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
Why CO₂ Neutral Fuels?

- UNFCCC Paris 2015: CO₂ emission curbed by 80%-95% in 2050 vs. 1990
- Transport target EU-RED 2050:
  - 60% CO₂ emission reduction
  - Aviation 40% RE by 2050 (~2% of global CO₂ emission)
- Transport makes up ~25% EU primary energy consumption

→ Batteries and Hydrogen emission free, but
  → low volumetric energy density
    (hence mobility range limit)

→ Bio Fuels
  → limited by Fuel vs. Food/Flora trilemma
    (jet fuel alone 5M barrels/day kerosene)
Aimed at phasing out Fossil and Nuclear and replace by Renewables

- Goal 80% electricity from Renewables in 2050
- Presently: 30% RE, 45GW installed wind power
- 30% RE on average: sunny and windy day 90% RE (8 May 2016). Cloudy and Calm: fossil coal, lignite and gas scrambled to cover demand
- Result: Dynamic grid control problem and CO₂ emissions up
- Objectives: clean, affordable, reliable energy supply not met
- Subsidised through guaranteed 20 yr electricity price (20B€/yr)
- Reform now drafted: Auction on generating capacity
- Needed: System Approach of generation, transmission, distribution to customers consistently managed
- Includes Energy Storage: BMBF Kopernikus Programme P2X
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 = 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
Direct air capture of CO₂

Klaus Lackner Tree captures 1 tonnes CO₂/day. Wet-dry cycle epoxy. To supply wind farm with CO₂ to be split by P2X, an approximately equally sized Lackner wood is needed.

First commercial CO₂ air capturing plant, Hinwil (CH), capacity 900 ton CO₂ /yr, swept area 6x12m² amine granules
Coupling Electricity, Gas and Oil infrastructure

**Surplus renewable electricity expected 2050:**
Germany 110-148 TWh, France 44-91 TWh, The Netherlands 30-55 TWh
Energy Storage capacity NL gas net 552 TWh

*Renewable energy: intermittency, mismatch supply and demand*

**Electricity Grid** - sustainable electricity

- **CO₂**
  - Point source capture
  - Electrolysis
  - Plasmolysis
  - Surplus electricity
  - H₂O
  - CO₂

**Gas Grid** - synthetic natural gas (SNG)

- **Power-to-Gas (P2G)**
- **Domestic use**
  - Heating, cooking, mobility
- **Liquid fuel production**
  - Alcohols, ethers, FT fuels
- **Synthesis gas**
  - CO + H₂
- **Methanation**
- **Chemical industry**
  - Carboxylic acids, aldehydes, etc
- **Power-to-Fine Chemicals**
- **Power-to-Liquid (P2L)**
  - Dispersed emission

Energy storage, transport, distribution
Splitting H$_2$O and/or CO$_2$ by electrolysis

- **Alkaline** electrolyte (100 yrs large scale, mature technology)
  - Power density low (< 0.5W/cm$^2$)
  - Hydrogen output pressure low (< 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°C, pressure 50-100 bar)
  - Co-electrolysis H$_2$O and CO$_2$
  - Degradation under high current density operation
  - Upscaling from kW range hampered
SOEC Co-Electrolysis at DTU

- External DC voltage pumps O^{2-} ions from porous **cathode** (Ni/YSZ)
- through dense solid **electrolyte** (YSZ = Yttrium Stabilised Zirconia)
- to porous **anode** (La_{1-x}Sr_{x}MnO_{3}/YSZ) at high temperature (800 °C)
Electrolysis is a surface process happening at the nm interface between electrode, electrolyte and catalyst a 3-phase boundary phenomenon not understood


Fuel Cell mode
a. $\text{H}_2$ absorption and dissociation on Ni surface to form $\text{H}^+$ migrating to site for water formation

b. Migration of $\text{O}^{2-}$ or $\text{OH}^-$ along electrolyte and Ni surface to form water

c. Water formation at electrolyte surface and electron transport through the electrolyte

d. Role of impurities (glassy Silicate) at the 3PB to block the water formation reaction
**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 gas flow and power flow density (45W/cm$^2$)
- Fast dynamic response (intermittent power supply)
- No scarce materials employed (Pt catalyst in PEM)

IGVP: 30 kW @ 915 MHz
**Chemical reaction scheme**

\[ \text{CO}_2 \rightarrow \text{CO} + \text{O} \quad (\Delta H = 5.5 \text{ eV}) \]

followed by reuse energetic \( \text{O} \) radical

\[ \text{CO}_2 + \text{O} \rightarrow \text{CO} + \text{O}_2 \quad (\Delta H = 0.3 \text{ eV}) \]

Net

\[ \text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2 \quad (\Delta H = 2.9 \text{ eV}) \]

**Efficiency to be increased by**

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

\[ \eta = \frac{CF}{W} = \alpha \frac{H}{E_v} \]

**Arrhenius/Fridman:**

Activation energy reduced by vibration energy

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

Out of equilibrium \( T_{\text{vib}} > T_0 \) chemistry

\[ \lambda = 4.24-4.28 \mu\text{m} \ (750 \text{ THz}, \tau = 14 \text{ fs}) \]
Experimental Results: Mass Spectroscopy

- CO and O$_2$ production as function RF Power

![Graph showing CO and O$_2$ production as a function of RF Power.](attachment:graph.png)
Optical Spectroscopy

- CO third positives, fourth positives, Angstrom and Triplet identified.
- CO line intensity increases linear with RF power and gas pressure.
Experimental Results

- CO production as function **Gas flow**

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

\[ \eta [\%] \]

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

Particle conversion vs. reduced E-field
Energy efficiency of CO₂ plasma conversion

**Fridman Energy efficiencies:**
- Microwave: ○
- Supersonic: ▲
- Radiofrequency (RF): □

**DIFFER & IPF Energy efficiencies:**
- High CO₂ flow (75 slm): ★★★
- Low CO₂ flow (11 slm): ★★

Conversion efficiencies:
O₂ separation from CO (similar sized)

- MIEC mixed ion electron conductive membrane (pressure driven) BSCF (Ba\textsubscript{0.5} Sr\textsubscript{0.5} Co\textsubscript{0.8} Fe\textsubscript{0.2} O\textsubscript{3-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 $\text{H}_2\text{O}$ and $\text{CO}_2$ to sustainable hydrocarbons

**CO$_2$ hydrogenation**

- methanol (Sabatier),
- methanol synthesis

**reverse water-gas shift reaction**

- $+41 \text{ kJ/mol}$

**Syngas-to-fuel chemistry**

- methane, methanol,
- Fischer-Tropsch fuels (higher alkanes), etc

**splitting reactions**

- $+242 \text{ kJ/mol}$

**water-gas shift reaction**

- $-41 \text{ kJ/mol}$

reaction enthalpies calculated for gaseous products at standard conditions
**Objectives** high CO$_2$ reduction with max CO$_2$ valorisation, decentralisation, upscaling, public acceptance and export

**Yr 1 to 3**
- 6 Research Clusters; FZ Jülich, RWTH Aachen, Dechema together with Associated Partners (KIT Energy Lab 2.0)
- Electrolysis, Catalysis, Material and Process design to produce Hydrogen and Syngas
- P2X Road mapping together with Socio-Economic groups and SME

**Yr 4 to 7**
- 4 Technology Clusters for validation, integration and Pilot projects

**Yr 8 to 10**
- 3 System Demonstration and Application (Industry lead)
Conclusions

• P2X provides vast seasonal energy storage capacity and provides flexibility in the energy 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
• In 10 yrs time, cost Wind and Solar tumble, whilst cost of decommissioning, waste disposal and climate change factored into cost of nuclear and fossil power.
• System approach is essential in future energy system, incl. waste disposal, storage and customer acceptance