Toward biomass-derived renewable plastics: Production of 2,5-furandicarboxylic acid from fructose

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We report a process for converting fructose, at a high concentration (15 weight %), to 2,5-furandicarboxylic acid (FDCA), a monomer used in the production of polyethylene furanoate, a renewable plastic. In our process, fructose is dehydrated to hydroxymethylfurfural (HMF) at high yields (70%) using a γ-valerolactone (GVL)/H2O solvent system. HMF is subsequently oxidized to FDCA over a Pt/C catalyst with 93% yield. The advantage of our system is the higher solubility of FDCA in GVL/H2O, which allows oxidation at high concentrations using a heterogeneous catalyst that eliminates the need for a homogeneous base. In addition, FDCA can be separated from the GVL/H2O solvent system by crystallization to obtain >99% pure FDCA. Our process eliminates the use of corrosive acids, because FDCA is an effective catalyst for fructose dehydration, leading to improved economic and environmental impact of the process. Our techno-economic model indicates that the overall process is economically competitive with current terephthalic acid processes.

INTRODUCTION

Biomass is an abundant renewable carbon source for the sustainable supply of valuable intermediates for the production of fuels, chemicals, and bio-based plastics (1). Furan-2,5-dicarboxylic acid (FDCA) is an important renewable building block because of its potential as a substitute for a variety of petrochemicals, such as terephthalic acid and adipic acid (2). Potential applications for FDCA include polyesters, polyurethanes, and polyamides (3). A bio-based polymer of commercial interest is polyethylene furanoate (PEF), a copolymer of ethylene glycol and FDCA. PEF has improved mechanical properties compared to polyethylene terephthalate, such as higher glass transition temperature and improved tensile modulus (4). In addition, PEF has better gas barrier properties for oxygen [9× lower (5)], carbon dioxide [11× lower (6)], and water vapor [2× lower (7)]. Avantium has shown that PEF can be used for the production of water bottles, food packaging, sports apparel, and footwear. Accordingly, a strategic consortium of global companies is developing technology for the production of this bioplastic (8). Economic production of bio-based ethylene glycol from carbohydrates has been recently achieved, and as such, the current limitation for commercial production of 100% bio-based PEF is the economical production of pure FDCA.

The general reaction scheme for the production of FDCA is shown in Scheme 1. Fructose [(2R,3S,4S,5R)-2,5-bis(hydroxymethyl)oxolane-2,3,4-triol] is selectively dehydrated to produce 5-(hydroxymethyl)furan-2-carbaldehyde (HMF), which is subsequently oxidized to yield FDCA. Unfortunately, as noted by various investigators (9–11), economical production of FDCA must address technological challenges, such as (i) instability of HMF caused by undesirable condensation reactions at moderate temperatures (for example, 373 K), especially in the presence of an acid and/or a base; (ii) low solubility of FDCA in commonly used solvents; and (iii) incomplete oxidation of HMF toward FDCA, producing small quantities of partially oxidized intermediates, that is, 5-formylfuran-2-carboxylic acid (FFCA) and 5-(hydroxymethyl)furan-2-carboxylic acid (HMFCFA), that terminate the chain growth during downstream polymerization process, leading to a poor-quality polymer (10). Avantium has developed a homogeneous process that uses methoxymethylfurfural (obtained from dehydration of fructose in methanol) as the substrate; acetic acid as a solvent; and Co(OAc)2, Mn(OAc)2, and HBr as the homogeneous catalyst system to overcome the abovementioned challenges to produce FDCA (11). The homogeneous process of HMF oxidation is effective, yielding more than 96% FDCA; however, a small fraction of FFCA is retained with FDCA in solid state and requires further purification by catalytic hydrogenation of FFCA. This step requires control of hydrogenation conditions to reduce/avoid reduction of FDCA (12). Moreover, catalyst recovery and recycle require additional unit operations, and a process using a heterogeneous catalyst is desired.

Oxidation of HMF has been extensively investigated over various heterogeneous catalysts (13–21). Although high yields of FDCA are reported for HMF oxidation in water, there are potential problems with this approach. First, production of FDCA by dehydration of fructose in water is not effective because of excessive HMF degradation, leading to low HMF yield (<20%) (22). Organic solvents, such as dimethyl sulf oxide (22) and γ-valerolactone [5-methylidihydropuran-2(3H)-one] (GVL) (23), have been used to achieve high yields of HMF (>70%). However, these solvents have high boiling points, and the high reactivity of HMF at elevated temperatures prohibits the use of traditional separation techniques, such as distillation, for separation and purification of HMF (24). Another limitation of HMF oxidation in water is that FDCA has low solubility in water, and stoichiometric amounts of base (for example, sodium hydroxide) are required to keep FDCA dissolved in solution and prevent its precipitation onto the catalyst surface. The requirement of a homogeneous base is disadvantageous because mineral salt (for example, NaCl) is produced along with FDCA.

Here, we present a strategy for the conversion of fructose to HMF and the subsequent oxidation of HMF to FDCA in an organic solvent mixture using a heterogeneous catalyst. In our proposed process, HMF is obtained at high concentrations by fructose dehydration, and it is subsequently oxidized over a heterogeneous catalyst to produce FDCA at high yields. We show that the heterogeneous catalyst is stable and can be recovered and recycled, a significant advantage over previous processes based on homogeneous catalysis. We demonstrate that the
The use of a GVL/H₂O solvent system enables the formation of HMF at high yields and at high concentrations from fructose dehydration, and the high solubility of FDCA in this solvent system at reaction temperatures (for example, 383 K) enables the oxidation of HMF to FDCA at high concentrations. This latter attribute of the GVL/H₂O solvent system alleviates the need for a homogeneous base, such as NaOH or Na₂CO₃, to enhance FDCA solubility, thereby eliminating the production of undesired salts along with the production of FDCA. Our process also replaces corrosive mineral acids, such as hydrochloric acid and sulfuric acid, which are frequently used as catalysts for fructose dehydration, with an organic acid, FDCA, which is also the desired product of the process. Moreover, we demonstrate that FDCA can be separated from the GVL/H₂O solvent system by cooling the reaction system, leading to crystallization and facile product separation and solvent recycling. Furthermore, we show, using techno-economic analysis (TEA), that the proposed process is a cost-effective route for the synthesis of FDCA.

RESULTS AND DISCUSSION

Carbon-supported platinum catalysts (Pt/C) have been studied in the literature for the oxidation of HMF to FDCA in aqueous medium both in the presence (17) and absence (16) of a homogeneous base. Accordingly, we studied HMF oxidation in the GVL/H₂O solvent system over a Pt/C catalyst without using a homogeneous base. Oxidation of HMF catalyzed by 5% Pt/C at 383 K under an oxygen pressure of 40 bar for 20 hours leads to complete conversion of HMF and 95% yield of FDCA (Table 1, entry 1).

The stability of the Pt/C catalyst was investigated in a continuous tubular fixed bed reactor with 0.5 weight % (wt %) HMF feed in the GVL/H₂O (80:20) solvent system. Under the specified reaction conditions, complete HMF conversion, 60% yield of FDCA and 38% yield of FFCA, was achieved. Figure 1A shows that the Pt/C catalyst is stable for the oxidation of HMF in the GVL/H₂O solvent system. Thus, HMF can be selectively oxidized to FDCA in the GVL/H₂O solvent system where it can be produced at high yields from fructose.

Table 1. Results for HMF oxidation reactions. Reaction was carried over the 5% Pt/C catalyst (under 40-bar O₂ pressure and 383 K). DFF, furan-2,5-dicarbaldehyde.

| # | HMF concentration | Solvent (GVL/H₂O) | HMF/Plat* | Time (hours) | HMF conversion (%) | DFF yield (%) | FFCA yield (%) | FDCA yield (%) |
|---|--------------------|--------------------|-----------|-------------|-------------------|---------------|---------------|---------------|
| 1 | 0.5 wt %           | 80:20              | 15:1      | 20          | 97                | –             | –             | 95            |
| 2 | 5 wt %             | 80:20              | 20:1      | 20          | 100               | 9             | 31            | 11            |
| 3 | 7.5 wt %           | 50:50              | 30:1      | 20          | 100               | –             | 94            | –             |
| 4 | 7.5 wt % F-D HMF   | 50:50              | 30:1      | 16          | 100               | –             | –             | 93            |
| 5 | 7.5 wt % F-D HMF using HCl + ion exchange + humin adsorption | 50:50 | 30:1 | 16 | 100 | – | – | 93 |
| 6 | 7.5 wt % F-D HMF using FDCA + humin adsorption | 50:50 | 30:1 | 16 | 100 | – | – | 91 |

*Molar ratio of HMF to platinum.
Fig. 1. HMF oxidation, FDCA solubility, and fructose dehydration. (A) HMF oxidation over 5 wt % Pt/C. 0.5 wt % HMF in GVL/H₂O (80:20) solution; temperature, 373 K; pressure, 40 bar; 5 wt % Pt/C, 2.0 g; solvent flow rate, 0.05 ml/min; O₂ flow rate, 20 ml/min. Black squares represent FDCA yield. Red circles represent FFCA yield. (B) HMF oxidation over 5 wt % Pt/C. 1.0 wt % HMF in GVL/H₂O (50:50) solution, temperature, 373 K; pressure, 40 bar; 5 wt % Pt/C, 2.0 g; solvent flow rate, 0.02 ml/min; O₂ flow rate, 25 ml/min. Black squares represent FDCA yield. Red circles represent FFCA yield. (C) FDCA solubility as a function of GVL concentration. Red circles represent solubility of FDCA at 303 K. Red triangles represent solubility of FDCA at 373 K. Black squares represent heat of mixing of GVL and H₂O. (D) FDCA solubility as a function of temperature. Red circles represent GVL/H₂O (50:50). Black squares represent H₂O. (E and F) Fructose conversion and HMF yield for fructose dehydration at 453 K. Black squares represent fructose dehydration using 3 mM HCl. Blue triangles represent fructose dehydration using 0.53 wt % FDCA. Red diamonds represent FDCA stability under dehydration reaction. Solid lines are visual guides.
Fig. 2. Process and economics for the production of FDCA from fructose. (A) Pictorial representation of FDCA production from fructose. (i) 15 wt % fructose in GVL/H₂O (50:50) containing 0.53 wt % FDCA. (ii) Solution after dehydration at 453 K containing 7.5% HMF and humins. (iii) Humin removal by adsorption over activated carbon (a red colored solution instead of a black solution is obtained). (iv) Solution obtained after oxidation over a Pt/C catalyst. (B) Sankey diagram for FDCA production process and (C) costs and revenues. LA, levulinic acid; AC, activated carbon; ROI, return on investment.
solute determines its solubility in the solvent system (25). We observe that the increase in solubility of FDCA with GVL concentration correlates well with the enthalpy of mixing of GVL and water (Fig. 1C) (26). Accordingly, we performed HMF oxidation over a 5% Pt/C catalyst with high HMF concentration in GVL/H2O (80:20) (Table 1, entry 2). This experiment resulted in lower FDCA yield, in part, due to the low water content, because HMF oxidation is shown to proceed through the formation of geminal diol, and the equilibrium shifts toward the formation of the corresponding carbonyl compound in the solution with low water concentration (27). In addition, water is shown to be the oxygen source in HMF oxidation (17). Thus, we performed HMF oxidation with a solvent system containing higher water content while maintaining high FDCA solubility, that is, GVL/H2O (50:50). Figure 1D shows a comparison between the solubility of FDCA in water and in GVL/H2O (50:50) as a function of temperature. It can be seen that the solubility of FDCA increases exponentially in the GVL/H2O (50:50) with temperature, and at the temperature of 383 K, the solubility of FDCA in the GVL/H2O (50:50) system is >9 wt %. Oxidation of 7.5 wt % HMF solution in GVL/H2O (50:50) over the 5% Pt/C catalyst resulted in 94% FDCA yield (Table 1, entry 3). As the liquid product stream cooled, FDCA crystallized out from the solution, leading to facile product separation and solvent recycling. Moreover, we show that the Pt/C catalyst is stable for the oxidation of HMF in the GVL/H2O (50:50) solvent system using a three-phase trickle bed reactor (see Fig. 1B and the Supplementary Materials). In addition, we studied the influence of transport resistances in the trickle bed reactor by changing the flow rates while keeping space velocities of the liquid we studied the influence of transport resistances in the trickle bed reactor (see Fig. 1B and the Supplementary Materials). In addition, we studied the influence of transport resistances in the trickle bed reactor by changing the flow rates while keeping space velocities of the liquid feed and gaseous oxygen constant. We observe that the changing hydrodynamic properties of the flow have minimal effects on the yield of FDCA produced (table S9), indicating that there are negligible external transport resistances present in the reactor. We also probed the effects of oxygen pressure by performing the oxidation under two different oxygen pressures (40 and 20 bar). We observe that the oxygen pressure has no effect on the FDCA yield, indicating that HMF oxidation is zero order with respect to oxygen pressure. Our results are in agreement with the recent findings of Davis et al. (17).

We have previously shown that high yields of HMF are obtained by dehydration of fructose using HCl as catalyst and with GVL/H2O solvent containing high GVL content (90 wt % GVL and 10 wt % water) (23). Here, we show that similar yields (for example, >70%) are obtained using the GVL/H2O (50:50) solvent with 15 wt % fructose (Fig. 1, E and F), yielding a liquid product stream containing 7.4 wt % HMF. It is desirable to use glucose instead of fructose as the feed material, but we obtained low HMF yield from glucose dehydration (~20%), and as such, oxidation of glucose-derived HMF was not performed. However, we found that direct oxidation of the fructose-derived HMF (F-D HMF) is complicated by the by-products of the dehydration reaction, especially humins, which are produced by the polymerization of HMF and/or fructose (Table 1, entry 4). Oxidation of HMF using the homogeneous Co/Mn/Br system has been reported to suffer from deactivation of the catalyst (28).

Oxidation of F-D HMF solution obtained in GVL/H2O (50:50) resulted in low FDCA yield due to catalyst deactivation (see the Supplementary Materials). We determined that both Cl− ions and humins lead to catalyst deactivation (see the Supplementary Materials). Treatment of F-D HMF by ion exchange to remove Cl− ions and by contacting with activated carbon to remove humins produced a liquid stream of GVL/H2O containing HMF that could be oxidized over Pt/C to FDCA, resulting in 93% FDCA yield (Table 1, entry 5). In addition, FDCA crystallized out as the solvent was cooled, and solid FDCA was obtained with >99% purity (see the Supplementary Materials).

Note that complete removal of FDCA from the GVL/H2O (50:50) solvent is not achieved during crystallization. Specifically, crystallization at 277 K leads to two phases, a substantially pure crystallized solid FDCA phase that accounts for 94% of the FDCA produced in the oxidation step and can be directly used in downstream processes without further purification and a liquid phase containing ~0.5 wt % FDCA in the GVL/H2O (50:50) solvent system. FDCA is stable under the conditions used for fructose dehydration, and thus, the liquid phase obtained after crystallization can be recycled to the HMF production reactor. To avoid the use of corrosive mineral acids, we replaced HCl with FDCA, creating a more sustainable system capable of achieving high yields of HMF (Fig. 1, E and F). Replacing the mineral acid, HCl, with an organic acid, which is the product of the process, improves the economics of the process, because the Cl− ion is eliminated and the ion exchange operation is not required. In addition, the capital cost of the process decreases because FDCA is not as corrosive as the mineral acid. Oxidation of HMF obtained by the dehydration of 15 wt % fructose in GVL/H2O (50:50) using 0.53 wt % FDCA as catalyst resulted in 91% FDCA yield (Table 1, entry 6). Figure 2A shows pictorially each step of the process.

On the basis of our experimental data, we developed a process model and performed TEA of the process. The analysis suggests that our approach can produce FDCA at a minimum selling price (MSP) of $1490/metric ton (Fig. 2, B and C). The reduced MSP for the approach described in the present paper is due to the enhanced solubility of FDCA in the GVL/H2O solvent system, the ease of product separation, the use of stable heterogeneous catalysts, and the use of FDCA as a dehydration catalyst. A detailed description of the process, the assumptions made, and the model used are available in the Supplementary Materials. Among the process sections, the HMF production section is the highest contributor due to the high feedstock cost ($650/metric ton), whereas the FDCA production section is the second highest contributor due to the long residence time (4.3 hours), requiring a large volume for the HMF oxidation reactor. If a 40% reduction in the residence time can be achieved, via increased catalyst activity, and the feedstock cost is reduced by 10%, then the MSP of FDCA can be reduced by 11.9% to $1310/metric ton. Thus, the proposed approach could become an economically competitive alternative to current terephthalic acid processes based on fossil fuels [that is, a benzoic counterpart of FDCA ($1445/metric ton)].

**MATERIALS AND METHODS**

**Fructose dehydration reactions**

Fructose (>99%; Sigma-Aldrich), GVL (>99%; Sigma-Aldrich), HCl (0.5 M; Sigma-Aldrich), and FDCA (>98%; TCI Chemicals) were used as received. Milli-Q water (~18 megohm-cm) was used in all experiments.

Fructose dehydration to produce HMF was carried out in 10-ml thick-walled glass reactors (Alltech Inc.) heated in a temperature-controlled oil bath on a digital stirring hot plate (Thermo Fisher Scientific). The temperature in the oil bath was monitored by a K-type thermocouple (OMEGA Engineering). In a typical experiment, 0.88 g of fructose, along with 2.5 g of GVL, 2.5 g of Milli-Q water, and the required amount of catalyst [HCl (30 μl) or FDCA (31 mg)], was loaded into the glass reactor. The reactor was placed in an oil bath at 453 K for a specified reaction time. The mixture was stirred by a magnetic stir bar in the reactor at 600 rpm. After the desired reaction time had elapsed, the reaction was stopped by cooling the reactor in an ice bath.
The concentrations of the products were measured by high-performance liquid chromatography (HPLC) using a Bio-Rad Aminex HPX-87H column on a Waters 2695 system equipped with RI-2414 and PDA-2998 detectors. An aliquot of the product mixture was diluted 10 times with Milli-Q water and filtered with a 0.2-μm polytetrafluoroethylene (PTFE) filter before analysis. The temperature of the HPLC column was maintained at 338 K, and the flow rate of the mobile phase [water (pH 2), acidified by sulfuric acid] was 0.6 ml/min. Fructose, formic acid, and levulinic acid were analyzed with the refractive index (RI) detector, whereas the concentrations of HMF and furfural were measured with the photodiode array (PDA) detector at 320 and 210 nm, respectively. Yields of HMF, formic acid, and levulinic acid were calculated with respect to the total fructose present in the starting material. Table S1 shows typical product composition, and fig. S1 shows a typical chromatogram for fructose dehydrogenation conducted with 0.53 wt % FDCA as the dehydrogenation catalyst at 453 K for 70 min.

**Humin separation**

Activated carbon (Norit SX Ultra) was received from Cabot Corporation and used as received. Humins generated during fructose dehydrogenation were adsorbed on Norit SX Ultra carbon at 303 K. In a typical experiment, 60 mg of activated carbon was added for each gram of product solution generated by fructose dehydrogenation. The above solution was stirred at 500 rpm for 30 min. After adsorption, the solution was centrifuged at 5000 rpm for 10 min to remove the activated carbon. An aliquot of the solution after adsorption was diluted 10 times with Milli-Q water and analyzed using HPLC as described for the fructose dehydrogenation studies. More than 97% of the HMF was obtained after humin separation. Table S2 shows the typical product composition before and after humin adsorption on activated carbon.

**Ion exchange**

Ion exchange resin, Amberlite IRA400 hydroxide form, was purchased from Sigma-Aldrich. This resin was thoroughly washed with Milli-Q water and activated by passing ~500 ml of 1 M NaOH through a bed (323 K, 500 mbar). Dihydrogen hexachloroplatinate(IV) hexahydrate (H2PtCl6·6H2O, 99.99%; Sigma-Aldrich) was used as the Pt precursor. For oxidation reactions with low HMF concentrations (0.5 wt % HMF), the reaction mixture was filtered with a 0.2-μm PTFE filter to separate the catalyst. The filtrate was diluted with Milli-Q water in a 1:10 sample/water ratio. The diluted sample was injected in HPLC for product quantification.

For oxidation reactions with high HMF concentrations (5 to 10 wt % HMF), a known volume of 1 M NaOH solution was added to dissolve the products that may have precipitated. This slurry was filtered with 0.2-μm PTFE filter to separate the catalyst, and the filtrate was diluted with Milli-Q water in a 1:30 sample/water ratio. The diluted sample was injected in HPLC for product quantification.

The concentrations of products were measured by HPLC using a Bio-Rad Aminex HPX-87H column on a Waters 2695 system equipped with the PDA-2998 detector. The temperature of the HPLC column was maintained at 338 K, and the flow rate of the mobile phase [water (pH 2), acidified by sulfuric acid] was 0.6 ml/min. HMF, DFF, and FFCA were measured with the PDA detector at 320 nm, and FDCA was quantified by the signal at 290 nm. Yields of DFF, FFCA, and FDCA were calculated with respect to the total HMF added to the reactor.

**Catalyst preparation**

**5% Pt/C catalyst**

Vulcan XC-72 was purchased from Cabot Corporation. Carbon was washed thoroughly with Milli-Q water and dried in a vacuum oven (323 K, 500 mbar). Dihydrogen hexachloroplatinate(IV) hexahydrate (H2PtCl6·6H2O, 99.99%; Sigma-Aldrich) was used as the Pt precursor without further treatment.

The 5% Pt/C catalyst was prepared by incipient wetness impregnation of H2PtCl6·6H2O on carbon. For each gram of carbon support, 0.135 g of H2PtCl6·6H2O was weighed and dissolved in 1.7 g of Milli-Q water to reach the wetness point of the carbon (1.7 ml/g carbon). The dissolved precursor solution was then added to the support, and the impregnated support was dried at 383 K. The catalyst was reduced at 533 K under flowing H2 (100 ml/min) for 3 hours and passed with a mixture of 1% O2 in Ar at room temperature.

**Catalyst characterization**

**CO chemisorption**

Carbon monoxide chemisorption studies were carried out using a Micromeritics ASAP 2020C system. The catalysts were reduced under H2 flow at 533 K. After reduction, CO adsorption was performed at 308 K. The stoichiometry for adsorption of CO on surface metal atoms was assumed to be 1:1. Figure S2 shows a typical CO adsorption isotherm.
for the Pt/C catalyst. The total surface sites and the metal dispersion are shown in table S3.

**Inductively coupled plasma atomic emission spectroscopy**
The metal contents of the catalysts were determined by inductively coupled plasma atomic emission spectroscopy analysis. A PerkinElmer 400 ICP Emission Spectrometer was used for the determination of the metal loading of the catalyst. Typically, 50 mg of catalyst samples was digested in 10 g of aqua regia by refluxing at 423 K for 12 hours. The digested mixture was cooled to room temperature, diluted with Milli-Q water to 25 ml, filtered, and analyzed for the metal content. The metal loading of the catalyst are reported in table S3.

**FDCA solubility**
Solubility of FDCA as a function of GVL concentration in the solvent system at 303 K was measured in 10-ml thick-walled glass reactors heated in a temperature-controlled oil bath on a digital stirring hot plate. The reactor was capped and placed in an oil bath maintained at 303 K (±1 K). The mixture was stirred by a magnetic stir bar in the reactor at 600 rpm. After 4 hours, the reactor was opened, and an aliquot was taken while the mixture was still stirring in the oil bath. The sample withdrawn was quickly filtered through a 0.2-μm filter to minimize FDCA crystallization during filtration. The filtered sample was analyzed using HPLC to determine the FDCA concentration.

Solubility at elevated temperatures was determined as follows: A required amount of FDCA was added to a 3-ml HPLC glass vial. To the vial, 3 ml of water, GVL/H2O (50:50), or GVL/H2O (80:20) solvent system, along with a magnetic stir bar, was added. The vial was sealed and immersed in a temperature-controlled oil bath on a digital stirring hot plate. The mixture was stirred at 600 rpm. The temperature of the oil bath was increased in an increment of 3 to 5 K from 303 K. Each temperature increment was followed by 1-hour waiting time to achieve thermal equilibrium between the oil and the solution in the vial. The temperature at which no FDCA particles were visually observed was considered as the temperature at which FDCA was completely soluble.

**SUPPLEMENTARY MATERIALS**
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/1/eaap9722/DC1

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