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Purification of Biomass-Derived 5-Hydroxymethylfurfural and Its Catalytic Conversion to 2,5-Furandicarboxylic Acid

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A simple and effective water extraction method is presented for the purification 5-hydroxylmethylfurfural (HMF) obtained from a biomass dehydration system. Up to 99% of the HMF can be recovered and the HMF in aqueous solution is directly converted to 2,5-furandicarboxylic acid (FDCA) as the sole product. This purification technique allows an integrated process to produce FDCA from fructose via HMF prepared in an isopropanol monophasic system, with an overall FDCA yield of 83% obtained. From Jerusalem raw artichoke biomass to FDCA via HMF prepared in a water/MIBK (methyl isobutyl ketone) biphasic system, an overall FDCA yield of 55% is obtained.

The depletion of fossil resources has generated world-wide interest in the development of renewable and sustainable alternatives for fuels and chemicals.^[1-9] Chemical industries are shifting their focus to the development of sustainable manufacturing processes by utilizing abundant biomass in environmentally benign solvents.^[10-14] In this context, 2,5-furandicarboxylic acid (FDCA) has received significant attention as a possible replacement for terephthalic acid for the production of polyamides, polyesters, and polyurethanes.^[15] A furan-based polymer poly(ethylene-2,5-furandicarboxylate) (PEF) has been prepared from renewable sources, and it has demonstrated comparable thermal stability to polyethylene terephthalate (PET), a polymer commonly made into consumer goods for thousands of applications.^[16]

The biomass-derived FDCA can be produced by aerobic oxidation of 5-hydroxymethylfurfural (HMF) with various metal catalysts, while HMF can be prepared by acid-catalyzed dehydration of sugars or cellulose. Although the process for HMF oxidization to FDCA has been reported in literature, most of the investigations used pure/commercial HMF for the transformation with almost quantitative FDCA yield.^[17,18] Only a few examples considered the direct conversion of fresh biomassderived HMF into FDCA or combined an acid-catalyzed dehydration step with a metal-catalyzed oxidization step.^[19,20] When adopting this strategy, one critical challenge is the deactivation of oxidization catalysts as the impurities in the biomass-derived HMF will seriously affect the subsequent reaction.^[12] A recent report described a two-step process converting glucose to FDCA.^[12] In this process, HMF was produced and purified by

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distillation or multiple-cycle extraction with cyclopentane. Subsequently, the HMF was further oxidized to FDCA with Au/TiO₂ catalyst in concentrated NaOH solution, with about 80% FDCA yield of purified HMF by distillation, and 60% FDCA yield of purified HMF with cyclopentane extraction. The overall yields from glucose to FDCA were 50% and 35%.

During the past few decades, a variety of methods have been developed to convert biomass to HMF.^[11] HMF can be produced from single-phase systems by using solvents such as water, dimethyl sulfoxide,^[21] ionic liquids,^[22] isopropanol,^[23] THF, and γ -valerolactone (GVL).^[12] It can also be produced from biphasic systems, using the aqueous layer for reaction, and solvents like alcohols and ketones as extracting layers.^[24,25]

As HMF is an intermediate molecule and the market for HMF itself is small, it is important not only to optimize its synthetic process, but also to develop an efficient isolation/purification method that could be integrated into its subsequent upgrading reactions, in order to render the whole process economically viable for large-scale production. One of the problems during HMF production is the presence of impurities like humins, which are soluble in many organic solvents and coexist with HMF.^[26] The impurities will not only affect the appearance of the final product, but also affect the downstream conversion of HMF to other useful products.^[12,14]

Various methods, including extraction, column/HPLC, and activated carbon absorbent, have been used to isolate and purify HMF.^[11] The extraction method typically requires multiple cycles that not only consume large amount of solvents, but also introduce noticeable impurities to the organic layer. Column or HPLC methods can generate a high purity of HMF.^[23] However, these methods are more suitable for smallscale production rather than mass production. Activated carbon can efficiently remove impurities from HMF solution,^[27] but up to 50% of HMF was also lost and absorbed onto the absorbent in our experiments (Supporting Information, Figure S1). All these methods are costly and not suitable for mass production.

Our group recently reported an isopropanol system for the production of HMF from fructose.^[23] HMF can be easily separated from the reaction system by distillation of solvent for recycling. In our study, during the further oxidization of the crude HMF to FDCA using literature reported method with Au/HT^[18b] or Pt/C^[28] catalysts, it was found that the impurities significantly affected the catalytic oxidization reaction. In both cases, impurities deposited on the surface of the metal catalyst, resulting in the deactivation of the catalyst. As a result, a mixture of FDCA and 5-hydroxymethyl-2-furancarboxylic acid (HFCA) was observed (Supporting Information, Figure S2).

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Further investigation found that the dark humin impurities are highly soluble in isopropanol or other organic solvents (e.g., methanol, methyl isobutyl ketone (MIBK), THF, and DMSO), but insoluble in water. Since HMF is soluble in both water and organic solvent, we have devised a simple yet effective method to remove these impurities from HMF. As shown in Figure 1 a, the original HMF solution after the process of de-



Figure 1. a) As-synthesized HMF in isopropanol solution (left), crude HMF product after evaporation of solvent (middle), and HMF re-dissolved in water (right). b) Extraction times versus HMF recovery rate. Each time 5 mL of water was used for extraction.

hydration of fructose in isopropanol^[23] was dark brown in color, whereas pure HMF solution is pale yellow. Apparently, the dark brown color came from the impurities, which are mainly humins. After evaporation of isopropanol, a viscous black liquid was obtained. Water was then added into the vial to this viscous liquid. HMF was dissolved in water, and formed a transparent yellow color solution. Most of the impurities were insoluble and remained at the bottom as black solid (Figure 1a). Further study showed that the water-extraction process is very efficient and 99% of HMF could be recovered within two rounds of extraction (Figure 1b).

It was found that the complete removal of the solvent from the original HMF solution was a key to achieving high quality HMF. This was done by first evaporating isopropanol from the original solution of HMF at 90 mbar, 40 °C, followed by evaporation at lower vacuum conditions (using the continuous evaporation mode of the rotary evaporator) to completely remove the solvent. Without the second evaporation step, the trace amount of isopropanol that remains in the crude HMF will introduce noticeable impurities to the subsequent water extraction solution, and as a result, a darker color aqueous solution will get, and a slower catalytic reaction to FDCA will usually occur. This was also achieved by first evaporating isopropanol from the original solution of HMF at 90 mbar, 40 °C, and subsequently leaving the crude HMF drying in air overnight.

Alternatively, an equal volume of water was mixed with the HMF-containing isopropanol solution, and isopropanol was evaporated from the solution. After removing the impurities from the aqueous solution by either filtration or centrifugation, > 99% of HMF remained in the water solution. However, more impurities were observed in the aqueous solution. This was also due to the small amount of isopropanol remaining in the

solution, which dissolved more impurities into the water phase.

After that, oxidation reactions using Au/HT^[18b] or Pt/C^[28] catalyst were carried out with HMF before and after purification, following the reported methods. As described in the literatures, Au/HT^[18b] was used in a base-free aqueous solution, resulting in 99% FDCA yield, and Pt/C^[28] was used in NaOH aqueous solution, resulting in FDCA yield of >95%. Both literatures use high purity HMF as a starting material. It was reported that FDCA as an acid can dissolve HT (hydrotalcite) and destroy Au/HT catalyst.^[29] In our experiment, a molar equivalent of Na₂CO₃ was added to the reaction solution in order to neutralize FDCA and protect HT from dissolving. As a control, nearly quantitative yield of FDCA could also be achieved without the addition of any base. As shown in Table 1, all reactions

Table 1. Oxidation of HMF to FDCA.					
Entry	HMF	Catalyst	Time	FDCA Yield	
1 ^[a] 2 ^[b] 3 ^[a] 4 ^[b]	no extraction no extraction water extraction water extraction	Au/HT Pt/C Au/HT Pt/C	20 h 20 h 7 h 4.25 h	39% + HFCA 51% + HFCA 99% 98%	

[a] Reaction conditions: 1 mmol HMF in 10 mL H₂O, 0.25 g Au/HT catalyst, HMF/Au = 40 (mol/mol), 1 mmol Na₂CO₃, O₂ bubbling, 50 °C, 2 h, 95 °C. [b] Reaction conditions: 10 mL H₂O, 0.4 g Pt/C catalyst, HMF/Pt = 10 (mol/mol), 0.5 g NaOH; 1 mmol HMF in 5 mL H₂O was added dropwise, O₂ bubbling, 24 °C.

with unpurified HMF encountered the problem of catalyst deactivation. A mixture of HFCA and FDCA was obtained as a final product. Even with an extended reaction time to 20 h, no improvement was observed. However, for the HMF after purification, the reaction was completed in 7 h over Au/HT catalyst and in 4.25 h over Pt/C catalyst, and most importantly, only FDCA (>98% yield) was detected as the final product (Scheme 1).

A kinetics study was conducted for both pure HMF and our fructose-derived HMF with Au/HT catalyst under the same reaction conditions. It was shown that the conversion of HMF to FDCA with fructose-derived HMF was completed within 7 h. This was slightly slower than the reaction with pure HMF in which the reaction was finished in 4 h (Figure S3). After further investigation, the optimized reaction conditions for fructosederived HMF were found to be as follows: Firstly, oxygen gas was bubbled through the reaction mixture at 50°C for 2 h, during which HMF was nearly guantitatively converted to HFCA.^[30] The reaction temperature was then raised to 95 °C for another 7 h, during which the HFCA was fully converted to FDCA with yields up to 99%. Alternatively, a palladium-modified gold catalyst (Au₈Pd₂/HT) could convert purified HMF to FDCA in 7 h with 99% yield, without the need for pretreatment at lower temperature (Supporting Information, Figure S3).

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Scheme 1. Process for conversion of fructose to FDCA.

The tolerance of Au/HT catalyst for this biomass-based HMF was also studied. The Au/HT catalyst showed high activity for the first 2 runs with an FDCA yield of 98–99% (Supporting Information, Figure S4). However from the 3rd run, a significant slowdown of reaction speed was observed (\approx 56%). In a parallel experiment with pure HMF (from Aldrich) as the starting material, a lower reaction speed of 78% was also observed for the 3rd run (Supporting Information, Figure S4). To increase the durability of the catalyst, we have prepared palladium-modified Au/HT (Au₈Pd₂/HT) as a new catalyst, which showed excellent recyclability. The catalyst was kept at high activity for at least 5 runs with FDCA yield of 98–99% (Supporting Information, Figure S5), using the purified HMF from fructose. A carbon-supported Au–Pd (Au–Pd/C) catalyst was also reported to have good recyclability over Au/C in a recent literature.^[18d]

We have successfully demonstrated the conversion of fructose to HMF in isopropanol and the purification of HMF, followed by oxidation of HMF to FDCA. The two-step reactions were then integrated for the direct conversion of fructose to FDCA. In this process, fructose was converted to HMF in isopropanol with 5 mol% of HCl as catalyst. After the reaction, isopropanol was separated by evaporation and collected for the next run reaction. Then, HMF was purified with water-extraction and this aqueous solution was directly used for the oxidization reaction. As shown in Table 2, an overall FDCA yield of 83% was achieved. During this integrated process, both the

solvent (isopropanol) and catalyst were recycled. The whole process did not produce any additional waste and only water was consumed during the HMF purification process (Scheme 2). This method allows FDCA to be produced from fructose in a highly efficient, costly-effective, and environmentally benign way.

The key step for this process is to use water to extract and purify HMF. This method not only removes impurities in a simple and effective way, but also generates HMF aqueous solution that can be used directly for the next step catalytic reaction. This purification process could be simply incorporated into the mass production of FDCA or other processes.

A biphasic system is another widely used method for HMF production from fructose, as well as glucose or cellulose.^[24,25] Herein, we tested our integrated process for the conversion of fructose to FDCA by using a biphasic fructose dehydration method. In a water/MIBK biphasic system,^[25] HMF product (\approx 55% yield) in the organic layer was dried, extracted with water, and then directly used for oxidization reaction (Supporting Information, Figure S6). Under our standard conditions, > 97% FDCA yield with 100% HMF conversion was achieved. We also tested HMF prepared from glucose in a biphasic

Table 2. Integrated Process from Fructose to FDCA.						
Entry	Fructose [mmol]	$HMF^{\scriptscriptstyle{[a]}}$ Yield $[\%]^{\scriptscriptstyle{[c]}}$	$FDCA^{[b]} Yield [\%]^{[c]}$			
1	1	85.3 (84.0)	83.0			
2	5	80.2 (79.4)	78.0			

[a] Reaction conditions for step one: fructose 1 mmol, isopropanol 1.94 mL, H₂O 0.06 mL, HCl 0.05 mmol, 120 °C, 3 h. Entry 2: $5 \times$ scale up. [b] Reaction conditions for step two: HMF in step 1 was extracted in 10 mL H₂O, Au/HT 0.25 g, Na₂CO₃ 1 mmol, O₂ bubbling, 50 °C 2 h, 95 °C 7 h. [c] HMF yield is based on HPLC analysis. Isolated yield is given in parenthesis. FDCA overall yield is based on fructose.



Scheme 2. Integrated system for the conversion of fructose to FDCA: apart from the reactants only water is consumed during the reaction.

system of water/THF using HCl/AlCl₃ as catalyst with a HMF yield of 52%.^[12] For as-prepared HMF in THF solution, with our standard process, >99% of HMF was recovered after purification, and the final overall FDCA yield was 50%. We have therefore demonstrated that this HMF purification method can also be applied in other reaction systems with different solvents and different starting materials.

So far, we have successfully demonstrated the conversion of fructose and glucose to FDCA in an integrated process. It would be more interesting and challenging if we were able to convert raw biomass rather than pure sugar to FDCA. Jerusalem artichoke tuber (JAT) is an abundant, easy and fast growing biomass with very high inulin/fructose component (\approx 68-83% fructans).^[31] As an example, the conversion of JAT biomass to FDCA was tested by first converting JAT to HMF in a water/MIBK biphasic system. Compared to the monophasic system, the biphasic system works better for the conversion of JAT to HMF/FDCA, as impurities in JAT, such as biomolecules (proteins, DNA, RNA, vitamins), ions (Na⁺, K⁺, Mg²⁺, Ca²⁺, Fe³⁺), fibers and gels, will remain in the water layer, and the HMF will be extracted to MIBK, making the HMF purer. After the reaction, the crude HMF in MIBK was evaporated to remove MIBK for reuse, and the raw HMF was purified with our water extraction method to achieving a light yellow aqueous solution. The HMF aqueous solution was then used as feedstock for the Au/HT-catalyzed oxidization reaction. In this process, HMF was produced in 57% yield in the first step and the overall yield for FDCA was 55% (based on the fructose component in JAT) (Scheme 3).



Scheme 3. Integrated process for the conversion of JAT biomass to FDCA.

In summary, we have reported a simple and effective water extraction method to purify HMF obtained from a biomass dehydration system. Up to 99% of the HMF could be recovered and the HMF in aqueous solution could be directly used for further catalytic oxidization reaction to FDCA, the sole product. With this purification technique, an integrated process from fructose to FDCA via HMF prepared in an isopropanol monophasic system, we achieved an overall FDCA yield of 83%. We also used this process in a successfully demonstration of the direct conversion of JAT biomass to FDCA via HMF prepared in a water/MIBK biphasic system, with an overall FDCA yield of 55%.

Experimental Section

Materials: D-Fructose was purchased from Alfa Aesar. HMF and FDCA were purchased from Sigma–Aldrich. Anhydrous isopropanol and hydrogen chloride (37%) were purchased from Merck. All the

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chemicals were used directly without any pretreatment. Pt/C (5 wt %) was purchased from Aldrich.

General reaction procedure to produce HMF from fructose: The reaction procedure was based on our previous paper^[23] with minor adaptations. Briefly, in a 8 mL sealed glass tube fructose (2.5 mmol, 0.45 g), anhydrous isopropanol (4.85 mL), water (0.15 mL, 3 vol%), and 37% HCl (10 μ L, 5 mol%) were added. The solution was purged with argon gas 3 times until all the air was replaced. Under magnetic stirring at 700 rpm, the reaction was heated to 120°C in an oil bath for 3 h. After the reaction, the solution was cooled down in an ice bath. The solution was diluted in water for HPLC analysis. For an amount of starting materials of 1 mmol and 5 mmol, the experiments were conducted in 4 mL and 15 mL sealed glass tubes, respectively.

Reaction procedure to produce HMF from Jerusalem artichoke tuber (JAT): In a 8 mL sealed glass tube dried JAT powder (0.3 g, equivalent to 1.25 mmol fructose), HCl saturated with NaCl (1.2 mL, 0.25 M), and MIBK (4 mL) were added. The solution was purged thoroughly with argon gas 3 times until all the air was replaced. Under magnetic stirring at 700 rpm, the reaction was heated to 180 °C in a heating block for 30 min. After the reaction, the solution was cooled down in an ice bath and centrifuged. The MIBK layer was taken out for further usage.

General procedure to purify HMF: 1 mmol of HMF original solution in isopropanol was evaporated at 90 mbar and 40°C for 15 min, followed by another 15 min of a continuous evaporation process to completely remove the solvent. A dark brown viscous liquid of crude HMF product was obtained. After that, 5 mL of water was added and rotated at room temperature until the dark impurities were separated from the water solution. The transparent yellowish upper solution was taken out and the black impurities remained on the surface of the bottle wall. Another 5 mL of water

was added and rotated for another 15 min, before the upper solution was collected. The collected solution was mixed and centrifuged to remove any remaining residue, and a transparent yellowish solution was obtained. This solution was used for further reaction.

Preparation of Au/HT and Au₈Pd₂/HT catalysts: Au/HT was prepared according to the method reported in the literature.^[18b] Au₈Pd₂/HT was prepared following the same method with slight modifications. Briefly, HAuCl₄ (0.1 mmol) and NaPdCl₄ (0.025 mmol) were dissolved in water (40 mL). To this solution, hydrotalcite (1 g) was

added, followed by addition of NH_3 aqueous solution (29.5%, 0.425 mL) until pH 10 was reached. The solution was vigorously stirred for 6 h and refluxed for 30 min at 373 K. The resulting solid was filtered, washed thoroughly with water, and heated at 473 K overnight.

Catalytic reaction from HMF to FDCA: The reaction was conducted by using the method reported in the literature^[18b] with Na₂CO₃ as base. With oxygen gas bubbling, the solution was first heated to 50 °C for 2 h, and HMF was fully converted to HFCA. After that, the reaction was heated to 95 °C and kept for 7 h. The solution was diluted for HPLC analysis. For product isolation, the aqueous solution was adjusted to pH 1, and FDCA was precipitated from the solution. The precipitate was filtered and washed with ethanol. **Product analysis:** HMF and FDCA were analyzed by HPLC (Agilent Technologies, 1200 series) and confirmed with isolation yield. HPLC working conditions: column (Agilent Hi-Plex H, 7.7×300 mm, 8 µm), solvent 10 mM H₂SO₄, flow rate 0.7 mL min⁻¹, 25 °C, UV detector: 280 nm for HMF and 254 nm for FDCA. The retention times for detected compounds were 20.7 min, 24.4 min, 29.4 min, and 36.5 min for FDCA, HFCA, FFCA, and HMF, respectively. Fructose

was measured using a sugar analyzer (DKK-TOA Corporation, Japan. Model: SU-300).

Characterization: The product was characterized by ¹H and ¹³C NMR (Brucker AV-400). Au/HT catalyst was characterized by TEM (FEI Tecnai F20) and XRD (PANalytical X-ray diffractometer, X'pert PRO, with CuK_{α} radiation at 1.5406 Å). TEM, XRD, and NMR spectra are showing in the Supporting Information, Figure S7 and S8.

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- [1] J. P. Holdren, *Science* **2007**, *315*, 737–737.
- [2] A. M. Ruppert, K. Weinberg, R. Palkovits, Angew. Chem. Int. Ed. 2012, 51, 2564–2601; Angew. Chem. 2012, 124, 2614–2654.
- [3] J. N. Chheda, G. W. Huber, J. A. Dumesic, Angew. Chem. Int. Ed. 2007, 46, 7164–7183; Angew. Chem. 2007, 119, 7298–7318.
- [4] G. W. Huber, A. Corma, Angew. Chem. Int. Ed. 2007, 46, 7184–7201; Angew. Chem. 2007, 119, 7320–7338.
- [5] O. R. Inderwildi, D. A. King, Energy Environ. Sci. 2009, 2, 343-346.
- [6] Y. G. Zhang, J. Y. G. Chan, Energy Environ. Sci. 2010, 3, 408-417.
- [7] J. J. Bozell, Science 2010, 329, 522-523.
- [8] J. J. Bozell, G. R. Petersen, Green Chem. 2010, 12, 539-554.
- [9] E. L. Kunkes, D. A. Simonetti, R. M. West, J. C. Serrano-Ruiz, C. A. Gartner, J. A. Dumesic, *Science* 2008, 322, 417–421.
- [10] S. Dutta, S. De, B. Saha, ChemPlusChem 2012, 77, 259-272.
- [11] a) R. J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.* 2013, *113*, 1499–1597; b) S. P. Teong, G. Yi, Y. G. Zhang, *Green Chem.* 2014, *16*, 2015–2026; c) J. Wang, J. Ren, X. Liu, G. Lu, Y. Wang, *AlChE J.* 2013, *59*, 2558–2566.
- [12] J. M. R. Gallo, D. M. Alonso, M. A. Mellmer, J. A. Dumesic, Green Chem. 2013, 15, 85–90.

- [13] a) T. F. Wang, Y. J. Pagan-Torres, E. J. Combs, J. A. Dumesic, B. H. Shanks, *Top. Catal.* **2012**, *55*, 657; b) A. Rosatella, A. Dumesic, S. P. Simeonov, R. F. M. Frade, C. A. M. Afonso, *Green Chem.* **2011**, *13*, 754–793.
- [14] S. G. Wettstein, D. M. Alonso, Y. Chong, J. A. Dumesic, *Energy Environ. Sci.* 2012, *5*, 8199–8203.
- [15] C. Moreaua, M. N. Belgacemb, A. Gandini, Top. Catal. 2004, 27, 11-30.
- [16] A. Gandini, A. J. D. Silvestre, C. P. Neto, A. F. Sousa, M. Gomes, J. Polym. Sci. Part A 2009, 47, 295–298.
- [17] S. E. Davis, L. R. Houk, E. C. Tamargo, A. K. Datye, R. J. Davis, *Catal. Today* 2011, *160*, 55–60.
- [18] a) E. Taarning, I. S. Nielsen, K. Egeblad, R. Madsen, C. H. Christensen, *ChemSusChem* 2008, *1*, 75–78; b) N. K. Gupta, S. Nishimura, A. Takagaki, K. Ebitani, *Green Chem.* 2011, *13*, 824–827; c) S. E. Davis, M. S. Ide, R. J. Davis, *Green Chem.* 2013, *15*, 17–45; d) A. Villa, M. Schiavoni, S. Campisi, G. M. Veith, L. Prati, *ChemSusChem* 2013, *6*, 609–612; e) M. Krystof, M. Perez-Sanchez, P. D. de Maria, *ChemSusChem* 2013, *6*, 826–830.
- [19] M. Kröger, U. Prusse, K. D. Vorlop, Top. Catal. 2000, 13, 237-242.
- [20] M. L. Ribeiro, U. Schuchardt, Catal. Commun. 2003, 4, 83-86.
- [21] K. Shimizu, R. Uozumi, A. Satsuma, Catal. Commun. 2009, 10, 1849– 1853.
- [22] a) H. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, Science 2007, 316, 1597–1600; b) G. Yong, Y. G. Zhang, J. Y. Ying, Angew. Chem. Int. Ed. 2008, 47, 9345–9348; Angew. Chem. 2008, 120, 9485–9488; c) M. X. Tan, L. Zhao, Y. G. Zhang, Biomass Bioenergy 2011, 35, 1367–1370; d) J. Y. G. Chan, Y. G. Zhang, ChemSusChem 2009, 2, 731–734; e) L. K. Lai, Y. G. Zhang, ChemSusChem 2010, 3, 1257–1259; f) S. P. Teong, G. Yi, X. Cao, Y. G. Zhang, ChemSusChem 2014, DOI: 10.1002/cssc.201402131.
- [23] L. K. Lai, Y. G. Zhang, ChemSusChem 2011, 4, 1745-1748.
- [24] Y. Román-Leshkov, J. N. Chheda, J. A. Dumesic, Science 2006, 312, 1933– 1937.
- [25] Y. Román-Leshkov, J. A. Dumesic, Top. Catal. 2009, 52, 297-303.
- [26] K. D. O. Vigier, A. Benguerba, J. Barrault, F. Jerome, Green Chem. 2012, 14, 285–289.
- [27] P. Vinke, H. Van Bekkum, Starch/Staerke 1992, 44, 90-96.
- [28] W. L. Baak, US Patent 3326944, 1967, 1-3.
- [29] B. N. Zope, S. E. Davis, R. J. Davis, Top. Catal. 2012, 55, 24-32.
- [30] O. Casanova, S. Iborra, A. Corma, ChemSusChem 2009, 2, 1138-1144.
- [31] a) L. K. Zhou, A. Q. Wang, C. Z. Li, M. Y. Zheng, T. Zhang, *ChemSusChem* 2012, 5, 932–938; b) R. N. Razmovski, M. B. Sciban, V. M. Vucurovic, *Rom. Biotechnol. Lett.* 2011, 5, 6497–6503.

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Purification of Biomass-Derived 5-Hydroxymethylfurfural and Its Catalytic Conversion to 2,5-Furandicarboxylic Acid



Hell hath no furan: A simple and effective water extraction method to purify 5-hydroxylmethylfurfural (HMF) obtained from biomass dehydration system is reported. Up to 99% of the HMF can be recovered and the aqueous solution of HMF can be directly used for further catalytic oxidization reaction to 2,5-furandicarboxylic acid (FDCA) as the sole product. This purification technique allows an integrated process to produce FDCA from fructose via HMF