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Carbon Capture Technologies in the Cement Industry
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Membrane-assisted CO_2 liquefaction

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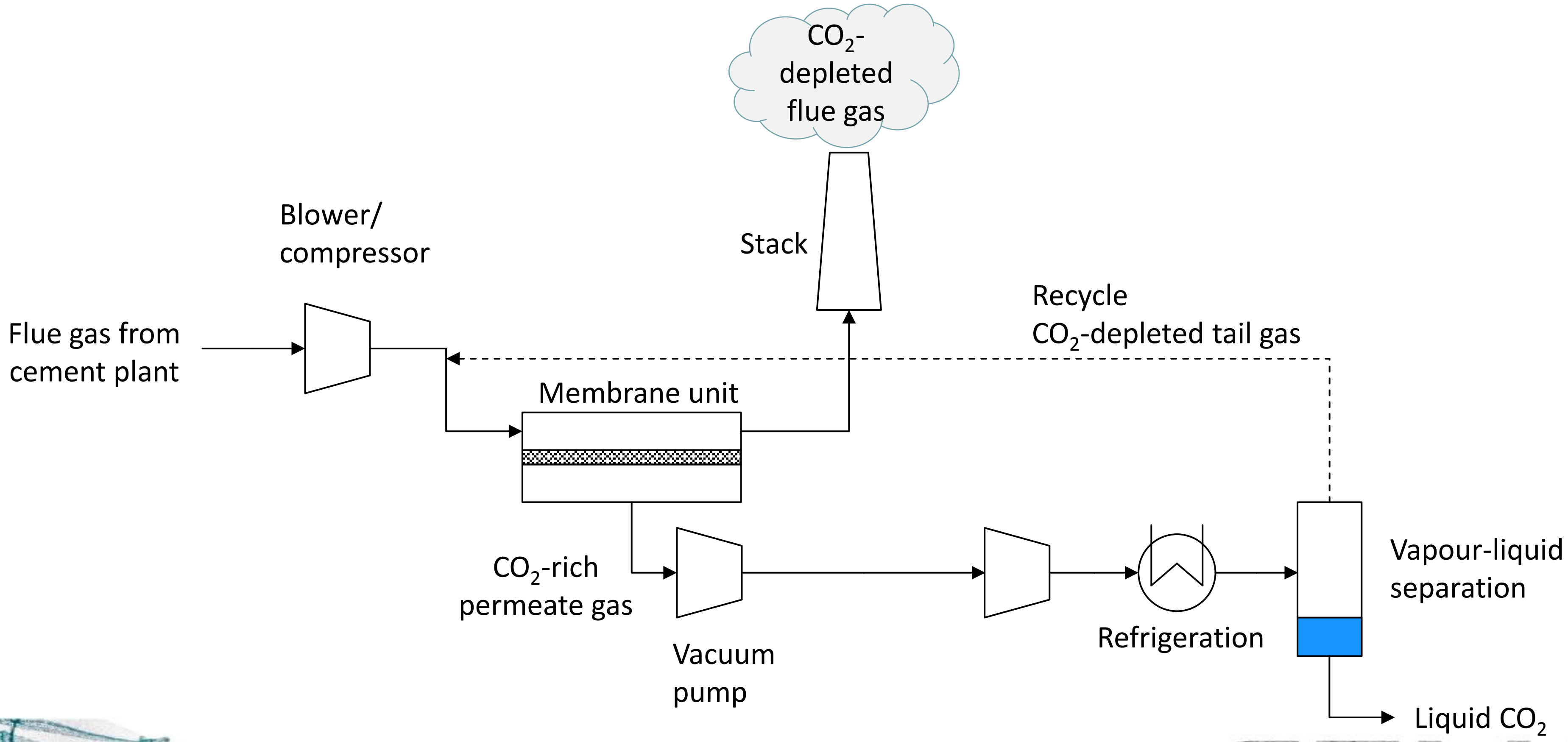
Basic system layout, membrane-assisted CO_2 liquefaction process

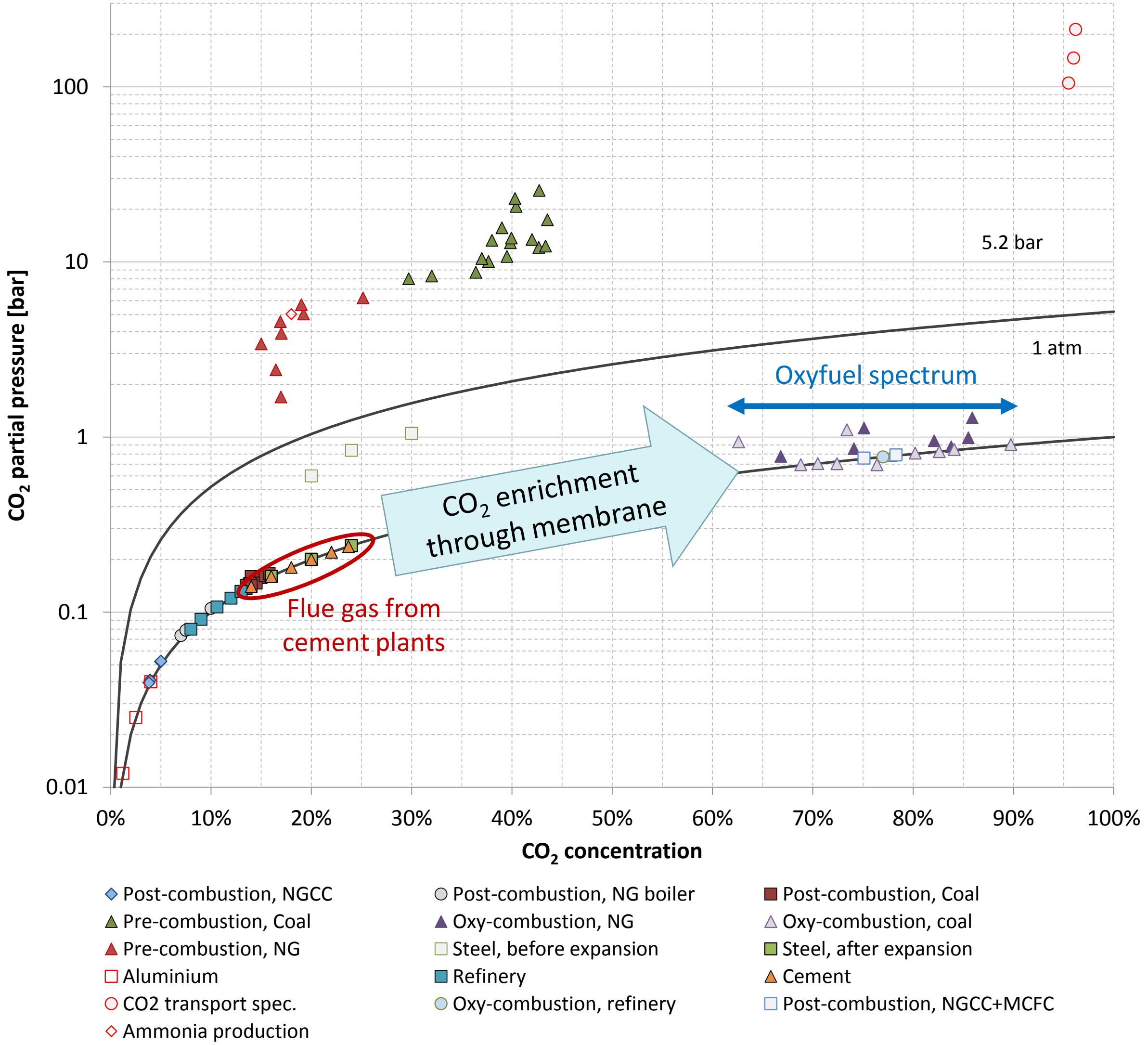
Neither sub-technology is particularly optimal for post-combustion capture in stand-alone application

By combining the technologies, both can operate in their optimal separation ranges



Motivation for combining membrane separation and CO_2 liquefaction

- The CO_2 concentration after a membrane stage can be configured to be typically 60–70 vol%
- These conditions are close to typical oxyfuel flue gas conditions, and can thus be otained with an "end-of-pipe" solution, without retrofitting a plant to oxy-combustion
- CO_2 liquefaction expected to be a better 2nd-stage option than another membrane stage
  - Superior scaling of liquefaction capacity
  - Superior purity of captured CO_2
  - Energy efficiency likely to be superior
  - The density of captured CO_2 in liquid form is 600–3000 higher than in gaseous from at vacuum or atmospheric pressure!



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Pros and cons about membrane-assisted CO_2 liquefaction

- Pros:
  - Performance of membranes improves dramatically with increased CO_2 concentration in flue gases
  - No need for handling large inventories of chemicals and disposal of degradation products
  - No need for large auxiliary steam generation plants → Mostly grid power is needed
  - Prospect for low investment cost for CO_2 capture
  - Potential for very competitive per-unit cost [€/ton CO_2 captured] at optimal CO_2 capture ratio
- Cons:
  - Generally lower optimal CO_2 capture ratio than solvents and sorbents
  - Scaleability: Generally limited size of each membrane module
    - Membrane unit scales linearly
    - NB: This is not an issue for the CO_2 liquefaction part of the process
  - Membranes are not yet mature technology for post-combustion CO_2 capture, but already shown to be mature in other demanding industries (e.g. natural gas upgrading)

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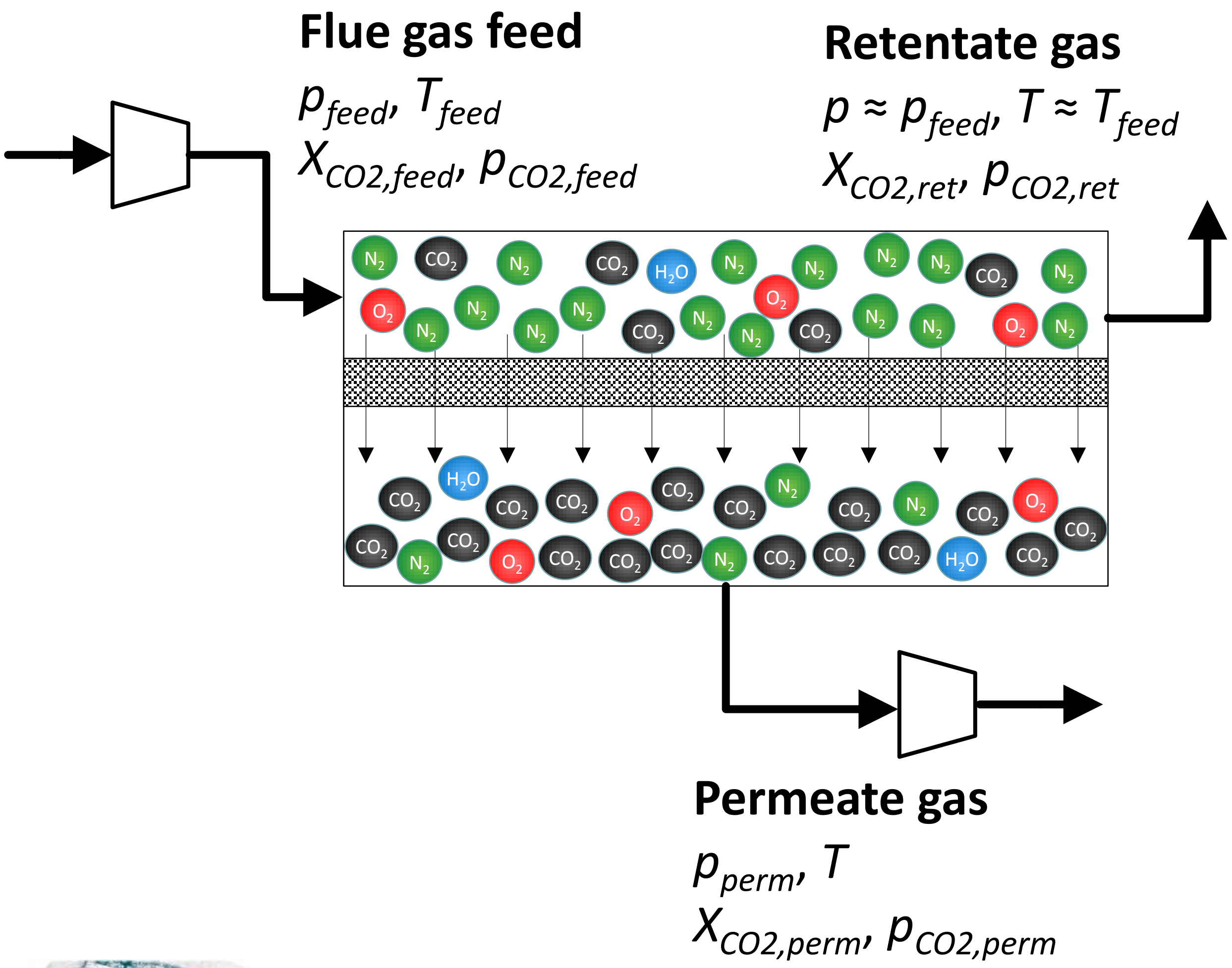
Membrane separation of flue gas – Process principle



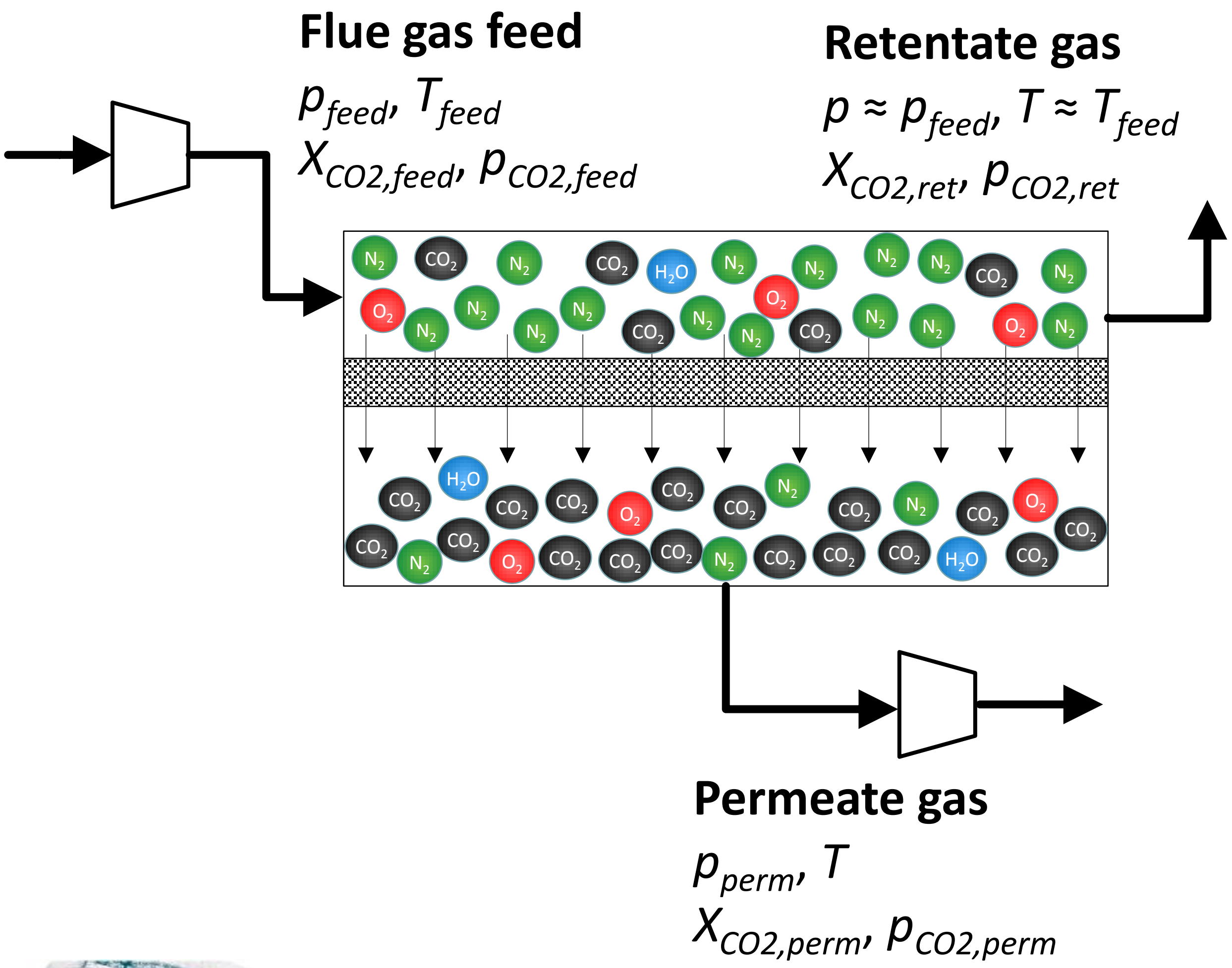
Partial pressure differences for CO_2, N_2, O_2 etc. between feed and permeate is the principal driving force of permeation of the difference gas components.

The membrane's ability to favour CO_2 over the other gas components is the membrane *selectivity*.

The selectivity of CO_2 over e.g. N_2 for membranes appropriate for post-combustion capture are typically from approximately 50 up to a few 100s.

The result is an increased CO_2 concentration on the other side of the membrane.

Membrane separation of flue gas – Pressure levels



Max theoretical enrichment of CO_2 through membrane:

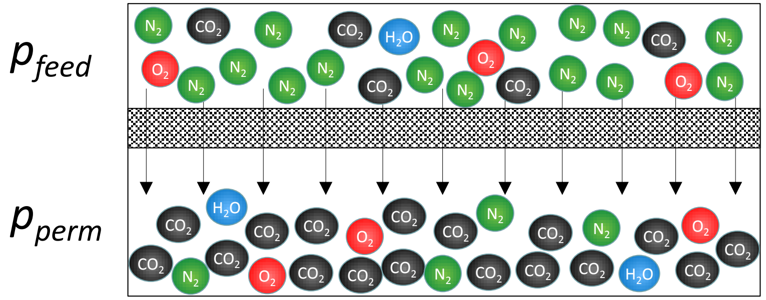
$$\frac{\mathrm{CO_2\ permeate\ concentration}}{\mathrm{CO_2\ retentate\ concentration}} \leq \frac{p_{feed}}{p_{perm}}$$

Example: CO_2 enrichment from 15 vol% to 75 vol%:

$$\frac{p_{feed}}{p_{perm}} \geq \frac{75\ \mathrm{vol\%}}{15\ \mathrm{vol\%}} = 5$$

The actual p_{feed}/p_{perm} pressure ratio must be even higher than this number, due to practicalities

Membrane separation of flue gas – Pressure levels



- **A membrane process will have typically a moderate flue gas pressure on the feed side and a moderate vacuum level on the permeate side**
- <u>Membrane pressure ratio</u> (p_{feed}/p_{perm}) must be high to allow high enrichment of CO_2
  - Can be promoted by having vacuum on the permeate side, i.e. p_{perm} < 1 atm
- <u>Membrane pressure difference</u> (p_{feed} - p_{perm}) must be relatively high to allow high flux through the membrane and thus reduce the overall membrane area requirement
  - Can be promoted by raising the feed pressure p_{feed} by using a blower/compressor
- There are, however, several trade-offs to consider:
  - Vacuum pumping power requirement + volume flow increase significantly at low vacuum levels
  - Feed gas compression is very power-demaning to the vast volume flows
  - Too high membrane pressure difference promotes flux of other components than CO_2 and therefore counteracts the desired CO_2 enrichment effect

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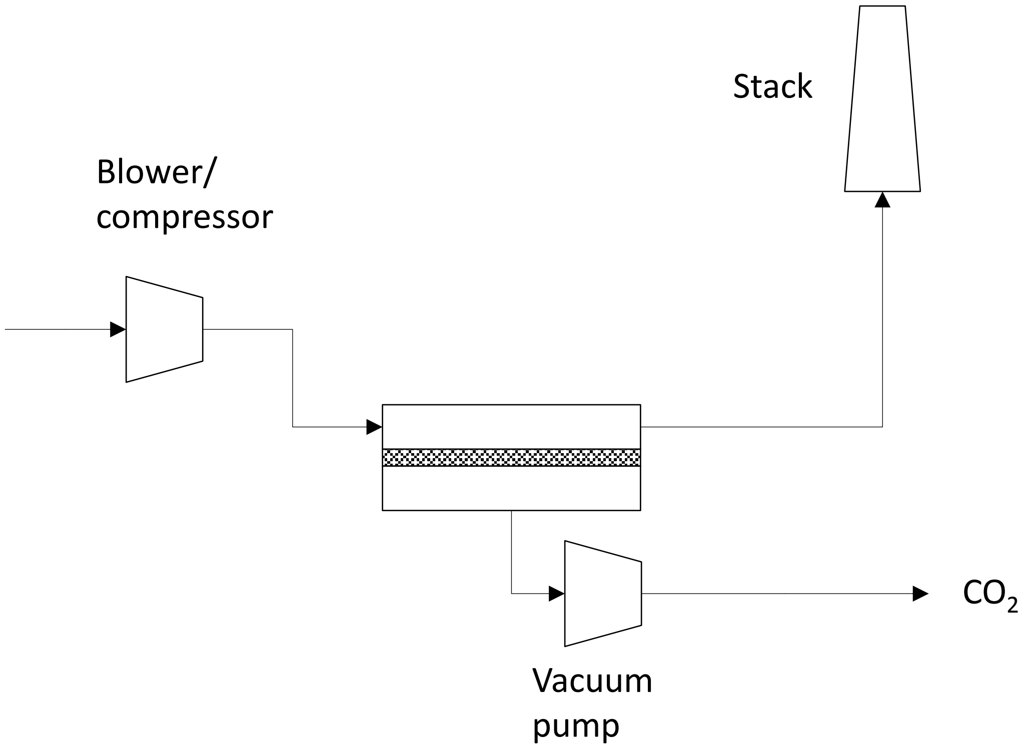
Single-stage membrane process

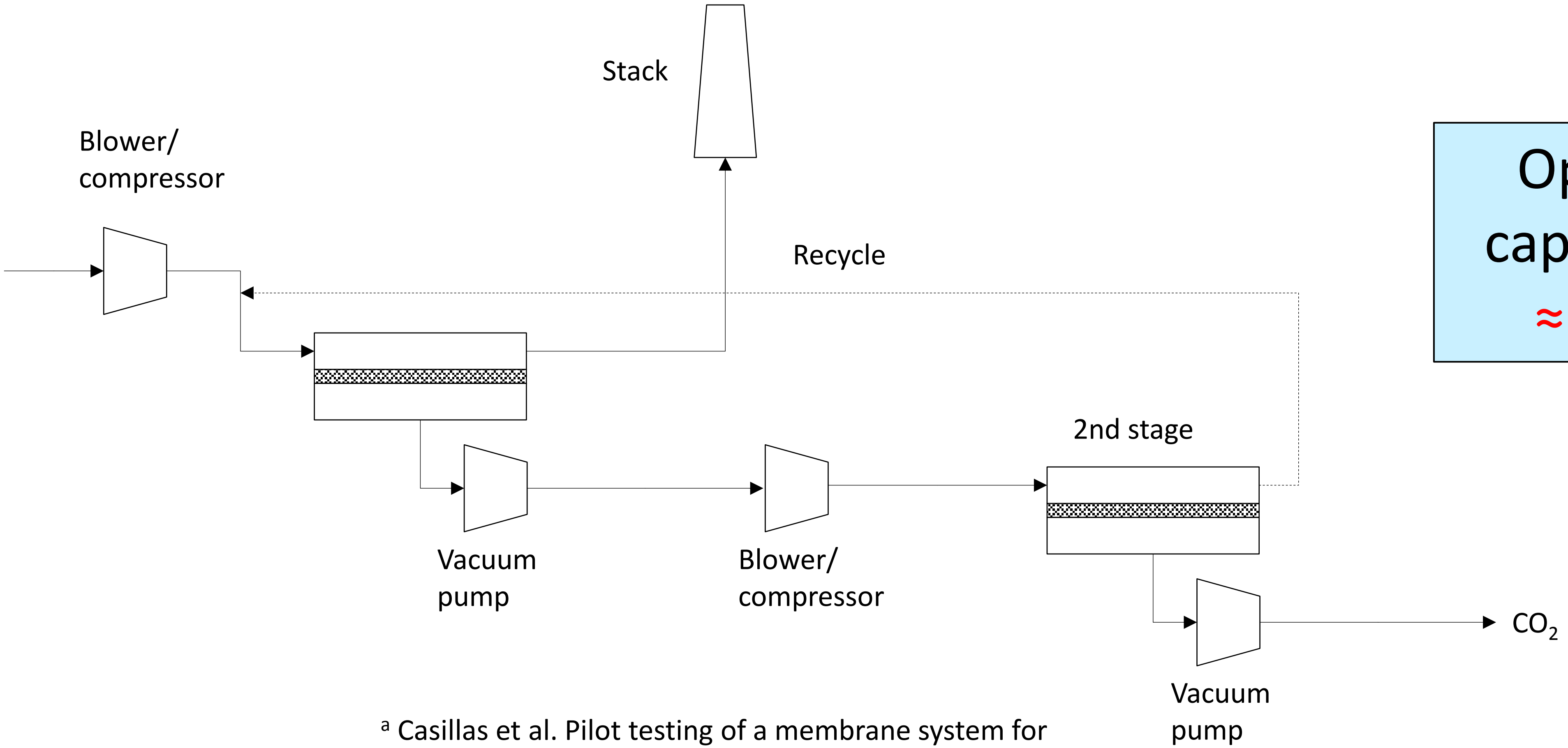


Optimal CO_2 capture rate[a]:

≈ 30 %

[a] Casillas et al. Pilot testing of a membrane system for post-combustion CO2 capture. NETL CO2 Capture Technology Meeting (2015)

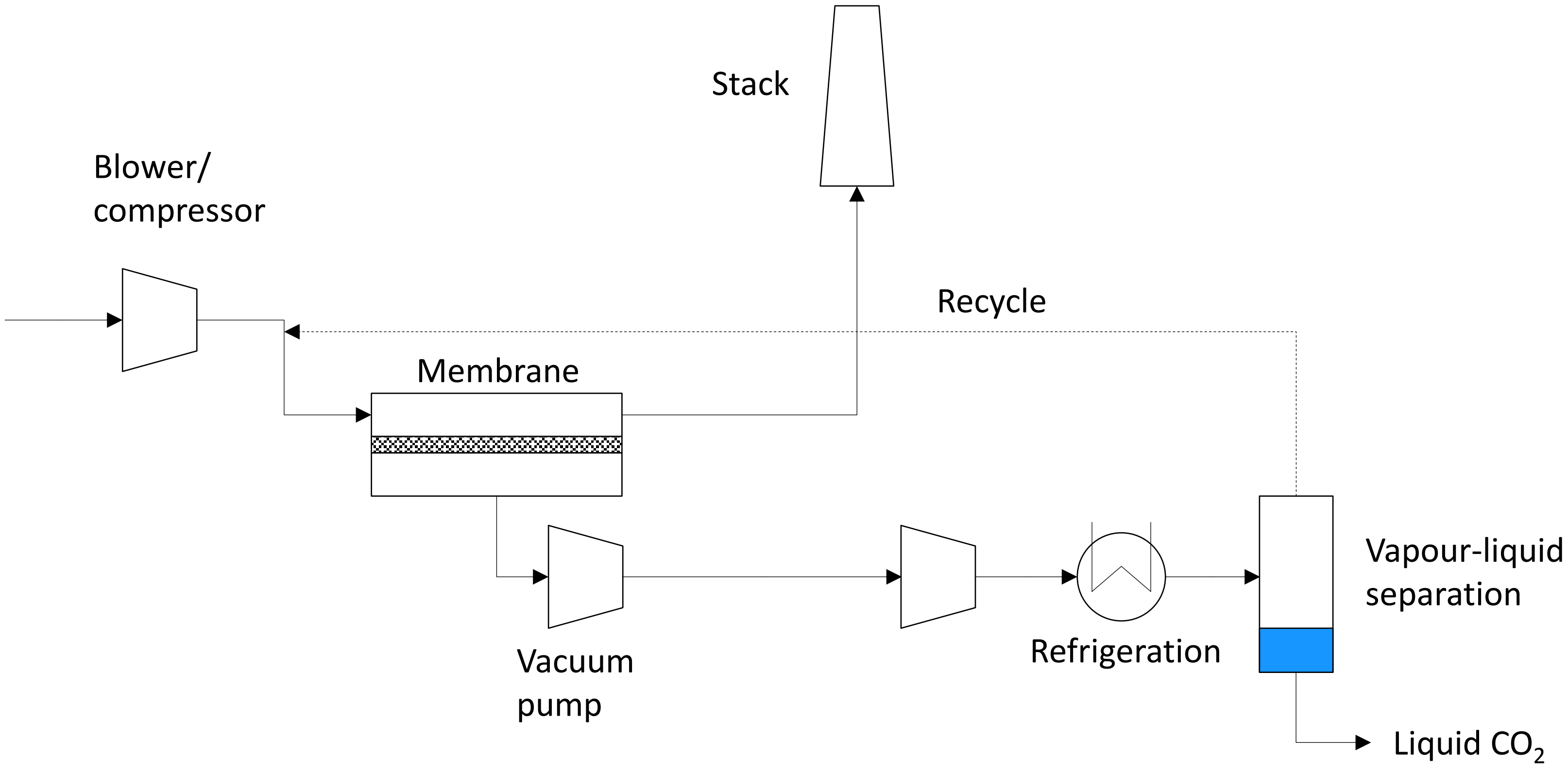
Two-stage membrane process with recycle loop



Optimal CO_2 capture rate[a,b]:
≈ 40–60 %

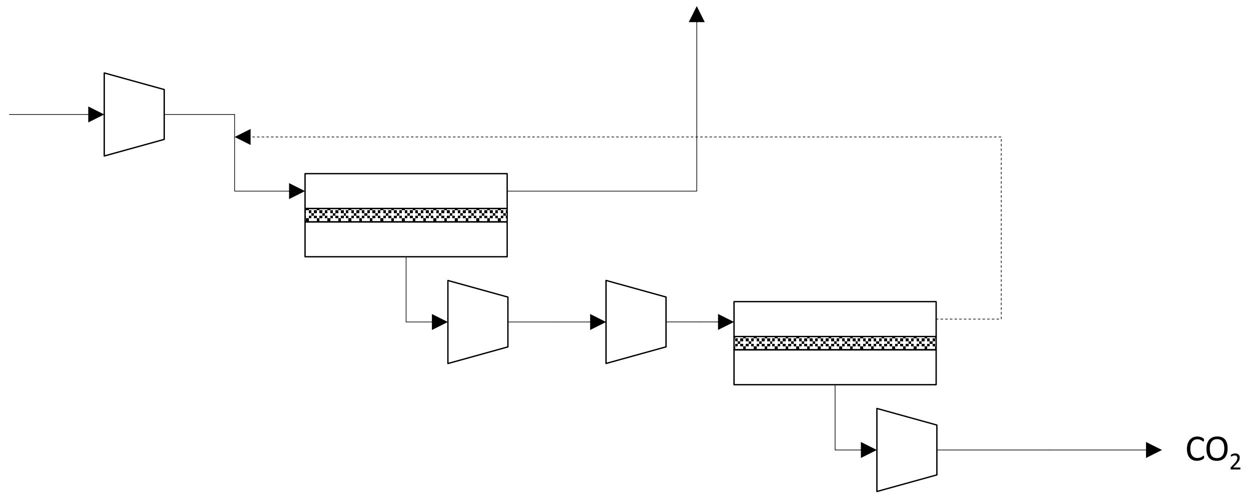
[a] Casillas et al. Pilot testing of a membrane system for post-combustion CO2 capture. NETL CO2 Capture Technology Meeting (2015)
[b] Internal optimisation analyses

Hybrid membrane-assisted CO_2 liquefaction process



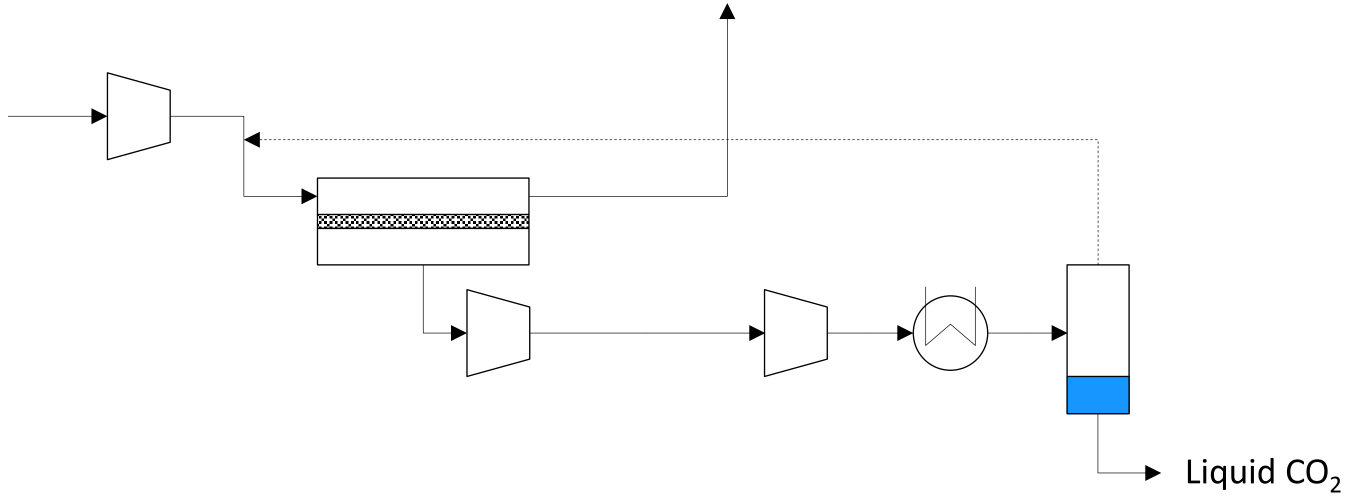
2-stage membrane CO_2 separation process

Optimal CO_2 capture rate:
≈ 40–60 %



Membrane-assisted CO_2 liquefaction process

Optimal CO_2 capture rate:
CEMCAP research task



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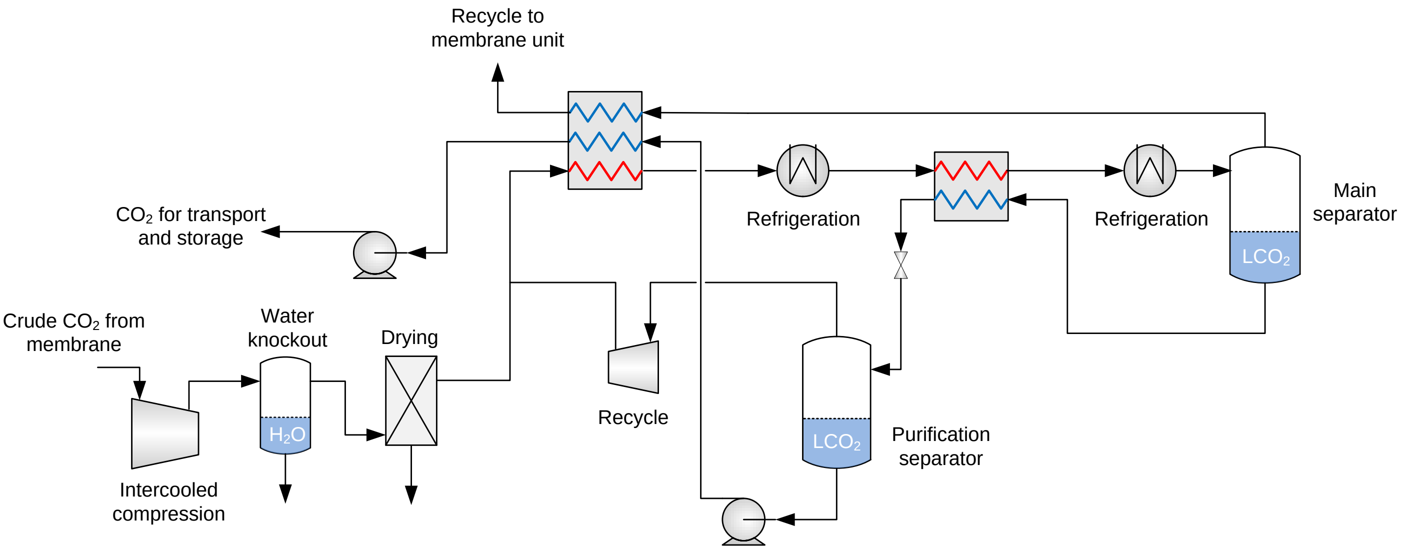
Liquefaction process for CO_2 purification

Simplified process layout



Separator	Pressure level	Temp. level	CO_2 purity
Main	30–40 bar	-53°C to -55°C	95–96 %
Purification	6–10 bar	-53°C to -56°C	99.5–99.9 %

CO_2 purity at -50°C (phase equilibrium)[a]

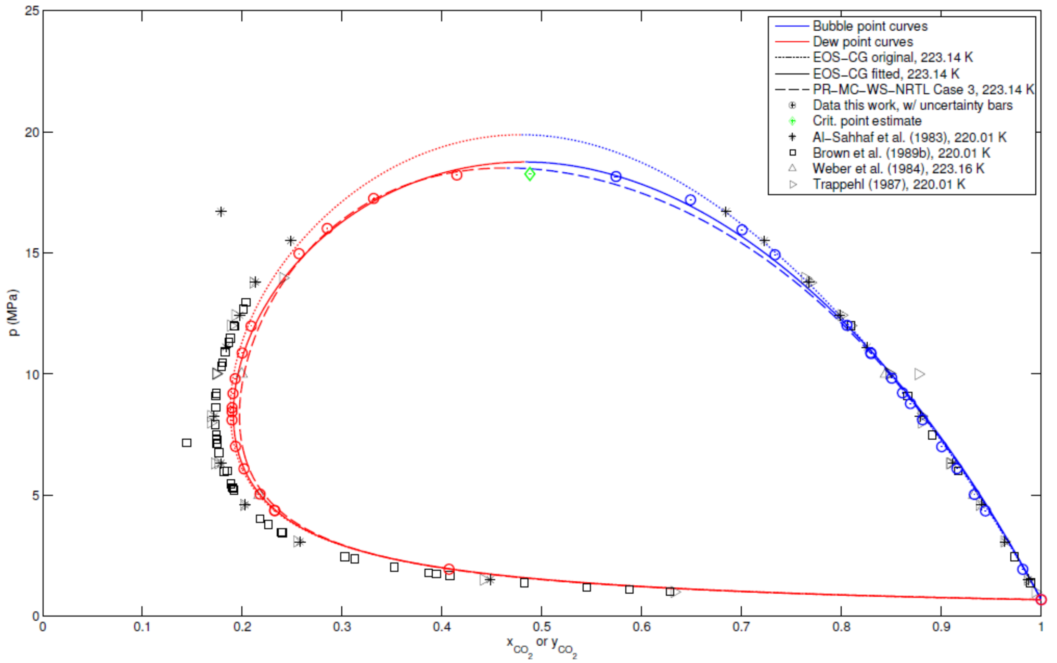
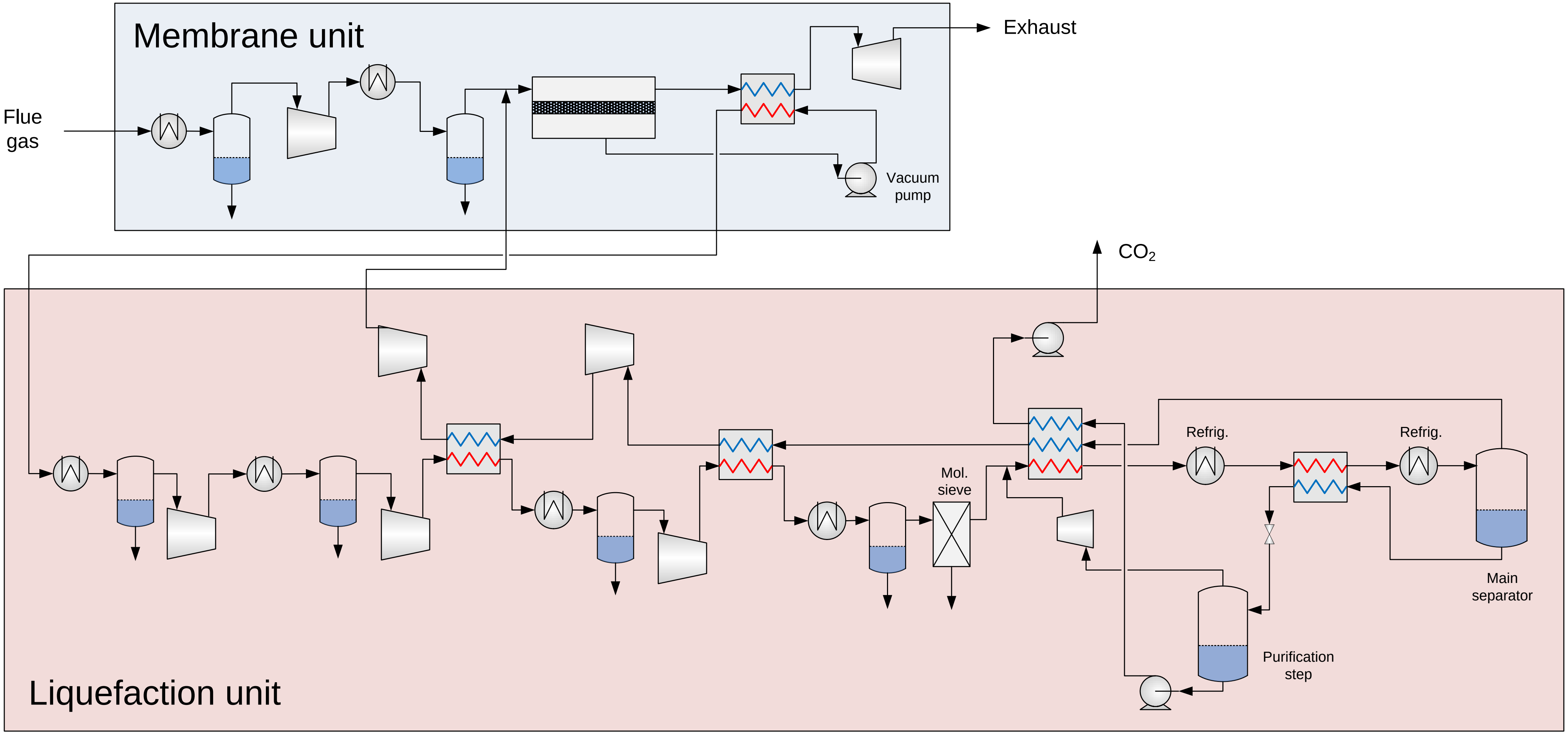


Fig. 7. Isothermal VLE data from literature [37, 28, 27, 52], EOS calculations at mean temperature $T = 223.14$ K, and measurements with estimated uncertainties from present work: $\bar{x}_{CO_2}$, $\bar{y}_{CO_2}$, $\bar{p}_f$, $u_c(\bar{x}_{CO_2})$, $u_c(\bar{y}_{CO_2})$ and $u_c(\bar{p}_f)$ from Tables 4 and 5. Critical point estimation and its uncertainties are from Section 5.2.

[a] Westman et al. Vapor–liquid equilibrium data for the carbon dioxide and nitrogen ($CO_2 + N_2$) system at the temperatures 223, 270, 298 and 303 K and pressures up to 18 MPa. Fluid Phase Equilibria 409, 207–241.

Principal layout of combined membrane and liquefaction capture process



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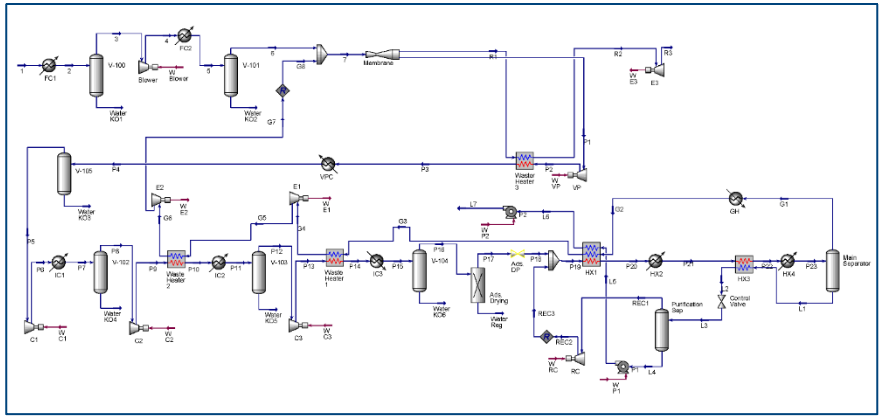
Ongoing and further work



- **Modelling and simulation of full-scale process configurations**
  - Includes in-house model for membrane unit
  - Foundation for the techno-economic analysis in CEMCAP
  - Determine optimal CO_2 capture ratio and specific cost and energy requirement
- **Bench-scale testing of (pre-)commerical membrane material**
  - Verify selectivity and flux appropriateness for CO_2 capture
- **Laboratory pilot testing of the CO_2 liquefaction and purification unit**
  - Test facility under commissioning
  - Capacity: Approximately 10 ton CO_2 per day
  - Experimental verification of CO_2 separation ratio and product purity
  - Comparison with theoretically obtainable performance

→ **Determine techno-economically optimum full-scale layout and KPIs**

→ **Propose layout of a scaled-up, on-site pilot plant**

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