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Production of 5-(formyloxymethyl)furfural from biomass-derived sugars using mixed acid catalysts and upgrading into value-added chemicals

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A B S T R A C T

In this work, 5-(formyloxymethyl)furfural (FMF) has been produced from biomass-derived hexose sugars within a biphasic reaction mixture consisting of aqueous formic acid (85%), a strong Brønsted acid catalyst, and 1,2-dichloroethane as an organic extractant. Using a combination of aqueous hydrobromic acid and formic acid, under optimized condition (80 °C, 8 h, 10 wt% substrate loading), 68% isolated yield of FMF was obtained from fructose. FMF has been demonstrated as a renewable chemical building block for the synthesis of renewable chemicals of commercial significance such as 5-methylfurfural, 2,5-diformylfuran, and 2,5-furandicarboxylic acid in good to excellent isolated yields.

1. Introduction

The transition from the petroeconomy to the bioeconomy is driven by incentives in renewable research, strict environmental regulations, and public outlook about a greener, sustainable future [1]. Biomass-derived carbohydrates have been envisaged as a source of renewable carbon that could potentially be transformed into fuels and value-added chemicals via the chemical-catalytic pathway to maximize the economic, environmental, and social benefits [2,3]. In this regard, the acid-catalyzed hydrolysis and dehydration of carbohydrates into furanics and levulinates is known for more than a century [4]. The reasonably fast and biomass agnostic process enables selective removal of oxygen atoms from the sugar molecules in the form of water without extensive defunctionalization or carbon-carbon bond scission reactions [5]. Production of 5-(hydroxymethyl)furfural (HMF **1**) by the acid-catalyzed dehydration of hexoses is a well-documented process in the literature [6]. As a biorenewable chemical intermediate, **1** has been used for the synthesis of a wide spectrum of products, including fuels and fuel additives, solvents, monomers, agrochemicals, surfactants, plasticizers, and pharmaceuticals [7]. One of the major advantages of **1** is that its structure contains only C, H, and O atoms. Though excellent yields of **1** have been realized from simple sugars like fructose, its production from polymeric carbohydrates requires special reaction conditions. Besides, the inherent hydrophilicity and instability of **1** in aqueous acid continue to dismay its purification, scalability, and process economics [8]. The isolation problem of **1** can be alleviated by transforming it into hydrophobic analogs like 5-(chloromethyl)furfural (CMF) and 5-(bromomethyl)furfural (BMF) (Scheme 1), both of which can be produced directly from carbohydrates in satisfactory yields [9]. The hydrophobic nature of CMF and BMF allows their relatively straightforward isolation from the aqueous media by solvent-solvent extraction. CMF and BMF have the potential to replace **1** in various derivative chemistry [10]. However, both CMF and BMF have halogen atoms in them that pose challenges in recycling the mineral acids used. The economic feasibility of many derivative chemistries of CMF and BMF mandate the efficient recovery of HCl and HBr, respectively, during the transformation [11]. Besides, the production of CMF and BMF requires the use of concentrated HCl and HBr, which are challenging to work with. Therefore, there is significant interest in developing new hydrophobic, stabler analogs of **1** that are straightforward to isolate from the aqueous reaction mixture, but not containing halogen atoms in their moieties [12]. Esters of **1**, such as 5-(acetoxymethyl)furfural (AMF) and 5-(formyloxymethyl)furfural (FMF **2**), have attracted significant attention over the past decade as non-halogenated, hydrophobic analogs of **1** by using inexpensive carboxylic acids [13]. Being hydrophobic but not containing halogen atoms, **2** enjoys the best of both worlds. Formic acid, used for the preparation of **2**, is a biogenic carboxylic acid and relatively innocuous for the environment. Although purified CMF or **1** can be conveniently converted into AMF or **2**, there is no significant advantage in doing so since the two-step process entails producing **1** in the first step [14]. One-pot preparation of **2** from biomass-derived carbohydrates using formic acid (FA) as the catalyst and reagent has also been reported [15]. However, the synthesis of **2** using FA alone requires relatively demanding conditions such as high reaction temperature and

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long duration [16]. 2,5-Dimethylfuran, a novel fuel oxygenate and chemical feedstock, has also been sourced from **2** [17]. FA is primarily sourced from methanol; however, novel synthetic routes have also been explored [18]. Biogenic FA can be produced by the selective oxidation of glucose or during the acid-catalyzed dehydration of hexoses [19]. FA has a multitude of applications in sustainable chemistry as a one-carbon (C1) compound, and show unusual reactivities when compared to other carboxylic acids in the homologous series [20]. We envisioned that a combination of FA with a strong Brønsted, non-nucleophilic acid would help in the dehydration of carbohydrates into **1** and its esterification with FA. Acid catalysts with a nucleophilic anion such as HCl and HBr would lead to CMF and BMF, respectively, that would react with formic acid in situ forming **2**. Since pure **1** or CMF reacts with formic acid to form **2**, we anticipated that it will form exclusively or as a major product in the reaction mixture. With no halogen atom incorporated into the product molecule, the recovery problem of HCl or HBr would be alleviated and make the process economically more attractive. Therefore, in the acid mixture, FA would act as a reagent rather than an acid catalyst. We propose using an aqueous-organic biphasic reaction mixture that would help **2** to sequester into the organic solvent as soon as it forms and shielded from hydrolysis and other decomposition pathways in aqueous acid. After the reaction, the organic solvent containing **2** could simply be phase-separated, and the aqueous acid recycled. FA can be isolated from the acid mixture by vacuum distillation. In this work, selective derivatization of **2** into important renewable chemicals has also been undertaken.

Table 1
Production of FMF **2** from fructose using a mixture of formic acid and a strong Brønsted acid catalyst. Reaction conditions: fructose (2 g), FA (20 mL, 85%), acid catalyst (160 mol%), DCE (40 mL).

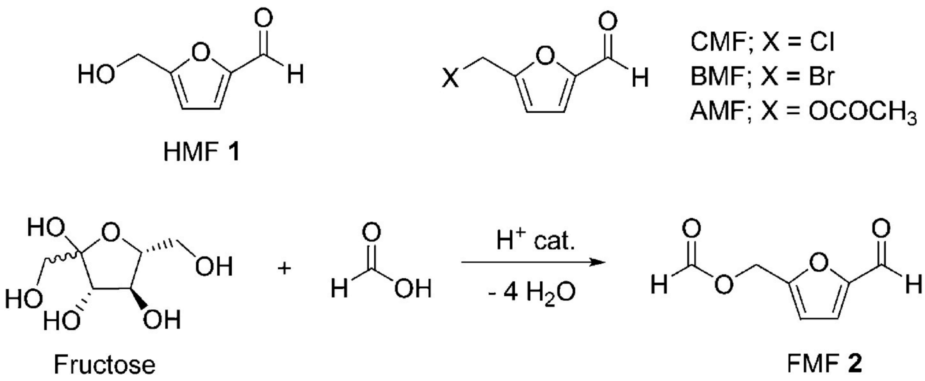
S/N	Acid catalyst	Reaction conditions	Yield of FMF (%)[a]
1	FA	Reflux, 20 h	15
2[b]	FA + HCl	Reflux, 8 h	48
3	FA + CH_3SO_3H	Reflux, 16 h	50
4[c]	FA + HBr	Reflux, 8 h	68
5	FA + H_2SO_4	Reflux, 16 h	38
6	FA + H_3PO_4	Reflux, 24 h	42

[a] Isolated yield.
[b] CMF formed as co-product was transformed into FMF.
[c] BMF formed as co-product (minor) was transformed into FMF. Around 10% LA was isolated from the aqueous layer along with 0.1 g of insoluble humin.

2. Results and discussion

Initially, the dehydration of fructose was attempted in FA alone using 1,2-dichloroethane (DCE) as the extracting solvent. DCE was chosen as solvent since chlorinated solvents work best in preparing furanics like CMF and BMF, has a decent boiling point, and chemically inert under the reaction conditions applied. In a typical reaction, fructose (2 g) was dissolved in 20 mL of FA (85%, aq.) and 20 mL of DCE was added. The biphasic mixture was placed in a pre-heated oil-bath and refluxed for 20 h under constant magnetic stirring. After cooling down the reaction mixture, the DCE layer was phase separated and distilled off to obtain **2** in only 15% yield (after chromatographic purification over silica gel). Slower kinetics of the dehydration of fructose by a weak acid like FA (pKa 3.74) was responsible for the low yield of **2** since prolonging the reaction time for another 12 h afforded additional 10% yield of **2**. The combination of FA with various strong Brønsted acids was then examined as a catalyst mixture for the production of **2** from fructose (Table 1).

When a mixture of HCl (35%, aq.) and FA was used (entry 2), the reaction kinetics accelerated significantly. However, even after using only a small quantity of HCl (5% of the total volume of acid catalyst), CMF formed in noticeable quantity along with **2**. The observation can be explained by the superior nucleophilicity of the chloride ion. Interestingly, when purified CMF was reacted with FA in the presence of an equivalent amount of ammonium formate, **2** was obtained in 87% isolated yield within 1 h at 60 °C. However, ammonium chloride is produced as a salt waste. Therefore, the DCE layer containing the mixture of CMF and **2** was phase-separated from the reaction mixture and then reacted with fresh FA at 80 °C till the conversion of CMF was complete. Evaporation of DCE and chromatographic purification gave a 48% isolated yield of **2**. When CH_3SO_3H was used as the Brønsted acid in combination with FA, **2** was isolated from the DCE layer in a 50% yield after refluxing for 16 h (entry 3). The longer duration was required due to the lower Brønsted acidity of CH_3SO_3H when compared to HCl. Shorter reaction time led to lower yields due to incomplete conversion of fructose. When sulphuric acid was used, under identical conditions, the yield of **2** was only 38%. Although the acidity of CH_3SO_3H and H_2SO_4 is similar, the lower yield of **2** can be attributed to indiscriminate dehydration of sugars by the latter, which led to noticeably more insoluble humin formation. When H_3PO_4 was used as the catalyst, the reaction provided only a 42% yield of **2** even after 24 h of refluxing. When HBr (aq, 48%) was used as the catalyst, a mixture of BMF and **2** was initially obtained, which was then transformed entirely into **2** by reacting with fresh FA. After purification, **2** was isolated in 68% yield. The higher yield of **2** in the case of HBr can be attributed to the stronger Brønsted acidity of HBr and the easier transformation of BMF into **2** during the reaction. The conversion of BMF to **2** also relatively faster when compared to CMF since the bromide group is considerably more labile and forms **2** by nucleophilic substitution reaction. Alternatively, **2** is formed by the esterification of **1**, formed as an intermediate by the hydrolysis of BMF. When the reaction was refluxed for 4 h, **2** was isolated in only 42% yield. The lower yield of **2** was due to the incomplete conversion of fructose. When the reaction time was extended to 12 h, the yield of **2** was 53%. This is due to the fact that **2** (also BMF) continue to degrade slowly in aqueous acid. Thus, the reaction should be quenched

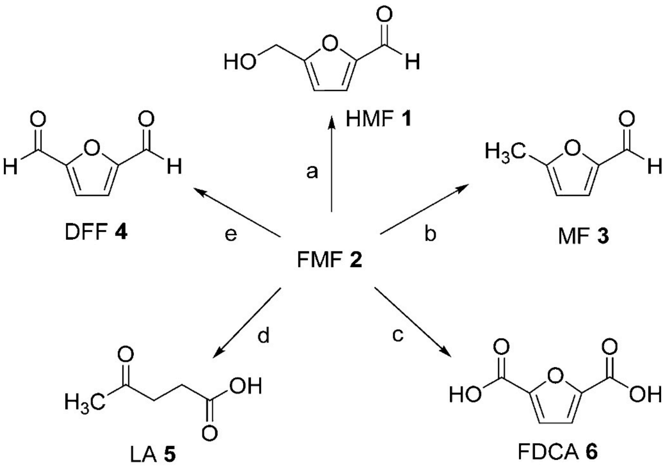


Scheme 1. Structure of HMF **1** and some of its hydrophobic congeners (top), and preparation of FMF **2** by acid-catalyzed dehydration of fructose in formic acid (bottom).

at optimum time (ca. 8 h) when the rate of decomposition of **2** becomes faster than its generation. The mixture of HBr and FA was then used as the catalyst mixture for the formation of **2** from other sugars and carbohydrates. Glucose afforded a 52% yield of **2** under identical conditions. The result may be explained by the relatively straightforward and more selective dehydration of fructose from its fructofuranose form. Glucose dehydrates into **1** directly or via isomerization into fructose first during the reaction. In both cases, more side products form, and the selectivity to **1** decreases. The trend is in accordance with most literature reports for the preparation of **1**. Sucrose gave a 58% yield of **2**, marginally better than glucose, possibly due to the presence of fructose (50 mol%) in the sucrose moiety. In the case of polymeric carbohydrates (e.g., starch, cellulose), the reaction mixture was refluxed for 24 h, but **2** was obtained in lower yields. The results may be explained by the feedstock's insolubility in the reaction mixture and slower kinetics of the depolymerization step, leading to more side reactions. Polymeric carbohydrates like starch (soluble) gave poor yield of **2** (ca. 10%) even after refluxing for 24 h. The result can be explained by the incomplete conversion of starch due to slow depolymerization under the reaction conditions used. However, a long time did not improve the yield any further.

In the present case, the dilution of the FA also plays an important role. When the reaction was carried out using 85% formic acid, **2** formed as the major product. The mixture was then converted entirely to **2** by reacting with fresh formic acid. When the reaction was repeated with 98% formic acid keeping all other parameters unaltered, BMF was found to form as the major product. This demonstrates that the transformation of BMF to **2** by nucleophilic substitution reaction is not the only mechanistic pathway. The hydrolysis of BMF to **1** followed by its esterification with formic acid, is also a viable route. When diluted formic acid (ca. 50%) was used, **2** formed almost exclusively. The exclusivity of **2** in the reaction mixture makes the next step of reacting with fresh formic acid redundant. However, the reaction takes a much longer time to give a decent yield. For example, after 20 h of reaction with 50% formic acid (along with 160 mol% HBr), fructose gave around 35% yield of **2**.

Hydrolysis of **2** in excess of boiling water afforded **1** in excellent isolated yield (ca. 90%). However, the extraction of **1** from the aqueous reaction mixture required excess of organic solvent [21]. Besides, chromatographic purification of **1** from levulinic acid (LA **5**), formed as a minor side product, was necessary [22]. However, when **2** was reacted with anhydrous methanol at a slightly elevated temperature (ca. 50 °C) in the presence of a catalytic amount of anhydrous K_2CO_3, **1** formed as the sole product in near-quantitative yield. Interestingly, the reaction did not work without the base catalyst. **1** was successfully isolated in 94% yield and in good purity by simply evaporating excess methanol. Methyl formate, the volatile by-product, escaped from the reaction mixture as soon as it formed. Catalytic reduction of **2** to 5-methylfurfural (MF **3**) was attempted by catalytic transfer hydrogenation conditions using a combination of FA and ammonium formate and 5%Pd/C as the catalyst. The reaction was conducted under conventional heating and magnetic stirring. The reaction was monitored by TLC for the disappearance of **2**. The reaction completed within 1 h at 70 °C and **3** was extracted from the reaction mixture by chloroform in 89% isolated yield.



a) MeOH, K_2CO_3 (cat.); b) $HCO_2H+HCO_2NH_4$, 5%Pd/C;
c) aq. HNO_3, 80 °C; d) H_2O, 120 °C; e) $Bi(NO_3)_3$, 50 °C

Scheme 2. Selective preparation of various renewable chemicals from FMF **2**.

MF **3** has been recognized as a potential fuel oxygenate and renewable furanic intermediate for further value addition [23]. Selective oxidation of **2** was also attempted. The formylmethyl arm of **2** was selectively oxidized to form 2,5-diformylfuran (DFF **4**), whereas complete oxidation of **2** led to 2,5-furandicarboxylic acid (FDCA **6**) (Scheme 2). Both **4** and **6** have received attention as biorenewable monomers for various polymeric applications [24,25]. Selective oxidation of **2** into **4** was achieved by using bismuth nitrate as the oxidant. Bismuth nitrate has already been used as an inexpensive, non-toxic oxidant for converting **1** into **4** in the presence of a heterogeneous catalyst [26]. In this work, the reaction was conducted at a slightly elevated temperature under the solvent-free condition without using any catalyst. In a typical reaction, a mixture of **2** and powdered $Bi(NO_3)_3 \cdot 5H_2O$ (0.8 eq.) was placed in a pre-heated (50 °C) oil bath and magnetically-stirred continuously during the course of the reaction. The reaction was *monitored by FTIR spectroscopy*, and stirring was continued till the conversion of **2** *was complete*. DFF **4** was separated from the reaction mixture by solvent extraction and isolated in 65% yield. When the oxidation of **2** was attempted in nitric acid (aq. 69%), FDCA **6** was isolated in a 48% yield. In a typical reaction, **2** was dissolved in excess aqueous nitric acid (8 mL for 0.5 g of **2**) and heated at 80 °C overnight under constant magnetic stirring. The reaction mixture was cooled down, and **6** was filtered off as a white crystalline solid. Rehydration followed by ring-opening of **2** in hot (ca. 120 °C) water led to the formation LA **5**. The reaction was conducted in a glass pressure reactor, and **5** was recovered from the aqueous mixture in 92% isolated yield using ethyl acetate as the extracting solvent.

2.1. *Conclusion*

In summary, FMF **2** has been produced in decent isolated yields from biomass-derived hexoses within an aqueous-organic biphasic system using a mixture of formic acid and a strong Bronsted acid catalyst. FMF **2** was catalytically reduced to MF **3**, a promising biofuel candidate, selectively. FMF **2** was also converted into DFF **4** and FDCA **6**, promising renewable monomers for biopolymers, by selective oxidation. Methanolysis and hydrolysis of FMF **2** led to HMF **1** and LA **5**, respectively, in excellent isolated yields. Lower concentration (ca. 50%) of formic acid along with HBr formed **2** almost exclusively; however, longer duration was required due to slower kinetics.

3. Experimental procedures

3.1. *Production of 5-(formyloxymethyl)furfural (FMF 2) from fructose*

Fructose (2.002 g) was added in a mixture of formic acid (FA, 20 mL) and hydrobromic acid (2 mL, 48% aq., 160 mol%) taken in a 100 mL round-bottomed flask and stirred to dissolve. To the solution, 20 mL 1,2-dichloroethane (DCE) was added, and the biphasic reaction mixture was placed in a pre-heated oil-bath and connected with a reflux condenser. The mixture was refluxed for 8 h under constant magnetic stirring. After the reaction, the mixture was cooled down to RT and filtered through a filter paper under vacuum. The mixture was then transferred in a separating funnel, and the DCE layer (bottom) was separated. The aqueous layer washed with fresh DCE (10 mL). The DCE layers were combined and washed with distilled water (10 mL). The DCE layer was then transferred in a 100 mL round-bottomed flask and 20 mL FA was added. The biphasic mixture was heated in an oil-bath (60 °C) till all 5-(bromomethyl)furfural (BMF), formed as a co-product, got converted into FMF **2**. The DCE layer was then phase-separated in a separatory funnel, washed with water, and dried over anhydrous Na_2SO_4. Evaporation of DCE under reduced pressure provided **2** as a brown liquid. The liquid was chromatographed (Silica gel 60–120 mesh, $CHCl_3$) to obtain purified **2** as a light yellow liquid (1.162 g, 68%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.64 (1H, s), 8.15 (1H, s), 7.28 (1H, d, 3.0 Hz), 6.68 (1H, d, 3.0 Hz), 5.25 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz) (δ ppm): 177.8, 160.1, 154.6, 152.8, 122.0, 112.9, 56.9. FTIR (ATR, cm^{-1}): 3003, 2931, 2841, 1724, 1670, 1521, 1148, 1020, 748.

3.2. *Isolation of levulinic acid (LA **5**)*

The aqueous layer was filtered through a filter paper, and the filtrate was saturated by adding sodium chloride. The saturated solution was cooled in ice-water and extracted with ethyl acetate (6 × 10 mL). The ethyl acetate layers were combined, dried over anhydrous Na_2SO_4, and evaporated in a rotary evaporator under reduced pressure to yield a brown liquid. The liquid was chromatographed over silica gel (60–120 mesh) using diethyl ether as eluent. Evaporation of the solvent provided levulinic acid as light yellow oil (0.132 g, 10%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.77 (t, 2H, $J = 6.6$ Hz), 2.64 (t, 2H, $J = 6.6$ Hz), 2.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) (δ ppm): 206.6, 177.8, 37.7, 29.8, 27.7; FTIR (ATR, cm^{-1}): 3300, 2928, 1704, 1211, 1161.

3.3. *Quantification of insoluble humin*

The aqueous layer was passed through a pre-weighed filter paper, and the filter paper was washed with an excess of distilled water. The filter paper was dried in a hot-air oven at 60 °C till a constant weight was achieved.

3.4. *Preparation of 5-methylfurfural (MF **3**) from FMF **2***

FMF **2** (0.498 g, 3.23 mmol) was taken in a 50 mL round-bottomed flask and dissolved in 3 mL of formic acid (85%). To the solution, ammonium formate (1.020 g, 16.18 mmol) and 5%Pd/C (0.050 g) were added. The flask was fitted with a magnetic stirring rod and a reflux condenser and placed in a pre-heated (80 °C) oil-bath. The suspension was stirred magnetically and monitored by TLC at regular intervals for the disappearance of **2**. After reaction (~1 h), the flask was cooled down to room temperature, and the content was transferred into a separating funnel. The reaction mixture was extracted with chloroform (3 × 10 mL). The chloroform layer was washed with distilled water, dried over anhydrous Na_2SO_4, and evaporated in a rotary evaporator under reduced pressure to provide crude **3** as a light-brown liquid. The slight colored impurity in **3** was removed by passing it through a plug of silica gel using chloroform as the eluent. Evaporation of the solvent under reduced pressure afforded MF **3** as a clear liquid (0.318 g, 89%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.34 (s, 1H), 7.04 (d, 1H), 6.10 (d, 1H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 176.7, 159.7, 151.7, 124.0, 109.4, 13.8; FTIR (ATR, cm^{-1}): 2923, 1673, 1218, 1020.

3.5. *Preparation of 2,5-diformylfuran (DFF **4**) from FMF **2***

FMF **2** (0.520 g, 3.37 mmol) was taken in a 100 mL round-bottomed flask, and powdered $Bi(NO_3)_3 \cdot 5H_2O$ (1.06 g, 2.68 mmol, 0.8 eq.) was added. A magnetic stirring bar was added, and the flask was placed in a pre-heated oil bath. The mixture was stirred magnetically and monitored by TLC for the disappearance of **2**. After a latent period of around 8–10 min, the evolution of brown NO_2 gas started. The reaction took nearly 45 min to complete. After the reaction, the flask was cooled down to RT, and the yellow paste was extracted with chloroform (6 × 10 mL). The chloroform layers were combined, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to yield **4** as a light-yellow solid (0.272 g, 65%). The compound was found to be NMR (^{1}H&^{13}C) pure; however, the trace colored impurity may be removed by passing through a plug of silica using chloroform as eluent. Alternatively, the trituration of the solid in hot petroleum ether (60–80) produced need-like colorless crystals of DFF **4**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.89 (s, 2H), 7.37 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 179.2, 154.2, 119.2; FTIR (ATR, cm^{-1}): 3132, 3101, 2852, 1674.

3.6. *Preparation of 2,5-furandicarboxylic acid (FDCA **6**) from FMF **2***

FMF **2** (0.500 g, 3.24 mmol) was taken in a 100 mL round-bottomed flask and dissolved in 8 mL aqueous HNO_3 (69%). The flask was placed in a pre-heated (60 °C) oil-bath and stirred magnetically for 2 h. Then, the temperature was increased to 80 °C and stirred overnight. After the reaction, the flask was cooled down to room temperature, and excess aqueous HNO_3 was distilled off under reduced pressure. The residue was then suspended in ice-cold water (10 mL) and filtered under vacuum. FDCA **6** was obtained as a white crystalline solid. The solid was dried in a hot-air oven at 60 °C until a constant weight was obtained (0.242 g, 48%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ (ppm): 7.29 (2H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm): 159.3, 147.5, 118.9.

3.7. *Preparation of levulinic acid (LA **5**) from FMF **2***

FMF **2** (0.496 g, 3.22 mmol) was taken in a 100 mL glass pressure vessel fitted with a Teflon-top and suspended in 20 mL water. A magnetic stir rod was introduced, the reactor was sealed, placed in a pre-heated (120 °C) oil-bath, and stirred magnetically for 4 h. After the reaction, the pressure vessel was cooled down to RT and opened. The solution was saturated with solid NaCl, transferred into a separating funnel, and extracted with ethyl acetate (5 × 10 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and evaporated in a rotary evaporator under reduced pressure to obtain crude LA as a brown oil. The oil was passed through a plug of silica gel (60–120 mesh) using diethyl ether as the eluent. LA was obtained as a clear liquid (0.344 g, 92%) by evaporating diethyl ether under reduced pressure.

3.8. *Preparation of 5-(hydroxymethyl)furfural (HMF **1**) from FMF **2***

3.8.1. *Strategy A*

FMF **2** (0.502 g, 3.26 mmol) was taken in a 50 mL round-bottomed flask and dissolved in 10 mL of dry methanol. To the solution, 0.020 g of anhydrous K_2CO_3 was added, and the suspension was stirred magnetically at 50 °C. The reaction was monitored by TLC for the disappearance of **2**. After the reaction, the reaction mixture was cooled down to RT and filtered. Methanol was distilled off using a rotary evaporator under reduced pressure to obtain crude **1**. The crude **1** was diluted in chloroform and passed through a plug of silica using 10% (v/v) ethyl acetate in chloroform as the eluent. The evaporation of the solvent under reduced pressure afforded **1** as a light-brown oil (0.386 g, 94%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 9.59 (s, 1H), 7.24 (d, 1H, 3.20 Hz), 6.54 (d, 1H, 3.20 Hz), 4.73 (s, 2H); FTIR (ATR, cm^{-1}): 2924, 2853, 1671, 1508, 1090.

3.8.2. *Strategy B*

FMF **2** (0.500 g, 3.24 mmol) was added drop-wise in 50 mL of boiling water taken in a 100 mL round-bottomed flask under vigorous magnetic stirring. The reaction was monitored by TLC for the disappearance of **2**. After the reaction, the homogeneous solution was cooled down to RT. The solution was transferred in a separating funnel and extracted with ethyl acetate (5 × 10 mL). The ethyl acetate layers were combined, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to yield **1** as a light yellow liquid (0.370 g, 90%).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carres.2020.108140.

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