Regeneration of cofactor used for CO_2 conversion into formate

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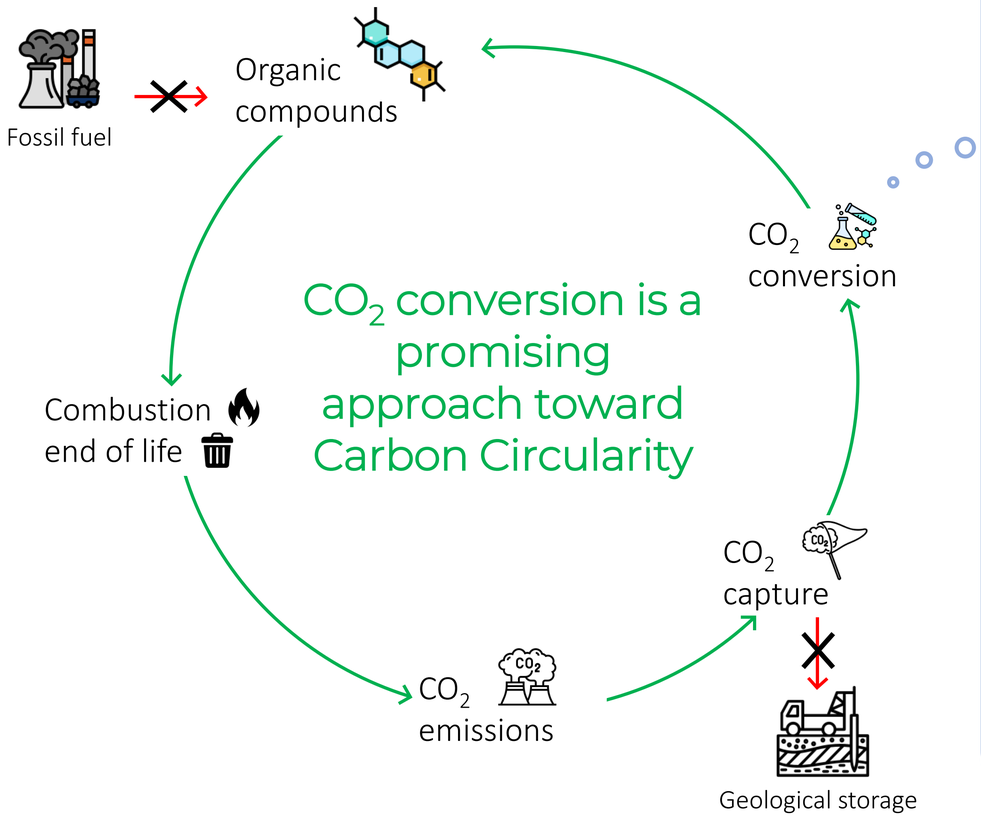
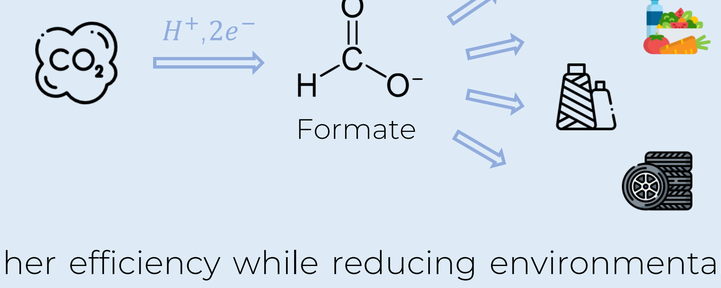
INTRODUCTION

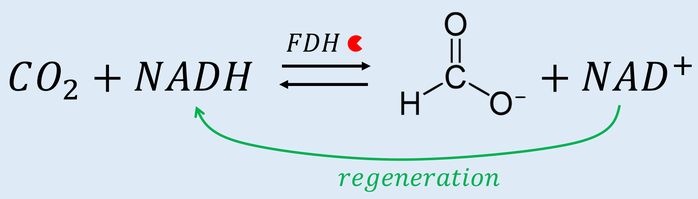


Formate is the first reduced form of CO_2 and can be used in a variety of fields, including medicines, conservation, textiles and rubber.



Enzyme-based CO_2 conversion enables higher efficiency while reducing environmental impact.

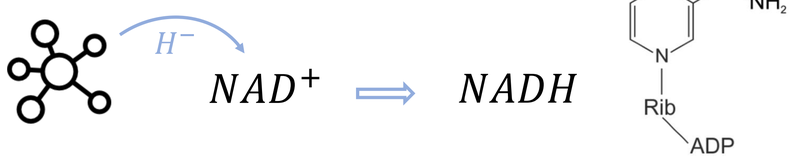
A method for converting CO_2 into formate using enzymes is inspired by a well-known biochemical pathway, which relies on a redox reaction between CO_2 and **NADH**, catalyzed by **formate dehydrogenases** (FDH).



Since NADH is expensive, its **regeneration** during the process is essential.

Hydride exchange

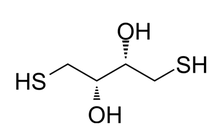
NADH regeneration can occur through **hydride transfer** from a reducing agent.

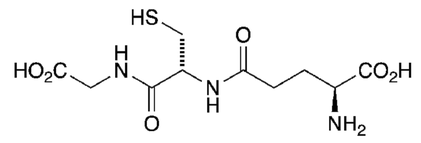


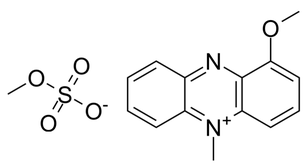
The reducing agent must be capable of regenerating the NADH without producing **intermediate radical species** that reduce the yield of the desired reaction, as is the case with electrochemical methods.

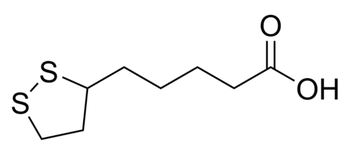
Potential reducing agents

No hydride exchange


dithiothréitol


glutathione


phenazine methosulfate

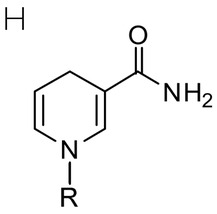

lipoic acid

No hydride exchange observed between sulphur compounds and NAD^+ or NADH

Successful hydride exchange

Hydride exchange observed between :

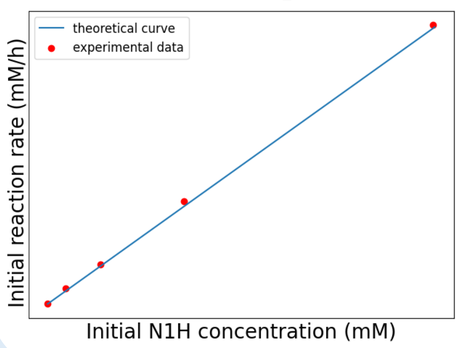
- reduced nicotinamides and NAD^+
- oxidized nicotinamides and NADH


Nicotinamides

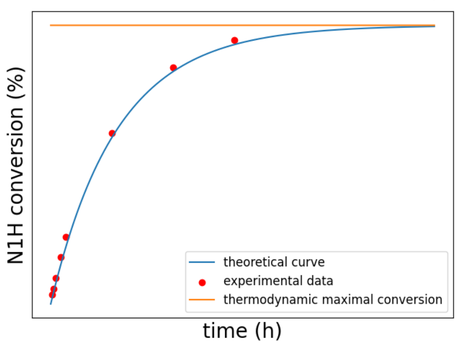
Performance

Some kinetic results with two natural nicotinamides

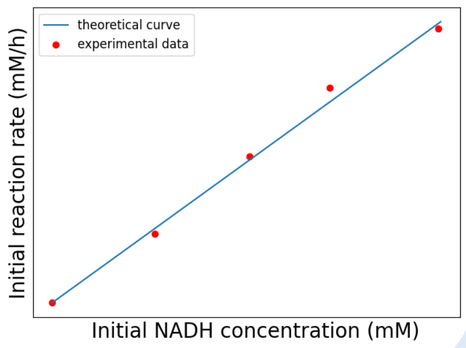
$N_1H + NAD^+ \rightleftarrows N_1^+ + NADH$



For twice as much NAD^+ as N_1H



$NADH + N_2^+ \rightleftarrows NAD^+ + N_2H$



Results with synthetic nicotinamides

- An easy to synthesise and low-cost synthetic nicotinamides in its oxidised form is able to oxides NADH while reducing itself .
- The inverse reaction is going to be tested and could lead to a cheap and easy to make NADH regeneration method.

Study of the reaction

Influence of :

- **Oxygen level**

  None on kinetics but the more oxygen, the less final reduced species due to oxidation :

  $NADH + O_2 + H^+ \rightleftharpoons NAD^+ + H_2O$

- **pH solution**

  None on kinetics but the more acidic the solution, the less final reduced species due to degradation:

  ~~pH~~ → ~~NADH~~

- **Buffer solution**

  Tris HCl or phosphate buffer : none on kinetics but higher degradation of reduced species in phosphate.

- **Temperature**

  The higher the temperature, the faster the reaction

  k_{cin} x2 when T° : 20°C → 37°C

Perspectives

- **Possibility of regenerating NADH or other high-cost reduced nicotinamides with easy to synthesise low-cost synthetic nicotinamides**
- **Development of a CO2 conversion process using NADH and FDH where NADH is continuously regenerated at low cost.**
- **Regeneration of NADH in the pharmaceutical industry, for which NADH is of great interest.**

CO_2-based Fuels and Chemicals Conference 2025