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CO_2 from flue gas to cultivation media

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Seminar: Algae as Carbon Capturer. Espoo, 22.4.2014

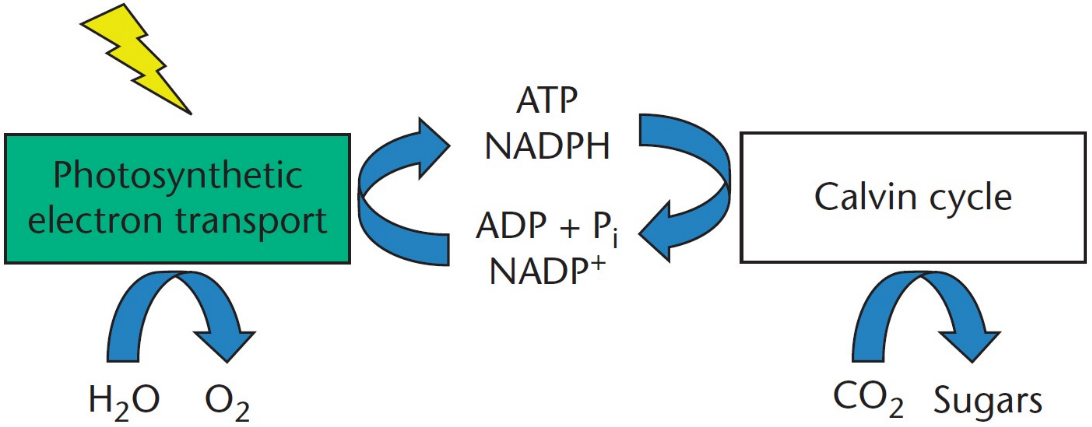
Goal of the study

- Identify means for transporting the CO_2 in industrial flue gases to algae in a cultivation for converting CO_2 → organic carbon in algae
- Focus on
  - maximizing CO_2 uptake and conversion to organic carbon
  - identifying restrictions
  - review of existing practices
- Part of CCSP Work Package 6

Contents

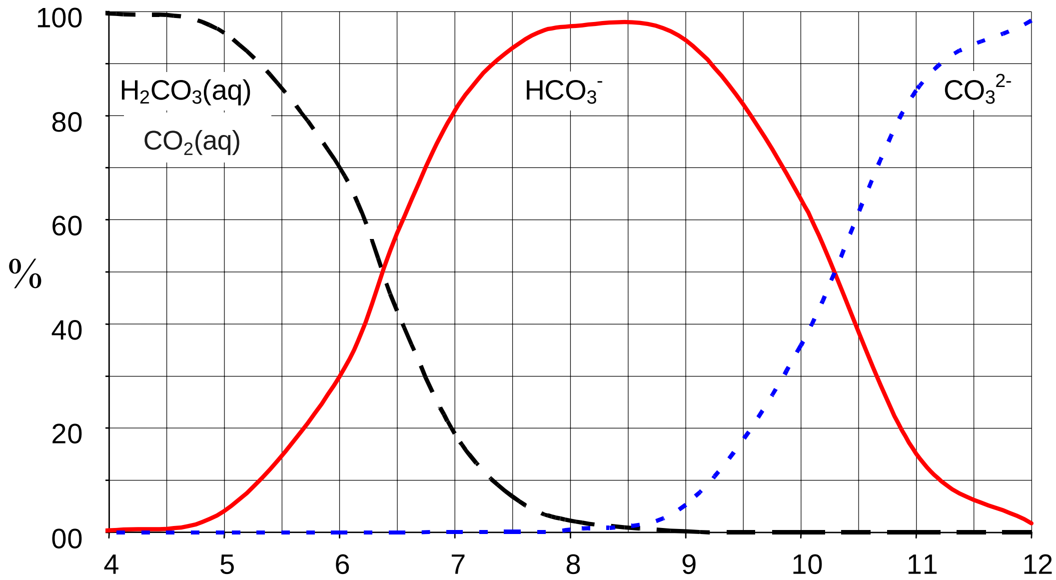
- How is CO_2 taken up by algae?
- Cultivation systems
- Restrictions
  - Species, flue gas quality, temperature, pH, light, nutrients, oxygen, retention time, land/water use
- CO_2 supply systems
- Potential and maturity
- Existing pilots

How is CO_2 taken up by photoautotrophic algae?



- Algae consume CO_2 and convert it into carbon molecules using photosynthetic processes similar to plants
  1. Light-dependent reactions absorb light and convert it into high energy molecules
  2. Light-independent Calvin cycle use these molecules to convert carbon dioxide and water into organic compounds
- CO_2 enters the cell by passive diffusion

In what form is CO_2 taken up?

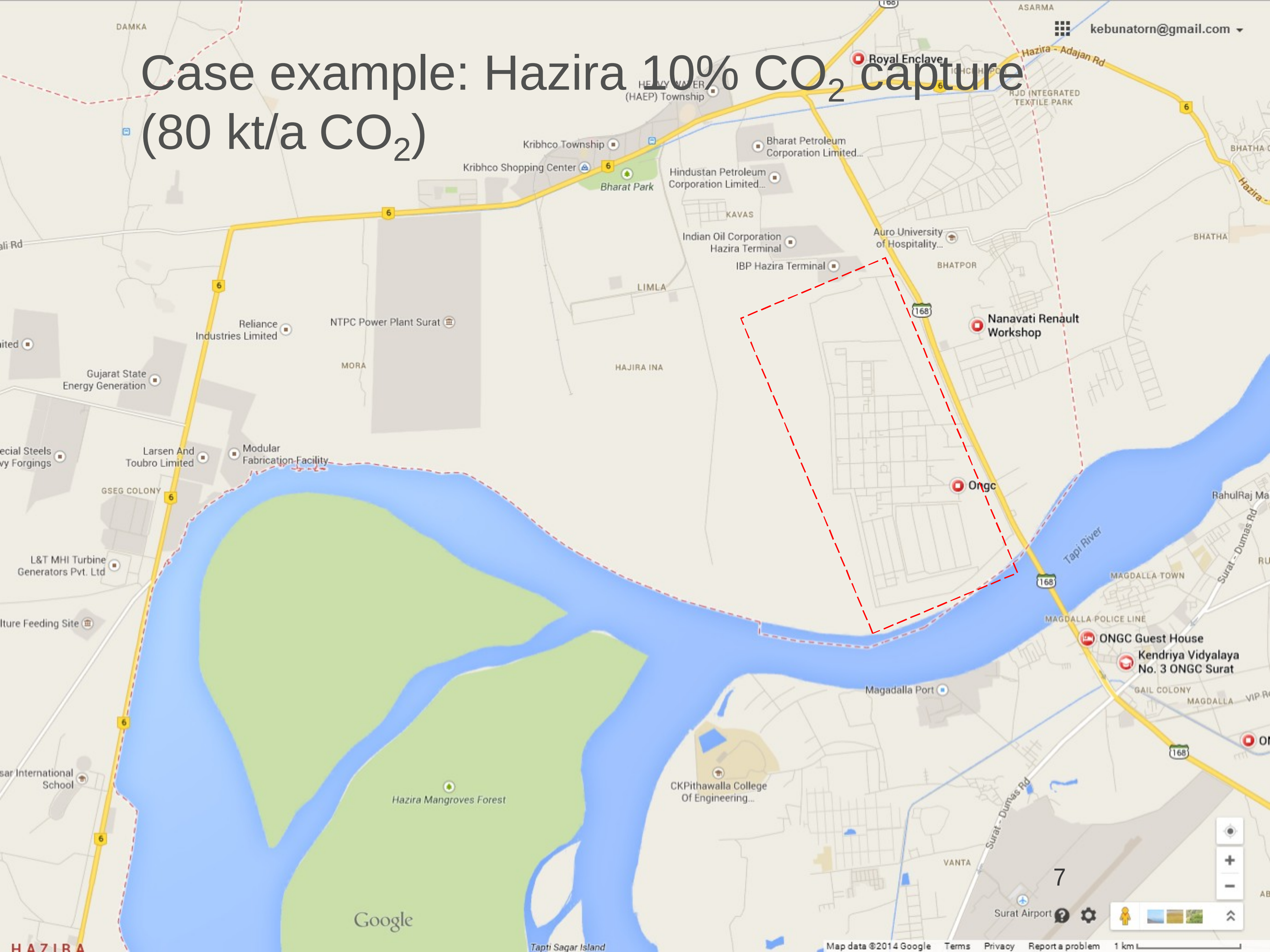


- Some algal species can only use (dissolved) CO_2, while others use bicarbonate (HCO_3^-) and a few use carbonate (CO_3^{2-}), although carbonate can be toxic to other species
  (Borowitzka & Borowitzka, 1988)

Cultivation systems

- Open ponds
  - \+ Common commercial method
  - \+ Cheap to build
  - \- Easily contaminated
  - \- Process control difficult
- Photobioreactors (PBR)
  - \+ Minimal CO_2 & water loss
  - \+ Not dependent on weather
  - \+ Process control, productivity, species selection
  - \- Wall growth, scale-up
  - \- Mixing and cooling
  - \- Expensive
- Closed tanks
  - – Only suitable for heterotrophic algae that consume organic carbon → unsuitable for CO_2 conversion

Case example: Hazira 10% CO_2 capture (80 kt/a CO_2)



Case example: Hazira 10% CO_2 capture

(83,000 tpa CO_2 → 46,000 tpa algal biomass)

Open pond system

- 58 MUSD construction costs
- 100,000 barrel algal oil per year

Photobioreactor system

- 201 MUSD construction costs
- 165,000 barrel algal oil per year

Current situation

- About 10,000 t/a microalgae biomass is produced commercially at facilities around the world, mainly for nutritional supplements

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Restrictions

- Flue gas quality: CO_2, NOx, O_2, **SOx, H_2S**, ash
- Temperature (< ~40 °C)
- pH: ~6-10
- Light
- Retention time, land use, water usage
- Algal species

Table 4. CO_2 tolerance of various species (review by Ono & Cuello, 2003)

Species	Known Maximum CO_2 Concentration
Cyanidium caldarium	100%
Scenedesmus sp.	80%
Chlorococcum littorale	60%
Synechococcus elongatus	60%
Euglena gracilis	45%
Chlorella sp.	40%
Eudorina spp.	20%
Dunaliella tertiolecta	15%
Nannochloris sp.	15%
Chlamydomonas sp.	15%
Tetraselmis sp.	14%

CO_2 supply systems

- Direct systems
  - Flue gas injection
    - Injection and dispersion of flue/vent gas as such into cultivation water
- Indirect systems
  - CO_2 injection
    - CO_2 separated from flue/vent gas and purified
    - Pure CO_2 injected into pond water (counter-current bubble carbonation in PBRs)
  - Water scrubbers/absorbers
  - Membranes
  - Chemical solvents

Direct gas injection

- Simplest and most common CO_2 supply
- Injection of CO_2 is regulated by monitoring the pH level
- Open ponds: major drawback of this type of CO_2 supply is that 80-90% of the CO_2 is lost to the atmosphere
- Photobioreactors: better suited, gas flow can be used for mixing the culture

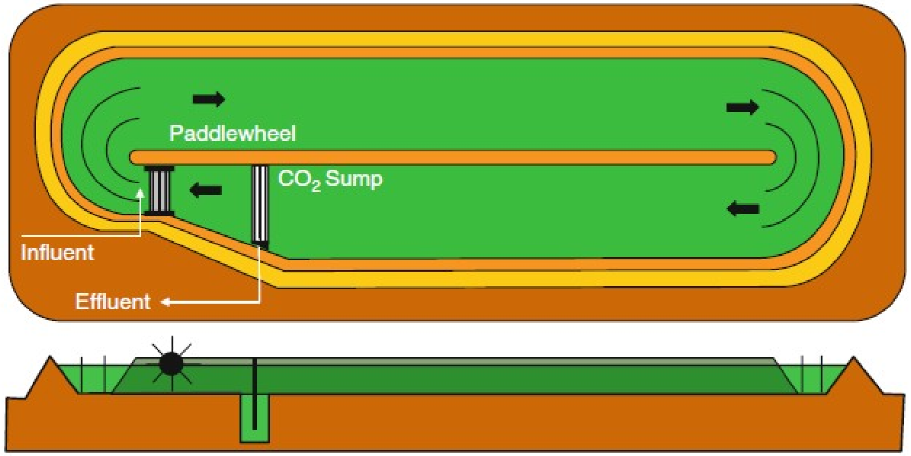


Figure 10. Plan view and side elevation of a high rate algal pond with CO_2 addition (Borowitzka & Moheimani, 2013).

Water absorbers

- Using a separate absorber allows for better process control
- Examples: packed bed towers, spray towers, bubble columns and hollow fibre modules
- Flue gas can be returned to the flue gas stack → only the dissolved CO2 (and other dissolved flue gas components) are transported to the open pond
- Cooling requirements of flue gases can be reduced, as the CO2-lean flue gases exiting the absorption column can be used for cooling the incoming CO2-rich flue gases

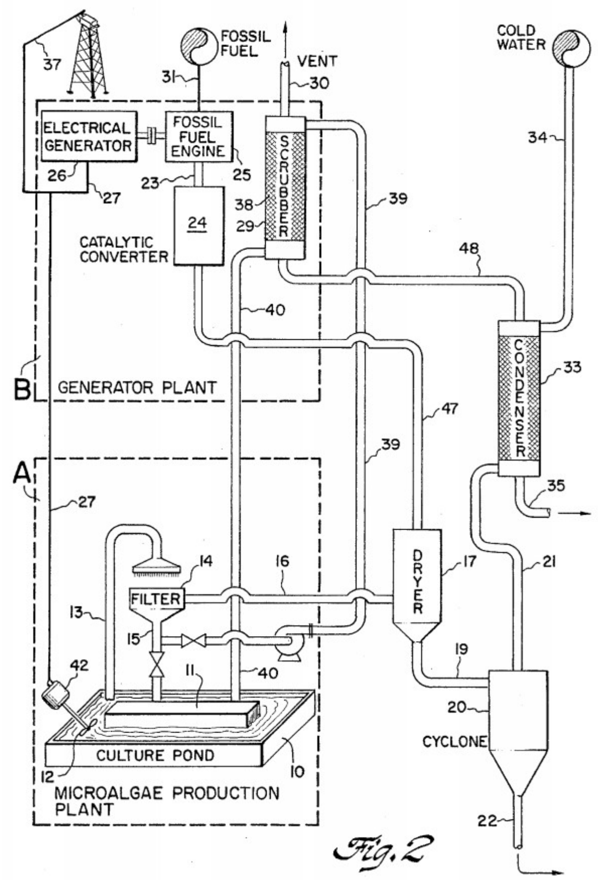


Figure 12. Cyanotech's patented concept for integrated microalgae production and electricity cogeneration (Jensen & Reichl, 1996).

Water absorbers for photobioreactors

- Lower energy requirements and simpler reactor design, as the flue gas stream does not need to be driven through the PBRs

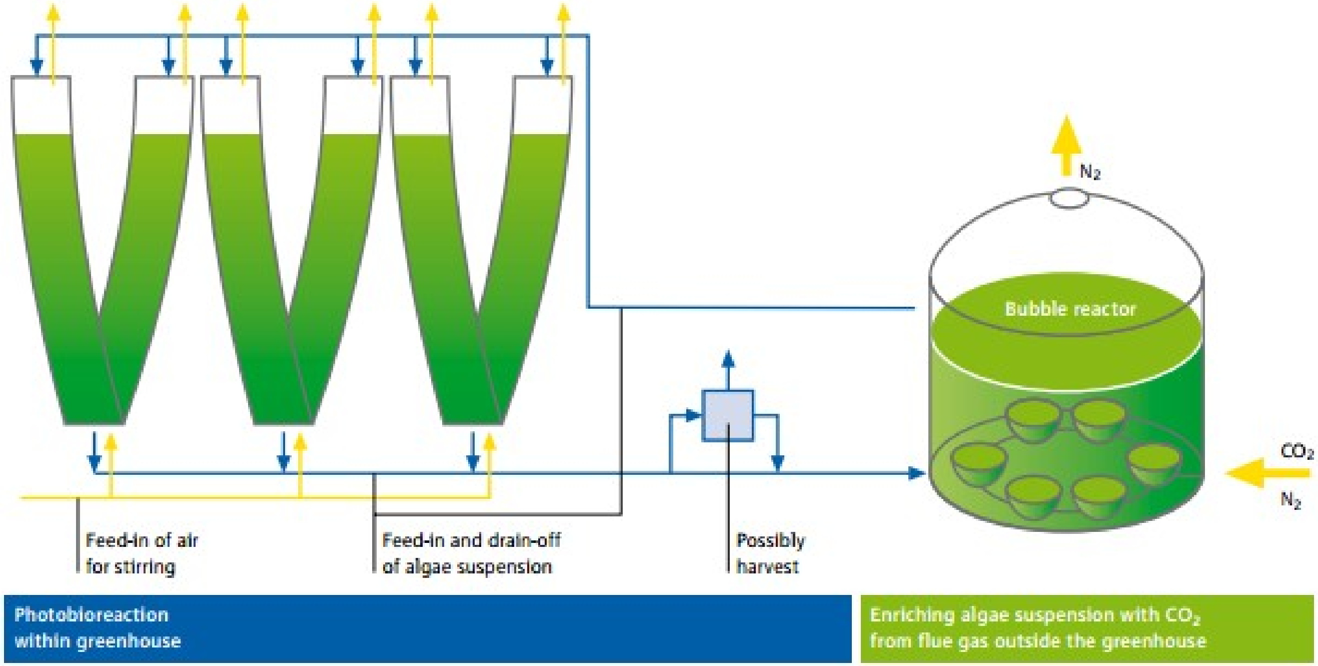
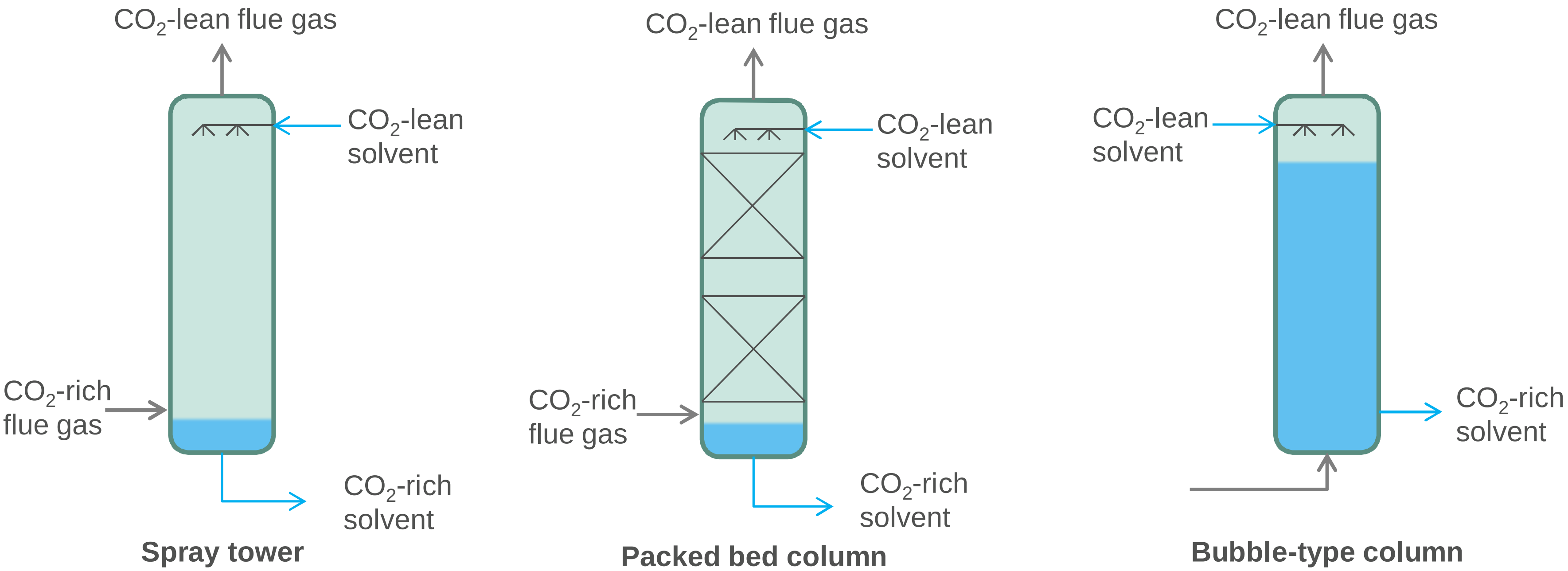


Figure 11. Process diagram of photobioreactor with separate bubble reactor for CO_2 absorption into cultivation media (RWE Power, 2009).

Types of absorption columns

- CO_2 dissolves **very** poorly into water
  - 2 g / kg H_2O, if gas is 100% CO_2 at 1 bar) and 20 ºC
- Bubble-type columns seem most suitable, as can be 3-10 times faster than in a packed bed column
- Packed beds more suitable when using a chemical solvent (e.g. amine)



Hollow-fibre modules

- Bundles of polymeric porous fibers with typical diameters of 250 µm, connected to inlet/oulet ports in their ends and contained in housing
  - Ratio between the membrane outer area and the external dimensions is quite high.
- Beneficial when the CO_2 source is purchased CO_2 gas and hence CO_2 losses to the atmosphere need to be minimized
- Better CO_2 mass transfer rates can be achieved using hollow-fiber modules in comparison to plain bubbling
- Membranes are relatively expensive and likely to be even more difficult to clean than other absorber types

Typical chemical absorbtion process for CO_2 separation / production

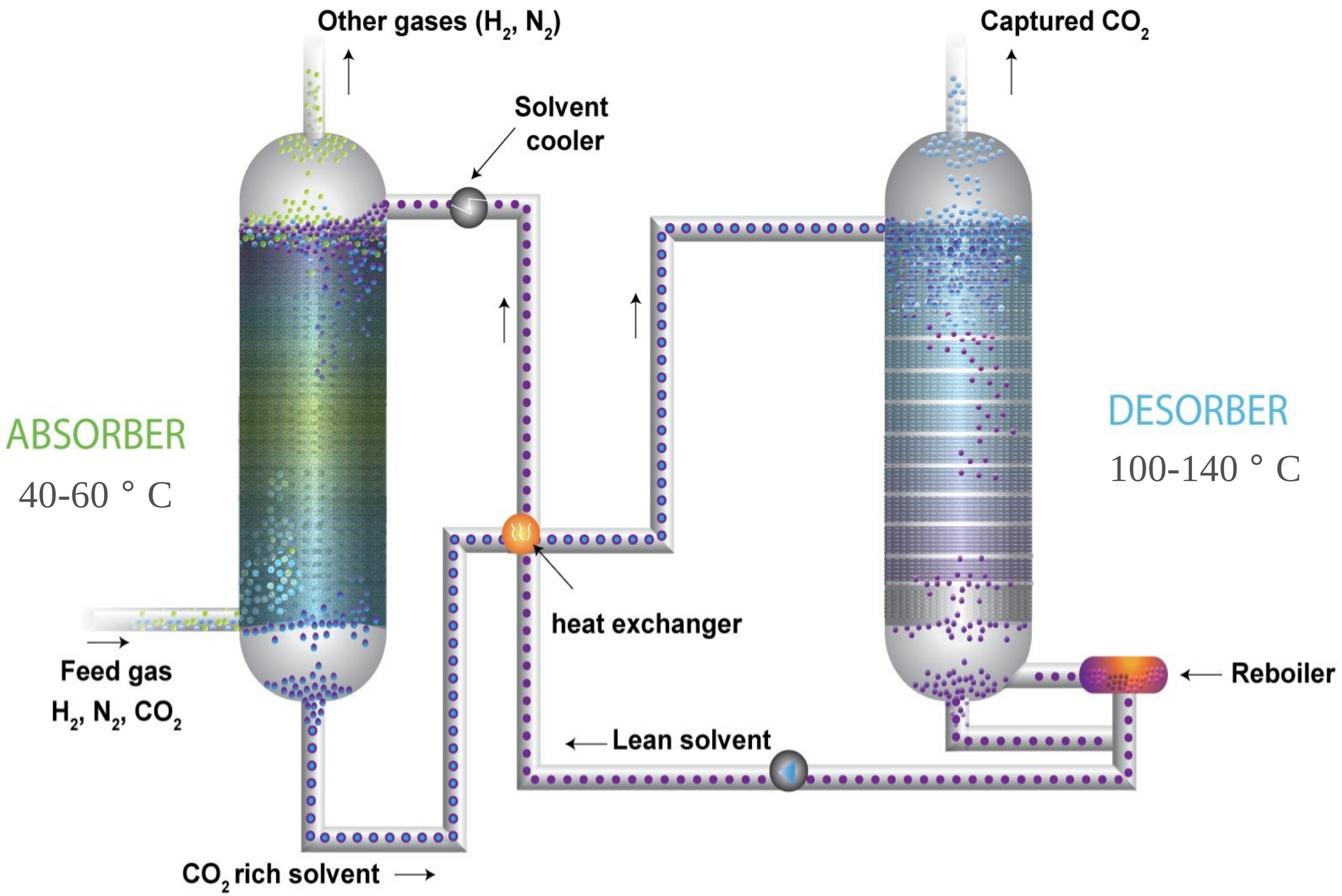


Image: CO2CRC

Chemical solvent for CO_2 capture AND as cultivation media

- For a chemical absorbent liquid, like an amine or amino acid solutions, the solubility of CO_2 is tenfold to that of CO_2 in water
- Some algal species can tolerate pH values higher than 8
  - Goetheer et al. (2011) tested the growth of micro-algae in 0.1-1 M solutions of amino acids, amines and carbonates
- Using a chemical solvent to increase the solubility of CO_2 in the cultivation water not only restricts the cultivation to algal species that can tolerate these chemicals but it is also likely to increase the operational costs due to requirements for make-up chemicals

Conclusions

- As algae can thrive using CO_2 from desulphurized flue gases injected into the cultivation water, there is no need for using costly CO_2 separation processes, as long as the algal cultivation unit is built next to a suitable industrial CO_2 source.
- The most promising systems for CO_2 capture seems to be the use of separate, bubbling, carbonation columns, both for open ponds and closed photobioreactors
- Using a separate bubbling column makes the design of the photobioreactors simpler, as CO_2 is fed readily dissolved by recycling the cultivation water through the bubbling columns

Conclusions

- Using separate bubbling columns for open ponds enables a higher CO_2 concentration in the ponds than what can be achieved by direct injection, and reduces the risk for release of gaseous harmful flue gas components into the area surrounding the ponds
- While the capacity of pure water to dissolve CO_2 is poor, the addition of alkaline salts can significantly improve the CO_2 uptake of water as well.

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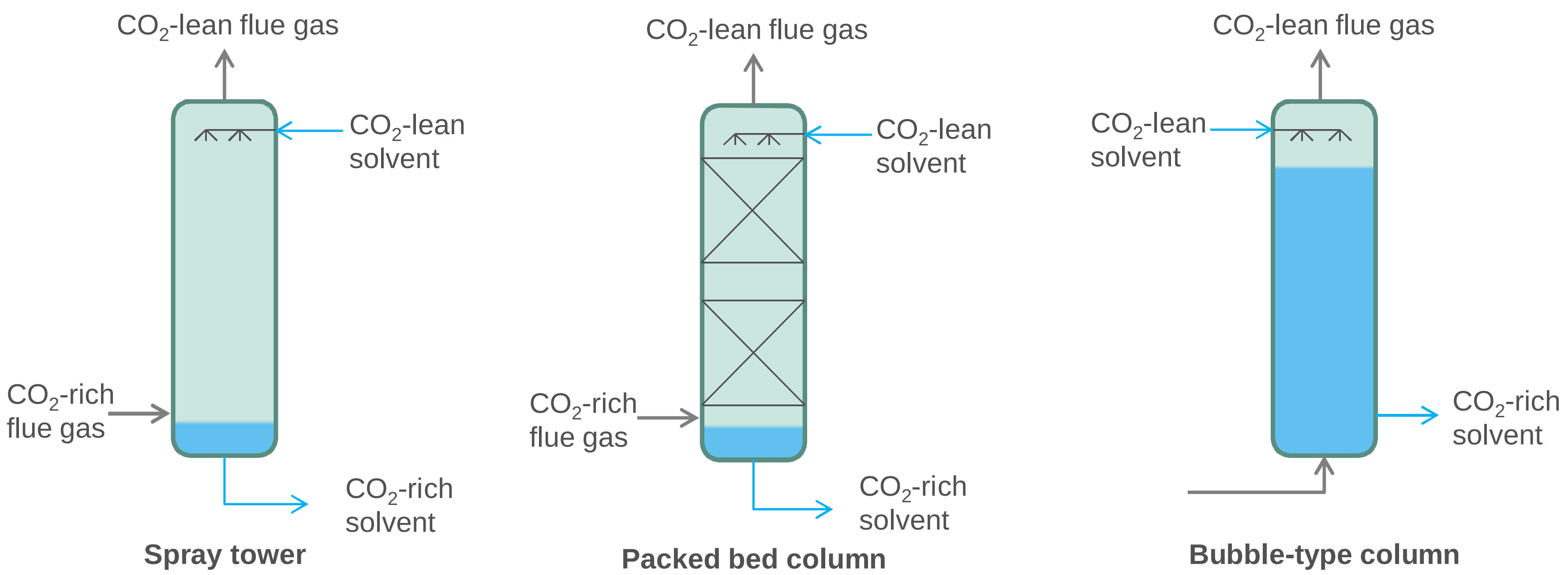
Thank you for your attention

Questions yet to be answered

- How does dissolved organic carbon affect the CO_2 uptake of algae?
- Are there high-CO_2 consuming heterotrophic algae?

Numbers used for potential calculation

- ~1 Mm^3/a vent gas (28-56% CO_2) → ~800,000 tpa CO_2
- Algae capacity: 1.8 t CO_2/t algae (best case)
- Algae production capacity
  - Open pond (HRAP)
    - 8000 t biomass/km^2/year
    - 2100 m^3 oil/km^2/year
    - Investment cost: 10 USD/m^2
  - PBR
    - 23000 t algae/km^2/year
    - 9800 m^3 oil/km^2/year
    - Operational costs: 100 USD/m^2


CO2-lean flue gas
CO2-lean solvent
CO2-rich flue gas
CO2-rich solvent
Spray tower
CO2-lean flue gas
CO2-lean solvent
CO2-rich flue gas
CO2-rich solvent
Packed bed column
CO2-lean flue gas
CO2-lean solvent
CO2-rich solvent
Bubble-type column