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Science **312**, 1933 (2006);
DOI: 10.1126/science.1126337

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Phase Modifiers Promote Efficient Production of Hydroxymethylfurfural from Fructose

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Furan derivatives obtained from renewable biomass resources have the potential to serve as substitutes for the petroleum-based building blocks that are currently used in the production of plastics and fine chemicals. We developed a process for the selective dehydration of fructose to 5-hydroxymethylfurfural (HMF) that operates at high fructose concentrations (10 to 50 weight %), achieves high yields (80% HMF selectivity at 90% fructose conversion), and delivers HMF in a separation-friendly solvent. In a two-phase reactor system, fructose is dehydrated in the aqueous phase with the use of an acid catalyst (hydrochloric acid or an acidic ion-exchange resin) with dimethylsulfoxide and/or poly(1-vinyl-2-pyrrolidinone) added to suppress undesired side reactions. The HMF product is continuously extracted into an organic phase (methylisobutylketone) modified with 2-butanol to enhance partitioning from the reactive aqueous solution.

We are entering an era of diminishing availability of petrochemical resources used to produce the energy and chemical materials needed by society. Abundant biomass resources are a promising alternative for the sustainable supply of valuable intermediates (such as alcohols, aldehydes, ketones, and carboxylic acids) to the chemical industry for production of drugs and polymeric materials. In this context, the high content of oxygenated functional groups in carbohydrates—the dominant compounds in biomass—is an advantage, in contrast to the drawbacks of such functionality for the conversion of carbohydrates to fuels. However, efficient processes must be developed for the selective removal of excess functional groups and the modification of others to create the desired products.

Here, we present a strategy for the selective dehydration of fructose to produce HMF, thereby providing a cost-effective route for the synthesis of this valuable chemical intermediate. Indeed, HMF and its ensuing 2,5-disubstituted furan derivatives can replace key petroleum-based building blocks (*1*). For example, HMF can be converted to 2,5-furandicarboxylic acid (FDCA) by selective oxidation, and Werpy and Petersen (*2*) and Pentz (*3*) have suggested that FDCA can be used as a replacement for terephthalic acid in the production of polyesters such as polyethyleneterephthalate (*2*) and polybutyleneterephthalate. They have also suggested that the reduction of HMF can lead to products such as 2,5-dihydroxymethylfuran and 2,5-bis(hydroxymethyl)tetrahydrofuran, which can serve as alcohol components in the production of polyesters, thereby leading to completely biomass-derived polymers when combined with FDCA. In addition, HMF can serve as a precursor in the synthesis of liquid alkanes to be used, for example, in diesel fuel (*4*).

Unfortunately, as noted by various authors (*5*–*8*), the industrial use of HMF as a chemical

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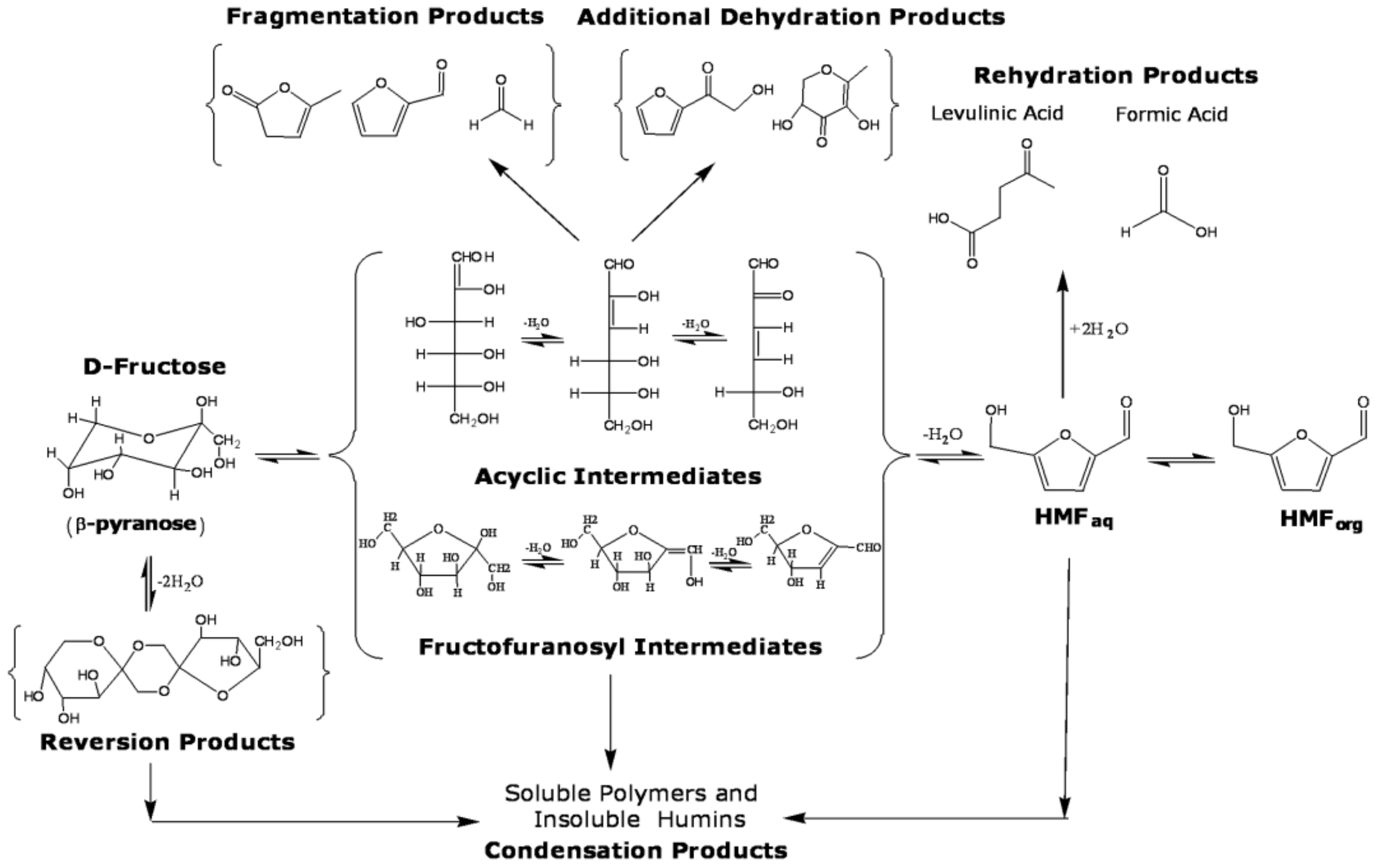

Fig. 1. Schematic representation of reaction pathways for acid-catalyzed dehydration of fructose. Structures in brackets correspond to representative species. Detailed chemistry is presented in (*20*, *23*).

intermediate is currently impeded by high production costs. Early work showed that HMF could be produced in high yields using high-boiling organic solvents [such as dimethylsulfoxide (DMSO), dimethylformamide, and mixtures of polyethyleneglycol with water] over various catalysts, including sulfuric acid and sulfonic acid resins. However, this approach necessitates difficult and energy-intensive isolation procedures (*6*, *9*–*13*). In pure water, fructose dehydration is generally nonselective, leading to many by-products besides HMF (*14*). Recent advances have shown improved results in pure water or in water-miscible solvent systems (such as acetonitrile or acetone), but only with the use of low initial fructose concentrations, which inevitably generate low HMF concentrations (*1*, *10*, *15*, *16*). Biphasic systems, in which a

Table 1. Results for acid-catalyzed dehydration of fructose. Runs 1 to 27 were carried out at 453 K for 2.5 to 3 min with 0.25 M HCl aqueous phase solutions; runs 28 to 39 were carried out at 363 K for 8 to 16 hours with an acidic ion-exchange resin at a 1:1 w/w fructose:resin ratio. Aqueous phase and organic phase compositions are reported as w/w ratios. Conversion is defined as the ratio of fructose consumed to fructose added initially. $R = [\text{HMF}]_{\text{org}}/[\text{HMF}]_{\text{aq}}$. Standard runs for HCl, H_2SO_4, and H_3PO_4 catalysts used 1.5 g of aqueous phase and 1.5 g of extracting solvent. Runs marked with an asterisk used 3 g of extracting solvent. Runs for resin catalyst used 5.0 g of aqueous phase and 5.0 g of extracting solvent. $V_{\text{org}}/V_{\text{aq}}$ was measured upon completion of reaction.

Run no.	Aqueous phase composition	Organic phase composition	Conversion (%)	Selectivity (%)	$[\text{HMF}]_{\text{aq}}$ (g/ml)	$[\text{HMF}]_{\text{org}}$ (g/ml)	R	$V_{\text{org}}/V_{\text{aq}}$
30 wt % fructose with HCl catalyst								
1	Water	none	50	51	0.060	–	0.00	0.00
2	Water	MIBK	91	60	0.056	0.050	0.90	1.51
3*	Water	MIBK	75	73	0.035	0.033	0.96	3.13
4	Water	7:3 MIBK:2-butanol	68	70	0.033	0.054	1.65	1.56
5*	Water	7:3 MIBK:2-butanol	86	80	0.026	0.045	1.73	3.68
6	8:2 Water:DMSO	MIBK	94	67	0.077	0.050	0.66	1.41
7	8:2 Water:DMSO	7:3 MIBK:2-butanol	80	75	0.050	0.064	1.30	1.49
8*	8:2 Water:DMSO	7:3 MIBK:2-butanol	87	82	0.034	0.046	1.39	3.65
9	7:3 Water:PVP	MIBK	74	66	0.055	0.041	0.81	1.56
10	7:3 Water:PVP	7:3 MIBK:2-butanol	62	76	0.042	0.047	1.25	1.57
11*	7:3 Water:PVP	7:3 MIBK:2-butanol	79	82	0.030	0.041	1.44	3.83
12	7:3(8:2 Water:DMSO):PVP	MIBK	79	75	0.071	0.047	0.71	1.52
13	7:3(8:2 Water:DMSO):PVP	7:3 MIBK:2-butanol	82	83	0.063	0.065	1.12	1.62
14*	7:3(8:2 Water:DMSO):PVP	7:3 MIBK:2-butanol	89	85	0.043	0.046	1.17	3.99
50 wt % fructose with HCl catalyst								
15	Water	none	51	28	0.064	–	0.00	0.00
16	Water	MIBK	65	47	0.049	0.051	1.11	1.80
17	Water	7:3 MIBK:2-butanol	71	59	0.049	0.079	1.73	1.91
18*	Water	7:3 MIBK:2-butanol	88	72	0.045	0.069	1.55	4.66
19	8:2 Water:DMSO	MIBK	71	57	0.076	0.060	0.86	1.69
20	8:2 Water:DMSO	7:3 MIBK:2-butanol	80	63	0.077	0.085	1.19	1.87
21*	8:2 Water:DMSO	7:3 MIBK:2-butanol	91	74	0.059	0.072	1.30	4.87
22	7:3 Water:PVP	MIBK	85	56	0.074	0.060	0.80	1.72
23	7:3 Water:PVP	7:3 MIBK:2-butanol	77	61	0.076	0.081	1.19	1.85
24*	7:3 Water:PVP	7:3 MIBK:2-butanol	90	77	0.062	0.070	1.22	5.15
25	7:3(8:2 Water:DMSO):PVP	MIBK	77	61	0.095	0.066	0.77	1.85
26	7:3(8:2 Water:DMSO):PVP	7:3 MIBK:2-butanol	72	62	0.068	0.074	1.25	1.89
27*	7:3(8:2 Water:DMSO):PVP	7:3 MIBK:2-butanol	92	77	0.076	0.070	1.03	5.11
10 wt % fructose with ion-exchange resin catalyst								
28	Water	MIBK	75	44	0.010	0.011	1.02	1.32
29	Water	MIBK	17	43	0.0021	0.0024	1.15	1.29
30	Water	7:3 MIBK:2-butanol	61	60	0.0086	0.014	1.61	1.31
31	8:2 Water:DMSO	MIBK	84	47	0.015	0.012	0.79	1.26
32	8:2 Water:DMSO	MIBK	19	80	0.0052	0.0045	0.87	1.24
33	8:2 Water:DMSO	7:3 MIBK:2-butanol	74	68	0.015	0.017	1.18	1.24
34	7:3 Water:PVP	MIBK	74	63	0.018	0.013	0.79	1.43
35	7:3 Water:PVP	7:3 MIBK:2-butanol	70	65	0.015	0.015	1.04	1.46
36	7:3(8:2 Water:DMSO):PVP	MIBK	80	71	0.026	0.013	0.54	1.38
37	7:3(8:2 Water:DMSO):PVP	7:3 MIBK:2-butanol	76	77	0.020	0.019	1.03	1.43
30 wt % fructose with ion-exchange resin catalyst								
38	7:3(8:2 Water:DMSO):PVP	MIBK	89	60	0.066	0.041	0.66	1.65
39	7:3(8:2 Water:DMSO):PVP	7:3 MIBK:2-butanol	83	65	0.053	0.051	1.07	1.74
30 wt % fructose with H_2SO_4 catalyst								
40*	Water	7:3 MIBK:2-butanol	80	66	0.022	0.035	1.63	3.54
41*	8:2 Water:DMSO	7:3 MIBK:2-butanol	85	71	0.029	0.040	1.35	3.59
30 wt % fructose with H_3PO_4 catalyst								
42*	Water	7:3 MIBK:2-butanol	65	65	0.016	0.029	1.89	3.47
43*	8:2 Water:DMSO	7:3 MIBK:2-butanol	51	76	0.016	0.025	1.58	2.95

water-immiscible organic solvent is added to extract continuously the HMF from the aqueous phase, have also been investigated with the use of mineral acid or zeolite catalysts at temperatures greater than 450 K (*6*, *17–21*). However, poor HMF partitioning into the organic streams used in these studies necessitated large amounts of solvent, thereby requiring large energy expenditures to purify the diluted HMF product (*22*).

Fructose is dehydrated in the presence of an acid catalyst to produce HMF and various by-products (Fig. 1). Although evidence exists supporting both the open-chain and the cyclic fructofuransyl intermediate pathways (*20*, *23*), it is clear that the reaction intermediates and the HMF product degrade by means of processes such as fragmentation, condensation, rehydration, reversion, and/or additional dehydration reactions. We used a modified biphasic system to address key HMF production limitations. Specifically, we improved the HMF selectivity (defined as the moles of HMF produced divided by the moles of fructose reacted) of the acid-catalyzed dehydration of concentrated [30 to 50 weight % (wt %)] fructose feeds by adding modifiers to both phases. The reactive aqueous phase containing the catalyst and the sugar was modified with polar aprotic molecules [DMSO or 1-methyl-2-pyrrolidinone (NMP)] and a hydrophilic polymer [poly(1-vinyl-2-pyrrolidinone) (PVP)]. The water-immiscible organic phase [methylisobutylketone (MIBK)] used during the reaction to extract HMF was modified with 2-butanol. The ratio of relative volumes of the organic and aqueous phases in the reactor (V_{org}/V_{aq}), as well as the ratio of the HMF concentration in the organic layer to that in the aqueous layer (defined as the extraction ratio, *R*) proved to be important variables in the process. Upon completion of the dehydration reaction, both phases can be separated for efficient product isolation. Although various acid catalysts can be used to perform the dehydration reaction, HCl showed the highest HMF selectivity of the common mineral acid catalysts (Table 1, runs 5, 8, and 40 to 43).

We performed experiments using 0.25 M HCl at 453 K under autonomous pressure. To optimize selectivity, we varied the concentrations of each aqueous phase modifier (Table 1 and Fig. 2) (*24*). Together, DMSO and PVP increased the selectivity from 60 to 75% (Fig. 2A). However, we also sought to optimize partitioning of the HMF product into the organic phase both to minimize degradation reactions arising from extended HMF residence in the reactive aqueous phase and to achieve more efficient recovery of HMF in the subsequent isolation step. Unfortunately, the aqueous additives are a liability in this respect, because they increase the solubility of HMF in the aqueous phase (thereby decreasing the *R* value). The addition of 2-butanol to the organic phase helped counteract this effect by increasing HMF solubility in the organic phase relative to pure MIBK (Fig. 2B). Although pure 2-butanol is moderately soluble in water [up to 19.5 wt % at 298 K, as measured by high-performance liquid chromatography (HPLC)], it partitioned effectively into the MIBK layer when mixed with MIBK at a 3:7 weight/weight (w/w) ratio (<5 wt % at 298 K was detected in the aqueous phase by HPLC). Starting with a 30 wt % aqueous fructose solution, our optimal results using all three modifiers (DMSO, PVP, and 2-butanol) yielded 0.065 g/ml of HMF in the organic layer, with 83% HMF selectivity at 82% conversion (Table 1, run 13).

The selectivity for production of HMF decreases when the initial sugar concentration is increased from 30 to 50 wt % (Fig. 2C). This result is in agreement with literature reports that increasing the fructose concentration leads to higher rates of condensation reactions (*6*, *13*). The addition of DMSO, PVP, and/or 2-butanol to the 50 wt % fructose systems in the same quantities used for lower fructose concentrations did not substantially improve the HMF selectivity. However, doubling the amount of the 7:3 MIBK:2-butanol extracting solvent increased the selectivity substantially. The optimal system using all three modifiers generated 0.070 g/ml of HMF in the organic phase at 77% HMF selectivity and 92% conversion (Table 1, run 27).

A heterogeneous catalyst is more easily separated from the product and recycled than a homogeneous catalyst, leading us to investigate fructose dehydration with the use of an acidic ion-exchange resin. These experiments were conducted at 363 K under autonomous pressure (Table 1, runs 28 to 39). When we used the resin catalyst, we observed trends in modifier impact that were similar to those we saw with HCl; however, the absolute selectivities were lower for the resin system. Kuster (*6*) reported that elevated temperatures (>453 K) favor higher HMF selectivity because at these conditions the rate of HMF formation is 4 to 10 times as fast as the rate of HMF degradation. Because ion-exchange resins degrade at these higher temperatures, it is desirable to replace HCl with a heterogeneous acid catalyst that is stable to 450 K. In this respect, and considering the favorable results we obtained using H_3PO_4 (Table 1, run 43), we tested a niobium phosphate catalyst at 453 K, obtaining promising results of 73% HMF selectivity at 62% conversion. In addition, Dias *et al.* (*25*) have shown that nanoporous materials possessing sulfonic acid groups can promote dehydration of xylose to furfural at elevated temperatures. Carlini *et al.* (*26*) observed fructose dehydration at low temperatures (353 K) and mostly at low conversion (<50%) with the use of vanadyl-phosphate–based catalysts, which may also withstand elevated temperatures.

Experiments conducted at low temperature and low conversions (Table 1, runs 29

Table 2. Simulation of HMF yield (*Y*) and energetic yield (*Y*η) for selected dehydration systems. $[HMF]_{aq}$ corresponds to the HMF concentration in the aqueous phase leaving the extractor, and $[HMF]_{org}$ corresponds to the HMF concentration entering the evaporator in Fig. 3. Runs are based on runs in Table 1. The selectivity is set to the value obtained experimentally, and conversion is assumed to be 90%. The yield is calculated based on the HMF present in the organic stream sent to the evaporator.

Run no.	Aqueous phase composition	Organic phase composition	Selectivity (%)	$[HMF]_{aq}$ (g/ml)	$[HMF]_{org}$ (g/ml)	*Y* (%)	*Y*η (%)
			30 wt % fructose				
2	Water	MIBK	60	0.0075	0.045	48	34
4	Water	7:3 MIBK:2-butanol	70	0.0001	0.057	61	43
6	8:2 Water:DMSO	MIBK	67	0.025	0.048	48	35
7	8:2 Water:DMSO	7:3 MIBK:2-butanol	75	0.0009	0.063	66	48
12	7:3(8:2 Water:DMSO):PVP	MIBK	75	0.024	0.057	56	44
13	7:3(8:2 Water:DMSO):PVP	7:3 MIBK:2-butanol	83	0.0032	0.071	73	56
			50 wt % fructose				
16	Water	MIBK	47	0.0026	0.054	39	27
26	7:3(8:2 Water:DMSO):PVP	7:3 MIBK:2-butanol	62	0.0019	0.091	53	43
27	7:3(8:2 Water:DMSO):PVP	7:3 MIBK:2-butanol	77	0.0055	0.071	67	51

and 32) offer mechanistic insight about the role of DMSO in enhancing HMF selectivity. The results show that DMSO primarily increases the rate of fructose conversion into HMF and to some extent decreases the rates of undesirable parallel reactions. Likewise, earlier work has suggested that DMSO suppresses both the formation of condensation by-products and HMF rehydration by lowering the overall water concentration (*6*, *13*). Similar studies have indicated that DMSO both favorably shifts the equilibrium of the rate-determining step in HMF production and inhibits acyclic reaction sequences that may lead to undesirable intermediates (*23*).

The reaction of 10 wt % fructose in 7:3 water:NMP with MIBK as the extracting solvent and an acidic ion-exchange resin catalyst generated 68% HMF selectivity at 80% conversion, indicating that the addition of NMP to water enhances the selectivity of HMF production from fructose. Because NMP is an aprotic solvent with properties similar to DMSO, NMP appears to act through mechanisms similar to those of DMSO to enhance HMF selectivity in the fructose dehydration reaction. However, whereas the carryover of DMSO from the aqueous phase into the organic phase is not considerable (<0.8 wt % DMSO in MIBK after contacting an 8:2 water:DMSO aqueous solution, as measured by HPLC), the carryover of NMP into the organic phase is high (~5 wt % NMP in MIBK after contacting a 7:3 water:NMP aqueous solution, as measured by HPLC), thereby complicating the subsequent separation of HMF from the organic phase by evaporation. Notably, we found that replacing NMP with PVP, a stable hydrophilic polymer that has NMP moieties along the polyethylene chain, preserves the benefits on selectivity produced by NMP but eliminates organic phase contamination due to the low solubility of PVP in the extracting solvent. In an analogous manner, grafting DMSO onto a hydrophilic polymeric backbone could be used as a strategy to eliminate trace amounts of DMSO in the organic phase.

The addition of 2-butanol to MIBK enhances HMF selectivity by removing HMF more efficiently from the reactive aqueous medium. Notably, increasing the extraction ratio *R* and/or increasing V_{org}/V_{aq} can counteract the faster rate of HMF degradation in the presence of fructose. This undesirable reaction between fructose and HMF is reflected in lower HMF selectivities at 50 wt % fructose when compared with 30 wt % (Table 1), and we observed directly that lower selectivities are obtained when controlled amounts of HMF are added initially to the fructose reaction system. In addition, separating HMF from the aqueous medium lowers the rate of HMF rehydration into levulinic and formic acids. Analyses by gas chromatography–mass spectrometry (GC-MS) of the aqueous and organic phases after conversion of 30 wt % fructose showed that the general composition of the by-products corresponds to typically 10% rehydration, 5% dehydration, 5% fragmentation, and 80% condensation compounds.

We performed simulations for selected experiments from Table 1 to estimate the HMF concentrations that would be obtained by combining our batch reactor experiments with a countercurrent extractor to remove the HMF remaining in the aqueous layer (Fig. 3). The final amount of HMF obtained by combining the organic streams from the reactor and the extractor (i.e., the stream entering the evaporator) is used to calculate the energetic yield ($Y\eta$) as a measure of the overall efficiency of our process for obtaining

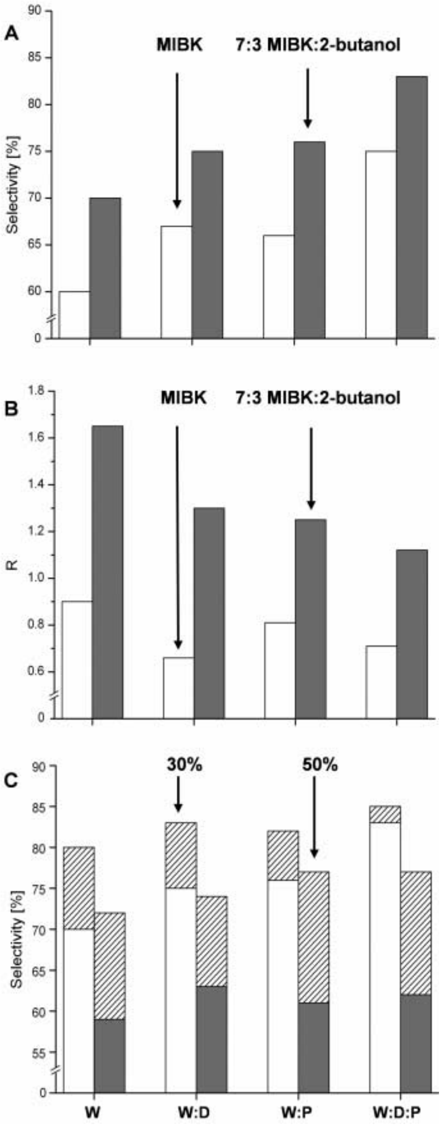

Fig. 2. Effects of changing the aqueous phase composition from water (W), to 8:2 w/w water:DMSO (W:D), to 7:3 w/w water:PVP (W:P), to 7:3 w/w (8:2 water:DMSO):PVP (W:D:P). (**A**) HMF selectivity with 30 wt % fructose feed. White and gray bars represent MIBK and MIBK:2-butanol extracting solvents, respectively. (**B**) Extraction ratio, *R*. White and gray bars represent MIBK and MIBK:2-butanol extracting solvents, respectively. (**C**) HMF selectivity with MIBK:2-butanol extracting solvent. White and gray bars represent 30 and 50 wt % fructose, respectively, and hatched bars show the improvement obtained with the use of double the amount of extracting solvent.

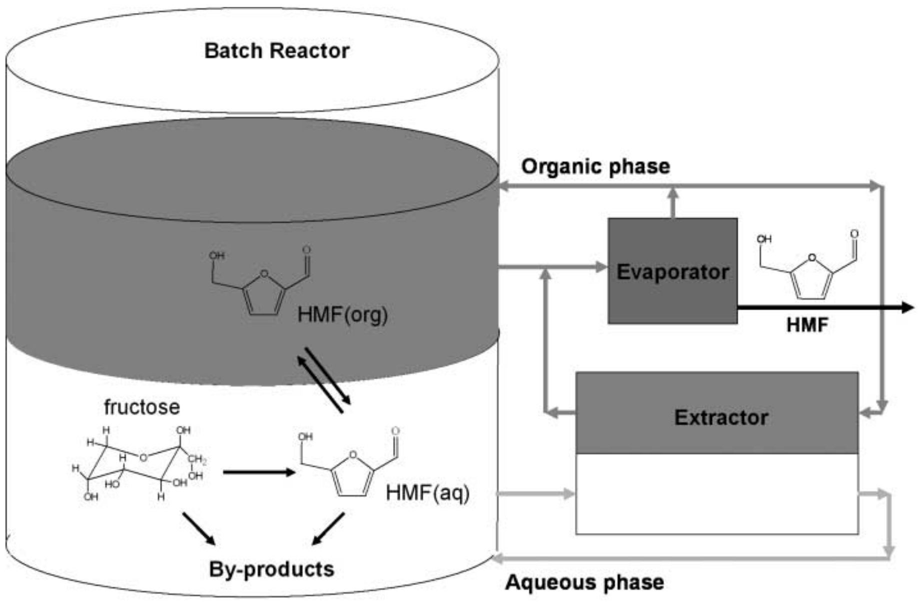

Fig. 3. Batch process for production of HMF from fructose with simulated countercurrent extraction and evaporation steps. The aqueous phase (white) contains fructose, DMSO, PVP, and the acid catalyst and is represented in the bottom half of the batch reactor. The organic phase (gray) contains MIBK or MIBK:2-butanol and is represented in the top half of the batch reactor.

HMF by solvent evaporation. The energetic yield is the product of the HMF yield (Y), defined as the moles of HMF in the stream entering the evaporator in Fig. 3 divided by the total moles of fructose fed to the batch reactor, and an energy efficiency (η), defined as the heat of combustion of the HMF product ($\Delta H_{\mathrm{C,HMF}}$) minus the energy necessary to evaporate the solvent ($\Delta H_{\mathrm{vap,org}}$), normalized by the energy content of the product [i.e., $\eta = (\Delta H_{\mathrm{C,HMF}} - \Delta H_{\mathrm{vap,org}})/\Delta H_{\mathrm{C,HMF}}$]. These simulations used the experimental selectivity for each system (Table 1), which was assumed to remain constant at 90% conversion, the experimental value of $V_{\mathrm{org}}/V_{\mathrm{aq}}$ for the batch reactor, and the experimental value of R to model a countercurrent extractor operating with equal volumes of aqueous and organic streams. Aqueous and organic phase modifiers improve the value of $Y\eta$, thus reducing energy expenditures required to obtain the HMF product when compared with the water/MIBK system (Table 2).

The value of $Y\eta$ alone does not address the difficulties of using high-boiling organic systems. For example, although a theoretical value of $Y\eta > 75\%$ can be obtained with pure DMSO, the HMF product cannot be separated from the solvent by simple evaporation. Previous work has shown that because of the reactive nature of concentrated HMF at high temperatures, distillation of HMF from DMSO leads to substantial carbonization of the product (*10*). Low-temperature separation processes such as vacuum evaporation and vacuum distillation have been used to separate various solvents and by-products from HMF mixtures, but no experimental data have been reported for DMSO (*27*–*29*). Accordingly, we used Aspen Plus Simulation Software (Version 12.1, Aspen Technology Inc.) to compare energy requirements for the separations of HMF from a low-boiling solvent (pure MIBK) and from a high-boiling solvent (pure DMSO) for vacuum evaporation and vacuum distillation processes (for HMF levels of 10 wt %). Vacuum evaporation simulations predicted that 99.5% of the MIBK solvent can be evaporated at 13 mbar and 343 K with a 2.5% loss of HMF, whereas evaporating DMSO at 1.3 mbar and the same temperature resulted in a 30% loss of HMF. Consequently, HMF separation from DMSO with minimal losses requires the more expensive vacuum distillation process (e.g., 0.66 mbar and a bottom temperature of 386 K). When comparing both solvents with the use of vacuum distillation, simulations predicted that an efficient separation of HMF from pure DMSO requires 40% more energy as compared with pure MIBK, clearly showing the advantages of using a low-boiling solvent system.

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30. This work was supported by the U.S. Department of Agriculture and the NSF Chemical and Transport Systems Division of the Directorate for Engineering.

Supporting Online Material

www.sciencemag.org/cgi/content/full/312/5782/1933/DC1
Materials and Methods

16 February 2006; accepted 30 May 2006
10.1126/science.1126337

An Octahedral Coordination Complex of Iron(VI)

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The hexavalent state, considered to be the highest oxidation level accessible for iron, has previously been found only in the tetrahedral ferrate dianion, $\mathrm{FeO_4}^{2-}$. We report the photochemical synthesis of another Fe(VI) compound, an octahedrally coordinated dication bearing a terminal nitrido ligand. Mössbauer and x-ray absorption spectra, supported by density functional theory, are consistent with the octahedral structure having an Fe≡N triple bond of 1.57 angstroms and a singlet d_{xy}^2 ground electronic configuration. The compound is stable at 77 kelvin and yields a high-spin Fe(III) species upon warming.

Iron, the most abundant transition element in the natural world, generally occurs in compounds of its divalent or trivalent ions. Iron ions in these two oxidation states occur in a wide range of minerals (*1*, *2*) found terrestrially as well as on Mars (*3*, *4*) and are widely used in biological electron transfer processes, such as those involving iron-sulfur clusters (*5*). Low-valent, electron-rich compounds play key roles in biological hydrogen production, for example, Fe(I) and Fe(0) (*6*–*8*). Nature also uses more electron-deficient iron centers for highly specific and efficient enzymatic oxidation (*9*–*11*), which has spurred chemists to prepare analogous coordination complexes for use in synthesis and oxidative waste remediation. Notable among these are Fe(IV) complexes that activate H_2O_2 (*12*) and Fe(IV)=O species that hydroxylate hydrocarbons (*13*, *14*), as well as several other Fe(IV) (*15*–*19*) and Fe(V) (*20*, *21*) compounds.

Although iron has eight electrons in its valence shell, only the +6 state is considered

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