extracting solvent. Phosphoric acid achieved the highest selectivity of 48% (Table 2, run 20), HCl had an intermediate selectivity of 41% (Table 2, run 9), whereas sulfuric acid showed the lowest selectivity of 34% (Table 2, run 19). Unfortunately, the high selectivities achieved using H_3PO_4 are accompanied by the need to use twenty times more acid compared to HCl to achieve the same pH. It is clear, however, that the nature of the acid can influence the production of HMF.

4.7. Influence of dichloromethane as extracting solvent

We further studied the effects of changing the extracting solvent from a mixture of 7 : 3 (w/w) MIBK : 2-butanol to pure DCM. As seen in Fig. 5, the 3 : 7 (w/w) W : DMSO–DCM system converts all the carbohydrate feed molecules described above at a temperature of 413 K without an acid catalyst, with selectivities similar to those achieved using the HCl catalyst at 443 K. Fructose shows the highest HMF selectivity of 87%, while glucose dehydration achieves a selectivity of 48% (Table 2, runs 21 and 24). Sucrose is converted with an HMF selectivity of 62% at 82% conversion, comparing well with a predicted HMF selectivity of 59% at 100% conversion of fructose and 64% conversion of glucose monomer units (Table 2, run 25). In a separate experiment, 10 wt% fructose was dehydrated to produce HMF in a first cycle. After separating both the layers, the HMF remaining in the aqueous layer was extracted by contacting with two additional batches of fresh DCM solvent before charging a fresh feed of fructose

to recycle the aqueous layer. The recycle reaction system showed a selectivity of 83% at complete conversion, indicating excellent recycling ability of the solvent mixture. We also increased the initial fructose concentration from 10 to 30 wt%, and we achieved 78% HMF selectivity at complete conversion (Table 2, run 22). The decrease in HMF selectivity (from the value of 87%) resulting from the increase in feed concentration could be because of higher rates of condensation reactions.[4] The ability of the W : DMSO–DCM system to process a variety of biomass feed molecules with good selectivity and recycling ability with no catalyst can prove beneficial to solve the corrosion problem caused by adding mineral acids. In addition, the extracting ratio of the organic phase is higher for DCM ($R = 1.35$) as compared to the mixture of MIBK : 2-butanol ($R = 0.8$). However, the DMSO carry over is higher in DCM (up to 20 wt%) than in the 7 : 3 (w/w) MIBK : 2-butanol solvent mixture, thereby increasing the subsequent recovery cost (see section 4.8). Thus, although the large-scale use of DCM would be restricted due to environmental concerns, DCM offers a valuable insight into the effects of different solvent properties on the selectivity.

DCM can undergo hydrolysis reactions in the presence of water at temperatures near 523 K to generate aqueous HCl.[39] In a blank run, we thus treated 3 : 7 (w/w) W : DMSO and DCM at 413 K for 3 h, and we observed a decrease of pH to 1.5, but no traces of HCl were observed by GC-MS analysis. These results suggest that water is not available for DCM hydrolysis to HCl, presumably because a high fraction of water is associated with DMSO.[40] However, traces of decomposition products from DMSO were observed that might impart acidity to the solvent mixture and cause the decrease in pH. Regardless of the origin for the decrease in pH upon reaction, this system shows promise because it can effectively deal with insoluble and soluble biomass feedstocks.

4.8. Effect of DMSO on energy requirements for separation

Previous work has shown that high yields (~90%) of HMF can be obtained by dehydration of fructose in pure DMSO as a solvent.[26] However, the reactive nature of pure HMF at high temperature leads to substantial carbonization of the isolated product upon distilling HMF from DMSO.[24] Low-temperature separation processes, such as vacuum evaporation and vacuum distillation, are thus necessary to separate HMF from DMSO.[24,41] During our process, a fraction of the DMSO from the aqueous layer is carried over to the organic layer (Table 1), thereby necessitating use of vacuum distillation to remove the small amounts of DMSO from the product. Since experimental data for separation of HMF from DMSO have not been reported in the literature, we performed process simulation calculations using Aspen Plus® Simulation Software (Aspen Technology Inc., Cambridge) to compare the energy requirements of our process using MIBK–2-butanol and DCM as solvents with a process using pure DMSO (see ESI†). For product purification in the biphasic system, the organic phases are fed first to an adiabatic flash unit to remove most of the volatile solvent (for a temperature at or above room temperature), followed by 2 vacuum distillation columns to remove the remaining organic solvent and DMSO, respectively. The initial

adiabatic flash does not prove to be useful for the pure DMSO system, because it leads to HMF loss (>20%). Simulation results show that a biphasic system using 7 : 3 MIBK–2-butanol and DCM solvents achieves 55% and 30% higher energy efficiencies, respectively, when compared to using pure DMSO. The separation schemes we have employed may not be the optimal strategies for each case, but they allow a preliminary comparative estimate of the energy requirements for the three processes on the same basis for similar equipment and operating conditions. To improve the energy efficiency further, the DMSO content can be optimized for each sugar by comparing the gain of HMF yield against the penalty paid by the increase in energy requirements caused by increasing the level of DMSO.

While volatile organic solvents such as DCM and aprotic polar solvents such as DMSO have benefits in terms of improved extracting capability and higher selectivity for HMF, their use poses environmental concerns, and future work must address this issue. As shown in our earlier work, the addition of the aprotic solvent N-methylpyrrolidone (NMP) to the aqueous-phase in the biphasic system increases the selectivity to HMF, similar to the effect of DMSO. Importantly, replacing NMP with PVP,[34] a hydrophilic polymer that has NMP moieties along the polyethylene chain, retains the advantage of increased selectivity, but significantly reduces carry over into the organic phase. In a similar manner, grafting DMSO onto a hydrophilic polymeric backbone[42] or a catalyst surface[43] could be used as a strategy to provide a suitable reacting environment for HMF production and avoid organic phase contamination. In addition, this strategy would eliminate the risk associated with DMSO handling in the aqueous phase. Similarly, environmentally benign solvents (such as lower alcohols like 2-butanol, esters, PEG) that exhibit desirable properties for HMF extraction from the reactive aqueous phase should be explored. As shown in our previous work, solid acid catalysts such as ion-exchange resins (at low temperature) and niobium phosphate (at high temperature) can be employed to replace the use of mineral acids.[34]

5. Conclusions

We demonstrate in this work that a biphasic system can be tuned to process diverse feedstock molecules to produce HMF and furfural. By using preferred reaction conditions for representative monosaccharide units, it is possible to process the corresponding polysaccharides, such as sucrose (from sugarcane), inulin (from chicory), starch (from corn, rice), cellobiose (from cellulose), and xylan (from hemi-cellulose), in the same reactor system with equally good selectivities (from 50 to 90%) at high conversions, thereby eliminating the separate hydrolysis step before the dehydration reaction. The process variables that influence the yields of HMF and furfural for different carbohydrate feed molecules are the pH of the solution, the DMSO content in aqueous phase, the initial sugar concentration, the nature of the acid, and the extracting solvent. This biphasic reaction system is a step toward the more economical production of HMF and furfural through the processing of inexpensive and abundantly available renewable feedstocks.

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