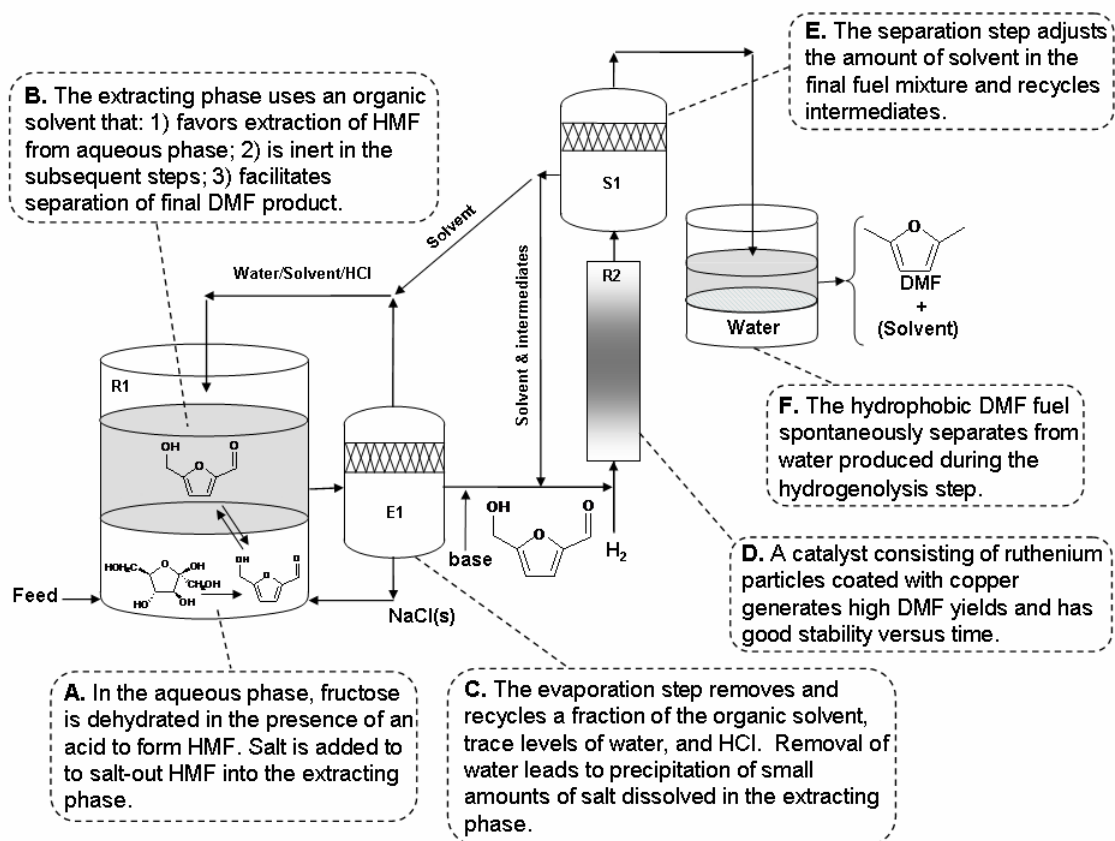
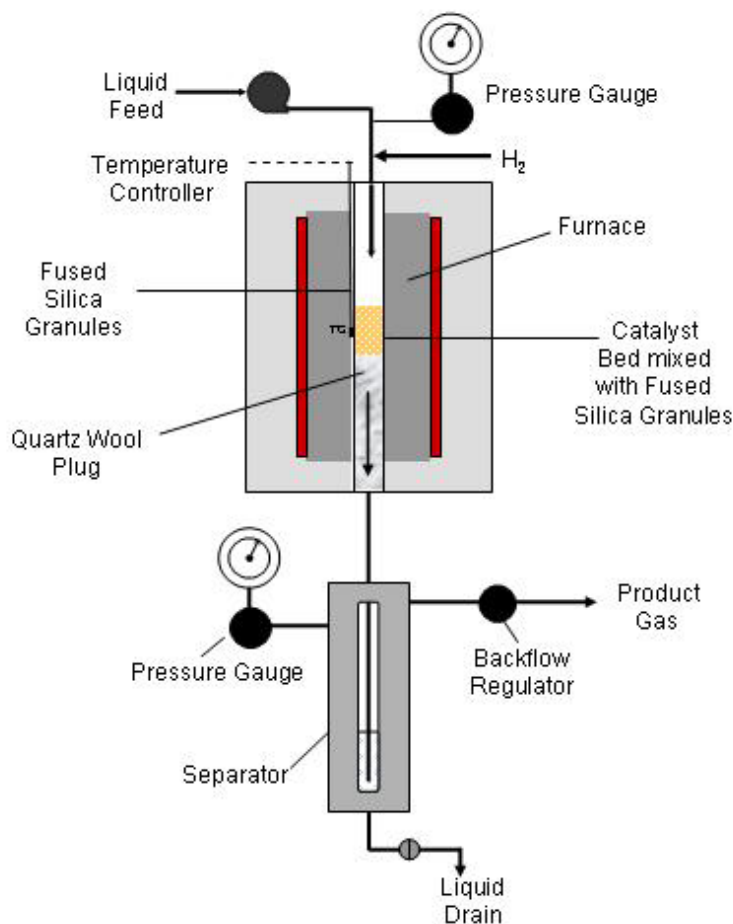


## Supplementary Figures and Legends:



Supplemental Figure 1. Annotated schematic diagram of the process for the conversion of fructose to DMF.



**Supplementary Figure 2. Schematic diagram of vapor-phase flow reactor.**

## Supplementary Methods

### Analysis Method

All liquid products were analyzed by HPLC (Waters 2695 system with a Zorbax SB-C18 5  $\mu\text{m}$  column from Agilent and PDA 960 and RI 410 detectors) and by GC (Shimadzu GC-2010 with an FID detector and a DB-5 column from Alltech). Product identification occurred by a combination of mass spectroscopy (Shimadzu QP5000 with gas chromatography inlet, electron impact ionization, and quadrupole analyzer), U.V. signature, and retention times in both HPLC and GC. Products were also purchased and calibrated for HPLC and GC analyses.

The gas stream was analyzed with two different gas chromatographs. A Hewlett Packard 5890A GC with a TCD detector and a Porapak QS 100/120 column (Alltech) was used to detect CO and H<sub>2</sub>. A Varian GC-MS (Saturn 3) using a FID detector and a GS-Q capillary column (J&W Scientific) was used to detect larger gas species. For both batch and flow reactor products, gas phase HMF-related products were negligible.

### **Method Used for GC/MS**

The method for the Shimadzu GC/MS (GC-17A, QP-5000) with Restek RTX-5 crossbond 5% diphenyl, 95% dimethyl, polysiloxane was as follows: An initial oven temperature of 323 K was held for 3 minutes; next, temperature was ramped at 20 K/min until 598 K was reached. Column pressure started at 100 kPa, held for 3 minutes, ramped at 1 kPa/min until 113 kPa was reached, and then held at 113 kPa for 0.75 minutes.

Column flow was 1.7 ml/min.

### **Method Used for HPLC with the Agilent Zorbax SB-C18 Column**

Column temperature was set at 308 K and flowrate at 0.7 ml/min. Gradient Used: 0-2 min., 100% water pH=2; 2-3 min transition and hold from 3-10 min with 80% water, 20% methanol; 10-11 min mark transition and hold from 11-15 min mark with 20% water, 80% methanol; 15-16 min mark transition and hold until 35 min mark with 100% water.

### **Compound Characterization**

Mass spectroscopy was performed starting at 33 m/z. The mass spectra and the retention times matched those of commercially available compounds and literature values from the SDBS database run by the National Metrology Institute of Japan<sup>26</sup>. Although mass spectroscopy data for **4** were not available, the mass spectrum of the target compound

matched that of the purchased version. For all the compounds described below, the retention times for the GC and the HPLC, as well as the UV signature in the HPLC (when available) matched those of the corresponding purchased compounds. The following compound numbers correspond to Figure 1 in the paper.

Compound **1**: **2,5-dimethylfuran** (CAS # 625-86-5), UV/vis:  $\lambda_{\max}$  221.5 nm; {Actual MW 96.13} M.S.: m/z (% of max intensity) 39 (14), 41 (12), 43 (100), 51 (11), 53 (41), 67 (5), 81 (16), 95 (34), **96** (37), 97 (3). Retention time in GC/MS is 2.17 min and 19.3 min in HPLC using the methods described above.

Compound **3**: **5-hydroxymethylfurfural** (CAS # 67-47-0), UV/vis:  $\lambda_{\max}$  226.2 & 282.8 nm; {Actual MW 126.11} M.S.: m/z (% of max intensity) 37 (10), 38 (18), 39 (56), 41 (100), 51 (12), 53 (14), 81 (3), 97 (43), 109 (4), 125 (4), **126** (22), 127 (2). Retention time in GC/MS is 8.5 min and 10.1 min in HPLC.

Compound **4**: **2,5-dihydroxymethylfuran** (CAS # 1883-75-6), UV/vis:  $\lambda_{\max}$  221.5 nm; {Actual MW 128.13} M.S.: m/z (% of max intensity) 38 (14), 39 (68), 41 (100), 42 (12), 43 (14), 50 (12), 51 (18), 52 (13), 53 (27), 55 (28), 65 (11), 69 (39), 97 (81), 109 (11), 111 (10), **128** (35), 129 (2). Retention time in GC/MS is 8.46 min and 9.7 min in HPLC.

Compound **5**: **2-methyl,5-hydroxymethylfuran** (CAS # 3857-25-8), UV/vis:  $\lambda_{\max}$  221.5 nm; {Actual MW 112.13} M.S.: m/z (% of max intensity) 39 (35), 41 (62), 43 (100), 50

(15), 51 (20), 52 (12), 53 (24), 55 (33), 67 (6), 69 (22), 84 (9), 95 (42), 97 (21), 111 (14), **112** (38), 113 (3). Retention time in GC/MS is 5.75 min and 16.0 min in HPLC.

Compound **6**: **2-methylfuran** (CAS # 534-22-5), UV/vis:  $\lambda_{\max}$  216.8 nm; {Actual MW 82.10} M.S.: m/z (% of max intensity) 38 (15), 39 (100), 41 (11), 43 (18), 50 (16), 51 (18), 53 (79), 54 (13), 81 (47), **82** (72), 83 (4). Retention time in GC/MS is 1.52 min and 17.8 min in HPLC.

Compound **7**: **furfural alcohol** (CAS # 98-00-0), UV/vis:  $\lambda_{\max}$  216.8 nm; {Actual MW 98.10} M.S.: m/z (% of max intensity) 37 (17), 38 (29), 39 (83), 41 (100), 42 (70), 43 (15), 50 (12), 51 (15), 52 (12), 53 (41), 55 (12), 69 (23), 70 (16), 81 (26), 97 (21), **98** (35), 99 (2). GC/MS ret. time 4.50 min. Retention time in GC/MS is 4.50 min and 11.7 min in HPLC.

Compound **9**: **2,5-dimethyltetrahydrofuran** (CAS # 1003-38-9), {Actual MW 100.16} M.S.: m/z (% of max intensity) 39 (25), 41 (100), 43 (74), 55 (14), 56 (55), 57 (12), 67 (10), 85 (27), **100** (1), 101 (0.1). GC/MS retention time 2.20 min.

**1-chlorobutane** (CAS # 109-69-3), {Actual MW 92.57} M.S.: m/z (% of max intensity) 40 (9), 41 (100), 42 (11), 43 (42), 51 (2), 56 (73), 57 (4), 63 (3), 65 (0.7), 73 (0.3), 75 (0.3). GC/MS retention time 1.73 min.

## Supplementary Discussion

### Vapor phase hydrogenolysis reaction

Detailed results for the vapor phase hydrogenolysis reaction are presented in Supplementary Table 3. We observed no signs of deactivation for feeds consisting of 1.5 wt% HMF. Runs 6-9, used the same 1 g of CuRu/C catalyst, which underwent overnight reductions at 493 K in flowing H<sub>2</sub> at 40 cm<sup>3</sup>(STP)/min. We observed signs of catalyst deactivation when 10 wt% HMF feeds were used. Deactivation was observed after processing an amount of HMF corresponding to around 1.7 times the catalyst mass. Notably, however, it was found that after deactivation became apparent, treatment for 2 h at 493 K in flowing hydrogen at 40 cm<sup>3</sup>(STP)/min was sufficient to regenerate the catalyst to initial performance, as shown by Runs 10-12, which showed 76 to 79% DMF yield. Specifically, after deactivation of the catalyst observed in Run 10, the aforementioned regeneration step was employed, followed by data collection in Run 11; after catalyst deactivation in Run 11, the catalyst was regenerated by treatment for 2 h at 573 K in flowing H<sub>2</sub> at 150 cm<sup>3</sup>(STP)/min H<sub>2</sub>, followed by data collection in Run 12. Run 14<sup>†</sup>, unlike all other runs which used purchased HMF, was an integrated run where the HMF was produced in the biphasic reactor and the 1-butanol layer was rotoevaporated, neutralized, and diluted (for comparison to the control Run 13) before being fed to the CuRu/C catalyst. In Run 15, DMF was used as the feed to the reactor, showing that approximately 7% of it remains on the catalyst. This buildup of carbon eventually leads to catalyst deactivation, such that the DMF yield starts to decrease and the yields of intermediates **4** and **5** increase. As can be seen by the carbon out/in column, approximately 80% of the carbon is recovered in a typical run.

## Supplementary Tables

Supplementary Table 1. Fructose dehydration using other inorganic salts

| Aqueous Phase   | Salt                             | Organic phase | Conversion (%)                     | Selectivity HMF (%) | R   |  |  |
|-----------------|----------------------------------|---------------|------------------------------------|---------------------|-----|--|--|
| 30 wt% fructose | NaBr                             | 2-butanol     | 83                                 | 78                  | 2.0 |  |  |
|                 | KCl                              |               | 89                                 | 82                  | 2.6 |  |  |
|                 | KBr                              |               | 86                                 | 76                  | 1.7 |  |  |
|                 | CaCl <sub>2</sub>                |               | 70                                 | 78                  | 2.7 |  |  |
|                 | CsCl                             |               | 72                                 | 76                  | 2.0 |  |  |
|                 | MgCl <sub>2</sub>                |               | 78                                 | 77                  | 2.8 |  |  |
|                 | NaNO <sub>3</sub>                |               | LOW REACTIVITY AND SOLID FORMATION |                     |     |  |  |
|                 | Na <sub>2</sub> SO <sub>4</sub>  |               |                                    |                     |     |  |  |
|                 | Na <sub>2</sub> HPO <sub>4</sub> |               |                                    |                     |     |  |  |

All dehydration reactions using the salts in the table above were carried out under the same conditions as the experiments reported in Table 1 using salt-saturated aqueous phases and an initial  $V_{\text{org}}/V_{\text{aq}} = 3.2$ .

Supplementary Table 2. Batch reactor liquid phase hydrogenolysis

| Run            | Catalyst                | Pre-contacted with H <sub>2</sub> O and NaCl | Solvent   | Conversion (%) | Selectivity |       |       |       |       | Carbon Out / In (%) |
|----------------|-------------------------|--|-----------|----------------|-------------|-------|-------|-------|-------|---------------------|
|                |                         |  |           |                | DMF (%)     | 5 (%) | 6 (%) | 7 (%) | 8 (%) |                     |
| 1              | 3:1 CuRuC               | Yes  | 1-butanol | 100            | 41.0        | 8.0   | 5.9   | 22    | 3.3   | 80                  |
| 1 <sup>†</sup> | 3:1 CuRuC               | Yes, and purified                            | 1-butanol | 100            | 61.0        | 9.4   | 3.6   | 11    | 1.8   | 86                  |
| 2              | 3:1 CuRuC               | No   | 1-butanol | 100            | 71.0        | 5.1   | 4.3   | 7.2   | 1.8   | 89                  |
| 3              | CuCrO (Barium promoted) | Yes  | 1-butanol | 18             | 0.0         | 0.0   | 0.0   | 0.0   | 0.0   | 82                  |
| 3 <sup>†</sup> | CuCrO (Barium promoted) | Yes, and purified                            | 1-butanol | 94             | 6.0         | 12.0  | 2.1   | 2.3   | 0.4   | 87                  |
| 4              | CuCrO (Barium promoted) | No   | 1-butanol | 100            | 61.0        | 29.0  | 0.0   | 0.0   | 2.8   | 92                  |

All runs were carried out at T=493 K, P=6.8 bar H<sub>2</sub>, stirred at 400 rpms with 5 wt% HMF feed, and sampled at 10 h. In Run 3 and especially 3<sup>†</sup>, significant amounts of **4** were observed and comprise the remainder of the carbon out/in balance. Runs pre-contacted with an aqueous phase saturated with NaCl contain 26 mmol/L of NaCl. <sup>†</sup>Runs pre-contacted with an aqueous phase saturated with NaCl and then purified by evaporation of 25% of the mass contain 1.6 mmol/L of NaCl.

**Supplementary Table 3. Flow reactor vapor phase hydrogenolysis**

| Run                  | Catalyst           | Solvent   | Pressure<br>(psi), H <sub>2</sub><br>flowrate<br>(cm <sup>3</sup> (STP)<br>/min) | HMF<br>(wt%) | Yield      |          |          | Carbon<br>Out / In<br>(%) |
|----------------------|--------------------|-----------|--|--------------|------------|----------|----------|---------------------------|
|                      |                    |           |  |              | DMF<br>(%) | 5<br>(%) | 6<br>(%) |                           |
| 5                    | CuCrO <sub>4</sub> | 1-butanol | 250, 19  | 1.5          | 52.0       | 0.0      | 0.0      | 52                        |
| 6                    | 3:2 CuRu/C         | 1-butanol | 250, 19  | 1.5          | 77.0       | 0.0      | 0.0      | 77                        |
| 7                    | 3:2 CuRu/C         | 1-butanol | 50, 19   | 1.5          | 62.0       | 0.0      | 4.0      | 66                        |
| 8                    | 3:2 CuRu/C         | 1-hexanol | 100, 42  | 1.5          | 78.0       | 0.0      | 0.0      | 78                        |
| 9                    | 3:2 CuRu/C         | 1-hexanol | 100, 42  | 10.0         | 78.0       | 4.0      | 2.0      | 84                        |
| 10                   | 3:2 CuRu/C         | 1-butanol | 250, 19  | 10.0         | 76.0       | 0.0      | 2.0      | 78                        |
| 11                   | 3:2 CuRu/C         | 1-butanol | 250, 19  | 10.0         | 79.0       | 6.0      | 1.0      | 86                        |
| 12                   | 3:2 CuRu/C         | 1-butanol | 250, 19  | 10.0         | 76.0       | 5.0      | 1.0      | 82                        |
| 13                   | 3:1 CuRu/C         | 1-butanol | 250, 19  | 1.5          | 72.0       | 0.0      | 0.0      | 72                        |
| 14 <sup>†</sup>      | 3:1 CuRu/C         | 1-butanol | 250, 19  | 1.7          | 72.0       | 0.0      | 0.0      | 72                        |
| Dimethylfuran wt (%) |                    |           |  |              |            |          |          |                           |
| 15                   | 3:2 CuRu/C         | 1-butanol | 250, 19  | 1.1          | 93.0       | 0.0      | 0.0      | 93                        |

All runs were carried out at T=493 K and 100% conversion of HMF. Data collected at steady state. Runs 6-9, used the same 1 g of CuRu/C catalyst and had overnight reductions at 493 K in flowing H<sub>2</sub> at 40 cm<sup>3</sup>(STP)/min. Run 11 occurs after Run 10 becomes deactivated and is regenerated through treatment at 493 K for 2 h in flowing H<sub>2</sub> at 40 cm<sup>3</sup>(STP)/min. Run 12 occurs after Run 11 becomes deactivated and is regenerated at 573 K for 2 h in flowing H<sub>2</sub> at 150 cm<sup>3</sup>(STP)/min. Runs 13-14<sup>†</sup> used the same catalyst. Symbol <sup>†</sup> indicates an integrated run using HMF produced from dehydration of fructose in which the 1-butanol layer was rotoevaporated, neutralized and diluted (for comparison to the control Run 13) before being fed to the CuRu/C catalyst.

## Supplementary Notes

### Estimation for the energy consumption in a distillation process for DMF and ethanol

In bioethanol production, a typical stream following sugar fermentation contains ~6 wt% ethanol in water. Cardona and Sanchez calculated that the distillation and dehydration of this stream would require approximately 27.4 MJ/(L of EtOH) to produce fuel-grade ethanol<sup>27</sup>. The majority of this energy is associated with phase change of water and ethanol from liquid to vapor. On the same basis, evaporating a stream containing 6 wt%

DMF in 1-butanol would require approximately 8.8 MJ/L of DMF. This value represents roughly 33% of the energy required in the ethanol process.

### **Toxicity Research on DMF and DMTHF**

Material Safety Data Sheets for DMF from 2006 show that the chemical, physical, and toxicology properties have not been thoroughly tested. Carcinogenic, mutagenic, reproductive, bioaccumulation, mobility, and ecotoxicity data are lacking. The limited information available suggests that DMF is not more toxic than current fuel components. For instance, the lethal DMF dose in rats is 1238 mg/kg body weight (gasoline is ~5000 mg/kg body weight). Also, DMF is a mutagen in hamsters at 8 mmol/L (benzene in gasoline is a mutagen in humans at 1 mmol/L) and is deadly to fathead minnows at 71 mg/L in a 96hr-LC50 test (aromatic chemicals in gasoline are lethal to fathead minnows at ~2 to 10 mg/L)<sup>28,29</sup>.

Long term studies performed at doses similar to those experienced while pumping gasoline or at a refinery (0.01 to 200 ppm, respectively) and long term oral dosages at levels similar to those of gasoline found in ground water will have to be performed before DMF fuel is approved for commercial use<sup>30</sup>. Similarly, since no data are available on 9 in regard to being carcinogenic, mutagenic, tetratogenic, a bioaccumulator, its mobility, or ecotoxicity, similar studies should be performed on this compound.

### Supplemental References

26. Spectral Database for Organic Compounds, search by CAS #,  
[http://www.aist.go.jp/RIODB/SDBS/cgi-bin/direct\\_frame\\_top.cgi?lang=eng](http://www.aist.go.jp/RIODB/SDBS/cgi-bin/direct_frame_top.cgi?lang=eng)
27. Cardona Alzate, C. A.; Sanchez Toro, O. J. Energy consumption analysis of integrated flowsheets for production of fuel ethanol from lignocellulosic biomass. *Energy* **31**, 2447-2459 (2006).
28. Sigma-Aldrich MSDS on 2,5-dimethylfuran from 2006, [www.sigmaaldrich.com](http://www.sigmaaldrich.com)
29. Russom, C.L. et al. Predicting Modes of Toxic Action from Chemical Structure Acute Toxicity in the Fathead Minnow (*Pimephales Promelas*). *Environmental Toxicology and Chemistry*, **16** (5), pg 948-967, 1997.
30. Poon, R. Inhalation Toxicology of Alcohol/Gasoline Fuels – Current Status. *Inhalation Toxicology*, 623-646 (2006).