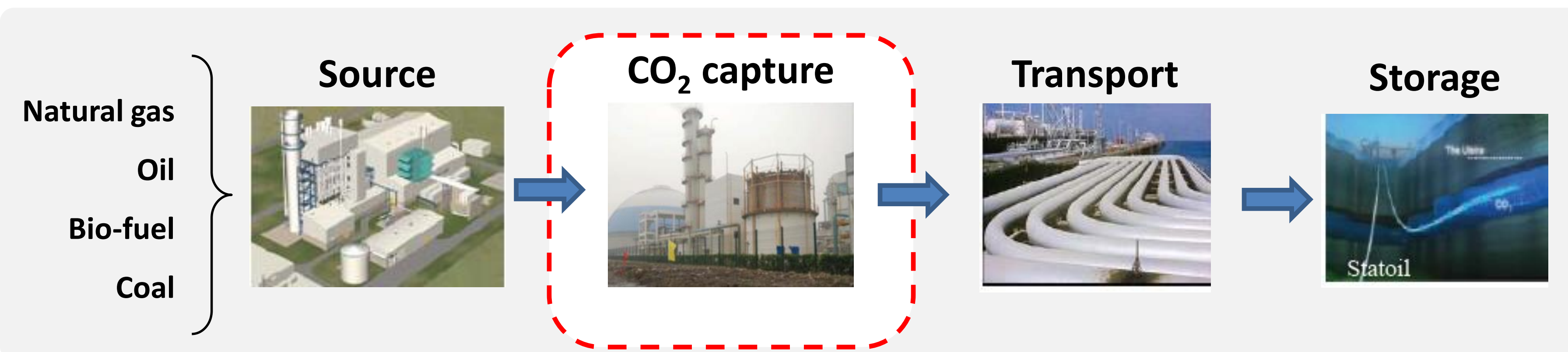
HiPerCap

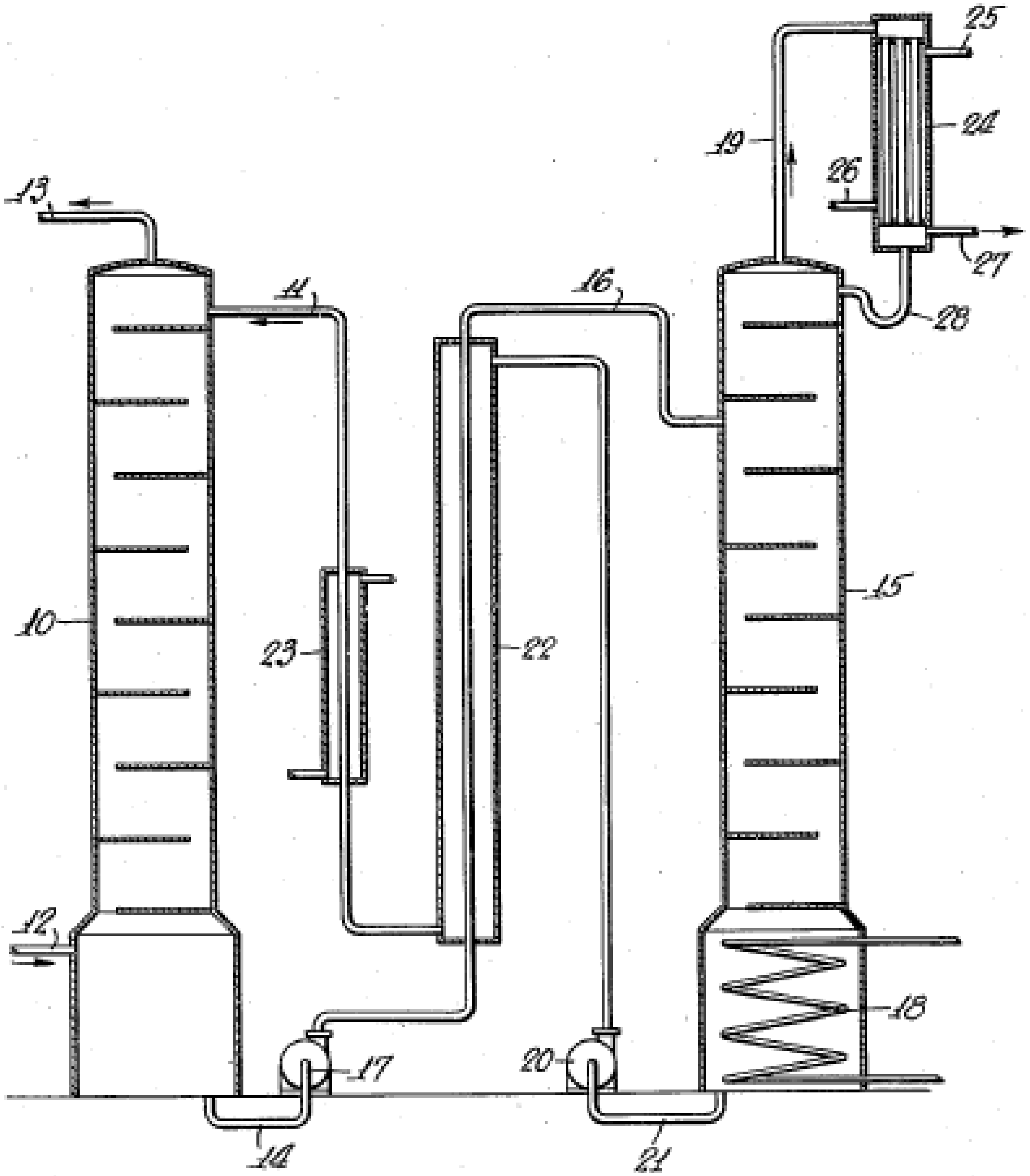
High **Per**formance **Cap**ture

Absorption Systems

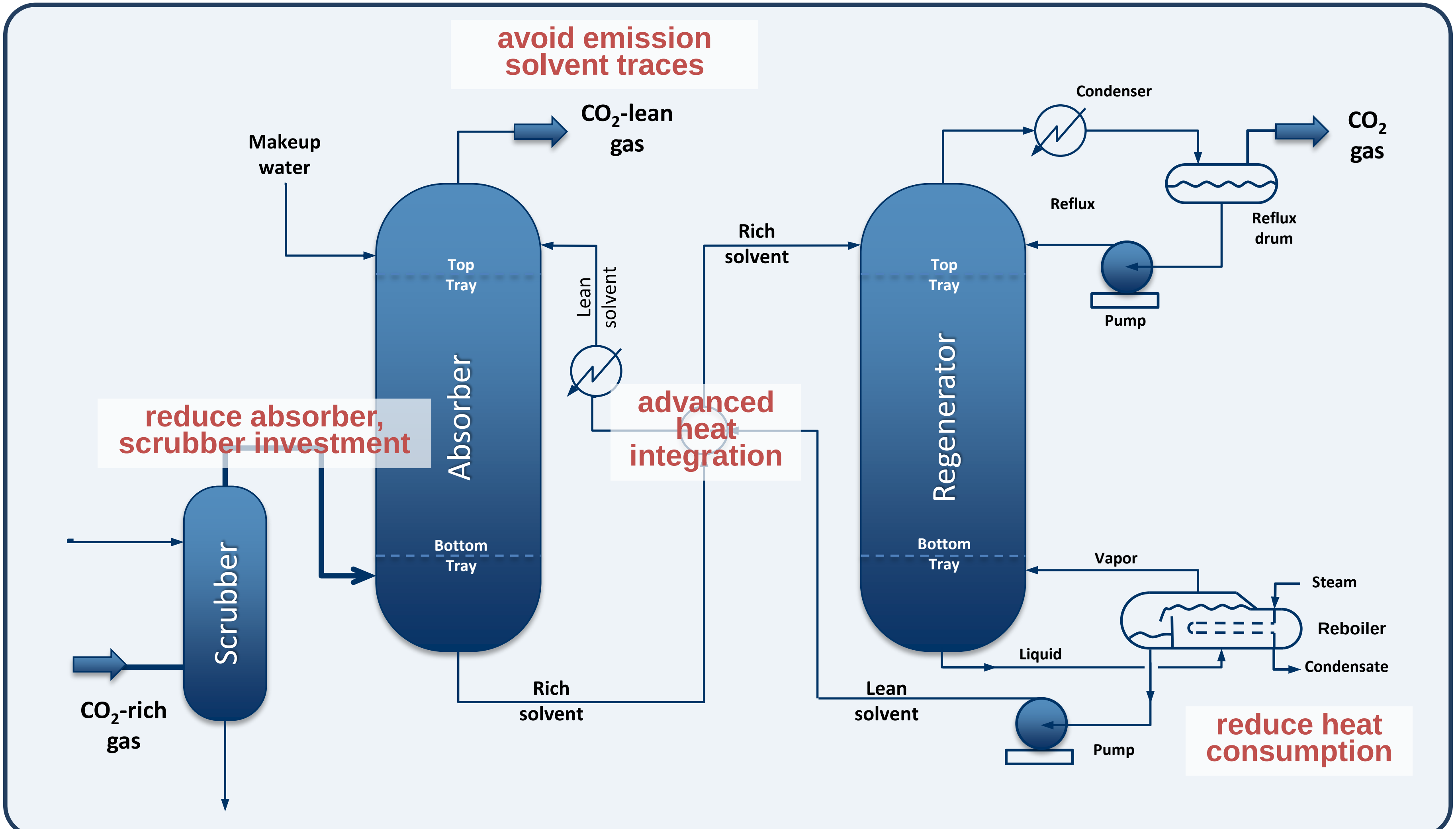


Earl Goetheer, Principal scientist at TNO

Capture in 1930

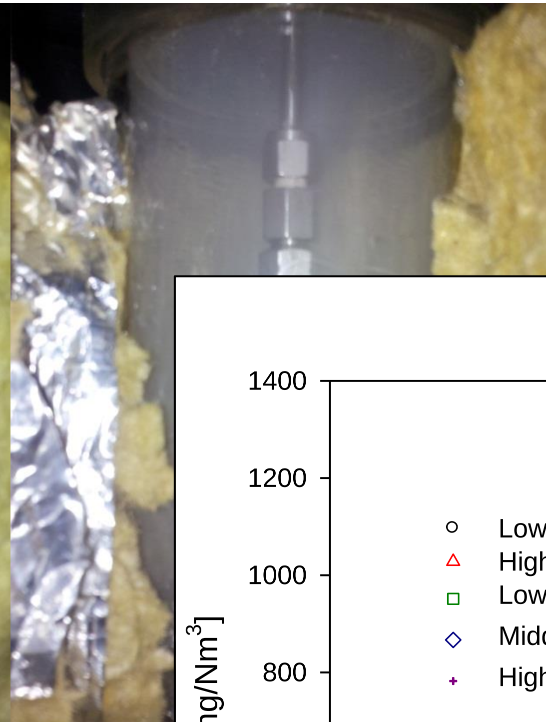


Challenges Post-combustion Capture

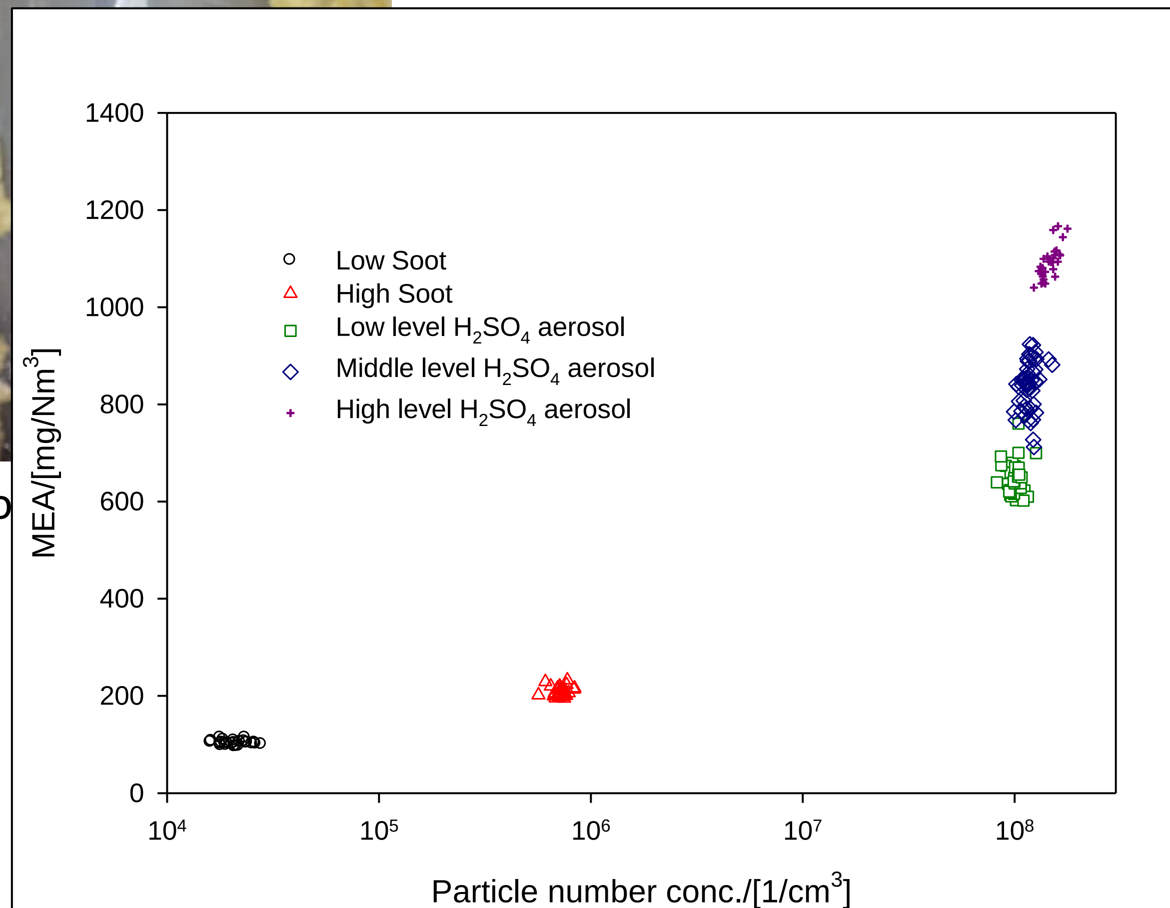


Emission

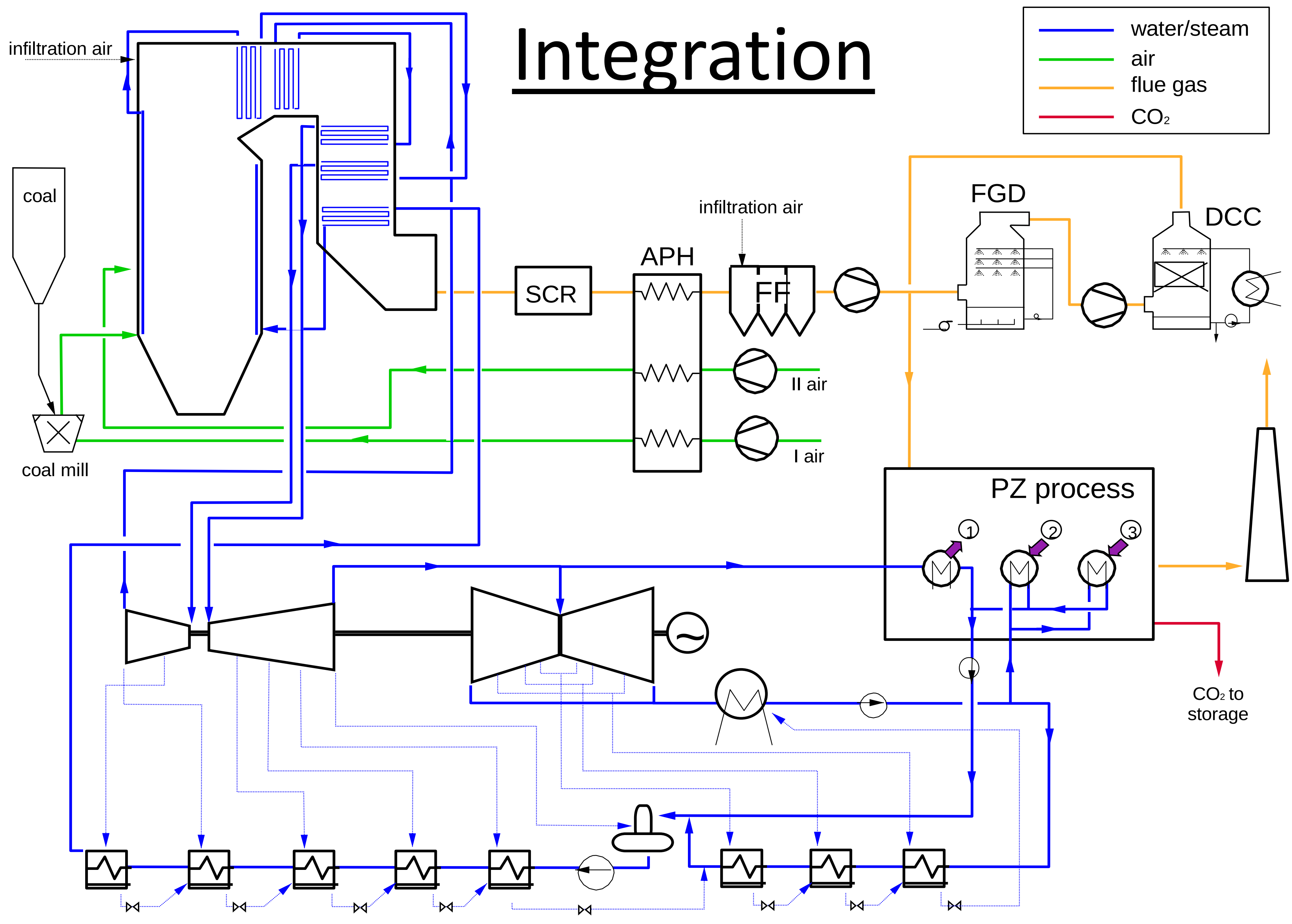
Volatile emission



Aero

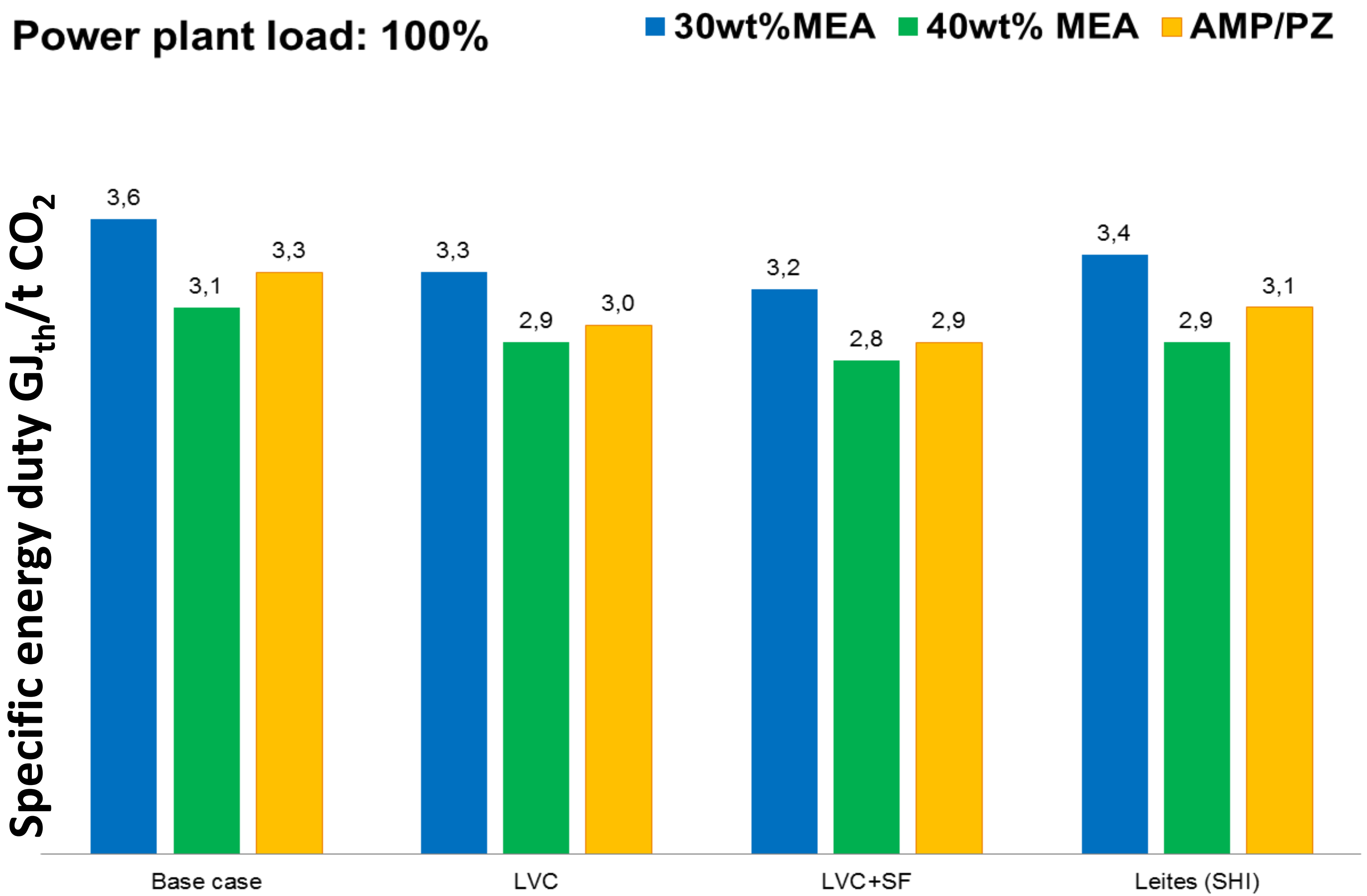


Integration



Energy Consumption

Power plant load: 100%



Technologies

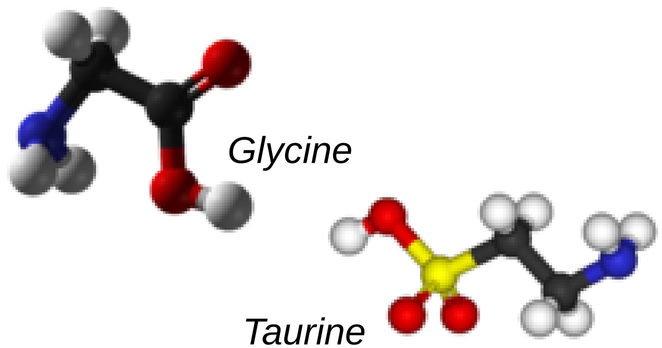
- Enzymatic catalysed CO2 capture
- Biomimicking
- Strong bicarbonate formers

- Precipitating solvent systems
- Capture integrated with algae cultivation

Precipitating solvent systems

TNO HiPerCap CO_2

CO_2 absorption with amino acid salts



- ✓ Resistant to oxidative degradation
- ✓ Less waste generated products
- ✓ Zero emissions of active reactant
- ✓ Potential energy savings
- Limited solubility in water

Ionic equilibria In water:

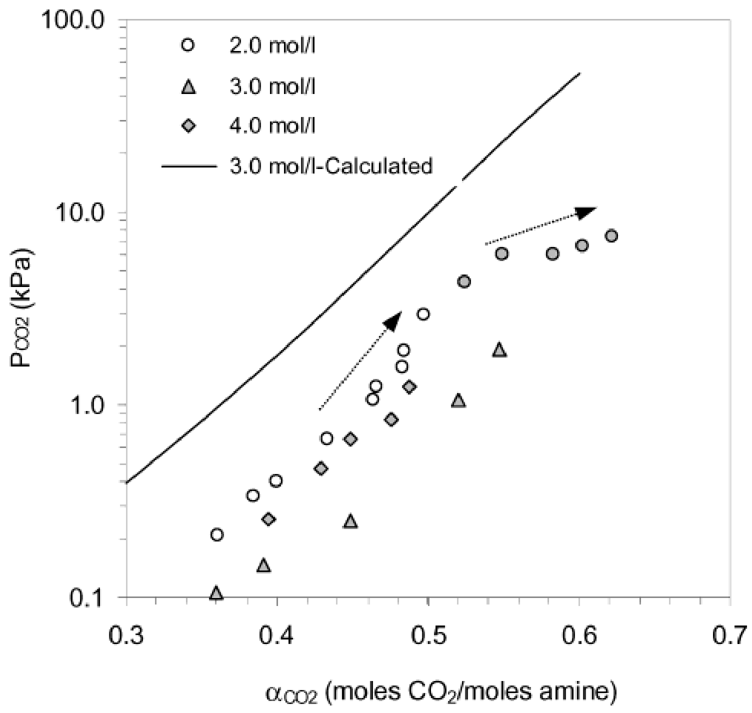
$R\text{-}(NH_2)COOH \rightarrow R\text{-}(NH_3)^+COO^-$ zwitterion

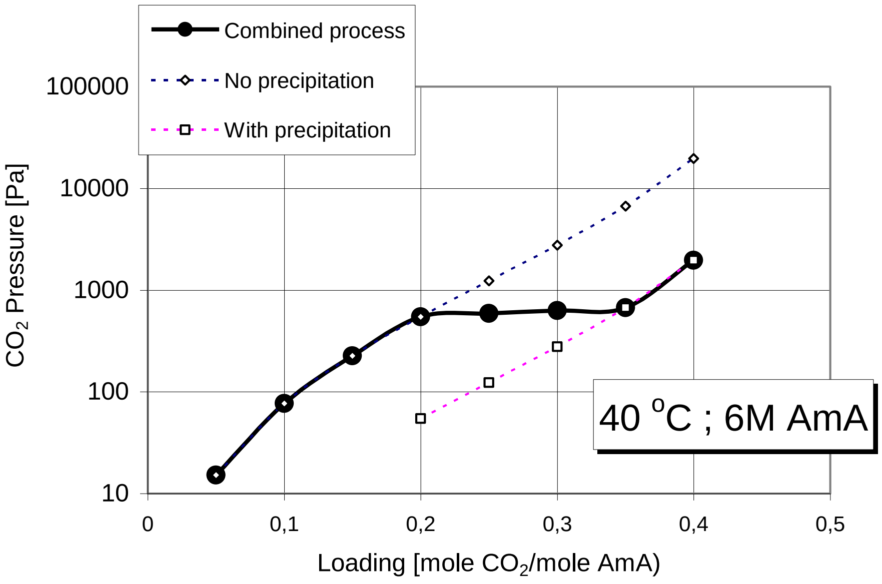
$R\text{-}(NH_3)^+ COOH \overset{-H^+}{\leftrightarrow} R\text{-}(NH_3)^+COO^- \overset{-H^+}{\leftrightarrow} R\text{-}(NH_2)+COO^-$

$R\text{-}(NH_3)^+COO^- + KOH \rightarrow R\text{-}(NH_2)COO^-K^+$ reactive

Effect of solid precipitation

Enhanced absorption capacity: DECAB principle





Experimental: Aqueous potassium taurate.

Dark points: precipitation

From: Kumar et al. Ind. Eng. Chem. Res. 42, 2003, 2841-2852

Schematic picture: effect of solvent precipitation

Why do you get higher capacity?

Reactions with CO_2 (similar to "normal" amine systems):

Carbamate formation (primary and secondary amines)

$CO_2 + 2\ ^{-}OOC\text{-}R\text{-}NH_2 \leftrightarrow\ ^{-}OOC\text{-}R\text{-}NH\text{-}COO^{-} + -OOC\text{-}R\text{-}NH_3^{+}$ (1)

amine — *carbamate* — *protonated amine*

Carbamate hydrolysis

$^{-}OOC\text{-}R\text{-}NH\text{-}COO^{-} + H_2O \leftrightarrow\ ^{-}OOC\text{-}R\text{-}NH_2 + HCO_3^{-}$ (2)

carbamate — *amine* — *bicarbonate*

Bicarbonate formation (tertiary amines, sterically hindered secondary amines)

$CO_2 + \ ^{-}OOC\text{-}R\text{-}NH_2 \leftrightarrow\ ^{-}OOC\text{-}R\text{-}NH_3^{+} + HCO_3^{-}$ (3)

amine — *protonated amine* — *bicarbonate*

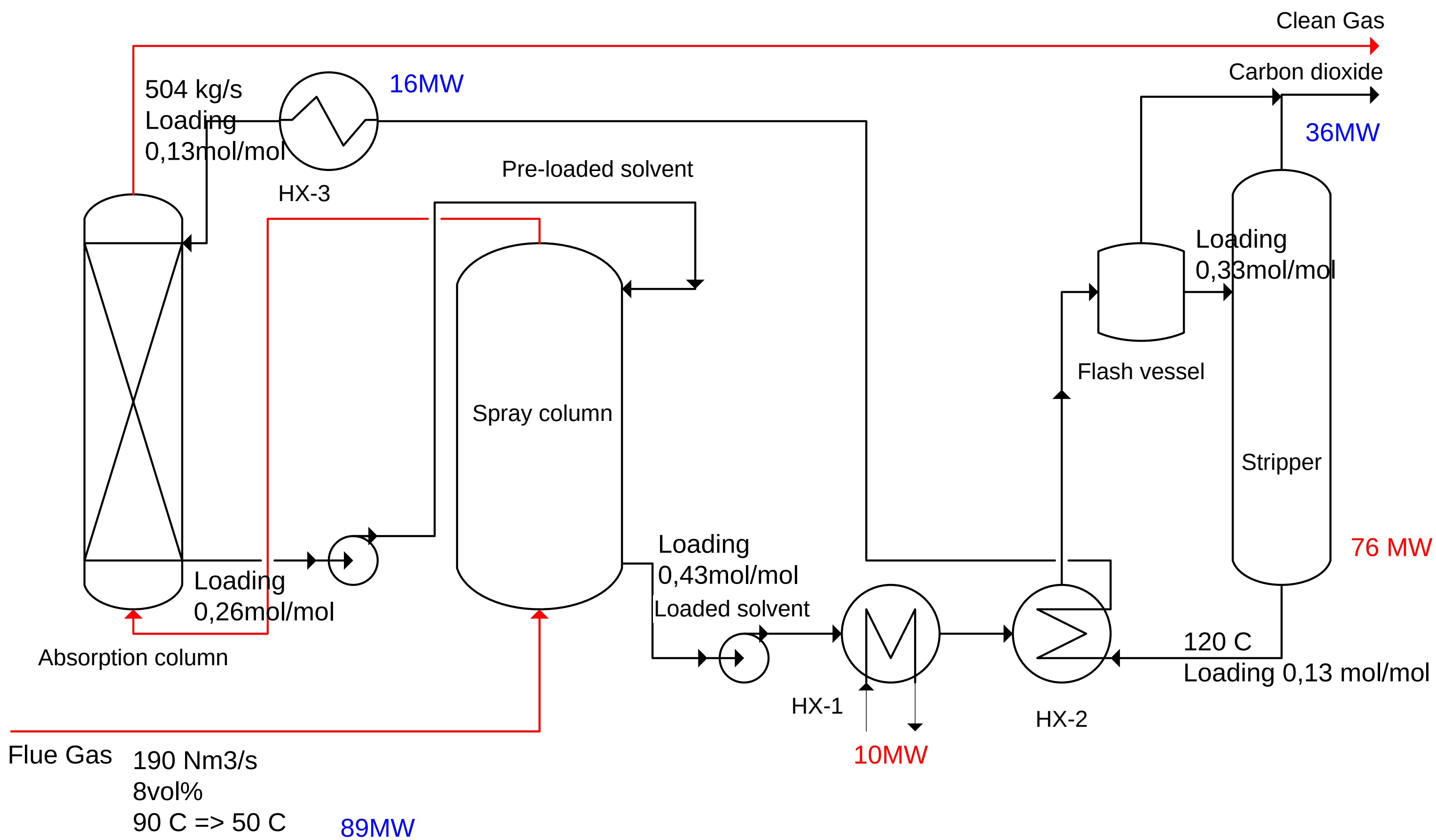
Removed by precipitation

Working with solids in the process

- Controlled precipitation of the solvent
- Solids should appear where they can be handled
- Equipment selected for solids handling
- Process complexity increased

Working with solids IF there is an economic breakthrough

DECAB Process (Design & Modelling Results)

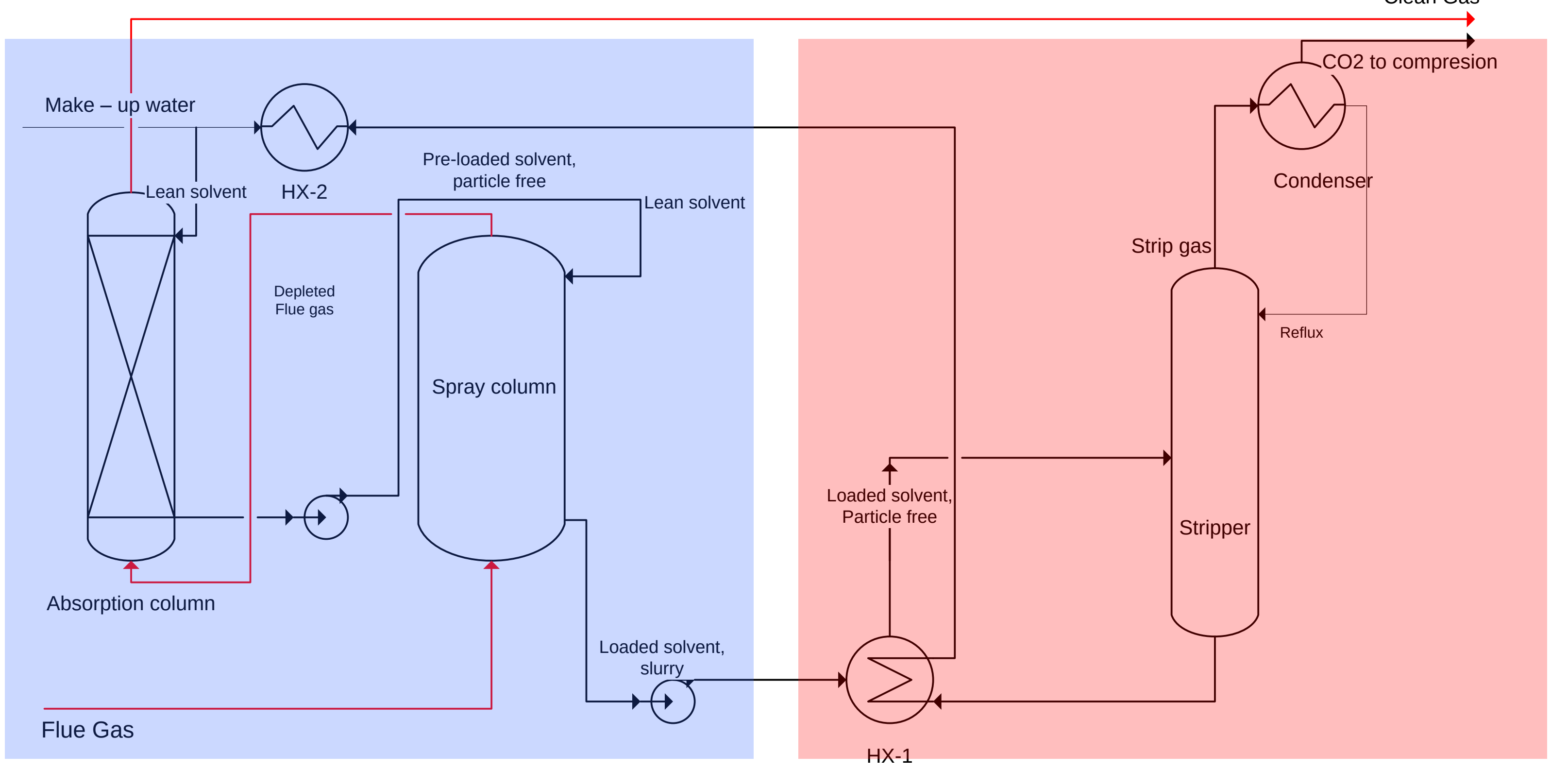


From DECAB to DECAB+

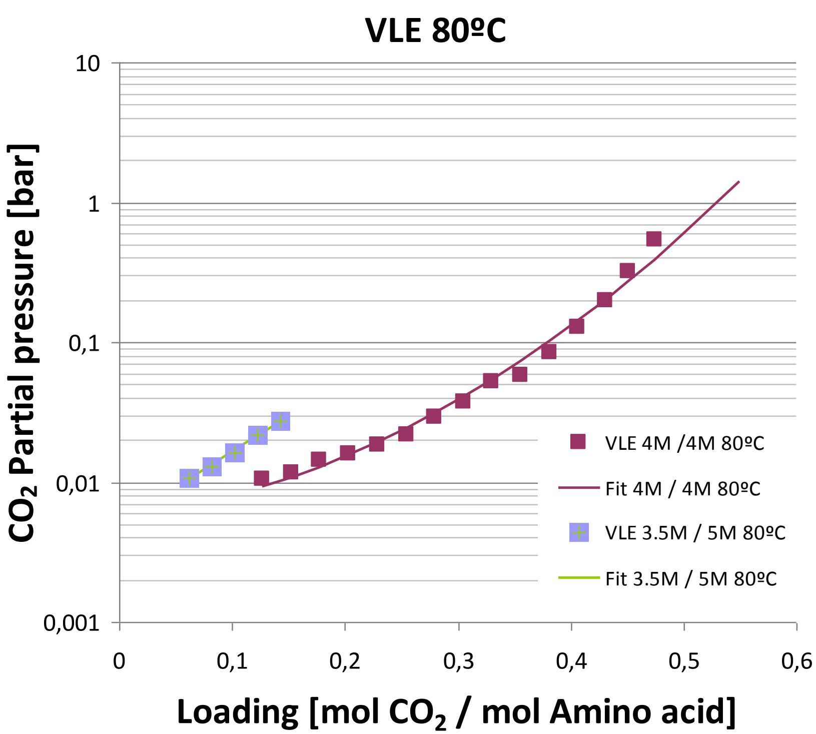
Conditions to enhance absorption and desorption

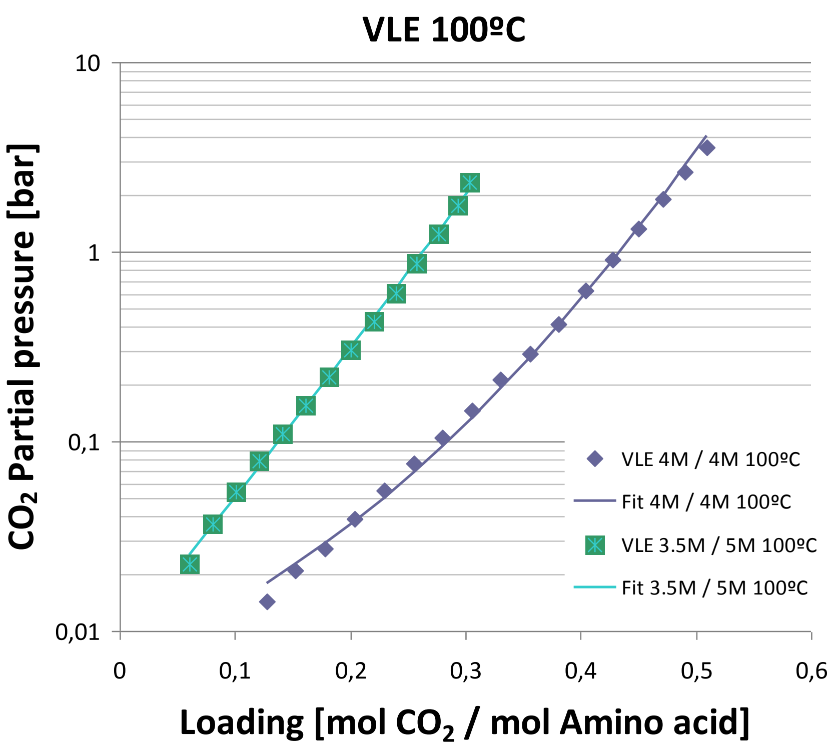
Absorption: High pH (basicity)

Desorption: Low pH (acidity)



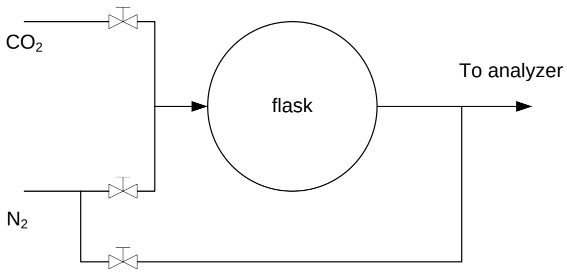
Effect of DECAB+. Enhanced desorption





The pH shift increases the partial pressure of CO_2 at a given loading

Proof of principle



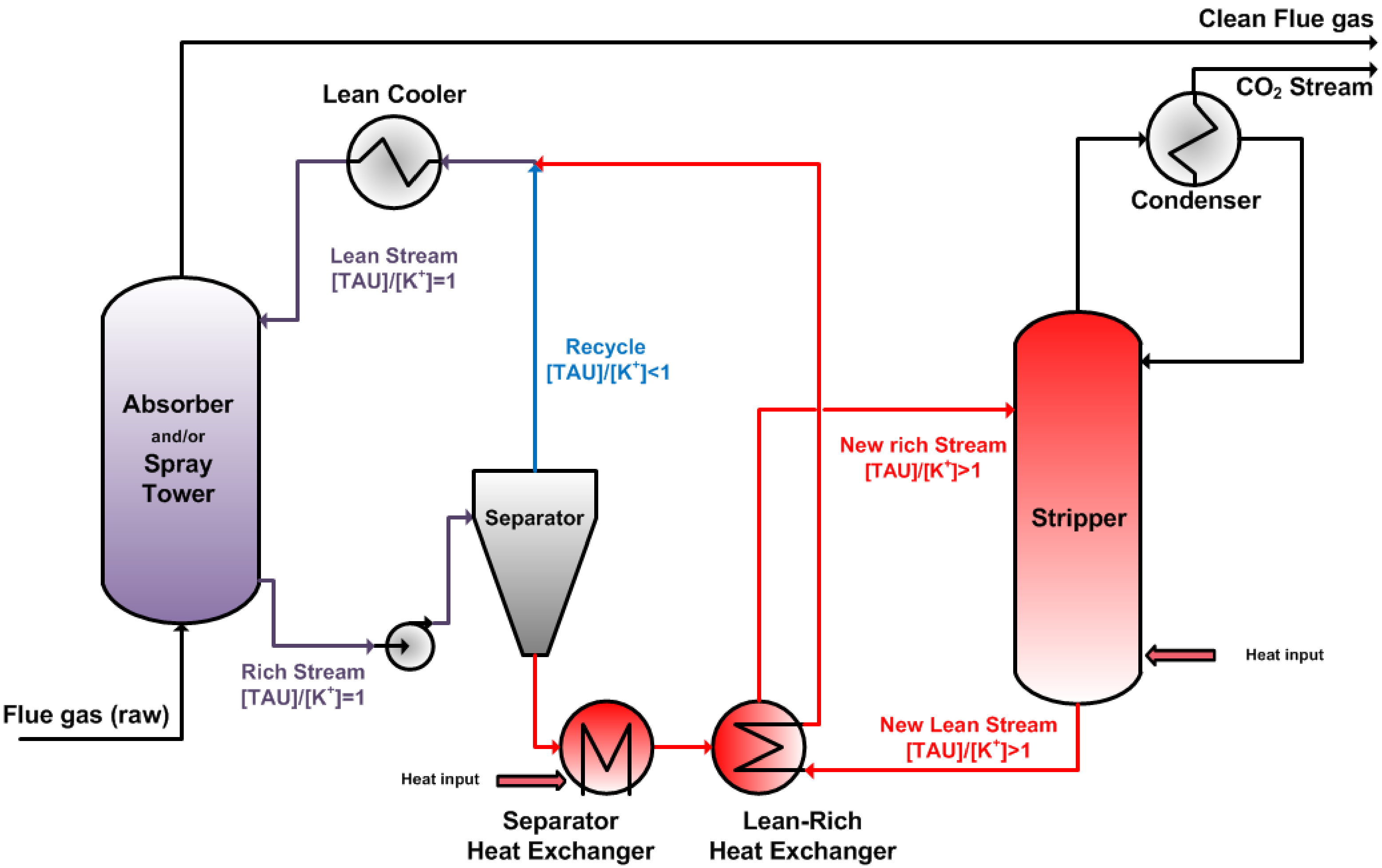
Liquid removed Vol (%)	Conc. M	T C	Rich Loading mol/mol	Lean Loading mol/mol
0%	4	74.1	0.65	0.36
21%	4.3	77.1	0.65	0.3
42%	4.9	76	0.65	0.17
0%	4	89.7	0.65	0.24
21%	4.3	95.4	0.65	0.13
42%	4.9	93.7	0.65	0.09

Low lean loadings are possible at relatively low temperatures

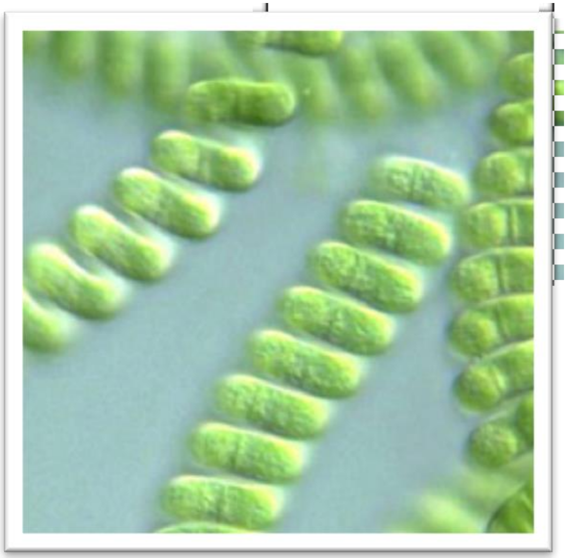
Key advantages of DECAB$^+$

- Low desorption temperature
  - Possibility to use low grade heat / waste heat (Ideal for the refinery case)
  - Possibility to achieve lower lean loadings without increasing reboiler temperature (Ideal for streams with low CO_2 concentrations such as flue gas from gas turbines combustion)
- High pressure desorption
  - Lower operating costs due to enhanced desorption
- All environmental advantages from amino acids

DECAB⁺ Process Concept



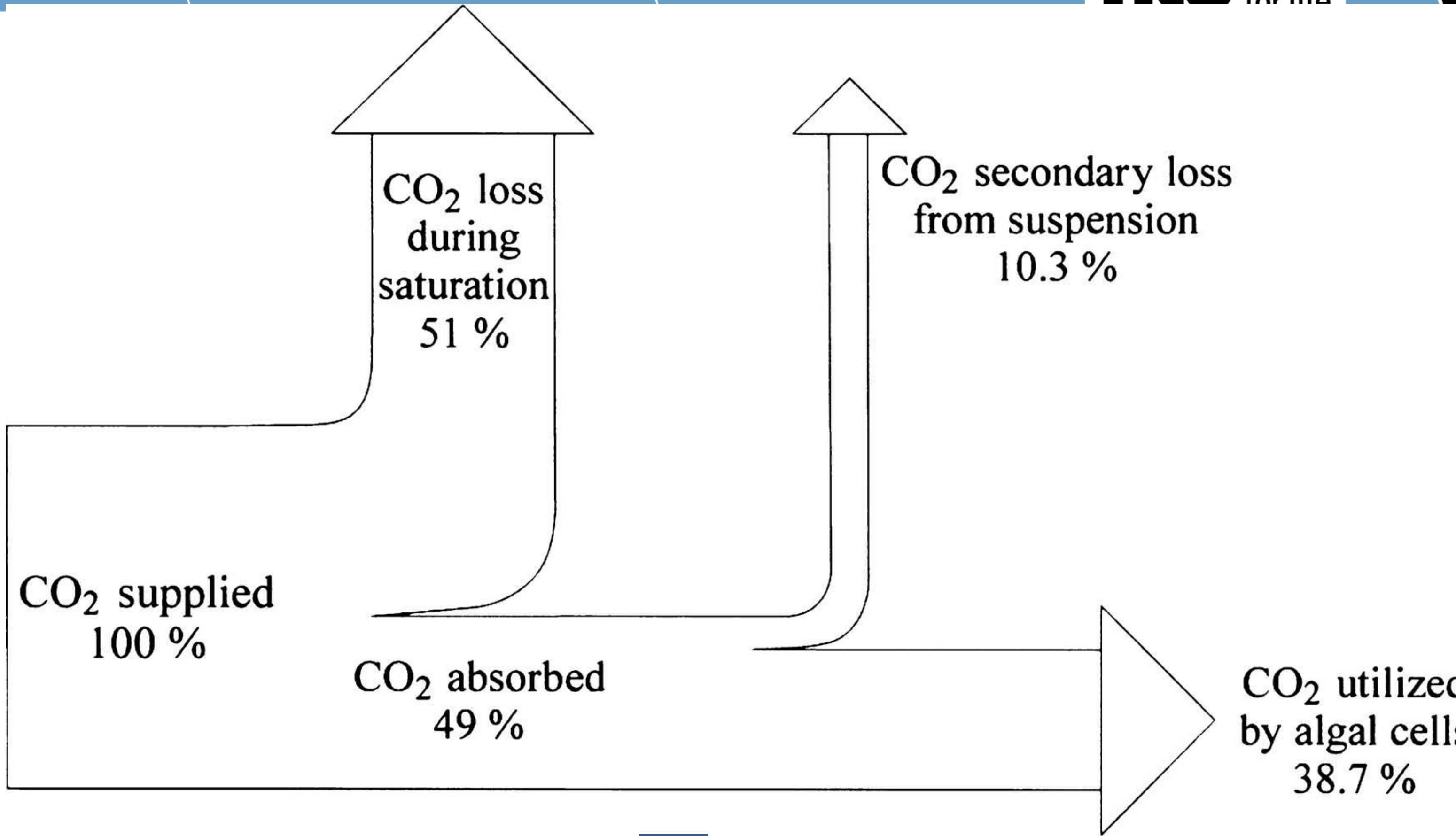
CO2 capture algae cultivation



EXAMPLES OF HIGH PRODUCTIVITY BIOMASS

Biomass community	Location	Yield (t d.w. ha^{-1} y^{-1})	Photosynthetic efficiency (%)
Hybrid poplar *(Populus spp.) (C3)*	Minnesota	8 -11	0.3- 0.4
Water hyacinth *(Eichornia crassipes)*	Mississippi	11 – 33 (>150)	0.3- 0.9
Switch grass *(Panicum virgatum) (C4)*	Texas	8-20	0.2- 0.6
Sweet sorghum *(Sorghum bicolor) (C4)*	Texas-California	22 - 47	0.6-1.0
Coniferous forest	England	34	1.8
Maize *(Zea mays) (C4)*	Israel	34	0.8
Tree plantation	Congo	36	1.0
Tropical forest	West Indies	60	1.6
Algae	Different locations	70	2-2.5
Sugar cane *(Saccharum officinarum)*	Hawaii-Java	64-87	1.8-2.6
Napier grass *(Pennisetum purpureum)*	Hawaii, Puerto Rico	85-106	2.2-2.8

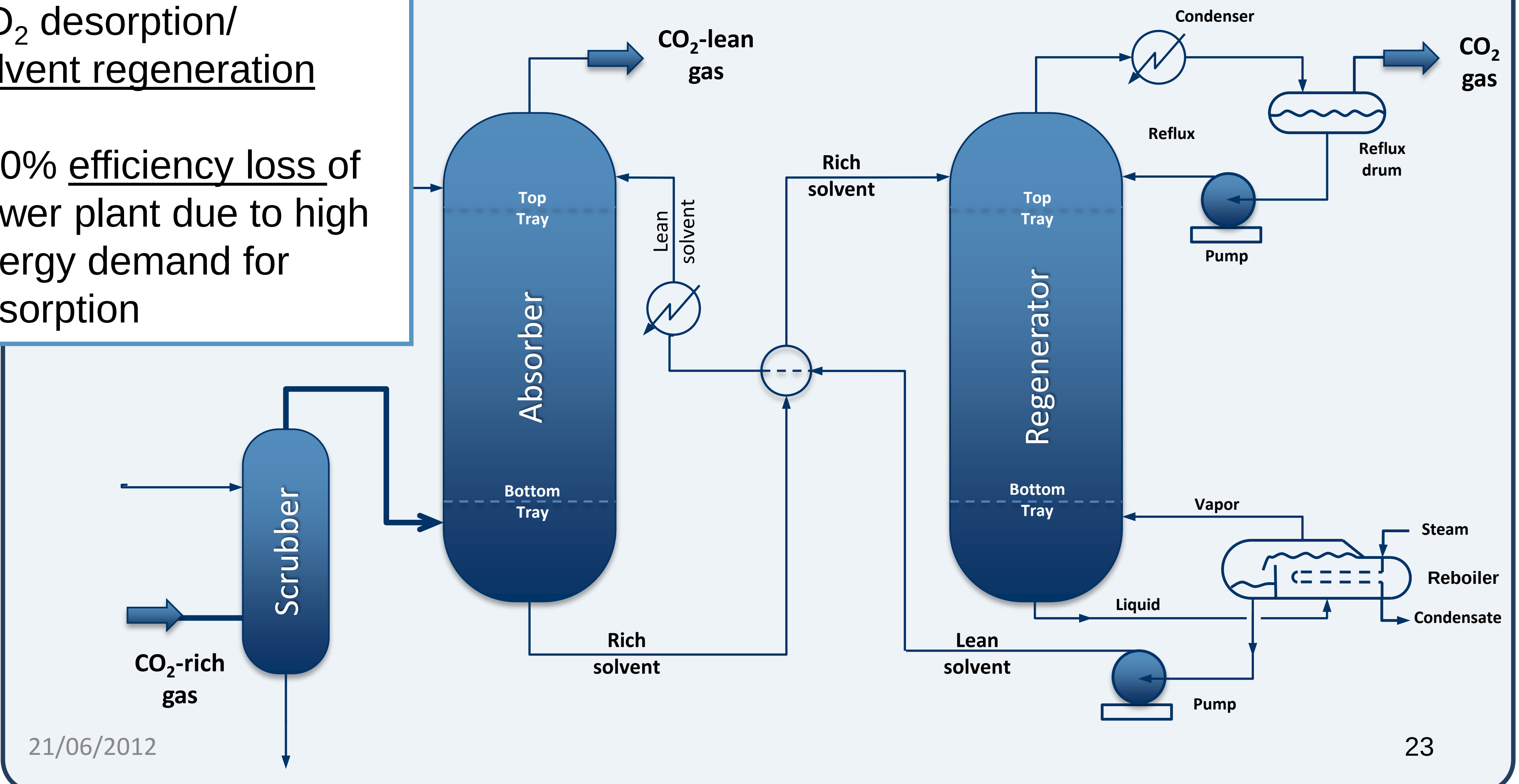
M. Tredici / Symposium " I Biocarburanti di seconda e terza generazione" Roma 14 April 2011



Per kg dry biomass ~ 4,4 kg of CO2 is needed

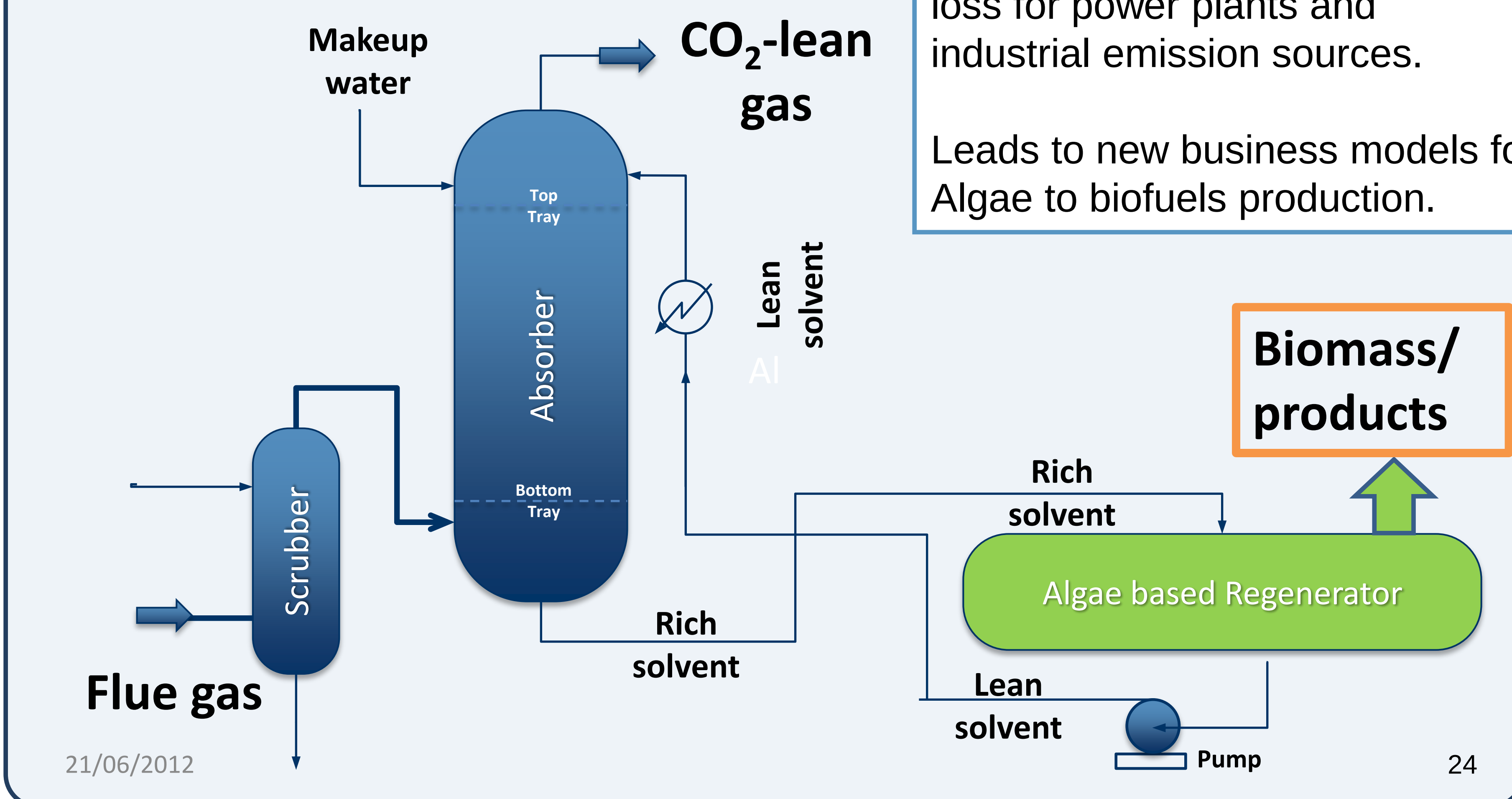
~75% OPEX is predominantly CO_2 desorption/ <u>solvent regeneration</u>

~20% <u>efficiency loss</u> of power plant due to high energy demand for desorption

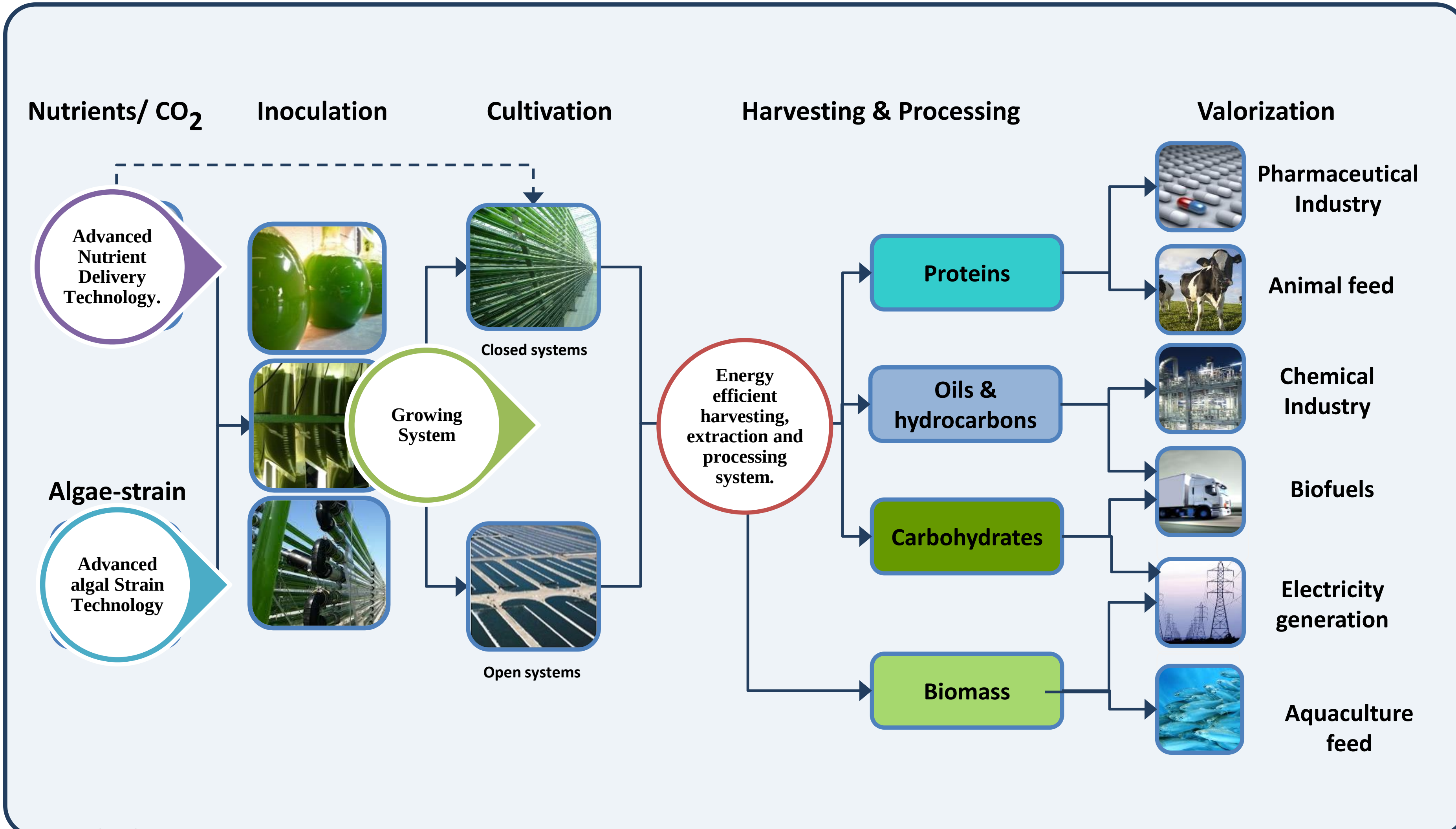


Need for <u>major cost reduction</u> of CO_2 capture and limited efficiency loss for power plants and industrial emission sources.

Leads to new business models for Algae to biofuels production.



From algae to products – improvement options



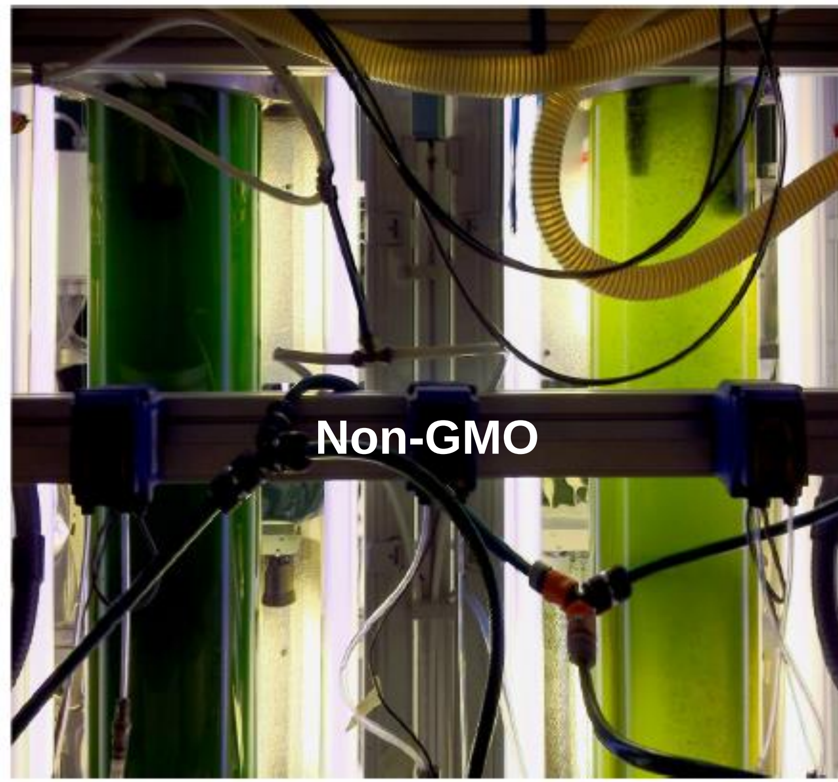
Advanced algal Strain Technology

Limitation: Mutual shading

Decreased light penetration
=
Slower growth
=
Lower biomass density

Solution: Light efficient strains
Same algal density **1,5 gr/ltr**

Wild strain | Improved Strain



Max. algal cell density of **8 gr/ltr** for Light Efficient Strain

Advanced Nutrient Delivery Technology.

Efficient CO_2-nutrient feeding

Current state-of-the-art

Pure CO_2 bubbling

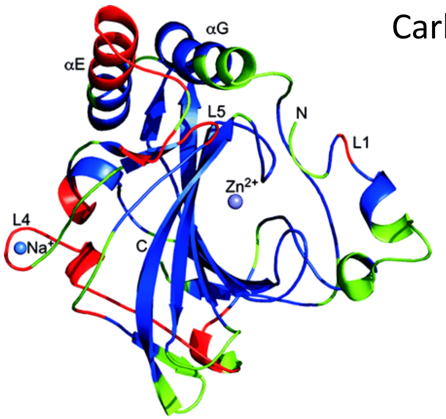
Flue gas washing/bubbling
(diluted CO_2 stream)

Two possible routes researched at TNO

Enzyme promoted CO_2 capture

- **Carbonic Anhydrase** enhances the uptake rate of CO_2 into an absorption liquid
- **Algae** regenerate the carbonate-based absorption liquid

Carbonic Anhydrase II

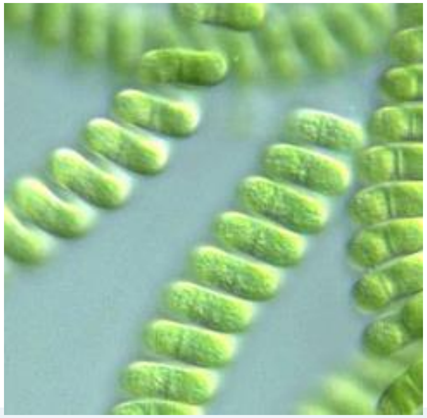


(source: Premkumar *et* al. (2005) PNAS, 102 (21) p,7493-7498)

Amine based CO_2 capture

- Cultivation of algae directly on CO_2 "captured" in **amine-based solvents**
- **Algae** regenerate solvent which can be reused for CO_2 capture

Spirulina platensis

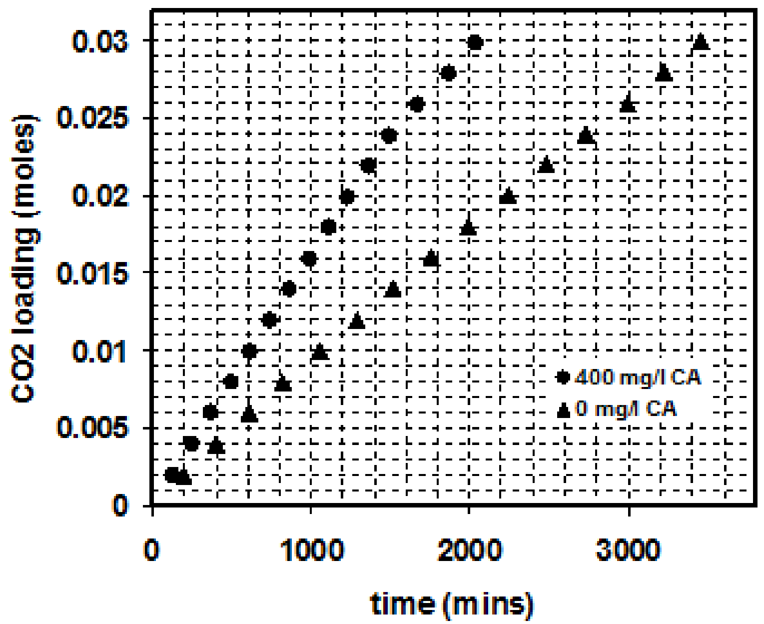


(source http://www.energen.it/inglese/olio_da_alghe.html)

Route 1: Enzyme promoted CO_2 capture

- Carbonate solutions are **cheap** compared to other CO_2 absorption liquids, but have a **slow CO_2 uptake rate**
- Addition of **carbonic anhydrase** to sodium carbonate solution **increases** the rate of CO_2 uptake

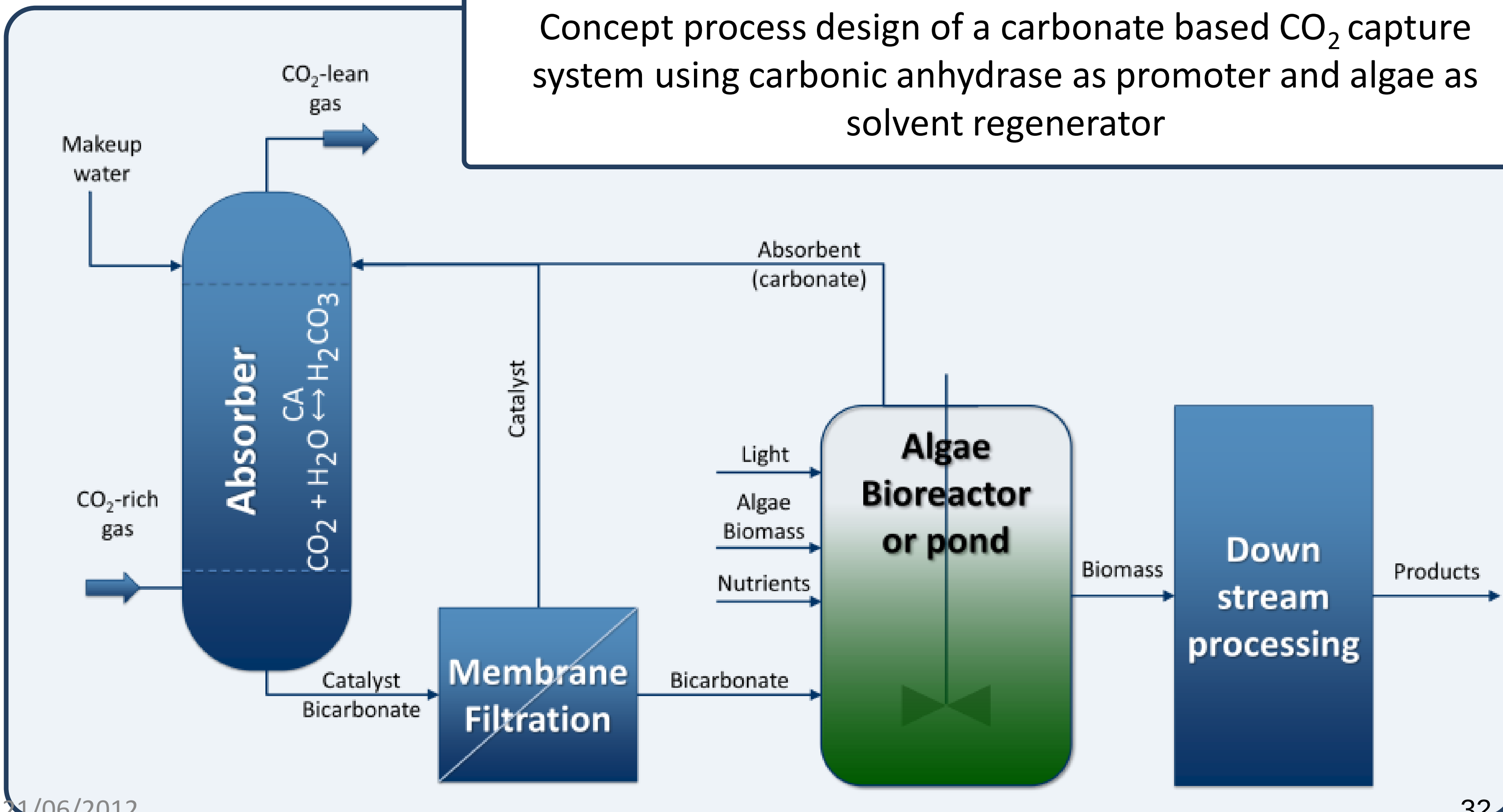
Carbonic Anhydrase effects on CO_2 loading



Kinetic experiments showing the rate of CO_2 loading in the reference (▲, 2M sodium carbonate) and catalyzed (●, 2M sodium carbonate plus 400mg/L carbonic anhydrase) tests

Route 1: Enzyme promoted CO_2 capture

Concept process design of a carbonate based CO_2 capture system using carbonic anhydrase as promoter and algae as solvent regenerator

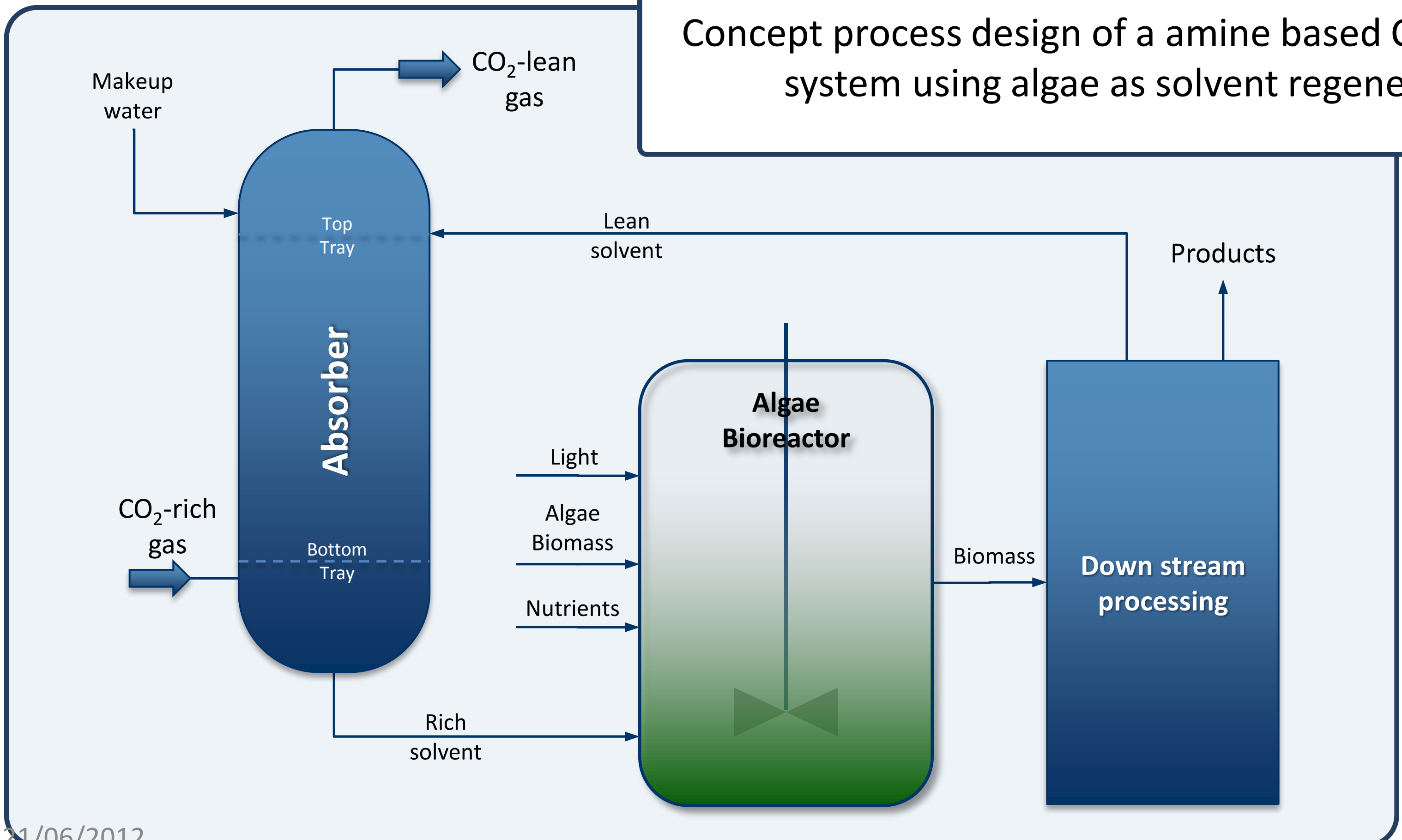


Route 2: Combining CO_2 capture with amine based solvents & algae cultivation

- The uptake of CO_2 by a amine-based solvent
- CO_2 stripping of solvent by consumption through algae in a solvent & medium solution
- Recycle of the solvent for new cycle of CO_2 uptake
- The algae biomass can be used for product.

Route 2: Algae-mediated CO_2 desorption from amine-based solvents

Concept process design of a amine based CO_2 capture system using algae as solvent regenerator



Capture solvent selection criteria

- 1. Non-toxic to algae culture
- 2. Slow biodegradable by algae culture
- 3. Cheap/abundant
- 4. Efficient capture of CO_2

(partly absorbed CO_2 should be bicarbonate species)

It is of importance to note that 90% CO_2 capture is **not** the objective

From problem to business

www.stichtingmilieunet.nl/.../sailing-algae.bmp

www.altdotenergy.com/wp-content/uploads/2009/...

Acknowledgement

HiPerCap CO2

Some references

US2014295531 (A1) - ENZYME PROMOTED CO2 CAPTURE INTEGRATED WITH ALGAE PRODUCTION – Goetheer et al.

WO2013022349 (A1) - COMBINING ALGAE CULTIVATION AND CO2 CAPTURE – Goetheer et al.