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Microwave-assisted tandem catalyst-free production of 2-methyl furoate from furfural

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ABSTRACT

The valorization of building blocks present in vegetal biomass using eco-efficient processes is an excellent alternative to reduce the demand for fossil fuels. Furfural is an encouraging renewable biomass-based platform chemical that can be transformed into several value-added chemicals. The transformation of furfural into methyl furoate through a tandem process that involves oxidation followed by esterification with methanol is widely studied since the selectivity towards the product is strongly dependent on numerous factors: reaction conditions, oxidant, and catalysts. Depending on them, more than ten different products can be obtained, making the process of no importance given the difficulty of separating each of these products. In this communication we study the reaction selectivity in a very simple procedure that is catalyst-free, using a clean oxidant and mild reaction conditions. Particularly as an alternative source of heat, and with the aim of reducing reaction times, said transformation was assisted by microwaves. In order to optimize the process, the reaction time and temperature, type of oxidant, amount of oxidant and molar ratio of reagents were studied. In this work, 100% conversion with 69% selectivity was achieved in 2 h at 120 °C using 1:3:20 M ratio of furfural, oxidant, and alcohol. The methodology represents a powerful alternative for the preparation of furoates through a low-cost and environmentally friendly process that does not use a catalyst.

1. Introduction

Lignocellulosic biomass represents more than 20% of the total mass of the biosphere on our planet. However, most of it is burned to produce heat. Therefore, biomass from waste can undoubtedly become a valuable source for the provision of energy, chemicals, and materials (Deepak and Ganapati, 2022). The need to reduce the carbon footprint through the development of new, more sustainable processes has led to a growing interest in establishing a bioeconomy based on biorefineries and biofactories (Ampelli et al., 2016). The specific use of biomass will reduce environmental problems and minimize our dependence on fossil fuels (Yu et al., 2023).

It is well known that biomass is made up of polymers: cellulose (15%–20%), hemicellulose (25%–35%), and lignin (40%–50%). Particularly, from cellulose and hemicellulose by depolymerization processes it is possible to obtain C5 or C6 monosaccharides that in turn produce furanic compounds such as 5-hydroxymethyl furfural (HMF) and furfural (F) (Deepak and Ganapati, 2022; De et al., 2015; Climent et al., 2014).

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Furfural is an important renewable, non-petroleum based, chemical feedstock. It is one of the platform molecules that can be obtained from a wide variety of renewable resources that occur abundantly in nature and at low cost e.g. of biomass waste by applying various catalytic materials such as sulfonated crab shell-based solid acid (Shen et al., 2023). It can be converted into a variety of compounds by hydrogenation, oxidation, condensation, isomerization, reductive amination, decarbonylation, among others (Tian et al., 2023). The hydrogenation of furfural leads to furfuryl and tetrahydrofurfuryl alcohol, the latter being used as a green solvent in agricultural formulations and as an adjuvant in herbicides. Furfural is used to make other chemical derivatives, such as furoic acid from rice straw by tandem catalysis via recombinant *E. coli* combined with Sn-sepiolite (Peng et al., 2019) or the synthesis of furfurylamine from sugarcane bagasse via chemoenzymatic cascade catalysis (Li et al., 2021) or from biomass through chemoenzymatically transforming to furfurylamine in a deep eutectic solvent (He et al., 2023). The chemistry of furfural and its derivatives has been well and extensively reviewed by Adhami et al. (2023) (Adhami et al., 2023).

Our research group has made some contributions to the valorization of different building blocks present in biomass through processes with low environmental impact, such as furfural, HMF, and levulinic acid. These compounds have great potential, such as biofuel additives, monomers for designing biodegradable polymers, and additives for the design of antifouling paints to control marine fouling (Portilla-Zuñiga et al., 2020; Pardo et al., 2019; Escobar et al., 2019a, 2019b).

One of the most relevant furfural oxidation processes is the one carried out to obtain alkyl furoates, which are used as additives in the formulation of fragrances and flavors. Particularly, methyl 2-furoate is a specialty fragrance with a market value of around USD 50–100/kg (two orders of magnitude higher than the substrate value) (Ampelli et al., 2016).

Usually, the preparation of methyl 2-furoate is carried out in two stages, the first of which involves the oxidation of furfural by means of a strong oxidant such as $KMnO_4$ and the second the esterification of furoic acid with methanol assisted by an acid catalyst such as H_2SO_4 (Fischer esterification).

The literature describes numerous oxidizing agents that act in stochiometric form or assisted by a catalyst (simple oxidants as well as more complex catalyst systems), for example, copper acetylacetonate; oxygen; sodium hydroxide; 1,3-bis(2,4,6-trimethylphenyl) imidazolidine, in water at 50 °C, under 760.051 Torr, for 12 h, sealed tube (99%) (Liu and Li, 2016), sodium carbonate in water at 30 °C, for 40 h, wavelength, irradiation (96%) (Zhou et al., 2017), manganese (IV) oxide, oxygen, sodium hydrogencarbonate, in water at 100 °C, under 7500.75 Torr, for 24 h (95%) (Hayashi et al., 2019), $Co_4HP_2Mo_{15}V_3O_{62}$, N-(4-sulfonic acid)butyl triethylammonium tetrafluoroborate, dihydrogen peroxide in water at 20 °C, for 4 h (94%) (Hu et al., 2015), *tert*-butyl hydroperoxide; ammonium cerium (IV) nitrate in water:acetonitrile at 20 °C, for 15 h (93%) (Gowda and Chakraborty, 2011), with immobilized lipase B from *Candida antarctica*; dihydrogen peroxide in ethyl acetate; *tert*-butyl alcohol at 40 °C, for 24 h (91%) (Krystof et al., 2013), pyridinium chlorochromate at 20 °C, for 6 h (82 %) (Salehi et al., 2001), among many others. For its part, the second stage (esterification of 2-furoic acid with methanol) is assisted by different catalysts, including phosphotungstic acid for 4 h, reflux (98 %) (Li and Peng, 2010); sulfuric acid for 4 h, reflux (93%) (Hasan et al., 2011); potassium carbonate in ethyl acetate for 1.5 h, heating (92%) (Won et al., 2007); beef pancreas lipase at 20 °C, for 7 h (81%) (Roy et al., 2006); oxone in toluene at 60 °C, for 48 h (28%) (Hou et al., 2018); hydrogenchloride (Gennari, 1894), and others.

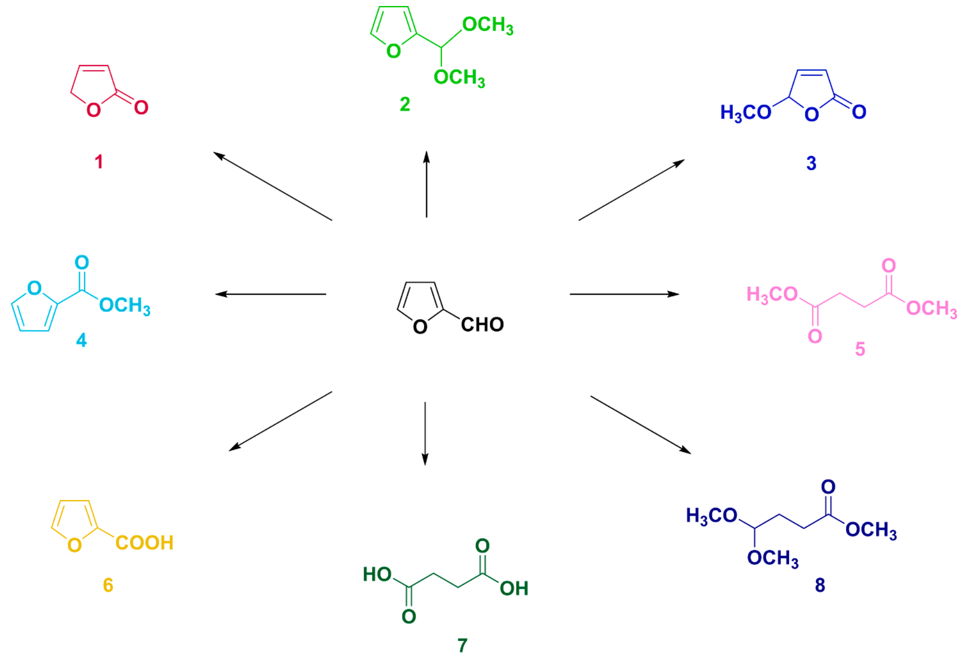
In the search for more efficient methods that promote the reduction of isolation and purification processes that generate waste through the elimination of stages to obtain the final product, a tandem process that involves carrying out both processes (oxidation-esterification) consecutively has been studied. Recently studied processes include dihydrogen peroxide; $Al_{1.3}SiW_{12}O_{40}$ at 80–250 °C (96%) (da Silva and Rodrigues, 2020); perchloric acid, sodium percarbonate, vanadia for 0.35 h (95%) (Gopinath et al., 2003); oxygen at 60 °C, under 760.051 Torr (88%) (Zhang and Wang, 2019); urea hydrogen peroxide adduct, *p*-toluenesulfonyl chloride at 60 °C, for 7 h (82%) (Jeong et al., 2017); dihydrogen peroxide/$VO(acac)_2$, at 20 °C, for 6 h (75%) (Talukdar et al., 2013) *tert*-butyl hydroperoxide; potassium iodide in water at 65 °C, for 20 h (74%) (Reddy et al., 2009); oxone at 60 °C, for 0.5 h, sonication (30%) (Aghayan et al., 2015), among others.

Given the importance of this reaction, recent studies have evaluated said transformation under different conditions that make it possible to evaluate its selectivity towards numerous high value-added products, including 2-methyl furoate, dimethyl succinate, dimethylester, furfural diethyl acetal, 5-hydroxymethyl furanone, 2-furoic acid, among others (Yin et al., 2021; Shahin and Rataboul, 2021; Zhang et al., 2020; Ning et al., 2018; Radhakrishnan et al., 2017; Manzoli et al., 2016).

Since the 90s, Green Chemistry has been implemented in all disciplines and has established itself as a work methodology in the different investigations that are carried out, generating important advances in science and technology. Organic synthesis in the absence of a solvent and especially without a catalyst has made a great contribution to organic synthesis with low environmental impact, since they are simple, low-cost, and convenient processes from the point of view of separation and purification. Catalysts are usually expensive, often difficult to recycle, with the consequent waste of money and problems associated with environmental pollution. Therefore, research on processes without the addition of a solvent and a catalyst is a necessity (Brahmachari, 2017).

In this regard, the use of microwave irradiation as an alternative energy source represents a very efficient way of heating the reaction mixtures and allows drastically reducing the conversion times of the substrates and, in many cases, it is also possible to dispense with the use of solvents or catalysts. The use of microwave irradiation has allowed the development of more eco-efficient processes: greater speed, efficiency and uniformity of heating of the reagents, low operating costs, reduction in the formation of secondary products, purity of the main product, and less heat loss to the environment (Avila-Ortiz and Juaristi, 2020; Lambat et al., 2020).

In this article we present a study for the production of 2-methyl furoate from furfural using a tandem catalyst-free procedure assisted by microwave (Scheme 1).



Scheme 1. Product formed during the tandem oxidation/esterification in catalyst-free conditions, using clean oxidation in methanol assisted by microwave.

2. Experimental

2.1. General

Chemicals were purchased from Aldrich (Buenos Aires, Argentina) and used without further purification. TLC was done on aluminum sheets precoated with silica gel and fluorescence indicator. The GC analysis was performed in a Shimadzu GC-2014 (La Plata, Buenos Aires, Argentina) with an FID detector. All products were identified by GC-MS using an HP 5971 mass detector coupled to an HP gas chromatograph.

Reactions were carried out by thermal heating using conventional equipment or assisted by microwaves. Microwave-assisted reactions were carried out in a glass vial G10, Anton Paar Monowave 400.

2.2. Experimental reactions

The tandem oxidation-esterification reaction of furfural with methanol to obtain methyl furoate was chosen for evaluating the optimal reaction conditions in the absence of a catalyst using microwave irradiation as an alternative heat source. Different oxidants were used (urea:hydrogen peroxide, UHP, 1:1 M ratio; *tert*-butyl hydroperoxide solution, TBHP, 5.0–6.0 M in decane; hydrogen peroxide, HP, 35% aqueous solution; and sodium percarbonate, NaPC, $Na_2CO_3.1.5\ H_2O_2$ 20%–30% avail. hydrogen peroxide), and different variables were evaluated such as the time (15, 30, 45, 60, 90, and 120 min), temperature (80, 100, 120, and 140 °C), furfural:methanol molar ratio (1:5, 1:10, 1:20, and 1:40) and furfural:oxidant molar ratio (1:2, 1:3, 1:5, and 1:10).

Prior to each chromatographic analysis, it is necessary to pre-treat the sample to eliminate both excess oxidant and water. This operation is carried out in the following way: 0.20 ml of crude oil is put in contact with 0.5 mL of chloroform and 2 x 0.5 mL of water. The organic phase is separated, dried with anhydrous Na_2SO_4 and filtered for subsequent chromatographic analysis.

The product was purified by liquid chromatography using hexane-ethyl acetate mixtures of increasing polarity. It was identified by CG-MS and was coincident with a sample of methyl furoate prepared by a method previously reported in the literature (Safdar et al., 2023).

3. Methods of analysis

The reactions were analyzed using a Shimadzu gas chromatograph model 2014 with an SPB-1 column (30 m, 32 mm, 1.00 μm), equipped with an FID detector. The carrier gas was high purity nitrogen (≥99.999%), splitless injection mode was used (1 μL), and the injector temperature was 280 °C. The oven temperature was kept at 70 °C for 3 min, then raised to 90 °C at 7 °C min^{-1}, and finally to 250 °C at 20 °C min^{-1} and maintained for 10 min.

3.1. General method to prepare alkyl furoates

In a specific tube for microwave-assisted synthesis 2.47 mmol of furfural, 7.41 mmol of the corresponding oxidant, 49.4 mmol of alcohol were mixed. Then, the mixture was stirred magnetically and was heated by microwave irradiation at a temperature of 120 °C for 2 h.

3.2. Mass spectrum of products

Compound 1: *m/z*: 84 (M^+, 50%), 55 (100%), 39 (15%), 27 (38%).

Compound 2: *m/z*: 142 (M^+, 16%), 129 (3%), 112 (9%), 111 (100%), 96 (15%), 95 (22%), 68 (5%), 55 (12%), 51 (3%), 43 (4%), 39 (11%).

Compound 3: *m/z*: 114 (M^+,10%), 113 (19%), 99 (5%), 85 (39%), 83 (100%), 70 (45%), 59 (10%), 55 (97%), 42 (28%), 39 (21%), 29 (40%), 27 (57%).

Compound 4 (methylfuroate): *m/z*: 126 (M^+,48%), 96 (10%), 95 (100%), 91 (1%), 81 (2%), 68 (4%), 59 (2%), 39 (29%), 29 (8%).

Compound 5: *m/z*: 146 (M+, -%), 115 (100%), 114 (109%), 101 (1%), 87 (29%), 73 (4%), 59 (49%), 55 (65%), 45 (9%), 27 (15%).

Compound 6: *m/z*: 162 (M+, -%), 131 (49%), 115 (2%), 99 (25%), 75 (100%), 71 (95%), 59 (8%), 47 (18%), 41 (32%), 29 (19%).;

Compound 7: *m/z*: 112 (M+, 100%), 95 (86%), 84 (9%), 55 (10%), 45 (10%), 39 (55%), 29 (5%).

Compound 8: *m/z*: 118 (M^+, 1%), 74 (78%), 73 (58%), 56 (31%), 55 (100%), 45 (84%), 29 (42%), 28 (52%). 27 (63%).

4. Results and discussion

4.1. Microwave reaction

Scheme 1 shows the reaction pathways for the synthesis of 2-methylfuroate from furfural with methanol in catalyst-free conditions using different clean oxidants, and assisted by microwave. All detected products are indicated.

The colors presented in this scheme serve as a guide for the interpretation of Fig. 2, **4**, **6** and **8**.

4.2. Effect of different oxidants

The performance of various friendly oxidants was investigated for oxidation/esterification (methanol) of furfural in catalyst-free conditions (Scheme 1). For comparative purposes, the following reaction conditions were established: Temperature: 120 °C; time: between 15 min and 120 min; microwave irradiation. Remarkably, there was a significant difference in both conversion and selectivity for different oxidant agent types. Fig. 1 shows the conversion of furfural as a function of time using the different oxidants and microwave irradiation at 120 °C. In all cases and for comparative purposes, the same amount of oxidant was used in millimoles (3 mmol of oxidant: 1 mmol of furfural). A reaction was also performed without any oxidant under similar reaction condition, but no conversion was observed.

Fig. 1 shows a higher conversion when the oxidants UHP and HP are used (100% and 96%), respectively, in a reaction time of 2 h. For its part, the use of TBHP gives a moderate conversion (51%) in the same reaction time, and there was practically no conversion when using sodium percarbonate (only 1.5%), concluding that the latter catalyst is not appropriate under the established reaction conditions. It is noteworthy that UPH was much more active than HP, since a conversion of 93% was reached in 15 min, compared to 28% obtained with HP.

The next step was to determine the selectivity of the reaction under the established conditions. Fig. 2 shows the selectivities obtained using UHP, HP, and TBHP.

Although the compound with the highest selectivity obtained was the desired product (methyl furoate, 41%, compound **4**) when the most active oxidant (UHP) was used, numerous secondary products that were not identified were obtained as well as 1% of 5-hydroxymethyl furanone (**3**). Then, the selectivity using *tert*-butyl hydroperoxide solution (TBHP, 5.0–6.0 M in decane) was evaluated. In addition to the fact that the conversion is moderate (51% in 2 h), various products are produced, including furfural diethyl

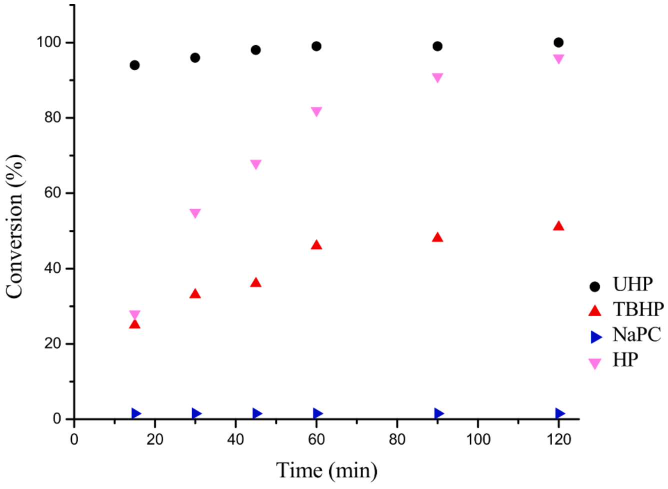


Fig. 1. Furfural conversion (%) using different oxidants.

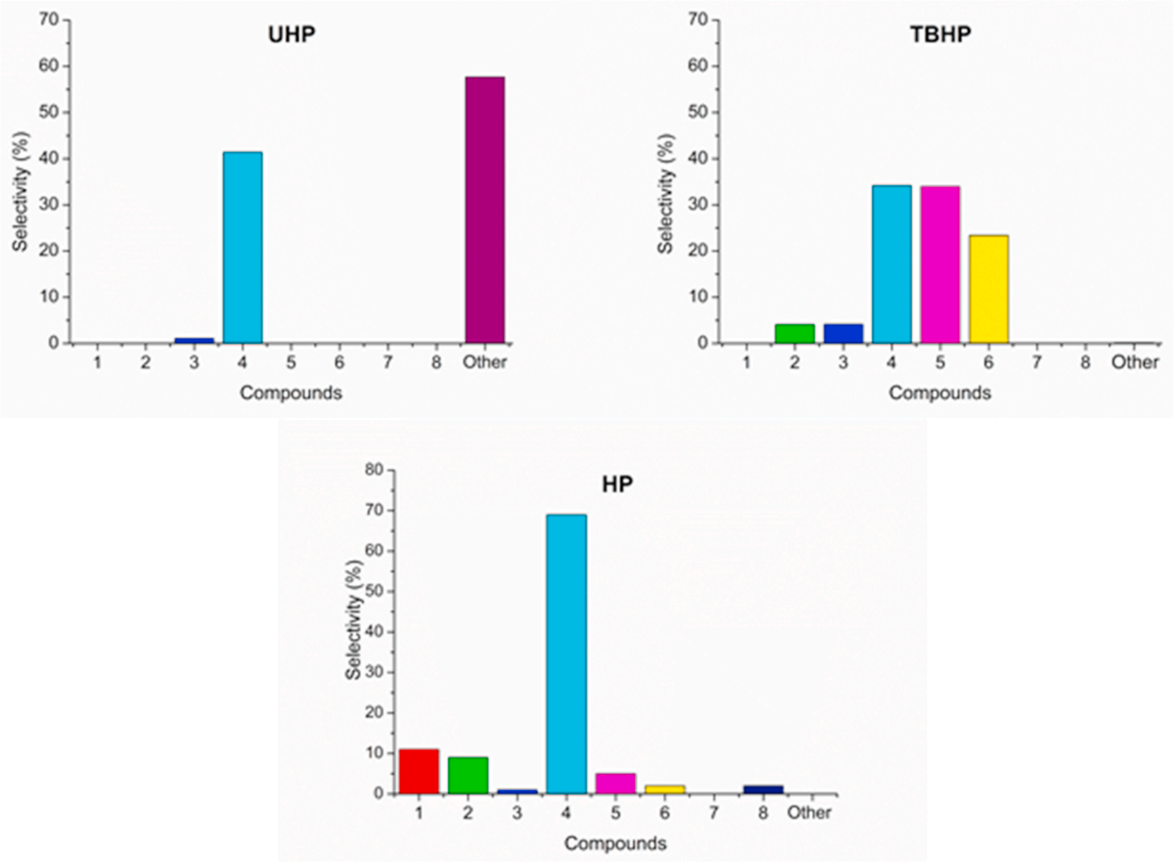


Fig. 2. Product selectivity (%) using different oxidants.

acetal (4%, compound **2**), 5-hydroxymethyl furanone (4%, compound **3**), methyl-2-furoate (34%, compound **4**), dimethyl succinate (34%, compound **5**), and 2-furoic acid (23%, compound **6**). Finally, we evaluated the selectivity of the reaction using 35% aqueous hydrogen peroxide (HP). As can be seen, the reaction is selective towards 2-methyl furoate (69%), and a small amount of secondary products were detected, including 2(5H)-furanone (11%, compound **1**), furfural diethyl acetal (2%, compound **2**), dimethyl succinate (17%, compound **5**), and 2-furoic acid (4%, compound **6**). From the results obtained, it can be seen that this last oxidant (35% of aqueous hydrogen peroxide) is the most appropriate to carry out the next optimization tests.

4.3. Effect of molar ratio of furfural to methanol

In this transformation, methanol acts as both a reactant and a solvent (excess). The effect of the molar ratio of furfural:methanol was studied from 1:5 to 1:40 under the same reaction conditions, leaving the amount of oxidant constant (3 mmol of 35% aqueous hydrogen peroxide x mmol of furfural). It was found that as the concentration of methanol increases, the rate of conversion decreases. For example, for 1 h of reaction, the following furfural conversions are observed for the respective ratios: 1:5 = 99%, 1:10 = 92%, 1:20 = 82%, and 1:40 = 60%. In addition, complete conversion is observed at 2 h using the ratios 1:5 and 1:10 (Fig. 3). Considering the proposed plausible mechanism, it proceeds through a radical mechanism (Scheme 3), this effect can be associated with the fact that some alcohols are inhibitors of free radicals, so an increase in the concentration of methanol would translate into a decrease in the production of methyl furoate via the formation of free radicals.

The selectivity of the reaction was evaluated for the four furfural methanol ratios established at 2 h of reaction (Fig. 4). It is observed that an increase in the amount of alcohol substantially improves the selectivity of methyl furoate, being, in both cases, the main product of the reaction (ratio 1:40, selectivity: 80%, and ratio 1:20, selectivity: 59%).

By reducing the amount of alcohol, a drastic reduction of the selectivity towards 2-methyl furoate is observed. For example, using a furfural/methanol ratio of 1:5 furfural selectivity is 14%, the main products 1 and 5 being those obtained with selectivities of 37% and 30% respectively. In addition, 14% of numerous products that were not identified are observed. Similarly, using a furfural methanol ratio of 1:10, 2-methyl furoate selectivity is very low (8%), in this case the main products formed are: 1, 3, and 5 with a selectivity of 21%, 35%, and 27% respectively.

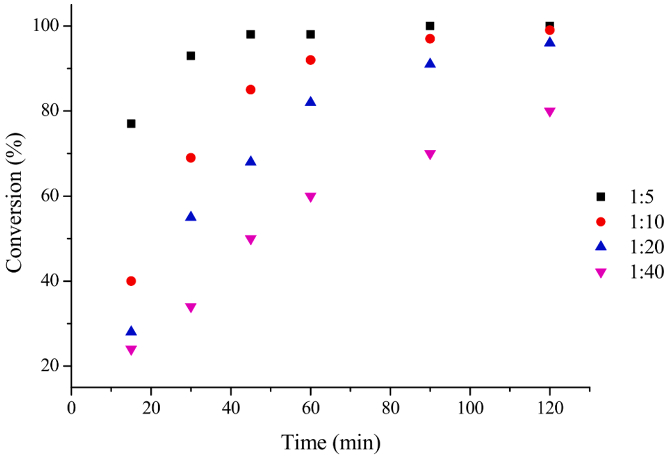


Fig. 3. Furfural conversion (%) using different furfural methanol ratios.

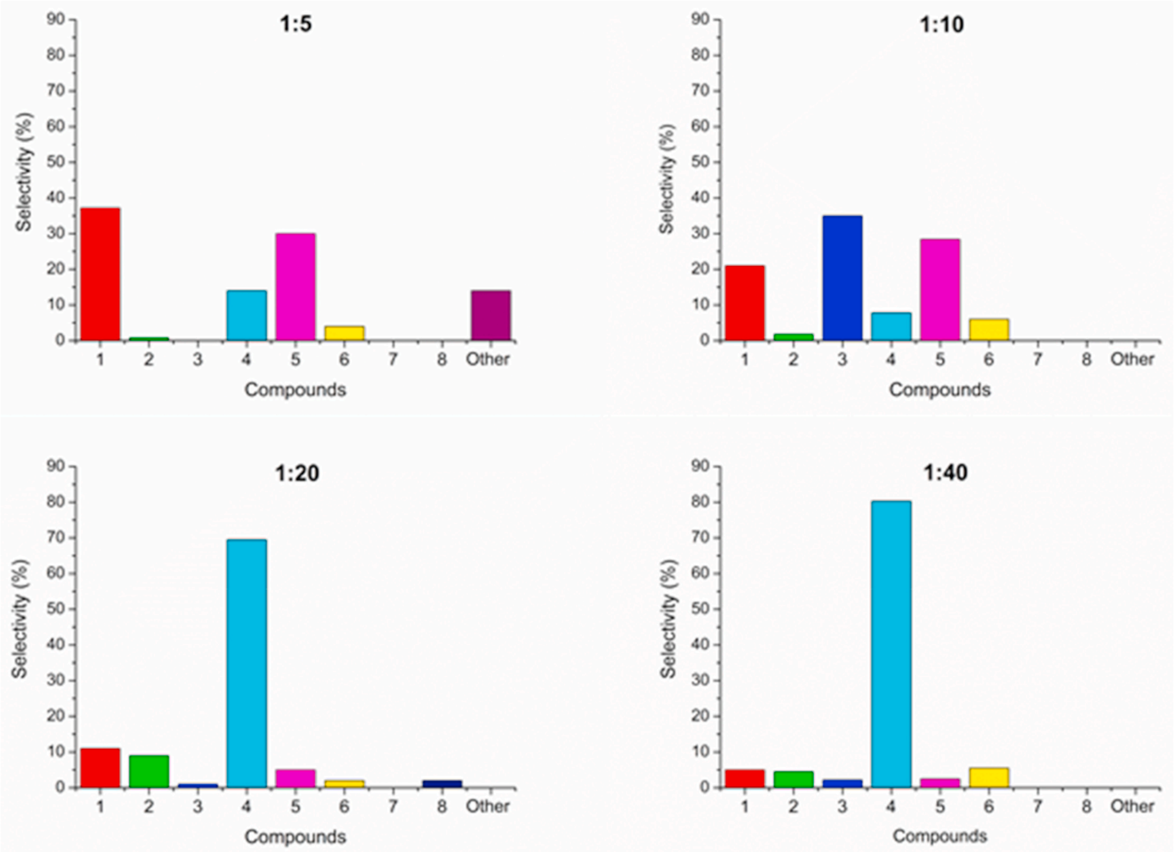


Fig. 4. Product selectivity (%) using different furfural methanol ratios.

4.4. Effect of molar ratio of furfural to oxidant (aqueous hydrogen peroxide)

The effect of the molar ratio of furfural to 35% aqueous hydrogen peroxide was studied over the furfural oxidant ratios of 1:2 to 1:10 (Fig. 5). Four furfural oxidant molar ratios were tested: 1:2, 1:3, 1:5, and 1:10. A reaction temperature of 120 °C and a constant furfural:methanol ratio of 1:20 were established.

As can be seen in Fig. 5, an increase in the amount of oxidant improves the oxidation rate of furfural. If the conversions of furfural at 1 h of reaction are compared for the different molar ratios of furfural to oxidant, the following increasing order is observed: furfural oxidant ratio: 1:2 (59%), 1:3 (82%), 1:5 (94%), and 1:10 (100%).

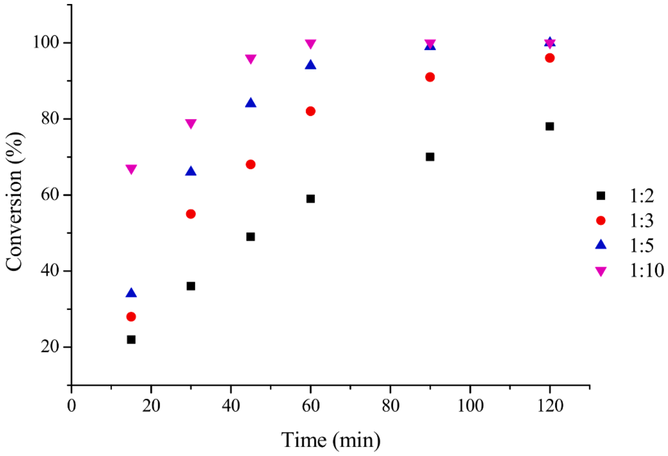


Fig. 5. Furfural conversion (%) using different molar ratios of furfural to 35% aqueous hydrogen peroxide.

The selectivity evaluated at 2 h of reaction for the four furfural oxidant ratios shows that with the low ratios 1:2 and 1:3 the reaction is selective towards the formation of methyl 2-furoate (68% and 59% respectively) (Fig. 6). In both cases the amount of secondary products is relatively small. However, using a 1:5 ratio, the selectivity drops drastically to 41%, forming appreciable amounts of compound **1** (19%) and **5** (24%). Finally, the addition of a large excess of oxidizing agent leads to the non-formation of methyl-2-furoates, obtaining compound **1** (35%) and **5** (43%), respectively, as the main products.

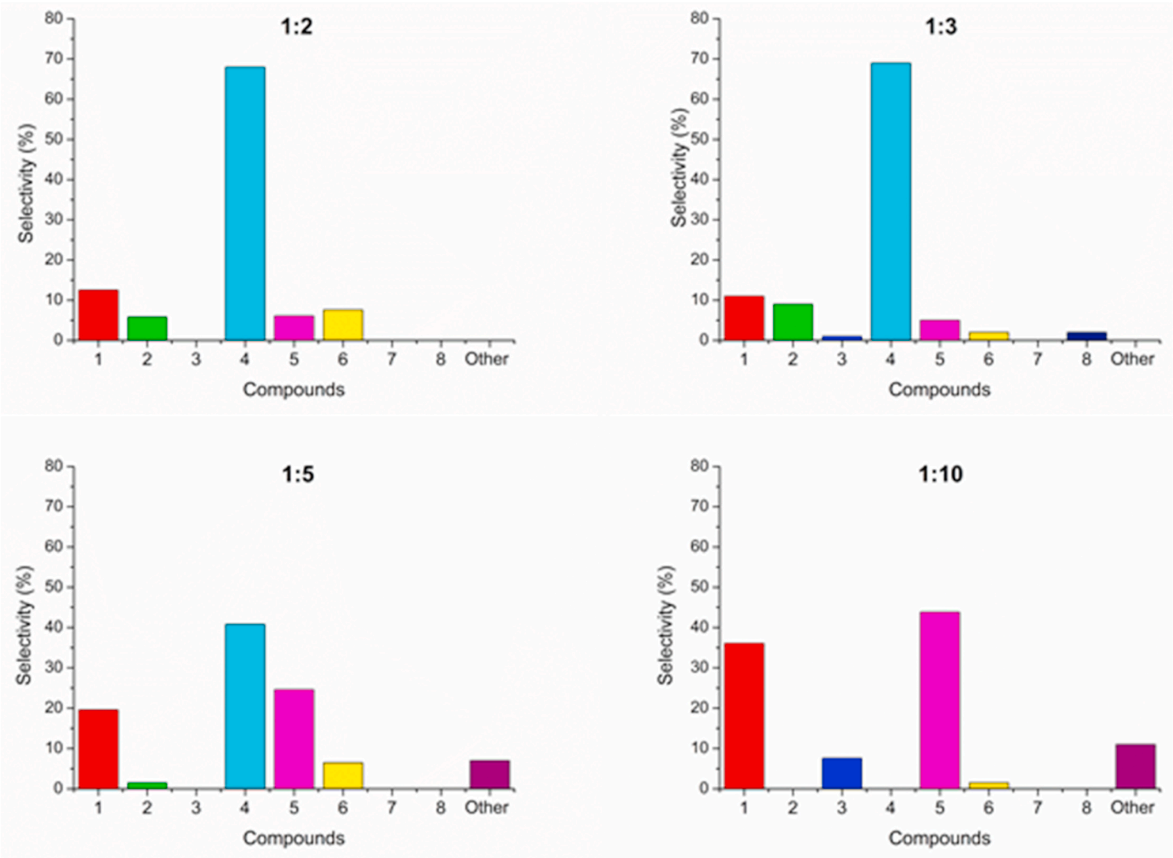


Fig. 6. Furfural selectivity (%) using different molar ratios of furfural to 35% aqueous hydrogen peroxide.

4.5. Effect of temperature

The effect of reaction temperature on the conversion of furfural was studied from 80 to 140 °C (Fig. 7). An increase in conversion is observed as a function of temperature, which supports that the reaction is kinetically controlled. Evaluating the conversion of furfural for a reaction time of 2 h, a very low conversion is observed at 80 °C (34%), moderate at 100 °C (68%), and high at 120 °C (96%). A temperature increase to 140 °C leads to the same conversion value (96%). It is also notable that, in the case of these last two temperatures, the conversion was also high, halving the reaction time by 82% (120 °C), and 89% (140 °C), respectively.

Then, the selectivity of the reaction was evaluated for the four temperatures: 80, 100, 120, and 140 °C (Fig. 8). In all the cases evaluated, the main product is methyl furoate **4**; however, a decrease in selectivity was observed with increasing temperature.

The effect of temperature on furfural conversion can be seen in Fig. 7. In general, an increase in temperature leads to an increase in furfural conversion. However, no significant differences are observed at 120 and 140 C. The order obtained for a reaction time of 2 h was: 140 °C (57%), 120 °C (60%), 100 °C (68%), and 80 °C (76%). In all cases, small amounts of secondary products are observed: **1, 2, 5,** and **6.** Particularly, at 140 °C in 2 h of reaction, the selectivity (Fig. 8) towards methyl furoate decreases considerably and a considerable increase in secondary products is observed such as: 2(5H)furanone (**1**), dimethyl succinate (**5**) and furoic acid (**6**). Considering the proposed plausible mechanism, it proceeds through a radical mechanism (Scheme 3). It is thus observed that an increase in temperature favors the homolytic breakdown of the oxidant, which translates into an increase in the conversion.

On the basis of both conversion and selectivity of the desired product, a temperature of 120 °C was selected as the optimum temperature to test the reaction using other alcohols of different structural nature.

4.6. Oxidative esterification of furfural with different alcohols

The oxidative esterification of furfural with other alcohols (ethanol, 1-propanol, 1-butanol, 2-propanol, and 2-butanol) (Table 1) was carried out under similar reaction conditions (120 °C, 120 min). The conversion of substrate varies with the type of alcohol. The main products obtained are furoic acid and the corresponding ester. In all cases the conversion was moderate, lower than that obtained with methanol. The branched alcohols resulted in less conversion than linear alcohol due to the higher steric hindrance.

4.7. Proposed reaction pathway for furfural oxidation

Scheme 2 indicates a plausible reaction pathway for furfural oxidation that allows justifying the formation of 2-methyl furoate and the other intermediate and secondary products. In general, the catalytic processes of furfural oxidation/esterification require the presence of acid and redox sites.

Here, in the absence of a catalyst, several paths lead to the formation of both the desired and secondary products. The oxidation of furfural under catalyst-free conditions can form 2-furoic acid (**6**), and 2(5H)-furanone (**1**) (by Baeyer- Villiger oxidation). Then, the esterification of furoic acid (**6**) with methanol, also in the absence of catalyst, gives the desired product (methyl 2-furoate, **4**). Another alternative path that leads to the formation of methyl 2-furoate (**4**) occurs when furfural reacts with two molecules of methanol to produce 2-furaldehyde dimethyl acetal (**2**), and this acetal is further oxidized to methyl-2-furoate (**4**).

This method has the advantage of being simple and fast, the use of microwaves allows energy savings compared to conventional heating methods and provides good yields. The absence of catalyst and co-solvents, and the moderate temperature used in the reactions, make this an environmentally friendly method. On the other hand, the use of microwaves would make it difficult to scale the reaction to industrial quantities.

4.8. Plausible reaction mechanism

The proposed mechanism is based on the work of Deepak S. Desai (Desai and Yadav, 2022).

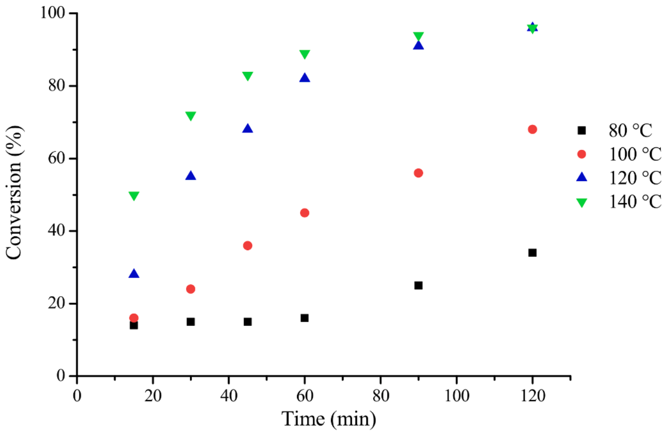


Fig. 7. Furfural conversion (%) using different temperatures.

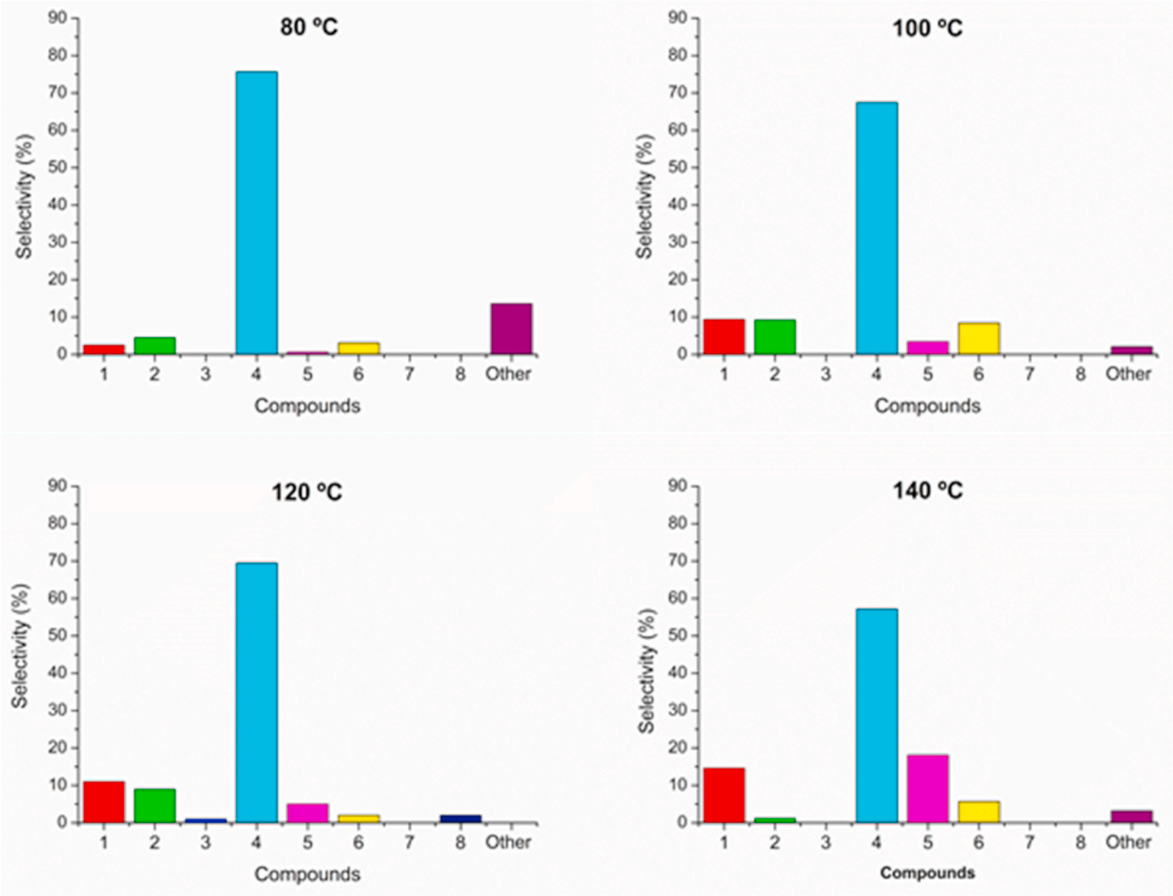


Fig. 8. Product selectivity (%) using different temperatures.

Table 1
Furfural conversion (%) and product selectivity (%) using different alcohols.

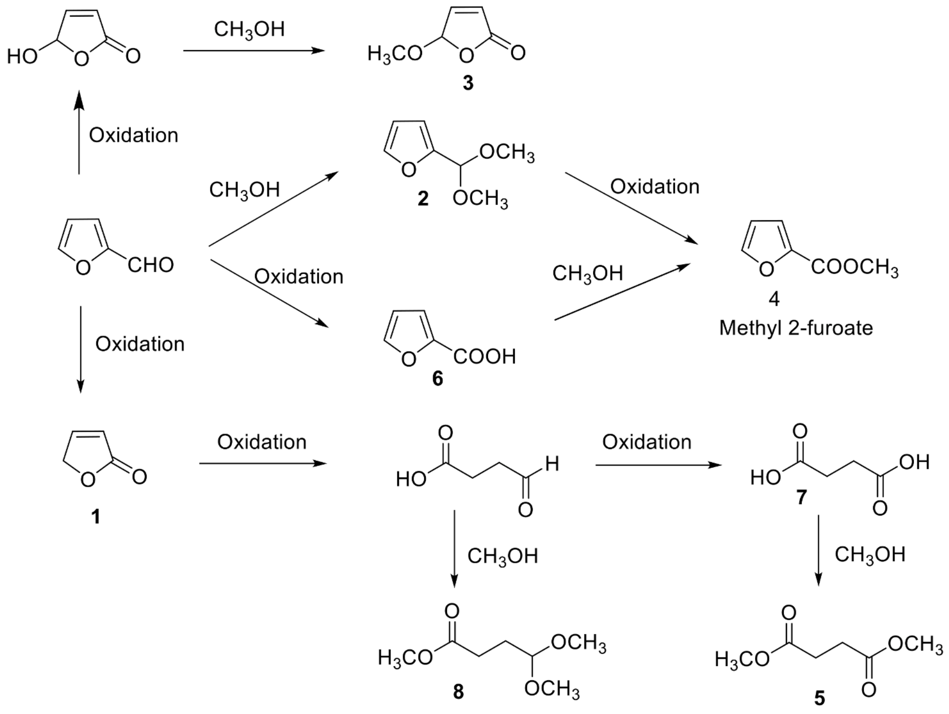
Entry	Alcohol	Conversion (%)	Furoic acid Selectivity (%)	Alkyl furoate Selectivity (%)	Other (%)
1	Methanol	96	–	69	30
2	Ethanol	63	47	28	25
3	1-Propanol	50	51	26	23
4	1-Butanol	53	51	28	21
5	2-Propanol	20	35	44	21
6	2-Butanol	52	56	15	18

Experimental conditions: furfural:oxidant:alcohol molar ratio, 1:3:20; microwave irradiation; 120 °C; 120 min.

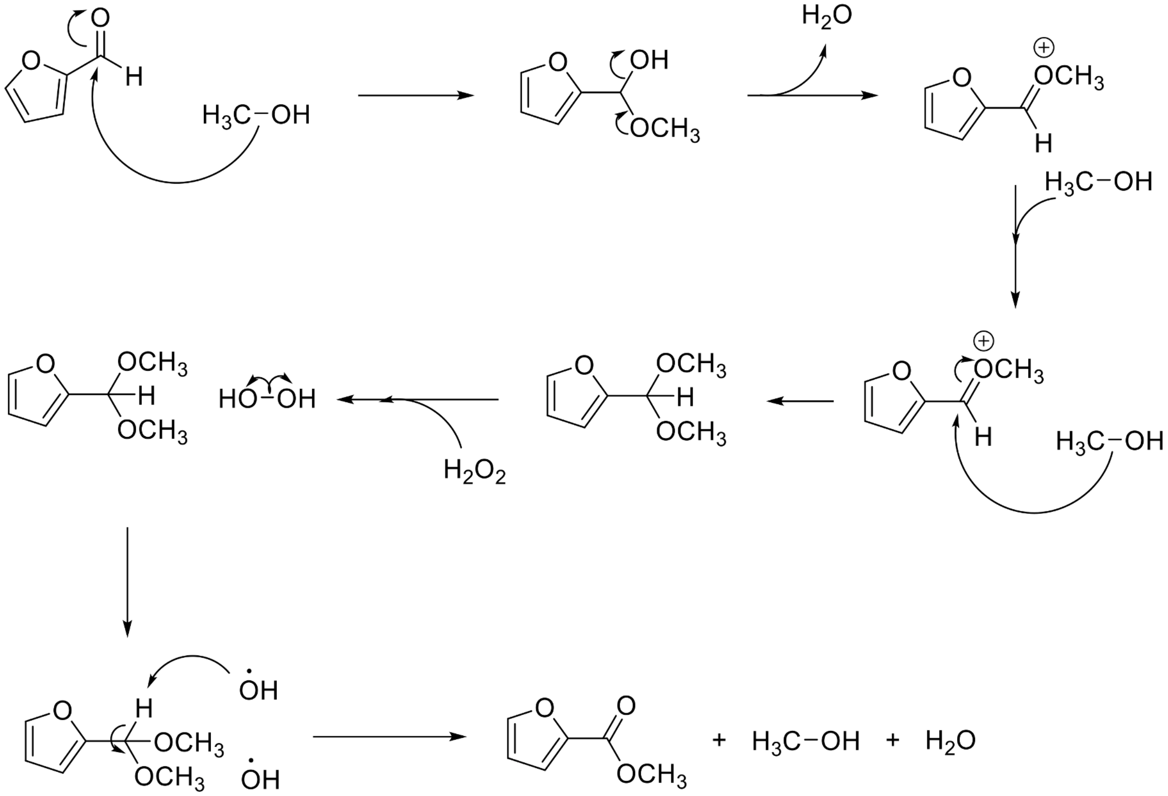
In a first stage, furfural reacts with methanol, obtaining the corresponding acetal (2-furaldehyde-dimethyl-acetal), in a second stage, the hydrogen peroxide undergoes a homolytic cleavage and the resulting radicals attack the acetal, producing methyl furoate, water and methanol.

5. Conclusion

Tandem oxidative esterification of furfural with methanol leads to the formation of methyl furoate, which is used as fragrance and flavor ingredients in food chemistry, as extracting agent, and in fine chemical industries. Numerous investigations seek to find a catalyst that provides excellent selectivity towards methyl furoate through low-cost and environmentally friendly procedures. Here we report a very simple procedure that is easy to implement through a tandem process that involves the oxidation of furfural, followed by an esterification of methanol, where we dispense with the use of catalyst and reaction solvent, the process being assisted by microwave irradiation. In this work, 96% conversion with 69% selectivity was achieved in 2 h at 120 °C using 1:3:20 M ratio of furfural, oxidant, and alcohol.



Scheme 2. Proposed reaction pathway for furfural oxidation.



Scheme 3. Reaction Mechanism.

The methodology represents a powerful alternative for the preparation of furoates through a low-cost and environmentally friendly process that does not use a catalyst.

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CRediT authorship contribution statement

Maira A. Guerrero: Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Ángel G. Sathicq:** Methodology, Funding acquisition, Formal analysis, Data curation. **Ileana D. Lick:** Data curation. **Mónica L. Casella:** Data curation. **María S. Legnoverde:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Gustavo P. Romanelli:** Writing – review & editing, Supervision, Project administration, Methodology, Formal analysis.

Declaration of competing interest

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

Data availability

Data will be made available on request.

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