Process modeling and optimization for production of carbon-neutral solar fuels

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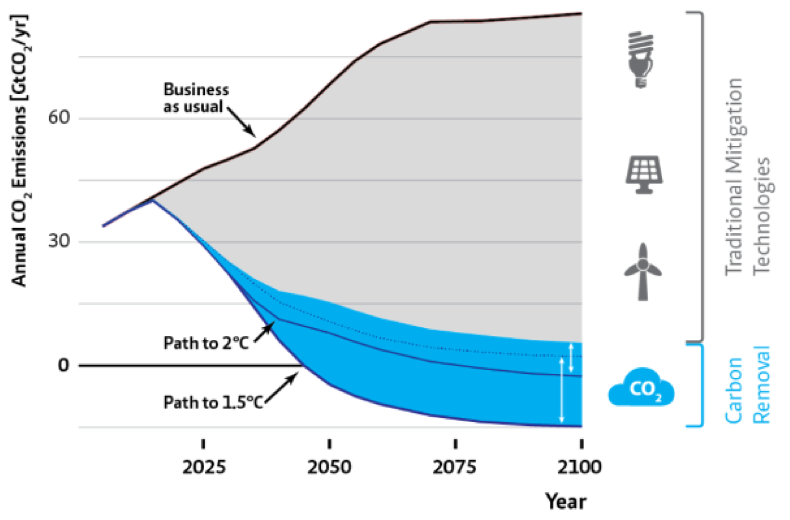
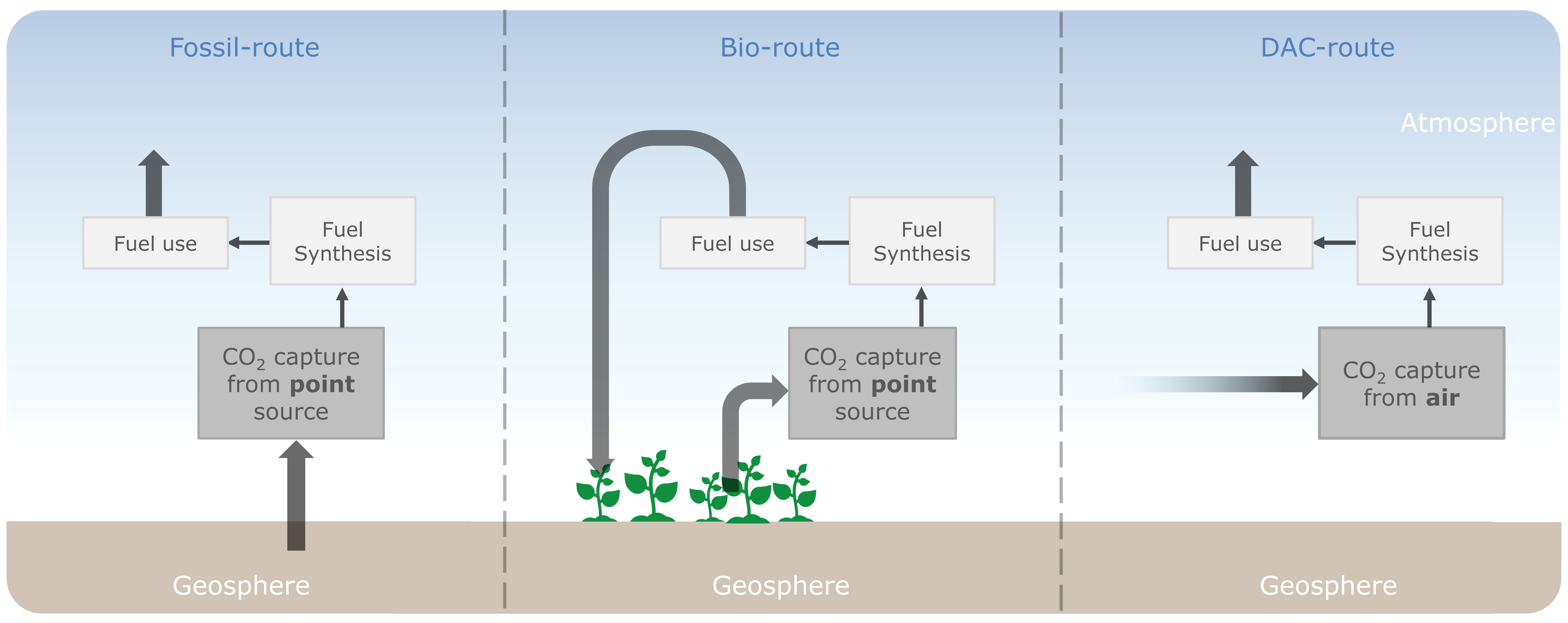
Overview

Introduction

- With the Paris climate agreement, the vast majority of world countries pledged to limit the increase in the global average temperature to 'well-below' 2 °C [1];
- Depending on the sector there are different pathways to reduce the CO_2 emissions.
- The role of carbon based chemicals and fuels will continue to play an important role in the future, e.g. for transportation, energy storage, chemical industry. Therefore a sustainable production is necessary.



Synthetic fuel production



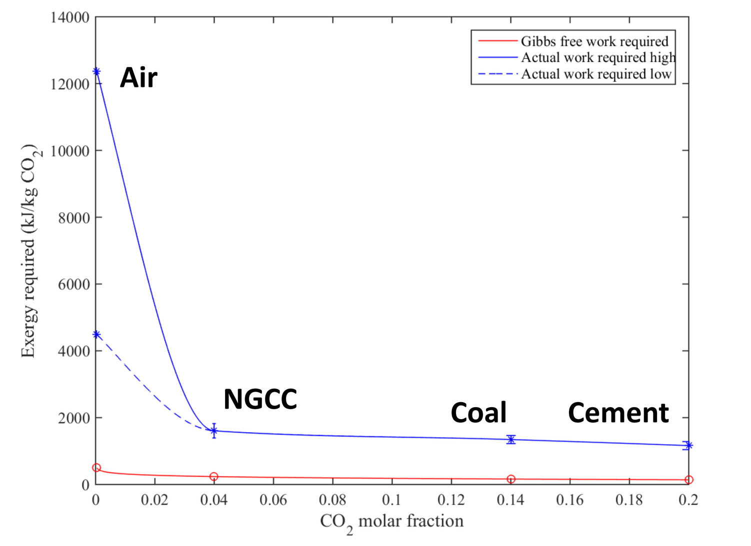
- Capturing CO_2 from a point source using fossil fuels, e.g. coal power plant.
- Not a sustainable process.

- Capturing CO_2 from a power plant using biomass as input.
- Competing with different utilization of biomass.

- Capturing CO_2 directly from the ambient air.
- Relatively new and innovative technology in early commercial stages.

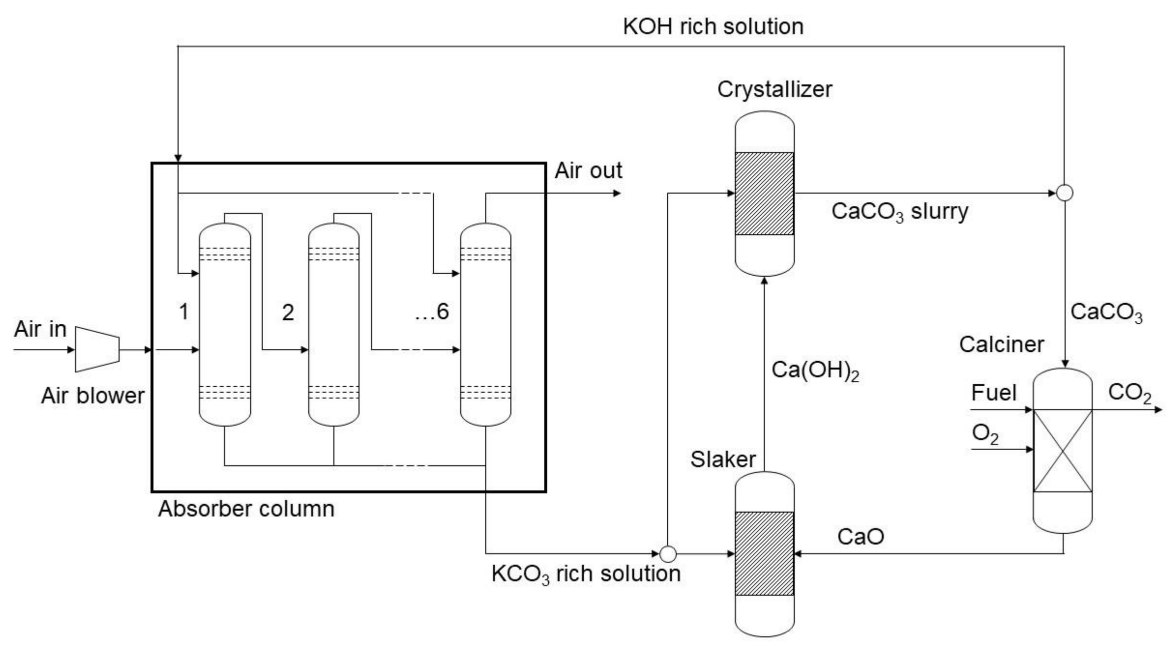
Energy requirements DAC

- From a theoretical perspective, the Gibbs free energy required to separate one mole of CO_2 from air at ambient conditions is 497 kJ/kg_{CO2};
- In practice, real processes require larger amount of energy. For air capture values in literature vary significantly;
- Estimated energy requirements for DAC range from about 4 GJ/ton_{CO2} to 12 GJ/ton_{CO2};



Liquid Scrubbing

Process design



Thermodynamics

Vapor: CO_2 H_2O

Liquid: CO_2 H_2O

$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$
$$HCO_3^- + OH^- \rightleftharpoons H_2O + CO_3^{2-}$$
$$CaOH^+ \rightarrow Ca^{2+} + OH^-$$
$$KOH \rightarrow K^+ + OH^-$$
$$Ca(OH)_2 \rightleftharpoons CaOH^+ + OH^-$$

Solid: $Ca(OH)_2$ K_2CO_3 $CaCO_3$ $KHCO_3$

Modeling approach

- The process is composed of two cycles: the *potassium cycle* (Absorber, Crystallizer) and the *calcium cycle* (Calciner, Slaker);
- The potassium cycle and the calcium cycle are modeled in Aspen Plus separately, using a rigorous thermodynamic model (E-NRTL framework [3]). The two environments are directly linked using MATLAB which ensures the consistency of the energy and mass balances.
- For the simulation of the air contactor section, a rate based model was developed;

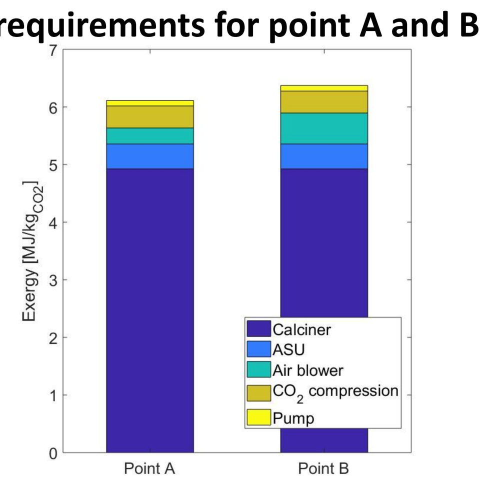
Optimization

- Multi-objective optimization to minimize the specific energy consumption and maximize productivity;
- Three decision variables are optimized: air velocity, absorber loading, water content in the Ca-loop;
- The production is fixed at 1$Mton_{CO2}$, while the CO_2 recovery is free to vary;
- Genetic algorithm NSGA-II used for optimization, implemented in MATLAB;

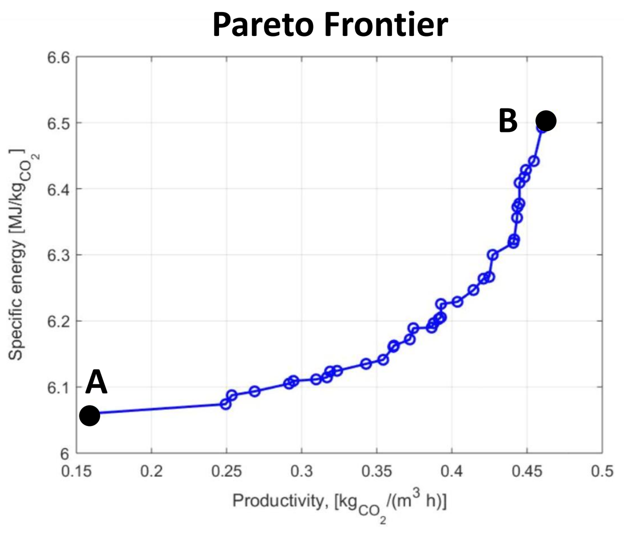
Results

- As expected, most of the energy is required for the calcination of $CaCO_3$;
- The productivity is way smaller than classical CCS;
- The optimal CO_2 recovery ranges between 50-70%;
- The results obtained are in line with previous estimates [4];

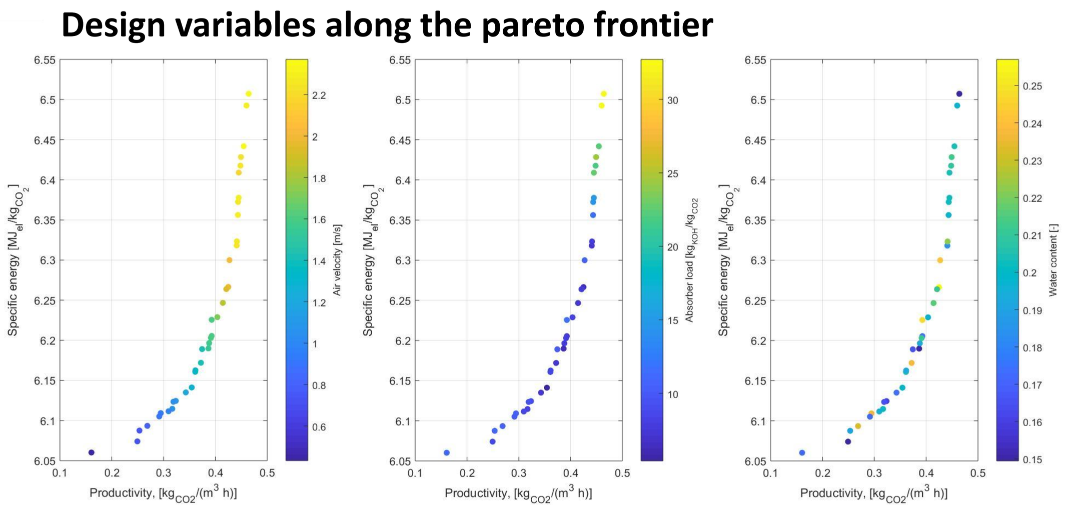
Breakdown of energy requirements for point A and B



Pareto Frontier

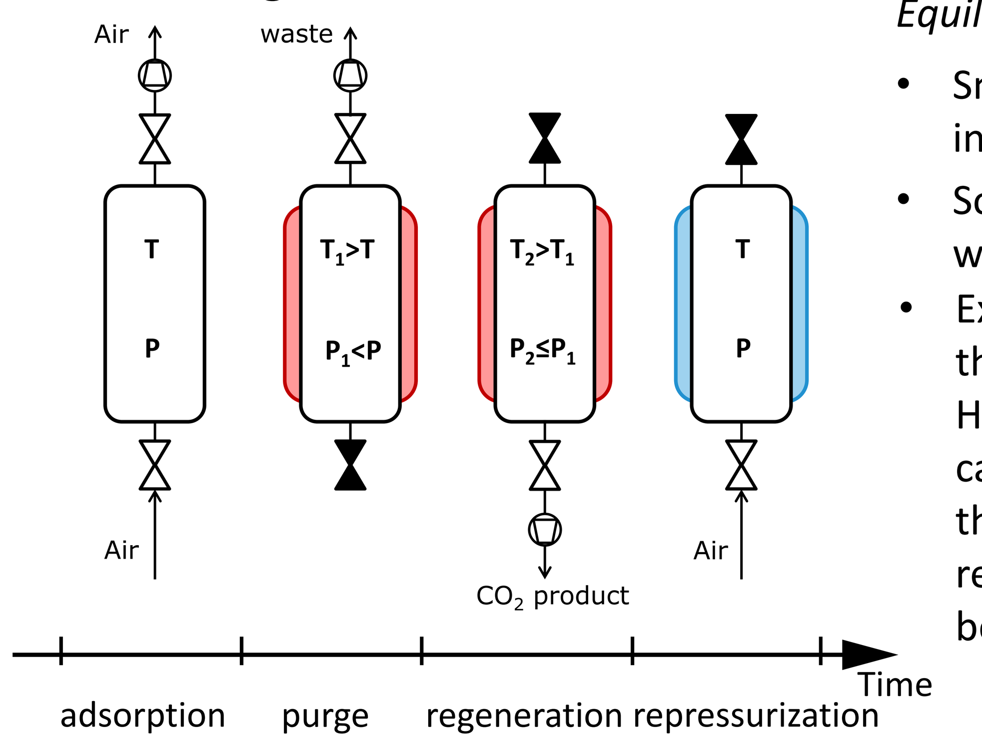


Design variables along the pareto frontier



Temperature-Vacuum Swing Adsorption (TVSA)

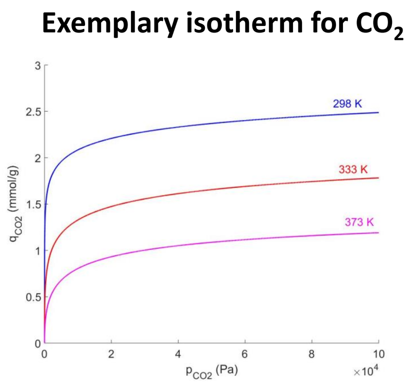
Process design



Equilibrium data:

- Small sorbent screening was carried out including data of 69 sorbents;
- Sorbents with negative working capacity were excluded;
- Exemplary isotherm for CO_2, H_2O and N_2 was calculated on the basis of the remaining sorbents;

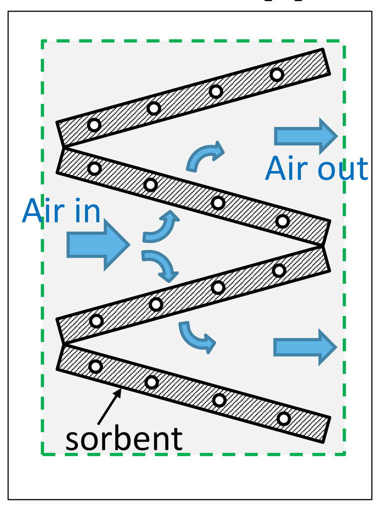
Exemplary isotherm for CO_2



Modeling approach

- Reactor design similar to air ventilation systems;
- Cyclic adsorption process is simulated by using a 1-D fixed bed model [2], [5];
- Adsorption data and isotherms [6]-[9], i.a.:
  - Exemplary isotherm for CO_2 and H_2O
  - Bed density: 55.1 kg/m³

Scheme of the air contactor [9]



Component and total mass balances:

$$\varepsilon_t \frac{\partial c_i}{\partial t} + \frac{\partial (uc_i)}{\partial z} + \rho_b \frac{\partial q_i}{\partial t} = 0 \qquad i=1,\dots,N$$

$$\varepsilon_t \frac{\partial c}{\partial t} + \frac{\partial (uc)}{\partial z} + \rho_b \sum_{j=1}^{N} \frac{\partial q_j}{\partial t} = 0$$

Energy balances for the fluid and solid phase:

$$(\varepsilon_t C_g + \rho_b C_s + \rho_b C_{ads}) \frac{\partial T}{\partial t} - \varepsilon_t \frac{\partial p}{\partial t} + u C_g \frac{\partial T}{\partial z} - \rho_b \sum_{j=1}^{N} (-\Delta H_j) \frac{\partial q_j}{\partial t} + 2\frac{h_L}{R_i}(T - T_{amb}) = 0$$

Momentum balance (Ergun equation):

$$\frac{\partial p}{\partial z} = -\frac{150(1-\varepsilon_b)^2}{\varepsilon_b^3 d_p^2} u - \frac{150(1-\varepsilon_b)^2}{\varepsilon_b^3 d_p} |u| u$$

Mass transfer (LDF model)

$$\frac{\partial q_i}{\partial t} = k_i (q_i^{eq} - q_i) \qquad i=1,\dots,N$$

Optimization

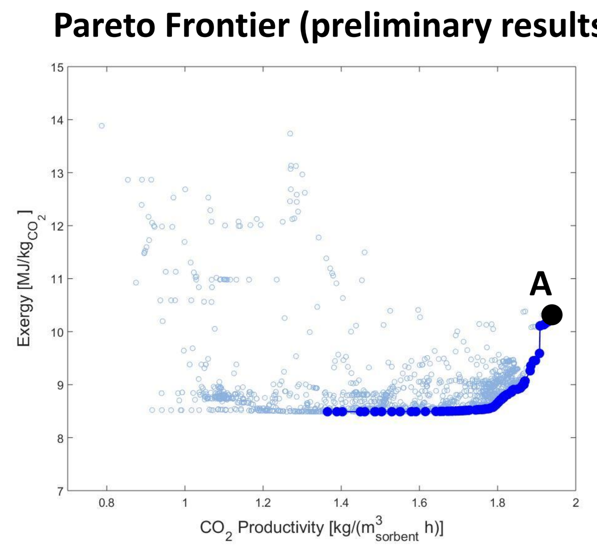
- Multi-objective optimization with productivity and specific energy consumption as objectives:

$$Pr = \frac{m_{CO2}/t_{cycle}}{V_{Ads}}$$

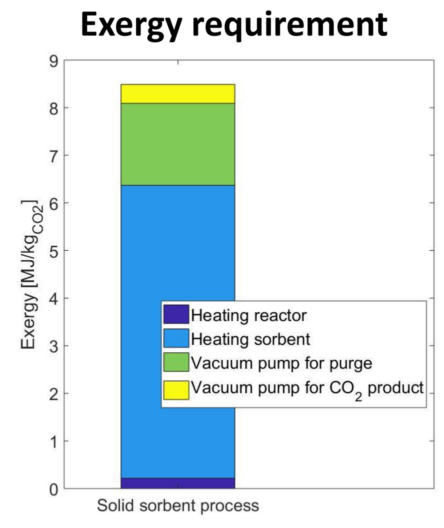
$$E = \frac{1}{m_{CO2}} \left(Q_{purge} + Q_{prod} + W_{vac,purge} + W_{vac,prod} \right)$$

- Six decision variables are optimized: time steps for adsorption, purge and regeneration, Temperature T_1 and T_2, vacuum pressure;

Pareto Frontier (preliminary results)



Exergy requirement



Preliminary Results

- CO_2 purities above 98% can be achieved, after condensing water at ambient conditions;
- High CO_2 recovery is less important in terms of separation, but affects the productivity;
- Reactor configuration strongly affects overall energy needs;
- Thanks to the low temperature of the heat required, exergy requirement is considerably lower than energy requirement;

Conclusions

- While the **scrubbing** process shows a lower exergy consumption, the **TVSA** has higher productivity, along with large room for decreasing the sorbent heat of regeneration;
- The **performance** of DAC processes is already quite good, with having an exergy efficiency (η_{ex}= 6-8.3%) in the lower range of classical CCS plants (η_{ex}=8.5-23%);
- The main challenge lies in reducing the **costs** significantly by keeping the energy performance (currently around 600 \$/t_{CO2});

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