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Highly Efficient Formic Acid-Mediated Oxidation of Renewable Furfural to Maleic Acid with H₂O₂

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Maleic acid and its anhydride are important intermediates in chemical industry that represent millions of tons of market demands. The synthesis of maleic acid/anhydride from renewable biomass resources such as furfural and 5-hydroxymethylfurfural is highly desirable for the sustainability of human society. Most of the previously reported processes for maleic acid/anhydride synthesis from biomass suffer from low efficiency, complicated conditions and poor catalyst recyclability. Herein, we demonstrate a highly efficient and simple system for the synthesis of maleic acid from furfural. An excellent yield (95%) of maleic acid was achieved under mild conditions in this very simple system which requires only H₂O₂ as an oxidant in formic acid solvent. Under similar conditions, an 89% yield of maleic acid was achieved from biomass-derived 5-hydroxymethylfurfural. This study presents a novel synthetic method and a promising process for maleic acid production from renewable biomass resources.

The unsustainable strain placed on non-renewable resources caused by the rapidly growing global economy has triggered a desperate need to find substitutes for the world’s limited reserve of fossil fuels. The wide availability and enormous potential of biomass has made it the ideal alternative source of hydrocarbon needed in the chemical industry. Maleic acid (MA), fumaric acid (FumA), and their anhydride (MAAnh) are critical chemical intermediates in the manufacture of unsaturated polyester resins, vinyl copolymers, surface coatings, plasticizers, and pharmaceuticals. As such, their synthesis from renewable biomass resources is highly sought after.

5-Hydroxymethylfurfural (HMF) and furfural, which are derived from cellulosic biomass, are the most extensively studied platform molecules for the green synthesis of maleic acid/anhydride and other organic acids. In terms of cost, furfural is more attractive as it can be produced on a large scale from abundant agriculture waste while HMF is obtained on small scales from the dehydration of sugars.

Various homogeneous and heterogeneous catalytic systems with molecular oxygen or hydrogen peroxide as oxidants have been developed for the conversion of furfural to MA or MAAnh. Currently, liquid phase oxidations of furfural with O₂ or H₂O₂ using homogeneous or heterogeneous acid catalysts typically offer MA in < 50% yield. Up to 70% MA yield can be achieved in the gas phase oxidation of furfural over vanadium-based catalysts at low feed concentrations (as low as 1 vol%). Heterogeneous catalytic conversion of furfural in the liquid phase is also challenged by the potential for catalyst leaching. In the case of a Mo-V-O catalyst developed for furfural oxidation to maleic anhydride in acetic acid solvent under 20 bar of O₂, the leaching of the vanadium species into the solution resulted in the MA yield decreasing from 65% to 23% in the fifth reaction with recycled catalyst. The highest yield of MA (78%) from furfural to date in an aqueous phase oxidation was obtained over a titanium silicate-1 (TS-1) catalyst with H₂O₂ as an oxidant, and significant Ti leaching was also observed in the reaction. The problems of low efficiency, complicated conditions, or poor catalyst recyclability facing these processes severely limit their potential for industrial application.

![Scheme 1. Oxidation of furfural and HMF to maleic acid with H₂O₂. Reaction conditions: furfural or HMF (1 mmol), formic acid (4 ml), 31% H₂O₂ (1 ml), 98% HSO₄ (d only, 1 mol% to H₂O₂).](Image)

To date, all transformations of furfural or HMF to MA utilizing H₂O₂ or O₂ require a single or combination catalyst. A metal catalyst-free system would simplify product isolation and avoid the issues of catalyst deactivation, offering an attractive alternative to catalyzed furfural-to-MA methods provided that the reaction efficiency is comparable to or better than those in the catalytic
cases. To the best of our knowledge, there has been no report of metal catalyst-free transformation of furfural or HMF to MA. Hence, we demonstrate a highly efficient and simple system for the conversion of furfural and HMF to MA. Using H$_2$O$_2$ as the oxidant and formic acid as the solvent, MA was obtained in an unprecedented 95% yield from furfural and 89% yield from HMF (Scheme 1).

In our study, furfural oxidation with H$_2$O$_2$ was initially performed in acetic acid as it is a good solvent for the homogeneous and heterogeneous catalytic oxidation of furfural and HMF to maleic anhydride. Complete furfural conversion and 65% yield of MA was observed in acetic acid solvent under conditions of H$_2$O$_2$/furfural = 10 (mol/mol) at 100 °C over 4 h (Table S1). Formic acid was observed as the only side product (Figure 1A). Using pure water as a solvent without any catalyst afforded maleic acid in a yield of 15% (Table S1). Other solvents showed no selectivity towards MA (Table S1) but 2-furoic acid and some unidentified products were observed.

It was therefore presumed that carboxylic acids play a critical role in furfural oxidation to MA with H$_2$O$_2$. Thus, C$_2$ to C$_4$ carboxylic acids were tested as solvents with the results shown in Figure 1A. Complete furfural conversions were achieved in all carboxylic acid solvents but the yields of MA decreased linearly with increasing length of the carboxylic acid carbon chain. The yield of MA in butyric acid was a modest 37% while conducting the reaction in formic acid returned an unprecedented 91% yield of MA, far exceeding those (< 78%) from the aforementioned catalytic processes. Organic acid solvents may play multiple roles in the oxidation of furfural with H$_2$O$_2$. Organic acids are readily oxidized to peracids by H$_2$O$_2$ even at room temperature. Due to the electron-withdrawing effect of the carbonyl group, the -O-O- bond in organic peracids should be stronger than that in H$_2$O$_2$. Moreover, in the acidic environment (lower pH value) of organic acid solvents, the oxidation potential should increase according to the Nernst equation ($E = E^0 - 0.059pH$). Thus, H$_2$O$_2$ and organic peracids should be stronger oxidants in the organic acid solvents than in H$_2$O$_2$ or other less acidic acids. The acidities of carboxylic acids decrease with the length of the carbon chain (pK$_a$ values: formic acid, 3.75; acetic acid, 4.76; propionic acid, 4.87; butyric acid, 4.82), and this is in good agreement with the observed yields in the four solvents.

The amount of formic acid is also important for high MA yields. From Figure 1B, MA yields increased with increasing amount of formic acid and > 90% yield of MA was achieved at formic acid to H$_2$O$_2$ volume ratios greater than or equal to three. The H$_2$O$_2$ oxidation of formic acid to performic acid is a reversible reaction and a high concentration of formic acid favors the peracid at equilibrium. The presence of additional water in the system is detrimental to the reaction. A volume ratio of water/formic acid 1:1 yielded 27% of MA, while a water/formic acid ratio of 3:1 yielded 13% of MA (Table S2). Additional water changes the pH value of the solvent and decreases the rate of performic acid formation. In the cases where formic acid was absent or present in low concentrations (5.5 vol%), 2(SH)-furanone was the major product and the yield for maleic acid was < 17%. As formic acid can also be produced from biomass, the H$_2$O$_2$ oxidation of furfural to MA in formic acid is essentially a green synthetic method. Additionally, the side products of this reaction are formic acid and water, which enables facile product isolation from the reaction system. After the reaction, the solvent could be removed by evaporation to give crude MA as a white solid (Figures S2 and S3).

Figure 1. (A) Furfural oxidation to maleic acid in organic acids with H$_2$O$_2$ as oxidant. Reaction conditions: furfural (1 mmol), organic acid (4 ml), 31% H$_2$O$_2$ (1 ml), 100 °C, 4 h. (B) Furfural oxidation to maleic acid with H$_2$O$_2$ in different forms of organic acid. Reaction conditions: furfural (1 mmol), 31% H$_2$O$_2$ (1 ml), 100 °C, 1 h.

Figure 2. Kinetics of furfural oxidation to maleic acid at different reaction temperatures. Reaction conditions: furfural (1 mmol), formic acid (4 ml), 31% H$_2$O$_2$ (1 ml).
The kinetics of furfural oxidation in formic acid at different reaction temperatures are presented in Figure 2. The reaction was very fast when performed at 100 °C, requiring just 5 minutes to achieve a 72% yield of MA. The maximum yield of MA (93%) was achieved in 40 min, while a 91% of MA yield was still retained on prolonged reaction times of one to four hours, indicating that MA is stable in this system. The reaction rate was slower when the experiment was performed at 60 °C, with the maximum yield of MA (95%) achieved in 4 h. The reaction even proceeds at room temperature (25 °C) and a MA yield of 80% can be obtained within 20 h. The high efficiency of the current H$_2$O$_2$ oxidation of furfural to MA is remarkable compared with previously reported catalytic processes.\cite{he2012,li2013,moroz-2012-482} The current reaction can also be performed in open system with a slightly lower MA yield (Table S3).

As H$_2$O$_2$ is consumed in the transformation of furfural to MA, the amount of H$_2$O$_2$ input is crucial for the economy of this synthetic route. Thus, the effect of varying H$_2$O$_2$ to furfural ratio was studied under various conditions (Figure 3). Longer reaction times were used at lower reaction temperatures according to the kinetic studies shown in Figure 2. The optimal H$_2$O$_2$/furfural ratios were 10, 6, and 12, respectively, at 100 °C, 60 °C, and 25 °C. The yield of MA when the reaction was conducted at 60 °C is generally higher than that achieved at 100 °C and 25 °C. The best MA yield of 95% was achieved at a H$_2$O$_2$/furfural ratio of 6 at 60 °C. It should be noted that the optimal H$_2$O$_2$/furfural ratio of 6 is lower than that (7.5) employed in the TS-1 catalyzed system.\cite{peng2013} The observed relationship between MA yield and H$_2$O$_2$/furfural ratio at different reaction temperature can be rationalized as a balance of furfural oxidation and peroxide decomposition. There were more gas bubbles in the reactor at a reaction temperature of 100 °C, less bubbles at 60 °C, and almost no bubbles at 25 °C, indicating faster decomposition of the peroxides at higher reaction temperatures. At 100 °C, the oxidation of furfural is fast; however, rapid peroxide decomposition leads to a high consumption of H$_2$O$_2$. At room temperature, the decomposition of the peroxide oxidants was slower; however, the rate of furfural oxidation was also slower and therefore larger amounts of H$_2$O$_2$ were required to obtain high MA yields. Thus, the reaction temperature of 60 °C allows the minimum amount of H$_2$O$_2$ to be employed. To further verify this deduction, the reaction was studied at different temperatures with the H$_2$O$_2$/furfural ratio fixed at 6. The results are shown in Figure 3B and confirm the optimal MA yield was achieved at 60 °C.

One attractive feature of this method is that the reaction proceeds even at room temperature, albeit at a much slower rate of MA formation. As a reaction performed at room temperature is more energy efficient and cost effective for industrial application, we tried to improve the reaction rate at room temperature. Based on the hypothesis that acid catalysts can promote the oxidation of formic acid to performic acid and enhance the acidity of the system,\cite{lam2007} we added soluble and solid acid additives into the system in order to promote the reaction. It can be seen from Figure 4 that both H$_2$SO$_4$ and Amberlyst 15 had a positive impact on MA formation. The addition of H$_2$SO$_4$ had a more pronounced effect, where the addition of 1 mol% afforded an 83% yield of MA within 7 h at room temperature, as compared to the 80% MA yield achieved in 20 h in the absence of acid additives (Figure 2). The wide range of reaction temperatures which can be employed for the current synthetic method allows flexibility in practical application.

In order to probe the influence that substrate structure has on the current reaction, various furan compounds were tested. All of the furan compounds shown in Scheme 2 can be derived from biomass platform molecules except unsubstituted furan, 2,5-Diformylfuran (DFF), 2,5-formylfurancarboxylic acid (FFCA), 2,5-furandicarboxylic acid (FDCA), and 2,5-dimethylfuran (DMF) can be
derived from the oxidation or hydrogenation of HMF,[11] while 2-furoic acid is obtained from the oxidation of furfural.[12] Using the method we developed, almost quantitative yield (99%) of MA was achieved from furan. When the furan ring was substituted with aldehyde group(s), as was the case with furfural, HMF, and DFF, good to excellent yields of MA (77–91%) were still achieved. When the furan ring was substituted with carboxylic acid group(s) - in FFCA, 2-furoic acid, and FDCA - the yield of MA decreased notably to lower than 33%. With methyl substitution (DMF), the yield of MA was only 5%. Thus, carboxylic acid and methyl-substituents on the furan ring have a deleterious effect on MA formation compared to aldehyde substituents.

The mechanism for acid-catalyzed H₂O₂ oxidation of furfural/HMF to MA is still under debate with two main reaction pathways that have been proposed.[12a, d, h, k, n, r, s] The first pathway is the 2-furoic acid route, that is, furfural is first oxidized to 2-furoic acid, which is then converted to furan by decarboxylation. Further oxidation of furan by H₂O₂ affords maleic acid (Scheme S1).[8h] In our reaction system, 2-furoic acid was not observed and the reaction using 2-furoic acid as the starting material yielded a much lower yield of maleic acid (15% yield). Therefore, the 2-furoic acid route could be discarded. The second pathway starts with Baeyer-Villiger oxidation of furfural to furan formate ester, which is hydrolyzed to formic acid and 2-hydroxyfuran. 2-Hydroxyfuran isomerizes to furan-2(SH)-one which is oxidized to maleic acid (Scheme S2).[6k- 3h] Because both formic acid and the key intermediate furan-2(SH)-one were observed in our control reactions (Figures S1 and S4), it is likely that the present reaction proceeds through the Baeyer-Villiger oxidation route. Fully elucidating the reaction mechanism requires further efforts and this will be the focus of our future research.

Conclusions

We have demonstrated a highly efficient and simple system for the conversion of furfural to maleic acid with H₂O₂ as oxidant and formic acid as the solvent. The nature of the solvent was crucial for the high efficiency of MA formation and formic acid was found to be the best simple organic acid. Under mild reaction conditions, an unprecedented 95% yield of maleic acid was achieved from furfural using H₂O₂ as the oxidant and formic acid as the solvent. Reaction temperature significantly affects the reaction rate and dictates the optimal H₂O₂ to furfural ratio. A H₂O₂/furfural ratio of 6 is optimal for achieving the highest yield of MA (95%) at 60 °C. Remarkably, acid additives promote the reaction rate even at room temperature. This method is also effective for the synthesis of MA from other biorenewable platform molecules such as HMF, from which an unoptimized 89% yield of MA was achieved.

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Notes and references


