

A facile and effective method for preparation of 2,5-furandicarboxylic acid via hydrogen peroxide direct oxidation of 5-hydroxymethylfurfural

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In this paper, 2,5-furandicarboxylic acid (FDCA) was efficiently prepared by the direct oxidation of 5-hydroxymethylfurfural (5-HMF) using hydrogen peroxide (H_2O_2) in alkaline conditions without any catalysts. The effects of reaction parameters on the process were systematically investigated and the optimal parameters were obtained as follows: molar ratio of 5-HMF:KOH: H_2O_2 was 1:4:8, reaction temperature and reaction time were determined as 70°C and 15 minutes, respectively. Under these conditions, the yield of FDCA was 55.6% and the purity of FDCA could reach 99%. Moreover, we have speculated the detailed oxidation mechanism of 5-HMF assisted by hydrogen peroxide in alkaline condition to synthesize FDCA.

Keywords: 5-hydroxymethylfurfural, 2,5-furandicarboxylic acid, hydrogen peroxide, oxidation.

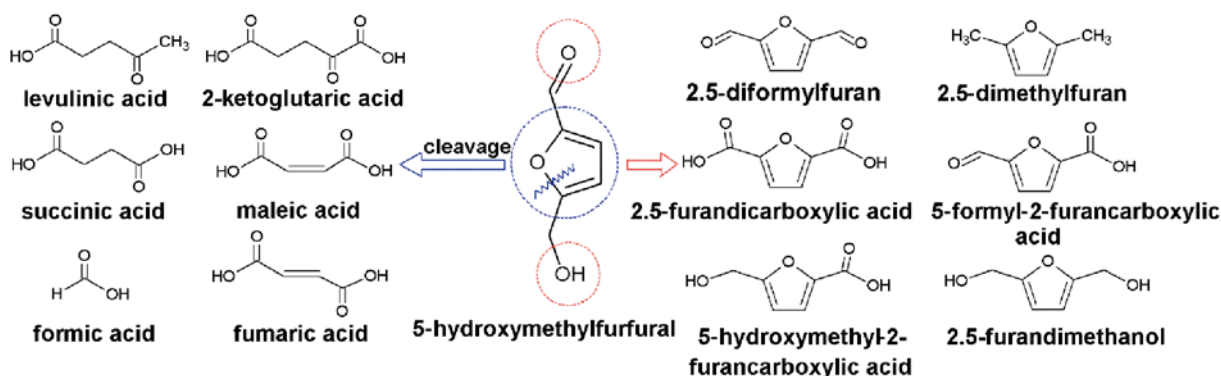
INTRODUCTION

Due to its renewability and abundance, biomass resources have been considered as one type of potential candidates to replace petroleum resources in producing various kinds of chemicals^{1–3}. Among them, 5-hydroxymethylfurfural (5-HMF) is an important raw material or building block for producing different intermediates during chemical industry fields, including pharmaceuticals, adhesives, sealants, resins, coating, spices and so on^{4–9}. And it can be easily synthesized by hydrolysis and dehydration of biomass materials in the previous reports^{10–12}. In terms of its structure, the special functional groups (hydroxymethyl and aldehyde groups) play crucial roles in synthesizing a series of derivatives (Scheme 1).

As one of common 5-HMF derivatives, 2,5-furandicarboxylic acid (FDCA) owns the similar structure with terephthalic acid^{13–15}. It was identified as the key sugar-based platform chemical for the production of green bio-based chemicals and materials in the future by U.S. Department of Energy¹⁶. Therefore, it has great possibility as substitute to replace terephthalic acid for the production of biodegradable polyesters materials¹⁷. However, in the most of the traditional synthesis approaches for oxidation of 5-HMF to prepare FDCA, noble metals and oxygen (or air) were essentially employed as catalyst and oxidant, respectively⁷. Verdeguer et al. have explored the oxidation of 5-HMF to FDCA and obtained a high yield of 99% within 2 h using Pt-Pb/C catalysts and oxygen at high pH. Furthermore, they found

the aldehyde side chain was first oxidized to carboxylic acid, followed by the second oxidation process of the hydroxymethyl side chain to produce FDCA¹⁸. Casanova et al. have investigated the effect of Au/TiO₂, Au/CeO₂, Au/C and Au/FeO₂ catalysts on the oxidation of 5-HMF in air. The results showed the activity and selectivity of Au/CeO₂ are better than that of Au/TiO₂. At 130°C the yield of FDCA reaches 96% over Au/CeO₂ catalyst after 8 h, while the yield was only 84% for Au/TiO₂ catalyst under the same reaction conditions¹⁹. Riisager et al. have studied the oxidation of 5-HMF using Ru(OH)_x and water as catalyst and solvent, respectively²⁰. Under the reaction conditions (2.5 bar O₂, 140°C, 6 h), the yield of FDCA was above 95%.

In general, most of the heterogeneous catalysts can achieve a higher yield of FDCA. Unfortunately, high cost, poor stability and catalyst deactivation of noble metal nanoparticles are still the key obstacle for the large-scale use of FDCA. In addition, another synthetic method of FDCA is to use homogeneous catalysts²¹. In the homogeneous oxidation of 5-HMF by air with Co(OAc)₂/Mn(OAc)₂/Br[−] as catalyst and acetic acid as solvent, the yield of FDCA was 61%²². The similar homogeneous catalyst of Co(OAc)₂/Zn(OAc)₂/Br[−] was used for the oxidation of 5-HMF into FDCA. But the reaction was prone to stay in the formation of intermediates such as 2,5-diformylfuran (DFF). After trifluoroacetic acid was added to promote the formation of FDCA, the yield of the FDCA reaches 60%²³. While homogeneous catalysts also have some drawbacks, such as bromine pollution,



Scheme 1. Examples of platform chemicals derived from 5-HMF

relatively low yield, difficult separation of metal salt catalysts and difficult purification of FDCA. Nowadays, extensive research has been performed to develop the efficient, low-cost, and sustainable commercial methods for the preparation of FDCA. However, there has been few reports about the efficient oxidation of FDCA with non-catalytic process.

In previous reports, the oxidation of HMF into FDCA was performed using stoichiometric oxidants such as KMnO_4 ²⁴. Although without employing any catalysts, the drawback of this method is generation of large amounts of high toxic waste manganese compounds to the environment. To solve this problem, hydrogen peroxide is chosen as an environmentally-friendly and green oxidation reagent²⁵. In this article, we explore the direct oxidation of 5-HMF by hydrogen peroxide for the preparation of FDCA, and the optimal reaction conditions were obtained. The molecular structure of FDCA was determined by Fourier Transform Infrared Spectrometer (FT-IR), Hydrogen Nuclear Magnetic Resonance (¹H-NMR) and Mass Spectrometry (MS). The purity of FDCA was obtained by High Performance Liquid Chromatography (HPLC).

EXPERIMENTAL

Material

5-HMF (>99%), FDCA (>99%), 5-hydroxymethyl-2-furancarboxylic acid (HFCA, >99%) and 5-formyl-2-furancarboxylic acid (FCA, >99%) were obtained from Sigma reagent company. Hydrogen peroxide (30%), potassium hydroxide (KOH), potassium carbonate (K_2CO_3), concentrated hydrochloric acid (HCl) and anhydrous magnesium sulfate (MgSO_4) were purchased from Beijing Chemicals Co. Ltd. The water used in this experiment was distilled followed by deionization.

Preparation of FDCA

First, potassium hydroxide and water were added into a 250 ml semibatch reactor with reflux-condenser, magnetic stirrer and temperature regulating devices. When potassium hydroxide was completely dissolved, an amount of 5-HMF was added. Then, 30% hydrogen peroxide solution was slowly added into the system under constant agitation. After the reaction finished, the system was cooled down. At the same time, concentrated hydrochloric acid was added to the solution to keep the pH value at 1.0 or less. Consequently, FDCA was precipitated from solution. The precipitate was separated by filtration under vacuum and washed with deionized water. The white powder (FDCA) was obtained by drying at 60°C for 24 h.

Analytical methods

FT-IR spectra of the sample were recorded on a Nicolet 380 FT-IR spectrometer. The state of hydrogen in the product was characterized by a Bruker AV500 ¹H-NMR analyzer, and the solvent used was dimethyl sulfoxide-d₆ (DMSO-d₆), the internal standard (for calibrating shift for ¹H) was tetramethylsilane (TMS).

The molecular weight of the product was measured by Waters Quattro Premier XE. The purity of the product

was analyzed by Agilent 1260 Infinity HPLC system equipped with a UV detector (278 nm) and a ZORBAX SM-C18 Column (150 mm*4.6 mm) at 25°C. The HPLC utilized 100% methanol used as the mobile phase flowing at 1.2 ml/min to analyze the purity. The product yields (mol%) can be calculated by the following formula:

$$Y = \frac{\text{Moles (FDCA)}}{\text{Moles (starting amount of 5-HMF)}} \times 100\%$$

RESULTS AND DISCUSSION

The effect of reaction temperature, the dosage of hydrogen peroxide, the dosage of potassium hydroxide and reaction time were systematically investigated.

Reaction temperature

As shown in Figure 1, reaction temperature affects the oxidation of 5-HMF significantly. When the reaction temperature increases from 40°C to 70°C, the yield of FDCA increases from 17.6% to 42.8% correspondingly. Although the higher temperature is feasible to accelerate the reaction, it will induce advanced oxidation that results in a decrease of yield when the temperature is above 70°C. Therefore, the optimal reaction temperature was chosen as 70°C in the following experiment.

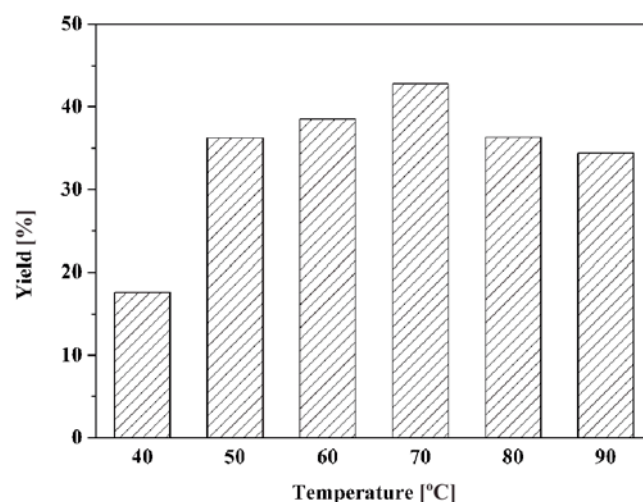


Figure 1. Effect of reaction temperature on the yield of FDCA (5-HMF 4 mmol, KOH 14 mmol, H_2O_2 36 mmol, H_2O 10 ml, reaction time 15 min)

The dosage of hydrogen peroxide

The effect of hydrogen peroxide loading on the reaction is shown in Figure 2. It can be observed that when the dosage of hydrogen peroxide increases from 12 mmol to 32 mmol, the yield of FDCA increases from 33.8% to 50.6%. When the loading of H_2O_2 is 32 mmol, the yield reaches the highest value. As we know, hydrogen peroxide is a strong oxidant, it can rapidly disintegrate into water and release oxygen in strong alkaline condition. When the dosage of hydrogen peroxide is low, the oxidation process is incomplete that the reaction in generating intermediate product will play a dominant role. On the contrary, an excess oxidant is added, advanced oxidation will occur that reactants turns into small molecule acid and results in a decline in yield.

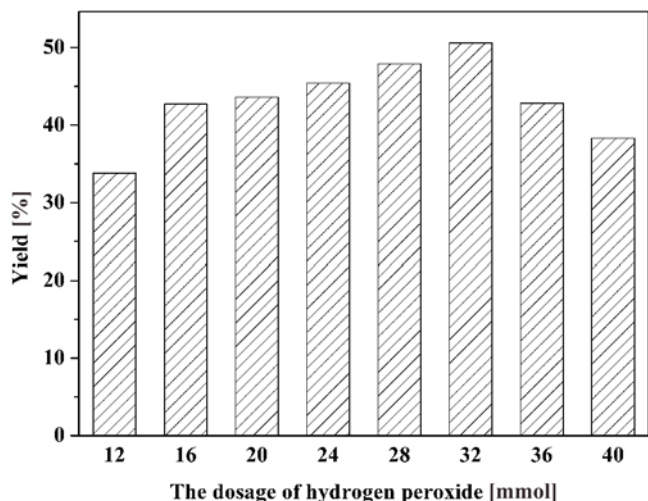


Figure 2. Effect of the dosage of hydrogen peroxide on the yield of FDCA (5-HMF 4 mmol, KOH 14 mmol, H₂O 10 ml, reaction temperature 70°C, reaction time 15 min)

The dosage of potassium hydroxide

As presented in Figure 3, when the dosage of potassium hydroxide increases from 6 mmol to 16 mmol, the corresponding yield of FDCA increases from 9% to 55.6%. When the content of KOH is 16mmol, the yield of FDCA reaches the highest value. It is reported that increasing the dosage of potassium hydroxide can accelerate the decomposition of H₂O₂ and be favorable for the formation of HOO⁻¹⁴. But when the dosage of KOH is higher, the yield of FDCA is reduced. This may be caused by disproportionation of 5-HMF due to the aldehyde without α -H. Thus, the reaction carried out under the effect of strong alkali can be divided into two portions: one portion of aldehyde is oxidized to acid; the another portion is reduced to alcohol that leads to the formation of 2.5-furandimethanol (FDM).

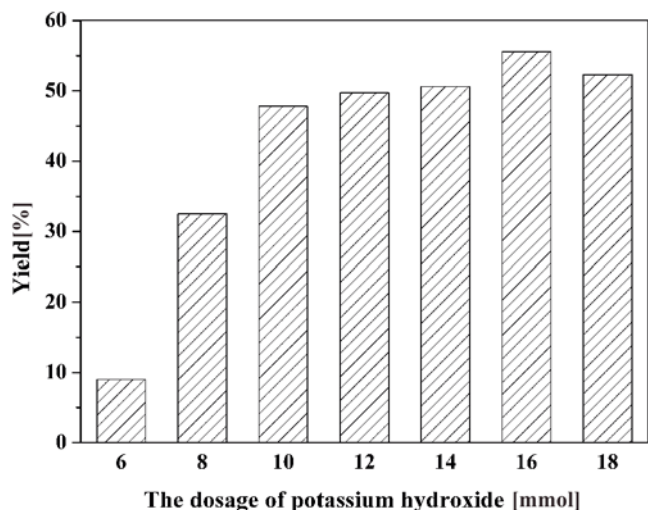


Figure 3. Effect of the dosage of potassium hydroxide on the yield of FDCA (5-HMF 4 mmol, H₂O₂ 32 mmol, H₂O 10 ml, reaction temperature 70°C, reaction time 15 min)

Reaction time

Figure 4 shows that when the reaction time is 15 min, the effect of oxidation is the best. When the reaction time is too short, reactants still stay in the intermediate stage, such as HFCA and FCA. Prolonging reaction time

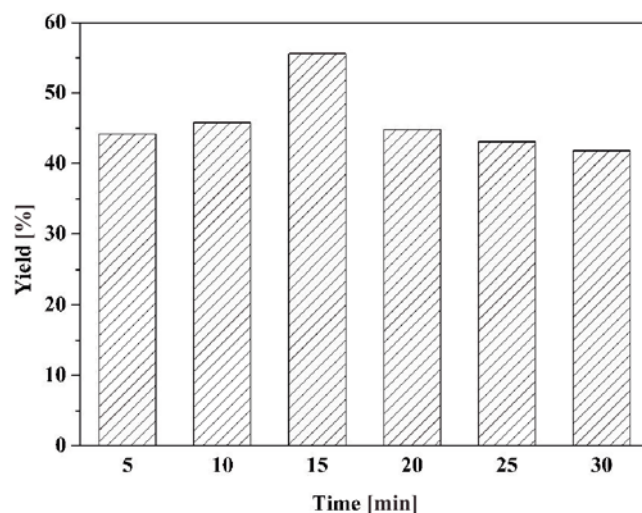


Figure 4. Effect of reaction time on the yield of FDCA (5-HMF 4 mmol, KOH 16 mmol, H₂O₂ 32 mmol, H₂O 10 ml, reaction temperature 70°C)

seriously promotes the advanced oxidation from FDCA to small molecule acid, such as levulinic acid, succinic acid and maleic acid. It will result in the decrease of the yield of FDCA.

Structure of the product

The analysis on the chemical structure of the product is shown in Figure 5, Figure 6 and Figure 7, respectively. FT-IR (ν , cm⁻¹): 3151, 3125 (-OH); 1701 (C=O); 1572, 1424 (C=C); 1276, 1229 (C-O); 962, 852, 763 (=CH). ¹HNMR (δ /ppm): 7.286 (s, 2H, CH); 13.575 (s, 2H, COOH). MS: [mass-to-charge ratio (m/z)]: Calcd for C₆H₄O₅, 156; found 156. The purity of FDCA as determined by HPLC with the normalization method is 99%.

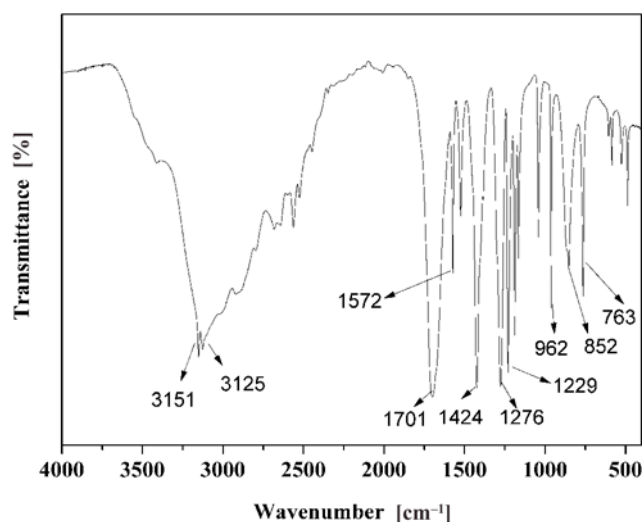


Figure 5. FT-IR spectrum of FDCA

Separation and recovery process of by-products

In order to accomplish separation and recovery of by-products, we have further carried out the experiments to investigate this process. The detailed reaction was conducted under the optimal conditions when the dosage of raw materials was magnified by 5 times on the basis of above formulation (5-HMF 20 mmol, KOH 80 mmol, H₂O₂ 160 mmol, H₂O 50 ml). When the reaction was finished, the system was cooled down to room temperature

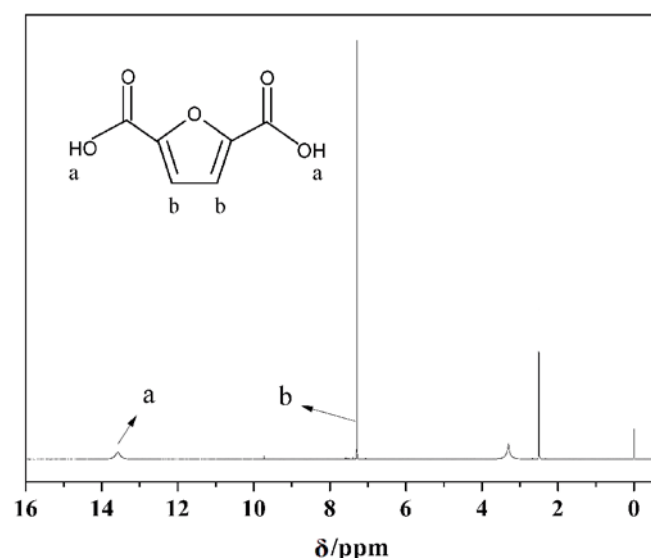


Figure 6. ¹H NMR spectrum of FDCA

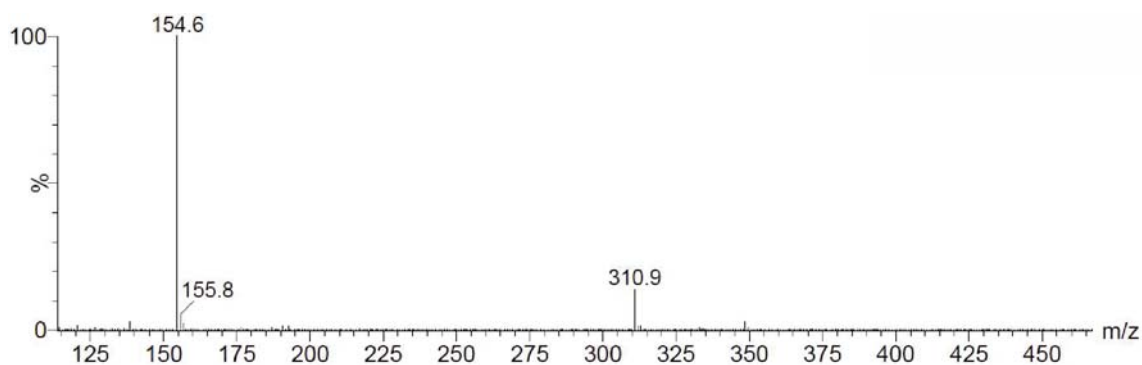


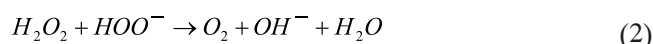
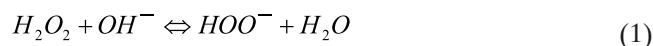
Figure 7. MS spectrum of FDCA

and concentrated hydrochloric acid (20 ml) was added to the reaction solution to obtain FDCA (1.735 g) until $\text{pH} < 1.0$. After vacuum filtration, the filtrate was adjusted to neutral by adding potassium carbonate (9.686 g). Thus, concentrated hydrochloric acid can be converted to potassium chloride (KCl). Simultaneously, the filtrate was dried by adding anhydrous MgSO_4 (72.290 g) in order to separate the organic phase. Subsequently, the organic phase was detected by HPLC. The results indicate that the organic phase is mainly composed of HFCA (3.2 mmol 0.454 g) and FCA (0.7 mmol 0.098 g). In addition, the mixture (169.620 g) of potassium chloride crystals and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ can be used as raw materials for fertilizers manufacture. Except for approximately 5% material loss in the experimental process, the amount of input and output is almost the same that is consistent

with the mass balance. The detailed separation and recovery process of by-products is listed in Scheme 2.

Potential reaction mechanism

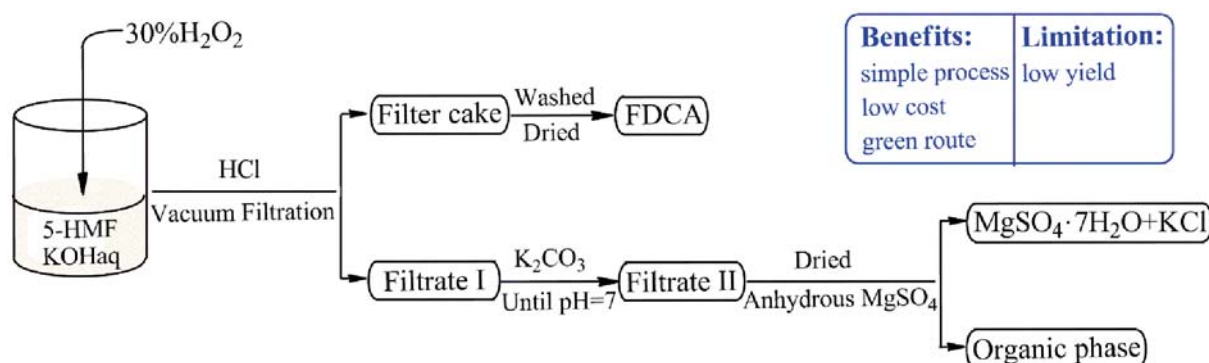
In the experiments, we have found that oxidation of 5-HMF by hydrogen peroxide for the preparation of FDCA without employing any catalysts is hard to accomplish no matter in acidic or neutral condition. In general, the decomposition mechanism of hydrogen peroxide under alkaline condition can be expressed by the following formula²⁶.



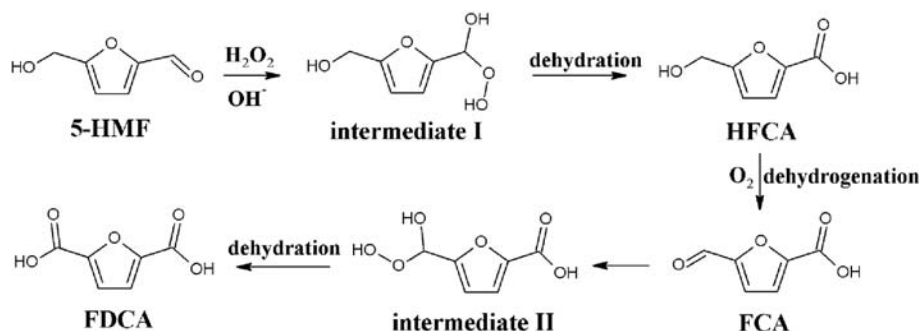
The first step is a reversible process and increasing the concentration of OH^- is favorable for the formation of HOO^- by accelerating the decomposition reaction of H_2O_2 . The second step is the reaction of H_2O_2 and

HOO^- to generate O_2 . We deduce that HOO^- plays an important role in the reaction of aldehyde groups turning into carboxyl groups and O_2 plays an important role in the reaction of hydroxymethyl groups turning into aldehyde groups. Therefore, the oxidation process of 5-HMF by hydrogen peroxide should be carried out in alkaline condition. In addition, the absence of formation of DFF in the organic phase is attributed to the fact that the aldehyde groups of 5-HMF are oxidized first, followed by the oxidation of the hydroxymethyl groups. Based on above mentioned facts, we have speculated the detailed oxidation mechanism of 5-HMF assisted by hydrogen peroxide in the alkaline condition to synthesize FDCA, as shown in Scheme 3.

First, hydrogen peroxide is decomposed into HOO^- under alkaline conditions. In the process, the aldehyde



Scheme 2. Separation and recovery process of by-products



Scheme 3. Putative oxidation mechanism of 5-HMF to FDCA

groups of 5-HMF are oxidized to form intermediate I²⁷. Then, the formation of HFCA is conducted by the dehydration of intermediate I. After that, the dehydrogenation of HFCA can produce FCA under the effect of oxygen that originates from the reaction between hydrogen peroxide and HOO[•]. At last, the aldehyde groups of FCA are further oxidized to form intermediate II. Furthermore, the target product FDCA was achieved by the dehydration of intermediate II.

CONCLUSIONS

In this article, hydrogen peroxide shows good oxidation performance for the conversion of 5-HMF into FDCA in alkaline condition. After systematically investigating reaction conditions, several important reaction parameters are confirmed. The optimal molar ratio of 5-HMF:KOH:H₂O₂ is 1:4:8 with the highest FDCA yield of 55.6% and the purity of 99%, which was carried out under 70°C for 15 min. This technology of preparation of FDCA has many advantages, such as simple process, saving time, easy separation of products and no catalyst. Moreover, this synthetic method can reduce the cost of FDCA production.

ACKNOWLEDGEMENT

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LITERATURE CITED

- Lichtenthaler, F.W. & Peters, S. (2004). Carbohydrates as green raw materials for the chemical industry. *Comptes. Rendus. Chimie*. 7, 65–90. DOI: 10.1016/j.crci.2004.02.002.
- Siankevich, S., Savoglidis, G., Fei, Z., Laurenczy, G., Alexander, DTL. & Yan, N., et al. (2014). A novel platinum nanocatalyst for the oxidation of 5-Hydroxymethylfurfural into 2,5-Furandicarboxylic acid under mild conditions. *J. Catal.* 315, 67–74. DOI: 10.1016/j.jcat.2014.04.011.
- Corma, A., Iborra, S. & Velty, A. (2007). Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* 107, 2411–2502. DOI: 10.1021/cr050989d.
- Chheda, J.N., Huber, G.W. & Dumesic, J.A. (2007). Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. *Angew. Chem.* 46, 7164–7183. DOI: 10.1002/anie.200604274.
- Gandini, A. & Belgacem, M.N. (1997). Furans in polymer chemistry. *Prog. Polym. Sci.* 22, 1203–1379.
- Moreau, C., Belgacem, M.N. & Gandini, A. (2004). Recent catalytic advances in the chemistry of substituted furans from carbohydrates and in the ensuing polymers. *Top. Catal.* 27, 11–30. DOI: 10.1023/B:TOCA.0000013537.13540.0e.

- Davis, S.E., Houk, L.R., Tamargo, E.C., Datye, A.K. & Davis, R.J. (2011). Oxidation of 5-hydroxymethylfurfural over supported Pt, Pd and Au catalysts. *Catal. Today*. 160, 55–60. DOI: 10.1016/j.cattod.2010.06.004.

- Boisen, A., Christensen, T.B., Fu, W., Gorbanev, Y.Y., Hansen, T.S. & Jensen, J.S., et al. (2009). Process integration for the conversion of glucose to 2,5-furandicarboxylic acid. *Chem. Eng. Res. Des.* 87, 1318–1327. DOI: 10.1016/j.cherd.2009.06.010.

- Jain, A., Jonnalagadda, S.C., Ramanujachary, K.V. & Mugweru, A. (2015). Selective oxidation of 5-hydroxymethyl-2-furfural to furan-2,5-dicarboxylic acid over spinel mixed metal oxide catalyst. *Catal. Commun.* 58, 179–182. DOI: 10.1016/j.catcom.2014.09.017.

- Su, Y., Brown, H.M., Huang, X., Zhou, X., Amonette, J.E. & Zhang, Z.C. (2009). Single-step conversion of cellulose to 5-hydroxymethylfurfural (HMF), a versatile platform chemical. *Appl. Catal. A: Gen.* 361, 117–122. DOI: 10.1016/j.apcata.2009.04.002.

- Moreau, C., Durand, R., Razigade, S., Duhamet, J., Faugeras, P. & Rivalier, P., et al. (1996). Dehydration of fructose to 5-hydroxymethylfurfural over H-mordenites. *Appl. Catal. A: Gen.* 145, 211–224. DOI: 10.1016/0926-860X(96)00136-6.

- Chheda, J.N., Leshkov, R.Y. & Dumesic, J.A. (2007). Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides. *Green. Chem.* 9, 342–350. DOI: 10.1039/b611568c.

- Gandini, A., Silvestre, A.J.D., Neto, C.P., Sousa, A.F. & Gomes, M. (2009). The furan counterpart of poly(ethylene terephthalate): an alternative material based on renewable resources. *J. Polym. Sci.* 47, 295–298. DOI: 10.1002/pola.23130.

- Jiang, M., Liu, Q., Zhang, Q., Ye, C. & Zhou, G.Y. (2012). A series of furan-aromatic polyesters synthesized via direct esterification method based on renewable resources. *J. Polym. Sci.* 50, 1026–1036. DOI: 10.1002/pola.25859.

- Ma, J.P., Pang, Y., Wang, M., Xu, J., Ma, H. & Nie, X. (2012). The copolymerization reactivity of diols with 2,5-furandicarboxylic acid for furan-based copolyester materials. *J. Mater. Chem.* 22, 3457–3461. DOI: 10.1039/c2jm15457a.

- Werpy, T. & Petersen, G. Report No. NREL/TP-510-35523 (2004).

- Yu, Z.L., Zhou, J.D., Zhang, J., Huang, K.X., Cao, F. & Wei, P. (2014). Evaluating effects of biobased 2,5-furandicarboxylate esters as plasticizers on the thermal and mechanical properties of poly(vinyl chloride) *J. Appl. Polym.* 40938, 1–10. DOI: 10.1002/app.40938.

- Verdeguer, P., Merat, N. & Gaset, A. (1993). Oxydation catalytique du HMF en acide 2,5-furane dicarboxylique. *J. Mol. Catal.* 85, 327–344. DOI: 10.1016/0304-5102(93)80059-4.

- Casanova, O., Iborra, S. & Corma, A. (2009). Biomass into chemicals: aerobic oxidation of 5-hydroxymethyl-2-furfural into 2,5-furandicarboxylic acid with gold nanoparticle catalysts. *Chem. Sus. Chem.* 2, 1138–1144. DOI: 10.1002/cssc.200900137.

- Gorbanev, Y.Y., Kegnæs, S. & Riisager, A. (2011). Selective aerobic oxidation of 5-Hydroxymethylfurfural in water over solid ruthenium hydroxide catalysts with magnesium-

-based supports. *Catal. Lett.* 141, 1752–1760. DOI: 10.1007/s10562-011-0707-y.

21. Zhang, Z.H. & Deng, K.J. (2015). Recent advances in the catalytic synthesis of 2,5-furandicarboxylic acid and its derivatives. *ACS. Catal.* 5, 6529–6544. DOI: 10.1021/acscatal.5b01491.

22. Partenheimer, W. & Grushin, V.V. (2001). Synthesis of 2,5-diformylfuran and furan-2,5-dicarboxylic acid by catalytic air-oxidation of 5-hydroxymethylfurfural. Unexpectedly selective aerobic oxidation of benzyl alcohol to benzaldehyde with metal=bromide catalysts. *Adv. Synth. Catal.* 343, 102–111. DOI: 10.1002/1615-4169(20010129)343:1<102::AID-AD-SC102>3.0.CO;2-Q.

23. Saha, B., Dutta, S. & Abu-Omar, M.M. (2012). Aerobic oxidation of 5-hydroxymethylfurfural with homogeneous and nanoparticulate catalysts. *Catal. Sci. Technol.* 2, 79–81. DOI: 10.1039/c1cy00321f.

24. Miura, T., Kakinuma, H., Kawano, T. & Matsuhisa, H. (2008). Method for producing furan-2,5-dicarboxylic acid. UK Patent 7411078.

25. Li, S., Su, K.M., Li, Z.H. & Cheng, B. (2016). Selective oxidation of 5-hydroxymethylfurfural with H₂O₂ catalyzed by a molybdenum complex. *Green. Chem.* 18, 2122–2128. DOI: 10.1039/c5gc01991e.

26. Duke, F.R. & Haas, T.W. (1961). The homogeneous base-catalyzed decomposition of hydrogen peroxide. *J. Phys. Chem.* 65, 304–306. DOI: 10.1021/j100820a028.

27. Sato, K., Hyodo, M., Takagi, J., Aoki, M. & Noyori, R. (2000). Hydrogen peroxide oxidation of aldehydes to carboxylic acids: an organic solvent-, halide- and metal-free procedure. *Tetrahedron. Lett.* 41, 1439–1442. DOI: 10.1016/S0040-4039(99)02310-2.