Letter

Selective Production of Maleic Acid from Furfural via a Cascade Approach Combining Photochemistry and Electro- or Biochemistry

Shanmugam Thiyagarajan,* David Franciolus, Roel J. M. Bisselink, Tom A. Ewing, Carmen G. Boeriu, and Jacco van Haveren

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ABSTRACT: Starting from furfural, maleic acid is efficiently synthesized in two steps under very mild conditions. In the first step, 5-hydroxy-2(5H)-furanone is synthesized via photochemical oxidation and proposed as a stable intermediate. Subsequent oxidation in the second step, by either an electrochemical or enzymatic process, results in maleic acid in high yield and selectivity.
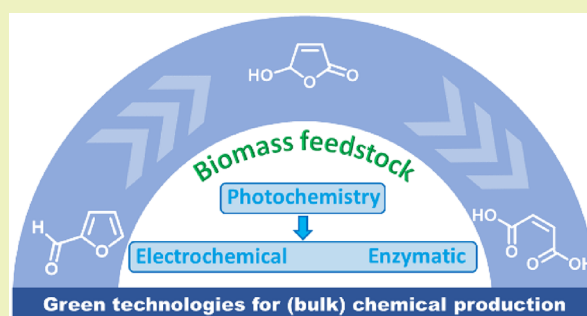
INTRODUCTION

In the past few decades, there has been a growing interest in reducing the dependency on fossil-based feedstocks and replacing them with renewable biomass as a sustainable source for the production of chemicals and materials.[1−4] In parallel to this quest, the investigation of greener technologies (such as photochemical, electrochemical, and biocatalytic processes) for the efficient conversion of such biomass into chemicals is also attractive. Most of these processes, in addition to high atom efficiency, will substantially reduce pollution and energy consumption, thereby lowering the production costs and resulting in less or no waste side-streams.[5,6]

Maleic acid (MA) is an important raw material that finds multiple applications in the chemical industry, such as in manufacturing of unsaturated polyester resins, lubricant additives, surface coatings, textiles, photographic chemicals, plasticizers, pharmaceutical products, and agricultural chemicals.[7−13] In our ongoing research, MA is widely being used to synthesize chemicals for different applications, in particular biobased aromatic (bulk) chemicals.[14,15] Biobased aromatic compounds can be conveniently synthesized via a Diels−Alder (DA) cycloaddition of furanics (as diene) with maleic acid anhydride (dienophile). Subsequent dehydration (also known as aromatization) of the DA adduct leads to aromatic compounds.[14,15] This strategy is regarded as an interesting technology for the production of biobased aromatic chemicals, since both diene and dienophile can be derived from cellulosic biomass. The most promising dienes, such as furan, (di)-methylfuran, and furfural, are synthesized from C5/C6 sugars in high yields according to procedures that are in agreement

with industrial demands for large-scale production.[16−18] Furfural is already commercially produced at a scale of around 280−400 kton/year from carbohydrates.[19−22] However, the development of cost-efficient routes for the production of MA starting from biomass is still challenging. To produce aromatic chemicals and other materials based upon biobased MA, it is essential to develop processes using green methodologies that can meet the industrial demands for the production of MA from renewable resources.

Currently, MA is commercially produced by hydrolysis of maleic acid anhydride, which in turn is obtained from the vapor-phase oxidation of benzene or *n*-butane.[23,24] Starting from 100 mol of benzene, 73 mol is oxidized to maleic anhydride and 23 mol is "burned off" under the applied conditions, leaving 4 mol of unreacted benzene in the commercial process.[23]

Lately, alternative resources have been investigated to circumvent the use of fossil derived feedstocks. In particular, biomass-derived platform chemicals like butanol, levulinic acid, 5-hydroxymethylfurfural (HMF), and furfural were investigated as starting materials for the synthesis of MA.[6−11] Among these platform chemicals, furfural is an interesting
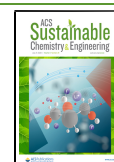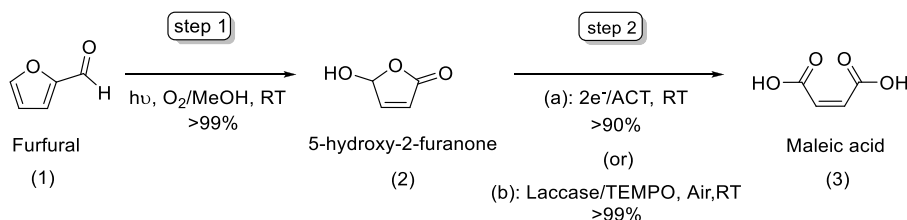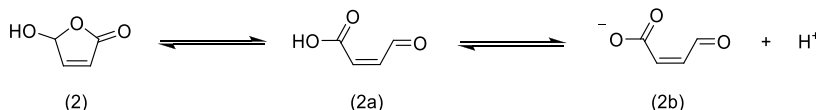
Scheme 1. Two-Step Strategy for Synthesizing Maleic Acid (3) from Furfural (1): Step 1, Photochemical Oxidation, and Step 2, (a) Electrochemical or (b) Enzymatic Oxidation

Scheme 2. Chemical Equilibrium between 5-Hydroxy-2(5H)-furanone (2), cis-β-Formylacrylic Acid (FAA, 2a), and the Conjugated Base 2b

substrate since its commercial production is already established starting from carbohydrates.[22,25]

The first report of the production of MA from furfural dates back to 1 century ago, when Yabuta patented the electrochemical oxidation of furfural to MA in sulfuric acid at lead (oxide) anodes.[26] This was followed by the work of Sessions, who in 1928 demonstrated the vapor-phase oxidation of furfural to MA at high temperature (300−350 °C);[27] however, the yields were not mentioned in that report. Since then, a wide range of investigations have been carried out to improve the process, including gas-phase reactions,[28,29] oxidation using a high pressure of O_2[30−32] or chemical oxidants,[33−35] and electrochemical oxidation.[26,36−42] In parallel to our investigations, we came across two recent reports: one by Wu et al., describing the use of metal chalcogenides as electrocatalyst and water as the oxygen source to produce 5-hydroxy-2(5H)-furanone from furfural at 83.6% selectivity and in parallel to MA at 8.8% selectivity,[43] and the other by Román et al., who oxidized furfural at platinum deposited on plain carbon cloth, thereby obtaining mainly 2-furoic acid, 5-hydroxy-2(5H)-furanone, and hydroxyfuroic acid, with MA being a minor product.[44]

Nevertheless, all these conditions require either high temperature, high oxygen pressure, a large excess of chemical oxidants like H_2O_2, or a large excess of charge to achieve maleic acid/anhydride in reasonable to good yields. These extreme conditions are unfortunately not favorable for producing such chemicals in large quantities at low to reasonable prices.

Herein, we describe a simple two-step procedure to synthesize MA efficiently starting from furfural. Step 1 is a photochemical oxidation of furfural to 5-hydroxy-2(5H)-furanone, and step 2 is a nitroxyl radical-mediated oxidation to MA via either an electrochemical or enzymatic oxidation process. It is important to mention here that the reaction conditions employed in both steps are very mild, resulting in higher selectivity to the desired product. This new strategy will promote not only the greener production of MA but also greener technologies for (bulk) chemicals production.

■ RESULTS AND DISCUSSION

Most of the reports dealing with direct oxidation of furfural (1) to maleic acid (3) describe as a common fact that furfural is first oxidized to several unstable intermediates and then finally

to MA.[30,45] Interestingly, a few of those reports discussed the formation of stable intermediates such as 2-furanone,[30,36] 2-furanol,[32] and 5-hydroxy-2(5H)-furanone.[26,37−40] These results prompted us to first synthesize one of these stable intermediates, i.e., 5-hydroxy-2(5H)-furanone (2), starting from furfural, and then subsequently oxidize the intermediate to MA in the second step (Scheme 1).

Since furfural is a highly reactive molecule, it is envisioned that converting it into a stable intermediate will circumvent undesirable byproduct formation under oxidation reaction conditions. Recently, a similar approach was employed to synthesize γ-butyrolactone starting from furfural via 5-hydroxy-2(5H)-furanone as an intermediate.[46]

**Step 1: Synthesis of 2 via Photochemical Oxidation.** The synthesis of **2** is well-documented in the literature: **1** is photochemically oxidized at room temperature by singlet oxygen generated using a catalytic amount of methylene blue as photosensitizer. The resulting endoperoxide is unstable and simultaneously decarbonylated to give **2**. Besides methylene blue, Rose Bengal was also used as photosensitizer, and typically quantitative yields of the desired product were reported.[47,48] The use of sunlight in solar photoreactors has also been successfully demonstrated for the synthesis of **2**,[49] which is already a convincing argument that the production of **2** at commercial scale can be performed economically in a green, sustainable manner. Besides furfural, **2** can also be synthesized starting from furan, 2-furoic acid, or furfuryl alcohol using similar conditions. While starting from 2-furoic acid or furfuryl alcohol results in similar yields,[50−52] a lower yield (35%) was reported when starting from furan.[53] Using a custom-made photoreactor setup (see Supporting Information), the photochemical oxidation of **1** was reproduced in good yield and high selectivity (>95%) to **2**. The crude product was further purified by Reveleris flash chromatography to obtain **2** in >99% purity. Spectroscopic investigations by ^{1}H and ^{13}C NMR and GC-MS confirmed the structure of the desired compound.

Step 2: (a) Electrochemical Oxidation of 2 to Maleic Acid 3. Under aqueous conditions, **2** is in equilibrium with various compounds, including its tautomer β-formylacrylic acid (FAA, **2a**) (Scheme 2). **2** accounts for 30−60% of the speciation under acidic conditions (0 < pH < 4), with the conjugated base of FAA, **2b**, being the dominant species at pH > 6.[46] The electrochemical oxidation of **1** to **3** using PbO_2 in
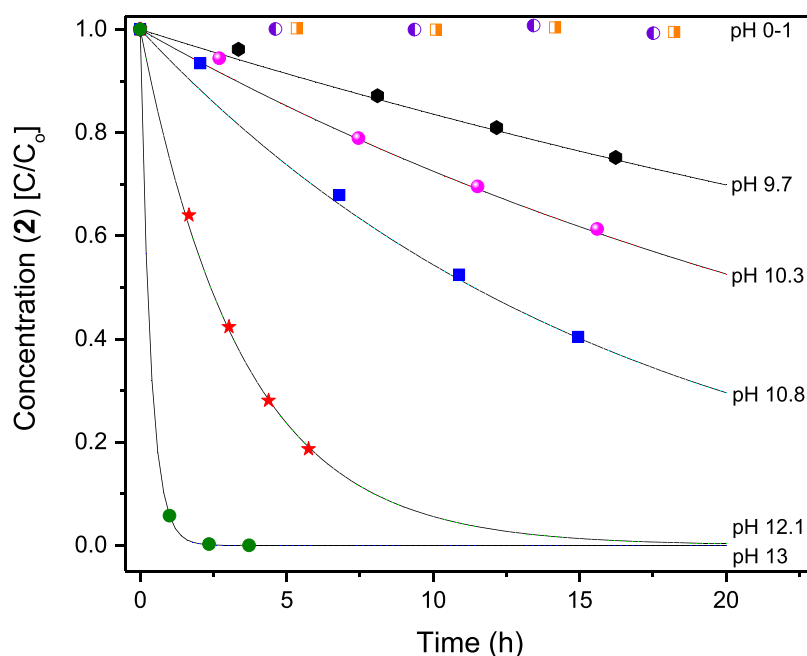
Figure 1. Degradation of **2** at room temperature under various pH conditions.
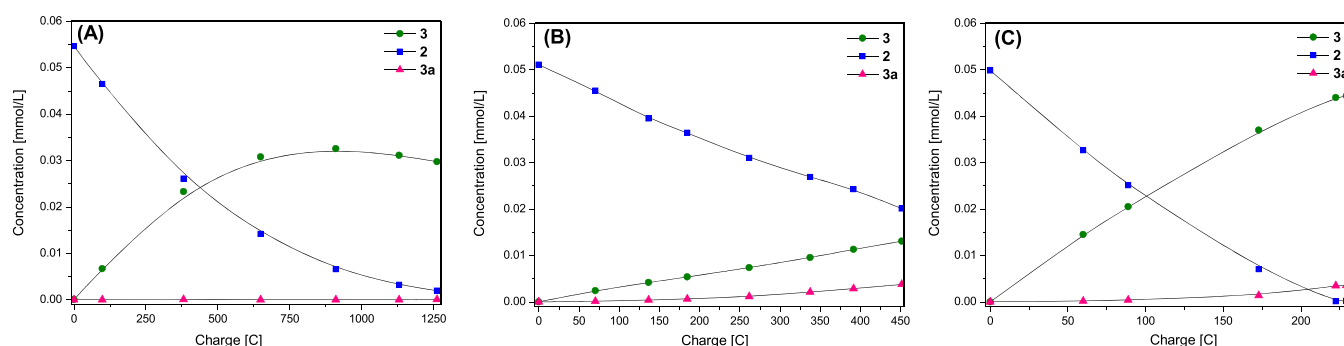
Figure 2. Oxidation of 0.05 M **2** to **3** and **3a** in an electrochemical cell divided by Nafion 117 at (A) 12.6 cm^2 β-PbO$_2$ at 1.8 V vs Ag|AgCl in 0.5 M H$_2$SO$_4$; (B) 11.0 cm^2 NiOOH at 0.9 V vs Ag|AgCl in 0.34 M Na$_2$CO$_3$ + 0.06 M NaHCO$_3$; and (C) 4 cm^2 45 ppi RVC at 0.8 V vs Ag|AgCl with 0.01 M ACT in 0.34 M Na$_2$CO$_3$ + 0.06 M NaHCO$_3$.

sulfuric acid solutions has already been known for almost 100 years[26] and proceeds through the intermediate **2a**.[37,38] Starting around 1970, Zverev, Mil'man, and co-workers published a series of works describing the electrochemical production of **2a** and **3** starting from **1** using PbO$_2$ and carbon anodes, including the use of various mediators.[39−42] As a result, **2a** could be produced in near to quantitative yields (90−95%) with high current efficiency (CE) at 1.3 V vs saturated calomel electrode (SCE). Increasing the potential further to >1.5 V vs SCE results in subsequent oxidation to **3**. However, this oxidation step appears to be less efficient, as furfural oxidation to **3** is faced by a low CE toward **3** (30%) and moderate yield (65%).[34] These moderate yields and low CE for **3** prompted us to investigate the viability of an electrocatalytic strategy for the production of **3** via **2** as an intermediate.

The oxidation of aldehydes to carboxylic acids using stable nitroxyl radicals or nickel oxide hydroxide (NiOOH) is well known. For example, the oxidation of HMF to 2,5-furandicarboxylic acid (FDCA) was demonstrated using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated electrochemical[54] or enzymatic[6] oxidation and via electrocatalytic oxidation using NiOOH.[55] The electrochemical systems

typically use alkaline conditions; therefore, we evaluated the stability of **2** at various pH values. The investigation revealed that **2** is stable in sulfuric acid solutions (pH 0−1) but starts to degrade under alkaline conditions, with an increasing degradation rate at increasing pH (see Figure 1). This observation is in line with the literature reports where **2a** readily polymerizes to a water-soluble resinous material,[56] and under alkaline conditions it isomerizes to the trans isomer, together with formation of a considerable amount of polymeric material.[57] In contrast to that of sulfuric acid, the electrocatalytic activity of TEMPO, 4-acetamido-TEMPO (ACT), and NiOOH increases at increasing pH.[58,59] Due to the reduced stability of **2** under strongly alkaline conditions, electrochemical oxidation was investigated at pH 10 using two different oxidative systems. The first one is ACT, which is low-cost, readily accessible, and outperforms other nitroxyls electrocatalytically,[59] and the second one is NiOOH, which circumvents downstream processing complexity compared to homogeneous catalysts.[55]

For comparison, electrochemical oxidation of **2** using β-PbO$_2$ in 0.5 M H$_2$SO$_4$ was performed under conditions similar to those described for **1**.[36] Initially a good selectivity was

Scheme 3. Mechanism for the Oxidation of Substrate by the Laccase-TEMPO System (Left)[63] and Electrocatalytic ACT System (Right)[64]
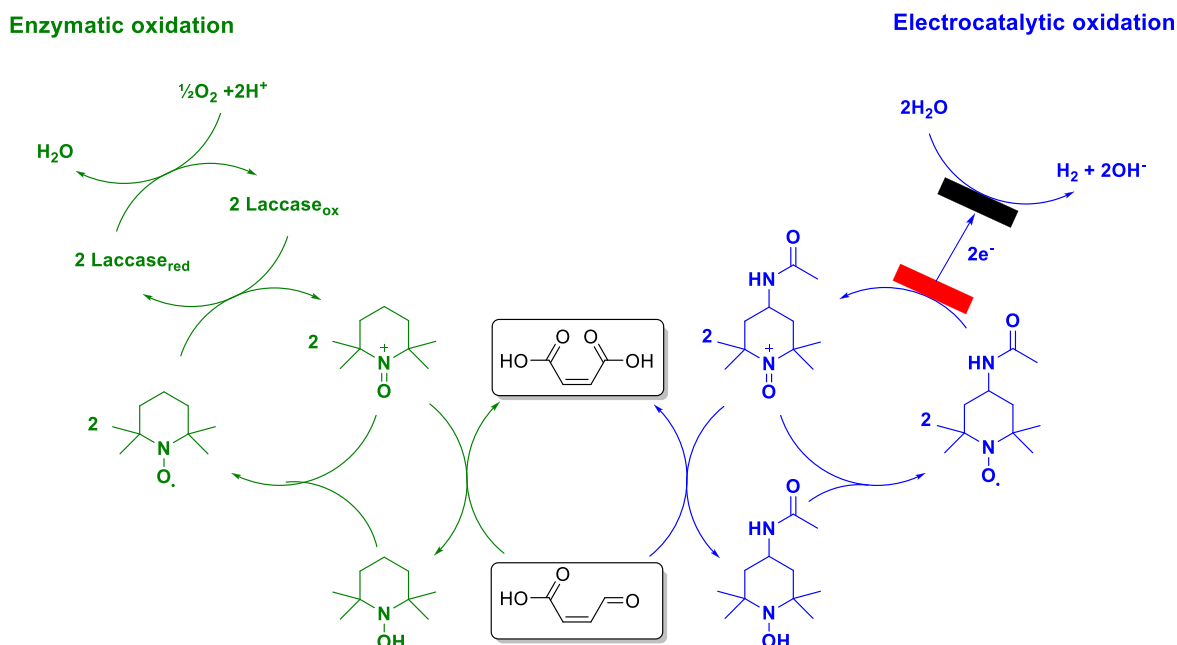
obtained, as illustrated in Figure 2a; however, at increasing conversion of **2**, the selectivity toward the product **3** decreases, resulting in a maximum yield of 60% at 911 C charge, 88% conversion of **2**, and 17% CE. These values are in line with the previous work of Kubota et al.[36] considering the near-quantitative conversion of **1** to **2**. At β-PbO$_2$, hydroxyl radicals are formed which degrade **3** ultimately to carbon dioxide.[60,61] At increasing electrochemical conversion of **2**, the concentration of **3** increases, thereby increasing the risk of degradation of **3** via hydroxyl radicals formed at β-PbO$_2$. The maximum yield of **3** is then probably limited by the decreasing conversion rates of **2** to **3** and increasing degradation rate of **3** to ultimately CO$_2$.

Oxidation of alcohols and aldehydes to the corresponding carboxylic acids can also be achieved using NiOOH under formation of Ni(OH)$_2$, which is continuously electro-regenerated to NiOOH.[55,62] The oxidation of **2** using NiOOH shows a similar trend to that with β-PbO$_2$ with respect to its conversion vs supplied charge (Figure 2b). In contrast to the reaction with β-PbO$_2$, the selectivity toward **3** remained constant at 42% during electrolysis, resulting in 26% yield at 61% conversion of **2** at 452 C charge. Next to preferred **3**, its isomer fumaric acid (**3a**) was also formed in 7.4% yield. The appearance of additional peaks in the HPLC analyses indicates the formation of byproducts during the electro-oxidation of **2** at NiOOH, thus resulting in a low selectivity. One of the additional peaks has been identified as the trans isomer of **2a** (see Supporting Information); analogous to the oxidation of **2a** to **3**, the trans isomer oxidizes to **3a**. The vicinity of a double bond, e.g. α,β-position, can result in cleavage at the double bond at NiOOH;[62] however, no oxalic acid or acetic acid was detected in the HPLC analyses.

TEMPO or ACT is first activated by its enzymatic or electrochemical oxidation to the oxoammonium ion. This species then reacts with the substrate, leading to the formation of product and the hydroxylamine TEMPO derivative. Comproportionation of the hydroxylamine TEMPO derivative

with the oxoammonium ion then regenerates the TEMPO/ ACT free radical. This free radical can then be reactivated for further rounds of catalysis.[63−65]

The formation of undesired products can be circumvented by using ACT instead of NiOOH. ACT is oxidized at the reticulated vitreous carbon anode under formation of the corresponding oxoammonium ion (ACT$^+$), which subsequently oxidizes **2** to **3** under formation of the hydroxylamine form of ACT (ACTOH). ACT is then regenerated by comproportionation of ACTOH and ACT$^+$.[64] This catalytic process is illustrated in Scheme 3. Using ACT, the total yield of products (**3** and **3a**) is enhanced up to 97%, including 7.1% of **3a**, as indicated in Figure 2c. Moreover, the combined CE of 90% achieved for ACT is significantly higher compared to those of NiOOH (18%) and β-PbO$_2$ (17%). Similar to the NiOOH system, the formation of **3a** and the presence of the trans isomer of **2a** were observed while using ACT. In both cases there is a progressive increase in the **3a** concentration, probably due to increasing concentration of **3**.

However, after reaching complete conversion (>99%) of **2**, electrolysis was continued further for approximately 40 min, at negligible conversion, during which the amount of **3a** remained constant. The formation of **3a** is attributed to the base-catalyzed (slow) isomerization of **2a** to the trans isomer,[57] followed by subsequent oxidation to **3a** under applied conditions.

The performance of ACT for the electrocatalytic oxidation of **2** to **3** is superior to that of NiOOH and β-PbO$_2$ in terms of the obtained selectivity, current efficiency, and applied electrode potential. In addition, to the best of our knowledge, this is the first report describing the nitroxyl-mediated oxidation of an α,β-unsaturated aldehyde to the corresponding acid.

Step 2: (b) Enzymatic Oxidation of 2 to Maleic Acid 3. Inspired by the electrochemical activation of nitroxyl radicals for the efficient oxidation of **2**, we were prompted to investigate its enzymatic oxidation in a similar fashion, i.e.,

conversion of aldehydes to carboxylic acids under mild reaction conditions using the laccase-TEMPO system.

The laccase-TEMPO system involves the action of the copper-dependent oxidative enzyme laccase and the mediator TEMPO, which enables the oxidation of substrates that are not directly oxidized by the enzyme. The mechanism of substrate oxidation by this system is shown in Scheme 3. TEMPO is first oxidized to its oxoammonium ion (TEMPO$^+$) by laccase.

Subsequently, TEMPO$^+$ oxidizes the substrate to give the desired product and a hydroxylamine TEMPO derivative (TEMPOH). TEMPO is then regenerated by comproportionation of TEMPOH with TEMPO$^+$. The reduced laccase is re-oxidized by molecular oxygen, enabling it to oxidize the TEMPO free radical, starting a new catalytic cycle.[63,66] The laccase-TEMPO system has previously been employed for the oxidations of alcohols to aldehydes, aldehydes to carboxylic acids, and amines to imines.[66,67] To develop our two-step reaction sequence for the conversion of **1** to **3** further, we investigated the potential of this mild oxidation method for the conversion of the intermediate **2** to **3**.

To this end, we have investigated the oxidation of **2** using the laccase-TEMPO system at different concentrations of laccase from *Trametes versicolor* and TEMPO. The results are shown in Table 1. At the highest laccase and TEMPO

Table 1. Conversion of 50 mM **2** to **3** by the Laccase-TEMPO System in 100 mM Sodium Acetate Buffer pH 4.5 and 15% Acetone at 25 °C

| | | | time duration | | | |
| | | | 6 h | | 24 h | |
entry	TEMPO (mM)	laccase (mg/mL)	2 conv (%)	3 yield (%)	2 conv (%)	3 yield (%)
1	50	2	75	75	>99	>99
2	50	0.2	17[a]	21[a]	64	61
3	10	2	26	19	23	22
4	10	0.2	6	6	22	16
5	50	—	<5	<5	<5	<5
6	—	2	—	—	—	—

[a]The conversion of **2** being lower than the yield of **3** at 6 h is attributed to experimental error in the determination of the concentration of **2**. The observed difference is explained by an error of <5% in this value.

concentrations tested, 75% conversion of **2** to **3** was observed after 6 h, and by prolonging the reaction to 24 h, quantitative conversion to the desired product with 100% selectivity was observed (Table 1, entry 1). At lower concentrations of either TEMPO or laccase, lower conversions to **3** were observed (Table 1, entries 2−4). In all reactions, the conversion of **2** to **3** was highly selective, with no byproducts being formed in quantifiable amounts. Control reactions from which either TEMPO or laccase was omitted were also performed. When **2** was incubated with TEMPO in the absence of laccase, trace amounts of **3** were formed (Table 1, entry 5). This is likely due to the direct oxidation of TEMPO by molecular oxygen, followed by its reaction with **2** to give **3**. On the other hand, no conversion was observed even after 24 h when **2** was reacted only with enzyme (laccase) in the absence of TEMPO. These observations clearly show that either laccase or TEMPO alone is not capable of efficiently oxidizing **2** (Table 1, entries 5 and 6).

Thus, the laccase-TEMPO system facilitates the oxidation strategy very efficiently by converting **2** to **3** in a quantitative yield with high selectivity. In addition, the reaction is performed under mild conditions (room temperature), which is attractive from the point of view of energy efficiency.

■ CONCLUSIONS

We have successfully demonstrated the use of greener technologies based on photo-, electro-, and biochemistry for the efficient synthesis of maleic acid from furfural. Furthermore, the work also reports two different promising strategies for the production of **3** starting from precursor **2**. The stable nitroxyl radicals TEMPO and ACT can be easily activated using both electrochemical and enzymatic methods favoring the efficient oxidation of **2** to **3** with excellent selectivity.

The electrocatalytic oxidation of **2**, utilizing ACT as catalyst, exhibited superior performance over other electrochemical systems in terms of conversion, current efficiency, selectivity, and overall 97% yield to **3** (including 7.1% of the other isomer, fumaric acid **3a**). Similarly, the laccase-TEMPO-catalyzed enzymatic oxidation is also highly effective in converting **2** to **3** in high selectivity with no formation of quantifiable amounts of byproducts. Further development will enable the enzyme and TEMPO loadings to be optimized to make this process feasible for large-scale industrial production. To the best of our knowledge, this is the first report describing the oxidation of **1** to **3** via the intermediate **2** using stable nitroxyl radicals.

To conclude, the technology integration of photocatalytic conversion of furfural to **2**, followed by oxidation via either an electrochemical or enzymatic approach, to produce maleic acid is an attractive, greener strategy and will certainly enable the large-scale production of bulk chemicals such as maleic acid at lower cost from biomass compared to current fossil-based feedstocks and production.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c02833.

> Materials and methods; details of synthesis, stability, and degradation experiments of 5-hydroxy-2-(5H)-furanone **2**; investigation on the identification of *trans-β*-formylacrylic acid; general procedure for the electro-chemical and enzymatic oxidation reactions (PDF)

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Notes
The authors declare no competing financial interest.

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