Electrochemical production of bio-based maleic acid

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Introduction

Industrially produced maleic acid (MA) currently is fossil based and is produced by hydrolysis of maleic anhydride, which on the other hand is produced by gas phase thermocatalytic oxidation of butane by oxygen catalyzed with vanadium-based V-P-O catalysts, however the process yields only 50-65 % maleic anhydride, therefore very inefficient.

Present work is aiming for development of the electrochemical production of MA from renewable feedstock, biomass, and demonstration of the continuous and economically feasible production at industrially relevant conditions.

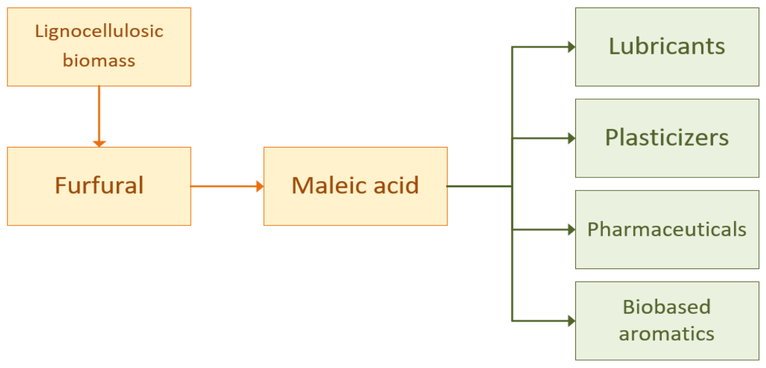

Figure 1 Production route and applications of MA.

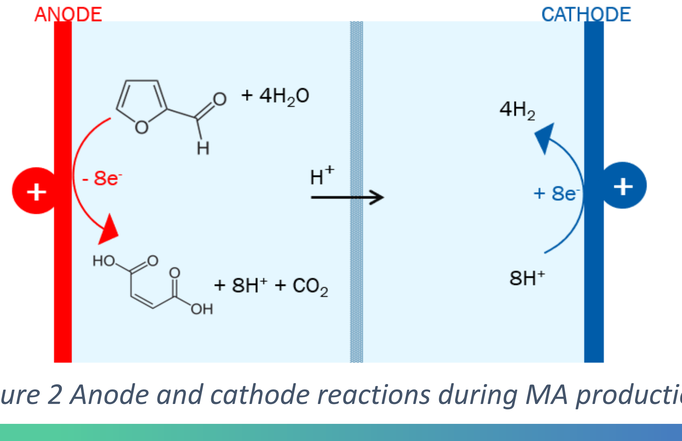

Figure 2 Anode and cathode reactions during MA production.

Results

Electrochemical direct oxidation of furfural to maleic acid is investigated in the EU Perform project. The project covers electrode and electrochemical reactor development, downstream process development, process and techno-economic assessment, demonstration of continuous production, sample generation and application testing.

Initially, reaction mechanisms (Fig. 3) studied and the main intermediate of furfural oxidation, was identified as 5-Hydroxy-2(5H)-furanone (5HFO). This was confirmed by NMR measurements and HPLC.

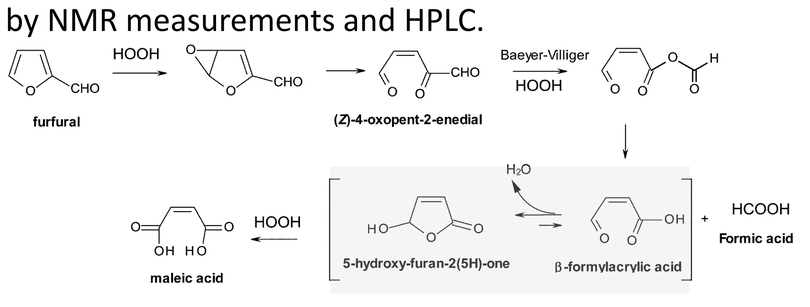

Figure 3 Reaction pathways of electrochemical oxidation of furfural to FAA and to MA.

Reactor scale up

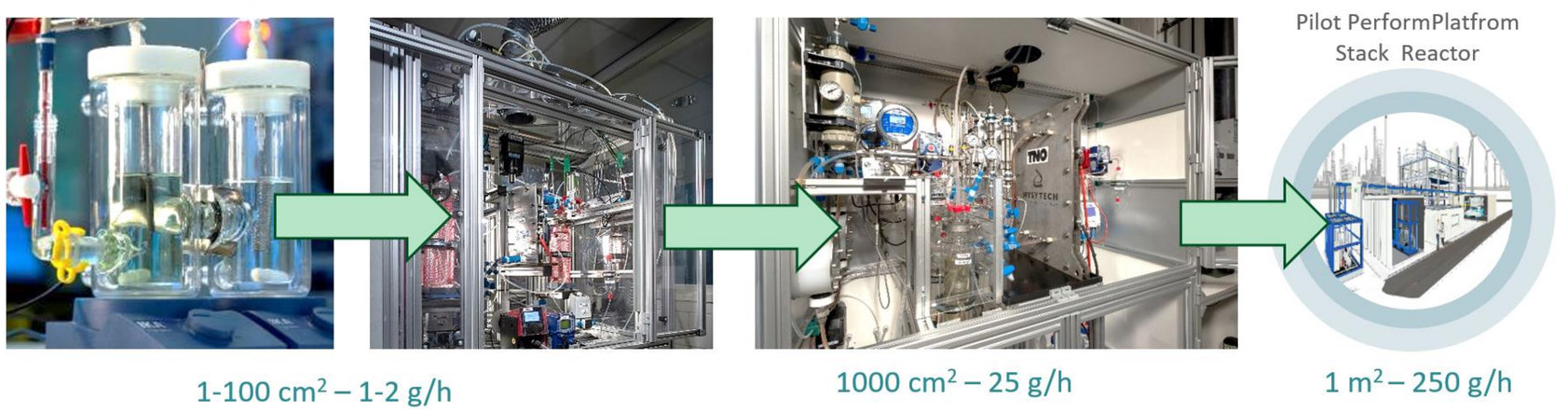

Figure 4. Electrochemical reactor scale up from 1 cm² to 1 m² stacked pilot unit (1000 cm²/cell)

The catalyst, electrodes and reaction conditions for the electrochemical MA production were optimized in 1-100 cm^2 reactors. The best catalyst materials and reaction condition selected: PbO_2 anode for oxidation of furfural to maleic acid at 25 ^0C in 1M H_2SO_4 (2.1 V vs RHE), while on the cathode H_2 or valeric acid are produced.

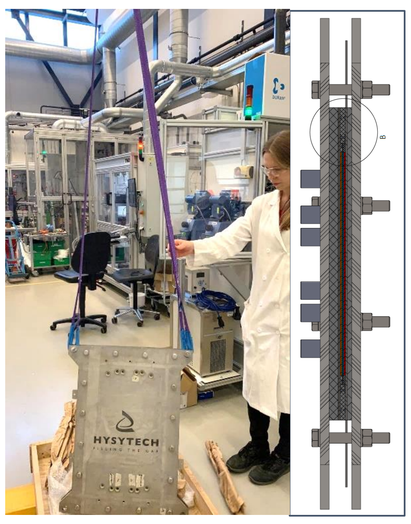

Figure 5 Electrochemical reactor, 0-gap configuration (1000 cm²).

Electrochemical reactor was scaled up from 1-10 cm^2 to 1000 cm^2. Flexible scaled up reactor was designed, performance simulated and optimized experimentally in a single cell flow reactor. Zero-gap reactor configuration was used for production of maleic acid. Electrochemical oxidation achieved with conversions of 99%, a combined yield of ~80% and `70% efficiency towards of MA + 5HFO, at current densities 20-100 mA/cm^2, cell voltage <3.5V (Fig. 6). Based on the obtained results stacked 1 m^2 electrochemical reactor (1000 cm^2 per cell) has ben designed and currently is under construction.

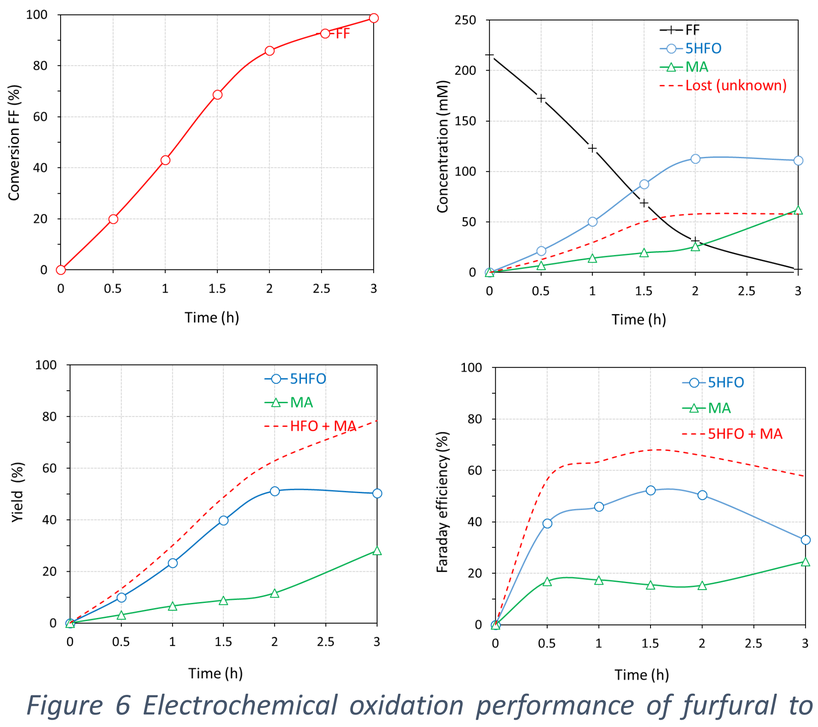

Figure 6 Electrochemical oxidation performance of furfural to MA in 0.5M H_2SO_4 on PbO_2 electrode, RT, 1000 cm^2 reactor.

Downstream process for maleic acid separation, consisting of concentration and crystallization steps, was optimized and 85% separation yield at >95% purity MA was produced in a laboratory scale separation units. Based on the results, pilot scale downstream processing units have been selected. Currently, pilot scale flexible electrochemical Perform PowerPlatform, reactor with semi-integrated separation units, is under construction. The demonstration tests in a 1 m^2 pilot unit to be performed by the end of 2022.

Techno-economic assessment of the electrochemical production of maleic anhydride was performed for various scenarios and product downstream separation options (assumed 300 ma/cm^2, 70% FE, 3V cell voltage). Results show that bio-based maleic anhydride/acid can be produced in an economically feasible manner under 1.5 Euro/kg via electrolysis of furfural (Fig. 7). The cost of the feedstock currently is the main contributor to the production costs. Further improvement of current density and current efficiency is required to lower the production costs.

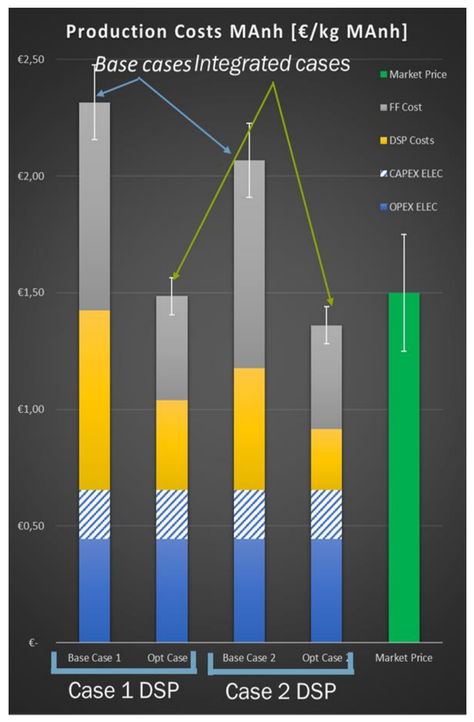

Figure 7 Techno-Economic Assessment of the electrochemical production of maleic anhydride.

Outlook

Direct electrochemical production of maleic acid from renewable resources is promising, as shown by the project results and techno-economic assessment. The reaction will be further demonstrated in 1 m^2 stacked reactor & pilot scale semi-integrated product separation, productivity ~250 g/h, TRL5-6. The methodology applied in this project is general and applicable to other electrochemical production of bio-based molecules.

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