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CO_2 abatement and renewable chemicals production by using microbial electrosynthesis within the framework of CO_2 biorefineries

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INTRODUCTION

Microbial electrosynthesis (MES) relies on **microorganisms** as catalysts for the anoxic **reduction** of organic compounds at the cathode, **CO_2** in this study, at the expense of oxidizing reactions performed at the anode. Due to the oxidized nature of the carbon molecule, **external energy** must be **supplied** for the reaction to be favourable. In a nutshell, MES can decrease surplus CO_2 in the environment while **synthesizing value-added compounds**.

OBJECTIVES*

(i) Evaluation of the current state of CO_2 emissions.
(ii) Study of materials and microorganisms.
(iii) Research on the economic viability and scale-up.
(iv) Review of real production schemes.

* Accomplished via a literary review of general and specific scientific papers.

GENERAL SCHEME

ANODE

WATER INPUT

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

O_2 finds application in the metal industry

Issues:
(i) OER overpotential; 600 mV are required for carbon electrodes to display intrinsic OER in a current density of 5 mA cm^{-2} .
(ii) Generation of oxygen, threatening the required anoxic conditions for the cathode.

WASTEWATER TREATMENT

Reduction of the Chemical Oxygen Demand (COD) using mixed enriched cultures.

Advantages:
(i) No oxygen generation.
(ii) Lower potentials required.
(iii) Cheaper electrodes
(iv) Simultaneous wastewater treatment (anode) and chemicals production (cathode).

FLUE GAS DESULPHURISATION

$2HSO_3^- + 2H_2O \rightarrow 2SO_4^{2-} + 6H^+ + 4e^-$

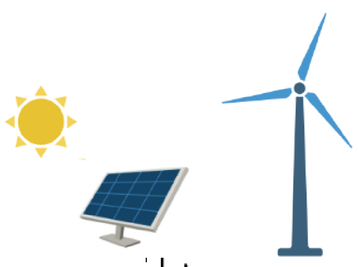
SO_4^{2-} is used as cleansing and foaming agent.

CHLORINE PRODUCTION

$2Cl^- \rightarrow Cl_2 + 2e^-$

Cl_2 is used in wastewater treatment and as a bleaching agent.

Electricity cost (EUR $ton_{product}^{-1}$):
(i) Non-renewable: **406**
(ii) Renewable: **162-243**



CATHODE

PRODUCTION OF VOLATILE FATTY ACIDS

$2CO_2 + 8e^- + 8H^+ \rightarrow CH_3COO^- + H^+ + 2H_2O$

Acetate: 1330 g m^{-2} d^{-1}, 99% CE
Ethanol: 8.46 g m^{-2} d^{-1}, 26% CE
Butyrate: 160 g m^{-2} d^{-1}, 99% CE
Butanol: 3.12 g m^{-2} d^{-1}, 12 % CE
Caproate: 46 g m^{-2} d^{-1}, 13 % CE

Prices (EUR kg^{-1}):
(i) Acetic acid: **0.6**
(ii) Caproic acid: **1.6**
(iii) Butyric acid: **3.5**

BIOGAS PURIFICATION

$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$

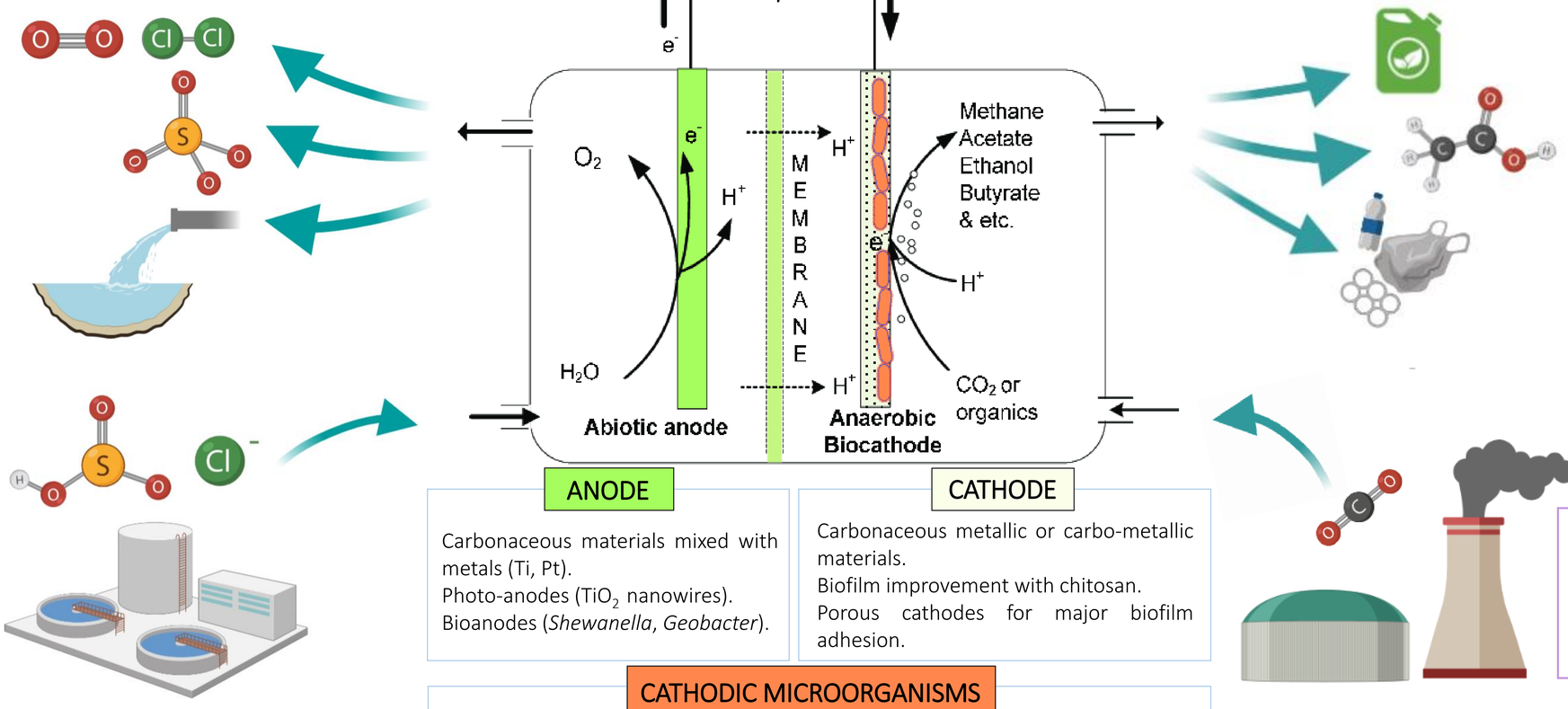
Upgrading the methane yield (0.16 g m^{-2} d^{-1}, 113% CE) of the obtained biogas from anaerobic digestion by methanogenic cultures.

Filters are required as the inlet of biogas usually contains toxic gases (H_2S, NH_3 and sulphur oxides).

BIOPLASTICS PRODUCTION

Acetate is generated at the cathode (5 g L^{-1}) and extracted in a central chamber. Later, the synthesized acetate is used by *Ralstonia eutopha ex situ* to produce polyhydroxybutyrate (PHB) (0.46 g L^{-1}, 71% CE).

PHB is an environmentally friendly and completely biodegradable product that finds application in the packaging industry.



ANODE

Carbonaceous materials mixed with metals (Ti, Pt).
Photo-anodes (TiO_2 nanowires).
Bioanodes (*Shewanella*, *Geobacter*).

CATHODE

Carbonaceous metallic or carbo-metallic materials.
Biofilm improvement with chitosan.
Porous cathodes for major biofilm adhesion.

CATHODIC MICROORGANISMS

From the genus: *Clostridium*, *Moorella* and *Sporomusa*.
Metabolic pathway: Wood-Ljungdahl.
Electron transfer: direct (NADH delivering enzyme, coenzyme Q, ubiquinone) or indirect (H_2, neutral red, methyl viologen, thionin).

WHY MES?

Solar panels with 40% efficiency sunlight to power conversion and 20% efficiency with a derived power of 2 V, require a current of 100 A m^{-2}. Thus, if 50% electron conversion efficiency from butyrate to butanol is assumed; 1.512 tonnes hectare^{-1} annum^{-1} can be produced, while 50 tonnes of algae biomass dry weight hectare^{-1} annum^{-1} are generated, from which biodiesel is obtained after a cumbersome process.

Atmospheric CO_2 levels (ppm):
(i) Pre-industrial: **278**
(ii) 2021: **417**

CO_2 capture cost (EUR ton CO_2^{-1}): **184** *

*For the steel and cement industry

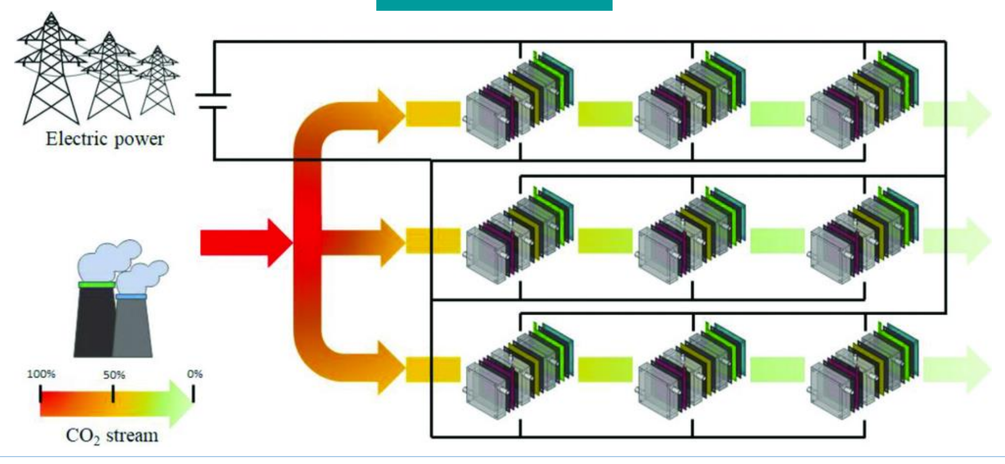
CONCLUSIONS AND FUTURE OUTLOOK

Strong points: **(i)** requirement for little amount of water and, sometimes not even freshwater, **(ii)** it does not need arable land, rendering it free from the debate of food vs. fuel, **(iii)** ease in the biofuel obtention process, and **(iv)** the possibility of (renewable) energy storage.

Economic viability: cost of electricity and reagents: **4,430** EUR year^{-1} and benefits: **3,356** EUR year^{-1} for 5.37 tonnes of acetate year^{-1} (3.94 tonnes CO_2 year^{-1}). Economically non-viable under the current state-of-the-art (**Technology Readiness Level 4**).

Future research: **(i)** good CO_2 availability, **(ii)** high couolombic efficiency with low overpotentials, **(iii)** increase production rates and specificity, and **(iv)** effective and economic downstream processing.

SCALE-UP



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