technische universität dortmund

TRONDHEIM CCS CONFERENCE
CO_2 CAPTURE, TRANSPORT AND STORAGE

Shell's research project:
Development of novel amine absorbents for CO_2 capture

TCCS-6, Session A2

Topic: Post-combustion Solvents

Improvement of lipophilic-amine-based thermomorphic biphasic solvent for energy-efficient carbon capture

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Fakultät Bio- und Chemieingenieurwesen

- Motivation
- Concepts
- Solvent performance
- Challenges and amelioration
- Summary

- **Motivation**
  - Global warming
  - Shortcomings of conventional solvents
  - Advantages of novel biphasic solvents
- Concepts
- Solvent performance
- Challenges and amelioration
- Summary

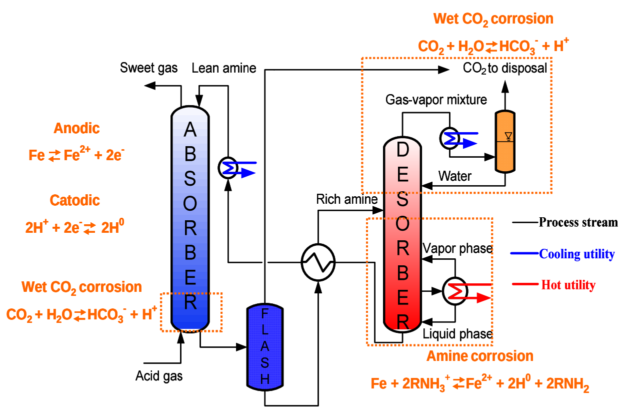
>120°C **80°C**

Challenges? → **New generation absorbents**

Technical shortcomings of conventional solvents:

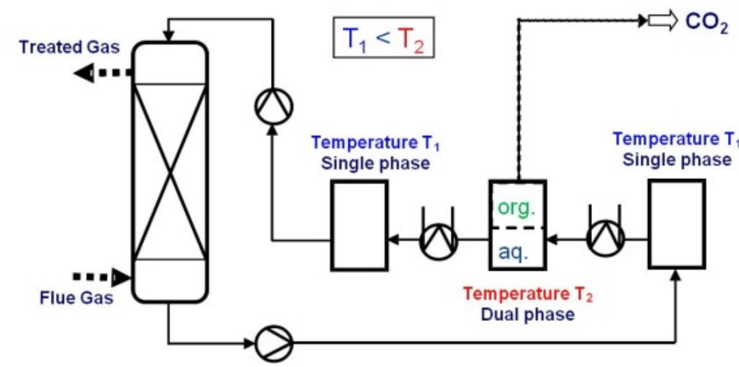
e.g. monoethanolamine (MEA)

- High **energy** consumption
- High quality of heat: **130-150 °C**
- Significant amine loss by **degradation**



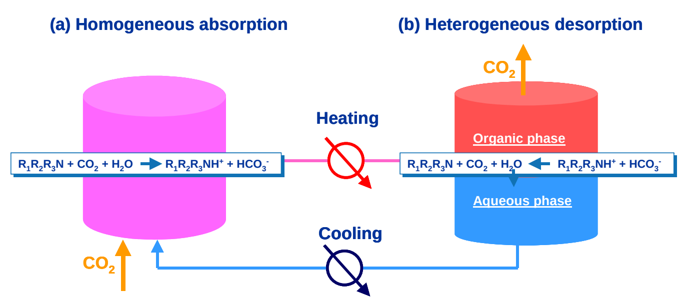
Major superiorities of novel biphasic solvents:

- Regeneration temperature **80°C**
- Use of **waste heat** for desorption
- Good chemical **stability**
- High net CO_2 loading **capacity**



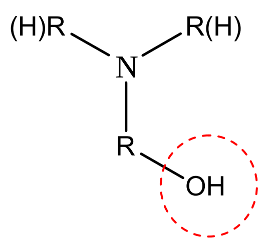
- Motivation
- **Concepts**
  - Lipophilic amine
  - Phase change
  - TBS absorbent
  - Other CO_2 capture process with LLPS
- Solvent performance
- Challenges and amelioration
- Summary

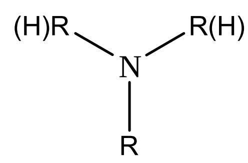
Liquid-liquid phase separation (LLPS)



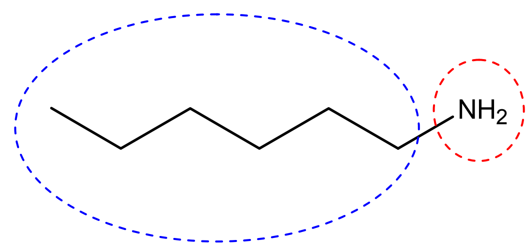
Novel amines

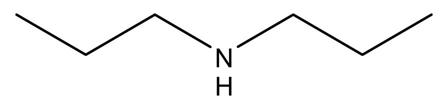
Alkanolamine vs lipophilic amine





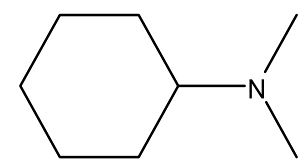
Hydrophobic **Hydrophilic**





Examples of lipophilic amine

- Hexylamine (I) HA
- Dipropylamine (II) DPA
- N,N-Dimethylcyclohexylamine (III) DMCA

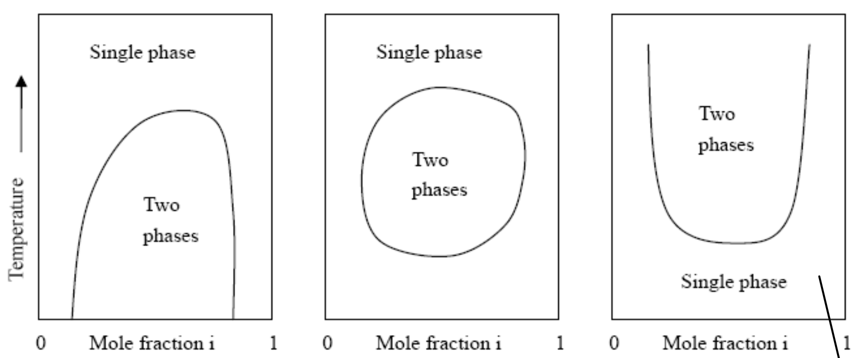


Phase change

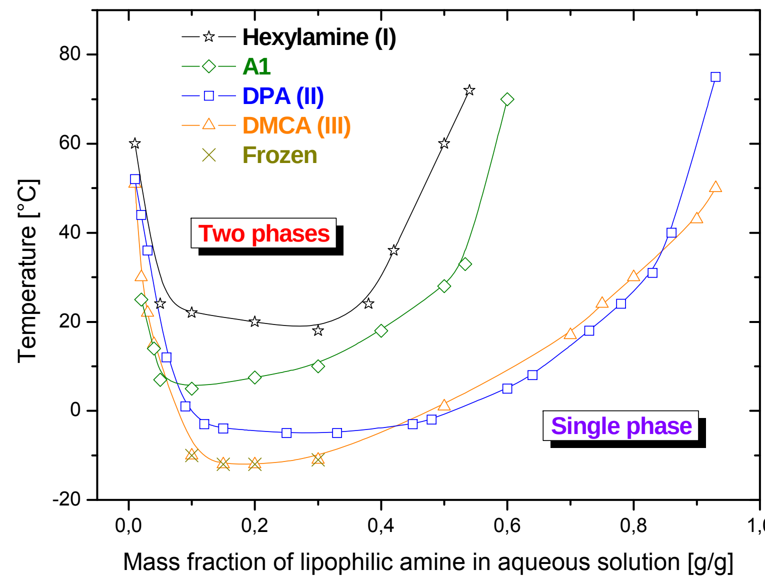
Thermomorphic phase transition

- Low temperature → single phase
- High temperature → dual phases

Lower critical solution temperature (LCST)

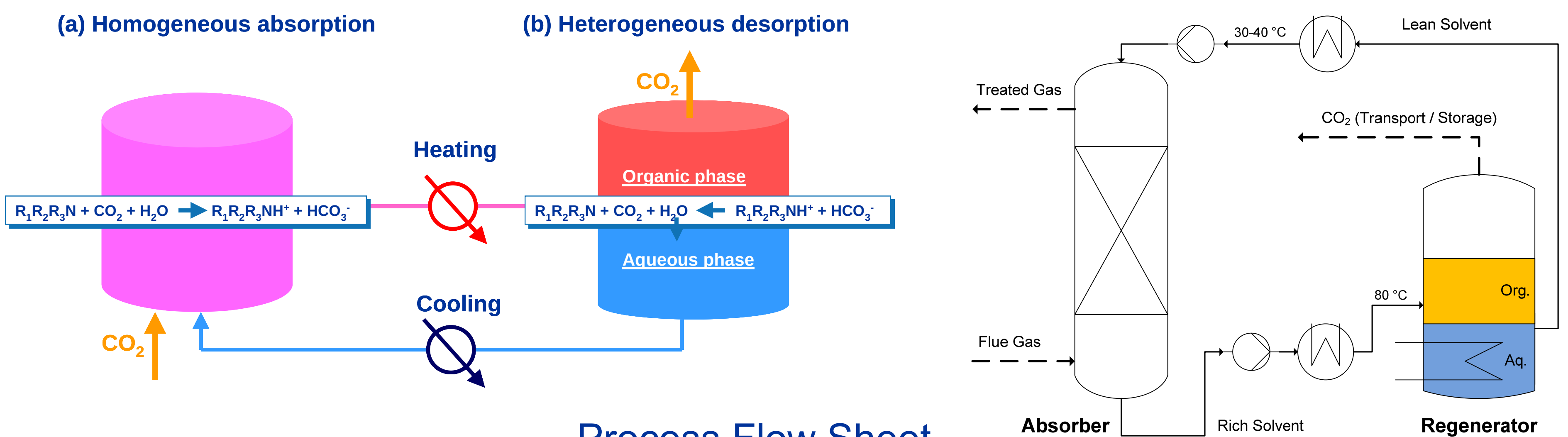


Expected



- Novel absorbent: thermomorphic biphasic solvent (TBS)
  - Absorption: single phase
  - Regeneration: two phases

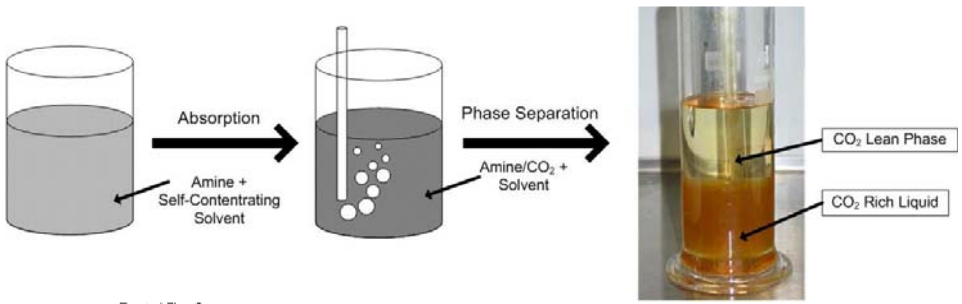
- Lean solvent → cooling to 30-40°C: homogeneous
- Rich solvent → heating to 70-80°C: biphasic

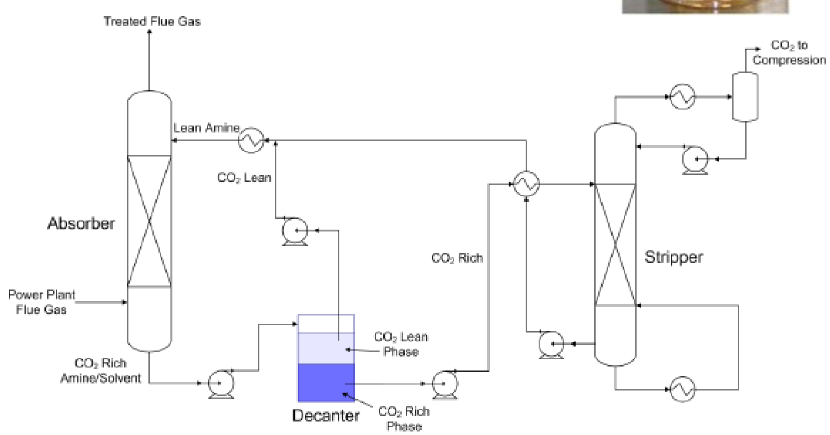


Process Flow Sheet

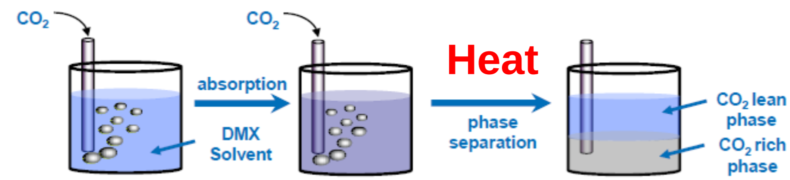
Other CO_2 capture process with LLPS

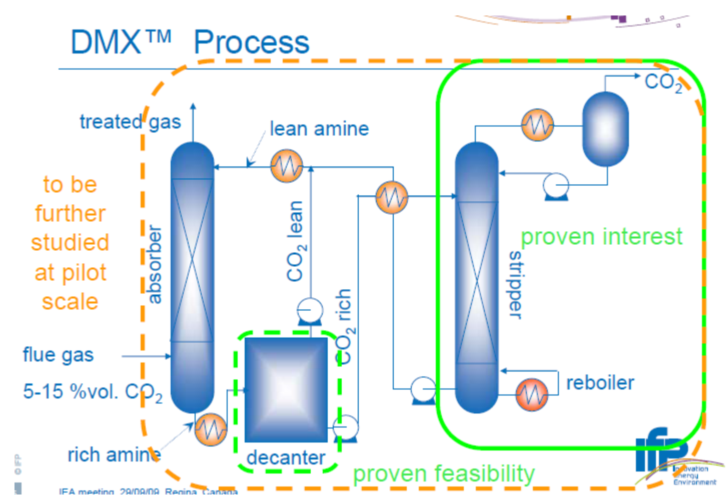
- ‘Self-Concentration’ CO_2 Capture Process
  - Univ. of Kentucky





- DMX™ process with demixing solvents
  - IFP Energies Nouvelles



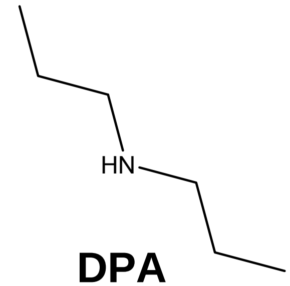


Ref.: Hu, 2010 Annual NETL CO_2 Capture Technol. R&D Meeting.

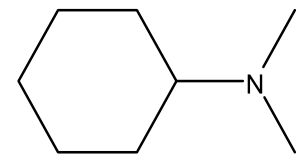
Lemaire, et al., 12th Intl. Network for CO_2 Capture, 2009

- Motivation
- Concepts
- **Solvent performance**
  - Amine selection
  - Absorption
  - Desorption
  - Chemical stability
- Challenges and amelioration
- Summary

- Screening tests – searching new amines
  - > 50 lipophilic amines (alkylamines)
  - < 10 comparable to MEA or MDEA
  - Criteria
    - **High loading capacity**: > 0.7 mol/mol (20% CO_2)
    - **Fast absorption rate**: comparable to MEA
    - **Good regenerability**: better than MDEA
    - **Low degradability**: comparable to AMP & MDEA
    - **Moderate heat of reaction**: lower than MEA
  - A: partially soluble in water, **rapid absorption rate**
  - B: less miscible with water, **high regenerability**

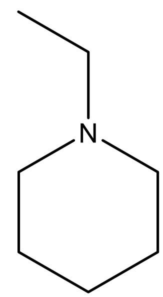


DPA



DMCA

- Recommended absorbent: Solvent blend A+B
  - A: as absorption activator → e.g. DPA, A1
  - B: as regeneration promoter → e.g. DMCA, EPD
  - **Blending A+B exploits the strengths of both components**

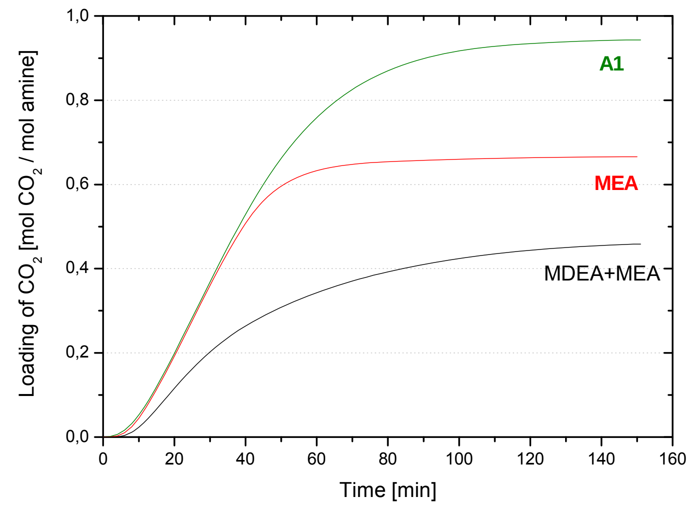


EPD

Absorption

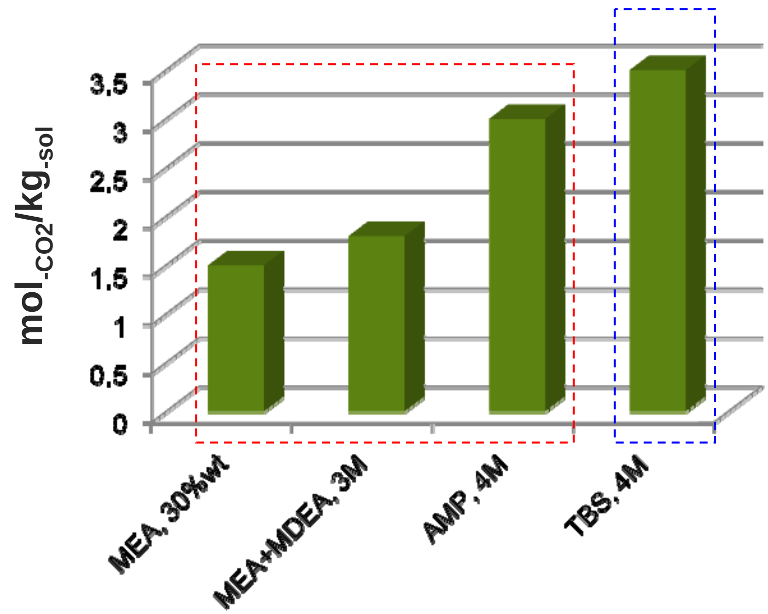
Reactivity

- Rapid reaction rate
- Comparable to MEA (when α<0.5)



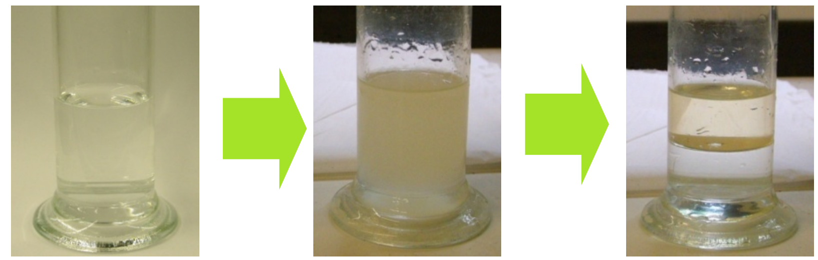
Loading capacity (net)

- Alkanolamine 40-120 °C
  w/ steam stripping
- TBS absorbent 30-80 °C
  w/o steam stripping
- CO_2 absorbed in TBS: 3.4 mol/kg
- Higher than MEA and AMP



Desorption

- Liquid-liquid phase separation →
- Low regeneration temperature
  - ca. 80°C
  - Low value heat
- High regenerability
  - > 80% at 80°C for most TBS
  - > 98% at 80°C for optimised TBS
- Estimated energy consumption →
  - MEA: 4.0 GJ/t_{-CO2}
  - TBS: 2.5 GJ/t_{-CO2}



Before regeneration | During regeneration | After regeneration

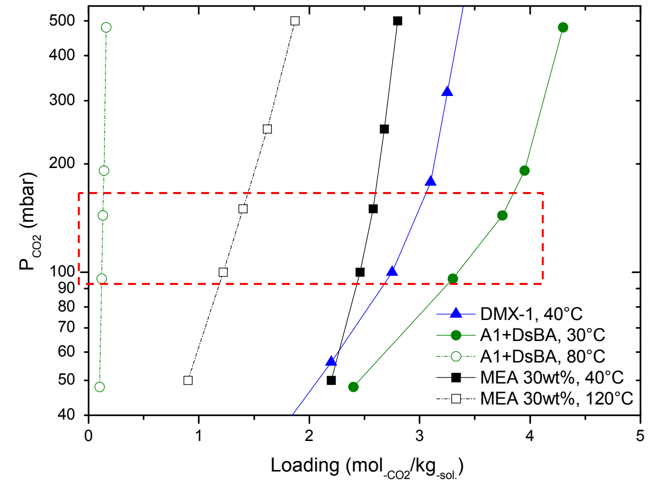
	Sensible Heat (ΔT = 15 °C) (MJ/kg CO_2)	Enthalpy of Reaction (MJ/kg CO_2)	Energy of Stripping (MJ/kg CO_2)	Heat Loss (MJ/kg CO_2)	Total (MJ/kg CO_2)
MEA	0.9 ($\Delta\alpha$ ~ 0.25 mol/mol; means 1.5 mol/kg)	1.8 (ΔH = 80kJ/mol CO_2)	~ 1.1 (Reflux Ratio ~ 2)	0.2 (ΔT ~ 90°C)	4.0
Bi-Ph	0.5 ($\Delta\alpha$ ~ 0.5 mol/mol; means 3 mol/kg)	1.6 (ΔH ~ 70kJ/mol CO_2)	0.3 (0.12 kg H2O vapor / kg CO2 at 80 °C)	0.1 (ΔT ~ 50°C)	2.5

Ref.: Geuzebroek, et al., TCCS-5, 2009

Solvent performance IV

Cyclic loading capacity

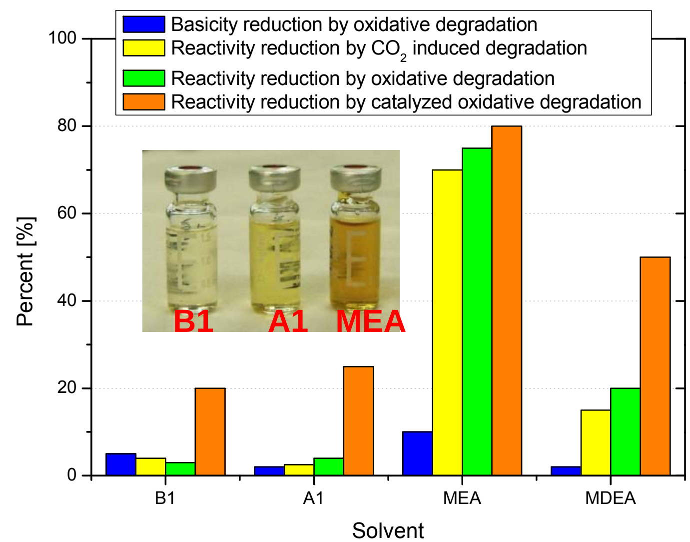
- Higher CO_2 loading
- Lower residual loading
- Better than benchmarks

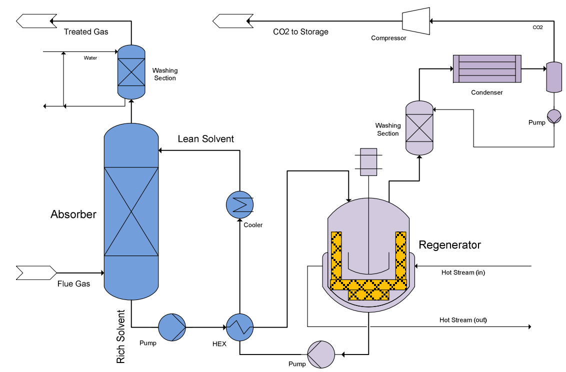


Ref.: Raynal et al., 2010 (DMX-1)

Chemical stability

- Low temperature (80°C) for desorption → less thermal degradation
- Low oxidability → less oxidative degradation





- Motivation
- Concepts
- Solvent performance
- **Challenges and amelioration**
  - Vaporisation loss
  - Phase transition
  - Regeneration techniques
  - Process development
- Summary

Amine vaporisation loss

- High volatility
- Significant volatile loss

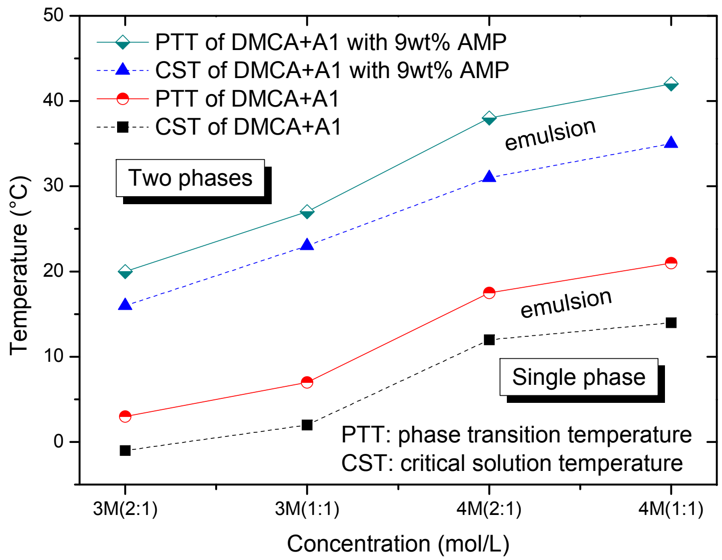
Amine	Temp.	Loss
	°C	*%/day*
A1	30	<0.5
	40	1.8
DMCA	30	4.8
	40	12
DMCA+A1 (3:1)	30	4.1
	40	10
	50	14
MEA	40	1.2
AMP	40	1.6

Countermeasures

- T for feed (top) at 30 °C
  - Reduced vaporisation
- Hydrophobic solvent scrubbing
  - e.g. Diphyl
  - Recovery >80%
- Water wash when using A1 as primary solvent
  - Reduced amine loss
  - Comparable to MEA or AMP

Phase transition

- Lower critical solution temperature (LCST): most lipo. Amines < 20°C
- Problem: biphasic solvent in absorber



Countermeasures

- Concentrating
  - Negative on vaporisation loss
  - Limited at 4M
- Using more A1
  - Negative on regeneration
  - LCST ≈ 20°C
- Partial deep regeneration
  - Residual loading 0.1
  - Increasing LCST to 30°C
- Adding solubiliser
  - <10wt%
  - Increasing LCST to 40°C

Regeneration techniques

Challenges

- Low temperature 80°C
- Without steam

- How to intensify the regeneration?

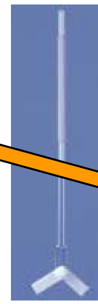
Regeneration intensification

- + Regeneration promoter

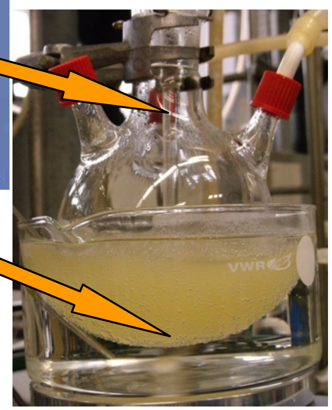
- **Agitation**
- **Nucleation**
- Nucleation + Agitation

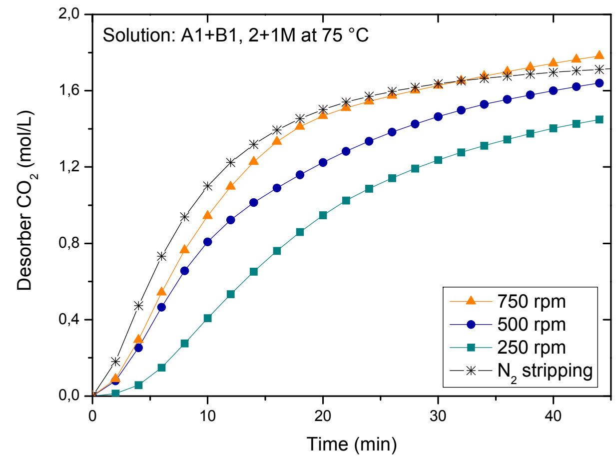
Regeneration techniques

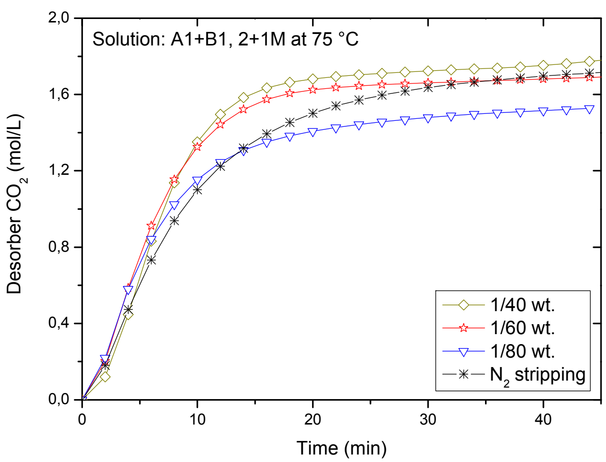
- Agitation
- Nucleation



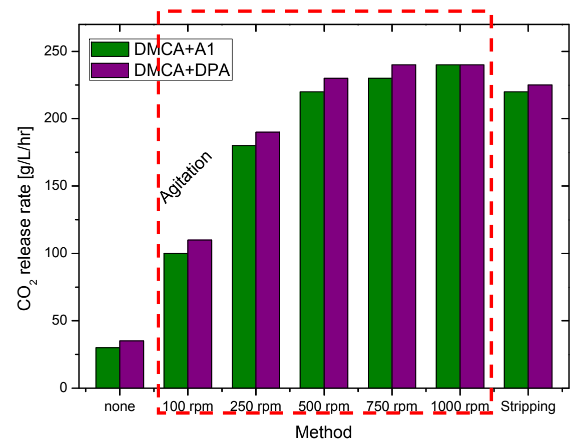
Stirring



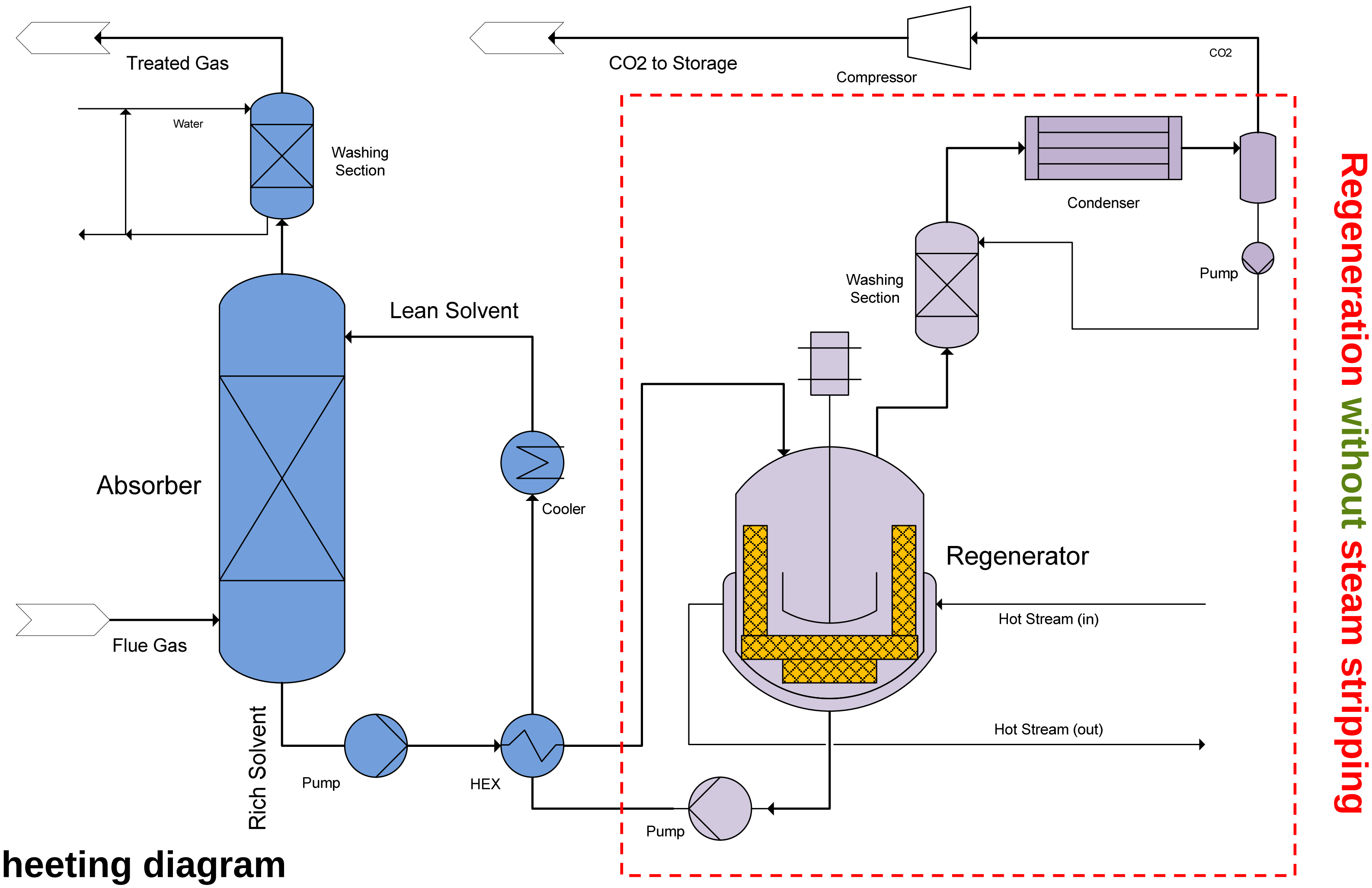




Porous particles for CO_2 bubble formation

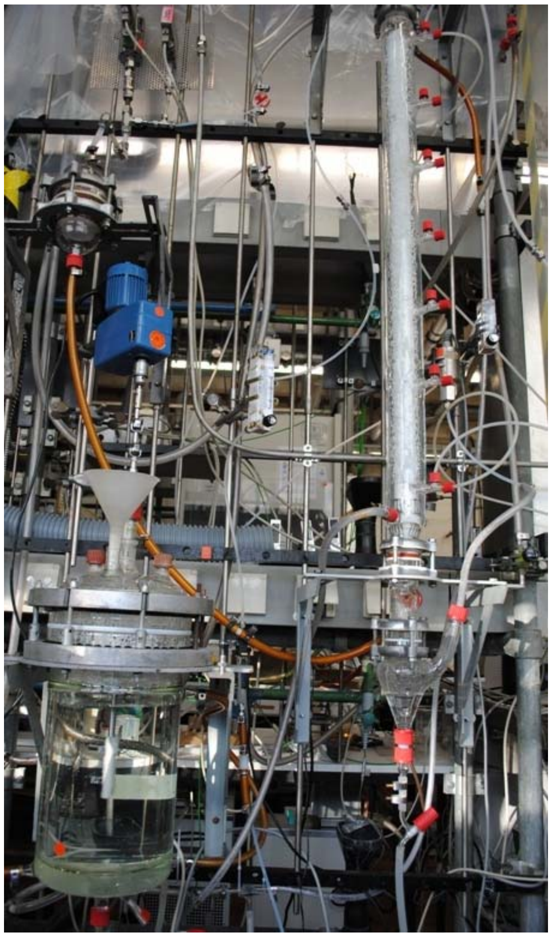


Process development

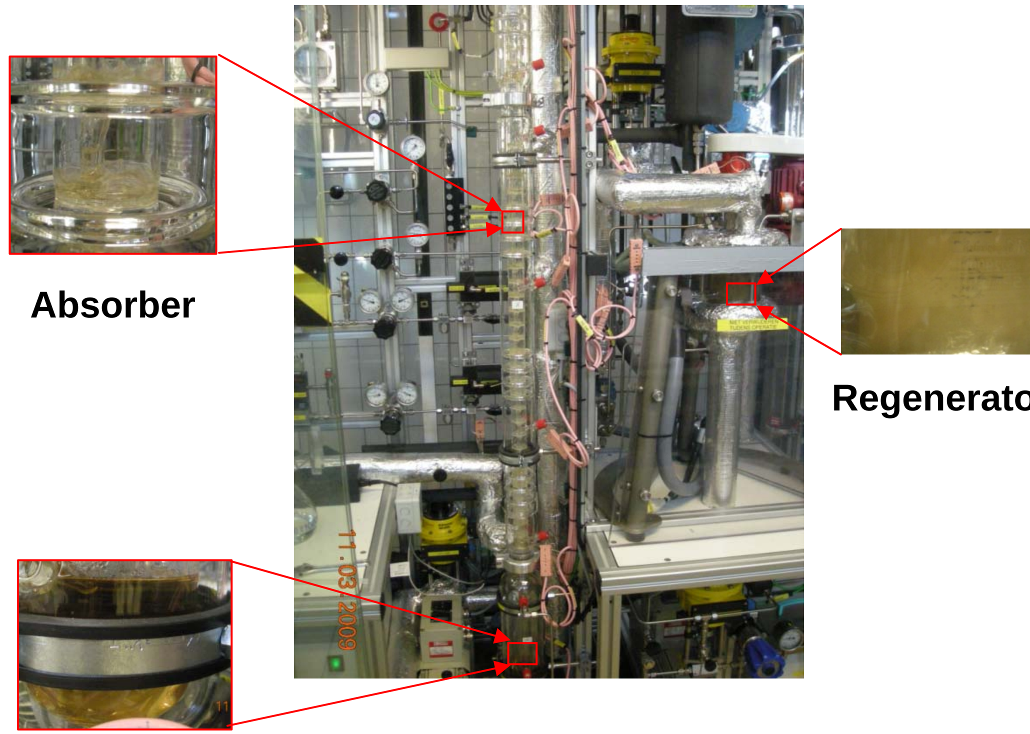


Flow sheeting diagram

Bench-scale experimentation in packed absorption columns



At TU Dortmund



At Shell G.S.

- **Novel absorbent**: lipophilic amine → TBS
  - Rapid absorption rate (due to activator A)
  - High regenerability (due to regeneration promoter B)
  - Excellent net CO_2 loading capacity
  - Low energy requirement
  - High chemical stability

- **Novel concept**: phase transition
  - LLPS ⇒ enhanced regeneration
  - Regeneration at **80°C** ⇒ use of waste heat ⇒ reduces CO_2 capture process costs

Acknowlegement

CO_2 Capture Research Group:

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Shell Global Solutions

Thank you

for your attention

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