

# Re-use of CO2 and intermittent renewables





# Re-use of CO<sub>2</sub> and intermittent renewables

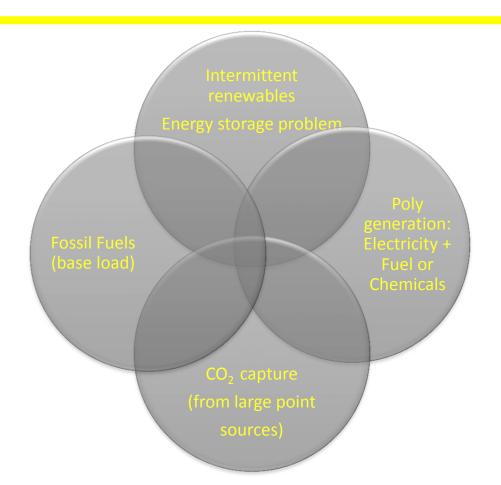
Wim Haije ECN/TUD
Stephane Walspurger ECN
Hans Geerlings TUD

CCCC 2013 05-06-2013

www.ecn.nl



## **Current situation**



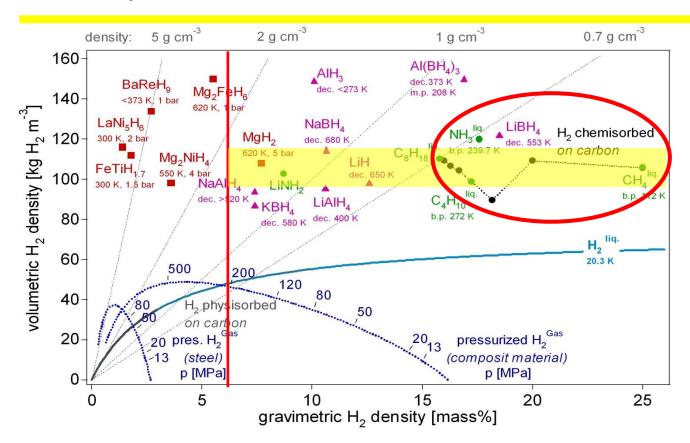


# Variability sustainable sources

- At present, countries like Germany and Spain have > 30 % power from intermittent sources, and are no longer able to "store" it in the grid when demand is low.
- IGCC installations cannot run in partial load
- In general this kind of large scale utilities, if they can be run at lower load, need quite some time for ramping up and down.
- Storage in the form of electricity on this scale is very difficult
- Storage in the form of hydrogen on this scale is not feasible.
- The gas grid (if present) has some capacity but H<sub>2</sub> concentrations are typically 10 % max
- "Wish storage material": something like gasoline!

# High gravimetric & volumetric density



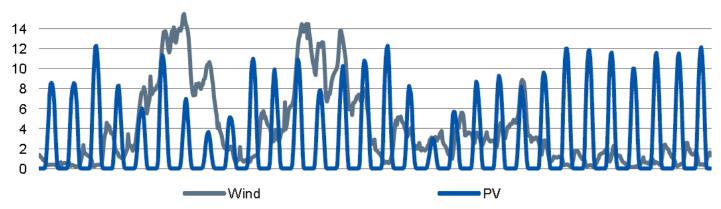




# Variability/Intermittency

### Fluctuations in wind and solar-generated electricity

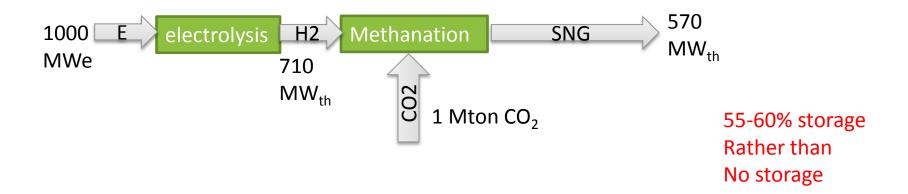
Hourly feed-in values (GW), Germany, September 2011



Source: ENTSO-E



# Storage-only efficiency

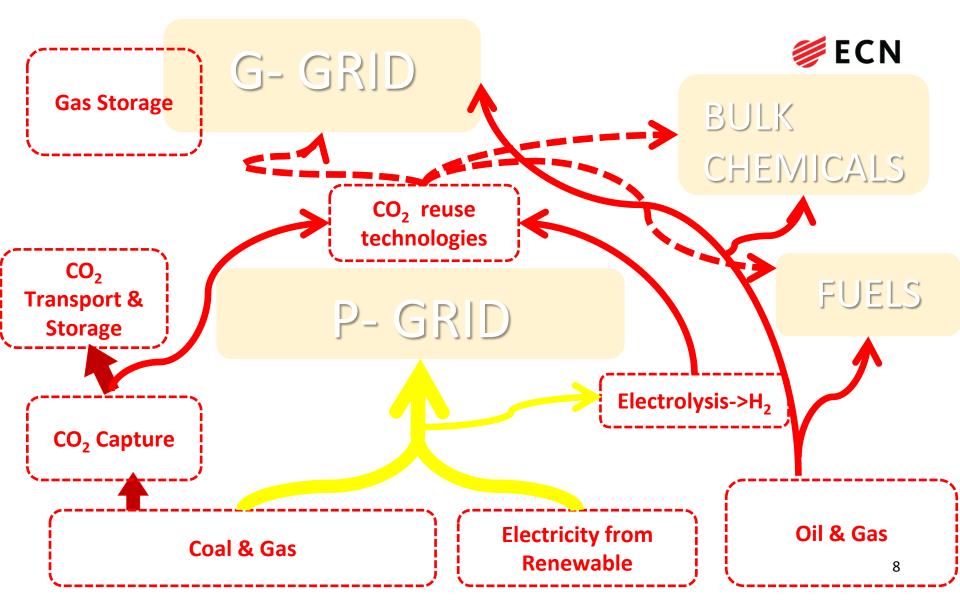




# Why CO<sub>2</sub> re-use/solar fuels

- CO<sub>2</sub> is an enabler for hydrogen transport and storage (energy carrier)
- CO<sub>2</sub> is available to answer the intermittent H<sub>2</sub> production from renewables
   (CO<sub>2</sub> is available continuously from a variety of sources)
- Chemicals/Fuels from CO<sub>2</sub> are a means to sustain a fossil fuel based economy (infrastructure, plants etc..) during the transition towards a completely renewable energy based economy (using <u>carbon</u> at least twice)
- CO<sub>2</sub> emissions are reduced by saving primary resources and optionally, depending on regional configuration, CO<sub>2</sub> storage/mineralisation
  - In chemical products (minor)
  - In energy systems (significant)

CO<sub>2</sub> re-use potential is about two orders of magnitude less than produced by the power production





Chemistry and technology



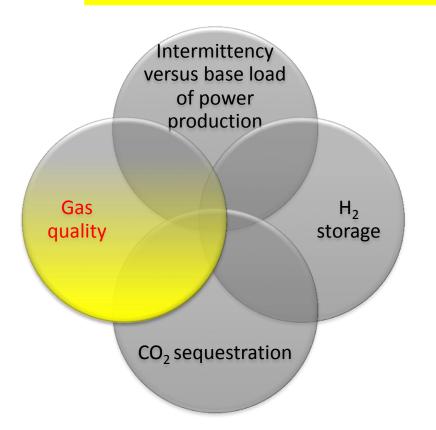
# Chemical products

- Main chemicals with a "green colour" are polymers (40-50w% CO<sub>2</sub>)
  - Polycarbonates and poly(ester-co-carbonate)s (DSM)
  - Polypropylene carbonate (PPC) and CO<sub>2</sub> polyols (BASF, Novomer)
  - Polyethylene carbonate (PEC) (Bayer)
- Bio Based
  - Food for bacteria and microalgea (final product Diesel)
- Artificial leaves
  - Formic acid (Panasonic)
- Inorganics
  - Solvay process (alkali carbonates)
  - Cement/concrete

Although the polymer market is huge, these activities will not have significant impact on the CO<sub>2</sub> levels in the atmosphere.



# Coupling of H<sub>2</sub> to CO<sub>2</sub>



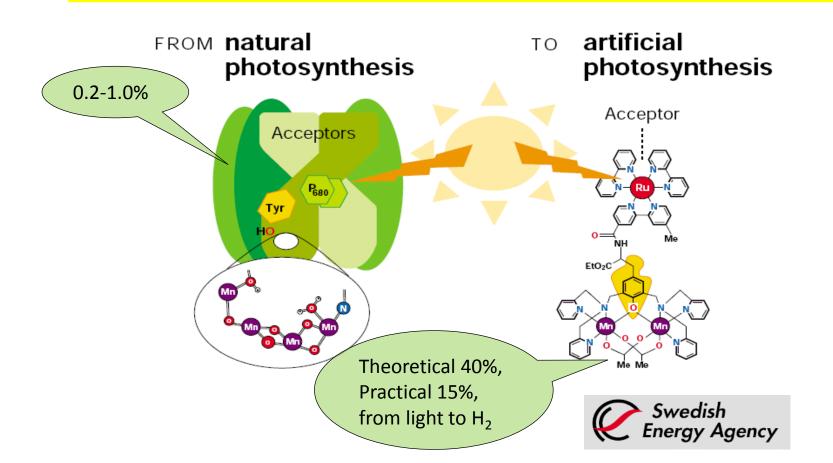
- Gas from high CO<sub>2</sub> content gas fields
  - $\triangleright$  Up to 60% CO<sub>2</sub>
- Digester gas is produced at small scale by manure digestion at farms.
  - Digester gas consists of 50 to 75%
     methane and 25 to 50% CO<sub>2</sub>
- Producer gas from biomass gasification
  - Biomass has higher carbon content than methane, which means that either CO<sub>2</sub> has to be removed from the gas or hydrogen has to be added.

#### But also

 Pure CO<sub>2</sub> from capture plants, industrial point sources etc..

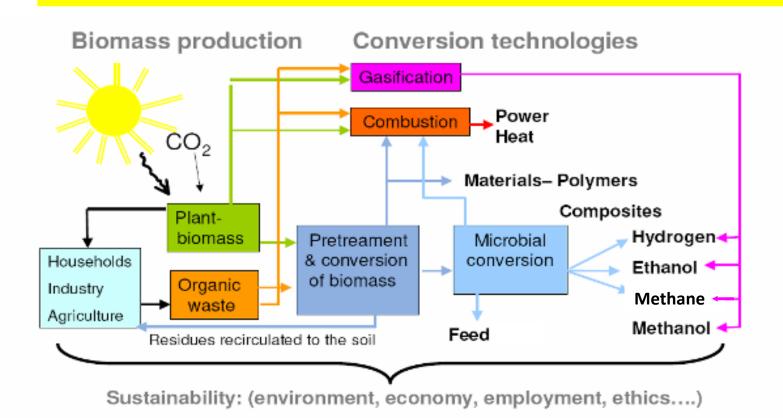


### How nature does it



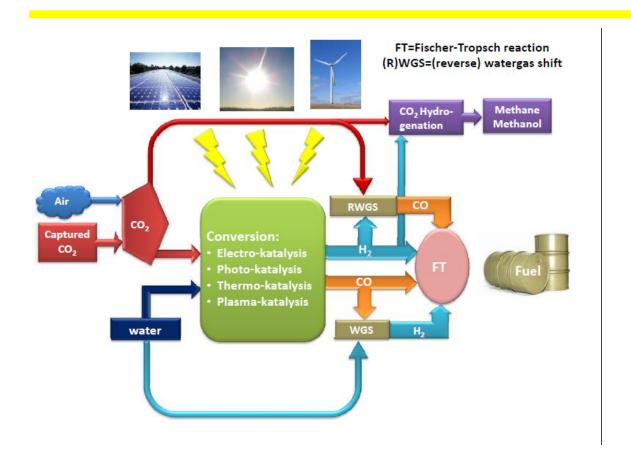


## What we do with it





## Can we do the same trick?





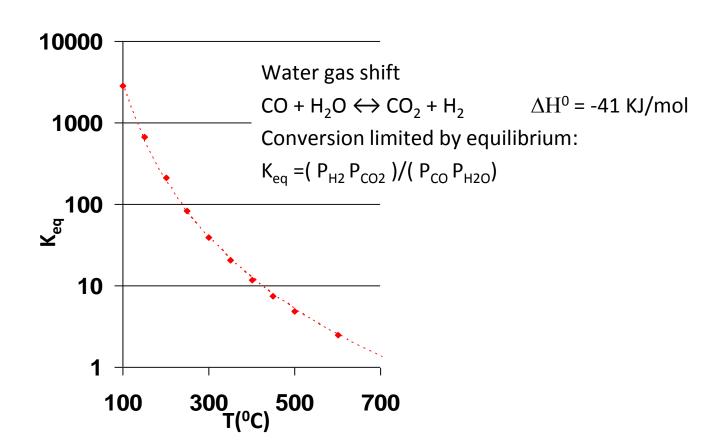
## Yes we can!.....

Reaction	ΔΗ	
	kJ/mol	
$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-167.0	methanation
$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-206.0	methanation
$CO_2 + H_2 \leftrightarrow CO + H_2O$	+41.3	reverse water gas shift reaction
$nCO + 2nH_2 \rightarrow -(CH_2)n - + nH_2O$	-126.0	Fischer-Tropsch
$CO_2 + 3H_2 \leftrightarrow H_2O + CH_3OH$	-49.6	methanol synthesis
$CO + 2H_2 \leftrightarrow CH_3OH$	-90.8	methanol synthesis

...... because CO<sub>2</sub> is always in equilibrium with other components and just needs a little help to go beyond that equilibrium!

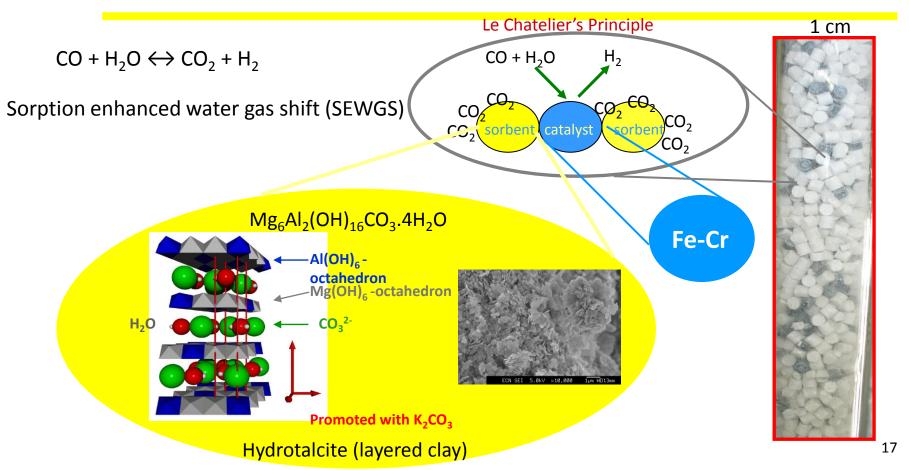


## **Fundamentals**





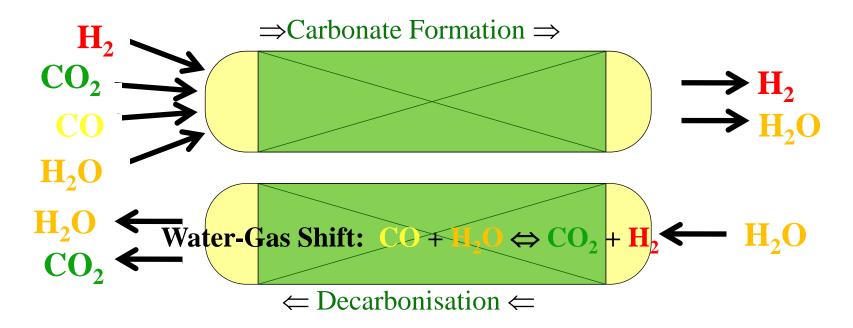
# How to produce pure H<sub>2</sub> and CO<sub>2</sub>?





# SEWGS the process

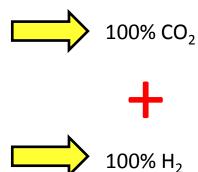
High temperature (400°C), high pressure (35 bar) production of H<sub>2</sub> from Syngas.



# SEWGS and what you can learn from it.....







Thermodynamics @ 400°C: 34% conversion

Two patent applications

- Sorbent
- Process for CO<sub>2</sub>/H<sub>2</sub>S separation

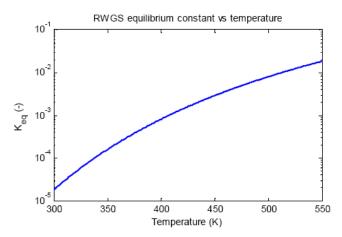


# Consequently:

 The reverse of the previous, the reverse sorption enhanced WGS, should work as well:

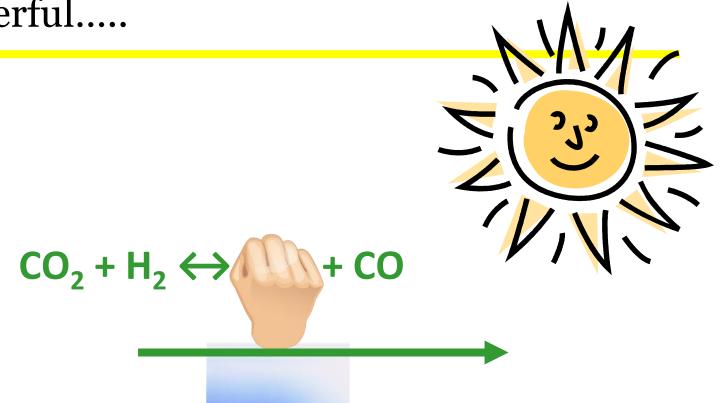
$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

 Idea: take out the water, yielding full conversion to CO, and with more H<sub>2</sub> any syngas composition can be tuned!!



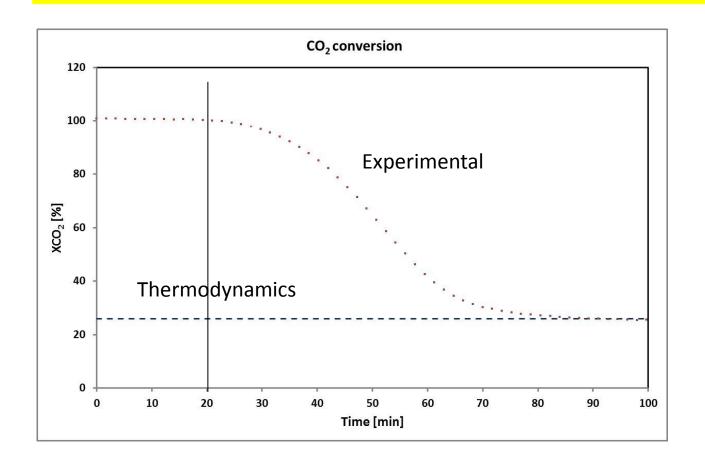


# Wonderful.....



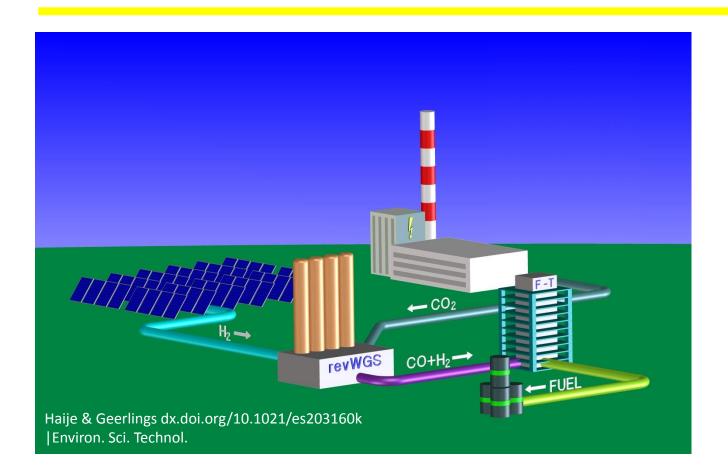


# 100% conversion!!





# Artist impression





# Efficiency estimate

- PV State of the Art :19%.
- High pressure electrolysis State of the Art: 85%
  - ► Solar hydrogen: 16%.
- Including a mismatch between photo-voltage and electrolysis potential: this number reduces to 13%.
- SERWGS: 90% (The only new technology in the process!)
- Fischer-Tropsch : 70%
  - ► Overall efficiency: Solar to fuels : 8.2%
- Including Carbon Capture penalty of 150 kJ/mol of CO<sub>2</sub>: 7.7%
- Alternative routes generally 1-2 orders of magnitude lower!!



# Economic viability



# Simple cost estimation

Equation

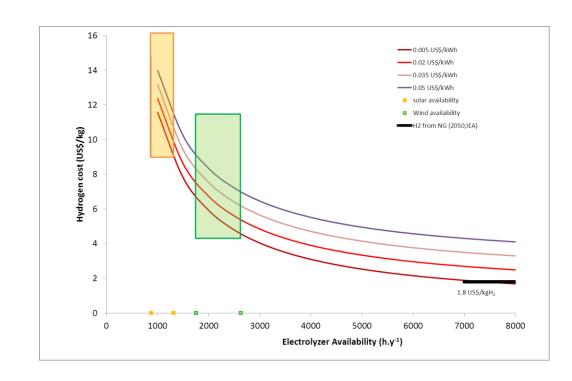
$$H_2 \cos t (Eur/kg) = Capital Cost + Power Cost$$
 $H_2 produced$ 

- Capital Cost:
  - Investment Cost Electrolyzer 700US\$/kW; CRF 20%; ISBL=2OSBL
- H<sub>2</sub> production:
  - Conversion power to H<sub>2</sub>: 62% efficiency, at 100-30% load.
- Power Cost:
  - 0 to 5 ctUS/kWh



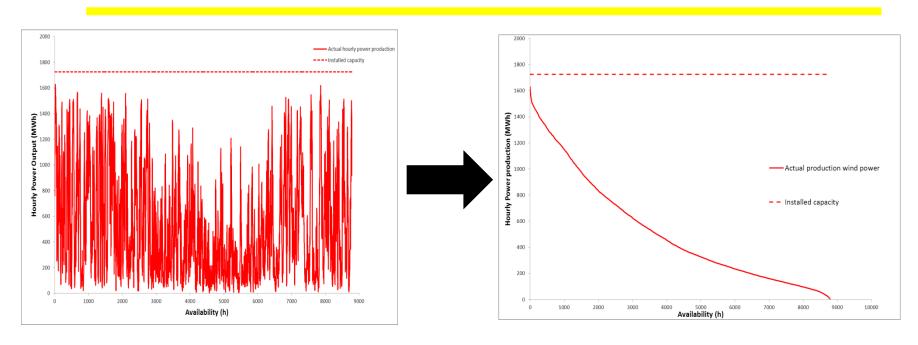
# Hydrogen costs from water electrolysis

- At high availability, H<sub>2</sub> cost mostly sensitive to power costs.
- At availability < 4000h cost increase due to capital intensive electrolyzer (low depreciation)
- Solar capacity factor around 10-15%
- Wind capacity factor 20-30%
- Still way above H<sub>2</sub> from fossil fuels (1.8U\$\$/kg, IEA forecast for 2050)





# Real case (Wind generation)



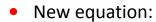
- Raw data sorted to determine electrolyzer's size
- Hourly Fluctuation neglected in first approach
- Source data: <a href="http://www.ieso.ca/imoweb/marketdata/windpower.asp">http://www.ieso.ca/imoweb/marketdata/windpower.asp</a> (Ontario, Canada)



# Real case (Hydrogen from Wind)

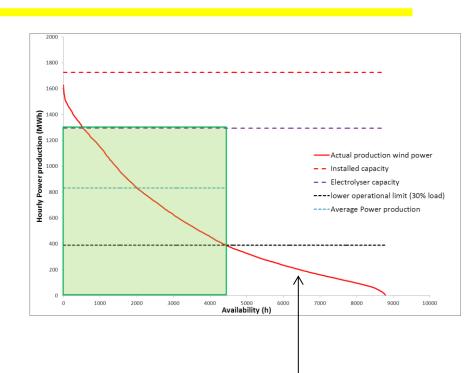
### • Assumptions:

- Electrolyzer capacity = 75% installed wind capacity
- Electrolyzer operational window at 62% efficiency: 100%-30% load.
- Surplus sold as power to the grid
- Downtime power sold to the grid
- Hydrogen Availability: 4440 hours/y
- Average power used: 831 MW
  - Equal to 64% of the electrolyzer capacity



**Power production Revenues** 

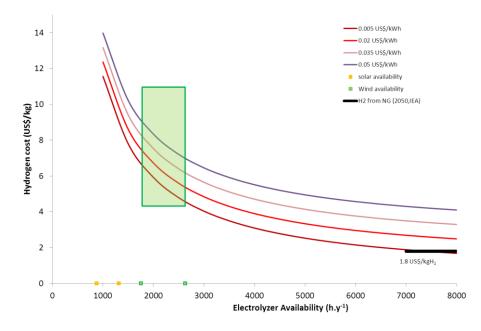
H<sub>2</sub> produced \* 0.64





# Real case (Hydrogen cost)

- Electrolyzer operation extended
  - From 1700-2700h/y-1 to 4000-5000h
- Electrolyzer average operation at 64% part-load (100-30%)
  - How about true efficiency?
- Number of start-up/shut down high
  - 96 interruptions / year (Power production below electrolyzer 30% capacity)
- Improvements:
  - Mixed renewable sources (wind+solar+hydro)?
  - Flexible modular electrolyzers
  - Higher Efficiency vs. load





# Real case (SNG cost)

### • Assumptions:

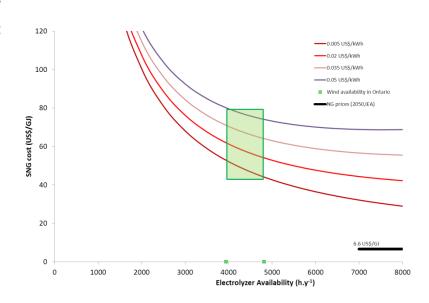
- Electrolyzer capacity = 75% installed wind capacity
- Electrolyzer operational window at 62% efficiency: 100%-30% load.
- Surplus sold as power to the grid
- Downtime power sold to the grid
- Power to SNG Availability: 4440 hours/y
- Average power used: 831 MW (64% electrolyzer capacity)

### SNG plant:

- 95% efficiency
- Investment costs: 40US\$/kWe electrolyzer installed
- SNG cost: from 45-80 US\$/GJ, 10 times NG prices

### Complementary questions:

SNG train response to part-load and shut down





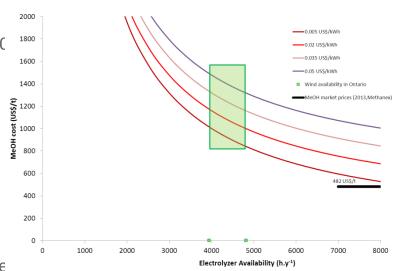
# Real case (MeOH cost)

### • Assumptions:

- Electrolyzer capacity = 75% installed wind capacity
- Electrolyzer operational window at 62% efficiency: 10
   30% load.
- Surplus sold as power to the grid
- Downtime power sold to the grid
- Power to SNG Availability: 4440 hours/y
- Average power used: 831 MW (64% electrolyzer capacity)

### MeOH plant:

- 95% efficiency
- Investment costs: 60US\$/kWe electrolyzer installe
- MeOH cost: from 800-1500 US\$/t, 2-3 times MeOH prices from NG
- Complementary questions:
  - MeOH conversion train response to part-load and shut down





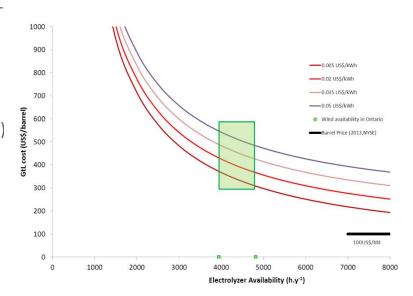
# Real case (GtL cost)

### • Assumptions:

- Electrolyzer capacity = 75% installed wind capacity
- Electrolyzer operational window at 62% efficiency: 100%-30% load.
- Surplus sold as power to the grid
- Downtime power sold to the grid
- Power to SNG Availability: 4440 hours/y
- Average power used: 831 MW (64% electrolyzer capacity)

### GtL plant:

- 95% efficiency
- Investment costs: 60US\$/kWe electrolyzer installed (150000US\$/tpd installed, 40% of mini GtL plant capital costs)
- GtL cost: from 300-550 US\$/barrel, 3-5 times oil prices
- Complementary questions:
  - GtL conversion train response to part-load and shut down





Wrap-up



# Take home messages

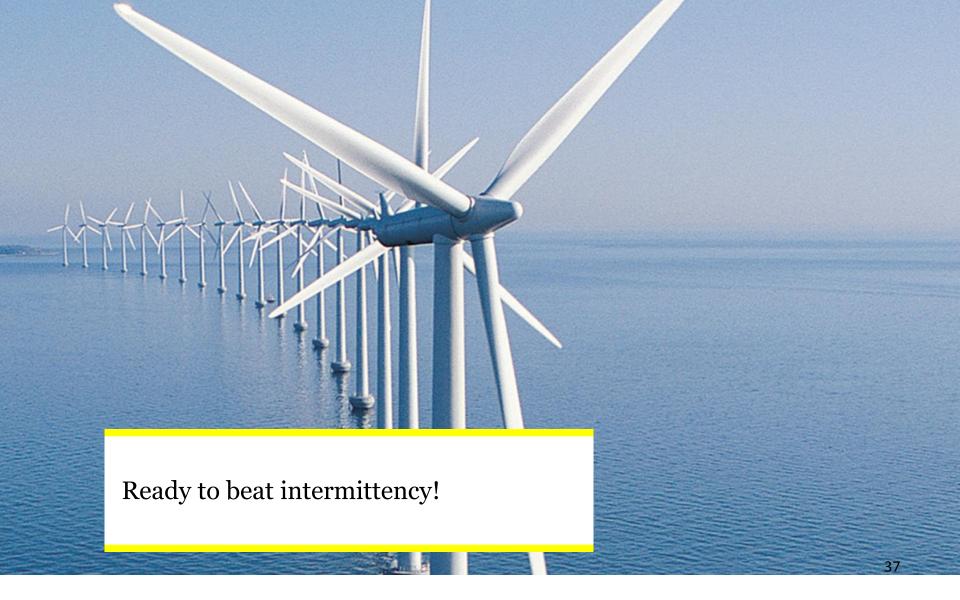
- Hydrogen will not prevail as sole energy carrier besides electricity
- CO<sub>2</sub> can be pushed into reaction with a.o. hydrogen (separation enhancement)
- Synthetic fuels are a logical route in intermittent demand/supply energy systems on large scale provided they can cope with intermittency
- There are many routes to chemicals and fuels
- There are clearly options on industrial scale in the near future
- What you don't take out of the earth's crust will not burn

# Developments in the Netherlands



- Program DIFFER (Dutch institute for fundamental energy research)
  - Four themes
    - Photons related
    - Out of equilibrium processes (plasmas)
    - Bio –mimetic photo systems
    - Downstream chemical processing

- Follow-up of CATO2
  - Capture and re-use and storage
  - Main message CO<sub>2</sub> is not waste but feedstock
  - Small impact: chemicals in industry
  - Big impact: energy storage related to intermittent energy sources





# Thank you for your attention

This research was performed in close cooperation with our Shell partners:

Mary Bastian, Donald Reinalda and Joost Smits.

#### **ECN**

Westerduinweg 3 P.O. Box 1

1755 LE Petten 1755 ZG Petten
The Netherlands The Netherlands

T +31 88 515 49 49 info@ecn.nl F +31 88 515 44 80 **www.ecn.nl** 

