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Deep eutectic solvent (DES) as both Solvent and Catalyst for Oxidation of Furfural to Maleic acid and Fumaric acid

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Efficient conversion of furfural to voluble chemicals is attracting for it is one of bulk feedstocks in biomass refinery. Maleic acid (MA) and fumaric acid (FA) are two kinds bulk monomers which can be prepared from furfural. Here, a simple method was developed to oxidize furfural to both MA and FA in a green solvent of deep eutectic solvent (DES). The DES contains of oxalic acid and choline chloride (ChCl), where oxalic acid worked as both the main content of the solvent and acidic catalyst for the conversion. It was found that the conversion of furfural can reach 100% while the yield of MA and FA reached 95.7% under mild reaction temperature of 50 °C, which provides a green and efficient route to synthesis valuable furfural. from

Introduction

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Maleic acid (MA), fumaric acid (FA), and their anhydride (MAnh) are important C₄ chemical intermediates with applications in multiple fields of the chemical industry, such as in the synthesis of unsaturated polyester resins, vinyl copolymers, surface coatings, lubricant additives, plasticisers, copolymers, agrochemicals, and pharmaceuticals.¹ The annual production of MA and FA is about 2 million tons, and it is still challenge to prepare them in new green and low-cost methods. Currently, MA is produced via aerobic oxidation of butane, benzene, or butadiene in industry while FA is manufactured by hydrolysis conversion of maleic anhydride or biological conversion by fungi.² FA was also prepared from succinic acid.

monomers

Preparation of MA and FA from lignocellulose is an attracting topic, especially from renewable resources such as furfural and 5-hydroxymethylfurfural (HFM), which are the most important bio-based chemical platforms that can be obtained from hemicellulose and cellulsoe.³ Various catalytic systems have been developed for the conversion of furfural/HMF to MA/FA or MAnh in the presence of molecular oxygen or hydrogen peroxide as oxidants, such as copper salts catalysis in liquid media with dioxygen,⁴ catalytic aerobic oxidation with phosphomolybdic acid,⁵ vanadium-oxide-based catalysis in a gas-phase oxidation of furfural with a up to 70% MA,⁶ titanium silicate-1 (TS-1) catalysis in a liquid phase oxidations of furfural to give 78% yield of MA,⁷ and Mo-V-O catalyst was also used for the heterogeneous catalytic

conversion of furfural to MAnh using acetic acid as solvent.8 Else, using an aqueous solution of betaine hydrochloride (BHC) in the presence of hydrogen peroxide, can get over 90% yield of MA and FA.⁹ Recently, Zhang et al. found that furfural can be oxidized by H_2O_2 in C1-C4 organic acids as both solvent and catalyst, and carboxylic acids play a critical role in the oxidation where organic acids can be oxidized to organic peracids by H₂O₂ which efficiently oxidize furfural to MA. Interestingly, the acidity of organic acid is a key parameter, and the yield of MA increased when the pK_a of organic acids increase from butyric (4.82), propionic acid (4.87), acetic acid (4.76), to formic acid (3.75), and get an excellent yield (95%) of MA when formic acid was employed.¹⁰ Is it possible to use a much strong organic acid to get the oxidation reaction more quick and efficient? Such as oxalic acid with pK_a of 1.23.

However, the molten point of oxalic acid is 189 °C, and a solvent should be added if oxalic acid was used. Green solvents are especially expectation, such as water or ionic liquids. Among ionic liquids, deep eutectic solvents (DESs) is a series of transparent liquid eutectic mixtures that obtained through strong hydrogen-bonding interactions between hydrogenbond acceptors (HBA) and hydrogen-bond donors (HBD),^{11, 12} which have been considered to be a new class of promising green solvent for their properties of both organic solvents and ionic liquids.^{13, 14} Oxalic acid/choline chloride (OA-ChCl) is a well-known DES where oxalic acid is the major content.¹⁵ So it is an ideal system for oxidation of furfural to MA/FA while it works as both green solvent and catalyst.

Here, OA-ChCl DES was used as solvent for furfural oxidation in the presence of H₂O₂, and the effect of OA/ChCl ratio, amount of H_2O_2 , water, time and temperature on the yield of MA and FA has been studied, and it provides a new and green route to convert furfural to MA and FA under mild reaction condition (Scheme 1).



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Reaction route

Scheme 1. Conversion of furfural to fumaric acid and maleic acid in ChCl-oxalic acid DES in the presence of $\mathsf{H}_2\mathsf{O}_2.$

Results and discussion

At first, OA was used as organic acid catalyst to replace formic acid for its higher acidity, but it was solid at room temperature. So solvent should be employed, and water was first selected. Saturated aqueous or ethanol solutions of oxalic acid were used as solvent to carry out the reaction, respectively. As control, pure water without OA was also studied. As shown in Fig.S1 and Table S1, the products contain many peaks, indicating a low selection to MA and FA, and the yield of MA/FA is low. Water is not the best solvent while the solubility of OA in ethanol is low, so more suitable solvent should be developed.



Figure 1. Effect of DES composites on the oxidation of furfural: (a) furfural/OA is 1:5.6, (b) furfural/OA is 1:4.3. Reaction condition: furfural (1 mmol), water (4 ml), H_2O_2 (10 mmol), 50 °C, 24 h.

As stated before, DESs are cheap ionic liquid-like green solvents, and here OA based DES was selected where OA

works not only as the HBD of DES but also catalyst for the furfural oxidation. Three kinds of OA based DESs has been used as solvent for the reaction, and they are OA-Betaine, OA-Proline, and OA-ChCl. Fig.S2 shows the typical HPLC curves of the products using the three DESs as solvent for the oxidation of furfural respectively, and clearly OA-ChCl is the optimal solvent for the reaction.

OA-ChCl DES was diluted by water to decrease its viscosity, and then the ratio of OA to ChCl was changed to study its effect on the yield of MA and FA. As shown in Figure 1, the amount of ChCl is a key parameter, and when the ratio of OA to ChCl is 1:4, the yield of FA (26%) and MA+FA is maximum (46.9%), and the yield of MA reach maximum (25.3%) when the ratio of OA to ChCl is 1:2. However, when the ratio of OA to ChCl is 1:5 all the yields decrease, and clearly some ChCl crystalline can be found at the bottom of the reactor, indicating some of the ChCl was not dissolved in the solvent. In addition, the viscosity of OA-ChCl (1:4, without water) is high, so we choice OA-ChCl (1:3) as the solvent for the next studies. In addition, increasing the amount of OA has little effect on the reaction.

The effect of ratios of H_2O_2 to furfural is another key parameter, and the results were shown in Figure 2. It's obvious that the yield of MA increased with the increase of hydrogen peroxide, but the yield of FA decreased slowly. Interestingly, the yield of MA/FA depended strongly on the amount of excess adding water. When more excess water was added (4 mL), the total tiled of both MA and FA is low, but decreasing of water will result in the increase of MA/FA, especially for FA, and the yield of FA reached 50% when no water was added while the ratio of H_2O_2 to furfural is 4. In addition, the cross point of the yield of MA and FA moved to higher $H_2O_2/furfural$ ratio, indicating FA is more easily oxidized to CO₂ than MA with more H₂O₂ and less water condition. For the yield of MA and FA, it reached the maximum when the molar ratio of H₂O₂/furfural is 10-12.



Figure 2. Effect of the amount of H_2O_2 on the oxidation of furfural in OA-ChCl DES with adding of excess water: (a) 4 mL excess adding water; (b) 1 mL excess adding water; (c)

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0 mL excess adding water. Reaction condition: furfural (1 mmol), furfural/OA is 1:5.6, OA/ChCl=1:3, 50 °C, 24 h.

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Figure 3. Effect of the amount of excess adding water on the oxidation of furfural in OA-ChCl DES: excess adding water (0-5 ml); Reaction condition: furfural (1 mmol), H_2O_2 (10 mmol), furfural/OA is 1:5.6, OA/ChCl=1:3, 50 °C, 24 h.

The effect of excess adding water content was also deep studied. As shown in Figure 3, increasing of excess adding water content has less effect on the yield of MA, but it has an obvious effect on the yield of FA, which decreasing rapidly with the increase of excess adding water. Thus, the total yield of MA and FA decreased with the increase of excess adding water, indicates that the presence of excess adding water may inhibit the reaction, and the results are consistence with that obtained from Figure 2. The effect of temperature on the conversion of furfural was also studied, and as shown in Figure 4, the yield of MA and FA changes regularly with the temperature. As the temperature rise, the yield of MA decreased, and the yield of FA increased, which lead to the highest yield of MA+FA occurs at near 50 °C. When the reaction occurs at temperature up 50 °C, the solution will release a lot of bubbles, and even turn black, indicates that the high temperature causes the quick decomposing of hydrogen peroxide, which is not favorable to the reaction.

Figure 5 shows the effect of reaction time on the yield of MA, FA and MA+FA when the reaction was carried out in 1 mL of excess adding water at 50 °C. Clearly, extending reaction time favors the conversion of furfural to MA and FA, especially at time after 15h, and the total yield of MA and FA up 65% while the yield of MA change little, indicating long reaction time (24h) promote the formation of FA.



Figure 4. Effect of the reaction temperature on the oxidation of further in OA-ChCI DES. Reaction conditions: furfural (1 mmol), excess adding water (139), suctoral (22) is 1:5.6, OA/ChCl=1:3, H₂O₂ (10 mmol), 24h.

As shown in both Figure 2 and Figure 3, it can be found that the amount of excess adding water in the reaction system is a key parameter, and low amount of water favors the high yield of MA and FA, especial FA. What will happen if no more water was added? As shown in Figure 6, the reaction was carried out in the system of OA-ChCl and H_2O_2 , no more water was added. Excitingly, the yield of FA increased quickly even after the reaction time is only 6h and it reaches 65.6%. The total yield of MA and FA reaches 94.4%, indicating an efficient conversion of furfural to FA and MA, and the high yield can maintain upto 15h reaction, and extending more reaction time will result in the over-oxidation of MA and FA, resulting in low yield of them.



Figure 5. Effect of the reaction time on the oxidation of furfural in OA-ChCl DES with excess adding of water (1 mL). Reaction condition: furfural (1 mmol), H_2O_2 (10 mmol), furfural/OA is 1:5.6, OA/ChCl=1:3, 50 °C.

Then, effect of reaction temperature on the conversion of furfural without adding water was studied. As shown in Fig.7, the optimal reaction temperature locates around 50-60 °C, and the yield of MA and FA even reached 95.7% when the temperature is 60 °C. Similarly, the major product is FA, indicating which is stable at the range of temperature. However, increasing the reaction temperature up 70 °C should decrease the yield of both MA and FA, indicating the furthermore oxidation of them.



Page 4 of 5

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Figure 6. Effect of the reaction time on the oxidation of furfural in OA-ChCl DES without excess adding water. Reaction condition: furfural (1 mmol), H_2O_2 (10 mmol), furfural/OA is 1:5.6, OA/ChCl=1:3, 50 °C.

The possible reaction mechanism was shown in Scheme 2. At first, oxalic acid reaction with hydrogen peroxide to generate peroxalic acid (PA), which works as the oxidant. The oxidation ability of -O-O- group in PA is stronger than H₂O₂ due to the electron-withdrawing effect of the carbonyl group. In the EDS, the pK_a of oxalic acid is 1.23, which makes the solvent more acidity than other C1-C4 organic acid. According to the Nernst equation ($E = E_0 - 0.059 \text{pH}$),⁸ it should be a strong oxidant for furfural. The in-situ formed peroxalic acid inserts an oxygen atom between the furan ring and the aldehyde group, and then the ester group is hydrolyzed to formic acid and the unstable intermediate 2-hydroxyfuran which arrange to get 2(5H)-Furanone rapidly.⁵ As the allyl hydrogen is easily oxidized, 2(5H) -furanone may be oxidized to maleic anhydride in the presence of hydrogen peroxide. Then maleic anhydride can be hydrolyze to maleic acid under acidic conditions, and it is easily converted to a more stable fumaric acid. This means that the yield of fumaric acid is higher than that of maleic acid in such condition. In HPLC studies, the peaks of formic acid and 2(5H)-Furanone can be directly detected (Fig.S3), which supports the rationality of the suggested mechanism.



Scheme 2. Suggested mechanism of the reaction



Figure 7. Effect of the reaction temperature on the oxidation of furfural in OA-ChCl DES without excess adding water. furfural (1 mmol), furfural/OA is 1:5.6, OA/ChCl=1:3, 50 $^{\circ}$ C, H₂O₂ (10 mmol), 6 h.

Experimental

Materials and Characterizations

All reagents and solvents mentioned were purchased from Furfural (98%), maleic acid (MA, 99.5%), 2-furoic acid (98%), phosphate (75%), L-proline (99%), betaine (98%), fructose (99%) were purchased from Aladdin. Hydrogen peroxide (30%), oxalic acid (OA, 99.5%), fumaric acid (FA, 99%), succinic acid (99.5%), glucose (AR), xylose (BR) were supplied by Sinopharm. Choline chloride (ChCl, 98%) was supplied by Macklin. 2-(5H)-Furanone (98%) was supplied by Sigma-Aldrich. Methanol (analytical purity) was supplied by Oceanpak, ultrapure water with resistivity of 18 M Ω ·cm was produced by a Milli-Q (Millipore, USA).

High performance liquid chromatograph (Shimadzu), C-18 Chromatographic column (5 μ m, 4.6×250mm, purchased from Agilent Technologies Inc.) with an ultraviolet detector. Mobile phase: 20% methanol + 80% Phosphoric acid solution(1‰), column temperature: 40 °C, and flow rate: 0.6 mL/min.

Oxidation of furfural

Firstly, Furfural was purified by vacuum distillation. For water/ethanol solvent, adding 0.5g oxalate and 4ml water/ethanol into a 25 ml flask, and heating the container at 50 °C under water bath for several minutes to get a clear solution. Then, adding 1 mmol furfural (83μ L) and 1ml H₂O₂ (30%). The reaction was carried out for 24 h at 50 °C. Next, diluting the reaction solution 100 times to quench the reaction, and then it was through a 0.22 µm syringe filter for HPLC analysis.

For DES, adding 0.4-1.0g oxalate and 0.4-3.0g ChCl (or betaine/proline) into a 25 ml flask, heating the container at 50 °C under water bath for several minutes to form the liquid, and 0-5 mL water was added next. Then, adding 1 mmol furfural (83 μ L) and 0.5-4ml H₂O₂ (30%) to the container. The reaction was carried out for 24 h at 50 °C. At the end of the reaction, diluting the reaction solution 100 times by water to quench the reaction, and then it was through a 0.22 μ m syringe filter for HPLC analysis.

Conclusions

Here, an efficient route was found to convert furfural to maleic acid (MA) and fumaric acid (FA) using an oxalic acid (OA) based deep eutectic solvents (DES) as both solvent and acidic catalyst. The reaction can be carried out under mild condition at low temperature (50-60 °C) with hydrogen peroxide as oxidizer, and the total yield of MA and FA reached 95.7%. It provides a new and green method to convert biomass to valuable chemicals.

Conflicts of interest

There are no conflicts to declare.

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