

## Catalyst-free process for oxidation of furfural to maleic acid by high frequency ultrasonic activation.

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### Supporting information

In this study, oxidation of furfural to maleic acid was carried out in a 250 mL high-frequency ultrasonic reactor (SinapTec Ultrasonic Technology, NextGen Lab 1000, 550 kHz, designed cylindrical stain steel reactor in a cup-horn configuration with a 75 mm diameter base-surface, and equipped with a cooling system, Fig. S1). The total material volume introduced in the reactor was 50 mL, which is the minimal capacity of the reactor.

For the optimal reaction, 0.12 mol of furfural (10 mL) and 0.46 mol H<sub>2</sub>O<sub>2</sub> (40 mL) were introduced in the reactor. A water-cooling stream (30°C) circulated in the double jacket reactor since the oxidation reaction is highly exothermic and may cause the increase of temperature for above 60 °C (maximal operating temperature) in about 30 minutes. In this way, we maintained the temperature of the reaction medium at 42 °C.

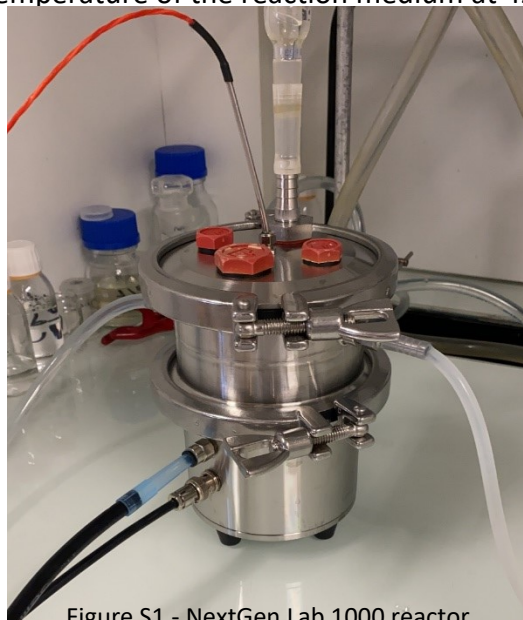


Figure S1 - NextGen Lab 1000 reactor

The reaction mixture was sampled and then analyzed using GC, HPLC and NMR.

Furfural was detected and quantified using by Gas Chromatography (Perkin Elmer instruments, AutoSystem XL) equipped with a Column Alltech Part No. 16368 AT-1ht 30m x 0.25mm D x 0.1µm. The injection volume 1µl, oven temperature 250°C, Q<sub>H2</sub>= 45 ml/min and

$Q_{\text{air}}=450$  ml/min. Method: 40°C constant for 2 min, then increase by 20°C/min for 10.5 min to 250°C, then plateau from 3 min to 250°C

MA, HFUR and FUR were analyzed on a Shimadzu HPLC equipped with a corgel 87H3 column, Mobile phase: aqueous formic acid  $8.10^{-3}$  M, flow 0.6 mL/min. Column Temp: 35°C.

Diacids such as succinic acid and malic acid were detected by refractive index detector.

Use of radical inhibitors:

In order to verify if the mechanism under HFUS is either ionic or radical, we used methanol as a radical inhibitor. We followed the same reaction protocol and we added 1.5 eq of methanol (29 mL). In addition, we investigated the effect of radical inhibitors without ultrasonic irradiations.

By comparing the obtained results, we demonstrate that the mechanism under HFUS is radical since furfural conversion drops from 92 to 21%, which is not the case in the absence of US where the mechanism is ionic.

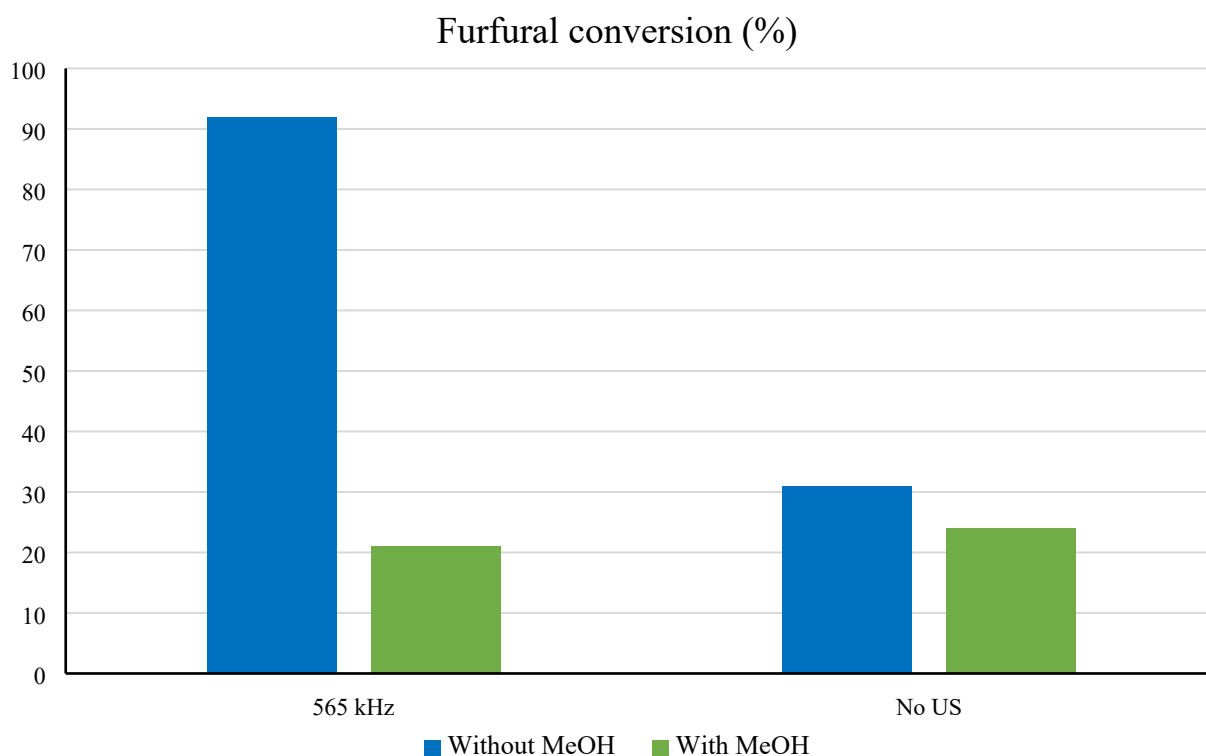


Figure S2: Furfural oxidation in presence or not of MeOH as inhibitor.

**Synthesis of 5-hydroxy-2(5H)-furanone**

In a 250 mL three-necked round bottom flask equipped with a cooler condenser and a thermometer was charged with freshly distilled furfural (5.0 g, 52.1 mmol) and methanol (150 mL). A catalytic amount of methylene blue indicator was added and oxygen (250 mL/min) was bubbled in the reaction mixture while stirring at room temperature. The set-up was fenced using two 400 watt construction lamps in such a way that the light falls on the reaction mixture. During the reaction, aliquots were taken and the GC-MS analyses showed full conversion of furfural in 5-hydroxyfuranone within 6 h. After evaporating the methanol at reduced pressure, the obtained crude product was further purified using automated column chromatography (5:1, PE:EtOAc eluents), yielding 5-hydroxyfuranone as yellow crystalline solid in >95% purity.

NMR:  $^1\text{H}$  NMR (400.17 MHz, D<sub>2</sub>O):  $\delta$ = 7.51 (d, H<sub>b</sub>, H-1,  $J$  = 5.7 Hz), 6.34 (m, a+a', 2H).  $^{13}\text{C}$  NMR (100.62 MHz, D<sub>2</sub>O):  $\delta$ = 173.8, 153.8, 123.6, 99.6.

#### **-Analytical instruments :**

##### **GC:**

Perkin Elmer instruments, AutoSystem XL Gas Chromatography. Column Alltech Part No. 16368 AT-1ht 30m x 0.25mm D x 0.1 $\mu$ m. injection volume 1 $\mu$ l, oven temperature 250°C,  $Q_{\text{H}_2}$ = 45 ml/min and  $Q_{\text{air}}$ =450 ml/min; Method: 40°C constant for 2 min, then increase by 20°C/min for 10.5 min to 250°C, then plateau from 3 min to 250°C

##### **RMN:**

$^1\text{H}$  NMR (frequency, D<sub>2</sub>O): Maleic acid:  $\delta$ /ppm 4.79 (s, 1H), 6.282 (s, 1H)

$^{13}\text{C}$  NMR (frequency, D<sub>2</sub>O): Maleic acid:  $\delta$ /ppm 130.5 and 169.4

##### **HPLC:**

HPLC MS Shimadzu equipped with a refractive index detector and an ICE-Coregel 87H3 column. Mobile phase: aqueous formic acid 8.10<sup>-3</sup> M, flow 0.6 mL/min. Column Temp: 35°C. The injection volume was 10  $\mu$ L.

#### **Energy consumption calculations:**

To estimate the heating energy necessary for maintaining oil bath at  $T_{set}$ , a thermal balance is done on three stages:

- 1- Warm-up
- 2- Heating stoppage
- 3- Re-heating

In all phases, the thermal balance is done by equating the sum of acting heat fluxes to the change in energy state of the system composed of oil bath, that is:

$$\rho_{oil} \times V_{oil} \times Cp_{oil} \frac{\Delta T_{oil}}{\delta t} = \Sigma Q$$

- 1- Warm-up

$$T_{plate} = T_{0,plate} + \alpha t$$

- 2- Heating stoppage

$$\rho_{oil} \times V_{oil} \times Cp_{oil} \frac{\Delta T_{oil}}{t} = \frac{-kA}{e} (T_{oil} - T_{plate})$$

- 3- Re-heating

$$T_{plate} = T_{0,plate} + \alpha t$$

We got  $t_1$ ,  $t_2$  and  $t_3$

At the end, we should calculate the number of times it turned off (x) and the number of times it went on (y) according to the reaction time.

$$\Leftrightarrow \text{Energy} = (t_{\text{warm-up}} + yt_{\text{on}}) \times \text{Power}$$

**Given:**

Specific heat capacity of oil:  $Cp_{oil} = 1510 \text{ J/Kg.K}$

Oil density:  $\rho_{oil} = 0,96 \text{ kg/L}$

Oil Volume:  $V_{oil} = 1 \text{ L}$

Convective coefficient:  $h = 10 \text{ W/m}^2.\text{K}$  (Heat loss through convection with air)

Thickness of the bath:  $e = 3 \text{ mm}$

Ambient temperature  $T_{amb} = 293 \text{ K}$

Lateral surface  $A = 0.035 \text{ m}^2$

**Example:**  $T = 50 \text{ }^\circ\text{C}$ ,  $t = 24 \text{ h}$  and  $P = 650 \text{ W}$  (ref [21] in the article)

$T_{set} = 323 \text{ }^\circ\text{K}$

$$T_{Li} = 321 \text{ } ^\circ K$$

$$t = 86400 \text{ sec}$$

$$t_{\text{warm-up}} = (T_{\text{set}} - T_{\text{amb}})/0.11 = 272.7 \text{ sec}$$

$$\Delta T_{\text{off}} = \frac{\rho_{\text{oil}} \times V_{\text{oil}} \times C_{p_{\text{oil}}} \times 2}{h \times A \times (T_{\text{set}} - T_{\text{amb}})} = 276.1 \text{ sec}$$

$$\Delta T_{\text{on}} = (T_{\text{set}} - T_{Li})/0.11 = 18.2 \text{ sec}$$

$$y = \frac{t}{(\Delta T_{\text{off}} + \Delta T_{\text{on}})} = 293.6$$

$$E = 368\,100.9 \text{ J}$$

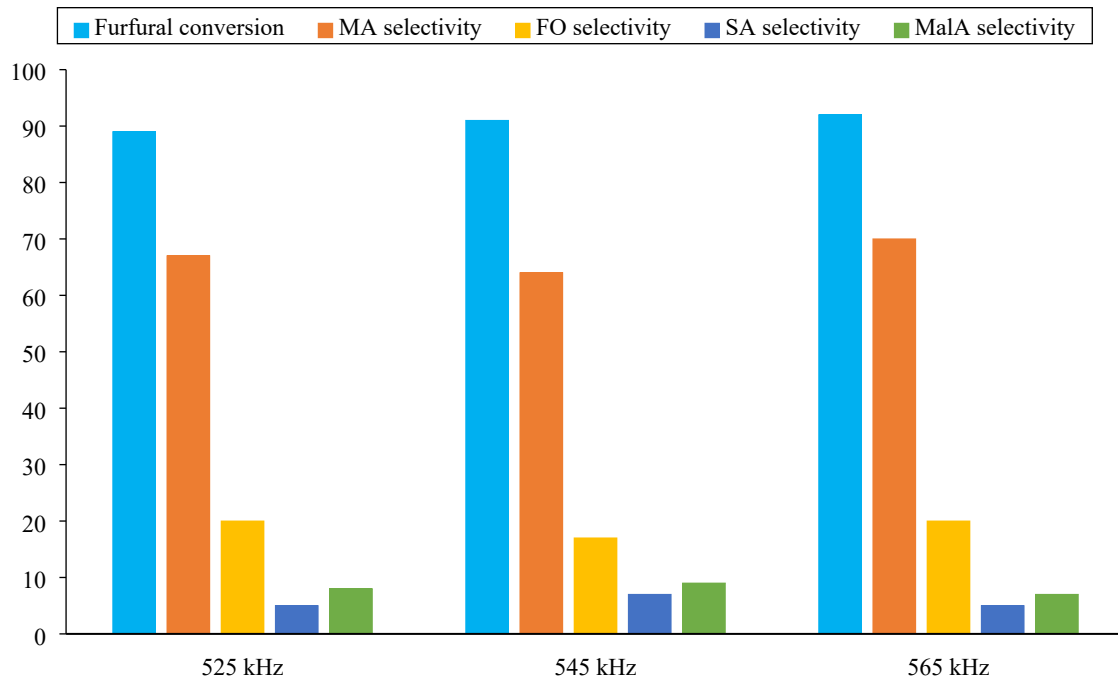


Figure S3 - Effect of the frequency (kHz); Furfural 10 mL (0.12 mol); H<sub>2</sub>O<sub>2</sub> 40 mL (0.46 mol), 2 h, 42 °C, 80 W, after boiling.

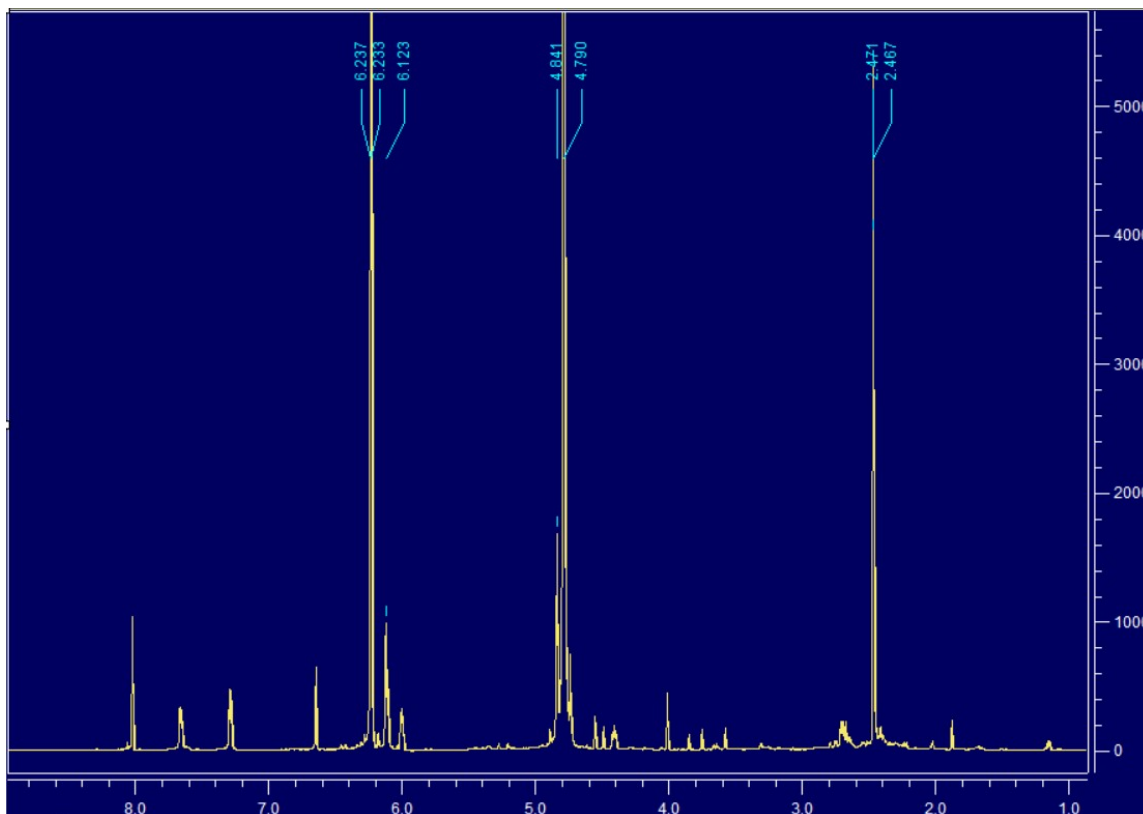


Figure S4 - <sup>1</sup>H spectrum; Furfural 10 mL (0.12 mol), H<sub>2</sub>O<sub>2</sub> 40 mL (0.46 mol), 42 °C, 2 h, 565 kHz, 80 W, after boiling.

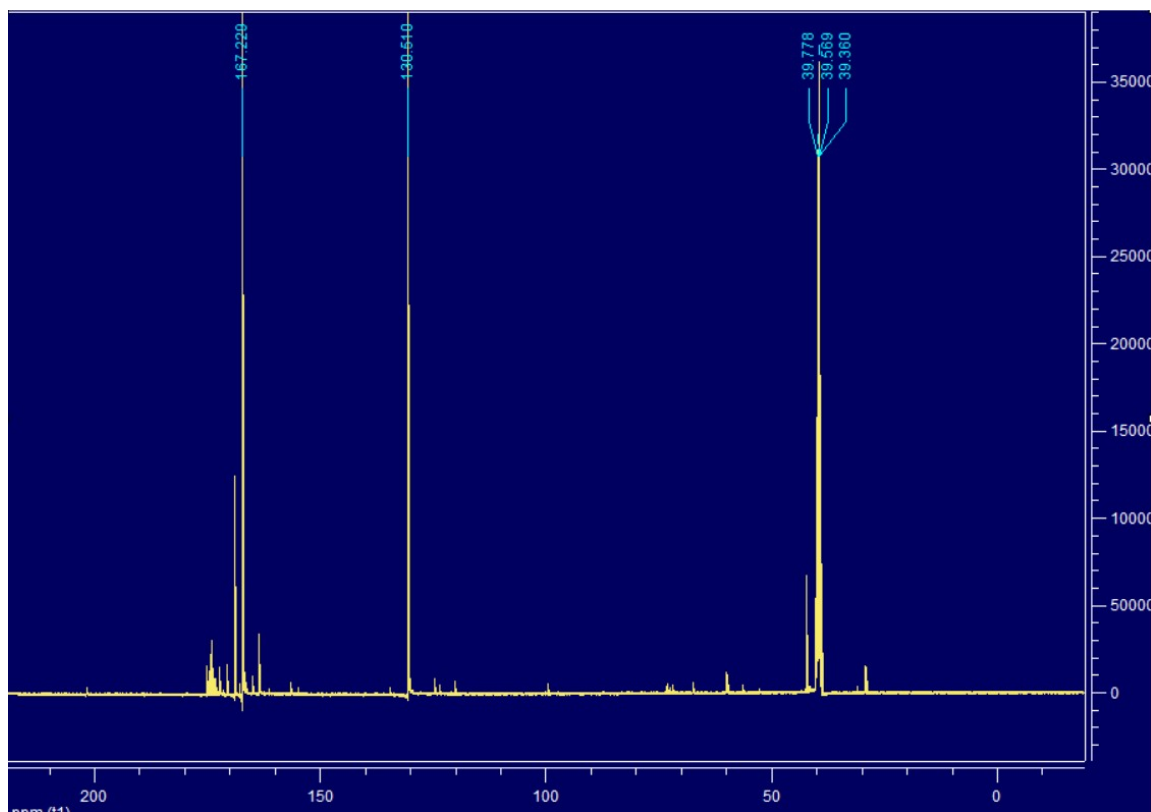


Figure S5 - <sup>13</sup>C spectrum; Furfural 10 mL (0.12 mol), H<sub>2</sub>O<sub>2</sub> 40 mL (0.46 mol), 42 °C, 2 h, 565 kHz, 80 W, after boiling.

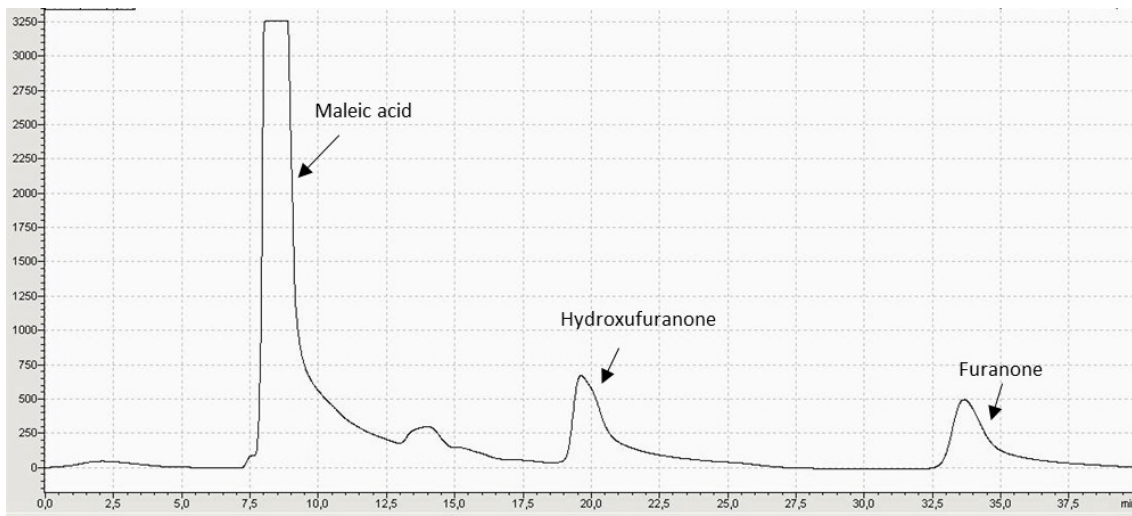


Figure S6 - HPLC chromatogram; Furfural 10 mL (0.12 mol), H<sub>2</sub>O<sub>2</sub> 40 mL (0.46 mol), 42 °C, 2 h, 565 kHz, 80 W, after boiling.

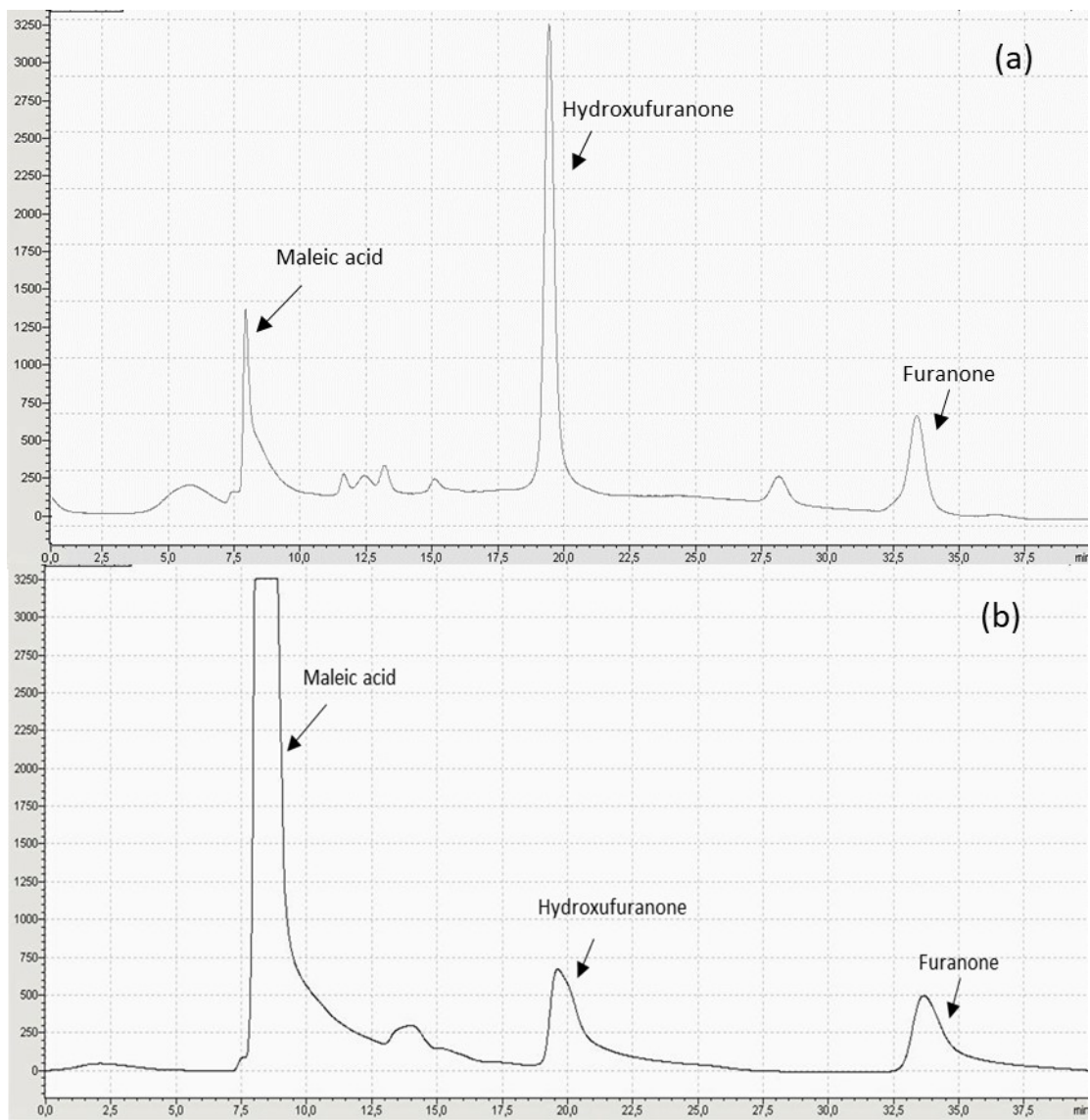


Figure S7 - HPLC chromatogram before (a) and after (b) boiling at 565 kHz, Furfural 10 mL (0.12 mol); H<sub>2</sub>O<sub>2</sub> 40 mL (0.46 mol), 2 h, 42 °C, 80 W, after boiling.



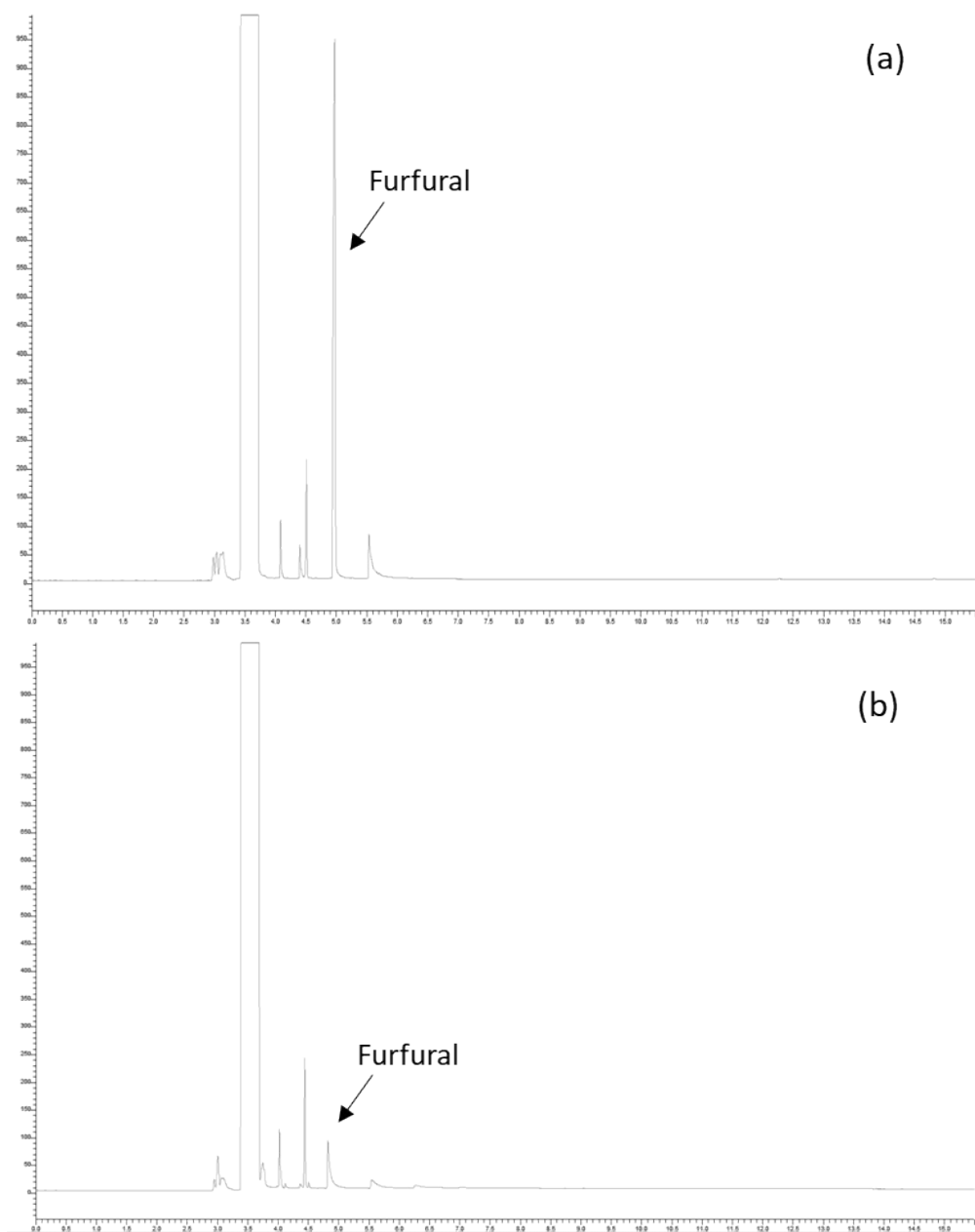


Figure S8 - GC chromatogram before (a) and after (b) boiling at 565 kHz, Furfural 10 mL (0.12 mol); H<sub>2</sub>O<sub>2</sub> 40 mL (0.46 mol), 2 h, 42 °C, 80 W, after boiling.