nature
Vol 447|21 June 2007|doi:10.1038/nature05923

LETTERS

Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates

Yuriy Román-Leshkov[1], Christopher J. Barrett[1], Zhen Y. Liu[1] & James A. Dumesic[1]

Diminishing fossil fuel reserves and growing concerns about global warming indicate that sustainable sources of energy are needed in the near future. For fuels to be useful in the transportation sector, they must have specific physical properties that allow for efficient distribution, storage and combustion; these properties are currently fulfilled by non-renewable petroleum-derived liquid fuels. Ethanol, the only renewable liquid fuel currently produced in large quantities, suffers from several limitations, including low energy density, high volatility, and contamination by the absorption of water from the atmosphere. Here we present a catalytic strategy for the production of 2,5-dimethylfuran from fructose (a carbohydrate obtained directly from biomass or by the isomerization of glucose) for use as a liquid transportation fuel. Compared to ethanol, 2,5-dimethylfuran has a higher energy density (by 40 per cent), a higher boiling point (by 20 K), and is not soluble in water. This catalytic strategy creates a route for transforming abundant renewable biomass resources[1,2] into a liquid fuel suitable for the transportation sector, and may diminish our reliance on petroleum.

The rationale for converting carbohydrates to 2,5-dimethylfuran (DMF) is outlined in Fig. 1. The selective removal of five oxygen atoms from a hexose (for example, fructose) to produce DMF not only decreases the boiling point to a value suitable for liquid fuels, but also attains the lowest water solubility and the highest research octane number[3] (RON) of the mono-oxygenated C_6 compounds, while preserving a high energy density (30 kJ cm^{-3}). This selective removal of oxygen atoms can be accomplished in two steps: first, removing three oxygen atoms by dehydration to produce 5-hydroxymethylfurfural (HMF); and second, removing two oxygen atoms by hydrogenolysis to produce DMF by way of intermediates **4** and **5**. Species **6**, produced by way of **7**, is a hydrogenolysis by-product that also possesses excellent fuel qualities.

A schematic representation of our process is outlined in Fig. 2. (An annotated version of this figure, summarizing the primary findings of this work, is presented in Supplementary Information.) The first step involves the acid-catalysed dehydration of fructose to produce HMF in a biphasic reactor. Because the normal boiling point of HMF is too high for it to be used as a fuel (Fig. 1), the HMF extracted by the organic phase of the biphasic reactor is subsequently converted to DMF by hydrogenolysis of C–O bonds over a copper-ruthenium (CuRu) catalyst. As described below, our process also involves two separation steps.

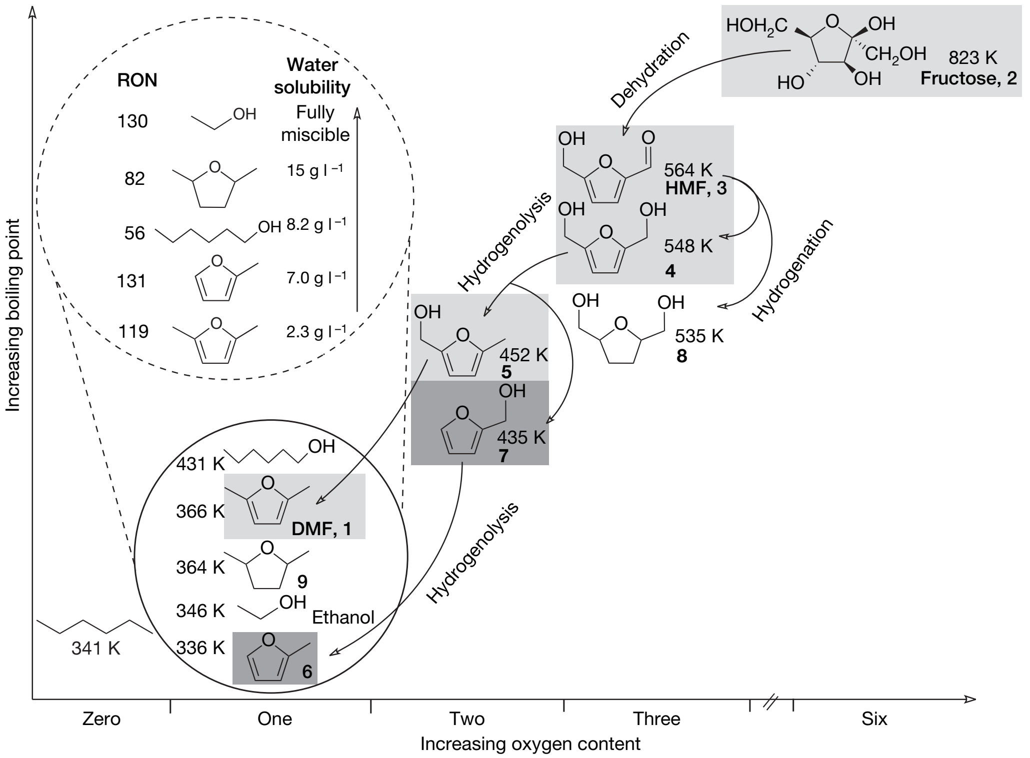

Figure 1 | Normal boiling points of representative C_6-hydrocarbons formed by removal of oxygen atoms from hexoses, compared to the normal boiling point of ethanol. Compounds as follows: 2,5-dimethylfuran (DMF, **1**); D-fructose (**2**), 5-hydroxymethylfurfural (HMF, **3**); 2,5-dihydroxymethylfuran (**4**); 2-methyl,5-hydroxymethylfuran (**5**); 2-methylfuran (**6**); furfural alcohol (**7**); 2,5-dihydroxymethyltetrahydrofuran (**8**); and 2,5-dimethyltetrahydrofuran (**9**). Light grey boxes highlight reactant, product and primary intermediates. Dark grey boxes highlight key by-products and by-product intermediates. Inset, water solubility and research octane number (RON)[3,24,25] of mono-oxygenated C_6-compounds and **6** compared to ethanol.

---

[1] Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA.

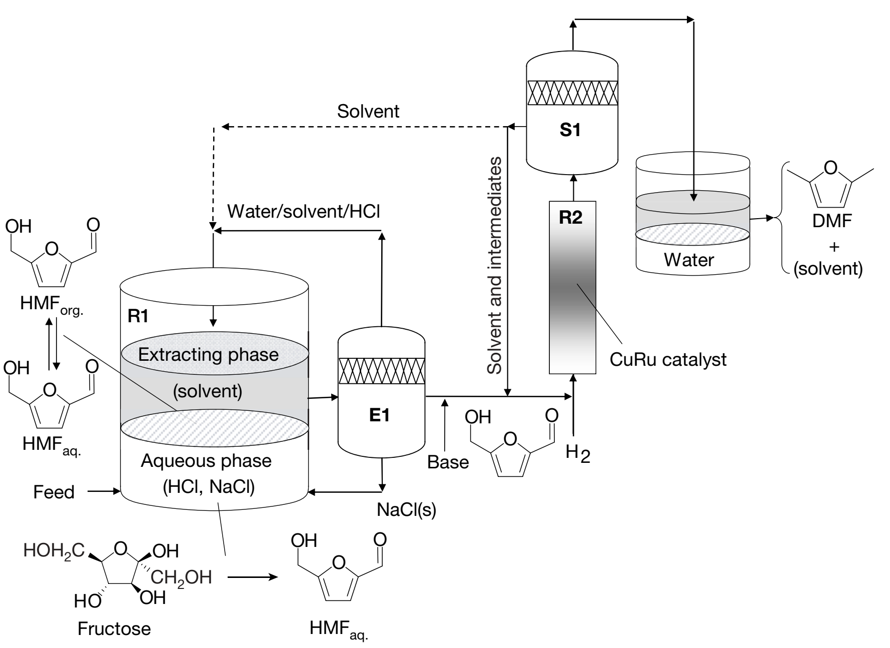

Figure 2 | Schematic diagram of the process for conversion of fructose to DMF. Diagram includes selective dehydration of fructose to form HMF in a biphasic reactor (R1); evaporation of water and HCl from the liquid solvent containing HMF, leading to precipitation of NaCl (E1); hydrogenolysis of HMF to DMF over a CuRu catalyst (R2); and separation of the DMF product from the extracting solvent and unreacted intermediates (S1). See text for details.

To implement our process, we developed a new catalytic system to produce HMF in high yields from concentrated sugar solutions (R1 in Fig. 2). Although multiple catalytic systems have been reported for the production of HMF in solvents containing high boiling point components (for example, dimethylsulphoxide) to suppress side reactions[4–9], trace amounts of such components are detrimental to fuel quality, and their removal necessitates energy-intensive purification procedures. We show that HMF can be produced in high yields by the acid-catalysed dehydration of fructose in a biphasic reactor using low boiling point solvents that themselves are excellent fuel components, thereby eliminating the need for expensive separation steps to produce the final liquid fuel mixture. The reactive aqueous phase in the biphasic reactor contains an acid catalyst and a sugar, and the extracting phase contains a partially miscible organic solvent (for example, butanol) that continuously extracts the HMF product. Importantly, the addition of a salt to the aqueous phase improves the partitioning of HMF into the extracting phase, and leads to increased HMF yields without the use of high boiling point solvents.

The capacity of the organic phase to extract HMF from the reactive aqueous phase, as measured by the extracting ratio *R* (the ratio of the HMF concentration in the organic layer to that in the aqueous layer), directly affects HMF selectivity, defined as the moles of HMF produced divided by the moles of fructose reacted (Fig. 3, Table 1). Our results demonstrate that HMF selectivity increases as *R* increases, indicating that a more efficient removal of HMF from the aqueous phase prevents undesired side reactions. The addition of salt to the reactive aqueous phase increases *R* by means of the salting-out effect, whereby electrolytes alter the intermolecular bonding interactions between liquid components, decreasing the mutual solubility of the aqueous and organic phases[10,11]. The *R* value for a specific extracting solvent depends not only on the affinity of the solvent for HMF, but also on the ability of the salt to separate both phases. In the present work, the addition of NaCl to the aqueous phase resulted in the largest increase in *R* of all the salts tested; results for other salts can be found in Supplementary Information. For example, compared to experiments without salt, a 30 wt% fructose solution saturated with NaCl (35 g of NaCl per 100 g of H_2O) using 2-butanol as the extracting solvent (with initial ratio of organic and aqueous phase volumes $V_{org.}/V_{aq.} = 1.6$) results in an increase in *R* from 1.6 to 3.3, leading to an improvement in HMF selectivity from 66% to 79% (Table 1, runs 1 and 6). Notably, the presence of NaCl has the additional benefit of allowing higher values of $V_{org.}/V_{aq.}$ to be used, thus leading to higher HMF selectivities, while maintaining biphasic reaction conditions. Specifically, when the ratio $V_{org.}/V_{aq.}$ is doubled, the 2-butanol system without salt becomes monophasic, whereas the system saturated with NaCl remains biphasic, with an *R* of 3.6 and an HMF selectivity of 89% (Table 1, run 5). The primary role of NaCl is to alter the solvent properties while remaining otherwise inert. Specifically, the dehydration of fructose in the presence of NaCl, but in the absence of an extracting solvent, leads to the same HMF selectivity as in the absence of NaCl (Table 1, runs 19 and 20).

Although various extracting solvents can generate high HMF selectivity (Fig. 3), the use of 1-butanol as a solvent is advantageous for biomass applications. For instance, solvents such as 2-butanol are obtained from petroleum-derived products (by the hydrolysis of 2-butene; ref. 12), whereas 1-butanol can be produced by the fermentation of biomass-derived carbohydrates[13,14]. Also, unlike unsaturated solvents such as toluene or methylisobutylketone, 1-butanol is inert in the hydrogenolysis step of our process. The dehydration

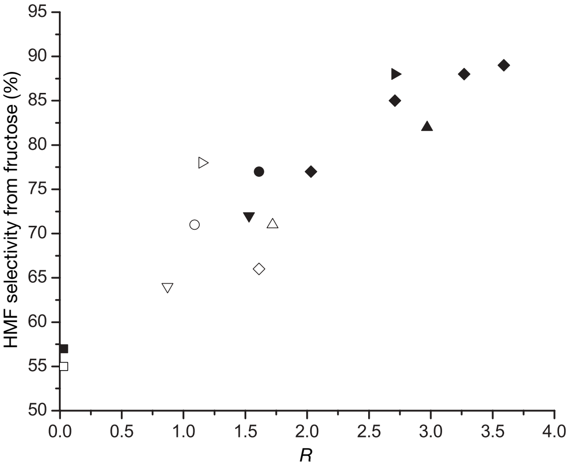

Figure 3 | Effect of extraction ratio *R* on HMF selectivity from fructose for various organic solvents. Open symbols, experiments without NaCl; filled symbols, experiments with an aqueous phase saturated with NaCl. Diamonds, 2-butanol (filled diamonds, experiments using 2-butanol as the extracting solvent and aqueous phases containing 5, 15, 25 and 35% NaCl; open diamond, experiments using 2-butanol with no salt and a $V_{org.}/V_{aq.} = 1.6$); upward-pointing triangles, 1-butanol; downward-pointing triangles, 1-hexanol; circles, methylisobutylketone; right-pointing triangles, 5:5 toluene:2-butanol; squares, no solvent. $R = [HMF]_{org.}/[HMF]_{aq.}$

reaction using 1-butanol and an aqueous phase saturated with NaCl shows an *R* value of 3.0 and an HMF selectivity of 82% (Table 1, run 8). When using 1-butanol, we observed that HMF selectivity was independent of acid content for experiments in the range of HCl concentrations from 0.01 to 0.25 M (Table 1, runs 8–12).

The extracting solvent containing HMF next undergoes a purification step (E1 in Fig. 2). For an experiment analogous to run 12 in Table 1, the stream entering the evaporator contains 260 mmol l^{-1} HMF (as measured by high performance liquid chromatography, HPLC), 2,800 mmol l^{-1} water (see Supplementary Information for calculation assumptions), 26 mmol l^{-1} NaCl (as measured by HPLC), 3.6 mmol l^{-1} HCl (as measured by acid titration with NaOH), and 1.1 mmol l^{-1} 1-chlorobutane (as measured by gas chromatography). Vacuum evaporation at low temperature (for example, 363 K) can be used to separate volatile impurities from components with lower relative volatility, such as HMF and 1-butanol. Furthermore, because the solubility of NaCl in anhydrous organic solvents is lower than in water, removal of water causes the salt to precipitate out of solution. Evaporation of 25% of the total mass of the entering stream lowers the impurity levels to 360 mmol l^{-1} water, 1.6 mmol l^{-1} NaCl, 1.5 mmol l^{-1} HCl, and 0.2 mmol l^{-1} 1-chlorobutane. Levels of 1-chlorobutane are lowered below our detection limits (<0.1 mmol l^{-1}) by neutralization with NaOH of the purified stream leaving the evaporator. Thus, the water, the NaCl, the fraction of 1-butanol that evaporates, and 58% of the HCl are recovered and recycled back into the biphasic reactor, whereas the purified liquid stream containing HMF and 1-butanol is sent for further processing.

Next, HMF is converted to DMF over a copper-based catalyst (R2 in Fig. 2). Previous studies have shown that copper chromite ($CuCrO_4$) selectively converts furfural into **7** and **6** without excessive hydrogenation of the furan ring or excessive ring decomposition products[15–17]. Accordingly, $CuCrO_4$ should be an effective catalyst for the hydrogenolysis of HMF to DMF, although no studies of this reaction have been reported. Our liquid-phase batch experiments of HMF hydrogenolysis using $CuCrO_4$ showed 61% yield (defined as the product of selectivity and conversion) for DMF and 29% yield for **5** (detailed results can be found in Supplementary Information). Importantly, however, trace levels of chloride ions in the solvent (introduced during the dehydration step and not completely removed during the evaporation step) deactivate the $CuCrO_4$ catalyst significantly. For instance, when this catalyst is used in a 1-butanol solution containing 1.6 mmol l^{-1} of NaCl, only a 6% yield of DMF is obtained. The literature regarding the deactivation of copper-based catalysts by p.p.m. levels of chloride species indicates that the primary mode of deactivation is chloride-induced sintering of copper[18].

To alleviate poisoning of the copper catalyst, we developed a chloride-resistant carbon-supported copper-ruthenium (CuRu/C) catalyst. The rationale for using this catalyst was that we first observed that a carbon-supported ruthenium catalyst was resistant to deactivation in the presence of chloride ions; however, this catalyst converted HMF primarily to **8**. Because copper and ruthenium are immiscible, and copper has a lower surface energy than ruthenium, their mixture creates a two-phase system in which the copper phase coats the surface of the ruthenium phase[19–21]. Accordingly, we hypothesized that a CuRu/C catalyst may exhibit copper-like hydrogenolysis behaviour combined with ruthenium-like chlorine resistance.

Liquid-phase hydrogenolysis experiments using a 3:1 (atomic ratio) Cu:Ru/C catalyst produce yields of 71% DMF, 4% **6**, and 12% intermediates. Notably, the same catalyst used with a purified 1-butanol solution containing 1.6 mmol l^{-1} of NaCl generates yields of 61% DMF, 4% **6**, and 20% intermediates. Thus, although CuRu/C is affected to some extent by the presence of chloride species, its performance is markedly superior to that of $CuCrO_4$.

Alternatively, because NaCl does not evaporate, vapour-phase hydrogenolysis experiments were performed using a flow reactor to eliminate effects of chloride ions on CuRu/C. Vapour-phase hydrogenolysis using a 3:2 Cu:Ru/C catalyst shows yields of 76–79% DMF and ~5% intermediates for 1.5 and 10 wt% HMF feeds (see

Table 1 | Dehydration results for 30 wt% fructose solutions

Run	Salt (%)	Organic phase	Conversion (%)	Selectivity (%)	$[HMF]_{aq.}$ (g l^{-1})	$[HMF]_{org.}$ (g l^{-1})	*R*	$[Salt]_{org.}$ (g l^{-1})	$[H_2O]_{org.}$ (wt%)
1	0*	2-butanol	58	66	28.6	46.0	1.6	0.0	31.4
2	5	2-butanol	65	77	16.8	34.1	2.0	0.9	16.4
3	15	2-butanol	65	85	12.7	34.4	2.7	1.1	9.6
4	25	2-butanol	75	88	11.6	37.9	3.3	1.2	6.8
5	35	2-butanol	74	89§	10.6	38.1	3.6	1.6	6.5
6	35*	2-butanol	71	79	18.0	60.0	3.3	1.6	7.4
7	0	1-butanol	52	71	15.1	26.0	1.7	0.0	23.1
8	35	1-butanol	85	82§	13.2	39.2	3.0	1.6	6.1
9	35†	1-butanol	80	83	12.0	39.0	3.3	1.6	6.1
10	35†	1-butanol	88	82	12.9	43.1	3.3	1.6	6.1
11	35†	1-butanol	77	84	12.4	37.8	3.0	1.6	6.1
12	35†	1-butanol	64	84	10.2	32.4	3.2	1.6	6.1
13	0	1-hexanol	50	64	21.1	18.4	0.9	0.0	7.9
14	35	1-hexanol	78	72	19.5	29.9	1.5	0.9	2.2
15	0	MIBK	50	71	20.0	21.8	1.1	0.0	0.9
16	35	MIBK	72	77	18.3	29.3	1.6	0.2	0.0
17	0	Toluene:2-butanol‖	64	78	27.7	31.7	1.2	0	6.7
18	35	Toluene:2-butanol‖	74	88	13.8	37.4	2.7	0.8	1.9
19	0	None	44	55	53.5	0.0	0.0	0.0	-
20	35	None	59	57	70.8	0.0	0.0	35.0	-
21	5‡	2-butanol	30	36	1.2	2.3	1.9	0.9	16.4
22	35‡	2-butanol	56	48	1.1	3.9	3.6	1.6	6.5

Fructose wt% is calculated on a salt-free basis. Standard reaction conditions: $T = 453$ K and $V_{org.}/V_{aq.} = 3.2$ with 0.25 M HCl catalyst (mol HCl per l of aqueous phase). Salt % is expressed as grams of salt divided by grams of water × 100.

* Runs that used $V_{org.}/V_{aq.} = 1.6$.

† Runs 9–12 used 0.12, 0.06, 0.03 and 0.01 M HCl, respectively.

‡ Runs that used a 10 wt% glucose (salt-free basis) feed.

§ Selectivity values for 1-butanol and 2-butanol systems saturated with NaCl are reported as means with s.d. of ±1.3% and ±1.5%, respectively ($n = 5$).

‖ 5:5 mass ratio.

Supplementary Information for detailed results). No chlorinated hydrocarbons were detected after reaction. Thus, although the vapour-phase process requires vaporization of the feed, it offers multiple benefits. First, when compared to the liquid-phase process, it generates no by-products and fewer intermediates. Second, it can process both dilute and concentrated HMF solutions. Third, because the same yields were obtained when using 1-butanol or 1-hexanol, other solvents can be used without altering the selectivity. Last, although the catalyst slowly deactivates after processing an amount of HMF equivalent to 1.7 times the mass of the catalyst, it can be regenerated fully by flowing hydrogen at the reaction temperature.

DMF can optionally be hydrogenated to **9** over a ruthenium catalyst. **9** contains a higher hydrogen to carbon ratio than DMF, which translates into a higher energy content. Moreover, **9** may provide additional stability on storage over extended periods of time because it contains a fully hydrogenated furan ring. The toxicological properties of neither DMF nor **9** have been thoroughly tested. The limited information available suggests that DMF is not more toxic than current fuel components; however, long-term studies must be performed before these furan components are approved for commercial use (see Supplementary Information for details).

The final step involves the separation of DMF from the solvent and the reaction intermediates (S1 in Fig. 2). The more volatile components (that is DMF, **6** and water) can be separated from the solvent and the intermediates; the latter stream can be then recycled back to the hydrogenolysis reactor. On condensation, the hydrophobic products DMF and **6** separate spontaneously from water. Depending on the final fuel composition requirements, a distillation process may be used to control more precisely the distribution of components and also to recycle a fraction of the solvent to the dehydration reactor. We note that the energy required to evaporate the stream containing DMF and 1-butanol, leading to product separation, is approximately one-third of the energy required to evaporate an aqueous solution of ethanol produced by fermentation for biofuel applications (see Supplementary Information).

The efficiency of wide-scale production of DMF from biomass would improve if a more readily available feedstock, such as glucose, was used. Although we have achieved moderate yields of HMF directly from glucose (Table 1, run 22), the conversion of fructose is more selective. In this respect, efficient processes already exist to produce high levels of fructose from glucose, such as enzyme-catalysed isomerization combined with a simulated moving-bed separation[22,23]. Although challenges remain for commercial application, this research opens a new path for the production of DMF as a biomass-derived liquid transportation fuel.

METHODS SUMMARY

Dehydration experiments. In a typical experiment, a hexose-containing aqueous solution (for example, 30 wt% fructose on a salt-free basis), an inorganic salt (for example, NaCl), an acid catalyst (for example, 0.25 M HCl) and an organic solvent (for example, 1-butanol) were mixed in a thick-walled glass reactor. The reaction was carried out at 453 K, at the total pressure generated by the vapour pressures of the volatile components at this temperature, and a constant initial volumetric ratio of organic and aqueous phases ($V_{\mathrm{org.}}/V_{\mathrm{aq.}}$). A reaction time of approximately 3 min was used to convert ~75% of the feed.

Hydrogenolysis experiments. Liquid-phase hydrogenolysis experiments were carried out using 5 wt% HMF in a 1-butanol solution at 493 K and 6.8 bar H_2 pressure. Vapour-phase experiments were performed in a flow reactor at 493 K with a liquid feed rate of 0.2 $\mathrm{cm}^3\,\mathrm{min}^{-1}$, and a weight hourly space velocity (defined as grams of HMF per hour per gram of catalyst) of 0.15 h^{-1} and 0.98 h^{-1} for 1.5 wt% and 10 wt% HMF solutions in 1-butanol, respectively. CuRu/C catalysts were prepared by incipient wetness impregnation (defined as the condition where the impregnation liquid containing the metal salt is added to fill the pore volume of the catalyst support, equal to 1.06 ml per gram of catalyst in this case) of a commercial catalyst consisting of 10 wt% Ru on carbon (C-10 catalyst consisting of high performance ruthenium on Vulcan XC-72 carbon, E-TEK Division, PEMEAS Fuel Cell Technologies) with a copper nitrate ($CuNO_3{\cdot}2.5H_2O$, Sigma-Aldrich) water solution.

Full Methods and any associated references are available in the online version of the paper at www.nature.com/nature.

Received 26 December 2006; accepted 11 May 2007.

1. Parikka, M. Global biomass fuel resources. *Biomass Bioenergy* **27,** 613–620 (2004).
2. Ragauskas, A. J. *et al.* The path forward for biofuels and biomaterials. *Science* **311,** 484–489 (2006).
3. Barlow, M. T., Smith, D. J. & Steward, D. G. Fuel composition. European patent EP0082689 (1983).
4. Román-Leshkov, Y., Chheda, J. N. & Dumesic, J. A. Phase modifiers promote efficient production of hydroxymethylfurfural from fructose. *Science* **312,** 1933–1937 (2006).
5. Brown, D. W., Floyd, A. J., Kinsman, R. G. & Roshan-Ali, Y. Dehydration reactions of fructose in non-aqueous media. *J. Chem. Technol. Biotechnol.* **32,** 920–924 (1982).
6. Kuster, B. M. F. 5-Hydroxymethylfurfural (HMF). A review focussing on its manufacture. *Starch* **42,** 314–321 (1990).
7. Moreau, C., Belgacem, M. N. & Gandini, A. Recent catalytic advances in the chemistry of substituted furans from carbohydrates and in the ensuing polymers. *Top. Catal.* **27,** 11–30 (2004).
8. Szmant, H. H. & Chundury, D. D. The preparation of 5-hydroxymethylfurfuraldehyde from high fructose corn syrup and other carbohydrates. *J. Chem. Technol. Biotechnol.* **31,** 135–145 (1981).
9. van Dam, H. E., Kieboom, A. P. G. & van Bekkum, H. The conversion of fructose and glucose in acidic media: Formation of hydroxymethylfurfural. *Starch* **38,** 95–101 (1986).
10. Eisen, E. O. & Joffe, J. Salt effects in liquid-liquid equilibria. *J. Chem. Eng. Data* **11,** 480–484 (1966).
11. Tan, T. C. & Aravinth, S. Liquid-liquid equilibria of water/acetic acid/1-butanol system—effects of sodium (potassium) chloride and correlations. *Fluid Phase Equil.* **163,** 243–257 (1999).
12. Neier, W., Webers, W., Ruckhaber, R., Osterburg, G. & Ostwald, W. Continuous production of sec-butanol. German patent DE3040997 (1982).
13. Jones, D. T. & Woods, D. R. Acetone-butanol fermentation revisited. *Microbiol. Rev.* **50,** 484–524 (1986).
14. Ramey, E. D. Continuous two-stage dual path anaerobic fermentation of butanol and other organic solvents using two different strains of bacteria. US patent US5753474 (1998).
15. Manly, D. G. & Dunlop, A. P. Catalytic hydrogenation. I. Kinetics and catalyst composition in the preparation of 2-methylfuran. *J. Org. Chem.* **23,** 1093–1095 (1958).
16. Rao, R. S., Baker, R. T. & Vannice, M. A. Furfural hydrogenation over carbon-supported copper. *Catal. Lett.* **60,** 51–57 (1999).
17. Zheng, H.-Y. *et al.* Towards understanding the reaction pathway in vapour phase hydrogenation of furfural to 2-methylfuran. *J. Mol. Catal. Chem.* **246,** 18–23 (2006).
18. Twigg, M. V. & Spencer, M. S. Deactivation of supported copper metal catalysts for hydrogenation reactions. *Appl. Catal. A* **212,** 161–174 (2001).
19. Helms, C. R. & Sinfelt, J. H. Electron spectroscopy (ESCA) studies of ruthenium-copper catalysts. *Surf. Sci.* **72,** 229–242 (1978).
20. Sinfelt, J. H. Supported bimetallic cluster catalysts. *J. Catal.* **29,** 308–315 (1973).
21. Sinfelt, J. H., Lam, Y. L. & Cusumano, J. A. Nature of ruthenium-copper catalysts. *J. Catal.* **42,** 227–237 (1976).
22. Broughton, D. B. & Gerhold, C. G. Continuous sorption process employing fixed beds of sorbent and moving inlets and outlets. US Patent US2985589 (1961).
23. Hashimoto, K., Adachi, S. & Shirai, Y. in *Preparative and Production Scale Chromatography* (eds Ganestos, G. & Barker, P. E.) 395–417 (CRC Publishing, New York, 1993).
24. Jones, J. H., Fenske, M. R. & Rusk, R. A. Vapor-phase oxidation as a process for raising octane number. *Ind. Eng. Chem. Prod. Res. Dev.* **10,** 57–65 (1971).
25. Graboski, M. S. *An Analysis of Alternatives for Unleaded Petrol Additives for South Africa* (Technical Report, United Nations Environment Programme, Nairobi, Kenya, 2003); available at ⟨http://www.unep.org/PCFV/PDF/PubGraboskiReport.pdf⟩.

Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

Acknowledgements This work was supported by the National Science Foundation Chemical and Transport Systems Division of the Directorate for Engineering, and the US Department of Energy Office of Basic Energy Sciences. We thank R. McClain and the UW Chemistry Department for access to their mass spectrometer. We also thank D. Simonetti, R. West, J. Chheda, E. Kunkes, S. Chen and S. Laumann for discussions and technical assistance.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to J.A.D. (dumesic@engr.wisc.edu).

METHODS

Dehydration reactions. Aqueous- and organic-phase components including reactants (fructose and glucose), inorganic salts (NaCl, KCl, NaBr, KBr, $NaNO_3$, Na_2SO_4, Na_2HPO_4, $CaCl_2$, CsCl and $MgCl_2$), organic solvents (2-butanol, 1-butanol, MIBK, toluene and 1-hexanol), and the acid catalyst HCl were obtained from Sigma-Aldrich.

Batch catalytic experiments were carried out in 10 ml, thick-walled glass reactors (Alltech) heated in a temperature controlled oil bath placed on top of a magnetic stirrer. The temperature in the oil bath was measured by a K-type thermocouple (Omega) and controlled using a series 16A temperature controller (Dwyer Instruments) coupled with a 150 W heating cartridge (McMaster Carr). In a typical experiment, 1.5 g of 0.25 M HCl aqueous phase solution composed of 30 wt% fructose (salt-free basis) and an amount of extracting solvent necessary to keep $V_{\mathrm{org.}}/V_{\mathrm{aq.}} = 3.2$ were poured into the reactor. Before use, the extracting solvent was pre-contacted with an aqueous phase containing the same amount of salt as the aqueous phase in the dehydration reactor. In this way, the extracting phase was saturated with water and salt before reaction. The reactor was placed in a preheating oil bath set at 353 K for 2 min, and then transferred into an oil bath set at 453 K to perform the reaction. Reaction times ranged from 2.5 to 3 min to obtain conversions close to 75%. The reaction was stopped by cooling the reactor in an ethylene glycol bath at 253 K. Next, on separation, the masses and densities of both phases were measured. For each phase, density values were measured by weighing a constant volume.

Sample analyses were performed by HPLC using a Waters 2690 system equipped with PDA 960 UV (320 nm) and RI-410 refractive index detectors. Fructose disappearance was monitored with an Aminex HPX-87H column (Biorad), using MilliQ water (pH 2) as the mobile phase at a flow rate of $0.6\,\mathrm{ml\,min^{-1}}$ and a column temperature of 333 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 $0.7\,\mathrm{ml\,min^{-1}}$ and a column temperature of 308 K. The gradient is described in Supplementary Information.

Fructose conversion and HMF selectivity were calculated from the product of the aqueous and organic phase concentrations obtained in the HPLC and their corresponding volumes after reaction.

After the dehydration reaction, impurity levels of the organic layer were measured using a combination of techniques. Levels of NaCl were measured using the Aminex HPX-87H column in the HPLC; acid content was measured by acid titration with NaOH; and 1-chlorobutane content was measured with gas chromatography (Shimadzu GC-2010 with an FID detector and a DB-5 column from Alltech). Water content before and after the purification step was obtained by mass balance. Specifically, given that the initial amounts of all components are known, as well as the final masses of the aqueous and organic phases and the concentration of the organic solvent in the aqueous layer (HPLC), it is possible to calculate the water content in the extracting solvent. For example, after mixing 5 g of water saturated with NaCl with 10 g of anhydrous 1-butanol, the mass of the organic layer is 10.6 g and it is determined that 0.06 g of 1-butanol is present in the aqueous layer. Then, assuming that a negligible amount of NaCl transfers into the organic layer, the water content in the organic layer is 0.66 g of H_2O in 10.6 g of extracting solvent or ~2,800 mmol of H_2O per l of extracting solvent. In a similar fashion, the amount of water remaining in the extracting solvent after the purification step can be calculated by subtracting the amount of water recovered from the evaporator from the initial amount of water present in the extracting solvent before evaporation.

Hydrogenolysis reactions: catalyst preparation. CuRu/C catalysts were prepared by incipient wetness impregnation of a commercial catalyst consisting of 10 wt% Ru on carbon (C-10: HP ruthenium on Vulcan XC-72, E-TEK Division, PEMEAS Fuel Cell Technologies) with a copper nitrate ($CuNO_3 \cdot 2.5H_2O$, Sigma-Aldrich) water solution. For a typical batch of 3:2 (molar ratio) Cu:Ru catalyst, 1.55 g of copper nitrate was dissolved in 5 g of deionized (DI) water. This solution was then added drop-wise to 4.58 g of Ru/C catalyst. Following impregnation, the catalyst was dried in air at 403 K for 2 h and reduced at 523 K in flowing hydrogen for 10 h ($0.42\,\mathrm{K\,min^{-1}}$ ramp for 6 h followed by 4 h at 523 K). After reduction, the catalyst was allowed to cool to room temperature and passivated in flowing 2% oxygen in helium for 3 h. All gas flow rates were maintained at approximately $110\,\mathrm{cm^3(STP)\,min^{-1}}$. Pre-reduced barium promoted $CuCrO_4$ was used untreated from Sigma-Aldrich.

Hydrogenolysis reactions: batch reactor system. All batch reactor runs were carried out using an autoclave reactor with external temperature and stirring controller (Models 4566 and 4836, Parr Instrument). For a typical hydrogenolysis run, 2.5 g of HMF (98%, Sigma-Aldrich) was dissolved in 47.5 g of organic solvent. The solvent used was either dry 1-butanol (99.9%, Sigma-Aldrich) or 1-butanol pre-contacted with a NaCl/water solution that simulated the final untreated organic layer from the biphasic fructose dehydration step. The NaCl/water solution was made by adding 6.7 g sodium chloride into 18.9 g DI water. Next, 51 g of 1-butanol was added to the NaCl/water solution and shaken vigorously. The resulting two phases were allowed to separate for 20 min. Afterwards the organic layer was siphoned off and used as the solvent. Next, 0.75 g of CuRu/C catalyst was added to the reactor. The reactor was sealed and purged of air by adding and releasing hydrogen to a pressure of 20 bar. Hydrogenolysis reactions were carried out at 493 K with 6.8 bar initial hydrogen pressure for 10 h while using a stirring speed of 400 r.p.m. These conditions were found to be optimal for DMF yield. After 10 h the reactor was cooled to room temperature before its contents were sampled, filtered (using 0.2 μm PES syringe membrane filter), and analysed.

Hydrogenolysis reactions: flow reactor system. Supplementary Fig. 2 shows the down-flow, vapour-phase, fixed-bed reactor set-up used to convert HMF to DMF. One gram of catalyst in powder form was mixed with 2.3 g of silicon dioxide fused granules with a 4–16 mesh size (Aldrich) and loaded into a 1/4-inch outer diameter tubular stainless steel reactor. The catalyst bed was contained in the tubular reactor by an end-plug of quartz wool (Alltech). A type-K thermocouple (Omega) attached to the outside of the reactor was used to measure the reactor temperature, which was controlled with a 16A series temperature controller (Dwyer Instruments). The flow rate of H_2 was controlled with a mass-flow meter (5850 Brooks Instruments). An HPLC pump (Model 301, Alltech) was used to introduce the feed solution into the down-flow reactor through a needle. The effluent from the reactor was condensed at room temperature in a separator, allowing for periodic sampling of the liquid product stream. The effluent gas stream passed through a back-pressure regulator (GO Regulator, Model BP-60), which controlled the system pressure, and through a flow meter to measure the gas flow rate.

All runs were carried out at 100% conversion at a temperature of 493 K, using a liquid feed rate of $0.2\,\mathrm{cm^3\,min^{-1}}$, and a weight hourly space velocity (defined as grams of HMF per hour per gram of catalyst) of $0.15\,\mathrm{h^{-1}}$ and of $0.98\,\mathrm{h^{-1}}$ for 1.5 and 10 wt% runs. Other process conditions used in the experiments are listed in Supplementary Table 2. Product sampling took place for approximately every $3–6\,\mathrm{cm^3}$ of liquid feed, and reported values are mean values over all steady state points.