CO$_2$-Neutral Fuels

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Kopernikus-P2X
Driver of the Energy Transition

CO\textsubscript{2} Emission Reduction

- Global CO\textsubscript{2} emissions from energy use roughly flat in 2016 (source BP)
- Year-on-year increase of 0.1% is well below 10-year average 1.6%
- Improved energy efficiency and slowing global economy partly responsible

- China world’s largest CO\textsubscript{2} emitter, but emissions fell by 41m tonnes in 2016
- India’s 2016 CO\textsubscript{2} emissions increased by 114m tonnes
- In 2016 the Asia-Pacific region produced half of global CO\textsubscript{2} emissions, up from 25% in 1990

Source: Economist, Jun 17\textsuperscript{th} 2017
Global CO$_2$ emission: EU 10.5%, NL 0.5%

**NL CO$_2$ emission budget**

- Power and Lightning (electricity) 26%
- Low temperature heat (domestic) 18%
- High temperature heat (industry) 19%
- Transport (cars, ships, planes) 17%
- Non-energy emissions (agriculture, waste, feedstock) 20%

*typically 20:20:20:20:20*
2050 UNFCCC agreement and EU Directives:

- $\text{CO}_2$ emission 80% to 95% below 1990 level
- Transportation: 60% $\text{CO}_2$ emission reduction
- Aviation: 40% sustainable fuel by 2050
- UN-ICAO: emissions 50% below 2005 level

Transportation sector: challenge to meet $\text{CO}_2$ reduction target, aviation being case in point
Energy Demand: The Netherlands (2015)

Electricity demand almost flat throughout the year ± 10% [GWh/day]

Gas demand (mainly heat): seasonal variation factor 4 [GWh/day]
UK energy demand: Electricity, Gas and Transportation

Seasonal and inter annual energy demand UK

- Transport: approx. flat over the year
- Electricity: ± 10% seasonal variation
- Gas: factor 5 seasonal variation and 2x electricity demand
Supply of Renewable Electricity - NL 2015

Sun: out of phase with seasonal heat demand at N-EU latitude. Winter insolation 10% of summer.

In phase with diurnal demand, but not quantitatively: surplus during day, shortage at night.

Wind: seasonal variation factor 2 to 3 in phase with heat demand but not quantitatively. Intermittent, with large dynamic range (factor 100).

Mix sun and wind 75%-25% projected by IEA not optimal.

Figures in GWh/day.
Projected Surplus Renewable Electricity

Current renewable energy scenarios rely on PV and Wind electricity. This leads to surplus electricity, whilst back-up power is still required.

Netherlands
- 2025: 1.5TWh (12GW wind)
- 2050: 30-55TWh

Germany
- 2035: 34.5 TWh
- 2050: 110-148 TWh

France
- 2030: 15 TWh
- 2050: 44-91 TWh

Need for large scale electricity storage on time scales ranging from msec to inter-annual in order to match renewable electricity supply with demand.
Two concepts:

- **Direct conversion** Solar photons into Fuel (Artificial Photosynthesis). Early days.
- **Indirect conversion** solar to electricity (PV, wind, waves, rivers). Followed by Electricity to Fuel = **Power to X**
- This P2X scheme is more advanced compared with AP
- As electricity makes up only 20% of demand, conversion into other energy sectors is needed: **Sector Coupling**
- Difficult to meet heat demand by renewable electricity: Capacity of the grid to be increased 3 to 5 times. Electricity transport is costly compared with gas (factor 20-40), whilst running idle half of time
- Difficult to meet transportation demand by electricity. Urban transport feasible, but long haul transportation probably not.
Energy Storage Systems

Energy Storage Capacity and discharge power

Chemical Energy Storage
Energy density and Specific energy high
**Hydrogen** low volumetric energy density: 3000 below *kerosene*
limits storage, transport and usage as a fuel

- liquefied at 20K still factor 3.7 lower energy density,
- pressurised at 700 bar factor 6.4 lower energy density
- Safety aspects: highly flammable
- LH2 Aircraft gas turbine redesign/qualification to operate cryogenic fuel
- New fuel system, new ground handling and storage (boil-off).
- Fuel to be stored in fuselage rather than wings, because of volume and heat transfer.
- Increased drag and fuel consumption
- Reduced lift-off weight

**DLR H2 Antares**
Hydrogen Fuel Cell powered
one seater glider
36 kW PEM Fuel Cell @ 80 kg
10 kWh battery 45-60kW @ 50kg
**Sustainable Aviation fuel - Batteries**

**Batteries** good for Urban transport, no air pollution, no noise, future self-driving/ride sharing/big-data also electricity dependent

Long Haul Transportation: Energy density most advanced Li-ion battery is factor 14 lower than kerosene, by weight factor 50 lower
Battery powered airbus 380 needs 14.000 ton battery, instead of 260 ton kerosene > It will never take off

*Long haul road transport, shipping and aviation are unlikely to be powered by electricity or hydrogen in the 2050 time frame*

Current EU Policy directed at **bio fuel**. However, biofuels do not meet sustainability and resource requirements set by projected 2050 global fuel demand. Example: 5 m barrels kerosene per day for jet fuel alone. Social Acceptance problem: Fuel vs. Food vs. Flora trilemma
**CO₂ Neutral Fuels**

**CO₂ Neutral Fuels offer an Alternative Sustainable Fuel**
Characterised by high energy density and existing infrastructure for Energy Storage, transport and distribution

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

**Power2X** connects sectors:
electricity to gas, to oil and to chemical sector.
Solves surplus, storage and transport by electricity
**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
From $\text{H}_2\text{O}$ and $\text{CO}_2$ to sustainable hydrocarbons

- **Sustainable energy**

- **CO$_2$ hydrogenation**
  - Methane (Sabatier), methanol synthesis
  - Reaction: $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$
  - Energy change: $-xx \text{ kJ/mol}$

- **Reverse water-gas shift reaction**
  - Reaction: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
  - Energy change: $+41 \text{ kJ/mol}$

- **Splitting reactions**
  - $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$
  - Energy change: $+242 \text{ kJ/mol}$
  - $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$
  - Energy change: $+283 \text{ kJ/mol}$

- **Syngas-to-fuel chemistry**
  - Methane, methanol, Fischer-Tropsch fuels (higher alkanes), etc
  - Reaction: $\text{H}_2 + \text{CO} \rightarrow \text{H}_2\text{O} + \text{CO}_2$
  - Energy change: $-41 \text{ kJ/mol}$

- **Carbon-containing fuels**

Reaction enthalpies calculated for gaseous products at standard conditions.
Sustainable Aviation Fuel

Input: surplus wind electricity followed by P2G
Output: synthetic methane for long-term, large-scale storage
Feedstock: CO\textsubscript{2} and H\textsubscript{2}O
Storage capacity Dutch gas system 552TWh
Recycling CO\textsubscript{2} emitted by re-capture from air

Research challenge: raise TRL from 2 to 5
CO\textsubscript{2} direct air capture, Efficient CO\textsubscript{2} and H\textsubscript{2}O splitting by electrolysis and plasmolysis, Gas separation

Sustainable aircraft grade Kerosene from Water and Air powered by Renewable Electricity, through splitting CO\textsubscript{2}, formation Syngas and Fischer-Tropsch synthesis.
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/cm²)
  – Low hydrogen output pressure (< 30bar)
  – Safety (caustic electrolyte)

• **PEM** (polymer electrolyte membrane), pre-commercial
  – Power density ~1W/cm²
  – 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 and pressure 50-100 bar)
  – Co-electrolysis $\text{H}_2\text{O}$ and $\text{CO}_2$
  – Degradation under high current density operation
Principle of Solid Oxide Electrolysis Cell

External dc voltage pumps $O^{2-}$ ions from porous **cathode** (Ni/YSZ) through dense solid **electrolyte** (YSZ = Yttrium Stabilised Zirconium) to porous **anode** (LSM/YSZ = La$_{1-x}$Sr$_x$MnO$_3$/YSZ)
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)

30 kW @ 915 MHz
Out of equilibrium $T_{\text{vib}} > T_0$ chemistry

**Chemical reaction scheme**

- $\text{CO}_2 \rightarrow \text{CO} + \text{O}$  \hspace{1cm} ($\Delta H = 5.5 \text{ eV}$)
- followed by reuse energetic O radical
- $\text{CO}_2 + \text{O} \rightarrow \text{CO} + \text{O}_2$  \hspace{1cm} ($\Delta H = 0.3 \text{ eV}$)
- Net
- $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$  \hspace{1cm} ($\Delta H = 2.9 \text{ eV}$)

**Efficiency to be increased by**

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

**Arrhenius/Fridman:**

Activation energy reduced by vibration energy

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

$\lambda = 4.24 - 4.28 \mu\text{m} (750 \text{ THz}, \tau = 14 \text{ fs})$
Experimental Results

CO and O₂ production as function RF Power

![Graph showing the production of CO and O₂ as a function of RF power.](image)

- Linear relationship between CO amount and RF power: \( y = 3.07E-04 \times x \)
- Linear relationship between O₂ amount and RF power: \( y = 1.54E-04 \times x \)

![Graph showing energy efficiency and energy per CO₂ molecule.](image)
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%
• CO 3\textsuperscript{rd} positives, 4\textsuperscript{th} positives, Angstrom and triplet bands identified.
• CO line intensity increases linear with power in supersonic regime
Experimental Results

![Energy efficiency vs. reduced E-field graph](image)

- Type I
- Type II
- Type III

**Energy Efficiency**

- **Energy per Charge** $E/n \times 10^{-16}$ V cm$^2$
- **Efficiency** $\eta$ [%]
Experimental Results

particle conversion vs. reduced E-field

E/n [10^{-16} V cm^2]
Separation of CO, O₂, CO₂ mixture

SOC oxygen separation membrane integrated with plasma reactor. Lanthanum based perovskites show superior oxygen flux. YSZ or SDC electrolyte sandwiched between perovskite electrodes: LSM/YSZ or LSCF oxygen electrode, Ni/YSZ or LSCM plasma electrode. Plasma sheath electric field meets with electrode polarisation critical I/F.
Conclusions

- P2X can provide vast seasonal energy storage capacity and flexibility of supply from Renewable Electricity though sector Coupling
- P2X enables distributed small scale production plants (Ex. Ammonia or CO)
- P2X-CCU enables a CO$_2$ neutral fuel cycle based on hydrocarbons and existing infrastructure
- Technical challenge: innovation in CO$_2$ splitting and CO-O$_2$ separation
- Economic challenge: cost reduction, business case expected to emerge around 2030, when cost of CO$_2$ reach € 200/ton
Future Energy System

• **Next 20 years**: fundamental shift in the way energy is generated, stored, delivered, valued and purchased

• Critical element: conversion renewable electricity into fuel

• Coupling of renewable electricity to the other 80% of CO₂ emitting sectors, including low and high temperature heat, transportation and chemical feedstock

• Incremental improvement: role of Industry

• Novel concepts, game changers: role of fundamental energy research

• Driver: CO₂ reduction targets, International (UNFCCC), EU directive (RED), National Policy. Targets for 2030 and 2050 are set, but

• **Road to get there is largely unchartered**
End of lecture

Thank you for your attention!

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