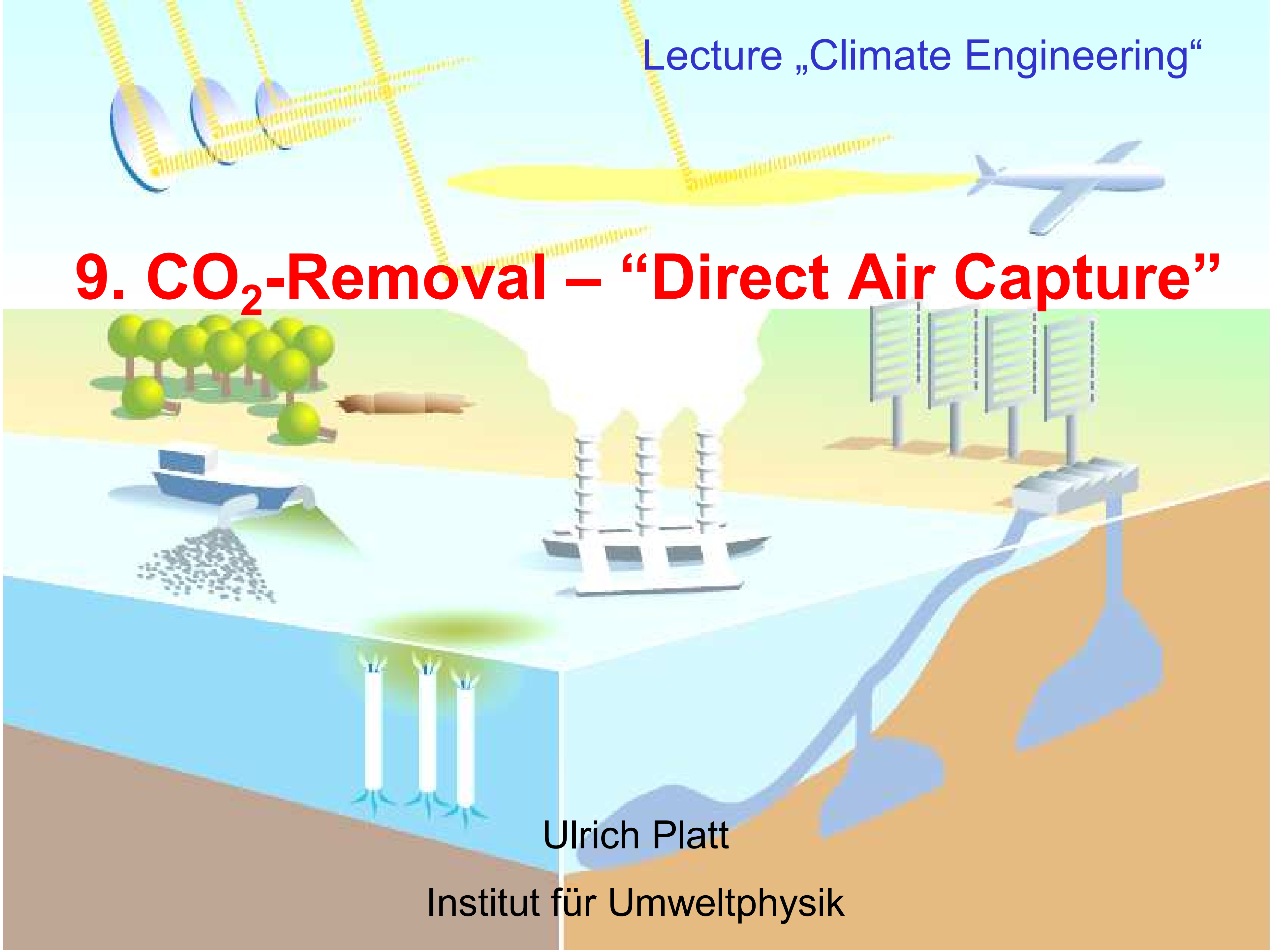
Lecture „Climate Engineering“

9. CO_2-Removal – “Direct Air Capture”



Ulrich Platt

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Lecture Program of „Climate Engineering

Part 1: Introduction to the Climate System (4 sessions)

1. Introduction and scope of the lecture
2. The Climate System – Radiation Balance
3. Elements of the Climate System - Greenhouse Gases, Clouds, Aerosol
4. Dynamics of the Climate System - Sensitivity, Predictions

Part 2: Climate Engineering Methods - Solar Radiation Management, SRM

1. SRM – Reflectors in space
2. SRM – Aerosol in the Stratosphere
3. SRM – Cloud Whitening
4. SRM – Anything else

Part 3: Climate Engineering Methods – Carbon Dioxide Removal, CDR

1. Direct CO_2 removal (CDR) from air
2. Alkalinity to the ocean (enhanced weathering)
3. Ocean fertilization
4. Removal of other greenhouse gases

Part 4: CE – Effectiveness, Side Effects (3 sessions)

1. Comparison of Techniques, characterisation of side effects
2. Other parameters than temperature
3. Summary

Literature

Appell D. (2013), Mopping up carbon, Physics World (June 2013), 23-27.

DePaolo and Orr (2008), Geoscience research for our energy future, Physics Today, Aug. 2008, 46-51.

Jones N. (2009) Sucking it up, Nature 458, 1094-1097.

Lackner K.S., Grimes P., and Ziock H.-J. (2011), Capturing Carbon Dioxide from Air, Report.

Lackner K.S. (2013), The thermodynamics of direct air capture of carbon dioxide, Energy 50 38-46.

Socolow, R. et al. (2011), Direct Air Capture of CO2 with Chemicals, A Technology Assessment for the APS Panel on Public Affairs, June 1, 2011.

Shepherd J.G. (2012) Geoengineering the climate: an overview and update, Phil. Trans. R. Soc. A 370, 4166-4175, doi: 10.1098/rsta.2012.0186.

Stephens, J. C. and D. W. Keith (2008). Assessing Geochemical Carbon Management, Climatic Change 90, 217-242.

Stolaroff J.K. (2006), Capturing CO_2 from ambient air: a feasibility assessment, Ph.D. Thesis, Carnegie Mellon University, Pittsburgh, PA.

Vaughan N.E. and Lenton T.M. (2012), Interactions between reducing CO_2 emissions, CO_2 removal and solar radiation management, Phil. Trans. R. Soc. A 370, 4343-4364, doi: 10.1098/rsta.2012.0188.

Sunho Choi, Taku Watanabe,Tae-Hyun Bae, David S. Sholl, and Christopher W. Jones (2012), Modification of the Mg/DOBDC MOF with Amines to Enhance CO_2 Adsorption from Ultradilute Gases, J. Phys. Chem. Lett. 3, 1136 − 1141.

Contents of Today's Lecture

- Taxonomy of CDR Methods
- The basic physics of removing CO_2 from air
- The basic chemistry of removing CO_2 from air
- Where to store the removed CO_2?
- Some „practical“ suggestions
- Summary

Taxonomy and Nomenclature for CO_2-Removal (CDR) methods

Direct Air Capture (DAC) usually refers to industrial direct capture of CO_2 to make a CO_2 product. (another taxonomy from Stephens and Keith, 2008)

Almost every carbon dioxide removal method by definition directly captures CO_2 from the atmosphere, and thus they may all be thought of as some form of direct capture of CO_2 from the air.

DAC is sometimes used to refer only to centralized chemical-industrial facilities that remove CO_2 form the atmosphere (rather than to nearly all carbon dioxide removal (CDR) approaches).

Important dimensions to consider are:

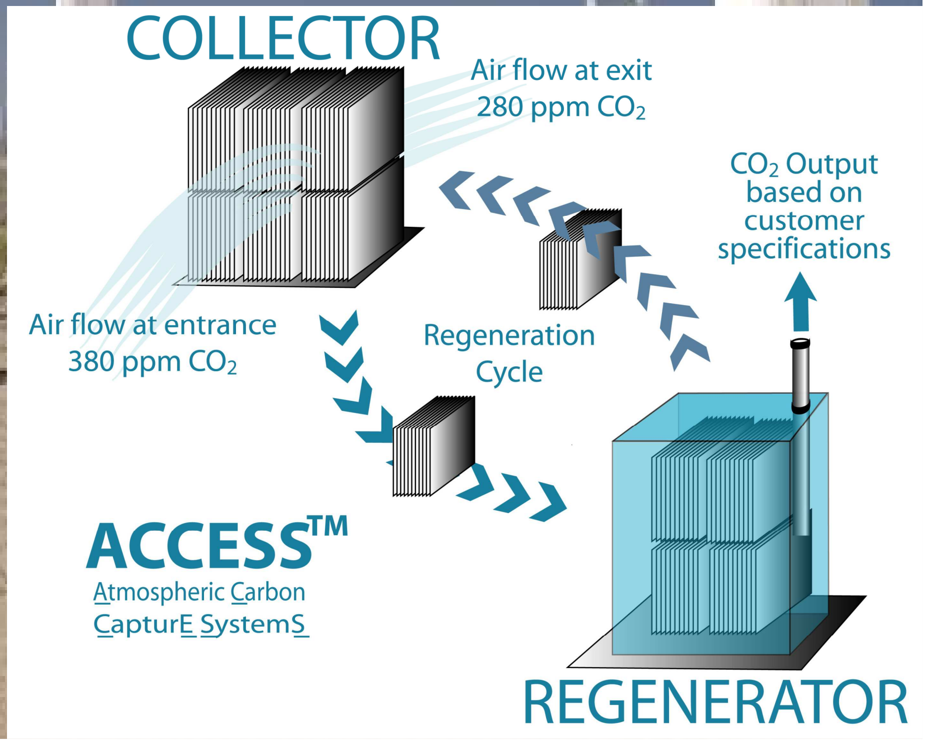
1. Biological (plants) vs. chemical approaches
2. Centralized vs. distributed approaches
3. Is the carbon stored as oxidized (molecular CO_2, HCO_3^-, etc) or re-used (organic carbon, black carbon)?

These 3 choices define 8 categories, examples:

- Centralized industrialized direct air capture is investigating (1) chemical approaches that are (2) centralized and (3) store the carbon as molecular CO_2 [oxidized].
- Ocean fertilization is (1) biological approach that is (2) distributed and (3) ultimately stores C as HCO_3^- [oxidized] carbon in the deep sea.
- Biochar is a (1) biological approach to capture that is (2) distributed and (3) stores C as reduced carbon. Liming the ocean is a (1) chemical approach that is (2) distributed over a wide area and (3) stores C as oxidized carbon (HCO_3^-).
- Afforestation is a (1) biological approach that is (2) distributed over a wide area and (3) stores the carbon as reduced [organic] carbon.

Which of these 8 basic categories are populated? Do we have clear an unambiguous terms to refer to each of the populated categories? There appear to be no feasible centralized biological approaches because photosynthesis by its very nature involves large areas to capture enough sunlight to be quantitatively important.

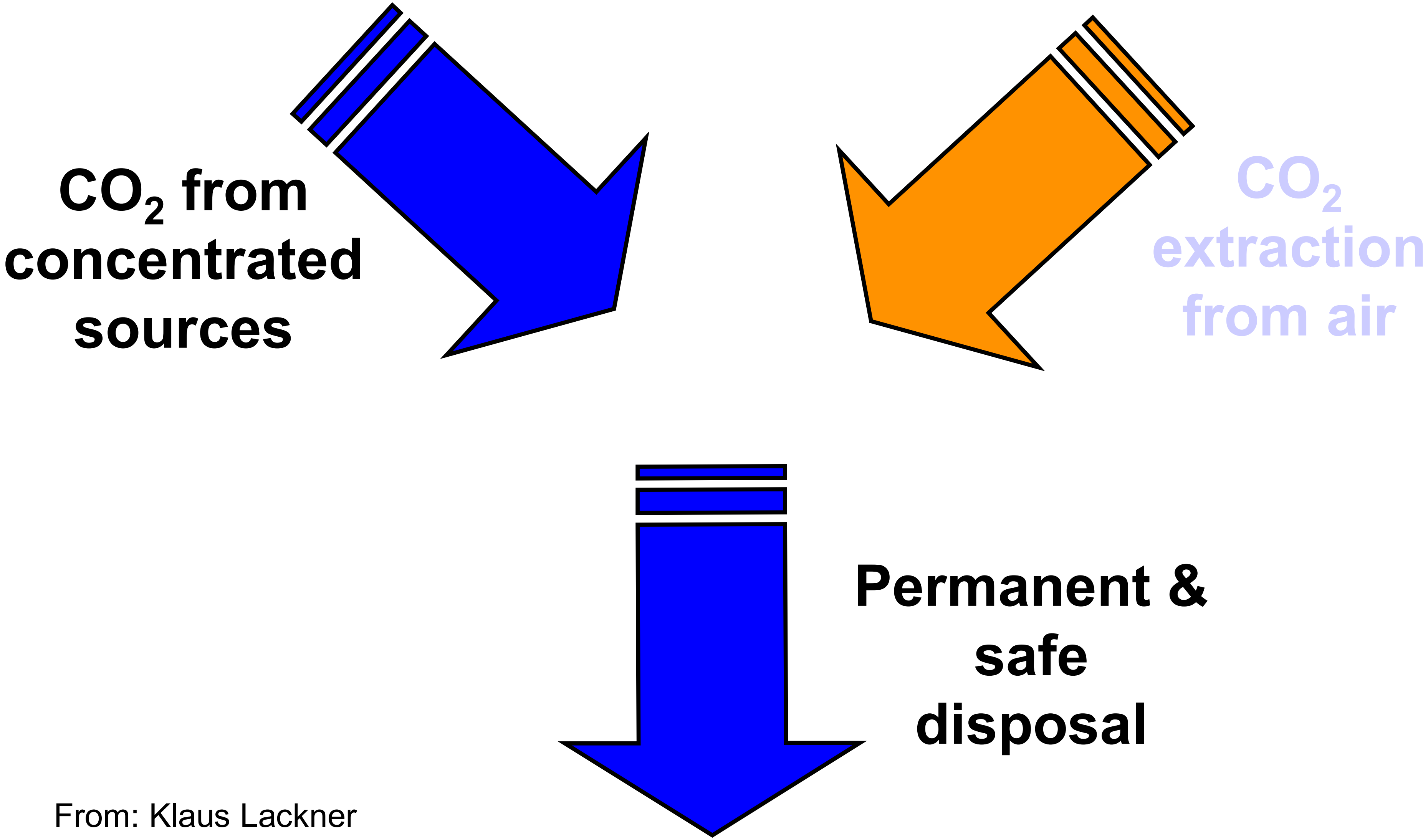
CO_2 – Removal from the Atmosphere



Art: Stonehaven CCS, Montreal,

from **Klaus Lackner**, Columbia University

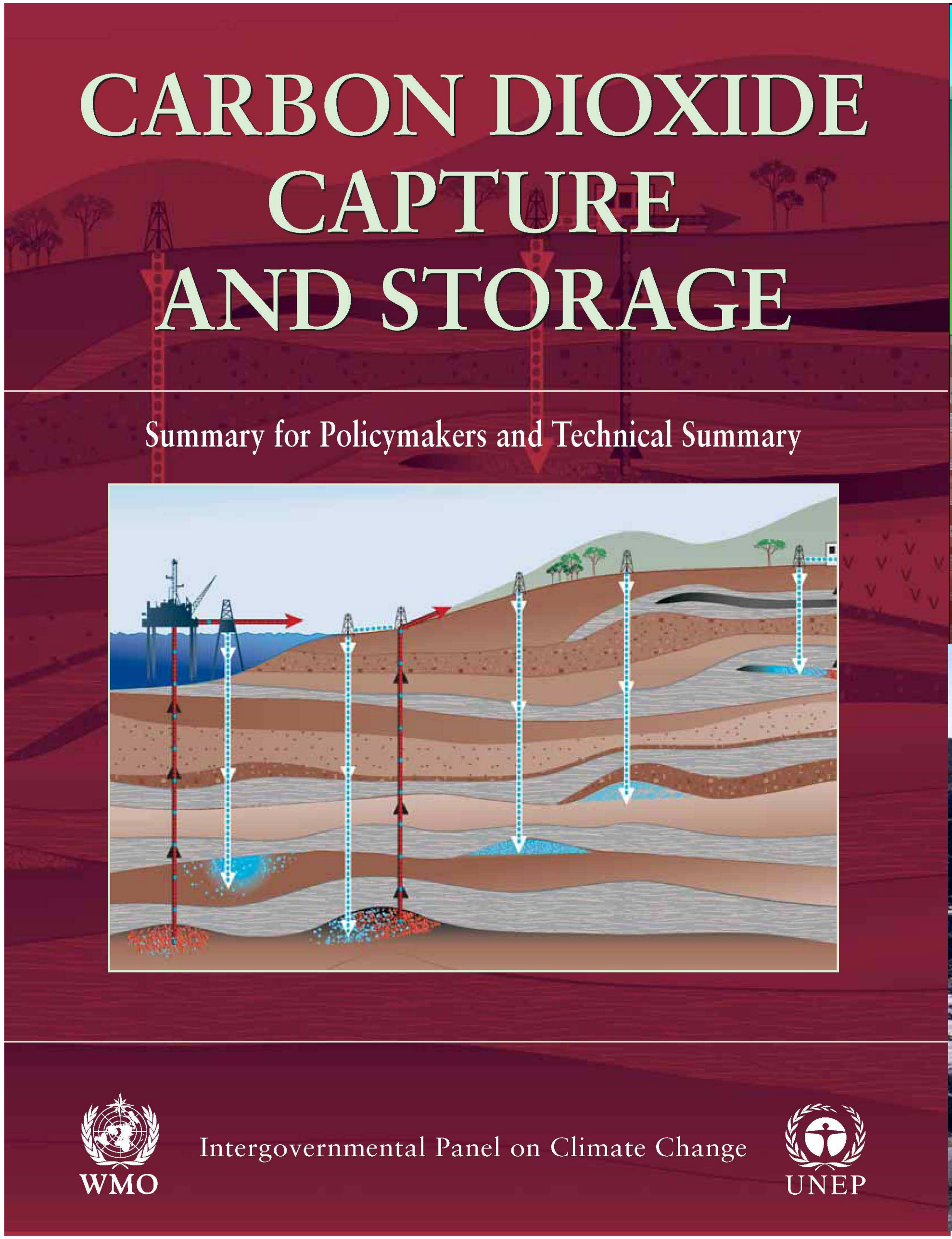
Net Zero Carbon Economy

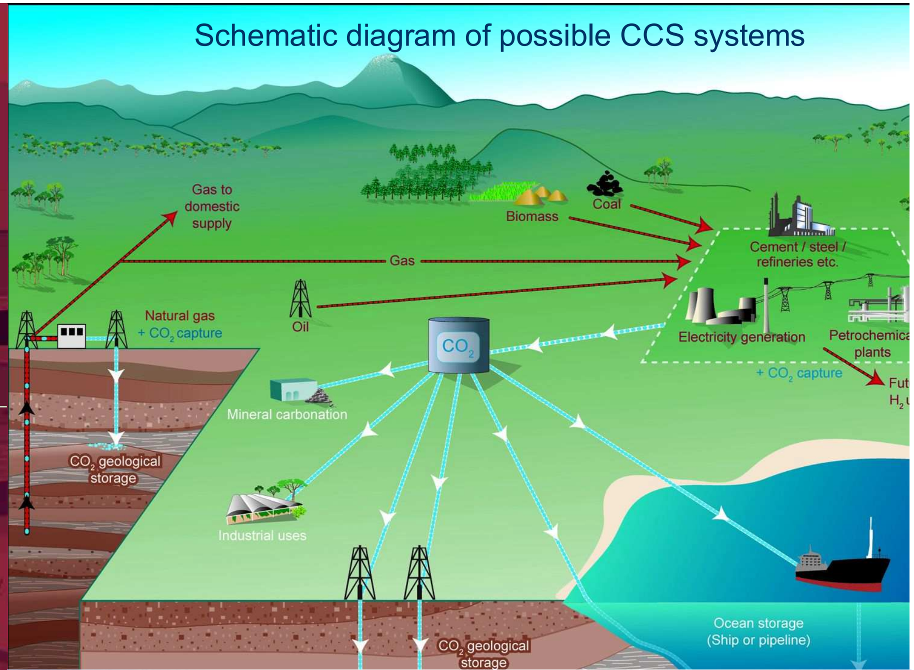


From: Klaus Lackner

LENFEST CENTER FOR SUSTAINABLE ENERGY

Initially Air Capture is Tied to CO_2 - Storage





Air Capture

- Takes CO_2 from the atmosphere to offset CO_2 emissions
- Can compensate for all CO_2 emissions
- Particularly interesting to offset emission from distributed, small and mobile sources (e.g. cars, aircraft)
- Hydrocarbon fuels could still be used

Natural Air Extraction

- Ocean Uptake

  30% of anthropogenic CO_2 emission

- Trees

  Biomass absorbs 100 GtC annually

  Capture cost ~ $27/ton of CO_2

  Land demand too large

  Leaves are underutilized for CO_2 extraction

From: Klaus Lackner

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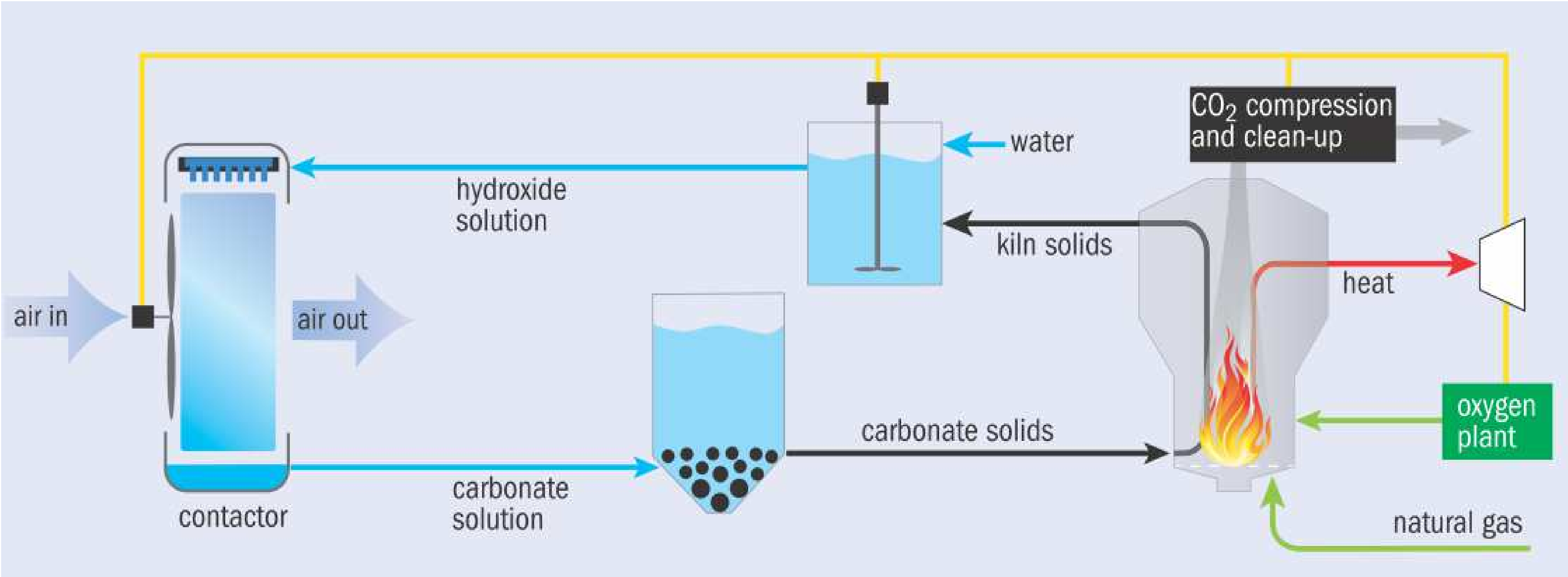
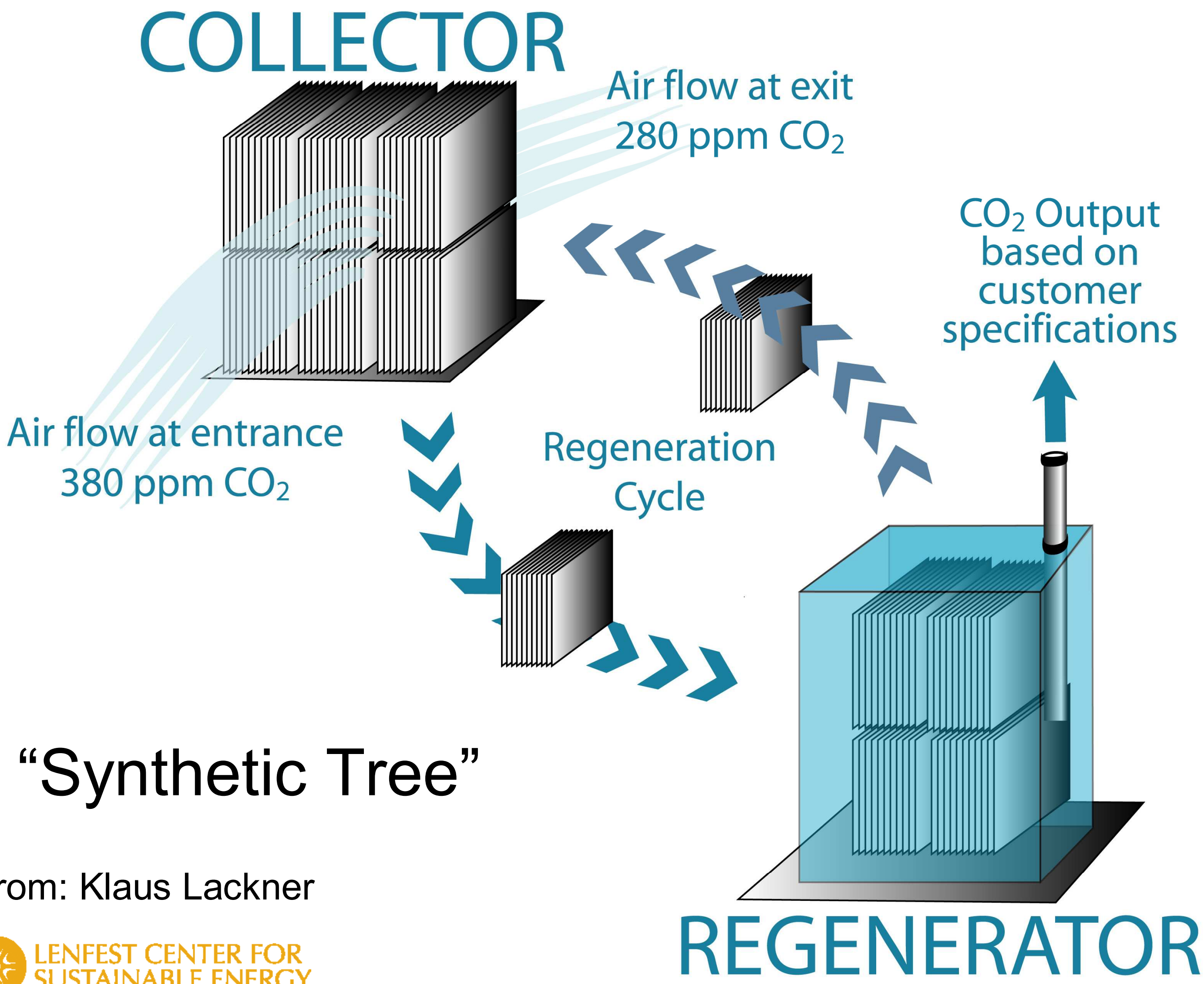
Chemical Capture



From Appell 2013

Air Capture: Collection & Regeneration



"Synthetic Tree"

From: Klaus Lackner

Courtesy GRT

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„Energy Contents“ of Air

Combustion, e.g.:

$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$ $\Delta H^o = -890.5$ kJ/mol

(This corresponds to 20.2 kJ/g of CO_2)

1 m^3 air at 293K (=41.6 moles) contains (at 400 ppm)
n=0.0166 moles of CO_2

→ $E = \Delta H^o \cdot n \approx 14.8$ kJ (a bit less, if gasoline or coal was burned)

→ If we remove all CO_2 from a m^3 of air, we offset the energy release from combustion of fossil fuels of about 10-15 kJ (approx. 3-4 Wh)

→ Energy consumption should for scrubbing 1 m^3 should be << 10 kJ!

Challenge: CO_2 in Air is Dilute

- Energetics limits options

  Work done on air must be small!

  - compared to heat content of carbon
  - 10 kJ/m^3 of air (equiv. to cooling 1m^3 of air (≈41.6 mol) by ≈8K)

- No heating, no compression, no cooling
- Low velocity 10m/s (60 J/m^3)

Solution: Sorbents remove CO_2 from air flow

From: Klaus Lackner

Minimum Energy Needed to Extract CO_2 from Air

Entropy relative to a component
with mixing ratio x for one mole of mixture:

$$\Delta S = -R \cdot \left[x \ln x + (1-x) \cdot \ln(1-x) \right] = \frac{\Delta W}{T}$$

$$\approx -R \cdot x \ln x$$

x = (molar) mixing ratio of species to be removed from mixture

$R \approx 8.31\ JMol^{-1}K^{-1}$ = gas constant

Atm. CO_2: $x \approx 4 \cdot 10^{-4}$ (400ppm) → $\Delta S \approx 0.026\ Jmol^{-1}K^{-1}$ for 1 mole of air

Entropy relative to a component for one mole of component:

$$\Delta S_x = -\frac{R}{x} \cdot \left[x \ln x + (1-x) \cdot \ln(1-x) \right] = \frac{\Delta W_x}{T} \approx -R \cdot \ln x$$

Minimum energy required to separate 1 mole of CO_2 at $x_{CO2} = 4 \cdot 10^{-4}$:

$$\Delta W_x = \Delta S_x \cdot T = -\frac{RT}{x} \cdot \left[x \ln x + (1-x) \cdot \ln(1-x) \right] \approx -RT \cdot \ln x$$

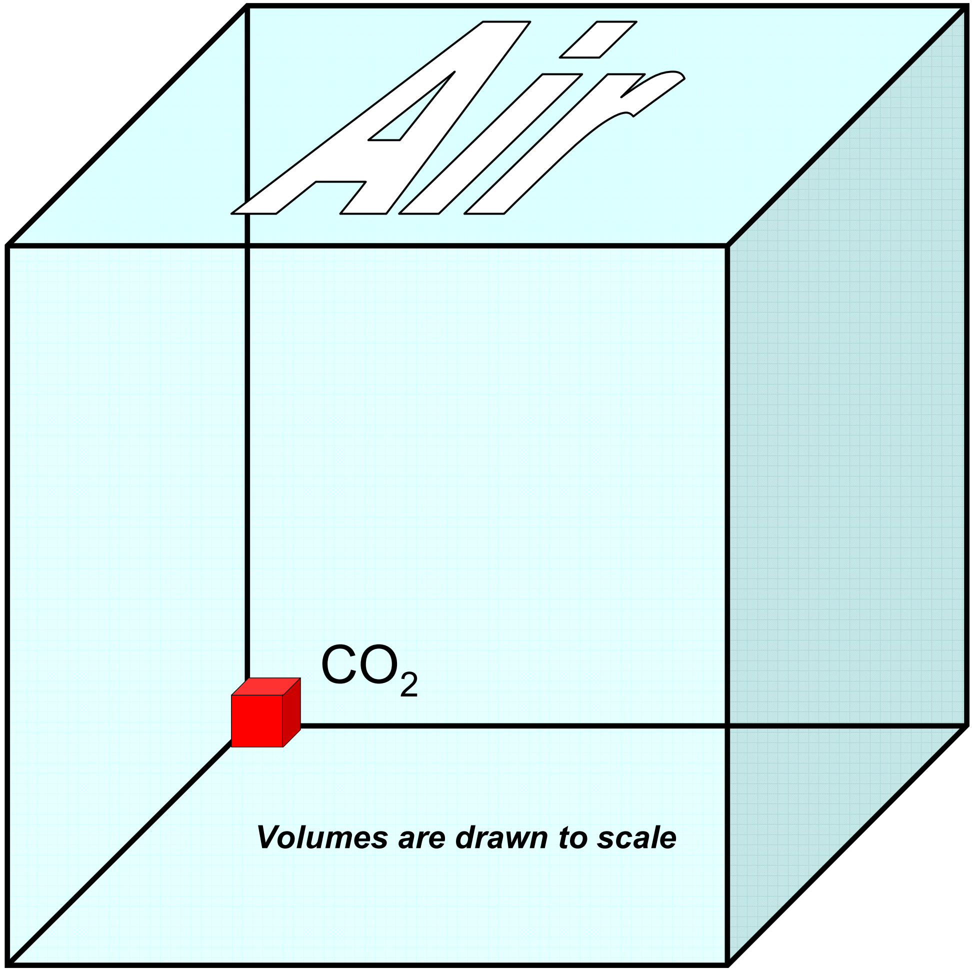
for $x \approx 4 \cdot 10^{-4}$ (400ppm) and 300K → $\ln(4 \cdot 10^{-4}) \approx -7.824$

→ ΔW_{CO2} ≈ 19.5 kJ/mol of CO_2 extracted (or 320J for all CO_2 of 1 m^3 air)

→ ≈ 443 kJ/kg of CO_2 extracted (M_{CO2}= 0.044 Kg/mole)

For comparison: ΔH(coal) ≈ 11 MJ/(kg CO_2), $\Delta H(CH_4)$ ≈ 20 MJ/(kg CO_2),

CO_2 Capture from Air



1 m³ of Air

≈40 moles of gas, 1.16 kg
wind speed 6 m/s:

$$E_{kin} = \frac{mv^2}{2} \approx 20\ \mathrm{J}$$

0.0166 moles of CO_2 (0.73 g)

produced by ≈11 kJ of gasoline

Minimum energy to remove:
320 J

From: Klaus Lackner

How much Wind?

equivalent to emission of 0.73g/s of CO_2

(6m/sec)

0.2 m^2 for CO_2

Area that carries 0.73g of CO_2 per second (22 tons/year)

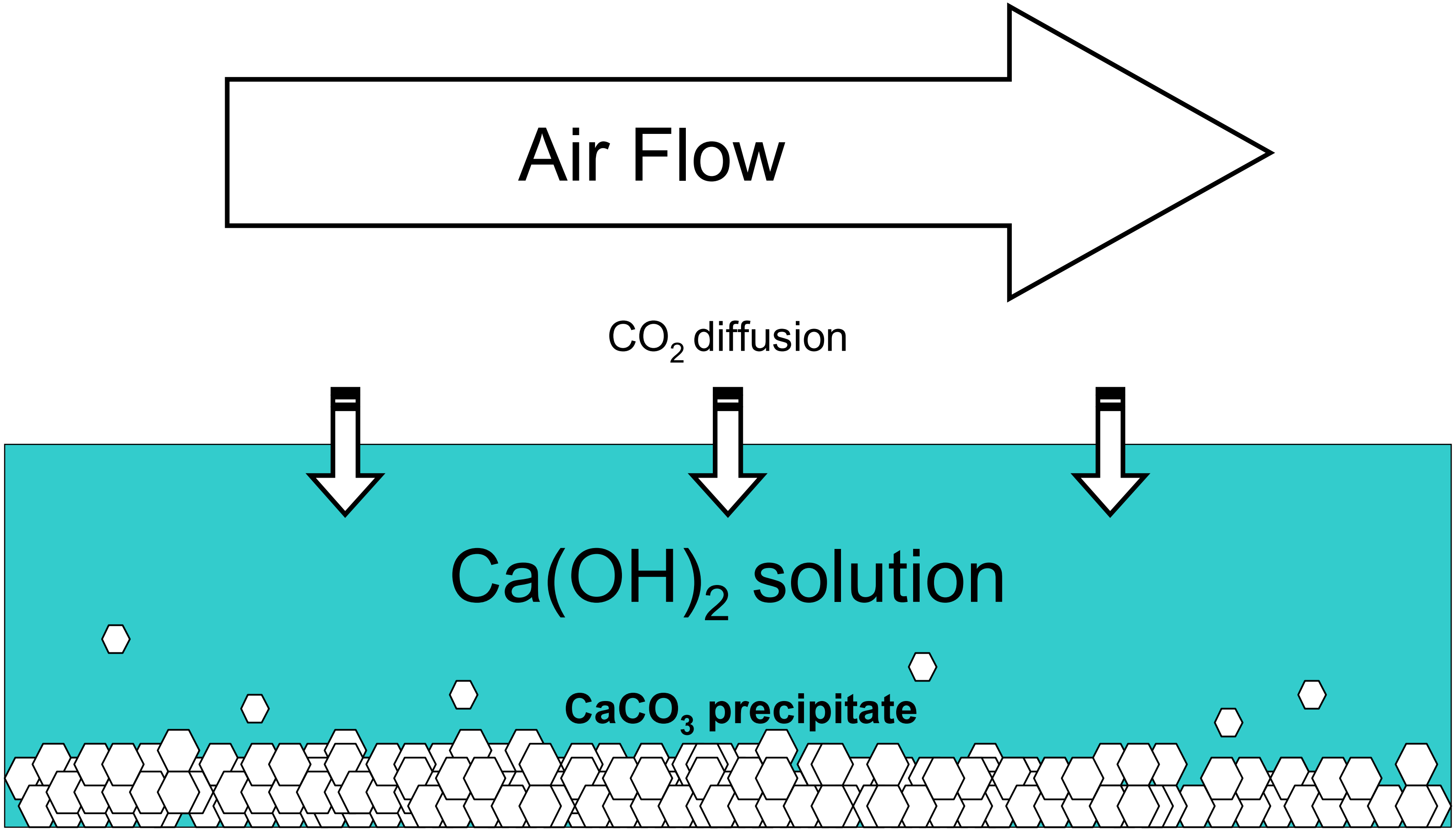
50 cents/ton of CO_2 for contacting

Wind area that carries 10 kW of wind power

80 m^2 for Wind Energy

From: Klaus Lackner

$Ca(OH)_2$ as an absorbent



CO_2 mass transfer is limited by diffusion in air boundary layer

From: Klaus Lackner LENFEST CENTER FOR SUSTAINABLE ENERGY

A First Attempt

From: Klaus Lackner

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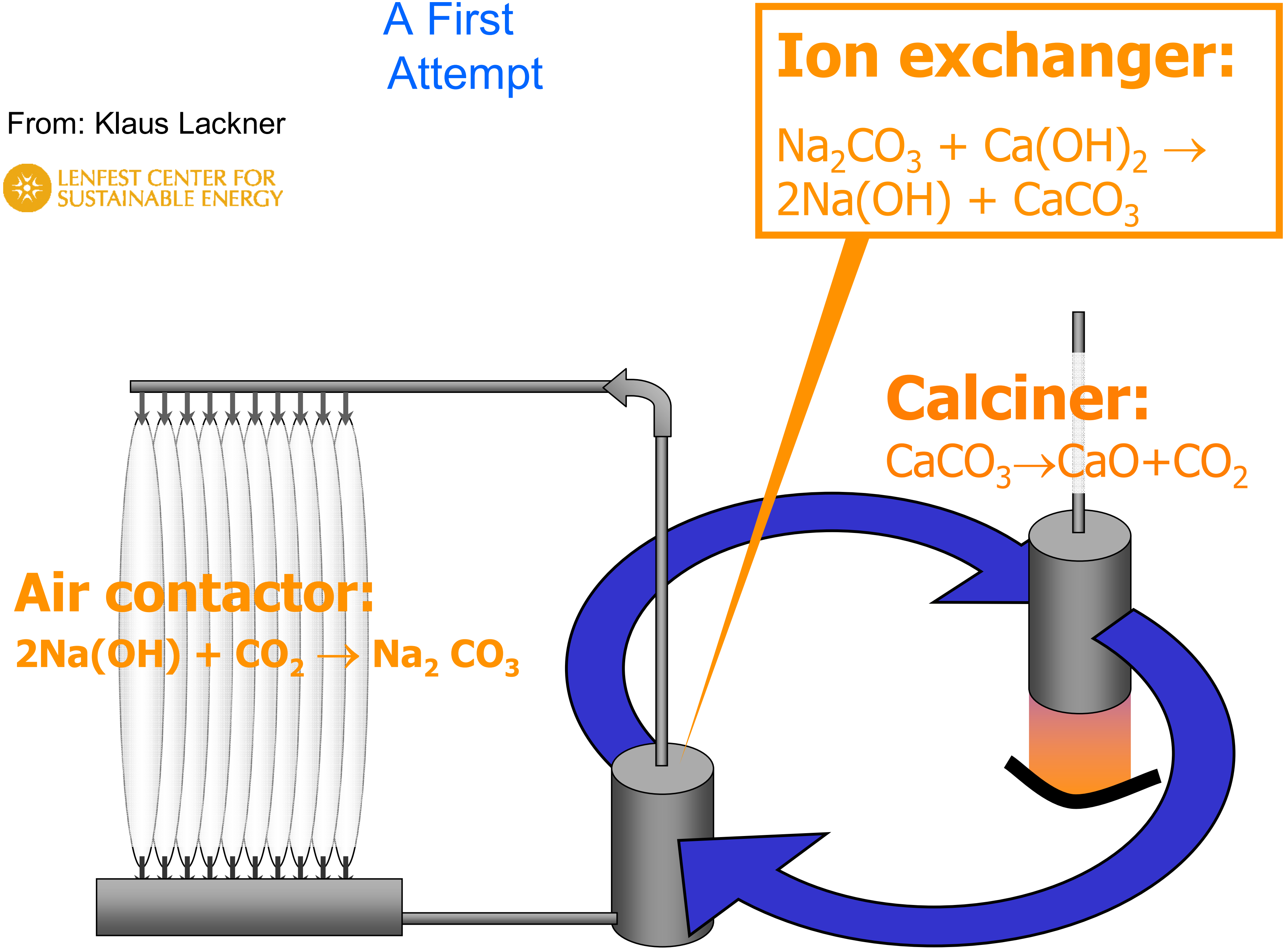
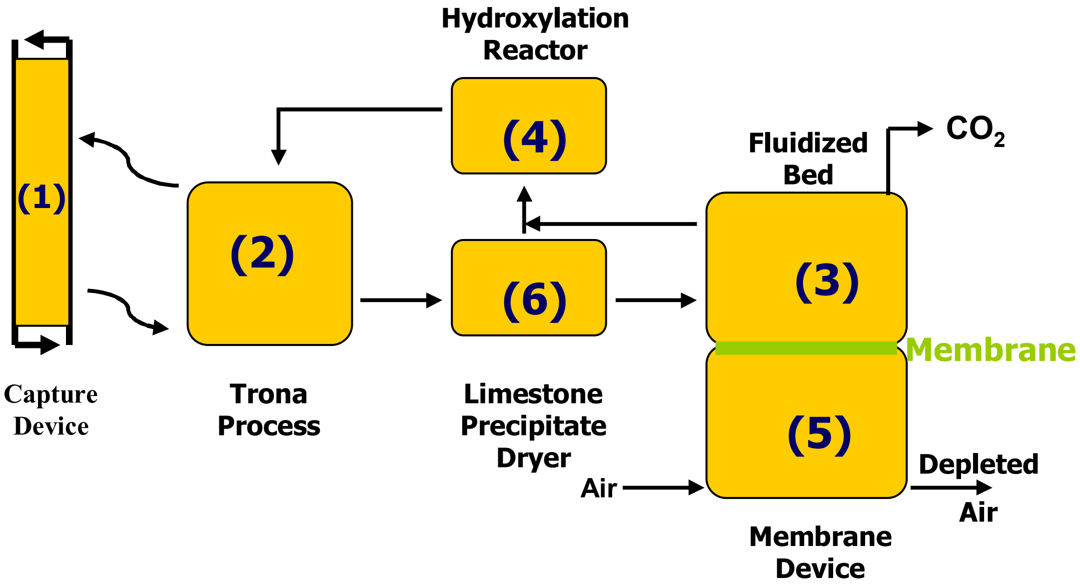


Process Reactions



(1) $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$ $\Delta H^{o} = -171.8$ kJ/mol

(2) $Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$ $\Delta H^{o} = 57.1$ kJ/mol

(3) $CaCO_3 \rightarrow CaO + CO_2$ $\Delta H^{o} = 179.2$ kJ/mol

(4) $CaO + H_2O \rightarrow Ca(OH)_2$ $\Delta H^{o} = -64.5$ kJ/mol

(5) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H^{o} = -890.5$ kJ/mol

(6) $H_2O_{(l)} \rightarrow H_2O_{(g)}$ $\Delta H^{o} = 41.$ kJ/mol

Source: Frank Zeman

Optimum Binding Energy?

Strong CO_2 - sorbent bond:

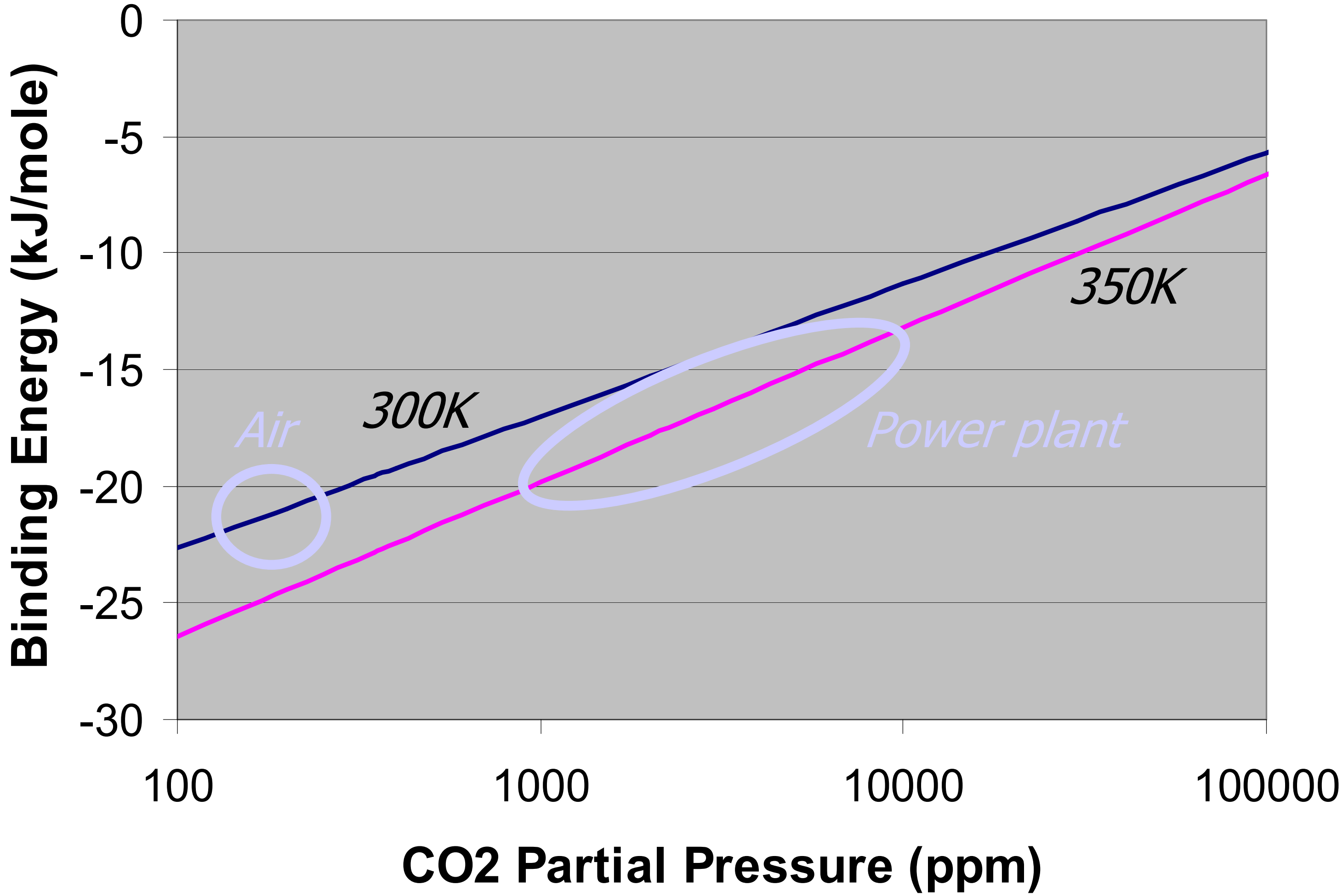
- Can remove all CO_2 (low residual concentration)
- Much energy needed to extract CO_2 from sorbent (= regeneration of sorbent)

Weak CO_2 - sorbent bond:

- Can only remove part of CO_2 (high residual concentration)
- Little energy needed to extract CO_2 from sorbent (easy regeneration of sorbent)

→ Search for Optimum

Sorbent Choices



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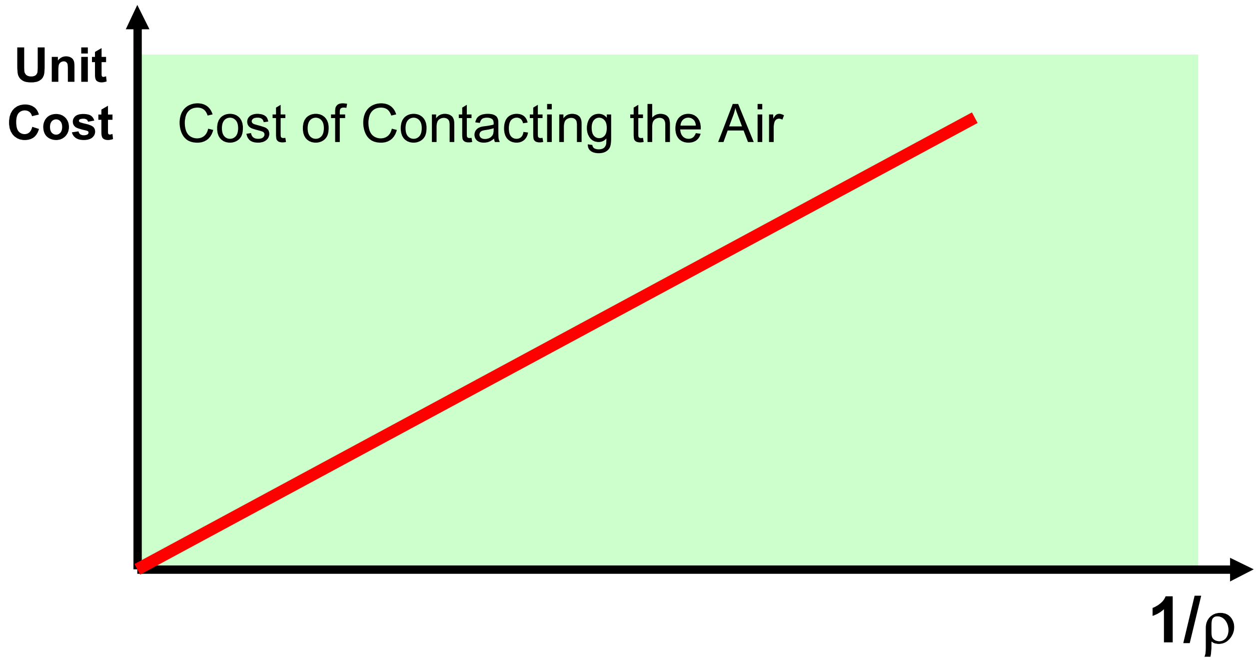
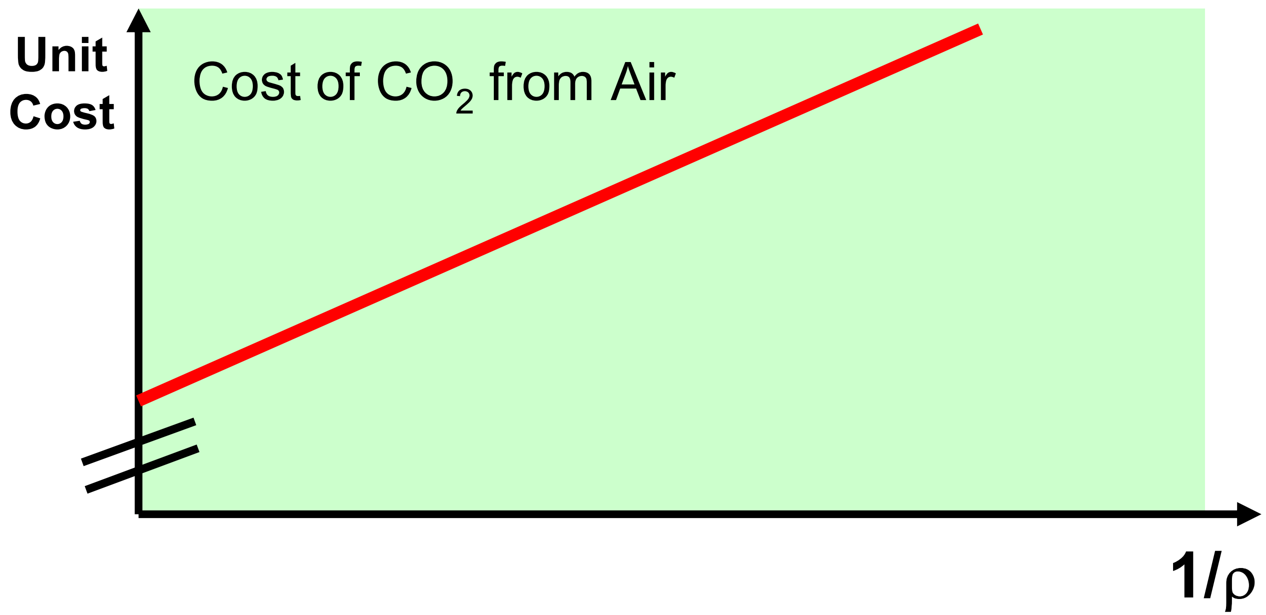
Remember: Minimum energy required (at 400ppm, 300K)

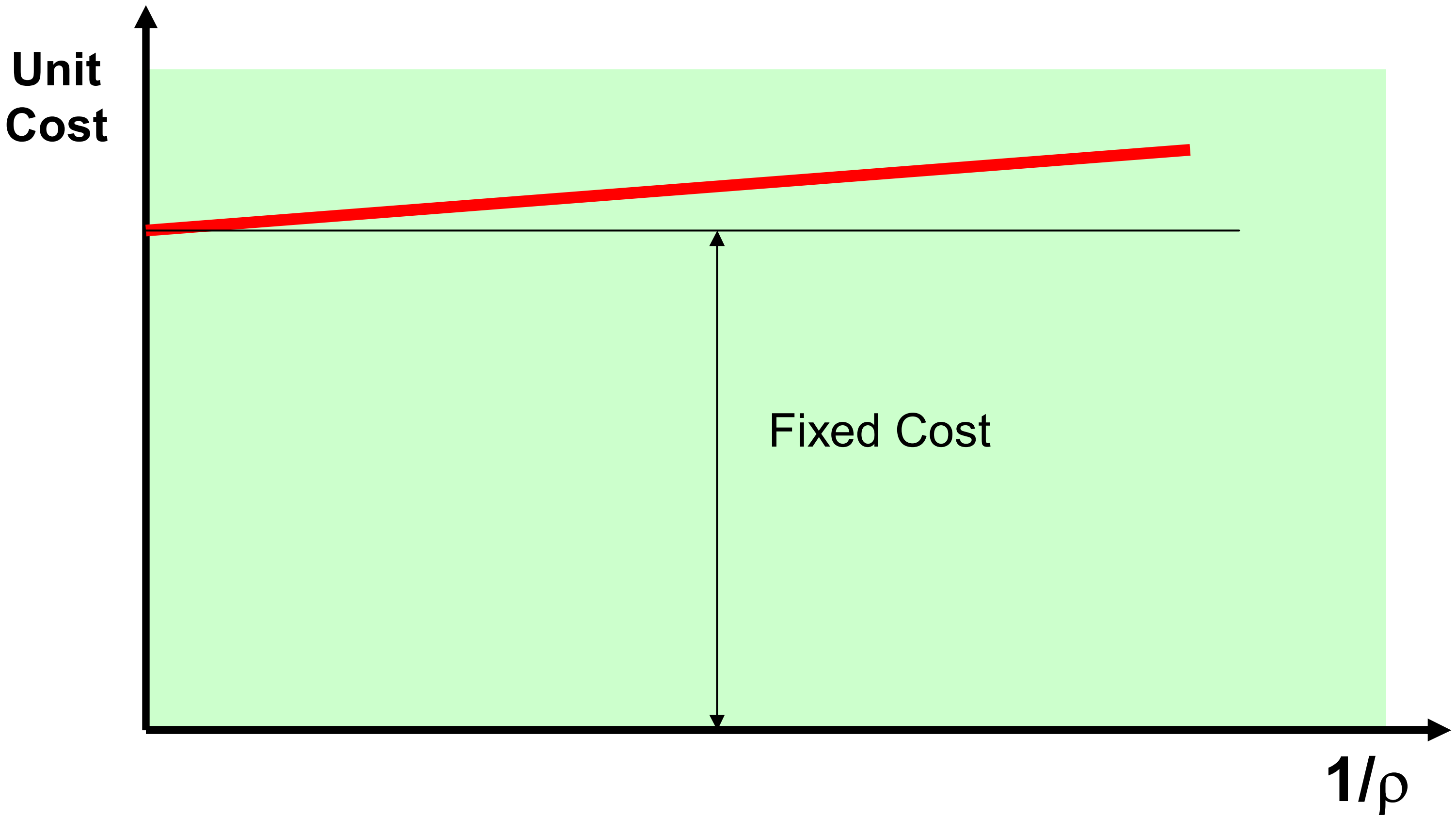
$\Delta W_{CO2} \approx 19.5$ kJ/mol of CO_2

Cost Components





Cost of CO_2 from Air (rescaled)



From: Klaus Lackner

Sketching out a design

Compare to windmills in 1960

Cost goal:

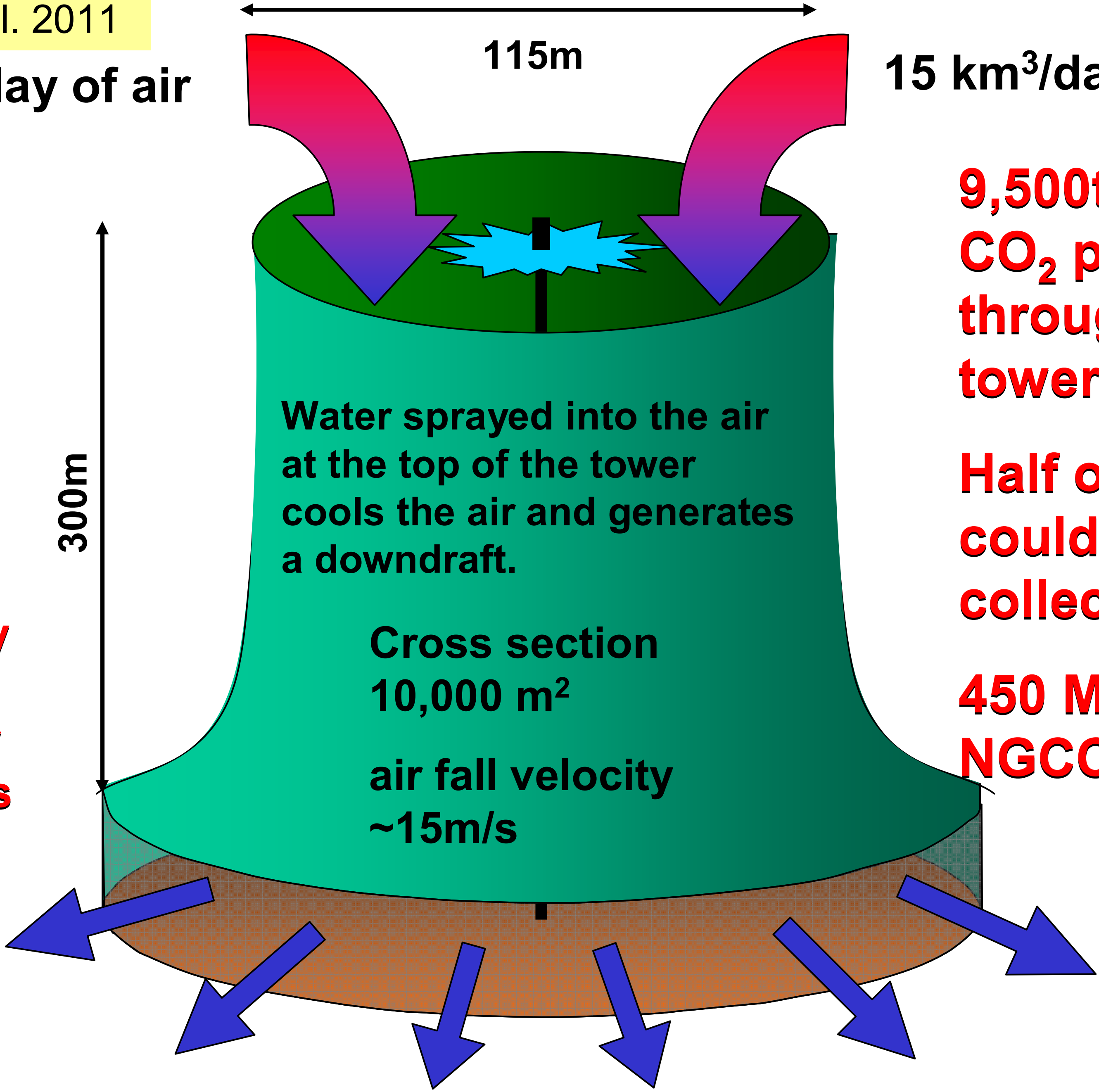
$30/ton of CO_2

Motivated by cost of fuel, oxygen, electricity, raw materials

From: Klaus Lackner

Convection Tower for CO_2-Removal

Lackner et al. 2011

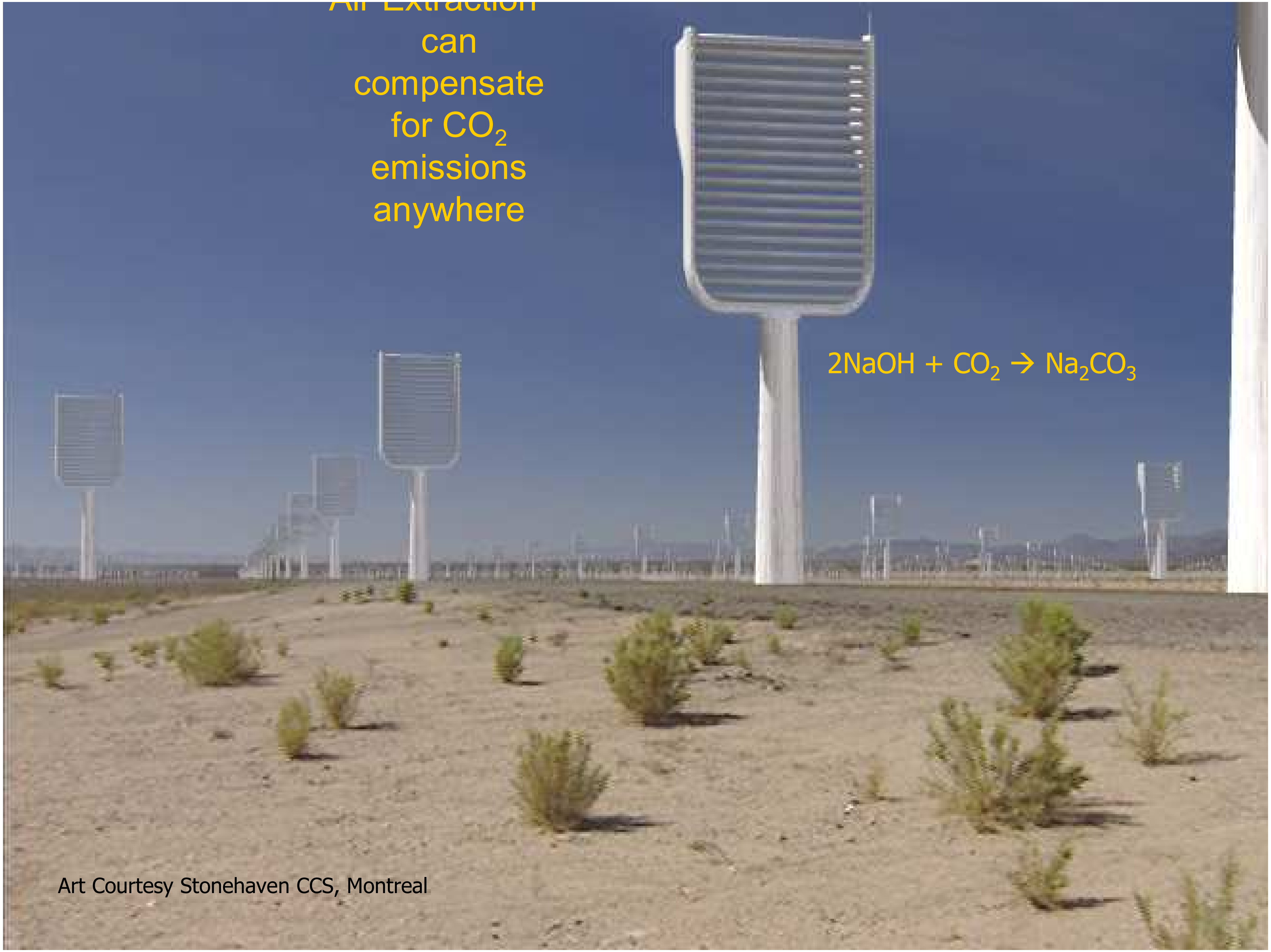


As electricity producer the tower generates 3-4 MW_e

9,500t of CO_2 pass through the tower daily.

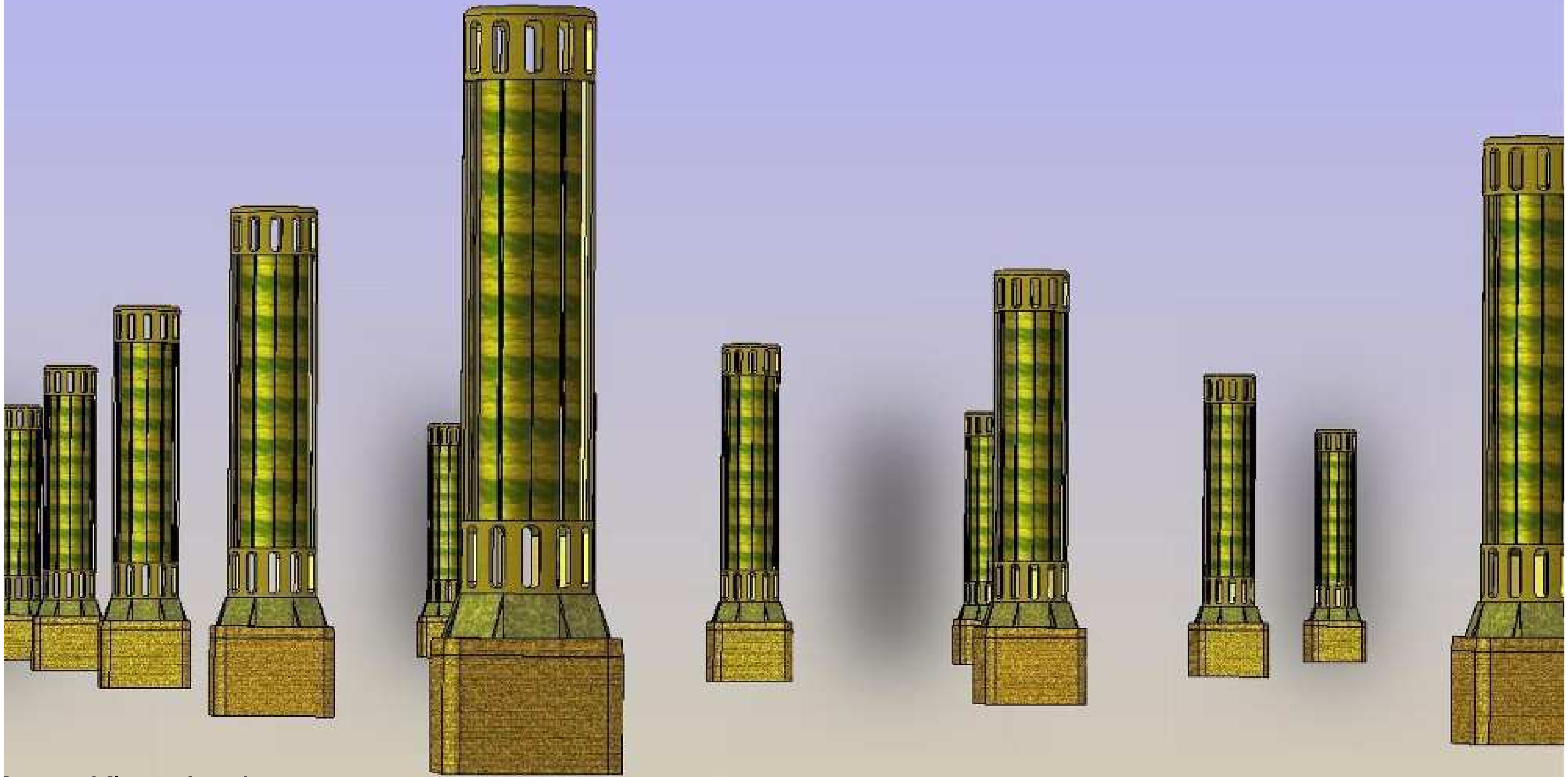
Half of it could be collected

450 MW_e NGCC plant


can compensate for CO_2 emissions anywhere
$2NaOH + CO_2 \rightarrow Na_2CO_3$
Art Courtesy Stonehaven CCS, Montreal

GRT

Small factory produced units can be packed into a standard 40 foot shipping container



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GRT’s Vision

'rst of a kind

From: Klaus Lackner

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Collection and Regeneration

Collection

- Natural wind carries CO_2 to collector
- CO_2 binds to surface on ion exchange sorbent materials

Regeneration

- CO_2 is recovered with:
  - liquid water wash
  - or carbonate solution wash
  - or low-temperature water vapor
  - plus optional low grade heat
- Regenerated sorbent is reused many times over

From: Klaus Lackner

Courtesy GRT

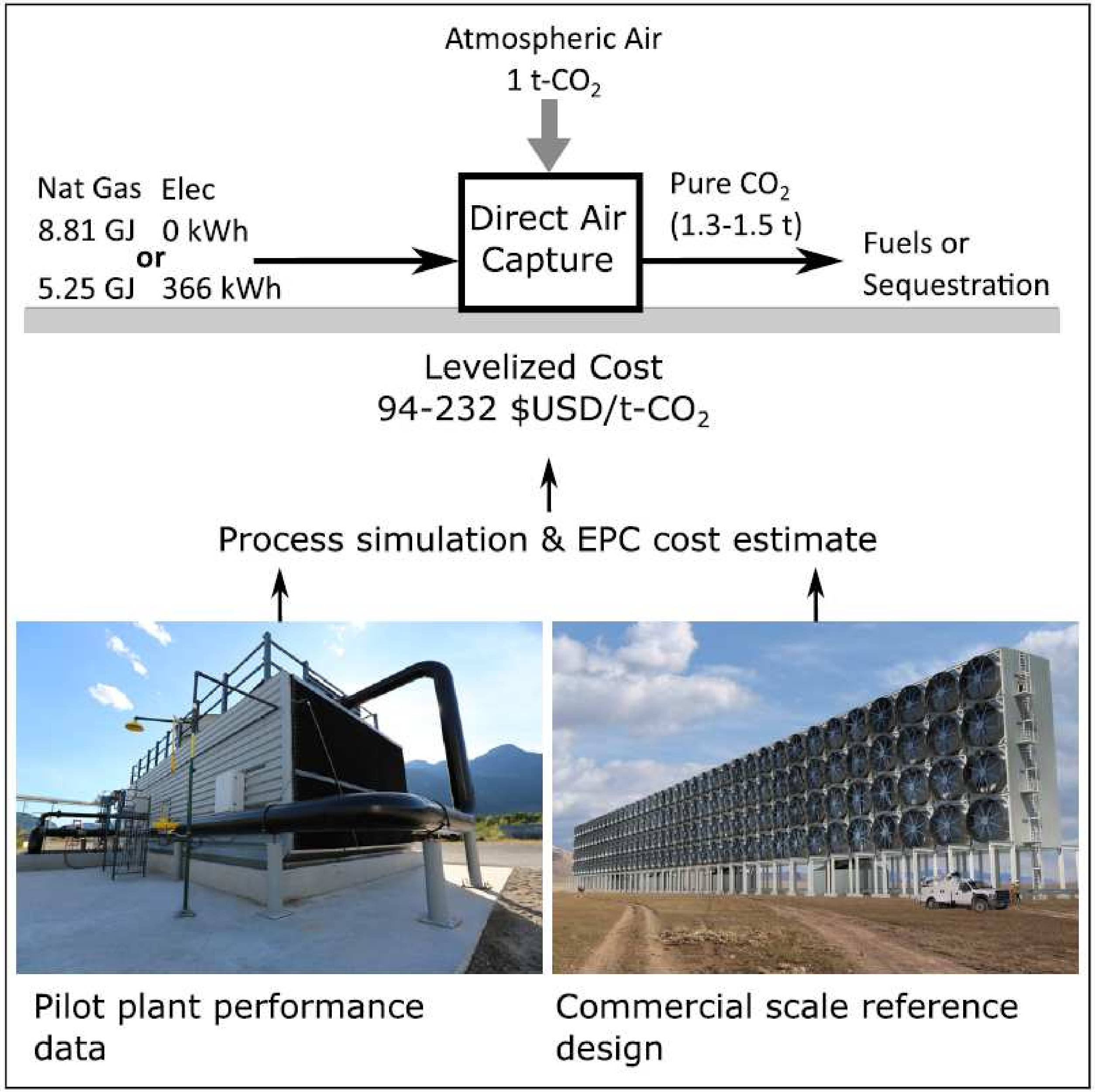
Options for Regeneration

- Pressure Swing
- Thermal Swing
- Water Swing
  - Liquid water – wet water swing
  - Water vapor – humidity swing
- Carbonate wash is a water swing
  - With CO_2 transfer
  - Salt splitter for CO_2 recovery

From: Klaus Lackner

CDR: Direct Air Capture Device

Cost per ton CO_2 captured from the atmosphere:
94 - 232 $.

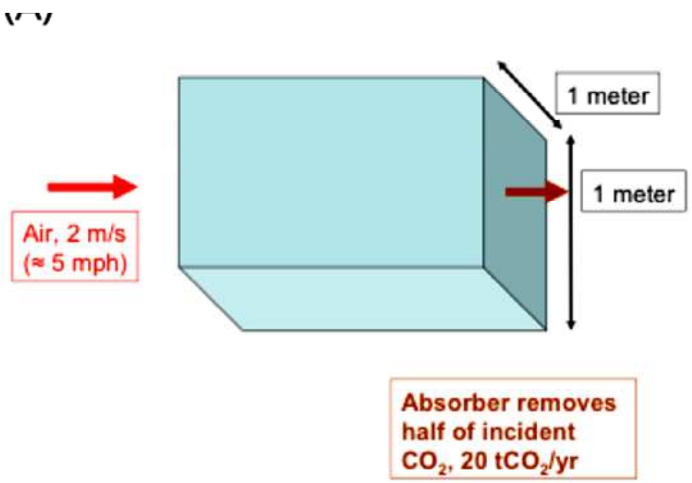


Keith et al. (2018), A Process for Capturing CO_2 from the Atmosphere, Joule, https://doi.org/10.1016/j.joule.2018.05.006

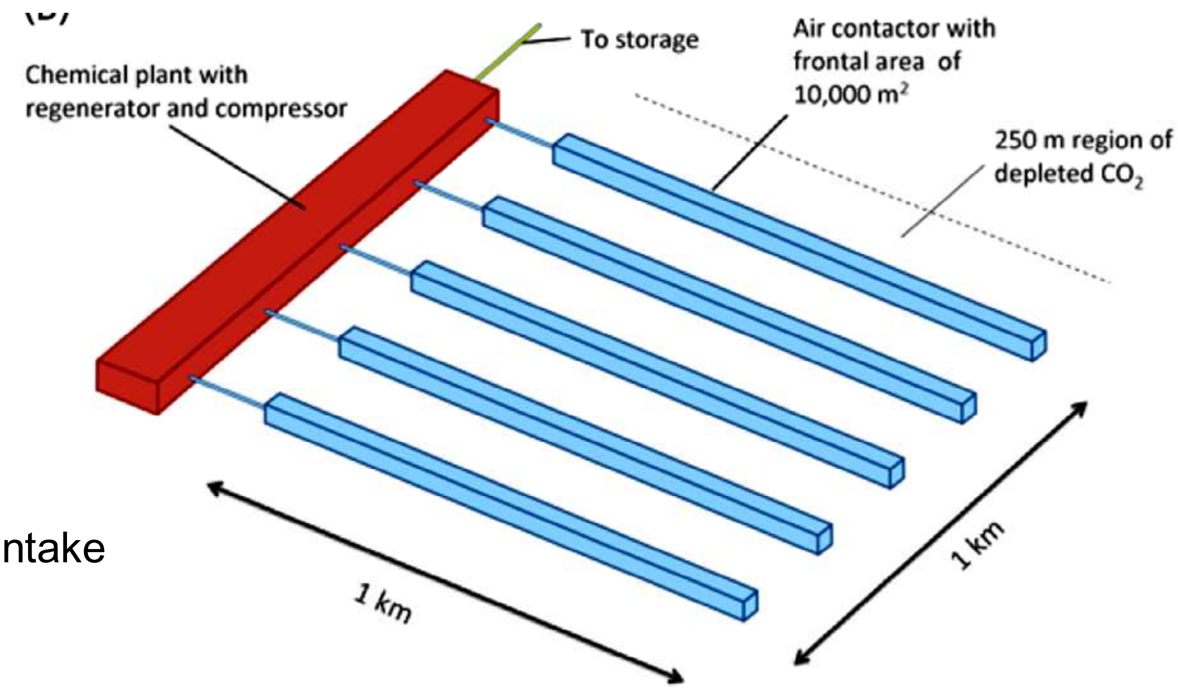
David Keith and his carbon-capture machine.

Another Practical Design …

From: Socolow et al. 2011



Schematic representations of a 1 m^2 intake area contactor capturing 20 tCO_2/yr



Schematic representations of a facility for capturing 1 $MtCO_2$/yr. It consists of five structures, each 10 meters high and 1 km long, and could collect 1 $MtCO_2$/yr if air passed through at 2 m/s and 50% of the CO_2 were collected. The structures are spaced 250 meters apart, and the footprint of the system is roughly 1.5 km^2 . Approximately six of these systems would be required to compensate for the emissions of a 1 GW coal plant. Buildings not to scale.

Removing CO_2 from the Ocean

Eisaman M.D., Parajuly K., Tuganov A., Eldershaw C., Chang N. and Littau K.A. (2012), CO2 extraction from seawater using bipolar membrane electrodialysis, Energy & Environmental Science, DOI: 10.1039/c2ee03393c

In principle not much difference in the effect of removing CO_2 from air (DAC) and removing CO_2 from ocean water, as long as CO_2 is extracted from surface ocean water. Advantage of removing CO_2 from ocean water: Higher volumetric density of CO2 (DIC) in ocean water.
Volume specific CO_2 concentration in sea water $\approx$120 times that of air.
→ 120-times less volume has to be processed.
However: water is much denser than air (which requires more power for pumping it),
Mass specific CO_2 conc. is only about 20% of that of air (at sea level pressure).
Neither pump air nor water to remove CO_2.
Rather rely on natural flow of the media (i.e. wind or ocean currents, respectively).
→ Compare the product of CO_2 volume specific concentration and typical velocities in air/water. Typical velocities in the ocean are 1-2 orders of magnitude slower than in the atmosphere,
→ This largely offsets the higher volume specific CO_2 density in ocean water.
Another problem is the energy consumption:
Eisaman et al. 2012 requires 242 kJ/mol to remove one mole of CO_2 from the ocean
→ 27% (or more) of the energy gained by burning fossil fuel.
Summary: The scheme does not appear to be a very bad idea, however advantages are no entirely obvious (although they may be there). Also, it may be possible to improve the technique.

Where to Store the Captured CO_2??

- Ocean
- Somewhere Underground
- Old oil/gas fields

Air Capture Supports Underground Injection

- Safety Valve
  - Unpredicted changes in the underground reservoir should trigger a safe release of CO_2
  - Compensated for by air capture
- Carbon Accounting
  - Losses can be made up by air capture
  - Air capture can introduce C-14 tracking

From: Klaus Lackner

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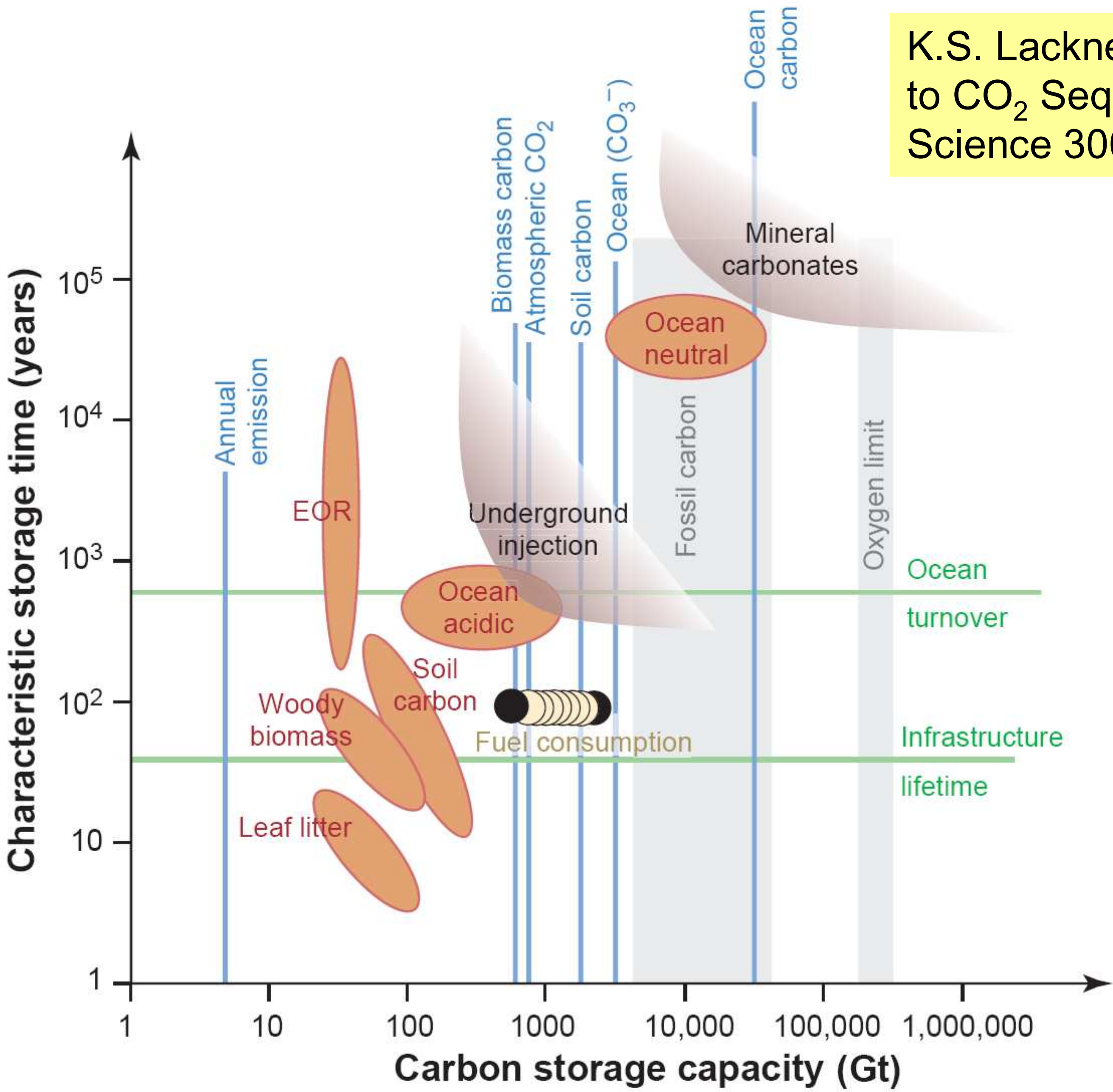
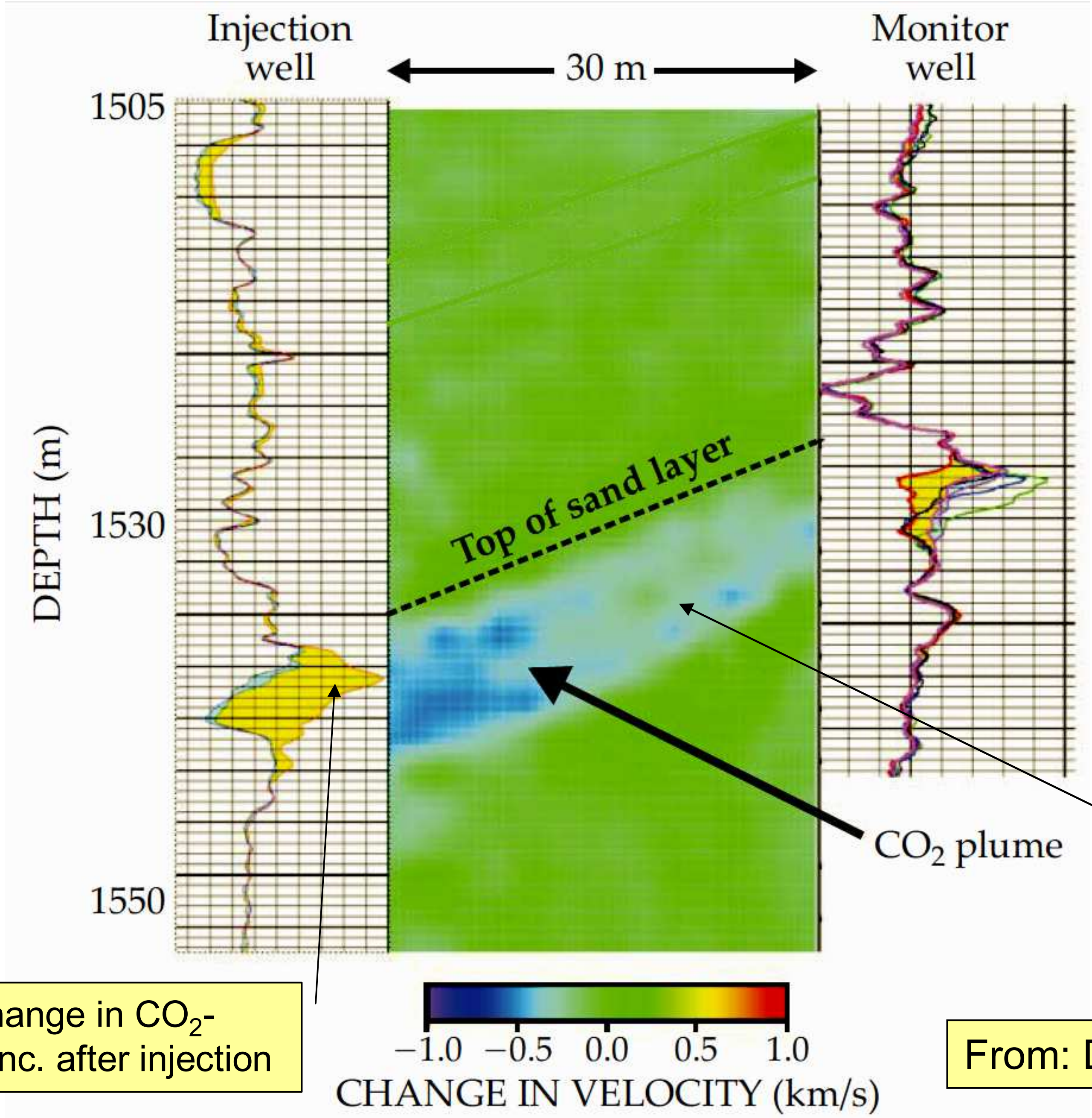
Carbon Storage

K.S. Lackner (2003), A Guide to CO_2 Sequestration, Science 300, 1677-1679.



A CO_2-Injection Experiment



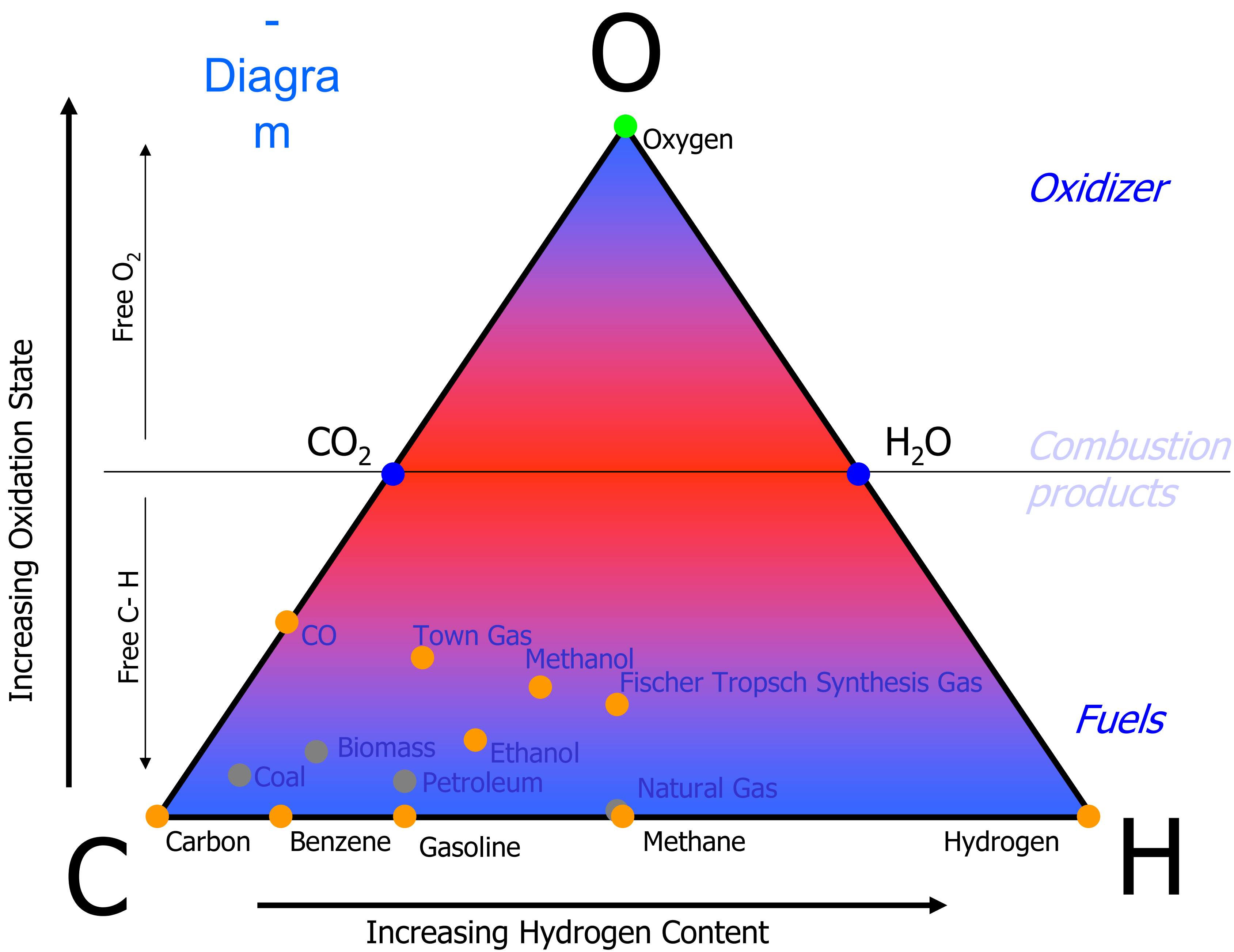
1600 t of CO2 injected at 1540 m depth in southeast Texas

Seismic Tomography Image

Change in CO_2-conc. after injection

From: DePaolo and Orr 2008

- Diagram



From: Klaus Lackner

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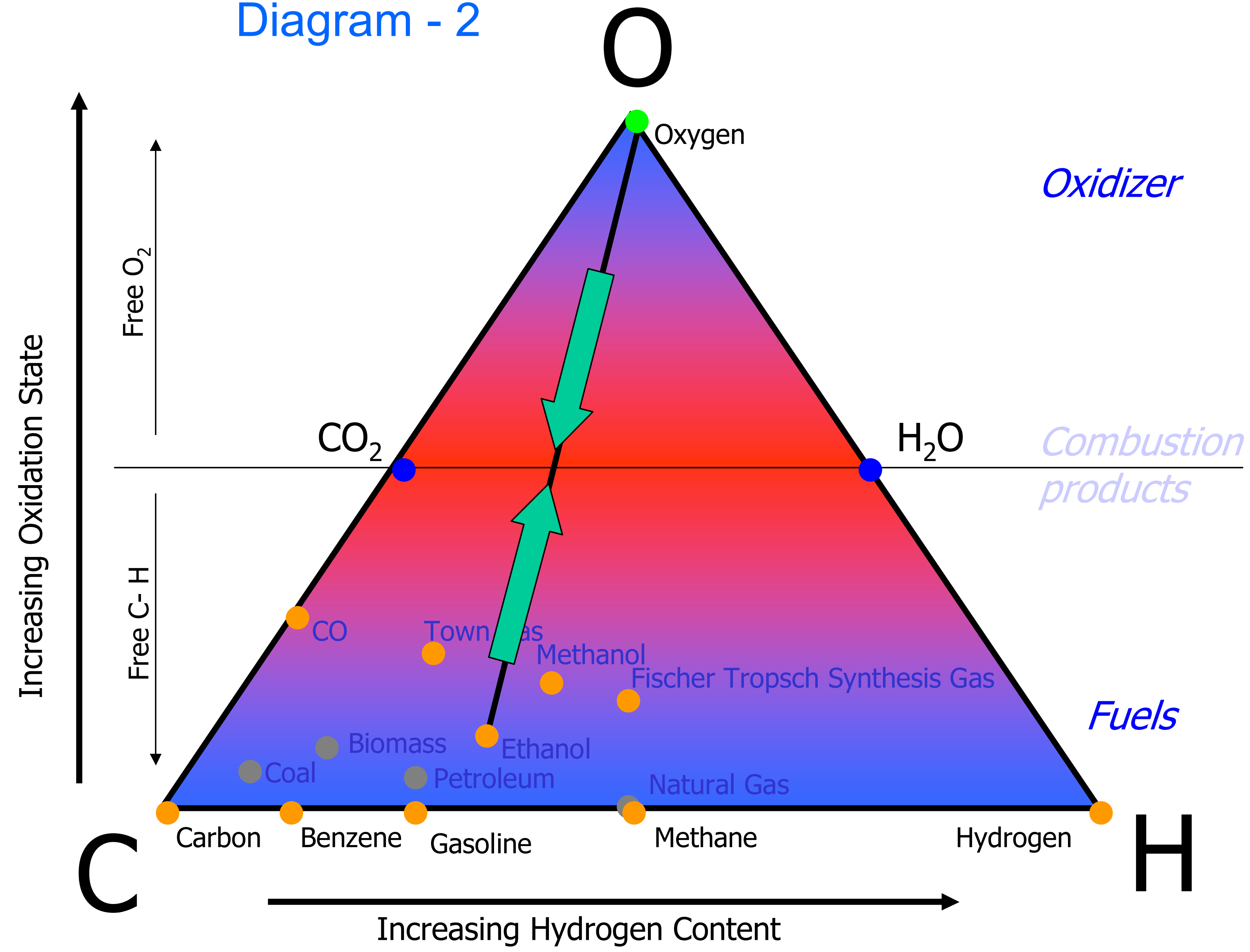
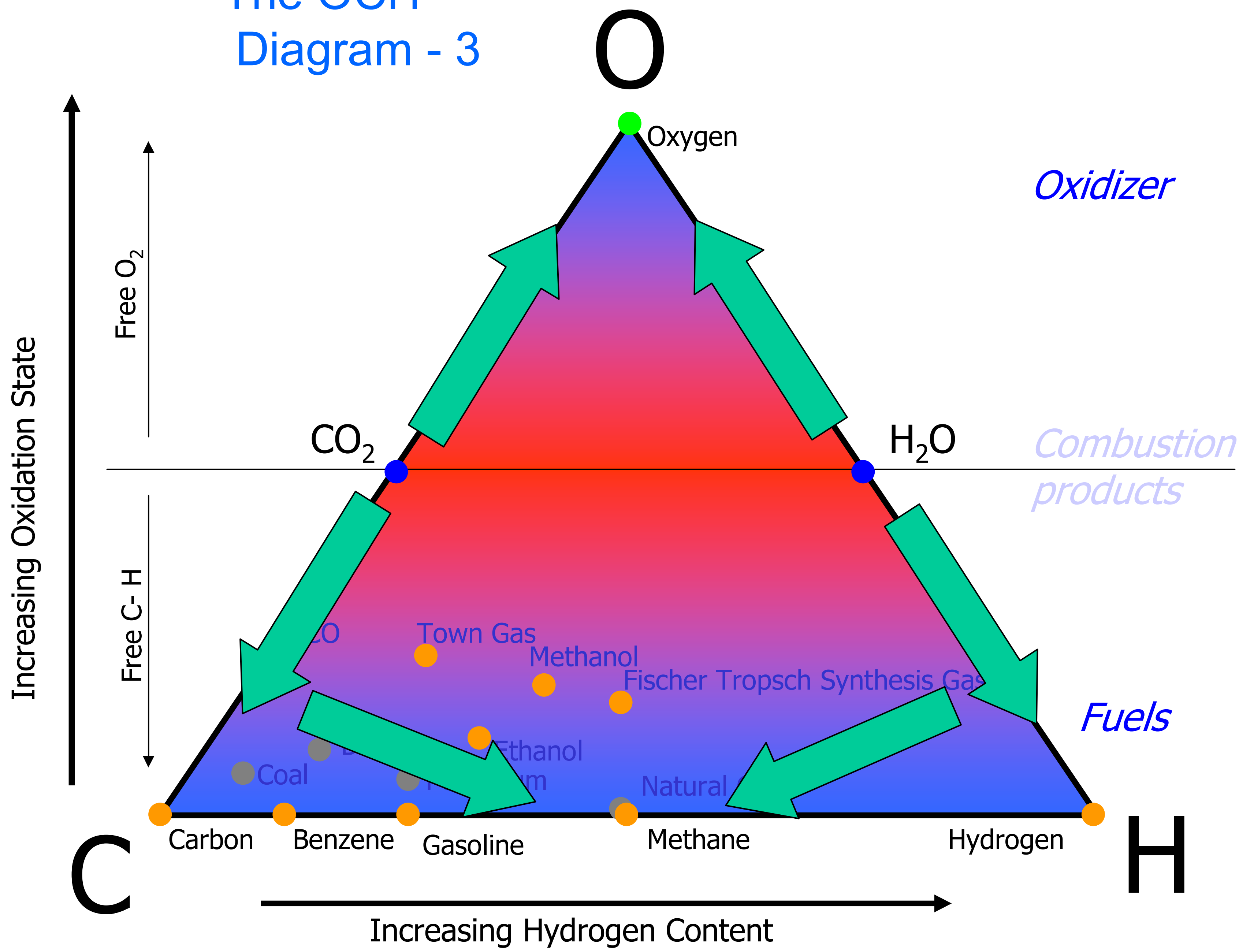
The OCH – Diagram - 2



The OCH – Diagram - 3



Cost of Air-Capture CDR Measures

1) Minimum Energy required: 443 kJ/kg of CO_2 extracted, corresponds to 0.12 KWh
→ at 0.25 €/KWh: 0.03 €/kg or 30 €/t of CO_2
(note that electricity becomes cheaper if you consume more, also there is cheaper energy than electricity.)

2) Estimate by Socolow et al. 2011 : 62$ (50€) per t of CO_2

3) Estimate by Stolarow 2006: 80-250$ per t of CO_2

For comparison: 1 barrel of oil produces about 0.5 t of CO_2
→ at 100$ (75€)/barrel it „costs“
200$ (150€) to produce a ton of CO_2

How much air do we need to treat annually?

1) Annual emission of C to the atmosphere: 10 Gt (does not all stay in the atmosphere, but this does not matter because of equilibrium)
2) Which is about 2.5% of the 800GtC that are already there.
3) Assuming that we remove all CO_2 in the treated air we need to blow 2.5% of the atmospheric volume through the plant annually.
4) Atmospheric volume: $V_{Atm} = A_{Earth} \cdot h_{Scale} \approx 5 \cdot 10^8\ km^2 \cdot 8\ km \approx 4 \cdot 10^9\ km^3/a$
5) At a wind (blower) speed of v=10m/s ($3.14 \cdot 10^5$ km/a) this corresponds to an Exchanger area of:

$$A_E = V_{Atm}/v \approx (4 \cdot 10^9\ km^3/a) / (3.14 \cdot 10^5\ km/a) \approx 10^4\ km^2$$

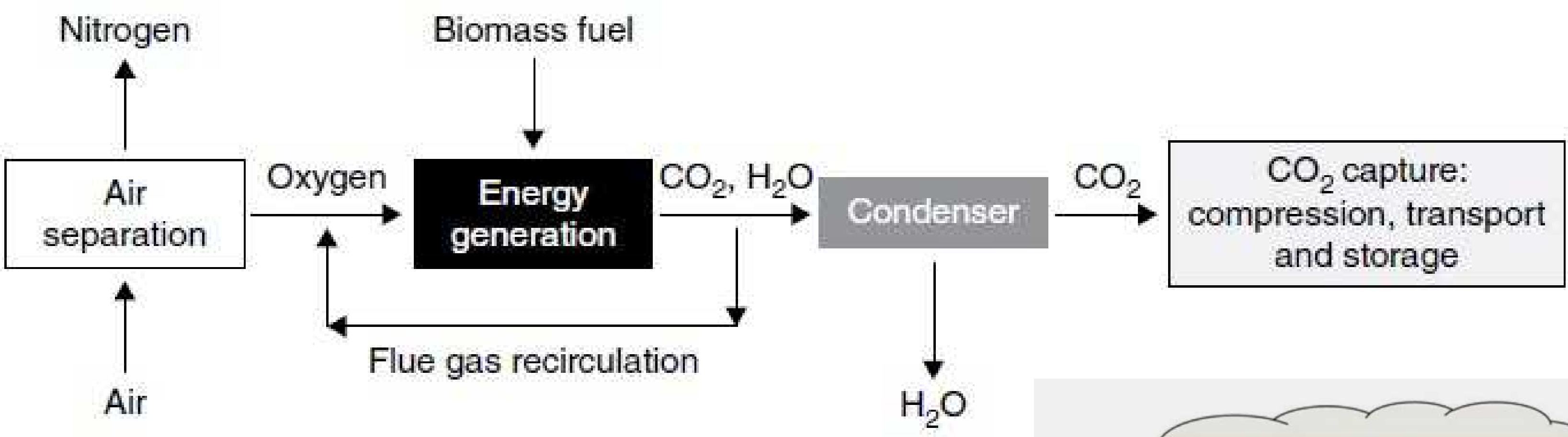
An „Artificial Forest“

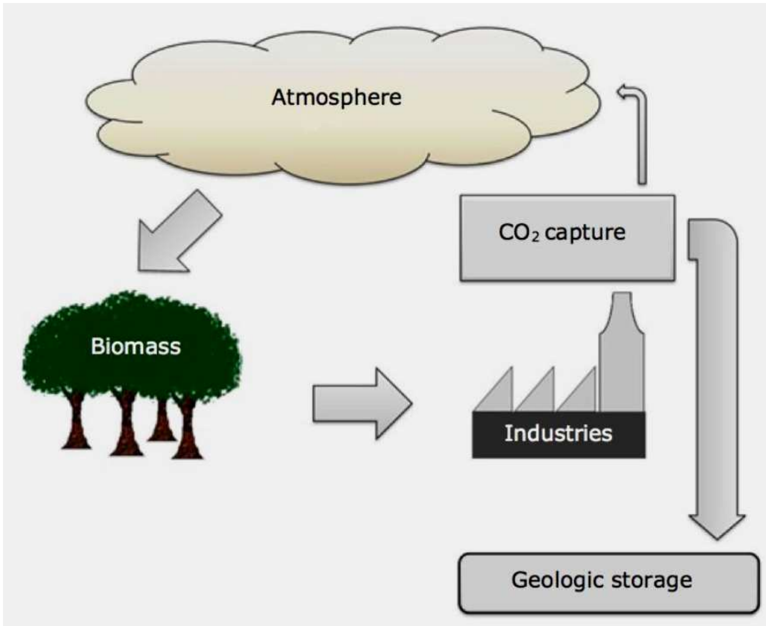
Klaus Lackner has imagined huge ‘farms’ featuring thousands of air-scrubbing devices that could soak up billions of tonnes of carbon from the atmosphere.

From: Jones 2009

CDR-3: Bioenergy + Carbon Capture & Stroage BECCS

The Idea: Burn biomass (containing carbon removed from the atmosphere by Photosynthesis), burn it and store the CO_2 underground:





Advantages:

Possibly cheap

Disadvantages:

Availability of Biomass?

Water demand

Proximity of suitable storage sites

Total annual capacity?

Competition to food production

Edström E. & Öberg C. (2013), Review of Bioenergy with Carbon Capture and Storage (BECCS) and Possibilities of Introducing a Small-Scale Unit, **Master's Thesis** KTH School of Industrial Engineering and Management Energy Technology EGI-2013-048MSC EKV950, Stockholm.

Summary

- Direct removel of CO_2 from air by technical means is possible
- Minimum energy required for CO_2 removal is 2-5% of energy gained by combustion of fossil fuel
- Cost needs to be determined, present estimates of the order of present cost of fossil fuel.
- Higher cost of CO_2 removal could be justified by emission from mobile sources
- There is the „Double Integral“ Problem
- Big problem: Where to put the CO_2?