Synthetic Fuels and Carbon Dioxide Capture From Air

Klaus S. Lackner
Columbia University

February 2011

After initial work at both Los Alamos and Columbia

GRT[*] demonstrated air capture in Tucson in 2007[**]

Klaus Lackner
Allen Wright
Gary Comer

Proof of principle

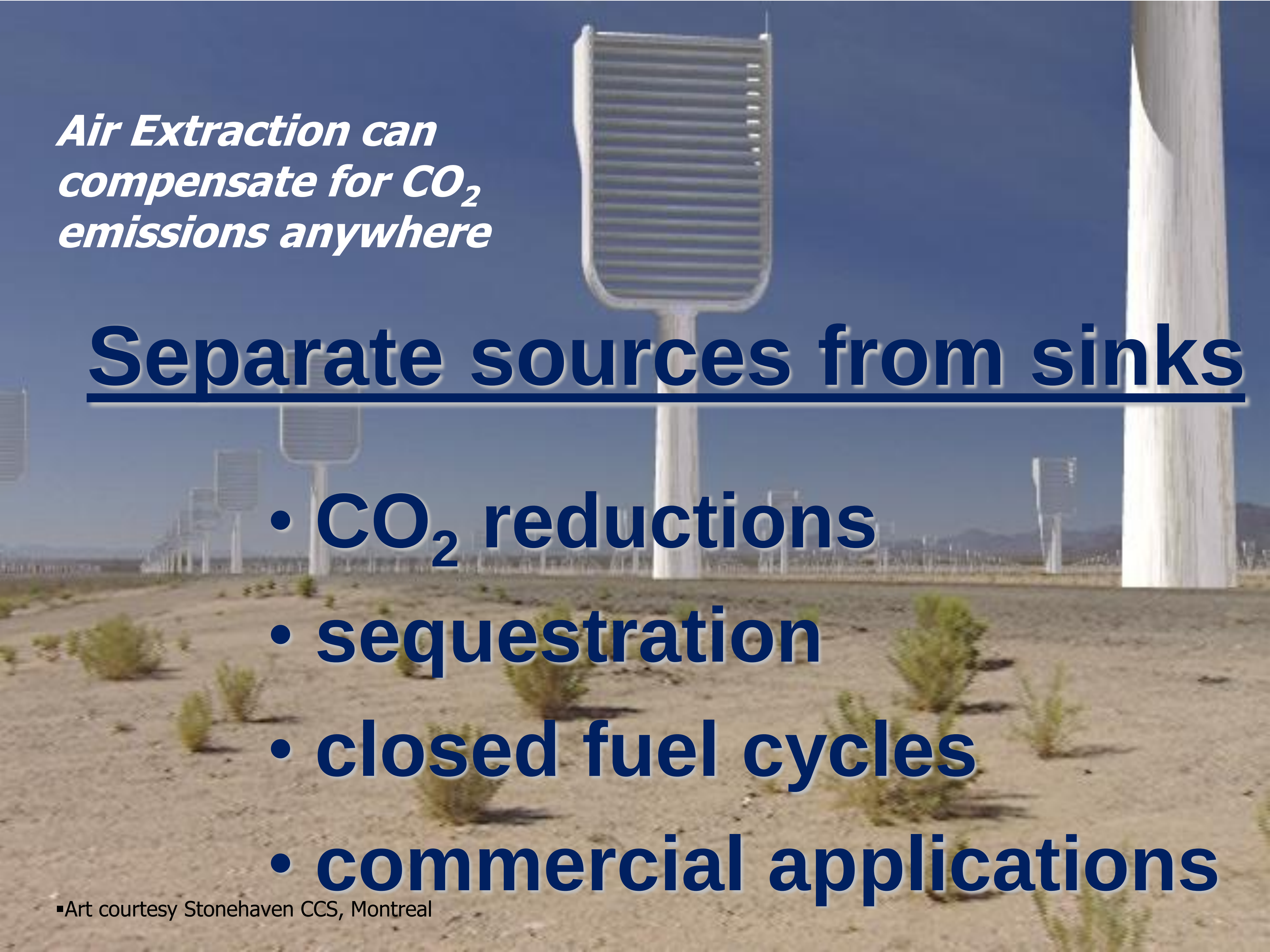
☑

---

[*] Now Kilimanjaro Energy, Inc.

[**] KSL is an advisor the company

INTRODUCTION



Air Extraction can compensate for CO_2 emissions anywhere

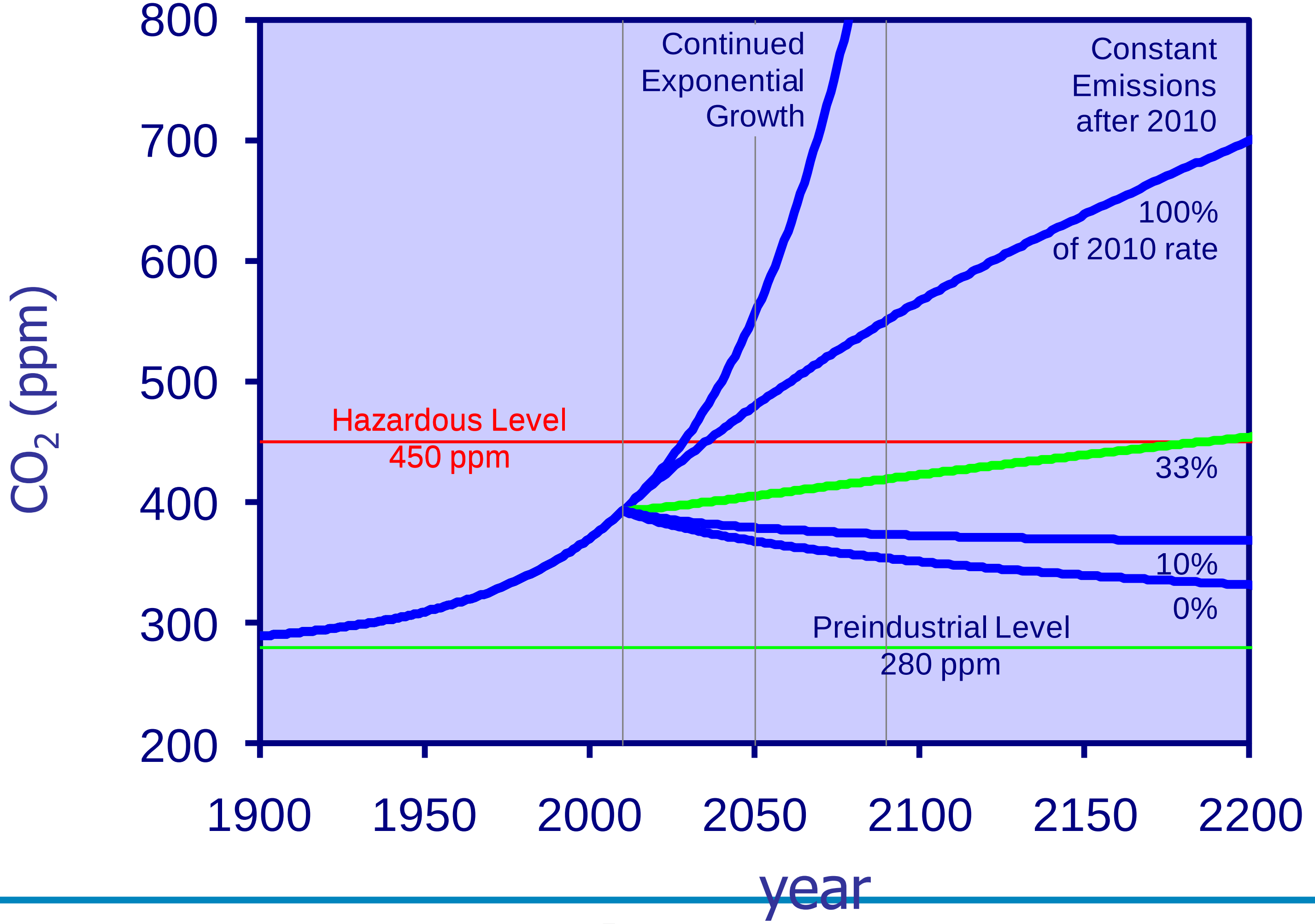
Separate sources from sinks

- CO_2 reductions
- sequestration
- closed fuel cycles
- commercial applications

▪Art courtesy Stonehaven CCS, Montreal

Environmental Limits – Not Resource Limits

Stabilize CO_2 concentration – not CO_2 emissions



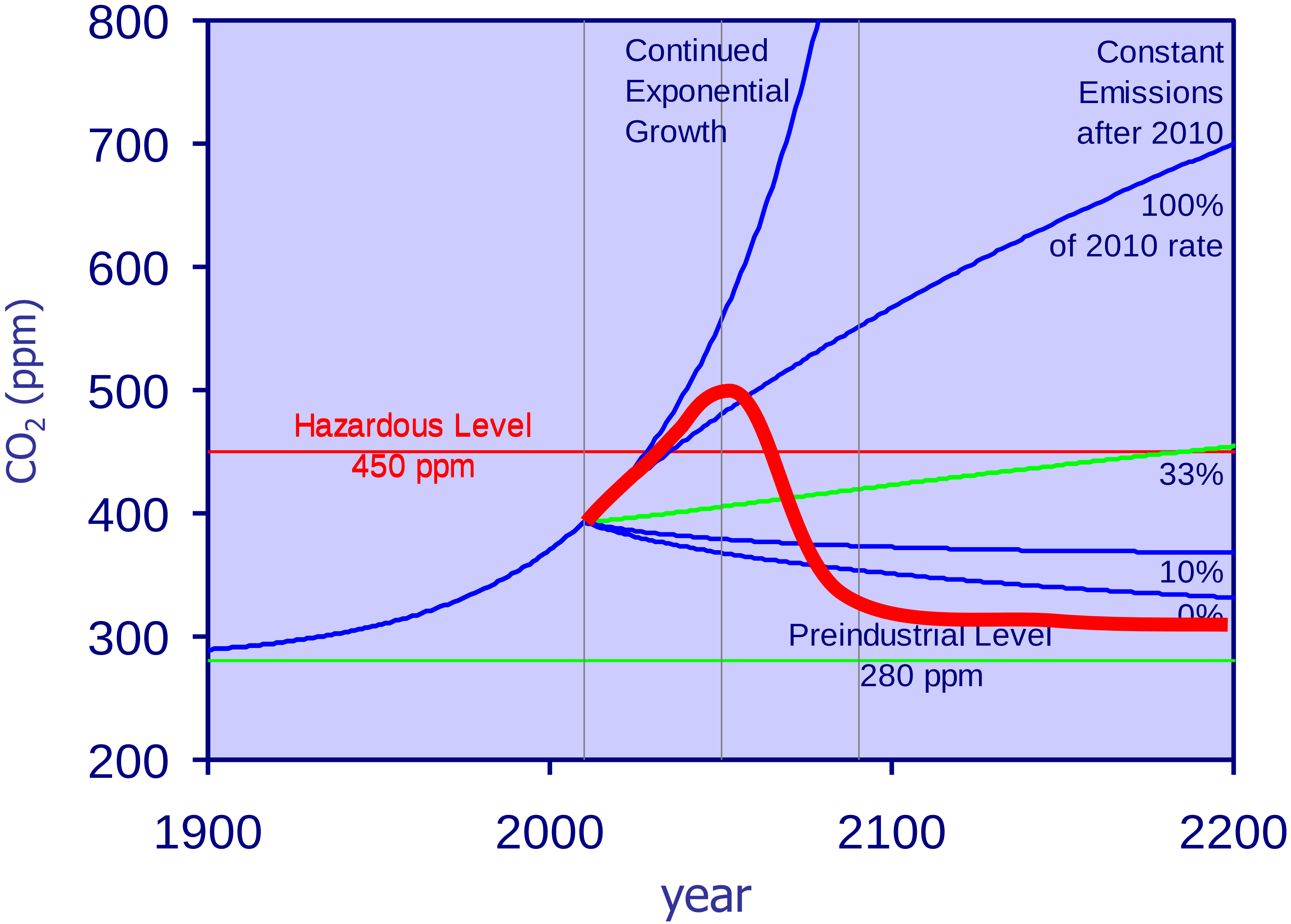
The personal carbon allowance

~ 30 tonnes for every person will reach 450 ppm

Total permanent allotment

Picture from emercedes online blog: http://www.emercedesbenz.com/Aug08/08_001327_Mercedes_Benz_Econic_Semi_Trailer_Tanker_Trucks_Enter_Service_At_London_Farnborough_Airport.html

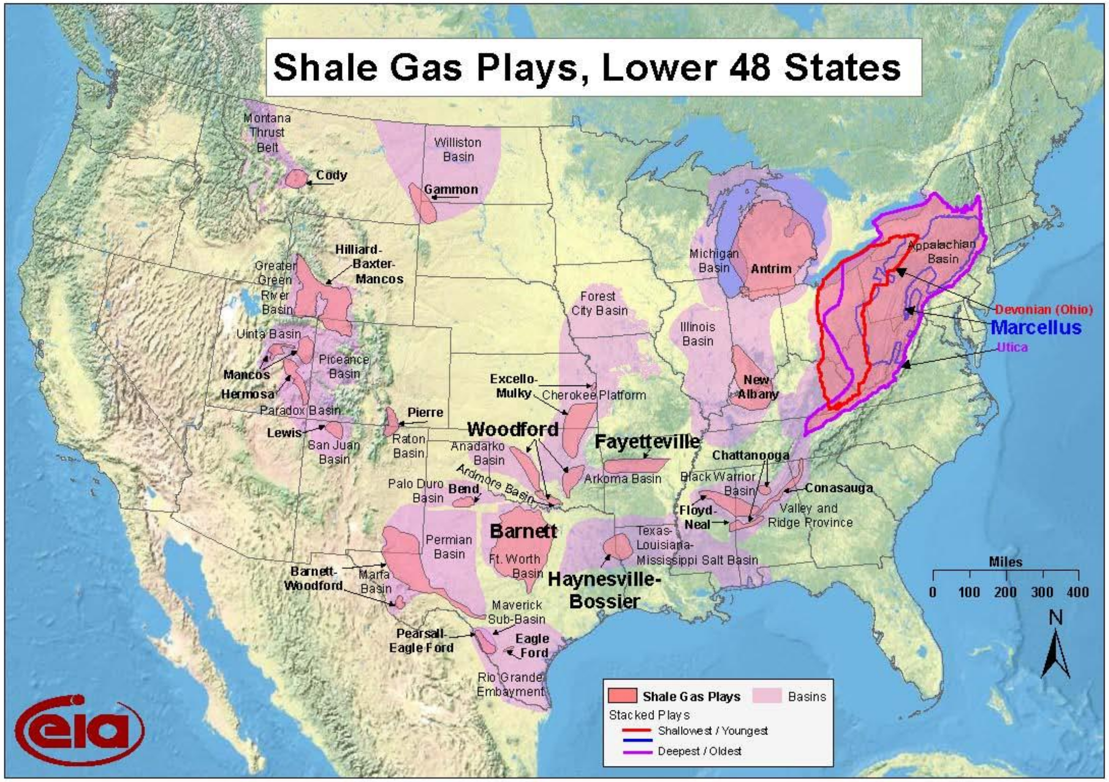
Coming back down



Fossil fuels are plentiful

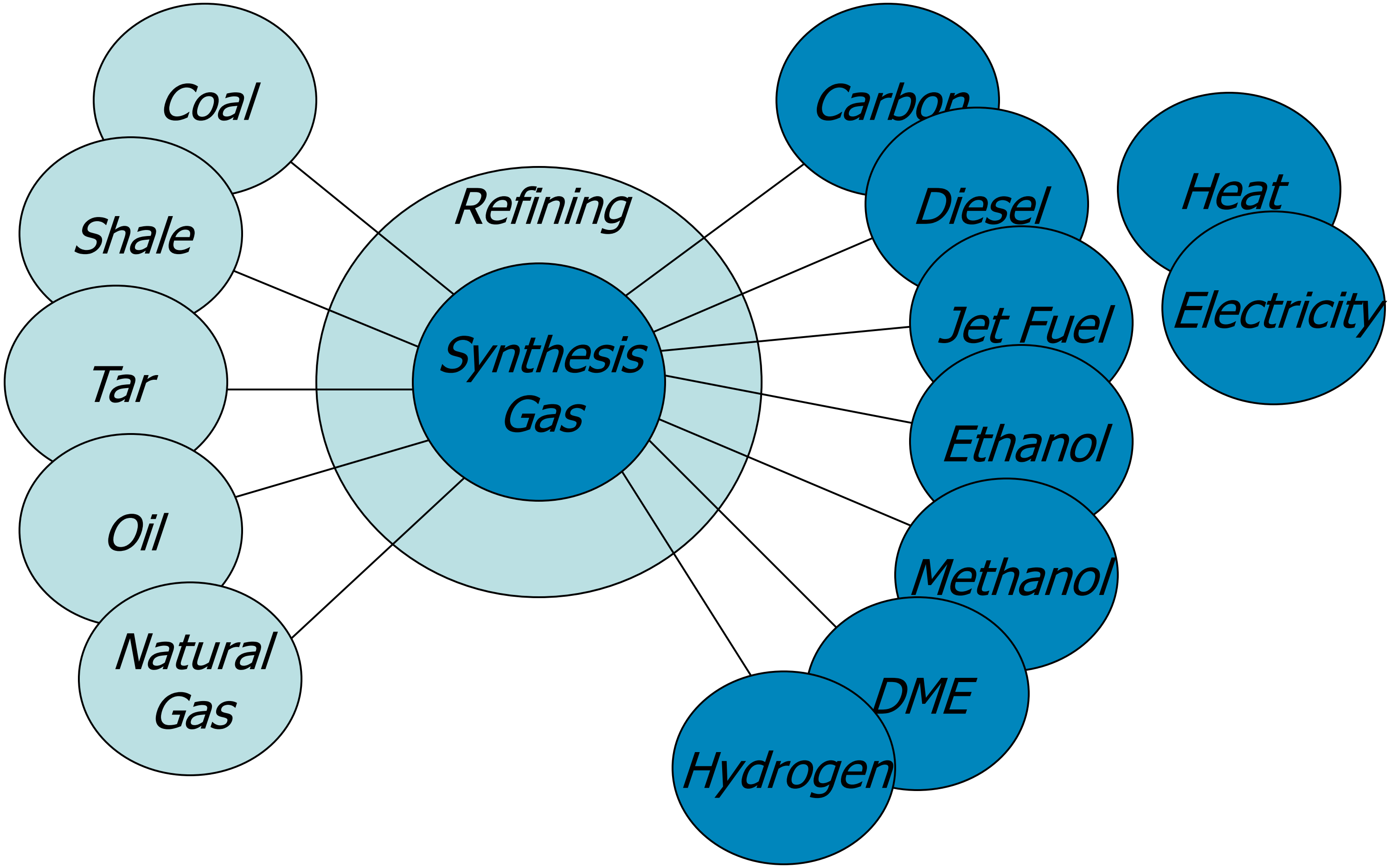
- Coal resources alone could be 3000 to 5000 Gt C
  - 400 Gt consumed since 1800
  - annual production of 8 Gt/yr of fossil carbon

- Natural gas reserves are growing rapidly
- Gas to liquid could support transportation sector



Source: Energy Information Administration based on data from various published studies.
Updated: March 10, 2010

Fossil fuels are fungible …



… and they are not running out

Without Carbon Capture and Storage fossil fuels will have to be phased out

The Big Three Energy Options

Air capture has a role in all

- **In Carbon Capture and Storage**
  - Capture of last resort
    - Cars, air planes, and “fugitive” emissions
- **In geo-engineering**
  - Reduction of atmospheric CO_2 concentration
  - Stabilizing CO_2 at the desired level
- **In non-fossil energy infrastructures**
  - Energy storage
  - Transportation fuels

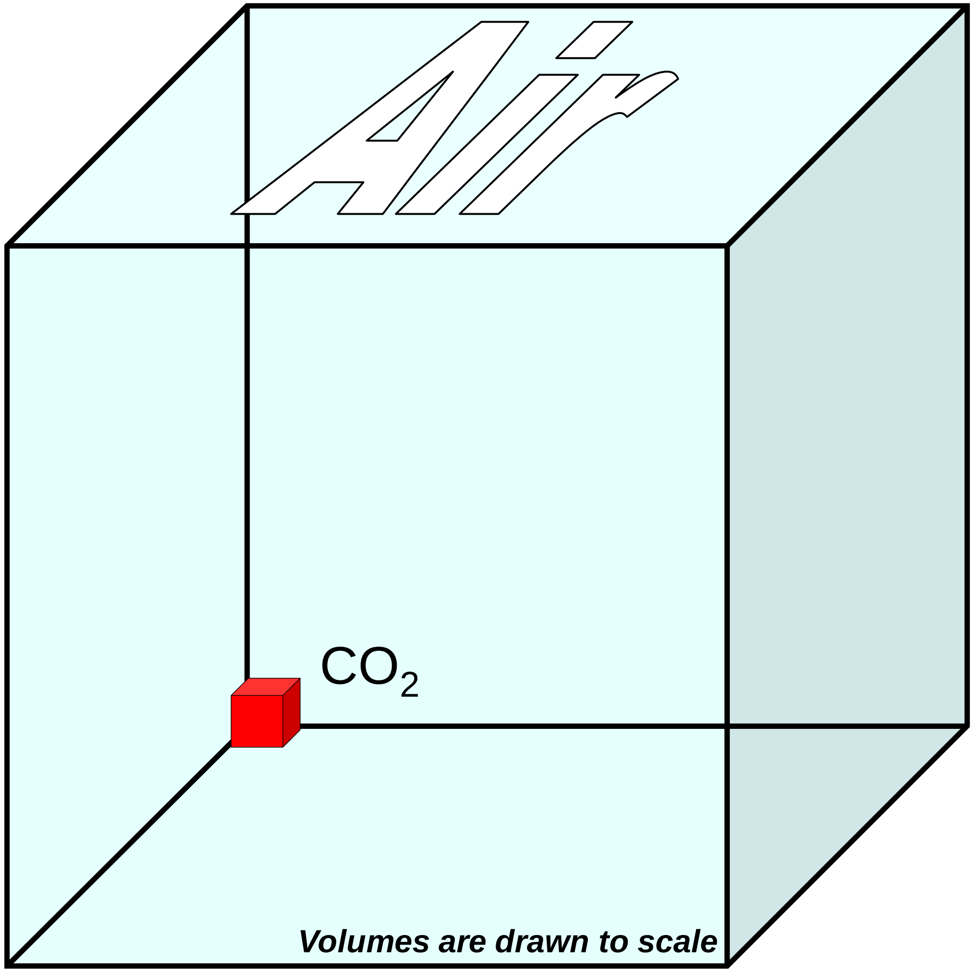
Liquid fuels vs. Batteries

- 2 orders of magnitude higher energy density in fuel
- CO_2 once emitted stays in the air unless captured

Summary

AIR CAPTURE TECHNOLOGY

CO_2 Content of Air



1 m^3 of Air

40 moles of gas, 1.16 kg

wind speed 6 m/s

$$\frac{mv^2}{2} = 20\,\mathrm{J}$$

0.016 moles of CO_2

produced by 10,000 J of gasoline

Wind energy – Air capture

Wikipedia picture

artist's rendering

Wind energy
~20 J/m^3

CO_2 combustion equivalent in air

10,000 J/m^3

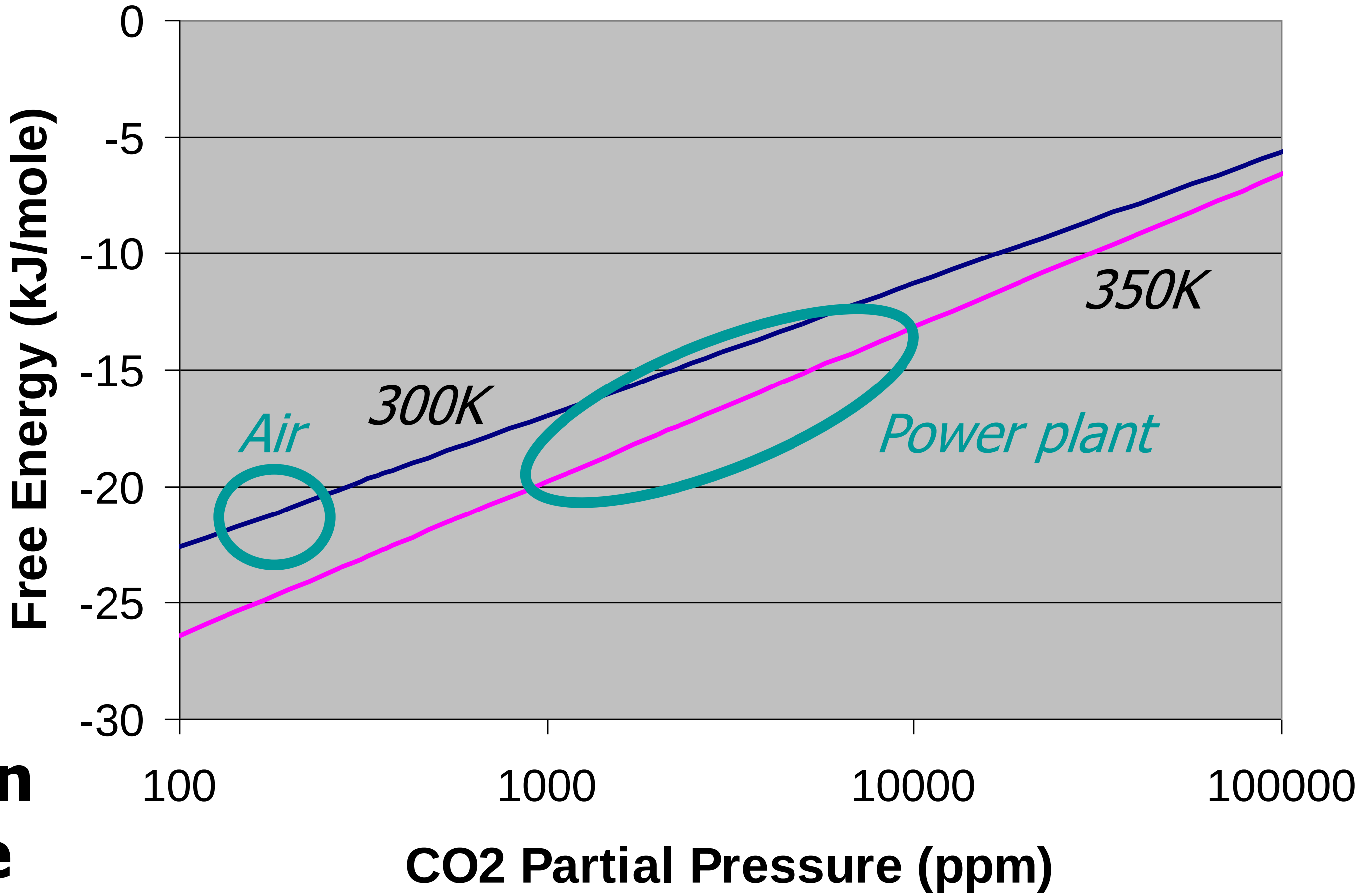
Passive contacting of the air is inexpensive

Air collector reduces net CO_2 emissions much more than equally sized windmill

Sorbent Strength

depends logarithmically on CO_2 concentration at collector exit

$$\Delta G = RT \log P$$

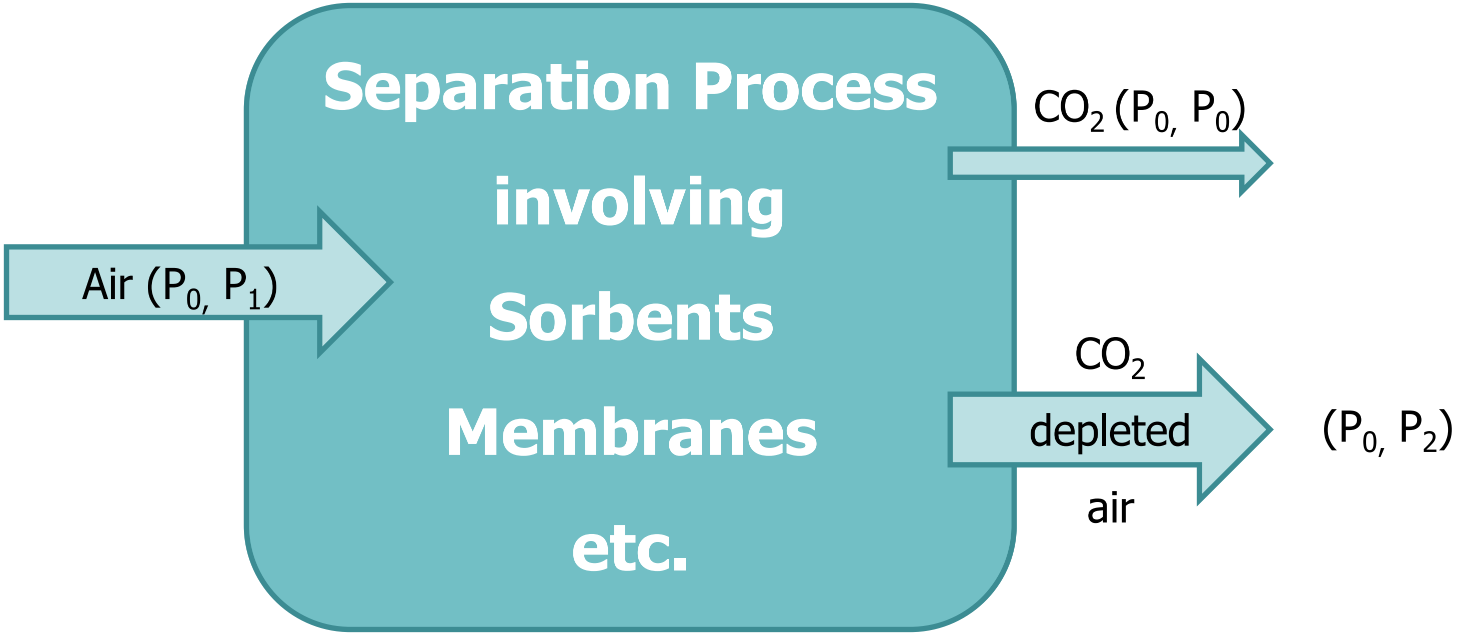


Sorbent regeneration is expensive

Separation of a gas stream

Theoretical minimum free energy requirement for the regeneration is the free energy of mixing

Gas pressure P_0
CO_2 partial pressure P_x
Denoted as $(P_{0,} P_x)$



Separation Process

involving

Sorbents

Membranes

etc.

Air $(P_{0,} P_1)$

CO_2 $(P_{0,} P_0)$

CO_2
depleted
air

$(P_{0,} P_2)$

$$\Delta G = RT\left(\left(\frac{P_0 - P_2}{P_1 - P_2}\right)\frac{P_1}{P_0}\ln\frac{P_1}{P_0} - \left(\frac{P_0 - P_1}{P_1 - P_2}\right)\frac{P_2}{P_0}\ln\frac{P_2}{P_0} + \left(\frac{P_0 - P_1}{P_0}\right)\left(\frac{P_0 - P_2}{P_0}\right)\frac{P_0}{P_1 - P_2}\ln\frac{P_0 - P_1}{P_0 - P_2}\right)$$

Specific irreversible processes have higher free energy demands

The limit of skimming

In this limit: $P_2 \to P_1$

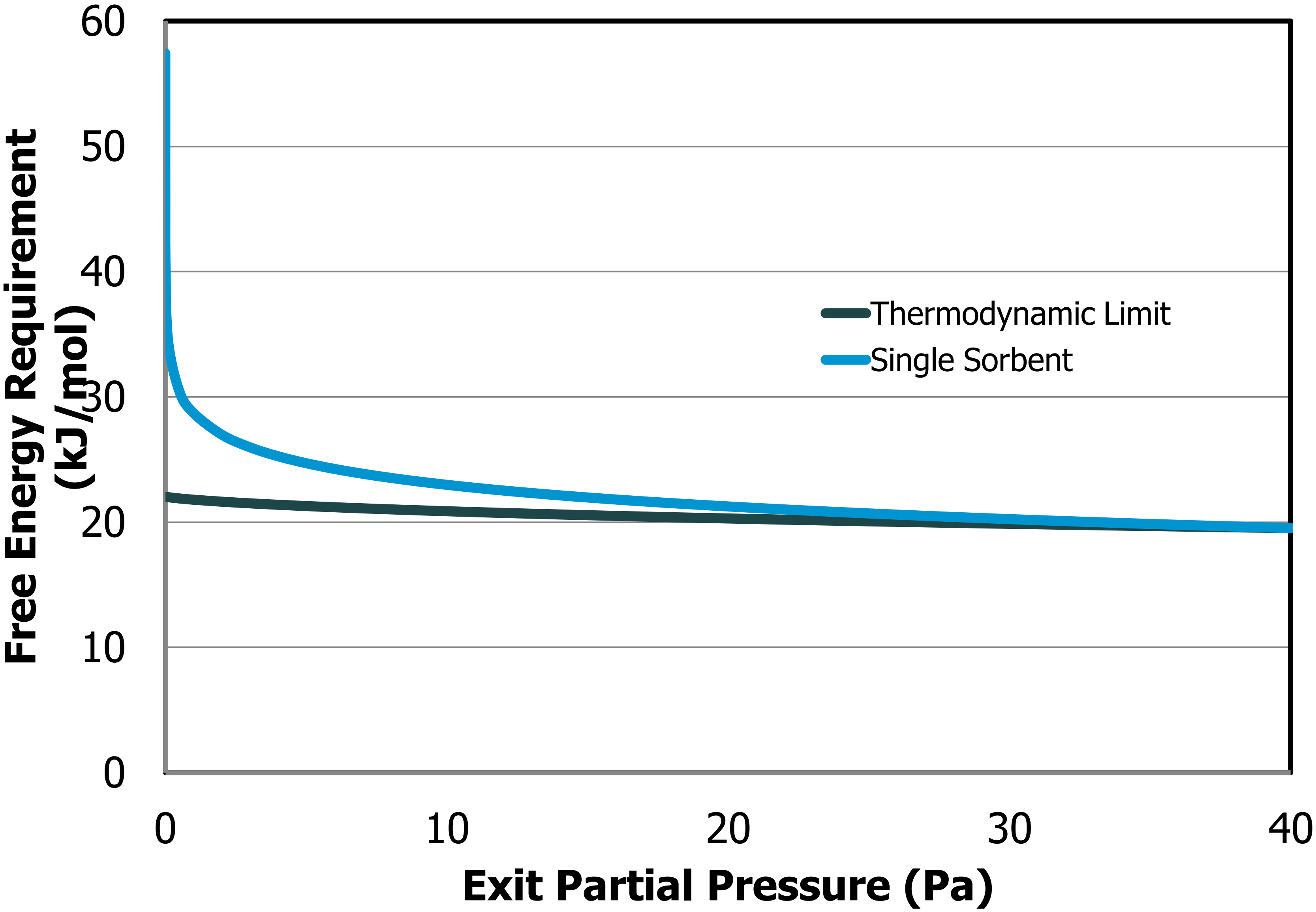
Simplify the general expression by expanding logarithms

$$\ln\left(\frac{P_1}{P_2}\right) = \ln\left(1 + \frac{P_1 - P_2}{P_2}\right) \approx \frac{P_1 - P_2}{P_2}\left(1 - \frac{P_1 - P_2}{2P_2}\right)$$

$$\ln\frac{P_0 - P_1}{P_0 - P_2} = -\ln\frac{P_0 - P_2}{P_0 - P_1} = -\ln\left(1 + \frac{P_1 - P_2}{P_0 - P_1}\right) \approx -\frac{P_1 - P_2}{P_0 - P_1}\left(1 - \frac{1}{2}\left(\frac{P_1 - P_2}{P_0 - P_1}\right)\right)$$

$$\Delta G_{\text{skimming}} = RT\ \ln\frac{P_1}{P_0}$$

Air Capture Free Energy



Flue Gas Scrubbing – Air Capture

Sorbent regeneration slightly more difficult for air capture than for flue gas scrubbers

artist's rendering

Dominant costs are similar for air capture and flue gas scrubbing

Sorbent choice is central

Low cost, rapid kinetics, easy regeneration


GRT photo

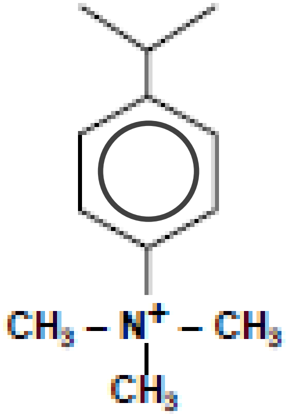
- Dilute CO_2 suggests carbonate chemistry
  - High dilution drives us to carbonate chemistry
  - $OH^- + CO_2 \rightarrow HCO_3^-$, $2HCO_3^- \rightarrow CO_3^{--} + H_2O$
- Fast loading and unloading is important
  - Solids proved interesting
- Materials must be affordable

Anionic Exchange resins

Anionic Exchange Resins

Solid carbonate "solution"
Quaternary ammonium ions form strong-base resin

Type I Strong Base Resins



- Positive ions fixed to polymer matrix
  - Negative ions are free to move
  - Negative ions are hydroxides, OH^-
- Dry resin loads up to bicarbonate
  - $OH^- + CO_2 \rightarrow HCO_3^-$ (hydroxide → bicarbonate)
- Wet resin releases CO_2 to carbonate
  - $2HCO_3^- \rightarrow CO_3^{--} + CO_2 + H_2O$

Moisture driven CO_2 swing

Membrane material

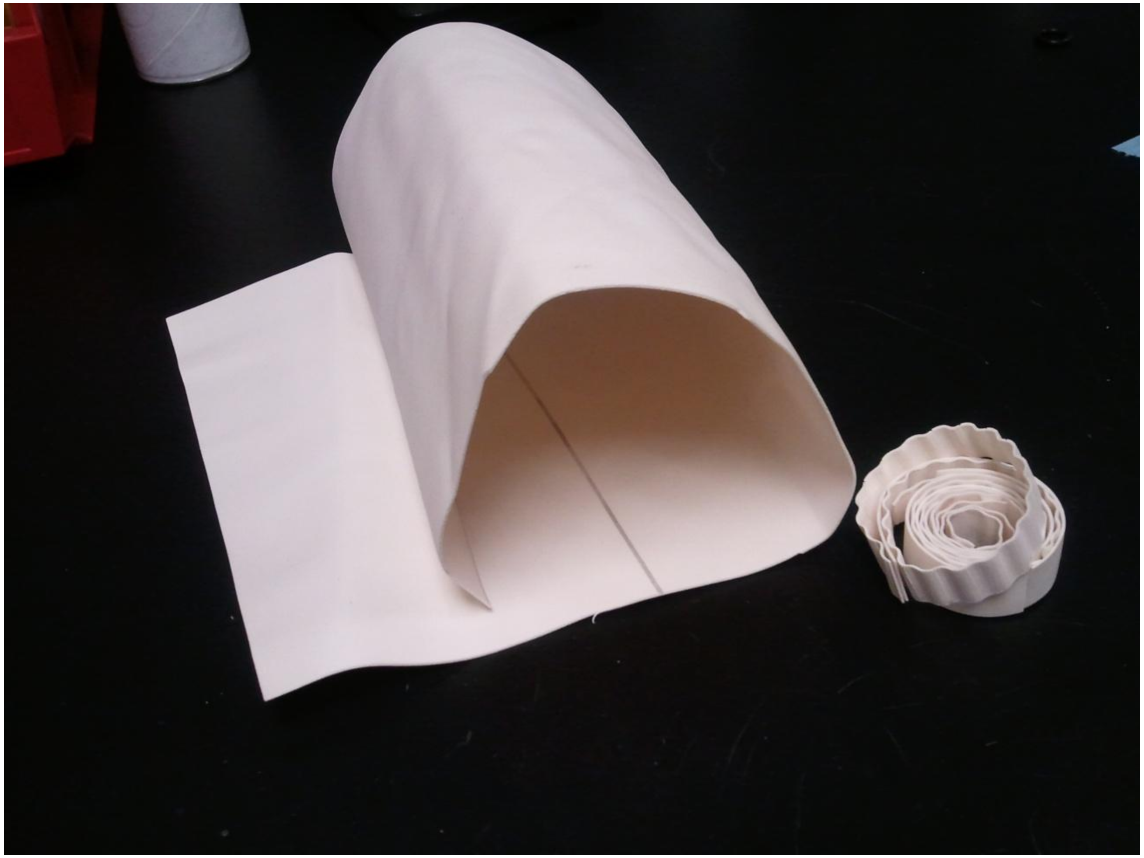
thin sheets

Snowpure electrochemical membrane (1mm thick)

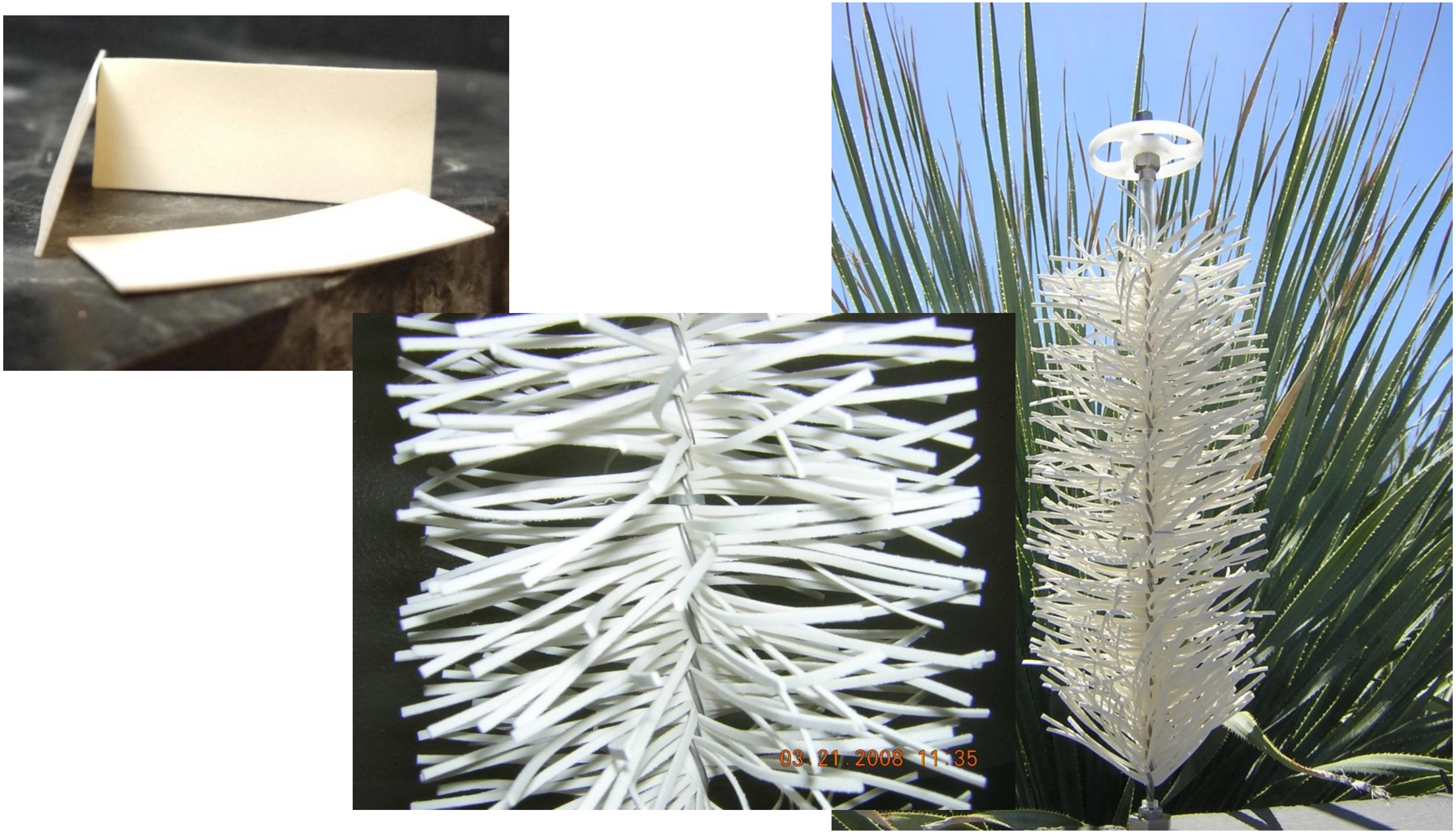
Polypropylene matrix with embedded fine resin particles (25μm)

Ammonium cations Carbonate/bicarbonate form

1.7 mol/kg charge equivalent



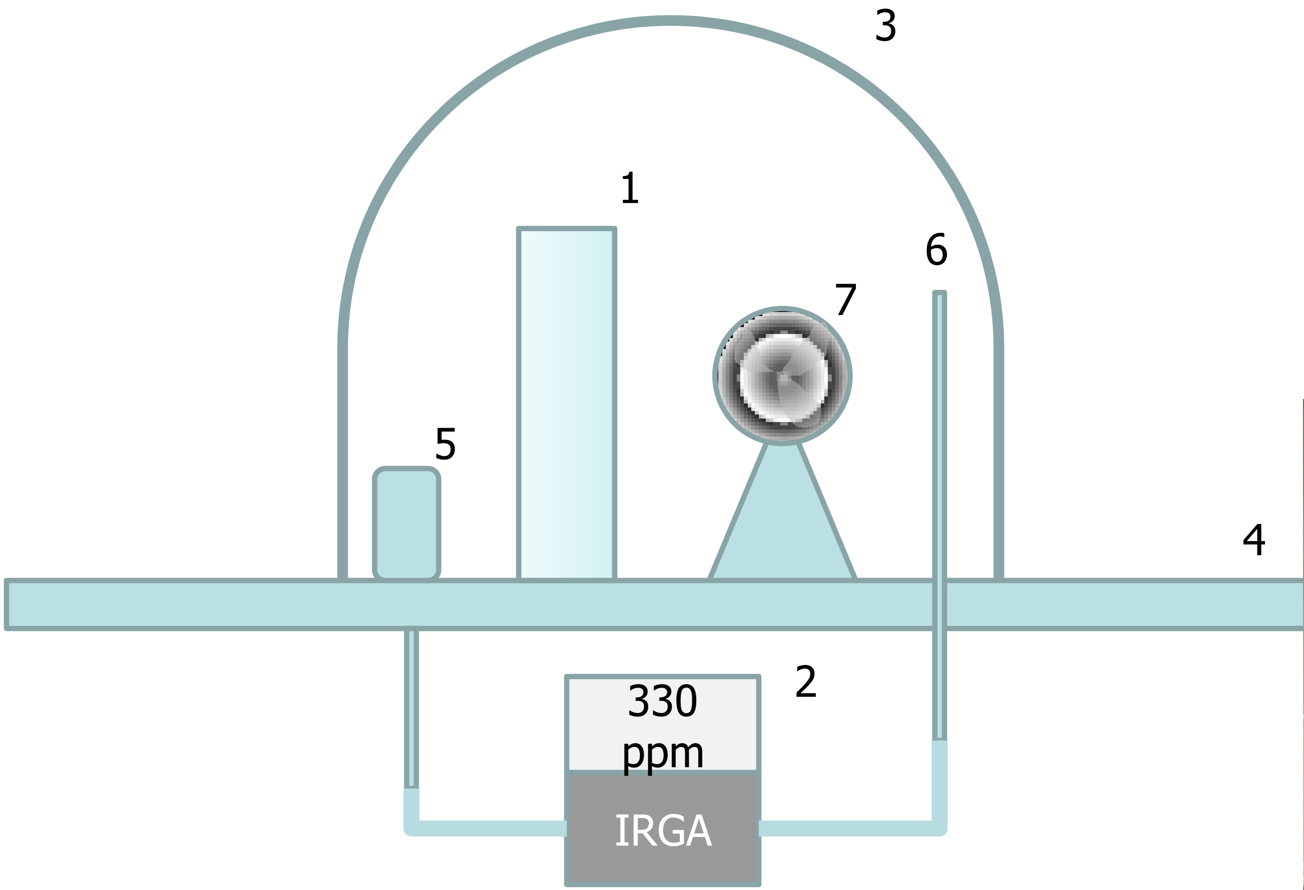
Resin material



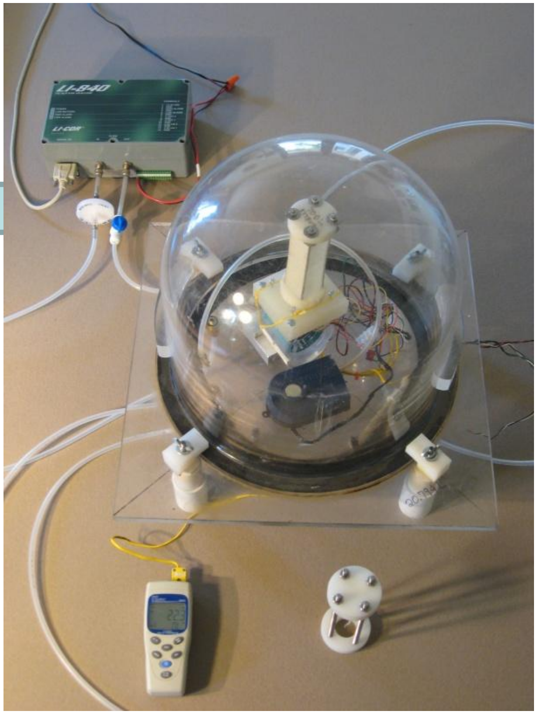
Observations on resin

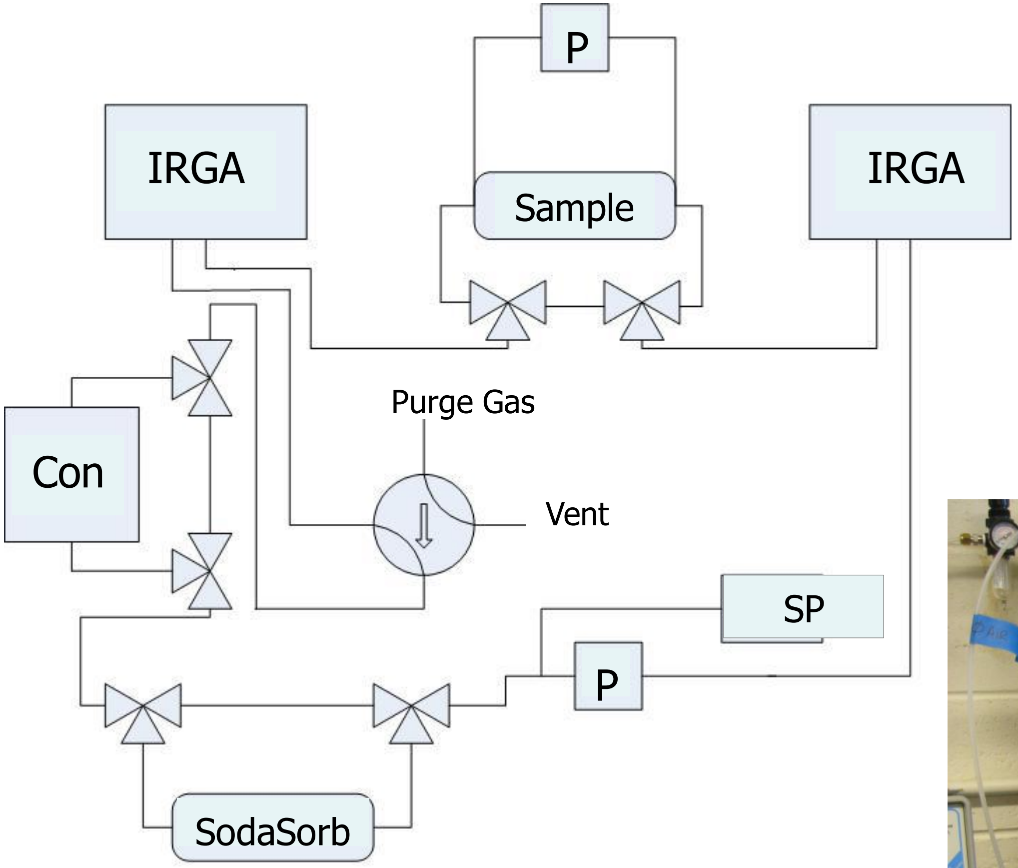
- **Resin sheets absorb CO_2 from air**
  - faster than equally sized sheets covered with 1-molar sodium hydroxide solution
- **Absorb to very low CO_2 partial pressures**
  - Scrubbing down to tens of ppm
- **Air loading can reach “bicarbonate”**
  - 1 mole of CO_2 per mole of fixed cations
- **Equilibrium loading is water sensitive**
  - Liquid wash drives resin to carbonate state

Closed Air Analyzing System



1. Resin Sample
2. Infrared Gas Analyzer
3. Glass Bell
4. Bottom plate with power and gas penetrations
5. Air pump
6. Air return
7. Fan to agitate air





P

IRGA

Sample

IRGA

Purge Gas

Con

Vent

SP

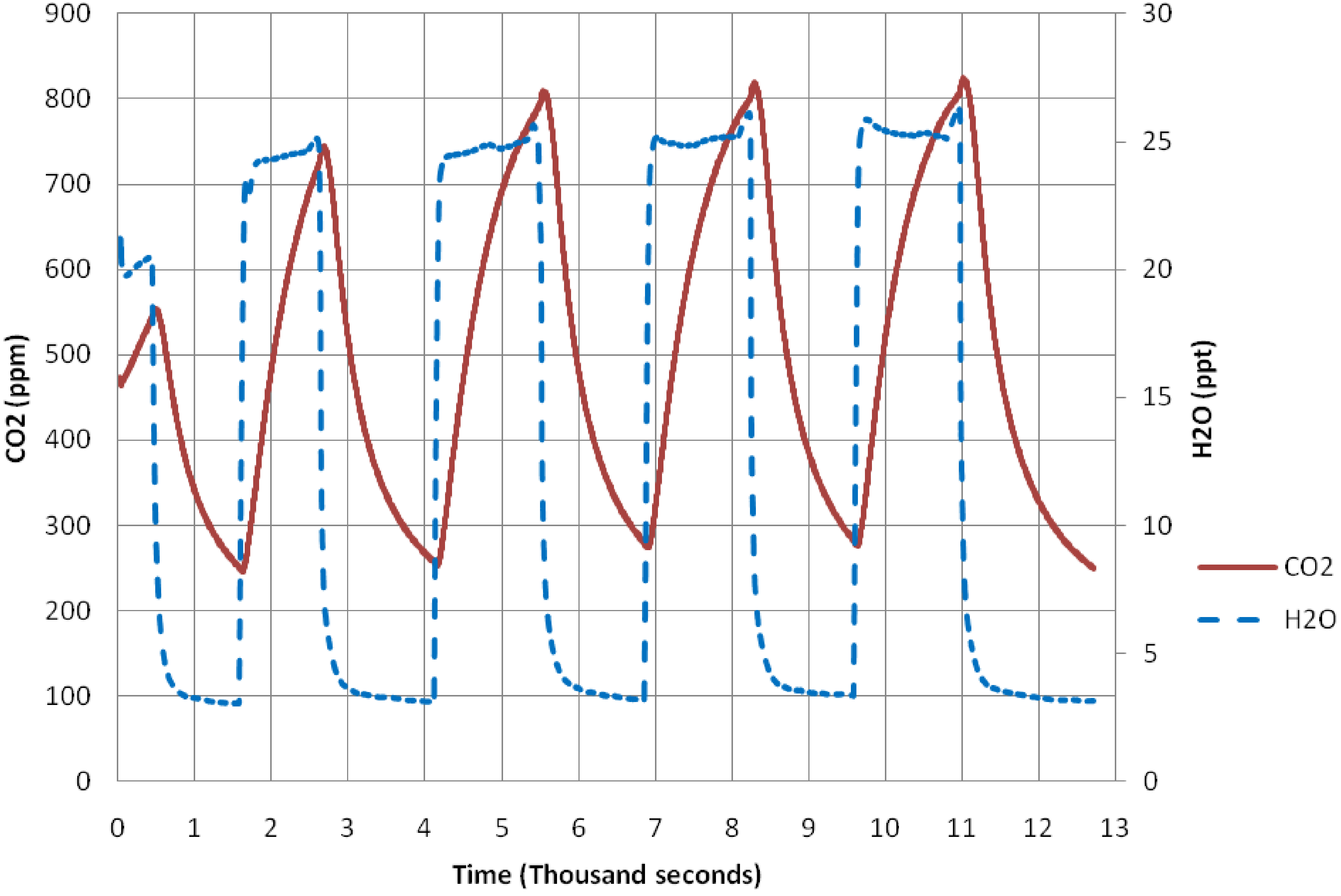
P

SodaSorb

Clockwise Flow

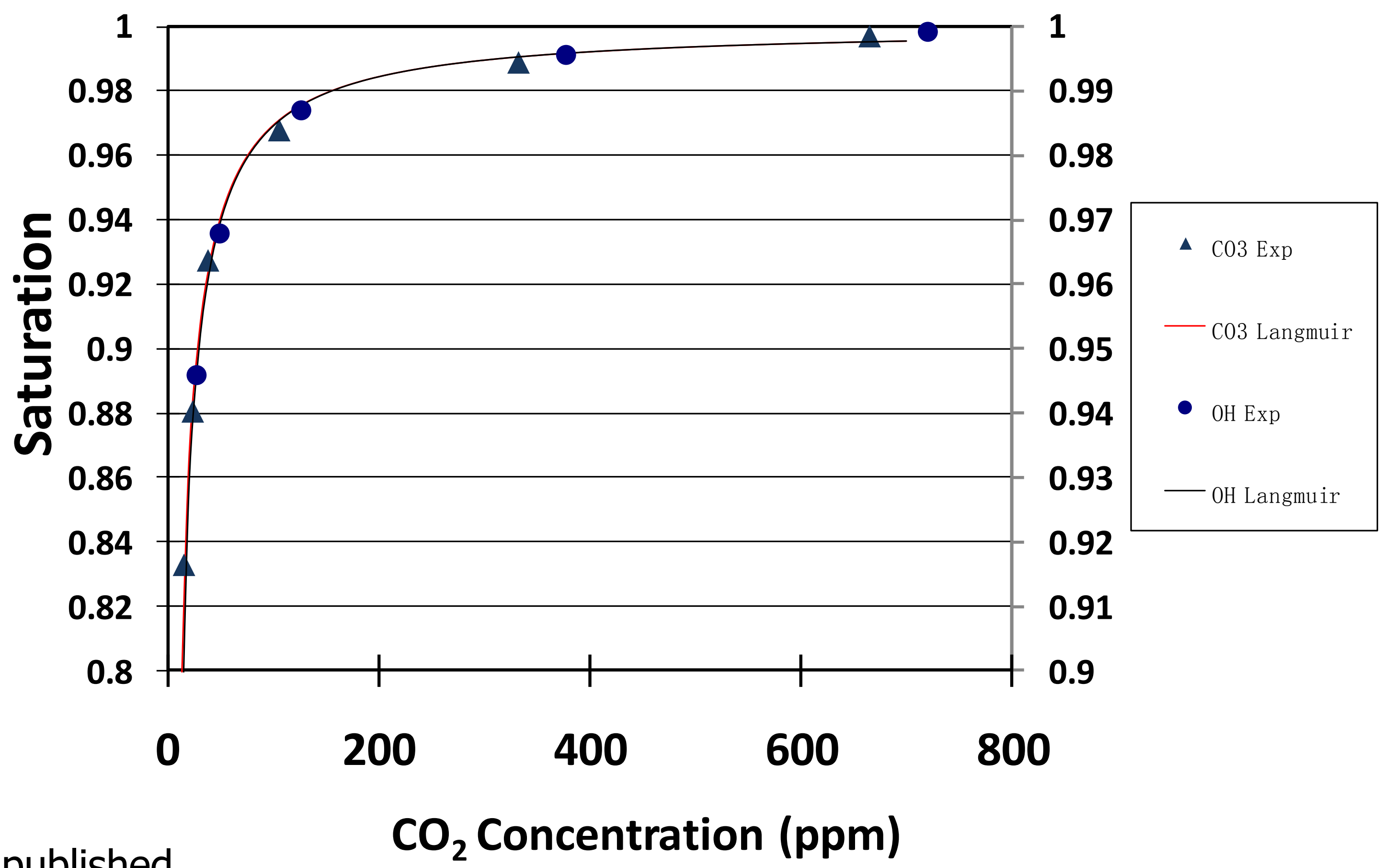
IRGA:	Infrared Gas Analyzer
P:	Pump
SP:	Syringe Pump
Con:	Condenser

Dowex® Marathon® MSA



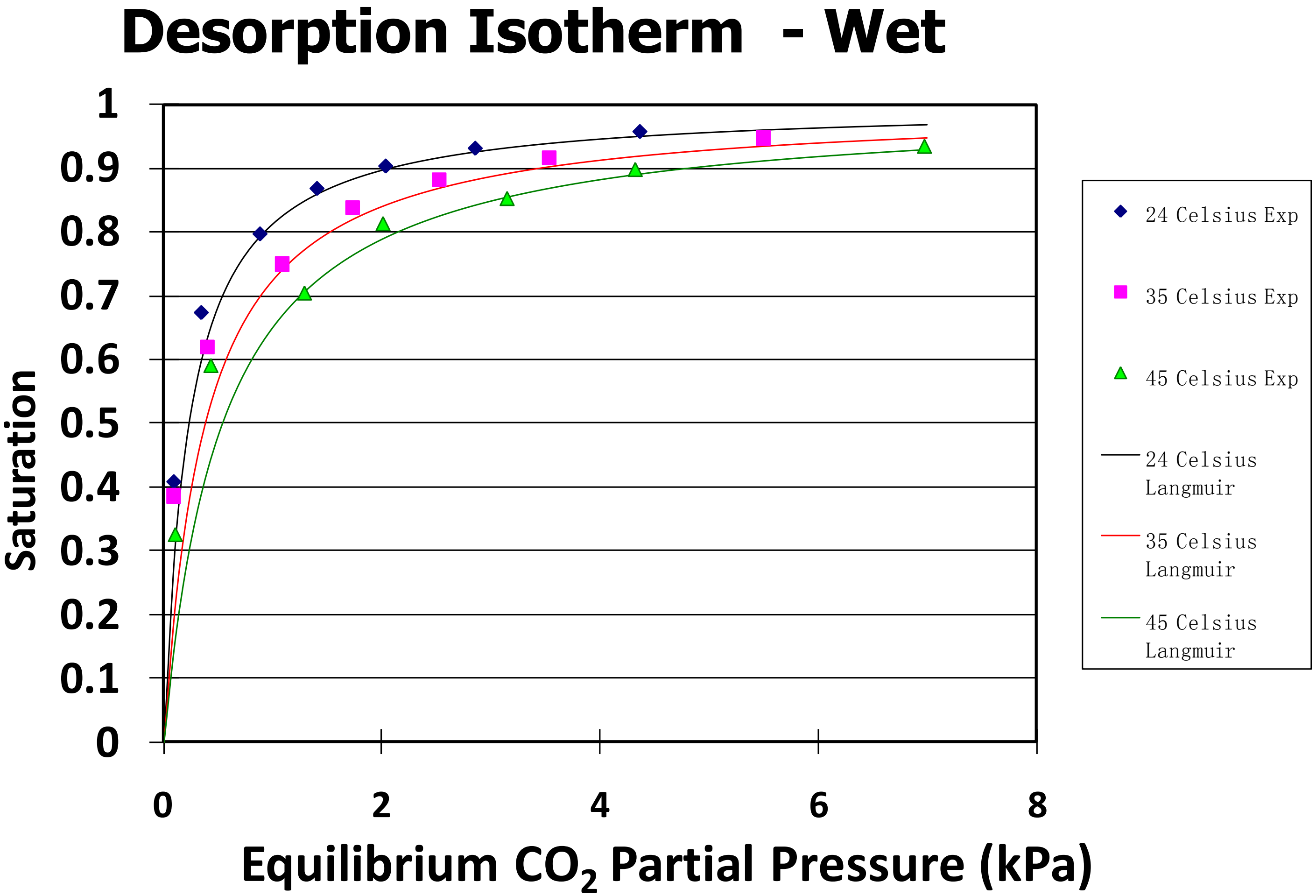
The Moisture Swing

Absorption Isotherm – Dry



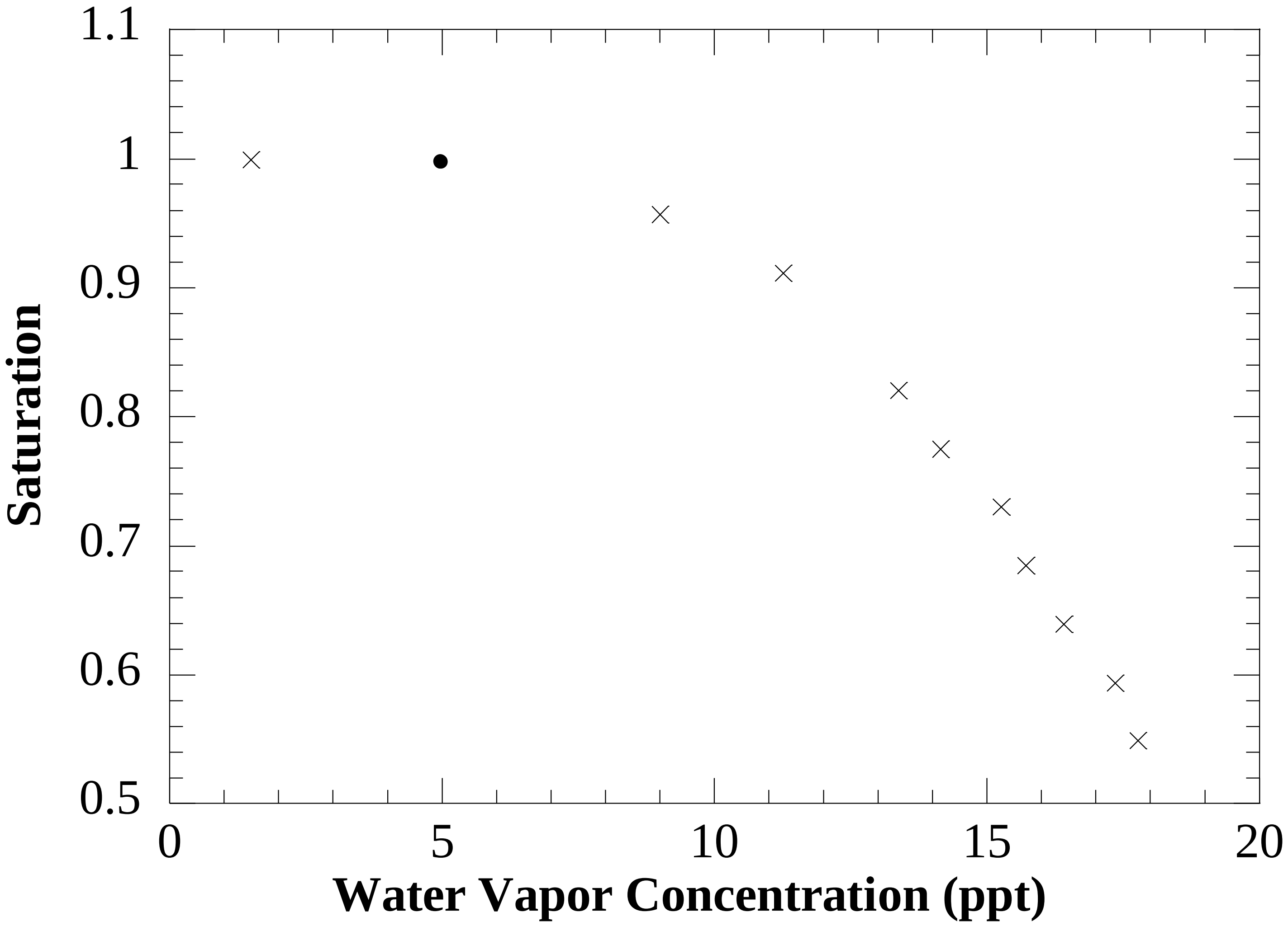
Tao Wang et al, to be published

The Moisture Swing



Tao Wang et al, to be published

Maximum loading drops with humidity

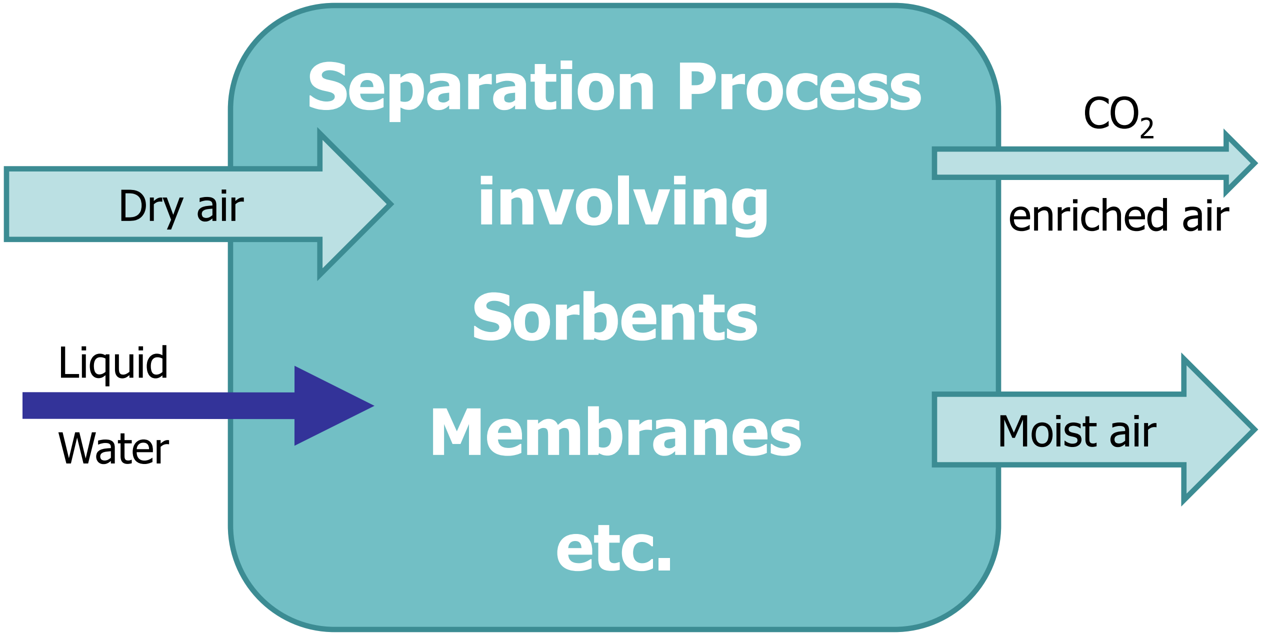


T = 23°C

CO_2 400 ppm

Free energy from water evaporation

Water evaporation can drive CO_2 capture



Separation Process

involving

Sorbents

Membranes

etc.

Free energy of water evaporation
at a relative humidity *RH:*
$\Delta G = RT \ln(P/P_{sat}) = RT\, ln(RH)$

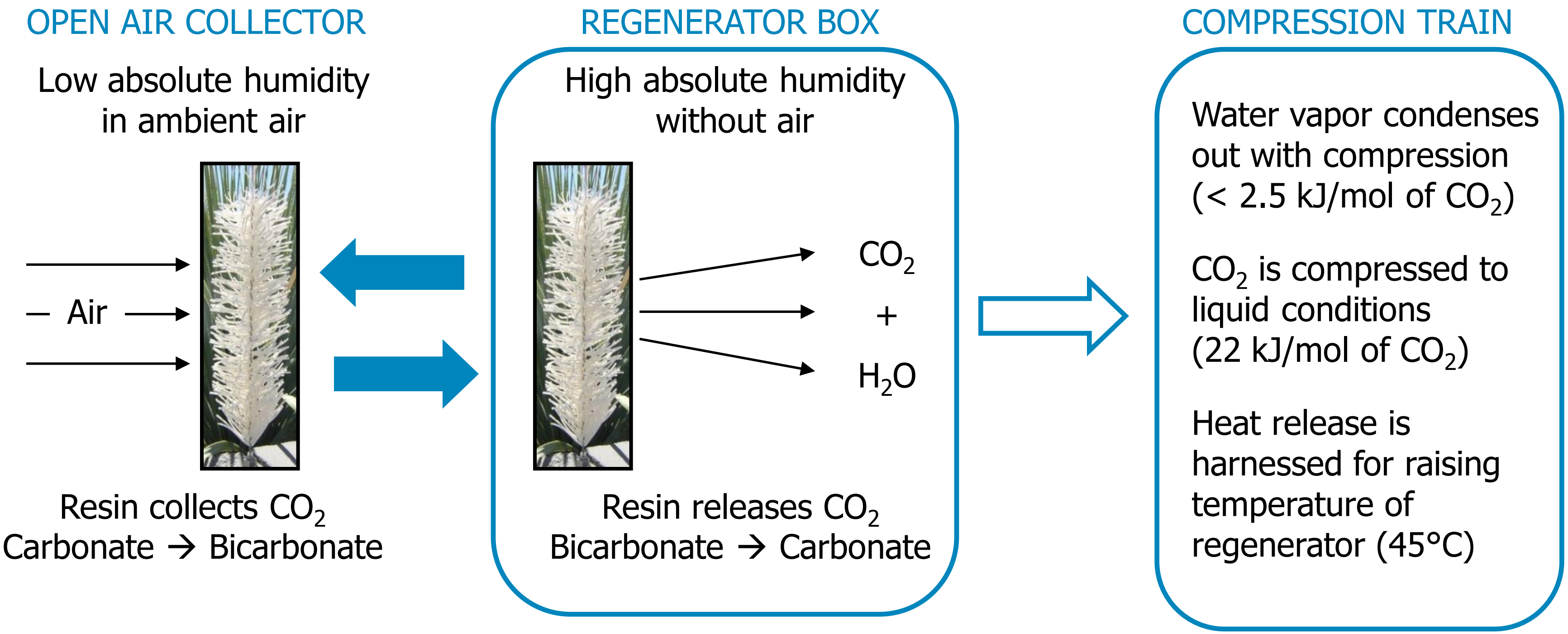
Ball park estimate: 2.5 kJ/mol
140 MJ/m^3
@ 20¢/m^3 0.5¢/kWh

Four steps in the moisture swing

- **Dry resin absorbs CO_2 from air**
  - Lowers free energy
- **Resin is wetted**
  - no free energy change in water transfer
  - water interaction with resin may change state
- **Wet resin releases CO_2 at higher pressure**
  - Total system lowers free energy
  - CO_2 has increased free energy (paid internally)
- **Resin dries**
  - Releases latent free energy available in the liquid water
  - This is the only source of free energy to drive the cycle

Novel Regenerator Chemistry

Moisture Swing Absorption



OPEN AIR COLLECTOR

Low absolute humidity
in ambient air

Resin collects CO_2
Carbonate → Bicarbonate

REGENERATOR BOX

High absolute humidity
without air

Resin releases CO_2
Bicarbonate → Carbonate

COMPRESSION TRAIN

Water vapor condenses out with compression (< 2.5 kJ/mol of CO_2)

CO_2 is compressed to liquid conditions (22 kJ/mol of CO_2)

Heat release is harnessed for raising temperature of regenerator (45°C)

- Moisture swing consumes water and electric power
  - 50 kJ/mol of CO_2
  - 10 liter of saline water per kg of CO_2

Dimensions

- Wind Speed
  - $1\ m\ s^{-1}$
- Uptake Rate
  - $25\ \mu mol\ m^{-2}\ s^{-1}$
- Release Rate
  - $25\ \mu mol\ m^{-2}\ s^{-1}$
- Specific Surface Area
  - $4 m^2\ kg^{-1}$
- Loading Factor
  - $0.25\ mol\ kg^{-1}$
- Resin Fill Factor
  - 10%

Setting the scale for 1 ton/day

- 2 × 30 panels
  - 2.5m × 1m × 0.3m
- 2 × 2500 kg of resin
  - 10,000m^2 of surface
- 6 × Chambers
  - 4m^3 each
- One Container
  - 86m^3
  - can hold all panels

Assembly line based automation

Cost of air capture?

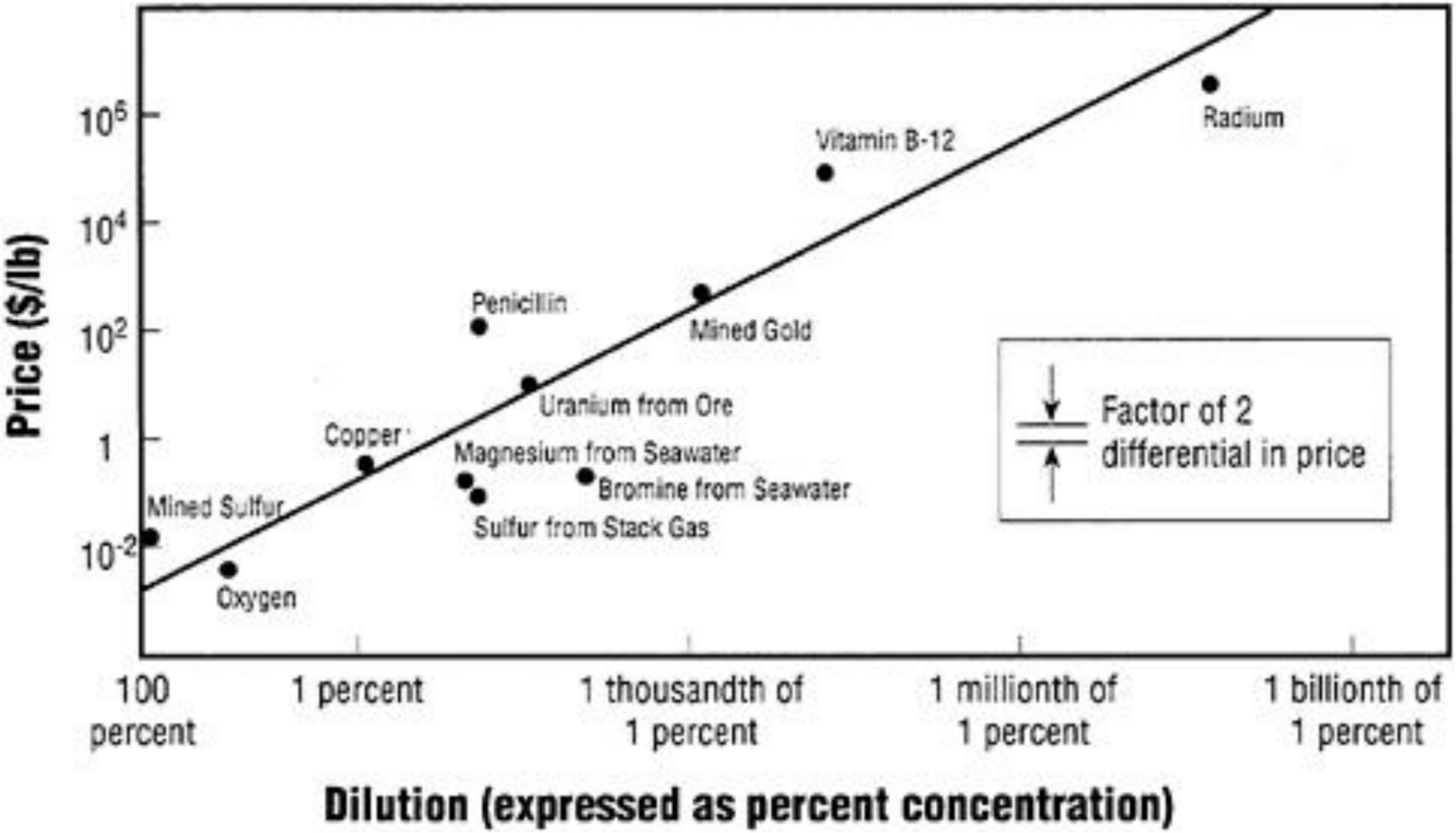
- Cost C as function of dilution D = 1/P

$$C = C_1 D + C_2 + C_3 \log D$$

- Constants depend on technology choice
  - ○ C_1 : contacting the air stream
    - Passive system sitting in the wind
  - ○ C_2 : handling of sorbent material (transport etc.)
    - Likely small, can be very much limited
  - ○ C_3 : sorbent regeneration
    - Not much different from flue gas scrubbing

Sherwood Plots and Cost

Sherwood's Law for Minerals ~ \$10/ton of ore



SOURCE: National Research Council (1987)

First cost estimates

- **Construction cost**
  - Materials – low
  - Manufacture – high
  - $200,000 per ton/day
- **Operating cost**
  - Inputs (power, water, etc.) – low
  - Maintenance – high
  - $120 per ton
- **Total including return on investment**
  - $200 - $250/ton CO_2

Building a car in a machine shop

Conversion

- **Air capture costs**
  - $100/t$CO_2$ ↔ 22¢/l (gasoline) ↔ 85 ¢/gallon
  - $30/t$CO_2$ ↔ 7¢/l (gasoline) ↔ 25 ¢/gallon

- **Energy content of gasoline**
  - 1 liter of gasoline ↔ 10 kWh (thermal)

The cost estimation fallacy

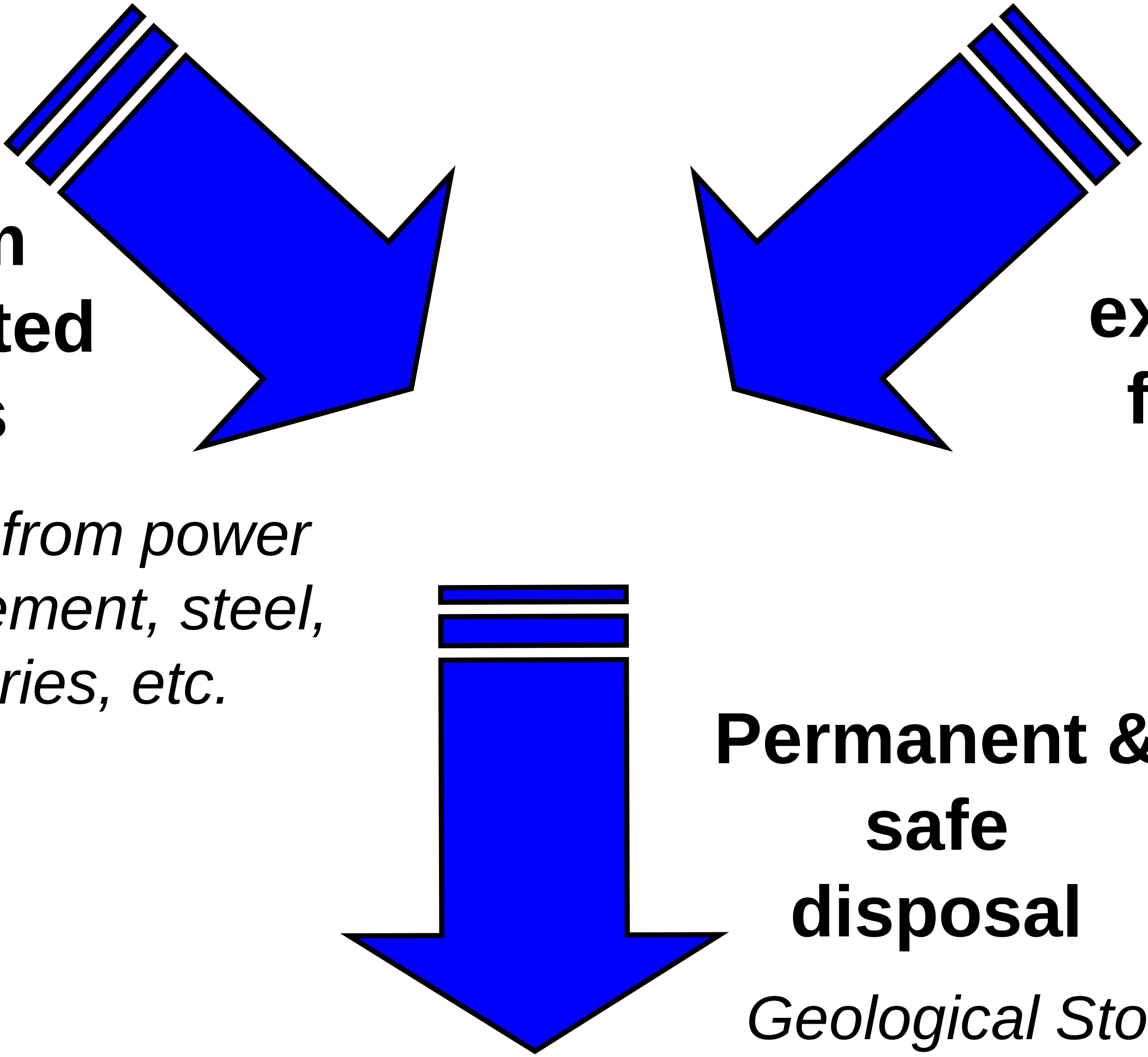
1980s: $20 per disk

2011: $0.10 per disk

Going to Scale (Mass Production)

- 10 million units @ 1/tonne per day
    - capture 3.6 Gt CO_2 per year (12% of emissions)
    - Require annual production of 1 million (10yr life)
        - Compared to 70 million cars and light trucks
- 100 million units would lower CO_2 in the air

Net Zero Carbon Economy



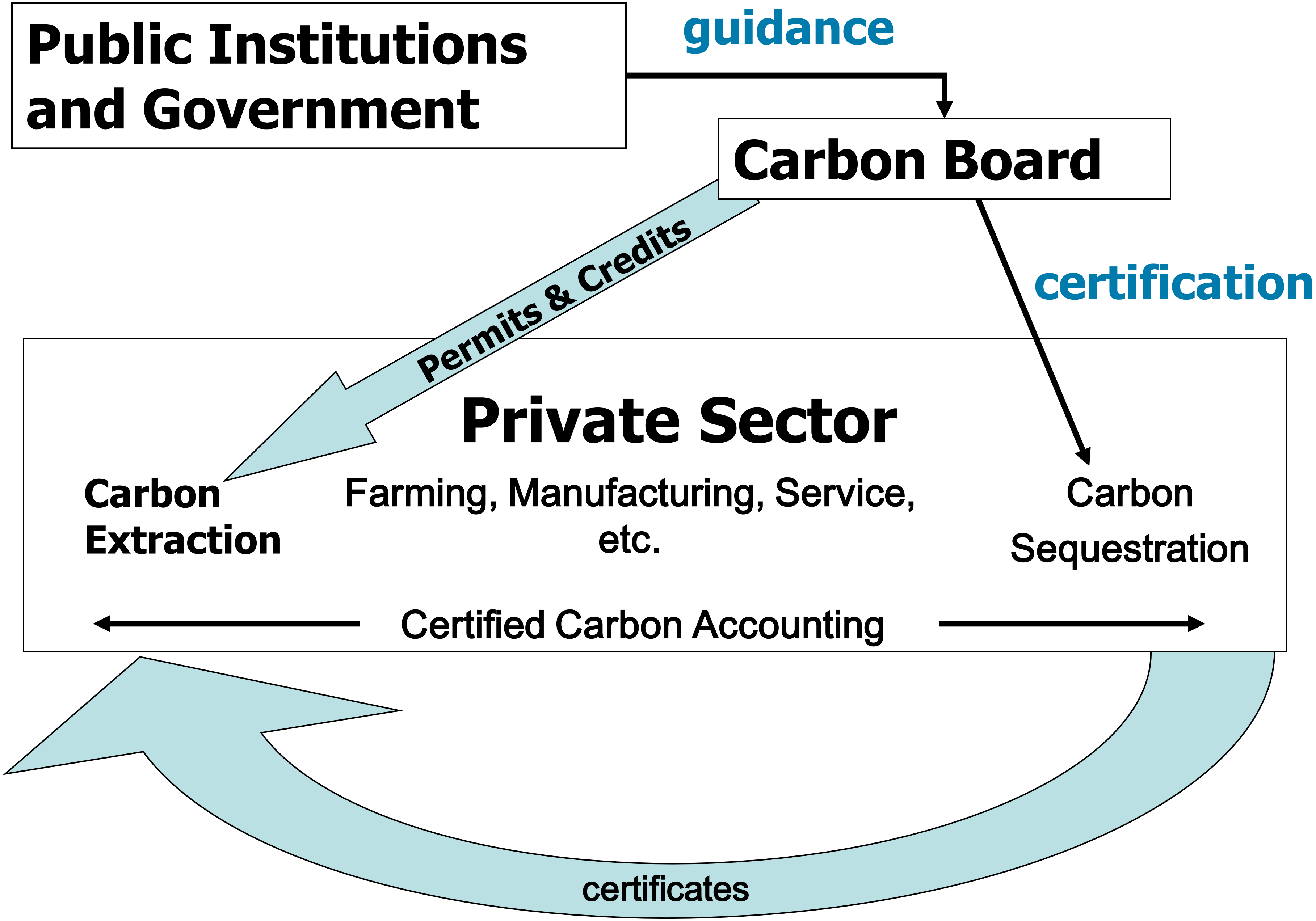
CO_2 from concentrated sources

Capture from power plants, cement, steel, refineries, etc.

CO_2 extraction from air

Permanent & safe disposal

Geological Storage
Mineral carbonate disposal



Public Institutions and Government

guidance

Carbon Board

Permits & Credits

certification

Private Sector

Carbon Extraction

Farming, Manufacturing, Service, etc.

Carbon Sequestration

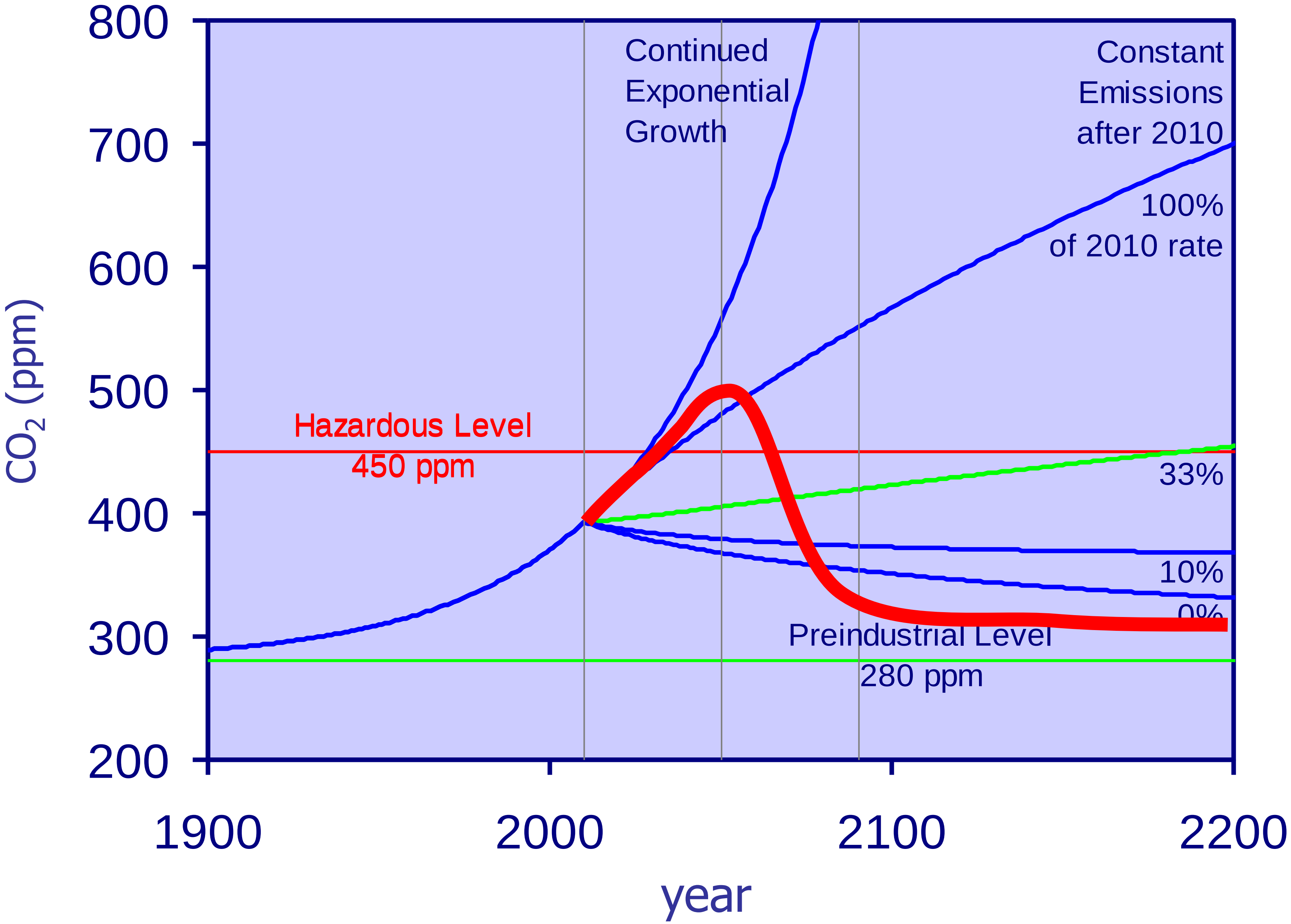
← Certified Carbon Accounting →

certificates

Air Capture as part of the mix

- **Capture option of last resort**
  - Air capture can deal with any CO2
  - Lower cost capture will go first
  - More expensive options cannot compete
- **Advantages of air capture**
  - Air capture eliminates transport costs
  - Air capture opens remote sites
  - Air capture can deal with past emissions
- **Air capture sets the marginal cost**

Coming back down by destroying certificates



Ultimate application

SYNTHETIC FUELS

Two complementary energy carriers

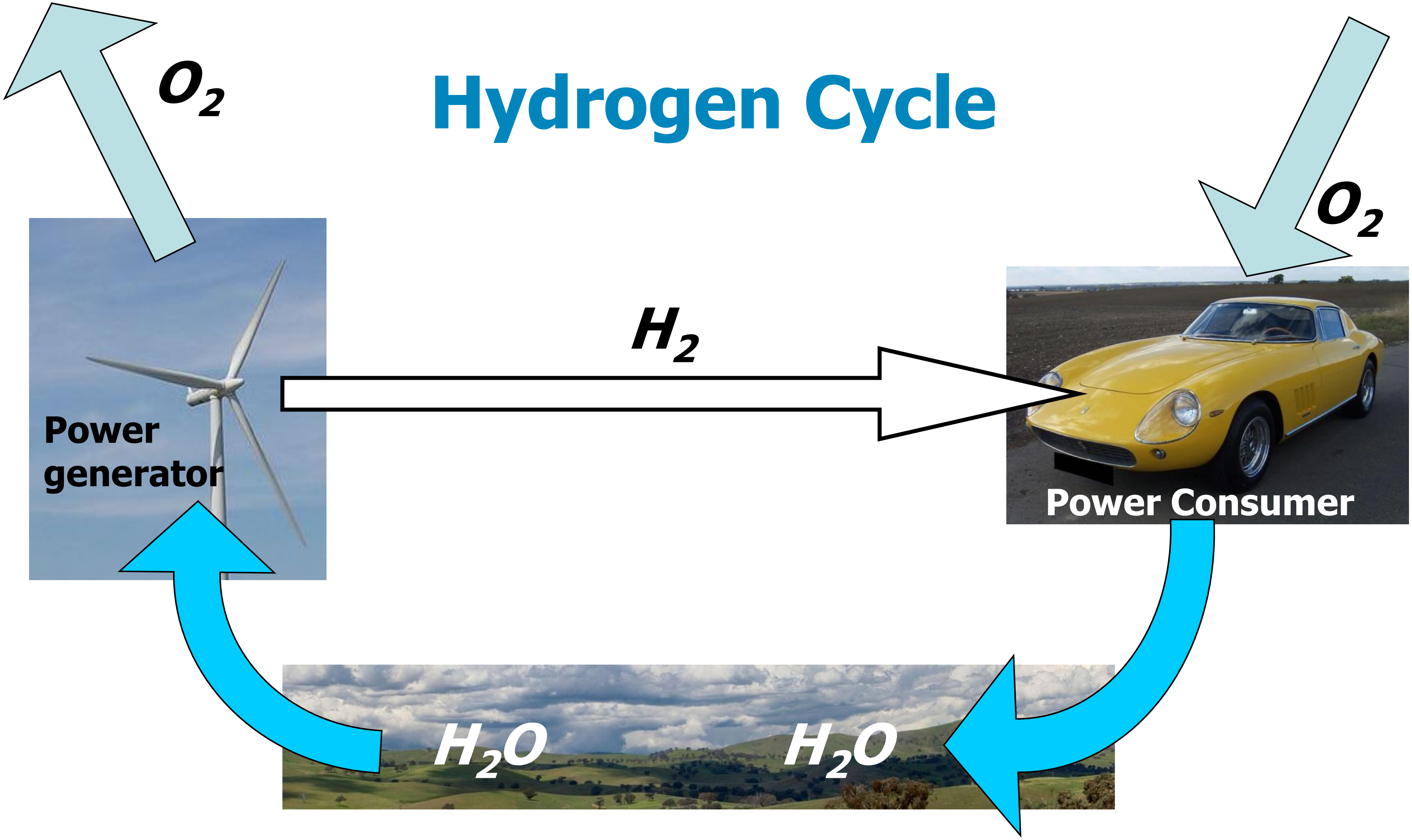
- **Electricity**
  - Responsive
  - No emissions at point of consumption
  - Stationary applications
  - No storage
- **Liquid fuels**
  - Easily stored
    - in transportation
    - for electricity
  - High energy density
  - Produce CO_2 at point of use

Connection between carriers

- **Electrolysis**
  - Low temperature (hydrogen from water)
  - High temperature (CO, H_2 from CO_2 and H_2O)
- **Fuel Synthesis**
  - Hydrogen, Methanol, DME, Gasoline, Diesel
- **Ingredients in a liter of gasoline**
  - 10¢ of carbon dioxide
  - 20 kWh of electricity (50% efficiency)
  - Off peak? 40 cents

Closed Cycle - Synthetic Fuels

Hydrogen Cycle



O_2

O_2

Power generator

H_2

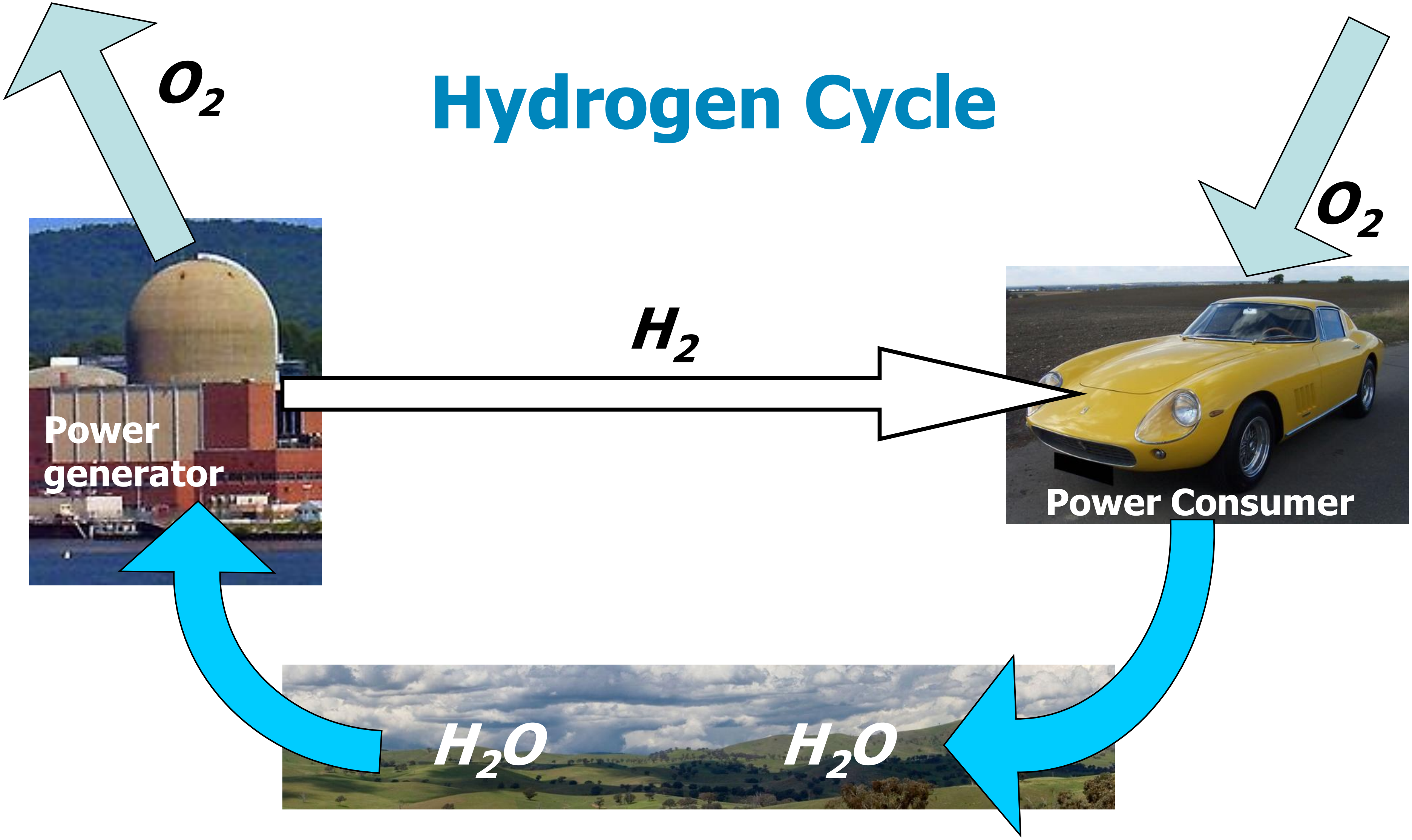
Power Consumer

H_2O

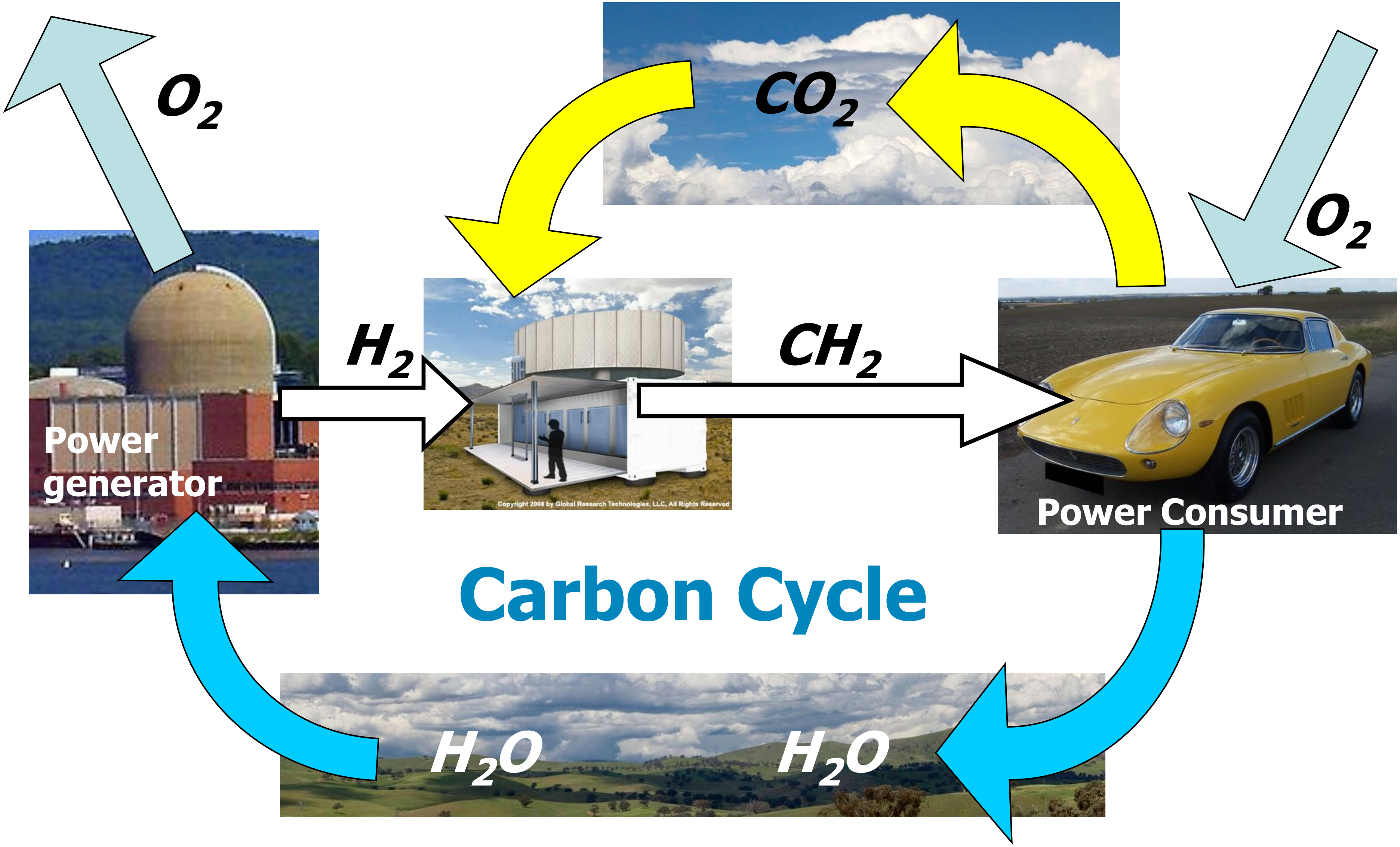
H_2O

Closed Cycle - Synthetic Fuels

Hydrogen Cycle



Closed Cycle - Synthetic Fuels



O_2

CO_2

O_2

Power
generator

H_2

CH_2

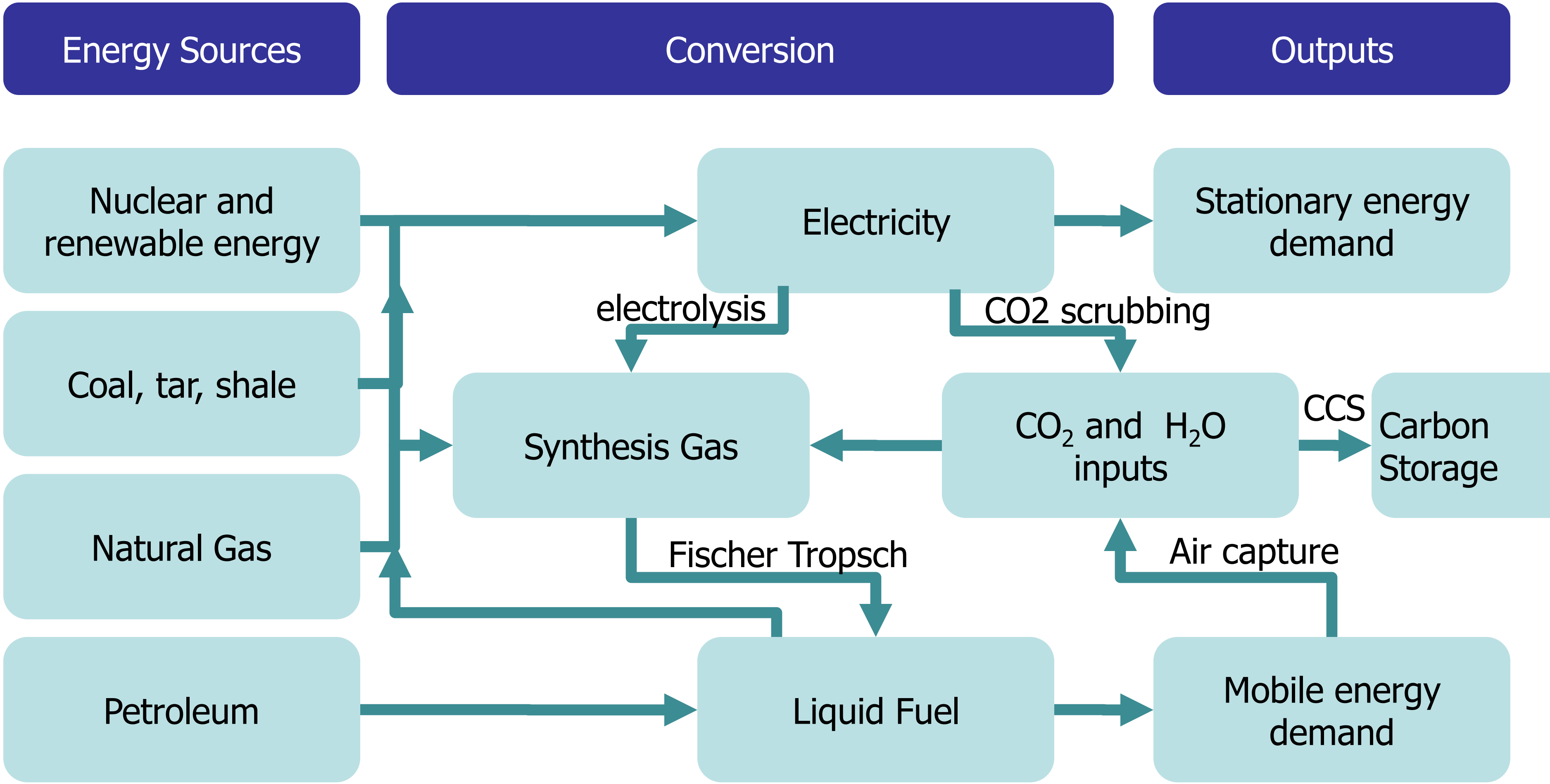
Power Consumer

Carbon Cycle

H_2O

H_2O

Carbon neutral energy systems



Energy Sources

Conversion

Outputs

Nuclear and renewable energy

Electricity

Stationary energy demand

electrolysis

CO2 scrubbing

Coal, tar, shale

Synthesis Gas

CO_2 and H_2O inputs

CCS

Carbon Storage

Natural Gas

Fischer Tropsch

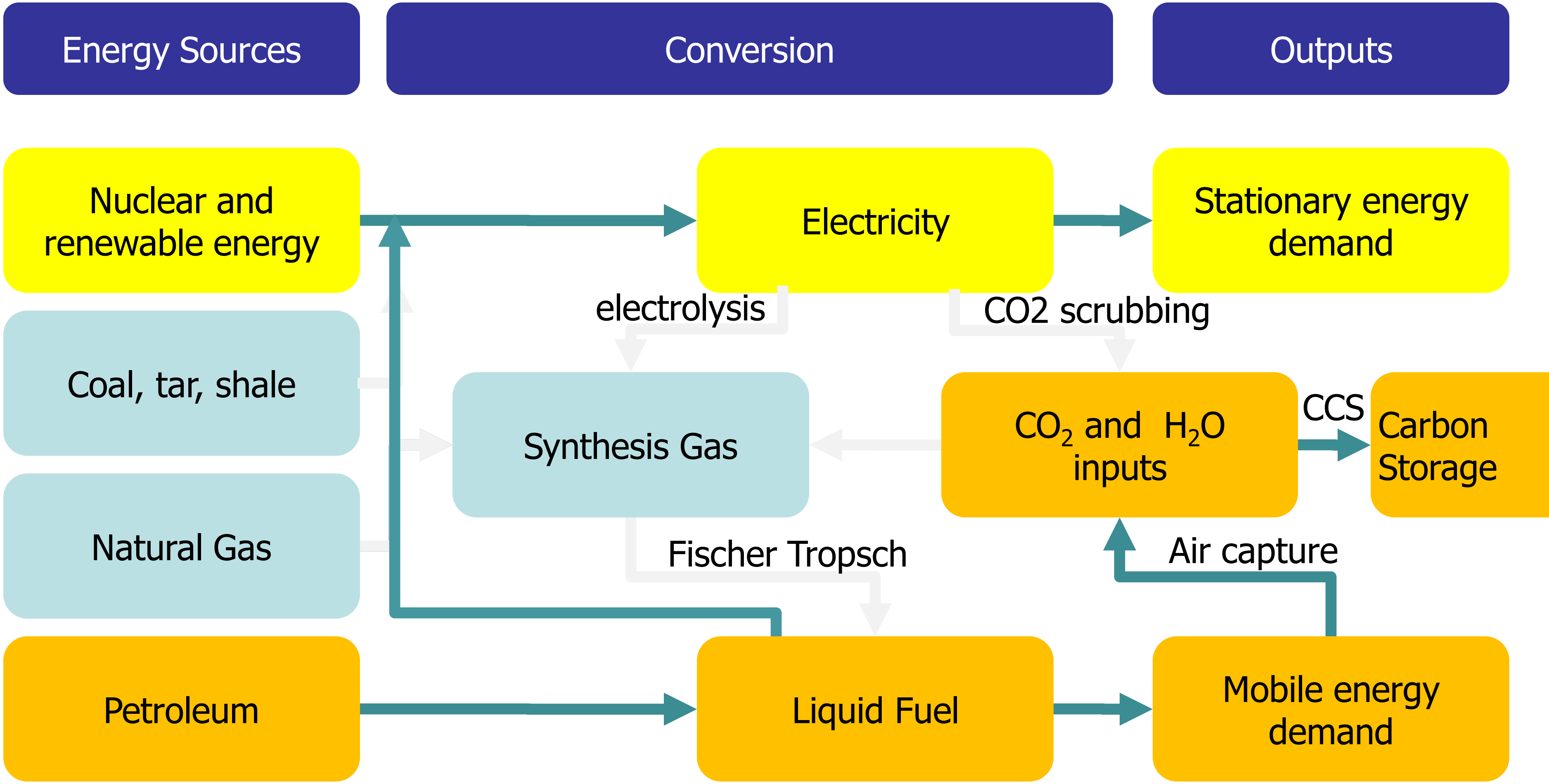
Air capture

Petroleum

Liquid Fuel

Mobile energy demand

Carbon neutral energy systems



Energy Sources

Conversion

Outputs

Nuclear and renewable energy

Electricity

Stationary energy demand

electrolysis

CO2 scrubbing

Coal, tar, shale

Synthesis Gas

CO_2 and H_2O inputs

CCS

Carbon Storage

Natural Gas

Fischer Tropsch

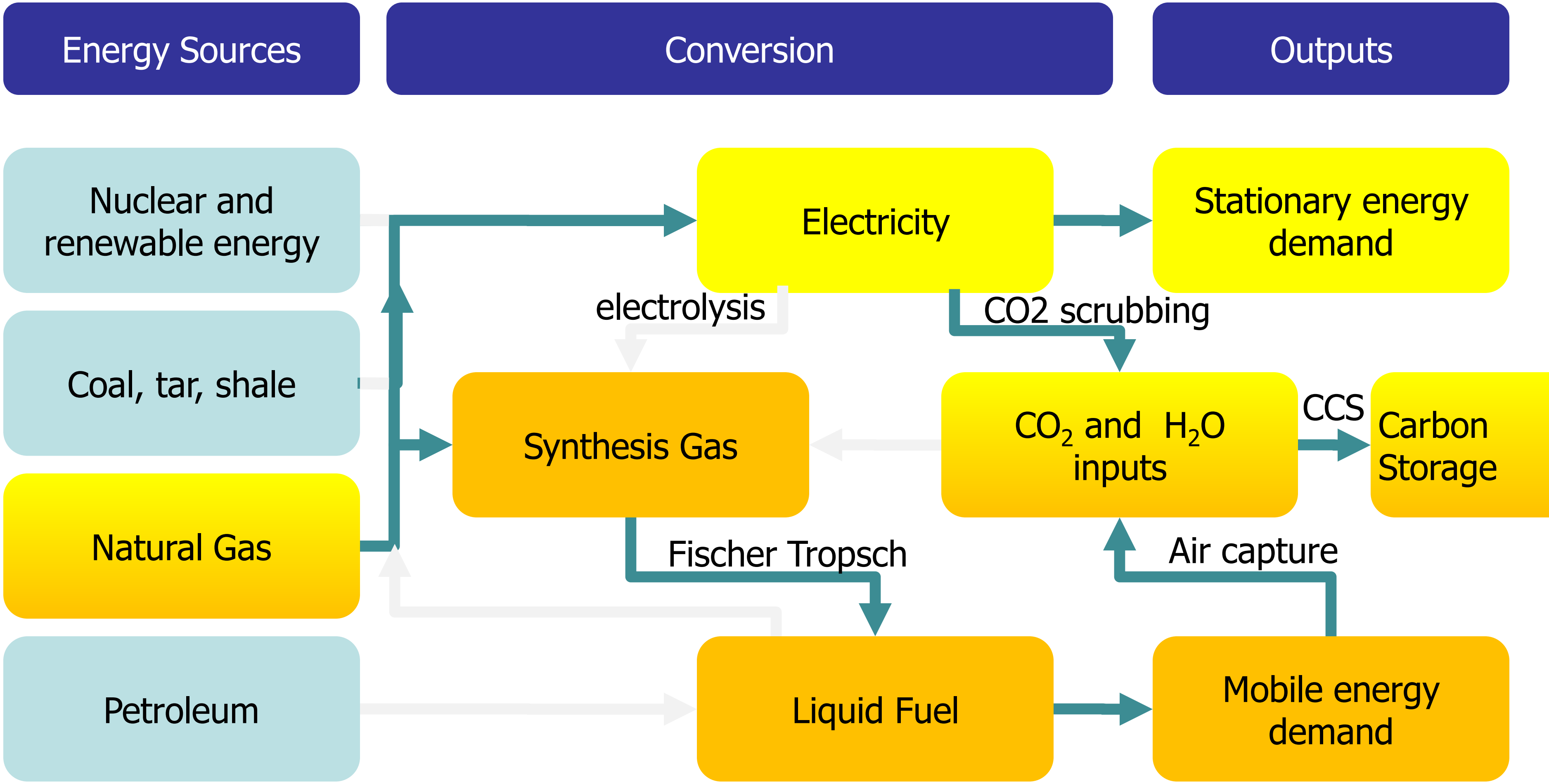
Air capture

Petroleum

Liquid Fuel

Mobile energy demand

Carbon neutral energy systems



Energy Sources

Conversion

Outputs

Nuclear and renewable energy

Coal, tar, shale

Natural Gas

Petroleum

Electricity

Stationary energy demand

electrolysis

CO2 scrubbing

Synthesis Gas

CO_2 and H_2O inputs

CCS

Carbon Storage

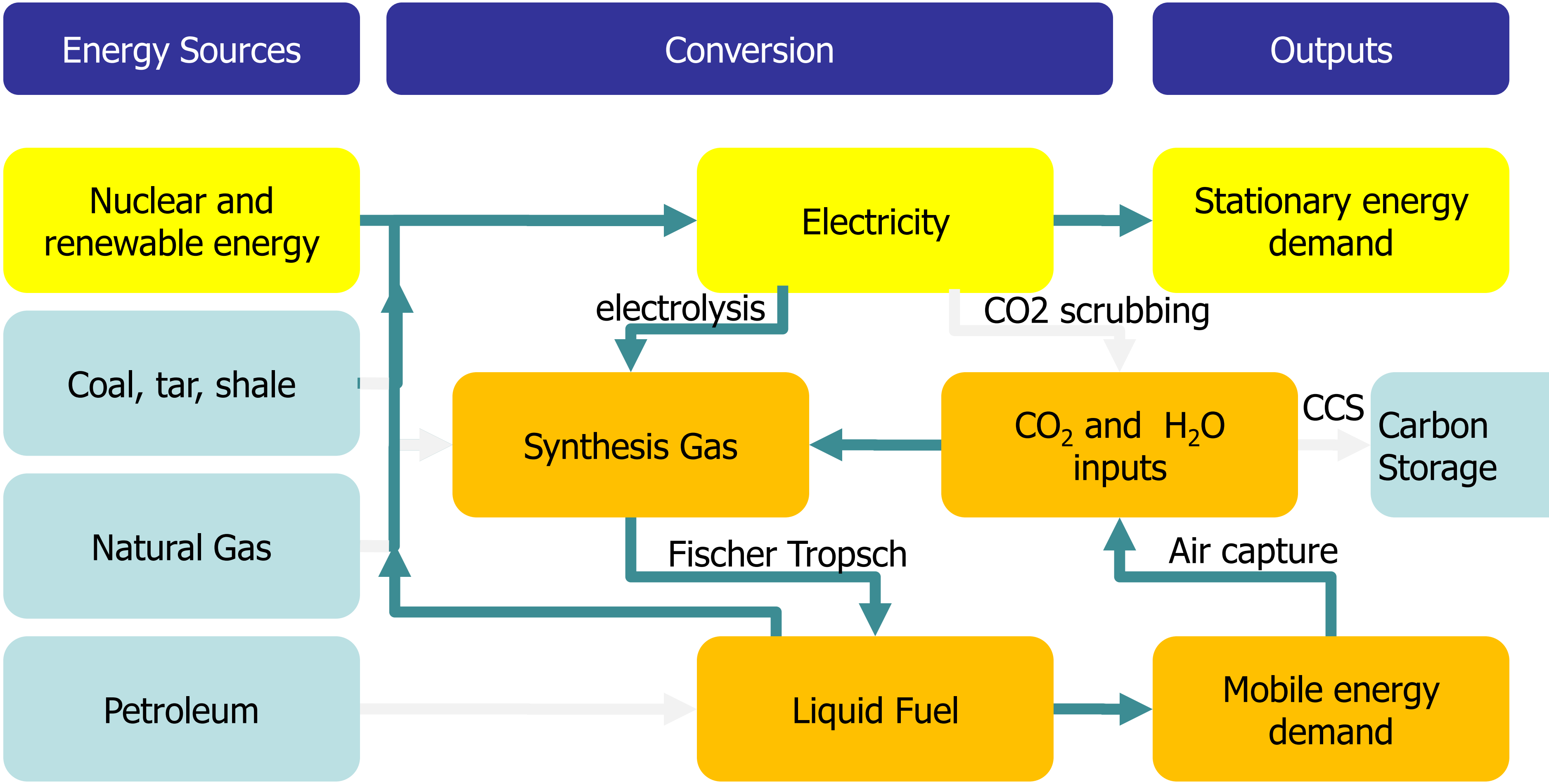
Fischer Tropsch

Air capture

Liquid Fuel

Mobile energy demand

Carbon neutral energy systems



Energy Sources

Conversion

Outputs

Nuclear and renewable energy

Electricity

Stationary energy demand

electrolysis

CO2 scrubbing

Coal, tar, shale

Synthesis Gas

CO_2 and H_2O inputs

CCS

Carbon Storage

Natural Gas

Fischer Tropsch

Air capture

Petroleum

Liquid Fuel

Mobile energy demand