Methodological evaluation of demixing solvents used for carbon capture by absorption-regeneration process

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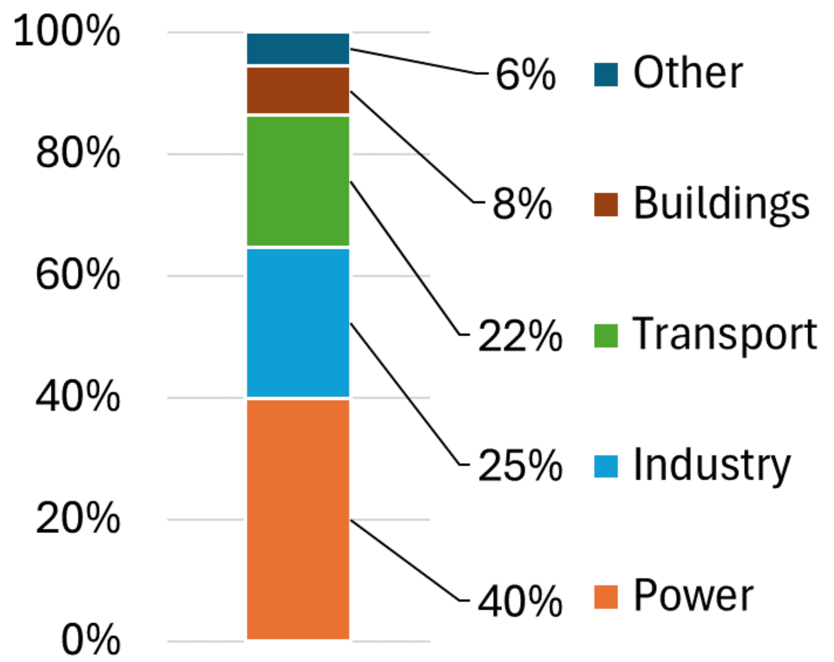
Context of the study

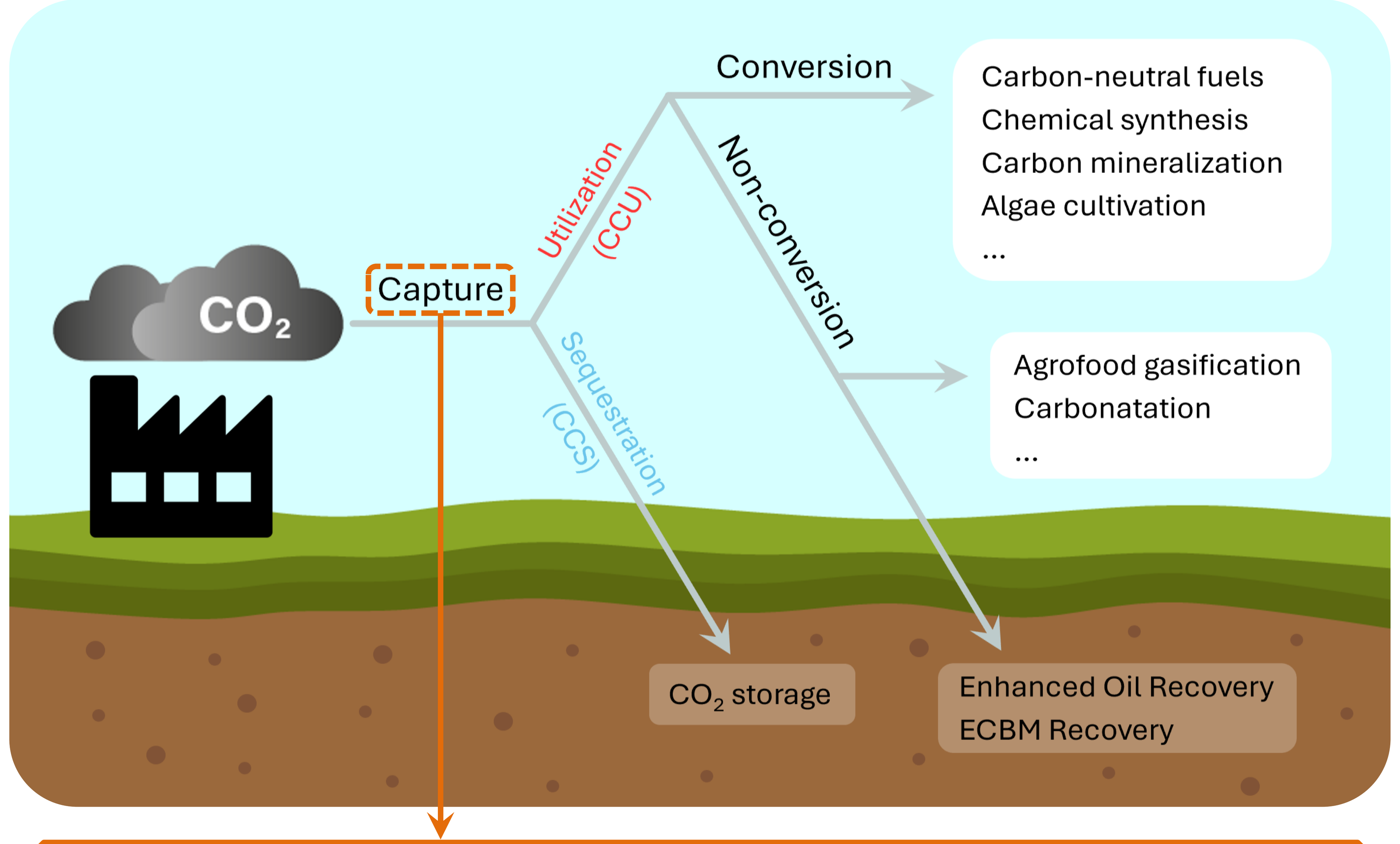
CO_2 emissions

37.4 Gt CO_2 Worldwide in 2023 [1]

Global CO_2 emissions by sector in 2022 [2]

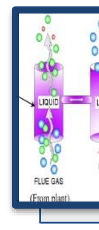


Carbon Capture Utilization and Storage (CCUS)

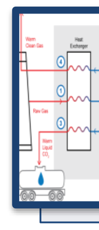


- Pre-combustion capture
- Oxy-combustion capture
- **Post-combustion capture**
  - *y_{CO2} between 5 and 30 mol.%*

Carbon capture technologies


Absorption


Adsorption


Cryogenics

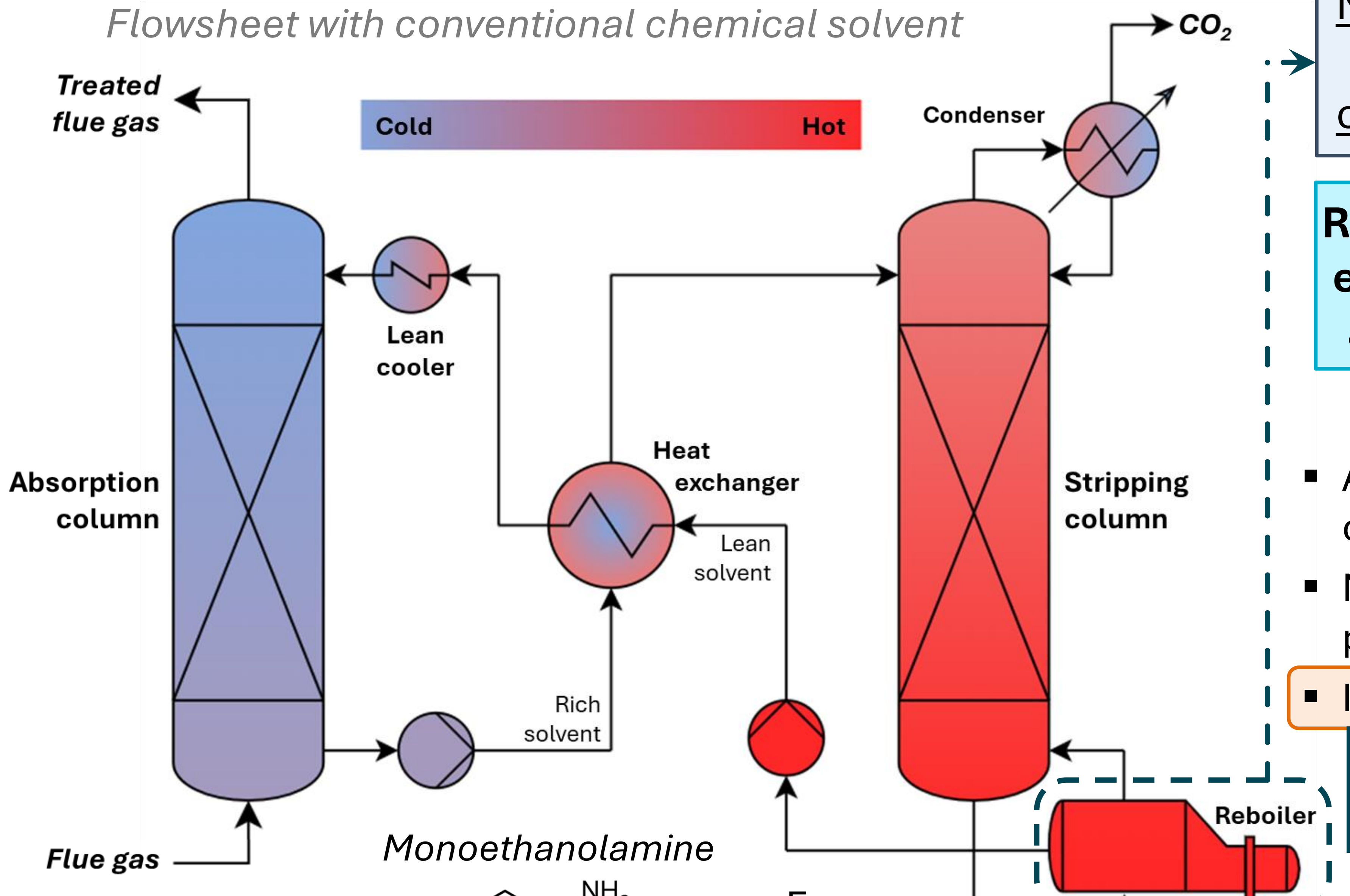

Membrane


Microalgae

Etc.

Carbon capture by absorption-regeneration process

Flowsheet with conventional chemical solvent



Benchmark: *Monoethanolamine* (HO–CH2–CH2–NH2), *MEA 30 wt.%*

$E_{regen} \approx$ 3.4 to 4 GJ/t_{CO2} [3]

Major challenge to reduce the operative costs:

Reduction of the energy demand at the reboiler

- Advanced process configurations
- New equipment & packed beds
- Innovative solvents [4]
  - *Ionic liquids, **demixing solvents**, amino-acid salts, ...*

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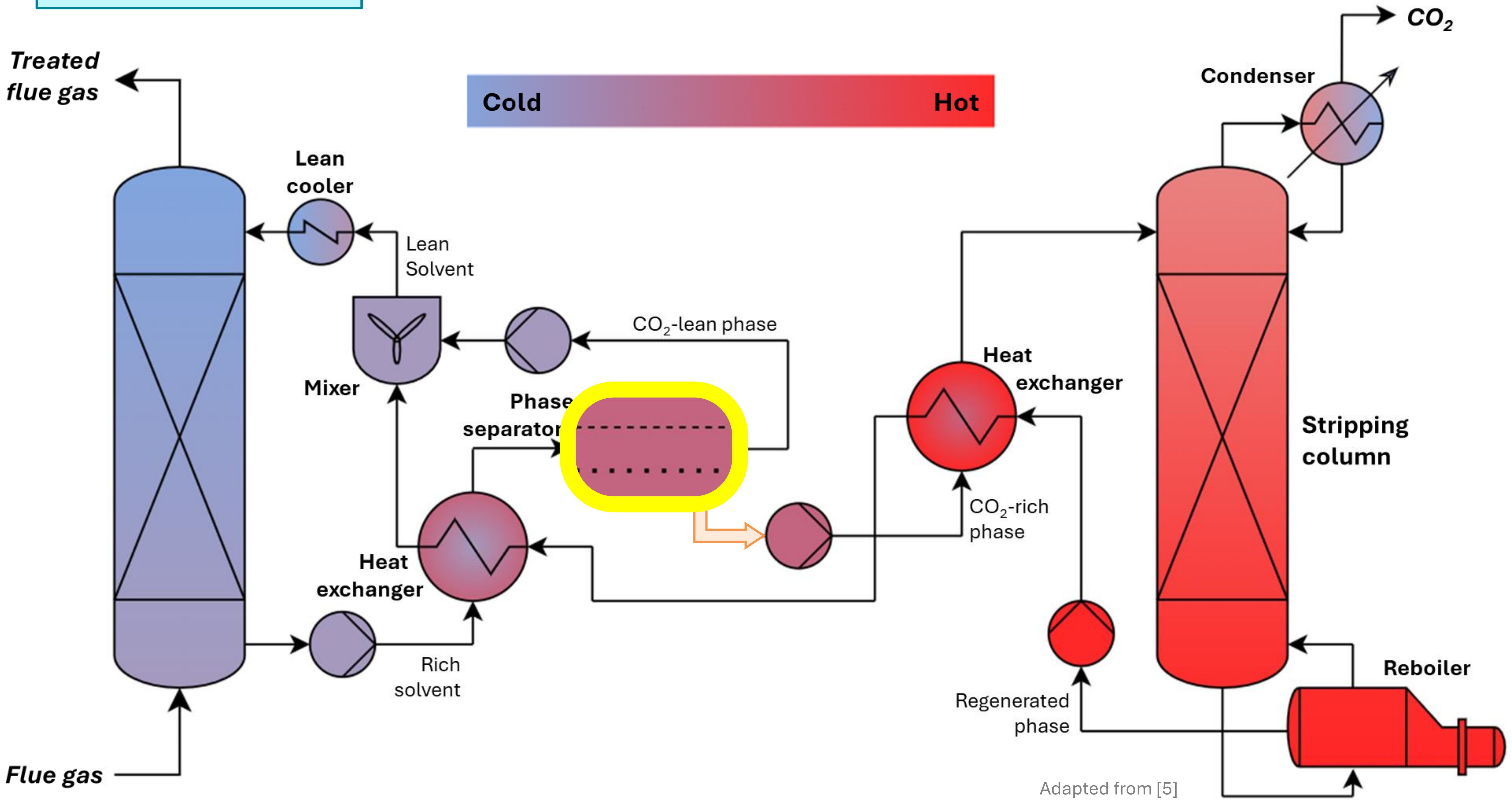
Bibliographic review

Carbon capture process using demixing solvents

Process flowsheet



Adapted from [5]

Advantages of the demixing solvents

Compared to non-demixing solvents

Only the CO_2-rich phase is regenerated in the stripping column → ✓ **Decreasing of the solvent flow** ✓ **Increasing of the CO_2 concentration**

Demixing phenomenon in carbon capture

CO_2 absorption reactions

Primary or secondary amines

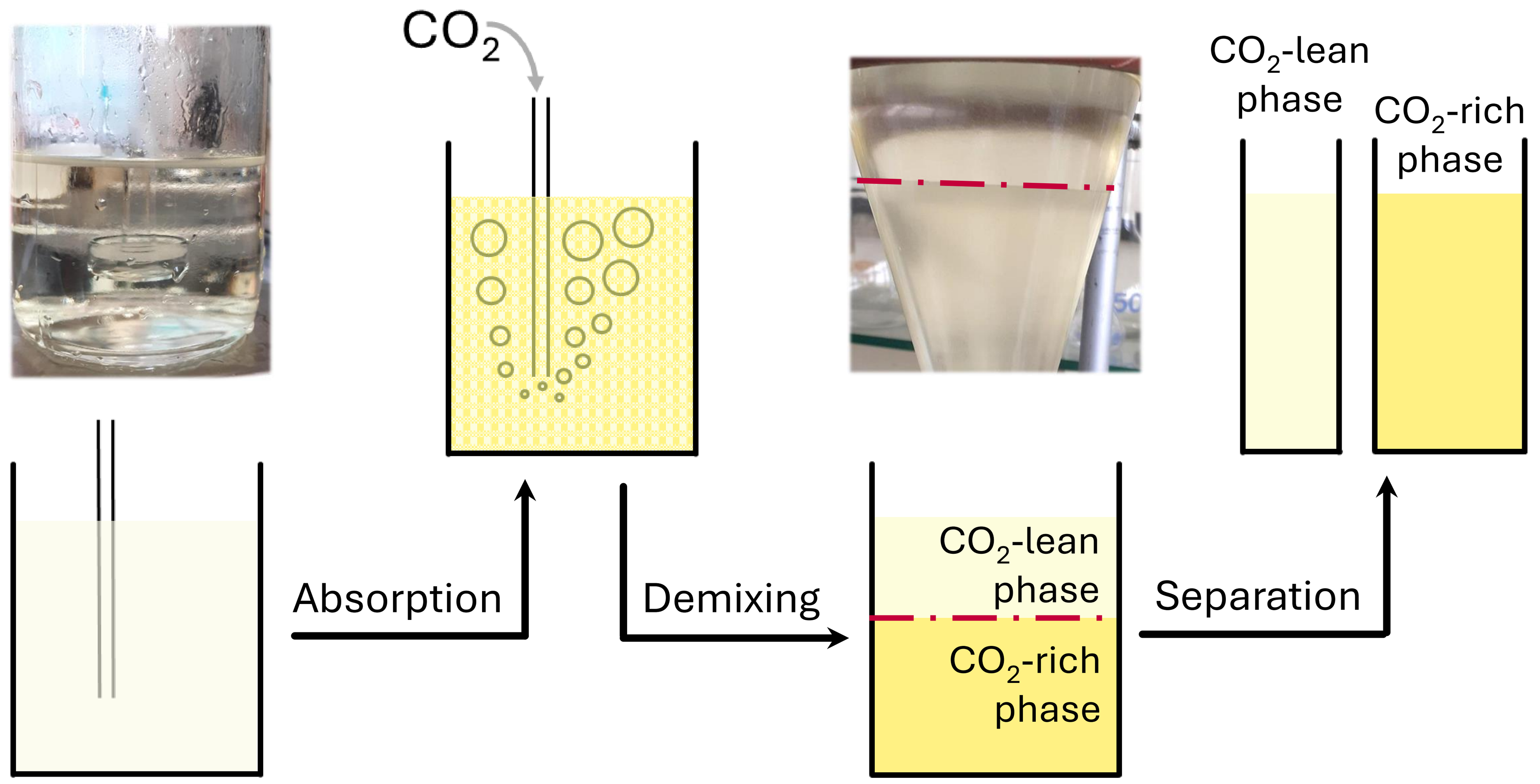
$$CO_2 + 2\,R_1R_2NH \rightleftarrows R_1R_2NCOO^- + R_1R_2NH_2^+$$

Tertiary amine

$$CO_2 + H_2O + R_1R_2R_3N \rightleftarrows HCO_3^- + R_1R_2R_3NH^+$$

Products: carbamate, carbonate and protonated amine

Phase change behaviour



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Bibliographic review

Biphasic solvents used for carbon capture

Solvents categories

- Amine functionalized ionic liquids
- Water-lean solvents
- Lipophilic amines
- Thermomorphic biphasic solvents
- Self-concentrating solvents

Solvents review

Aqueous mixtures

- No water-lean solvents ← Few data about water tolerance

Liquid-liquid phase separation

- No precipitating solvents ← Other challenges in the process design

Availability for large scale developments

- No ionic liquids ← Complex production process

Aqueous solvents used for carbon capture

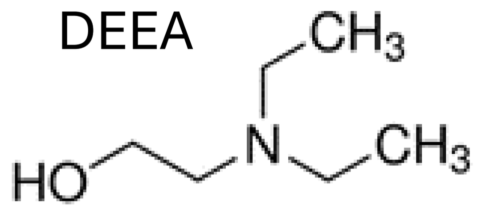
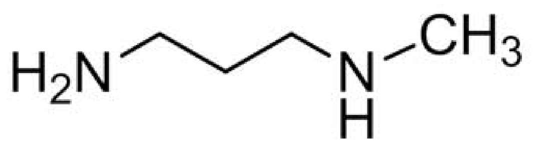
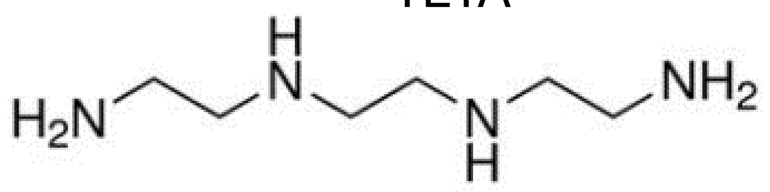
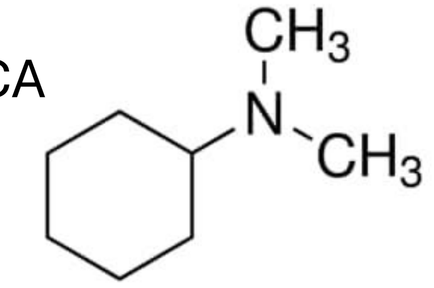
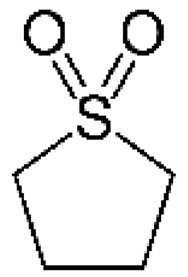
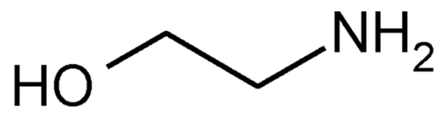
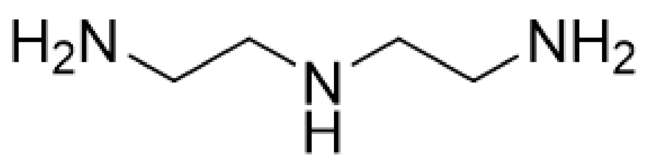
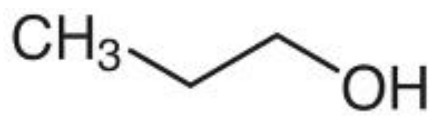
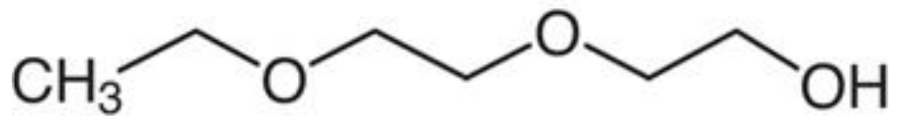
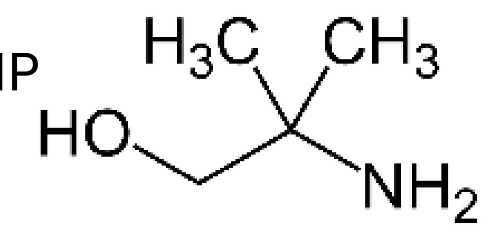
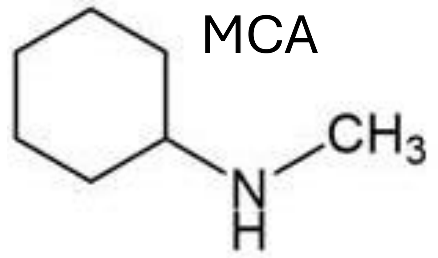
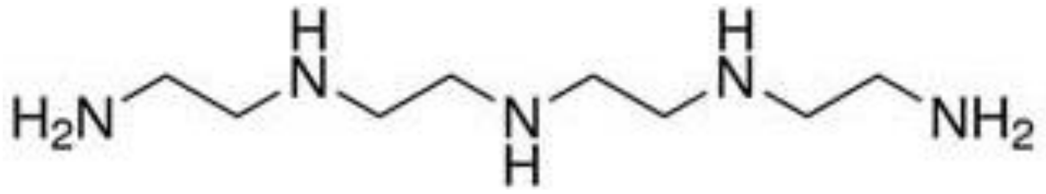
Solvents identified by the literature review

30 aqueous amine-based demixing blends

Demixing phenomenon dependent on temperature and CO_2 loading

- 2-amine blends
  - Often a primary/secondary amine with a tertiary amine
  - DEEA-MAPA, TETA-DMCA
- Presence of a phase-splitting agent
  - Used to induce or enhance the demixtion
  - Sulfolane: MEA-SULF, DETA-SULF
  - Alcohols: TETA-PROP, MEA-PROP
  - Others: DMCA-MCA-AMP, TEPA-DGME

Examples of blends

DEEA

MAPA

TETA

DMCA

SULF

MEA

DETA

PROP

DGME

AMP

MCA


TEPA

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Evaluation methodology

Literature review

30 aqueous amine-based solvents

Step 1: techno-economic classification

Classification method

Based on 6 key indicaotrs ... / ... having each a specific weight

Indicator	*Investigated parameters*	Weight
Regeneration energy (RE)	*Heat at reboiler*	0.42
CO_2 absorption rate (AR)	*Kinetics for CO_2-free solvent*	0.17
Demixing volume ratio (DR)	*$V_{CO2\text{-}rich}/V_{CO2\text{-}lean}$ at equilibrium*	0.15
CO_2 absorption capacity (AC)	*Max. CO_2 concentration at 1 atm*	0.12
Volatility of organic compounds (OV)	*$y_{organic}/x_{organic}$ at boiling point*	0.08
Solvent cost (SC)	*Commercial prices (free water)*	0.06

Scaling

- Based on the literature values
  - When missing values, based on estimated values through analogy or simulation (e.g., for volatility)
- Values normalized to the corresponding parameter for MEA 30 wt.% (indicators for MEA 30 wt.% equal to 1)
- Scaling from 1 (best case) to 5 (worst case) for each indicator

	Best value	*Worst value*	*MEA 30 wt.%*
RE	1.81 GJ/tCO_2	2.88 GJ/tCO_2	3.99 GJ/tCO_2
AR	9.12.V_{MEA}	0.52.V_{MEA}	V_{MEA}
DR	0.68	4.00	Not-applicable
AC	4.6 molCO_2/kg	1.39 molCO_2/kg	2.46 molCO_2/kg
OV	0.005	1.529	0.035
SC	9.89 €/kg	521.73 €/kg	4.48 €/kg

Weighting

- Weights calculated using the Analytical Hierarchy Process (AHP) [6] method
  - Based on relative importances for each couple of indicators
    - 1 → equal importance
    - 9 → very different importance
  - For 6 indicators:
    - 15 relative importances

Main advantage of the AHP method:
Consistency test of all the relative importances

Step 2: Health, safety and environment analysis

Rejection criteria

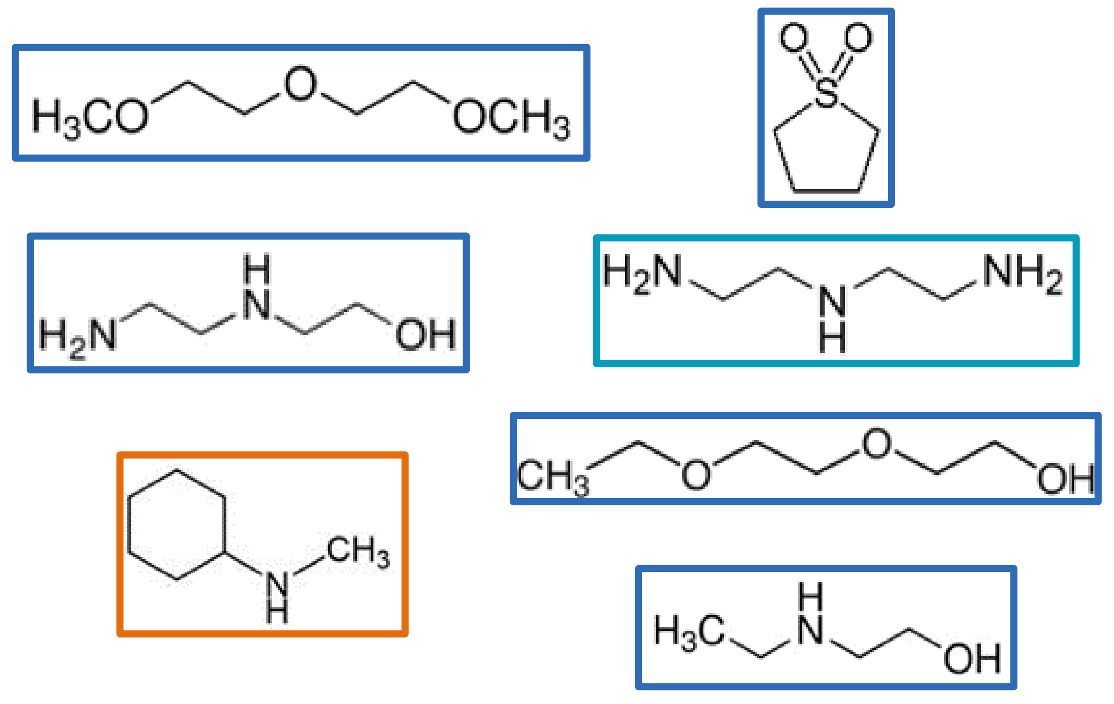
A solvent is excluded from the final ranking if at least one of its components causes:

Serious damage to the human
- Death
- Serious fertility problem

Serious damage to the process
- Corrosion to metals

Serious damage to the environment
- Very toxic to aquatic life

Concerned molecules



Exclusion of 17 solvents

Solvents ranking

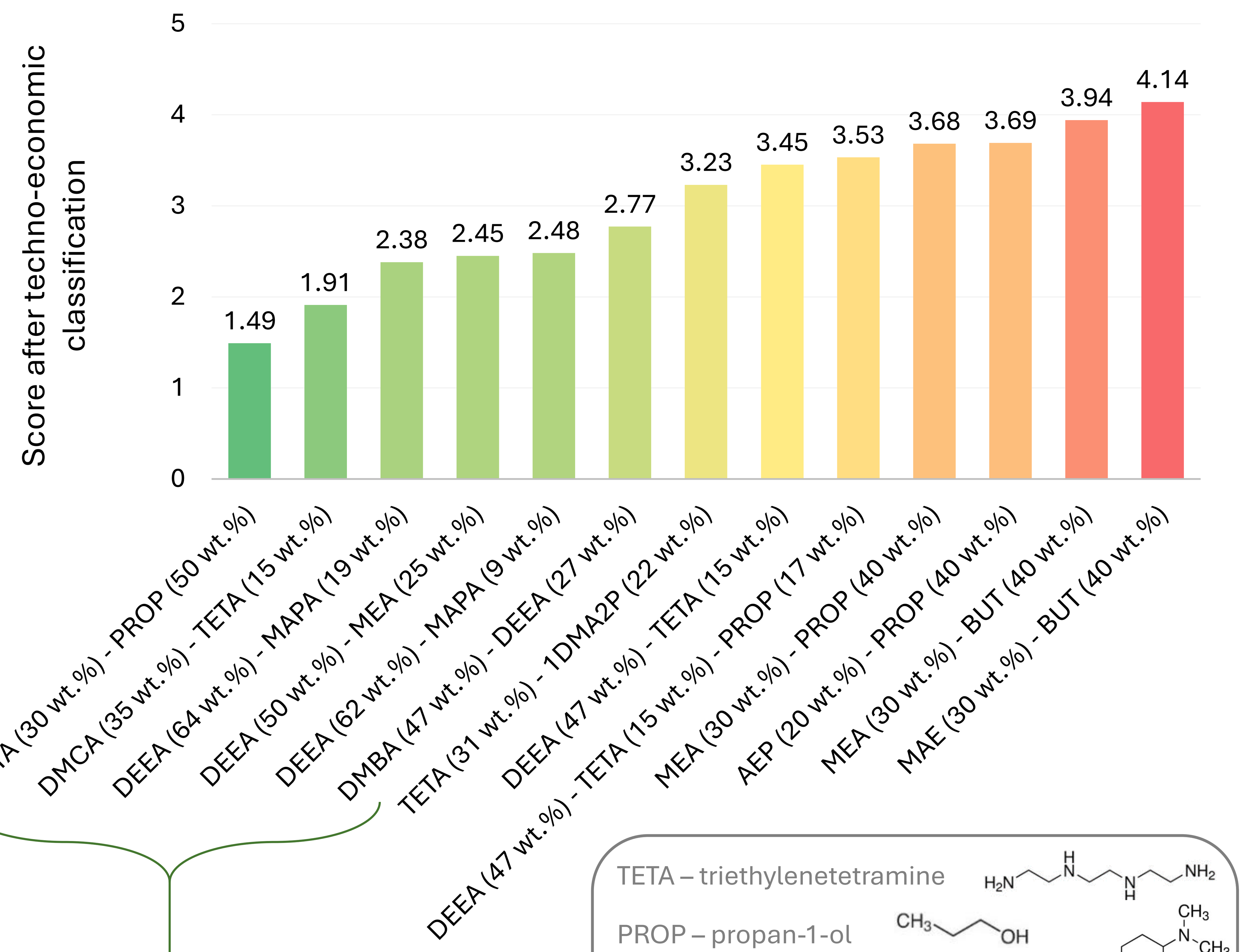
Selection of the most promising solvents

Methodological evaluation of demixing solvents used for carbon capture by absorption-regeneration process

Results and discussion

Final classification

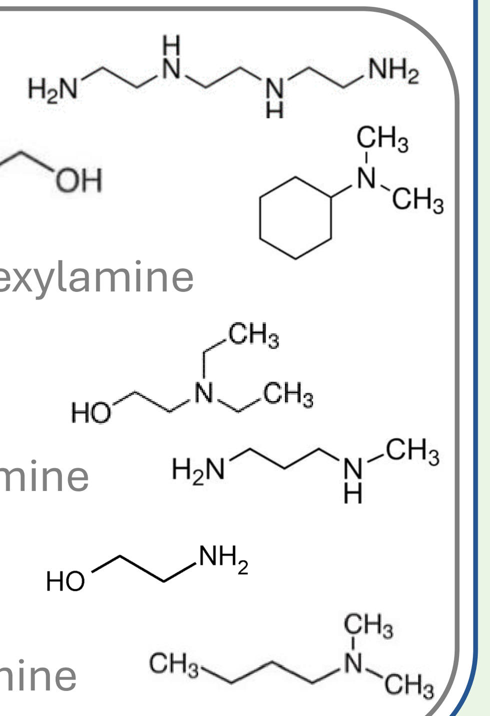
13 remaining solvents



6 blends get a global score below the mean score (= 3)

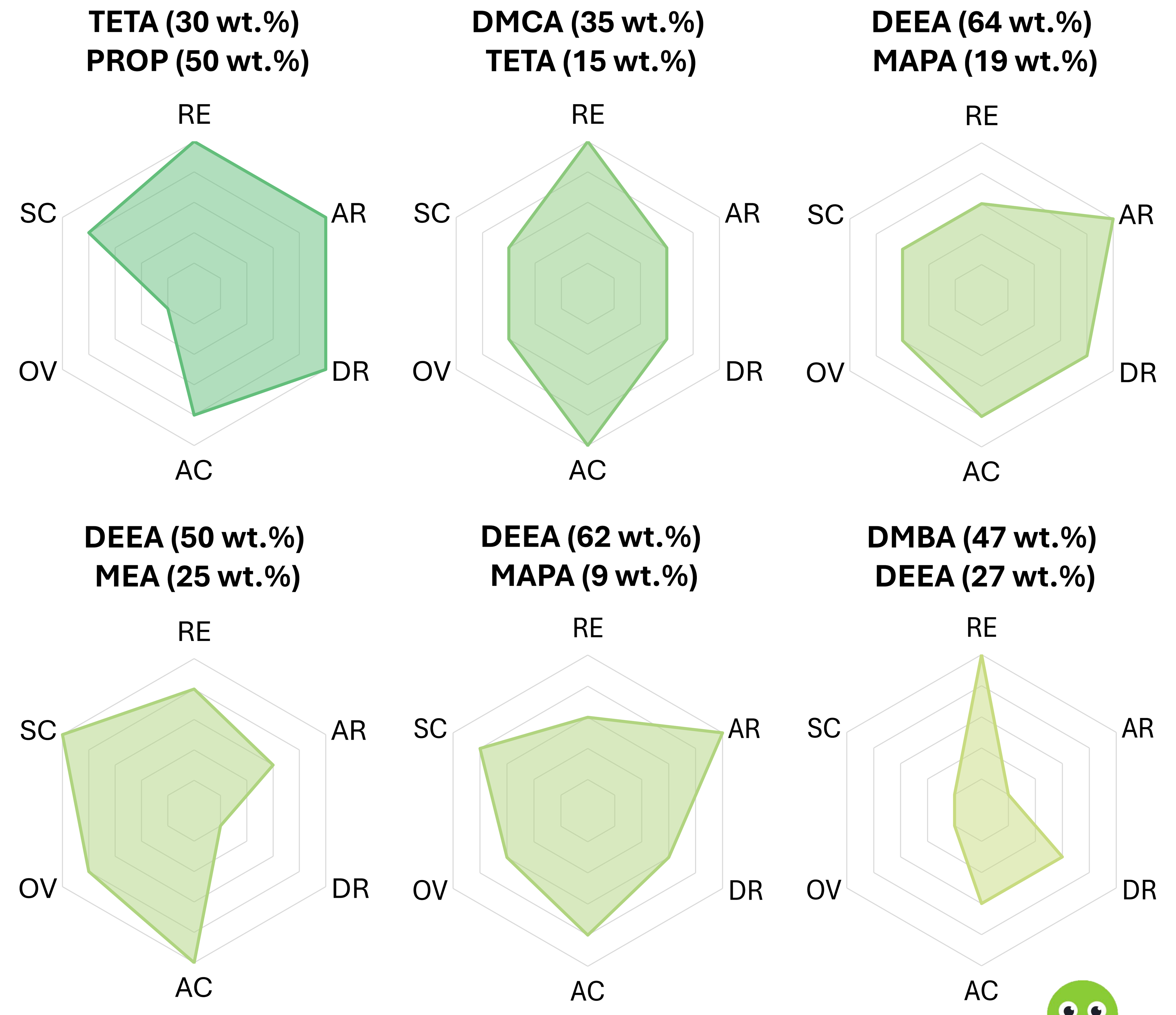
containing

- TETA – triethylenetetramine
- PROP – propan-1-ol
- DMCA – N,N-dimethylcyclohexylamine
- DEEA – diethylethanolamine
- MAPA – methylaminopropylamine
- MEA – monoethanolamine
- DMBA – N,N-dimethylbutylamine



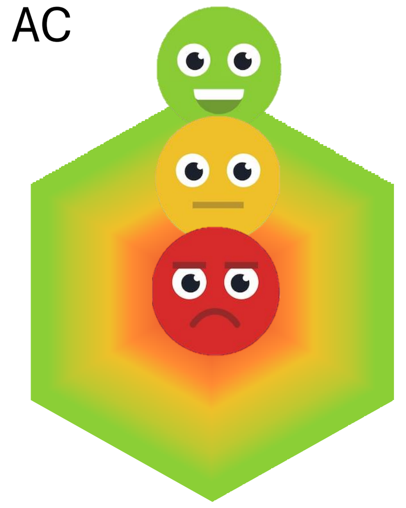
6 most promising aqueous solvents

Results for the 6 indicators



Legend

- RE → Regeneration energy
- AR → CO_2 absorption rates
- DR → Demixing volume ratio
- AC → CO_2 absorption capacity
- OV → Volatility of the organic compounds
- SC → Solvent cost



The most promising identified solvent

Triethylenetetramine (30 wt.%)
Propan-1-ol (50 wt.%)
Water (20 wt.%)

RE	2.06 GJ/tCO_2
AR	2.04.V_{MEA}
DR	0.68
AC	2.77 molCO_2/kg
OV	0.928
SC	27.60 €/kg

High volatility of the organic compounds

Mainly due to ***propan-1-ol***

Condenser at the top of the absorption column

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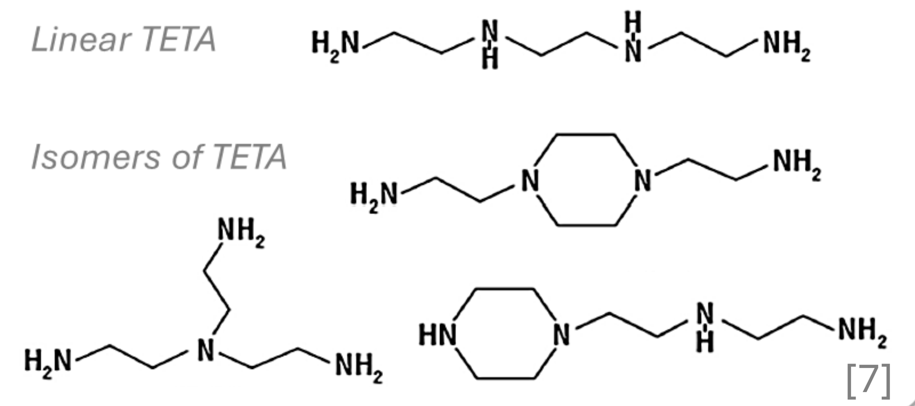
Conclusions and Perspectives

Selection of the solvents for further investigation

Triethylenetetramine (30 wt.%)
Propan-1-ol (50 wt.%)
Water (20 wt.%)

Isomeric mixture of triethylenetetramine (TETA)



[7]

Demixing
10th position in the final ranking of this evaluation

With 2 reference solvents

Monoethanolamine (30 wt.%)
Propan-1-ol (40 wt.%)
Water (30 wt.%)

Monoethanolamine (30 wt.%)
Water (70 wt.%)

Non-demixing
Benchmark in CO_2 absorption sector

Indicators of the techno-economic evaluation of the analysis for the selected blends

	TETA – PROP	MEA – PROP	MEA
RE	2.06 GJ/tCO_2	2.87 GJ/tCO_2	3.99 GJ/tCO_2
AR	2.04.V_{MEA}	1.28.V_{MEA}	V_{MEA}
DR	0.68	1.29	Not-applicable
AC	2.77 molCO_2/kg	2.32 molCO_2/kg	2.46 molCO_2/kg
OV	0.928	1.006	0.035
SC	27.60 €/kg	10.24 €/kg	4.48 €/kg

Possible improvements of the evaluation methodology

✓ Data acquisition of other key indicators

(eventually to include them in the evaluation)

For example,

Degradation
- Thermal degradation
- Oxidative degradation
- NO_x/SO_x degradation

Application of the method to newly studied blends

Possible with estimation of unknown parameters through analogy of simulation

Future steps for the selected solvents

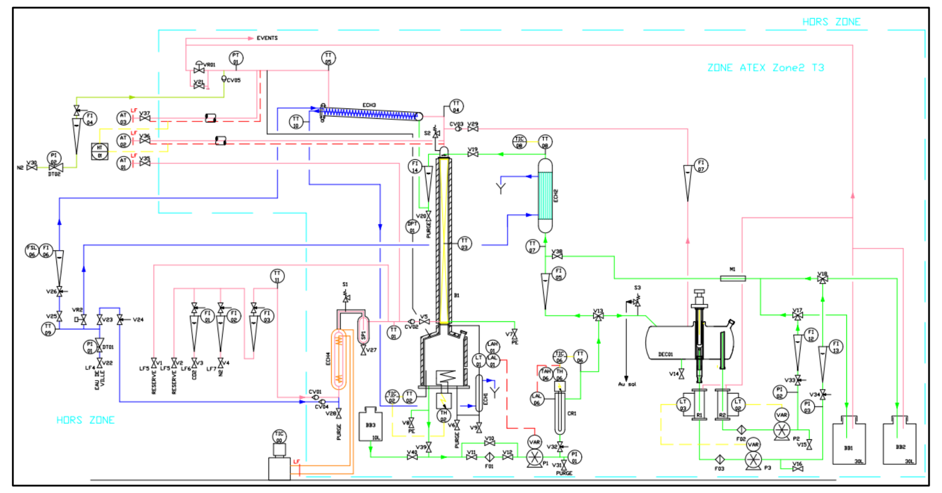
Demixing solvents review and selection ✓

Equilibrium and kinetic data acquisition

Micro-pilot scale solvents evaluation

Process modelling, simulation & LCA

New micro-pilot unit with phase separator (Delivering end of 2024)



References and Acknowledgments

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[2] IEA (2023), CO2 Emissions in 2022, IEA, Paris https://www.iea.org/reports/co2-emissions-in-2022
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