

# The Direct Conversion of Sugars into 2,5-Furandicarboxylic Acid in a Triphasic System

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A one-pot conversion of sugars into 2,5-furandicarboxylic acid (FDCA) is demonstrated in a triphasic system: tetraethylammonium bromide (TEAB) or water—methyl isobutyl ketone (MIBK)—water. In this reaction, sugars are first converted into 5-hydroxymethylfurfural (HMF) in TEAB or water (Phase I). The HMF in Phase I is then extracted to MIBK (Phase II) and transferred to water (Phase III), where HMF is converted into FDCA. Phase II plays multiple roles: as a bridge for HMF extraction, transportation and purification. Overall FDCA yields of 78% and 50% are achieved from fructose and glucose respectively.

At the current rate of consumption, the world's crude oil reserves can only last for several more decades.<sup>[1]</sup> Therefore there is an urgent need to develop renewable and sustainable alternatives for fuels and chemicals.<sup>[2-10]</sup> The use of renewable biomass, that is, lignocellulose, would be a good choice for the production of biofuels and biochemicals.<sup>[11-14]</sup> Recently, the use of biomass-derived 2,5-furandicarboxylic acid (FDCA) to replace terephthalic acid for the production of polyethyene terephthalate (PET) has received significant attention.<sup>[15]</sup> PET is usually used for the making of films, fibers, and in particular bottles for the packaging of soft drinks, water, and fruit juices. The PET bottle market alone amounts up to ca. 15 Mt per year, which is ca. 5.9% of the total global plastics production and consumes ca. 0.2% of the global energy supply.<sup>[16]</sup> A furan-based polymer poly(ethylene-2,5-furandicarboxylate) (PEF) was prepared from biomass-derived FDCA, which has demonstrated comparable properties to petroleum-based PET.<sup>[15,17]</sup> The Coca Cola company has collaborated with Avantium, Danone, and ALPLA to develop and commercialize PEF bottles.<sup>[18]</sup> Their research has shown that PEF bottles outperform PET bottles in many areas.<sup>[18,19]</sup> In view of this application, as well as its broad potential as versatile platform chemical, FDCA is listed as one of the top-12 value added chemicals from biomass by the US Department of Energy.<sup>[20]</sup>

Biomass-derived FDCA is usually produced by a two-step process from sugars or biomass.<sup>[12,21]</sup> 5-Hydroxymethylfurfural (HMF) was first prepared by acid dehydration of C6 sugars (like fructose and glucose) or cellulose.<sup>[22]</sup> HMF was then oxidized to FDCA with stoichiometric oxidants,<sup>[11]</sup> metal catalysts,<sup>[1,23]</sup> or

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enzyme.<sup>[24]</sup> The catalytic oxidization of HMF to FDCA is usually conducted in basic environment. The reaction is very sensitive to the purity of the HMF feedstock.<sup>[12,21]</sup> Acidic residues or other impurities, such as humins, in newly prepared biomass-derived HMF deactivate the catalyst in the HMF oxidization reaction.<sup>[21,25]</sup> As a result, prior to the second reaction step, separation and purification of HMF are usually required.<sup>[12,21]</sup> This multistep process inevitably leads to high costs, making the price of FDCA less competitive than terephthalic acid. Therefore, a more efficient process for the direct conversion of biomass derivatives into FDCA is highly demanded.

The direct conversion of sugars to FDCA has been a great challenge. Given the conditions for the two-step process are in conflict with each other, Kroger et al. reported a one-pot conversion of fructose to FDCA by using a specific membrane to separate the reactor.<sup>[26]</sup> The reaction lasted for 7 days, with a total FDCA yield of 25%. In another attempt, by Schuchardt et al., cobalt acetylacetonate encapsulated in silica was used to convert fructose to FDCA directly with a total yield of 72%.<sup>[27]</sup> However, the reaction was conducted in harsh conditions (160°C, 20 bar of air) and no mechanistic details were reported. Both processes used fructose as the starting material, where glucose is a more favourable starting material owing to its abundance and lower cost.

For the production of HMF from sugars, a two-phase reactor system has been widely studied.<sup>[28]</sup> In general, sugars are dehydrated to HMF in an aqueous layer with an acid catalyst, where HMF was extracted in-situ to the organic layer. HMF production has been demonstrated in biphasic systems with glucose, fructose, and even starch and cellulose feedstock.<sup>[11]</sup>

Herein, we report a triphasic reactor, which can convert biomass sugars to FDCA in one-pot. This reaction setup consists of three phases (Phase I, II, and III) as illustrated in Scheme 1. In the designed triphasic setup, sugars (fructose or glucose) were first dehydrated to 5-hydroxymethylfurfural (HMF) in Phase I. HMF was then extracted, purified, and transferred to Phase III via a bridge (Phase II). Finally, HMF was converted to FDCA in Phase III. With this setup, overall FDCA yields of 78%



Scheme 1. The triphasic system for the direct conversion of sugars to FDCA.





**Scheme 2.** Triphasic reactors: Phase I (grey): TEAB or water, for the conversion of sugar to HMF; Phase II (red): MIBK, for HMF extraction and transportation; Phase III (blue): water, for the conversion of HMF to FDCA.

and 50% were achieved from fructose and glucose, respectively, in one pot.

Several types of triphasic reactors were designed and tested, as shown in Scheme 2 and Figure S1 (Supporting Information). Setup A is not robust enough for the reaction conditions. For the HMF oxidization step in Phase III, the reaction was conducted under O<sub>2</sub> bubbling and stirring with solid Au<sub>8</sub>Pd<sub>2</sub>/HT catalyst.<sup>[21]</sup> As the result, setup A failed to separate Phase I and III completely. During this process,  $O_2$  bubbling in Phase III brought the reaction solution as well as catalyst up to Phase I and II. As a result, Phase I was interrupted and led to incomplete reaction. This also led to lower catalytic activity of Au<sub>8</sub>Pd<sub>2</sub>/HT in Phase III. An H-type reactor was then designed, as shown in Scheme 2(B) and Figure S1 to avoid the phase mixing issue. However, the HMF mass transfer efficiency was low. Therefore, an improved setup C was designed as shown in Scheme 2(C) where the problems observed in the previous setups were eliminated. Reactions in Phase I and Phase III were well-controlled and no mixing of reactants was observed. With that, the triphasic setup C was used for optimization.

The one-pot conversion of fructose to FDCA in the triphasic reactor was then conducted as shown in Figure 1A. 0.18 g fructose (1 mmol), 0.91 g TEAB, 0.09 mL water, and 0.018 g



Figure 1. A) The triphasic reaction setup, and B) FDCA yield vs reaction time.

smashed Amberlyst-15 were added into the reactor (Phase I). Au<sub>8</sub>Pd<sub>2</sub>/HT catalyst, Na<sub>2</sub>CO<sub>3</sub>, and water were added to the other side of the reactor (Phase III, right side of Figure 1 a) and MIBK was added on top of Phase I and Phase III. The reactor was placed in an oil bath preheated to 95 °C, where oxygen gas was bubbled into Phase III of the reactor throughout the reaction. Aliquots of the solution from left and right sides of Phase III were taken out and combined every 5 h for HPLC analysis. Figure 1 b shows the time study for FDCA yield. For the first 10 h, FDCA yield increased almost linearly over time, reaching a maximum overall FDCA yield of 78% at 20 h. After which, the FDCA yield decreased slightly, which may be due to the degradation of FDCA over prolonged reaction time.

To study the detailed kinetic process in this triphasic reactor, step-by-step reactions were conducted. Firstly, the conversion of fructose to HMF in TEAB was carried out based on a modified literature procedure<sup>[29]</sup> at a lower reaction temperature of 95 °C. The selection of 95 °C in Phase I was in consideration of the reaction in Phase III, where the optimized reaction temperature is 95 °C.<sup>[21,23a]</sup> The conversion of fructose to HMF in TEAB is a fast reaction. It was completed in 30 min with HMF yield of 86%, similar to Afonso's results (reaction completed in 20 min).<sup>[29]</sup> Concurrently, a control reaction was conducted in a biphasic system, with 4 mL of MIBK as the extraction solvent. As TEAB is immiscible with MIBK, a clear interface between TEAB and MIBK was formed during the reaction. After 30 min



at 95  $^\circ\text{C},$  0.6 mmol and 0.22 mmol of HMF were detected in TEAB and MIBK, respectively, when 1 mmol of fructose was used. The detected HMF distribution ratio between MIBK and TEAB was about 1:2.7. In parallel, the conversion of HMF (prepared from fructose and purified by a water extraction method<sup>[21]</sup>) to FDCA was also conducted separately in 10 mL of water, with Au<sub>8</sub>Pd<sub>2</sub>/HT catalyst and Na<sub>2</sub>CO<sub>3</sub>. The reaction was conducted at 95  $^\circ\text{C}$  with O\_2 bubbling and completed in 7 h with an almost quantitative yield of FDCA.<sup>[21]</sup> Au<sub>8</sub>Pd<sub>2</sub>/HT is a very efficient and robust catalyst for the conversion of HMF to FDCA,  $^{\left[ 21,23a,30\right] }$  however, from Figure 1, the whole process from fructose to FDCA was completed at nearly 20 h, with a total yield of 78%. This indicates that the bottleneck of the reaction is the mass transfer of HMF from Phase I to Phase III via MIBK, slowing down the whole process. HMF concentration in Phase I and II at different reaction time further confirmed the mass transfer limitation (Table S1, Supporting Information).

The reaction progress of the triphasic system was also monitored by analyzing the FDCA yield in Phase III with HPLC. As shown in Figure S2 (Supporting Information), the FDCA yield was gradually increased from 5 h to 20 h and reached a maximum yield of 78% at 20 h. As shown in Figure 2a, only HFCA



**Figure 2.** A) HPLC results for Phase III after 5 h reaction, and B) conversion pathway from HMF to FDCA in Phase III.

(retention time = 24 min) and FDCA (retention time = 21 min) were detected in Phase III where no HMF was observed (retention time = 37 min). As expected, high content of HMF was detected only in MIBK (Phase II) and TEAB (Phase I). This indicates that the conversion of HMF to FDCA occurs via HFCA (as showed in Figure 2b) intermediate, and fast conversion from HMF to HFCA was observed. This was attributed to the easy oxidization nature of the aldehyde group of HMF.<sup>[30]</sup> Once HMF diffused to Phase III, it was quickly converted to HFCA, which then converted to FDCA slowly. As a result, only FDCA and HFCA were detected in Phase III during the process.

The mass movement in this triphasic reactor was rather clear. In the reactor, fructose was converted to HMF which was extracted to MIBK. HMF in MIBK was diffused to Phase III where it was converted to HFCA and FDCA. HFCA and FDCA are highly soluble in Phase III in the presence of Na<sub>2</sub>CO<sub>3</sub>, but are insoluble in MIBK. Hence, the final product of FDCA was only found in Phase III. As HMF was continually consumed in Phase III, it drove the mass flow of HMF which led the overall reaction to completion.

A large triphasic reactor was also designed (OD=35 mm, height=80 mm, plate separator height=20 mm, Figure S1) to test for a scale-up reaction by a factor of 5. Under the same reaction conditions, we have achieved 74% FDCA yield over 20 h. This shows the feasibility of a large-scale FDCA production using this triphasic reactor.<sup>[31]</sup>

The direct conversion of glucose to FDCA in the triphasic reactor is challenging, however, more desirable as compared to fructose. To convert glucose to HMF in Phase I, TEAB was used as reaction media and Amberlyst-15/CrCl<sub>3</sub> were selected as catalysts.<sup>[32]</sup> CrCl<sub>3</sub> is important for the isomerization of glucose to fructose, and together with Amberlyst-15 made the system more efficient in the dehydration of glucose to HMF.<sup>[32]</sup> The first attempt was conducted at 95 °C. However, after 7 h, only negligible amount of FDCA was detected, with the glucose conversion of only 7.2%. The low glucose conversion may be due to the lower reaction temperature in Phase I. As reported in the literatures, the conversion of glucose to HMF in TEAB was conducted at 120 °C.<sup>[29,31]</sup> Therefore, the experimental setup was improved by tilting the reactor and heating only Phase I at 120 °C for 30 min. After that, the temperature was lowered and the whole reactor was heated at 95 °C. With O<sub>2</sub> bubbling in Phase III, the reaction proceeded smoothly and 50% FDCA yield was achieved with full glucose conversion, as shown in Table 1.

| Table 1. The conversion of glucose into FDCA in a triphasic reactor. <sup>[a]</sup> |                      |                   |                   |  |  |  |
|---|----------------------|-------------------|-------------------|--|--|--|
| Entry   | Reaction time<br>[h] | HFCA yield<br>[%] | FDCA yield<br>[%] |  |  |  |
| 1   | 10                   | 28                | 26                |  |  |  |
| 2   | 20                   | 17                | 43                |  |  |  |
| 3   | 30                   | 7                 | 50                |  |  |  |
| 4   | 40                   | 3                 | 49                |  |  |  |
| 5   | 50                   | 1                 | 48                |  |  |  |
| (10   |                      |                   |                   |  |  |  |

[a] Reaction conditions: 0.18 g glucose, 0.91 g TEAB, 0.09 g water, 18 mg Amberlyst-15, 26.6 mg CrCl<sub>3</sub>.6 H<sub>2</sub>O (10% mol), 0.25 g Au-Pd/HT catalyst, 10 mL water, 1 mmol Na<sub>2</sub>CO<sub>3</sub>. 120 °C 30 min, then 95 °C for 0–50 h with O<sub>2</sub> bubbling.

In the current triphasic reactor, we have selected TEAB as the reaction media for the conversion of sugars to HMF. The reason for this selection is due to the relatively high HMF yield (86% from fructose) that can be obtained under mild reaction conditions (95 °C for fructose and 120 °C for glucose).<sup>[29,32]</sup> Moreover, the price of TEAB is much lower as compared to imidazolium salts.<sup>[33]</sup> However, it would be advantageous if this reaction can be carried out in water. Dumesic et al. has reported a biphasic reaction system, using acid aqueous solution for sugar dehydration reaction and an organic layer for HMF extraction.<sup>[28]</sup> Similarly, we have tested to use NaCl-saturated HCI aqueous solution as the reaction media in Phase I in our triphasic system. The reaction was conducted at 95 °C and an overall FDCA yield of 41% was achieved, as shown in Table 2 below.

The low overall FDCA yield is due to the low HMF yield in the current reaction system. In a typical HCI/MIBK biphasic

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| <b>Table 2.</b> The conversion of fructose into FDCA in a triphasic reactor with an aqueous solution as Phase $I_{a}^{[a]}$ |                      |                   |                   |  |  |  |
|---|----------------------|-------------------|-------------------|--|--|--|
| Entry   | Reaction time<br>[h] | HFCA yield<br>[%] | FDCA yield<br>[%] |  |  |  |
| 1   | F                    | 12                | 10                |  |  |  |

15 3 41 20 3 4 30 1 38 [a] Reaction conditions: 0.18 g fructose, 0.6 mL 0.25 M HCI (NaCl saturated), 4 mL MIBK, 0.25 g Au-Pd/HT, 10 mL H<sub>2</sub>O, 1 mmol Na<sub>2</sub>CO<sub>3</sub>, 95 °C.

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system, the HMF yield is  $\sim$  50–70 %,<sup>[28]</sup> which was achieved in a closed reactor under reaction temperature of 150-180°C. The current triphasic system was an open system with a low reaction temperature of 95 °C. In a control experiment, fructose was converted in a similar open biphasic system at 95 °C and only 48% HMF was obtained after 20 h reaction. It is clear that the lower reaction temperature of Phase I lowered the HMF yield in the water/MIBK system and eventually led to a lower overall FDCA yield.

In conclusion, a triphasic reactor that can convert sugars into 2,5-furandicarboxylic acid (FDCA) in a one-pot process has been demonstrated. Overall FDCA yields of 78% and 50% were achieved with fructose and glucose feedstock, respectively. Kinetic studies revealed that mass transfer of HMF from Phase I to Phase III was the main bottleneck that impeded the overall reaction. This bottleneck may be overcome by better Phase II design.[31]

#### **Experimental Section**

Materials: D-Glucose and D-fructose were purchased from Alfa Aesar. TEAB, HMF, FDCA, and Amberlyst-15 were purchased from Sigma-Aldrich. MIBK was purchased from Merck. All the chemicals were used directly without any pretreatment.

The triphasic reactor was custom-made by UFO Labglass (S) Pte Ltd. Two sizes were made; the smaller one with OD = 23 mm and height = 75 mm, and the larger one with OD = 35 mm and height = 80 mm. Both reactors consist of glass plate separator with height = 20 mm. Pictures are shown in the Supporting Information, Figure S1.

Preparation of Au<sub>8</sub>Pd<sub>2</sub>/HT catalyst: Au<sub>8</sub>Pd<sub>2</sub>/HT was prepared based on our previous work.<sup>[21]</sup> Briefly, 0.1 mmol of HAuCl<sub>4</sub> and 0.025 mmol of NaPdCl<sub>4</sub> were dissolved in 40 mL of water. To this solution, 1 g of hydrotalcite was added, followed by addition of aqueous NH<sub>3</sub> solution (29.5%, 0.425 mL) until pH 10. 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.

General reaction procedure for fructose to FDCA: In the triphasic reactor, 0.18 g fructose (1 mmol), 0.91 g TEAB, 0.09 mL water, and 0.018 g smashed Amberlyst-15 were added into the reactor (Phase I). The reactor was preheated to 95°C under magnetic stirring to melt and mix all the reactants. 0.25 g Au<sub>8</sub>Pd<sub>2</sub>/HT catalyst, 0.106 g of Na<sub>2</sub>CO<sub>3</sub> (1 mmol) and 10 mL of water were added to the other side of reactor (Phase III). After that, the reactor was placed in an oil bath pre-heated to 95 °C, where 4 mL of MIBK was added on top of Phase I and Phase III. Oxygen gas was piped into the bottom of Phase III through a Pasteur glass pipette (230 mm long with open tip), with oxygen flow rate of 1 mLmin<sup>-1</sup>. Water was added if the water level decreased. The reaction was carried out for 1-30 h.

General reaction procedure for glucose to FDCA: In the triphasic reactor, 0.18 g glucose (1 mmol), 0.91 g TEAB, 0.09 mL water, 0.018 g smashed Amberlyst-15 and 0.027 g CrCl<sub>3</sub>.6H<sub>2</sub>O (0.1 mmol) were added into the reactor (Phase I) 0.25 g Au<sub>8</sub>Pd<sub>2</sub>/HT catalyst, 0.106 g of Na<sub>2</sub>CO<sub>3</sub> (1 mmol) and 10 mL of water were added to Phase III of the reactor. The reactor was tilted and Phase I of the reactor was heated to 120 °C for 30 min under magnetic stirring. After that, the reactor was placed in an oil bath pre-heated to 95°C, where MIBK was added on top of Phase I and Phase III. Oxygen was bubbled into Phase III of the reactor, where water was added if the water level decreased.

Product analysis: HMF and FDCA yields were analyzed by HPLC (Agilent Technologies, 1200 series) and confirmed with isolated yields. HPLC working conditions: column (Agilent Hi-Plex H, 7.7× 300 mm, 8  $\mu$ m), solvent 10 mM H<sub>2</sub>SO<sub>4</sub>, flow rate 0.7 mL min<sup>-1</sup>, 25 °C, UV detector, 280 nm for HMF and 254 nm for FDCA and HFCA. The retention times for detected compounds were 20.7 min, 24.4 min, and 36.5 min for FDCA, HFCA, and HMF respectively. Fructose and glucose conversions were measured using a Sugar Analyzer (DKK-TOA Corporation, Japan. Model: SU-300). For sugar analysis, during the reaction or after reaction, 10 µl of Phase I was taken out and diluted in 1 mL water (100 times dilution). The sugar concentration was measured with sugar analyzer. Before the measurement calibration was conducted with standard solution as a system requirement. Sugar conversion was then calculated based on the testing results.

Characterization: The product was characterized by <sup>1</sup>H and <sup>13</sup>C NMR (Bruker AV-400). Au<sub>8</sub>Pd<sub>2</sub>/HT catalyst was characterized by TEM (FEI Tecnai F20) and XRD (PANalytical X-ray diffractometer, X'pert PRO, with  $Cu_{K\alpha}$  radiation at 1.5406 Å). The characterization results are shown in the Supporting Information (Figure S3 and S4).

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# COMMUNICATIONS

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The Direct Conversion of Sugars into 2,5-Furandicarboxylic Acid in a Triphasic System



You can't win if you don't tri: The onepot conversion of sugars into 2,5-furandicarboxylic acid (FDCA) is demonstrated in a triphasic reactor. Sugars are first converted into 5-hydroxymethylfurfural (HMF) in Phase I, the HMF in Phase I is then extracted into Phase II and transferred to Phase III, where it is converted into FDCA. Overall FDCA yields of 78% and 50% are achieved from fructose and glucose, respectively.