Electrochemical oscillatory baffled reactors fabricated with additive manufacturing for efficient continuous-flow oxidations

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Table of contents

1 Gaskets .................................................................................................................................................. 2
2 Programming of the syringe pump used for oscillation ................................................................. 3
3 Geometry used for the CFD simulations .......................................................................................... 3
4 Study of higher currents in reaction ............................................................................................... 4
5 NAD+ quantification ......................................................................................................................... 5
1 Gaskets

Figure S1 A) Flexible resin gaskets degraded after working without limited current. B) Flexible resin gaskets status after a batch of experiments. C) TPU gaskets after a batch of experiments D) Comparison of the status between flexible resin and TPU gaskets.

Figure S2 A) Ammonite Spiral Reactor B) 3D Printed ECOBR C) Setup used for the ECOBR experiments.
2 Programming of the syringe pump used for oscillation

A Labview VI was developed to control the syringe pump that generates the oscillating flow. The front panel for the executable can be seen at figure S5A, there the user can input the desired oscillating conditions. The block diagram comprises a series of cases that activate different functions, including the start/stop of the oscillation and other processes like pump cleaning or initialization, an example can be seen at figure S5B. Finally, the oscillation order is sent to the pump as a string of commands in the required format generated using the code seen in figure S5C.

Figure S3 A) Front panel of the VI executable where user can select conditions. B) Part of the block diagram. C) Block diagram for the generation of the oscillation code.

3 Geometry used for the CFD simulations

Figure S4: A) Simplified 3D geometry used for the simulation. Red: electrodes. Green: inlet and outlet B) structure of the mesh

To accelerate the calculations, a subset of 5 cells was simulated (figure S4A), with proper inlet and outlet separation to minimize the effects of boundary conditions on the flow inside the cells. The surfaces marked in red represent the cell electrodes. Figure S4B shows a detail of the
fully structured 3D mesh that was generated, which is based on the O-GRID approach for the tubular regions.

Simulated flow field for non-oscillatory conditions

![Flow field for non-oscillatory conditions](image)

Figure S5: Flow field for the non-oscillatory conditions.

The flow is distributed evenly when the reactor is working under non-oscillatory conditions. Also, flow speed is extremely low and near the electrodes.

4 Study of higher currents in reaction

The use of higher currents lowered the yield presumably due to overoxidation of the substrate. Therefore, definitive experimental currents were selected using Faraday’s law, considering the concentration of NADH used, the cell’s volume, residence time and flow.

\[ i = \frac{m \cdot n \cdot F}{t} \quad \text{(Eq. S1)} \]

Where \( i \) = current, \( m \) = mol, \( n \) = electron number, \( F \) = Faraday constant, \( t \) = time.

Table S1 Results for experiments using higher currents in the commercial reactor.

| Entry | Flow / mL min\(^{-1}\) | \( t_{\text{res}} \)/ min | I / mA | Curr. dens. / mA cm\(^{-2}\) | Yield / % |
|-------|--------------------------|-------------------------|--------|-----------------------------|-----------|
| 1     | 0.02                     | 125                     | 0      | 0.0000                      | 0         |
| 2     | 0.02                     | 125                     | 0.32   | 0.0160                      | 68.59     |
| 3     | 0.02                     | 125                     | 0.64   | 0.0320                      | 39.48     |
| 4     | 0.02                     | 125                     | 1.29   | 0.0645                      | 23.08     |
| 5     | 0.02                     | 125                     | 2.57   | 0.1285                      | 0         |
5 NAD+ quantification

The NADH cofactor oxidation was quantified through its use in the enzymatic transformation of glucose into gluco lactone employing GDH enzyme. After the enzymatic reaction, the samples were analysed in UV-vis spectrophotometer at 340 nm and quantified through a calibration curve of NAD+

![Calibration curve for NAD+ concentration](image)