

Stripping the CO₂ capture process

Hanna Knuutila

Department of chemical engineering

NTNU

Department of Chemical Engineering

Research activities are focused on research related to:

- Environmental Engineering and Reactor Technology
- Catalysis
- Colloid and Polymer Chemistry
- Process Systems Engineering

Host for two Centres for Research-based Innovation (SFI):

- SUBPRO: Subsea production and processing
- iCSI: Industrial Catalysis Science and Innovation

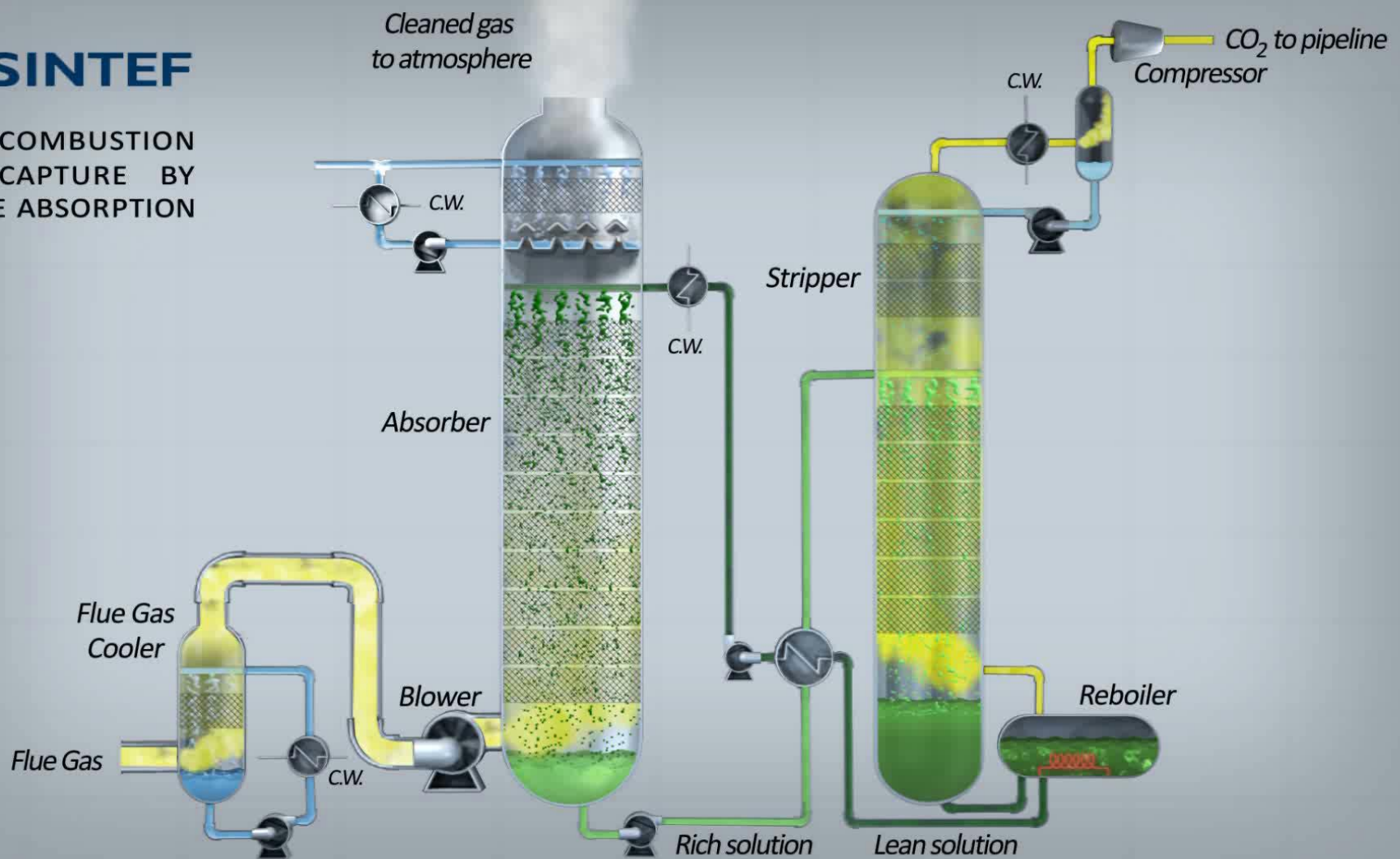
Participants in three Centres for Environment-friendly Energy Research (FME):

- NCCS, Bio4Fuels and HighEFF



STRIPPING THE CO₂ CAPTURE PROCESS

POST-COMBUSTION
CO₂ CAPTURE BY
AMINE ABSORPTION



Applications

$P_{\text{CO}_2} = 20\text{-}100\text{bar}$

$P_{\text{CO}_2} = 0.03\text{-}0.5\text{ bar}$

Natural
gas

Hydrogen

Coal flue
gas

Gas
turbines

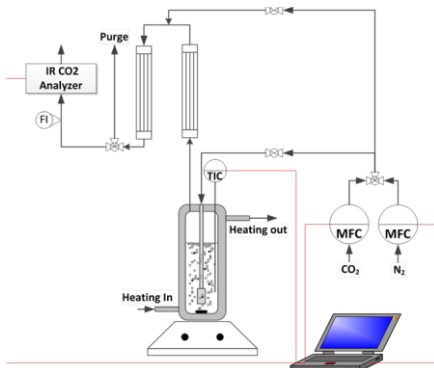
Biogas
upgrading

Solvent selection

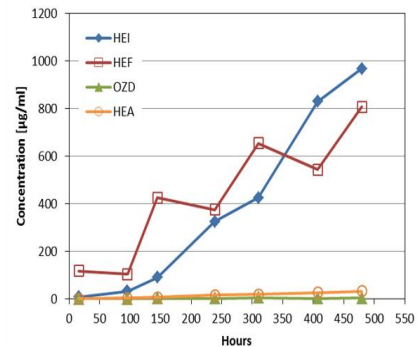
- Rate of reaction/mass transfer
- Gas/liquid equilibria
- Heat of reaction
- Cyclic capacity
- Chemical stability
- Corrosion
- Solvent vapor pressure
- Ecotoxicity and biodegradation
- Toxicity
- Cost and availability
- Foaming properties



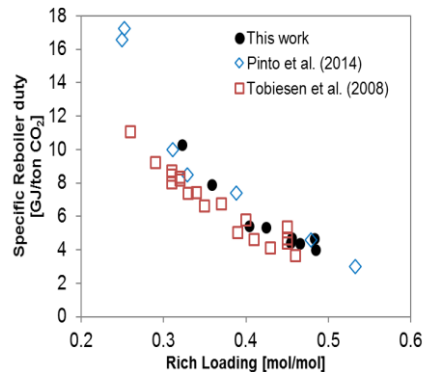
Solvents



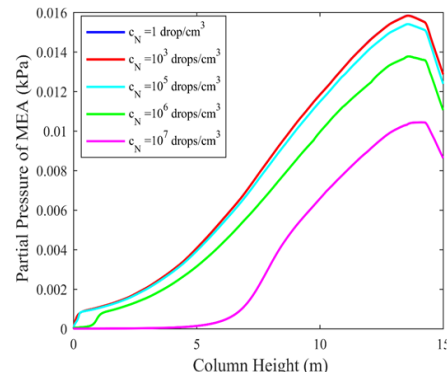
Solvent degradation



Energy consumption

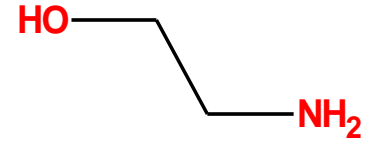


Solvent emissions



30wt% MEA (ethanolamine) used as a reference case

- A lot of data available
- Used industrially
- Used as reference/basecase in many papers



However, this can be considered to be old fashion.

SOLVENTS

Solvent types

Liquid solvents

- Amines
- Carbonates
- Ionic liquids
- Amino acids...

Solvents forming two liquid phases

- Amine blends

Precipitating solvents

- Amino acids
- Carbonate systems
- Ammonia systems

Solvent development

amines

- Primary
- secondary
- Tertiary
- Polyamines

Carbonates

- Sodium carbonate
- Potassium carbonate
- Ammonium carbonate
- Promoted systems

Amino acids

- Amine + amino acid
- KOH/NaOH + amine acid

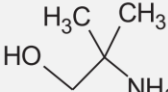
Ionic liquids

- Physical solvents
- Chemical solvents

Hybrid solvents

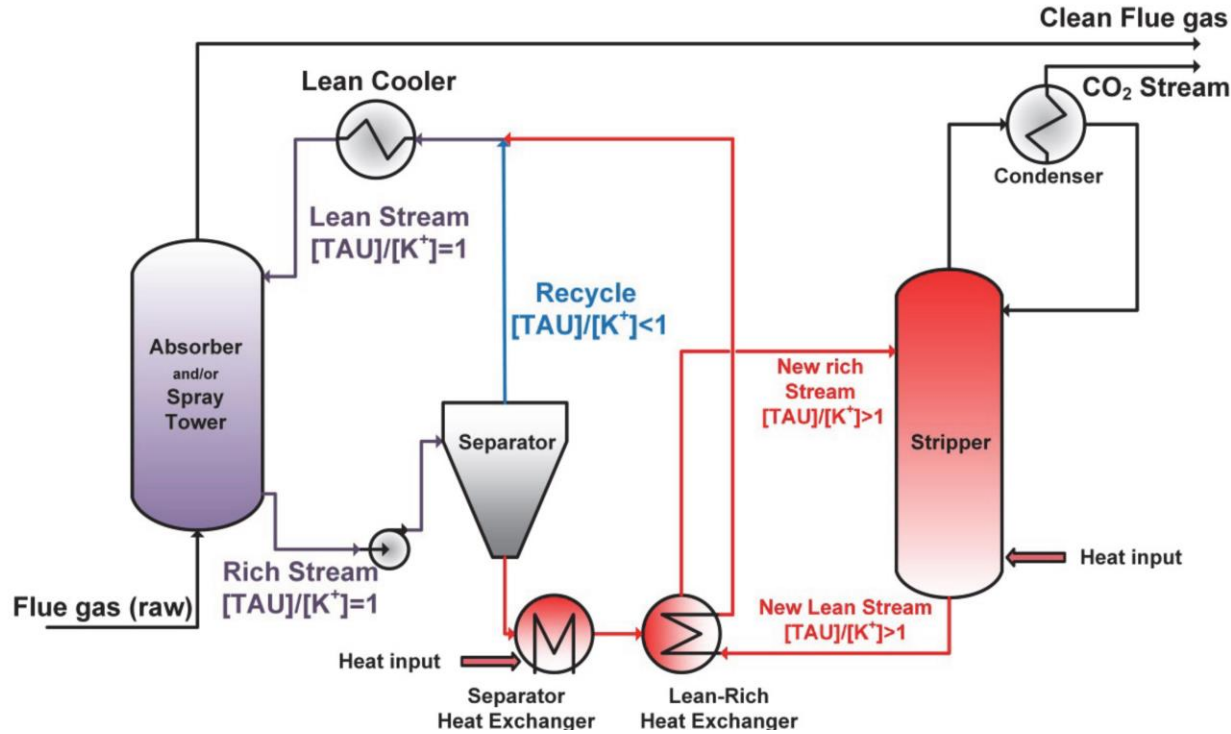
- Water lean solvents
- Combination of physical and chemical solvents

Heat of absorption >< kinetics

Class	Typical reaction	$-\Delta H_{\text{abs}}$ (kJ/mol)	Kinetics
Carbonate	$\text{CO}_3^{=}\text{ + CO}_2\text{ + H}_2\text{O} \leftrightarrow 2\text{HCO}_3^-$	40	Very slow
Tertiary amine	$\text{R}_3\text{N} + \text{CO}_2 \leftrightarrow \text{R}_3\text{NH}^+ + \text{HCO}_3^-$	60	Slow
Hindered amine	 $\text{NH}_2 + \text{CO}_2 \leftrightarrow \text{AMPH}^+ +$ HCO_3^-	60–70	Moderate
Secondary or primary amines	$2\text{R}_2\text{NH} + \text{CO}_2 \leftrightarrow \text{R}_2\text{NHCOO}^-$ $+ \text{R}_2\text{NH}_2^+$	70–80	Fast

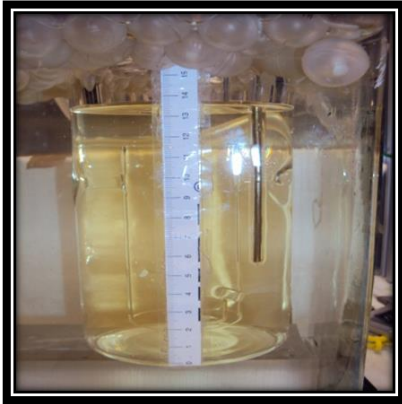
→ Blends are often used

Solvents forming two phases

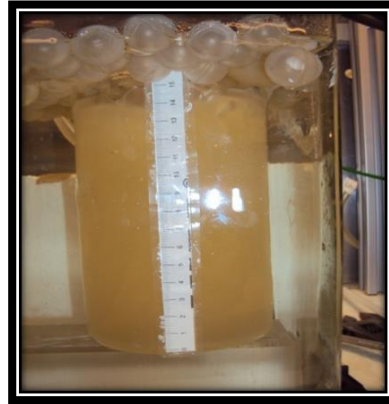


Eva Sanchez-Fernandez, Katarzyna Heffernan, Leen van der Ham, Marco J.G. Linders, Earl L.V. Goetheer, Thijs J.H. Vlught, Precipitating Amino Acid Solvents for CO₂ Capture. Opportunities to Reduce Costs in Post Combustion Capture., Energy Procedia, Volume 63, 2014, Pages 727-738,

Solvents forming two liquid phases



Before experiment

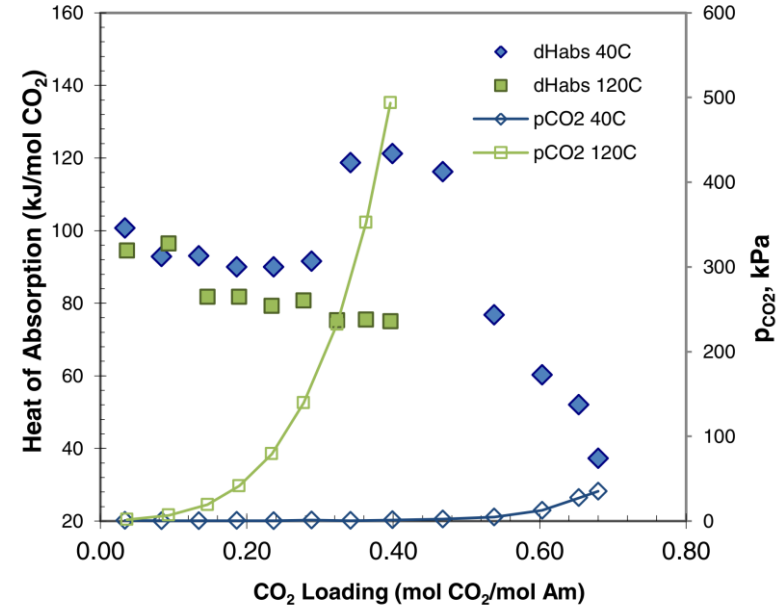
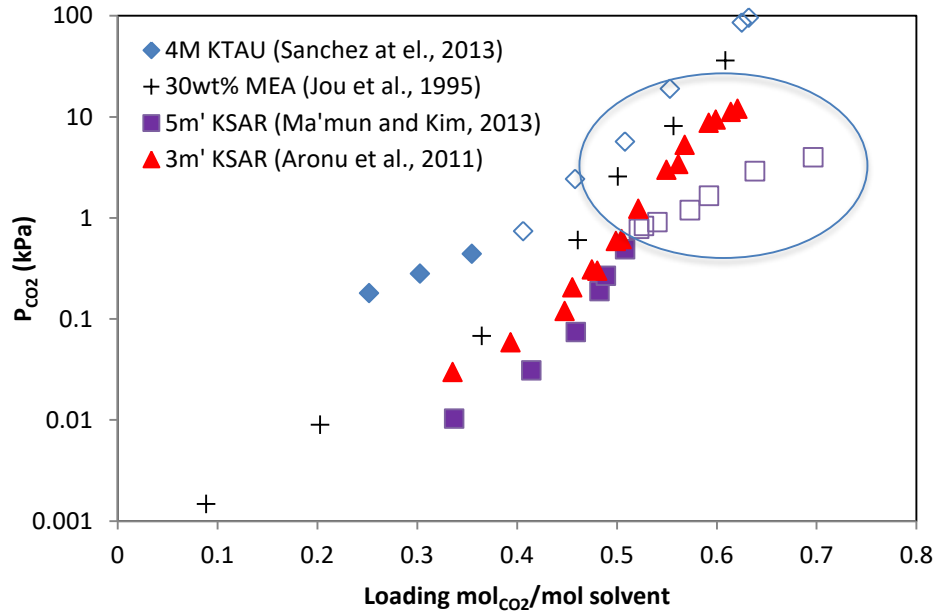


During Experiment



After separation

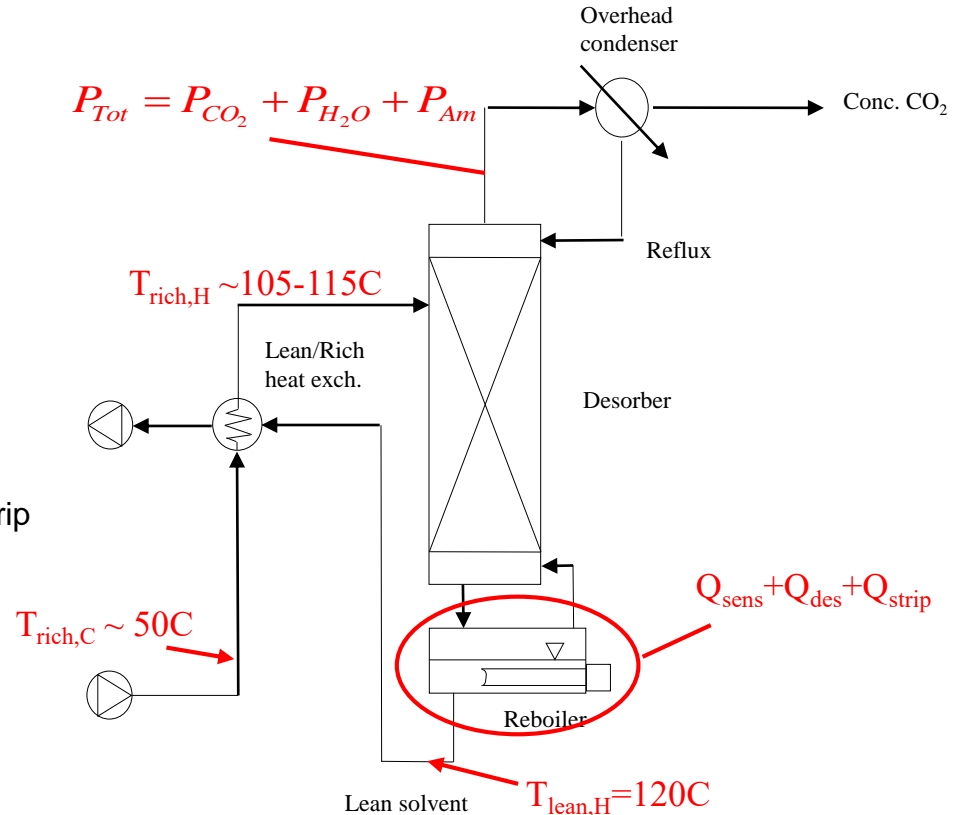
Precipitating solvents



Aronu, U., Kim, I., Haugen, G. Evaluation of energetic benefit for solid-liquid phase change CO_2 absorbents, Energy Procedia 63 (2014) 532 – 541

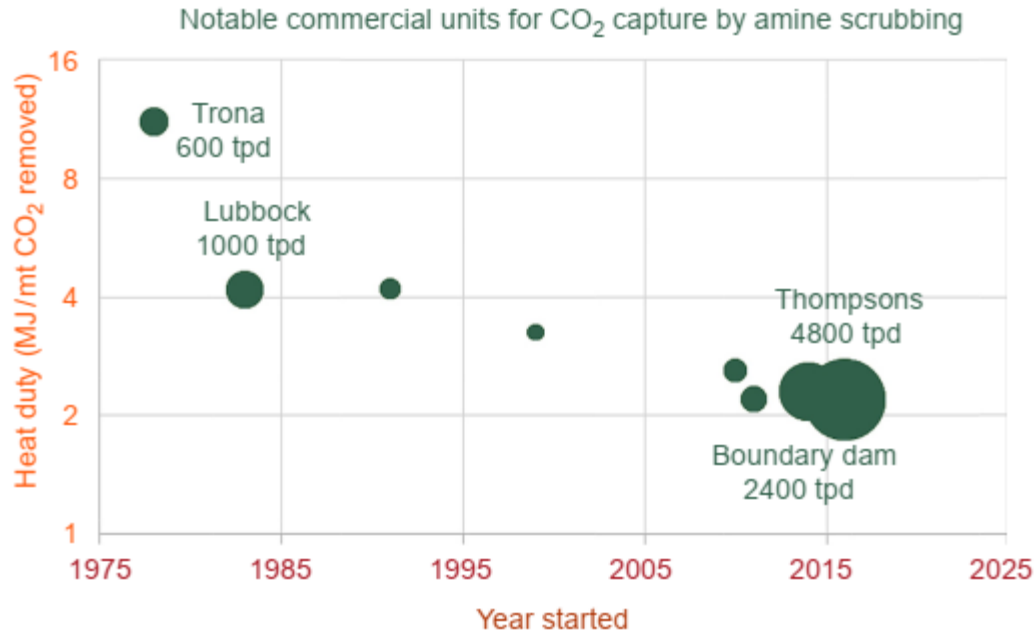
ENERGY CONSUMPTION

Energy consumption



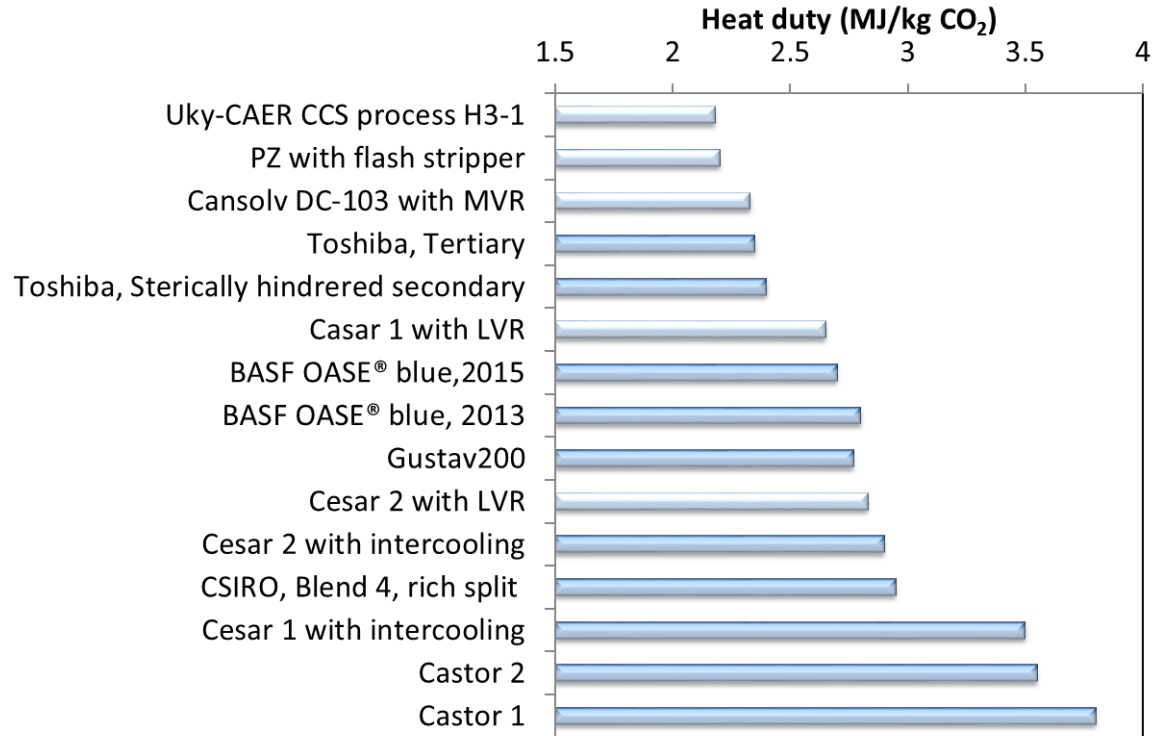
Total heat required = $Q_{sens} + Q_{des} + Q_{strip}$

Energy consumption of commercial units

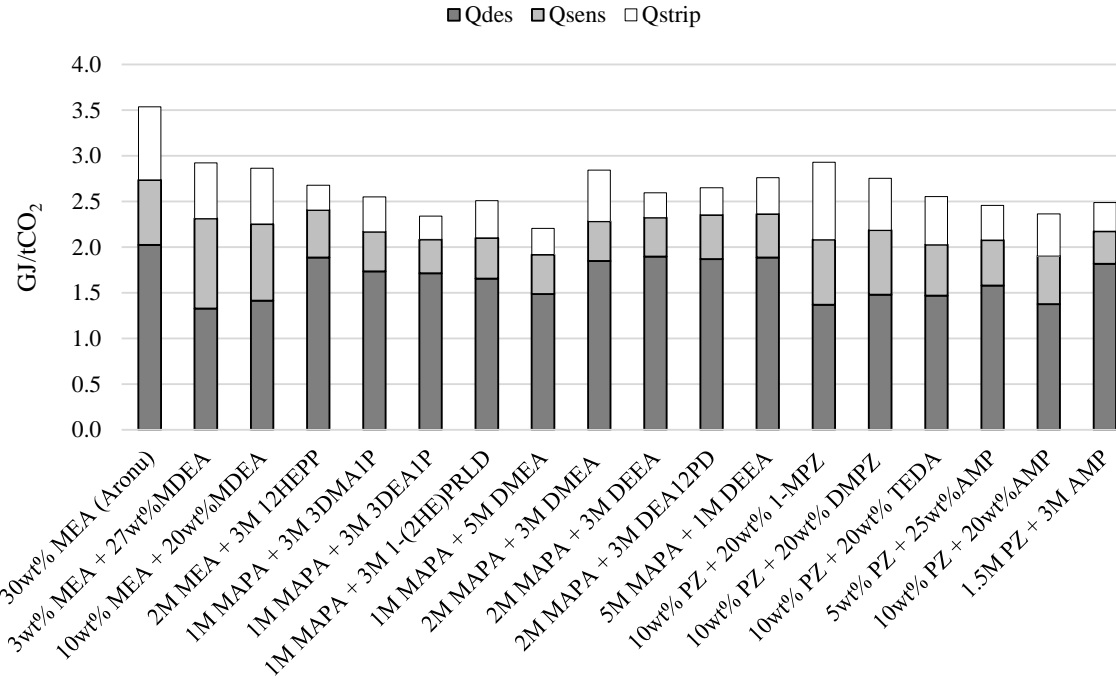


tpd= ton/day

Energy consumption - pilots



Estimated reboiler duties based on Vapor-liquid equilibrium



Towards lower energy consumption

High rich loading

- Close to equilibrium in absorber
- Fast absorbent, high heat of absorption

Low heat of reaction

- Low absorption rate

High equilibrium sensitivity

- High heat of absorption

Plant design

- Intercooler, Vapor recompression, Split flow
- High pressure stripping

SOLVENT DEGRADATION

Amine degradation: An overview

O₂

CO₂

Temp.

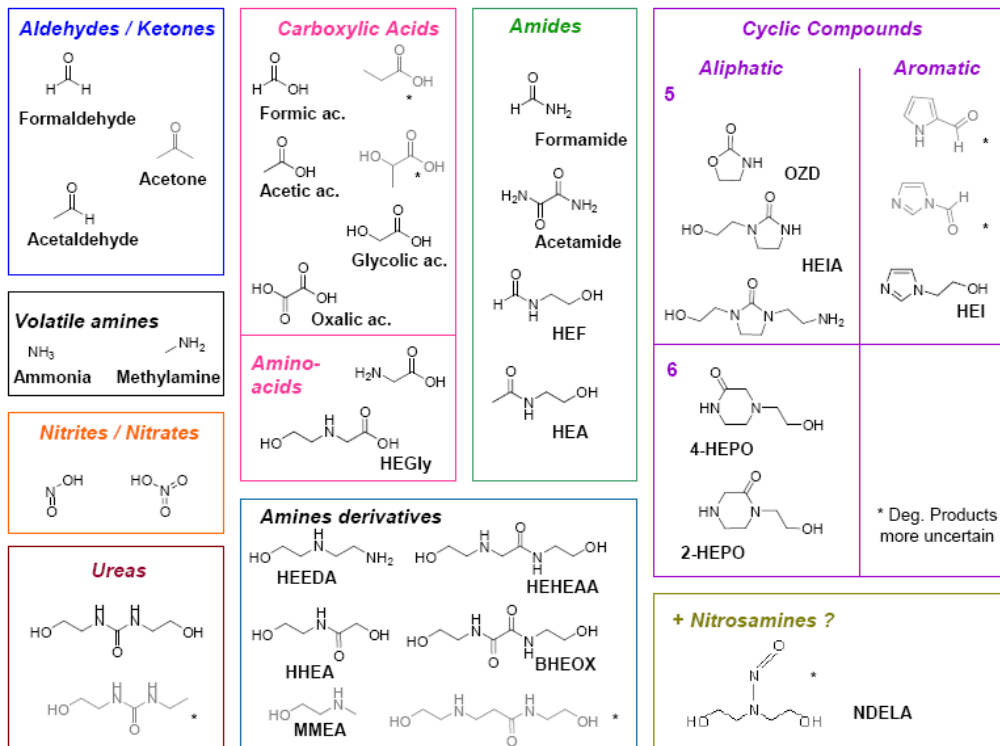
NO_x

SO_x

Particles

Iron

MEA degradation compounds



Analysis methods for MEA degradation products

Ion chromatography

- Anionic species: acetate, formate, oxalate, nitrate, nitrite, sulfate, propionate (glycolate not yet)

Liquid chromatography

- Nearly all degradation products
- No library of unknown degradation products
- Methods for each compound must be developed

Gas chromatography

- Not as sensitive as liquid chromatography, but unknown products can be matched with libraries

Solvent emissions

Products

Volatile

- Amine
- Ammonia,
- aldehydes etc.

- Low temperature in the water wash section
- Use of staged water wash
- Use acid wash

Non-volatile(Typically heat stable salts, organic acids, etc.)

Reclaimer waste

Mist

- High absorber top temperature
- Dry bed
- Brownian diffusion filter

Solvent degradation and emissions

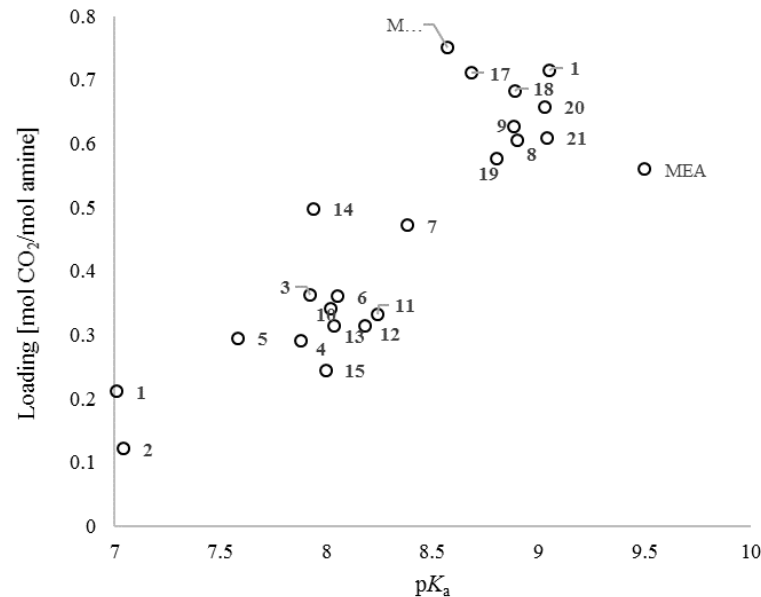
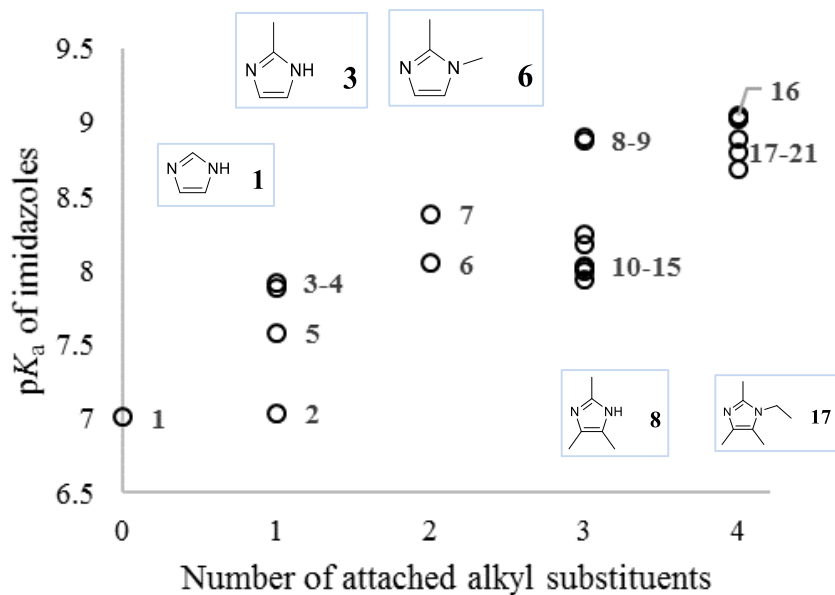
- summary

- Emissions of absorbent(amines) can be brought down to less than 0.02-0.03 ppm
 - If no aerosols are present
- Volatile degradation products can be handled by acid wash
- Methods for reducing degradation and corrosion rates are continuously being developed
 - Degradation inhibitors / corrosion inhibitors

FUTURE TRENDS

Task specific solvents

Polyalkylatedimidazoles



Evjen, S., Fiksdahl, A., Pinto, D.D.D., **Knuutila, H.K.**, 2018. New polyalkylated imidazoles tailored for carbon dioxide capture. International Journal of Greenhouse Gas Control 76, 167-174.

Solvent degradation and emissions

- Important for emissions and solvent management
- Countermeasures
 - Inhibitors
 - Filters to prevent aerosol emissions
 - O₂ removal from solvent
- Degradation prediction
 - Modelling
 - Black box
 - Reaction based

Process improvement

- High pressure stripping
 - Addition of volatile solvent
 - High temperature stripping



Reduces the CO₂ compression energy

- New contactors
 - 3D-printing, plastic materials
 - Membrane contactors
 - Compact contactors
 - Catalytic desorption



Less corrosion and degradation

Smaller contactors

No mist formation

Summary

Several solvents and processes available

Challenges – still

- Energy requirement
 - Degradation, oxidation, contaminants
 - Corrosion
 - Emissions to air (aerosols/mist)
-
- Methods to fast characterize degradation needed

THANK YOU!