CO$_2$-Neutral Fuels

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**CO₂ Neutral fuels: What are they?**

**Hydrocarbons** synthesised from water and air
- powered by Renewable Electricity
- CO₂ recirculated after use

Characterised by high energy density and existing infrastructure
Carbon neutral fuel cycle: P2X – CCU

**Point source capture** of fossil CO₂
→ not climate neutral, emission delayed

**Direct air capture** of CO₂
→ climate neutral fuel cycle

**Power-to-X**
\( X = \text{gas or liquid fuel or chemicals} \)

**P2X + CCU**
CCU: carbon capture and utilisation


**P2X is most critical part both technically and economically**

**Technology benchmark: costs of H₂**
- Electrolysis >6 €/kg H₂ (fossil fuel <1 €/kg H₂)
- CO₂ capture: point source 40 €/tonne, direct air 400 €/tonne
Splitting $\text{H}_2\text{O}$ and/or $\text{CO}_2$ by electrolysis

- **Alkaline** electrolyte (100 yrs large scale mature technology)
  - Power density low (< 0.5W/cm$^2$)
  - Low hydrogen output pressure (< 30bar)
  - Safety (caustic electrolyte)

- **PEM** (polymer electrolyte membrane), pre-commercial
  - Power density $\sim$1W/cm$^2$
  - Rapid dynamic response
  - Degradation membrane
  - Catalyst material Pt, Ir (Scarce)
  - MW unit (Siemens)

- **SOEC** (solid-oxide electrolyser cell)
  - High power density, energy efficiency, output pressure
  - High Temperature operation ($800^\circ\text{C}$ and pressure 50-100 bar)
  - Co-electrolysis $\text{H}_2\text{O}$ and $\text{CO}_2$
  - Degradation under high current density operation
**Mission:** Basic scientific research into Fusion Energy and Solar Fuels, Based on in house high-quality technical infrastructure, collaboration with Academia, National Research Organisations and Industry, building a national community in energy research.

**Relocated mid 2015**
University Campus Eindhoven
Why plasma for CO$_2$ conversion?

Characteristics of CO$_2$ plasmolysis

Ease conditions for CO$_2$ splitting by channelling energy in molecular vibration to break chemical bond, not to heat the gas (non-equilibrium)

- Energy efficiency comparable to Electrolysis (~60% demonstrated)
- High productivity: large gas flow and power flow density (45W/cm$^2$)
- Fast dynamic response to intermittent power supply
- No scarce materials employed (Pt catalyst in PEM)
Chemical reaction scheme

\[
\begin{align*}
\text{CO}_2 & \rightarrow \text{CO} + \text{O} \quad (\Delta H=5.5 \text{ eV}) \\
\text{CO}_2 + \text{O} & \rightarrow \text{CO} + \text{O}_2 \quad (\Delta H=0.3 \text{ eV}) \\
\text{Net} & \\
\text{CO}_2 & \rightarrow \text{CO} + \frac{1}{2} \text{O}_2 \quad (\Delta H=2.9 \text{ eV})
\end{align*}
\]

**Efficiency to be increased by**

Concentration of electron energy on vibrational excitation of \( \text{CO}_2 \) in asymmetric stretch mode

**Arrhenius/Fridman:**

Activation energy reduced by vibration energy

\[
k = A \exp \left( \frac{\alpha E_v - E_a}{kT} \right)
\]
Experimental Results

- CO and O₂ production as function RF Power

![Graphs showing CO and O₂ production as function of RF Power](image-url)
Experimental Results

• CO production as function **Gas flow**

![Graph showing CO production as function of gas flow](image)

- 10 kW RF absorbed
- 75 slm CO2, conversion 10% CO (non optimised for safety risk)
- Pressure 500 mbar,
- Energy Efficiency 30%
Experimental Results

Energy efficiency vs. reduced E-field

- Type I
- Type II
- Type III

$\eta [\%]$

$E/n [10^{-16} \text{ V cm}^2]$
Experimental Results

particle conversion vs. reduced E-field

E/n [10^{-16} V cm^2]
Energy efficiency of CO$_2$ plasma conversion

Fridman Energy efficiencies:
- Microwave: ◇
- supersonic: ▲
- Radiofrequency (RF): CCP: △, ICP: ▲

DIFFER & IPF Energy efficiencies:
- High CO$_2$ flow (75 slm): ★
- Low CO$_2$ flow (11 slm): ★

Conversion efficiencies:

![Graph showing energy efficiency vs. specific energy input](image)
O₂ separation from CO (similar sized)

- MIEC mixed ion electron conductive membrane (pressure driven) BSCF (Ba₀.₅ Sr₀.₅ Co₀.₈ Fe₀.₂ O₃-d) has been shown to produce an O₂ flux of 60-80 ml/cm² per min.
- Electro chemical Oxygen pump (Voltage driven) YSZ (Yttrium stabilized Zirconia).
Separation of CO, O₂, CO₂ mixture

YSZ Oxygen selective membrane to separate O₂ from CO, CO₂ mixture
Hairpin shaped membranes fitted into SS assembly
From H$_2$O and CO$_2$ to sustainable hydrocarbons

**sustainable energy**

**CO$_2$ hydrogenation**
- methane (Sabatier), methanol synthesis

**CO$_2$ splitting reactions**
- H$_2$O $\rightarrow$ H$_2$ + $\frac{1}{2}$ O$_2$ (splitting reactions)
- CO$_2$ $\rightarrow$ CO + $\frac{1}{2}$ O$_2$

**CO$_2$ water-gas shift reaction**
- H$_2$O + CO $\rightarrow$ H$_2$ + CO$_2$

**Syngas-to-fuel chemistry**
- methane, methanol, Fischer-Tropsch fuels (higher alkanes), etc

reaction enthalpies calculated for gaseous products at standard conditions
Conclusions

- P2X provides vast seasonal energy storage capacity and flexibility of supply from Renewables
- P2X-CCU enables a CO$_2$ neutral fuel cycle based on hydro-carbons and existing infrastructure
- Technical challenge: innovation in CO$_2$ splitting and CO-O$_2$ separation
- Economic challenge: cost reduction, government regulation, business case expected to emerge around 2030, cost of CO$_2$ to reach € 200/tonne