Imperial College London

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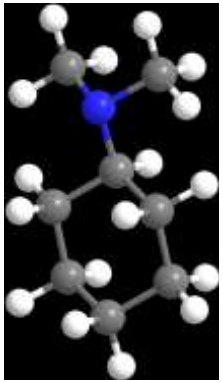
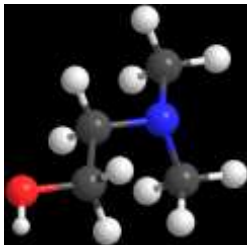
UKCCS RESEARCH CENTRE

UKCCSRC Biannual Meeting
Material Science for CCS Technical Session

Influence of amine molecular structures on CO_2 absorption



DMCA



DMAE

Jiafei Zhang

Cranfield, 21th April 2015

Outline

Introduction
- Solvents selection strategy
- Alternative amine solvents

Structural impact
- CO_2 capacity
- Absorption rate
- Regenerability
- Heat of absorption
- Degradation
- Viscosity
- Packing wettability

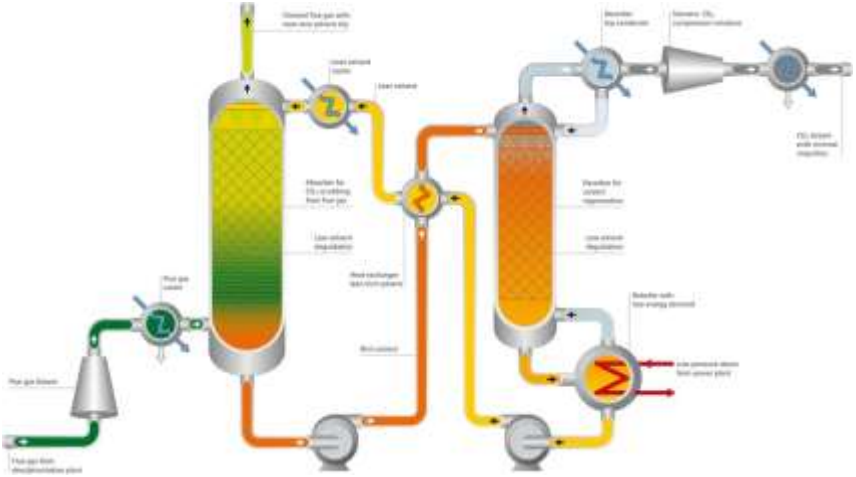
Summary

Amine solvents for CO_2 capture

Influence of molecular structure

Challenges?

Absorption Desorption



Δα

ΔH

Deg.

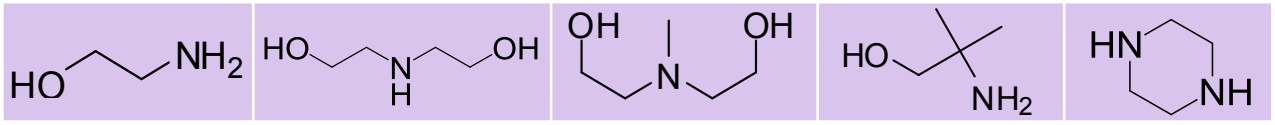
Image Source: Siemens

Strategy for solvent selection

CO_2 capacity	*Less solvent circulation*	*Tertiary, hindered, polyamines*
Reaction kinetics	*Smaller Column size*	*Primary, secondary amines*
Energy consumption	*Lower heat of reaction*	*Tertiary amines*
Solvent degradation	*Less solvent loss*	*Tertiary, hindered amines*
Technical feasibility	*Easy to operate*	*Viscosity, wettability, etc.*
Environmental impact	*Less negative effects*	*Volatility, toxicity, etc.*

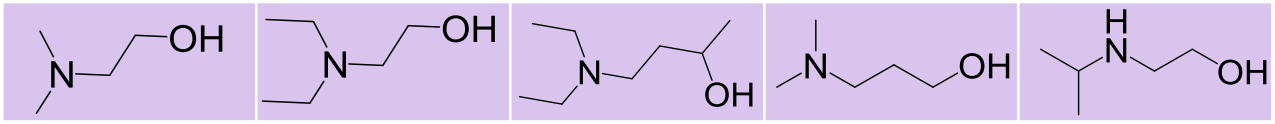
Amine solvents

Well studied solvents
- MEA, DEA, MDEA
- AMP, PZ



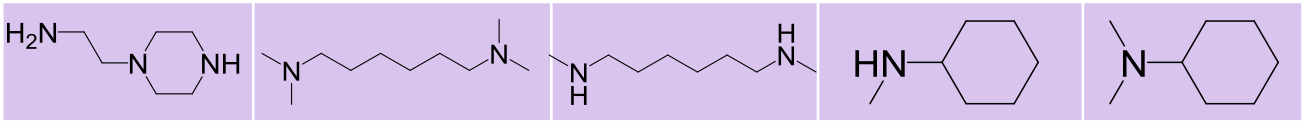
MEA	DEA	MDEA	AMP	PZ
Primary	Secondary	Tertiary	Hindered	Diamine

Alternative alkanolamines
- DMAE (IC, UK)
- DEAE (NTNU, NO)
- DEAB (Regina, CA)
- DMAP (RITE, JP)
- IPAE (RITE, JP)



DMAE	DEAE	DEAB	DMAP	IPAE
Tertiary	Tertiary	Tertiary	Tertiary	Hindered

Alternative Polyamines/alkanylamines
- PZEA
- TMHDA (IFP, FR)
- DMHDA (Twente, NL)
- MCA (Dortmund, DE)
- DMCA (Dortmund, DE)



PZEA	TMHDA	DMHDA	MCA	DMCA
I+II+III	Tertiary	Secondary	Secondary	Tertiary

CO_2 capacity

General knowledge (according to mechanism)

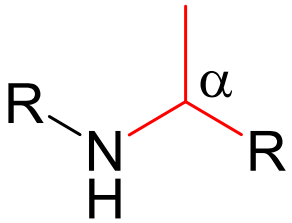
- Primary/secondary amine: $\alpha \approx 0.5$
- Tertiary amine: $\alpha \approx 1$
- Impact: sterical hindrance
- Compare: MEA, MDEA, AMP

$$CO_2 + 2RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^-$$

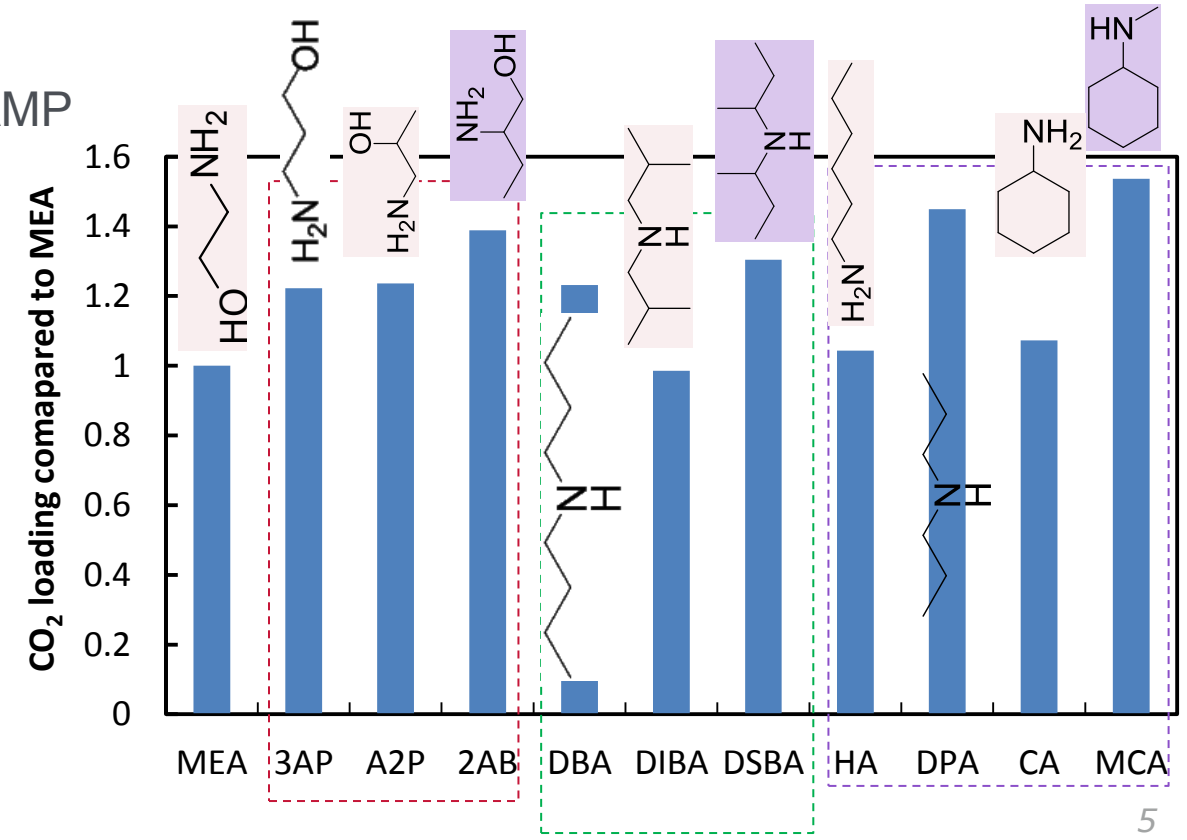
$$CO_2 + RNH_2 + H_2O \leftrightarrow RNH_3^+ + HCO_3^-$$

Structure influence

- Branched structure
  - Potential to increase
  - ***α*-Carbon** branch



- Polyamines



CO_2 capacity

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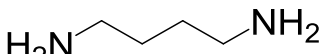
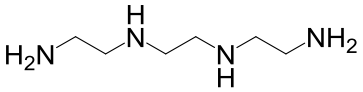
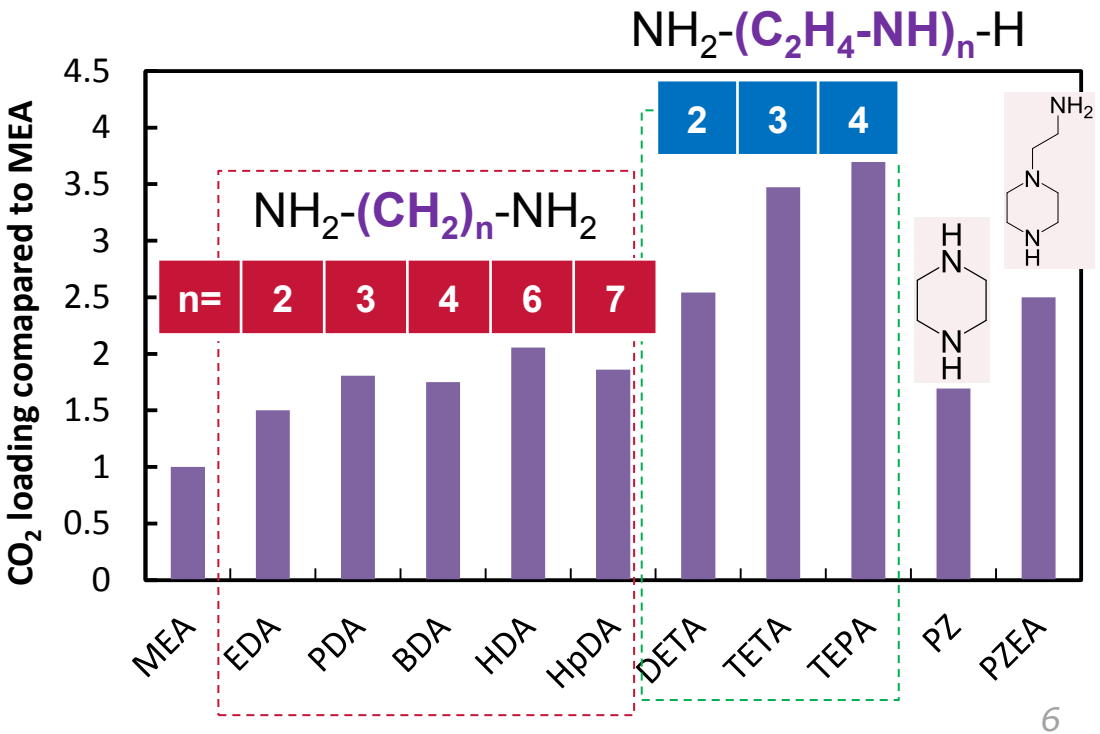
Structure influence

- Branched structure
  - Potential to increase
  - ***α*-Carbon** branch
- Polyamines
  - e.g. BDA 
  - TETA 
  - Increase α
  - Decrease per $-NH_x$



Data Source: Singh, 2009

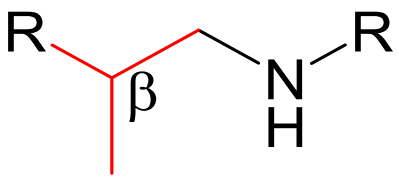
Absorption rate

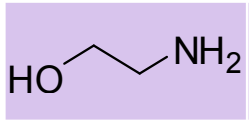
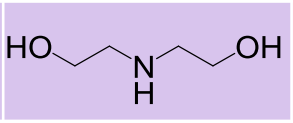
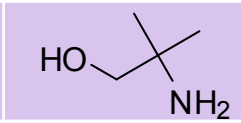
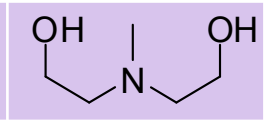
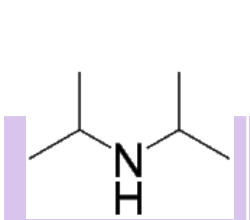
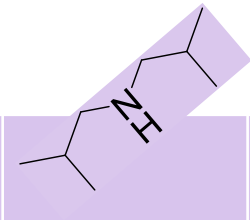
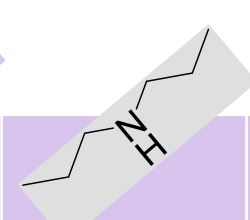
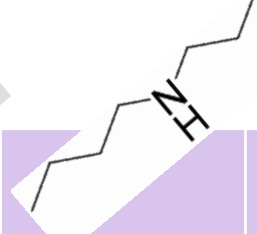
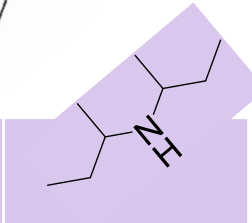
In general

- Primary/secondary amine: fast
- Tertiary amine: slow
- Hindered amine: slow (depend)

Structure influence

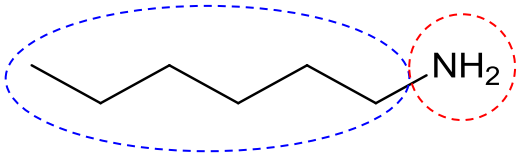
- Branched structure
  - Potential to increase
  - ***β*-Carbon** branch



				
MEA Primary	**DEA** Secondary	**AMP** Hindered	**MDEA** Tertiary	
Fast → Slow				
				
DIPA Secondary	**DIBA** Secondary	**DPA** Secondary	**DBA** Secondary	**DSBA** Secondary
Carbon	3+3	4+4	3+3	4+4	4+4

Regenerability

Hydrophobic **Hydrophilic**

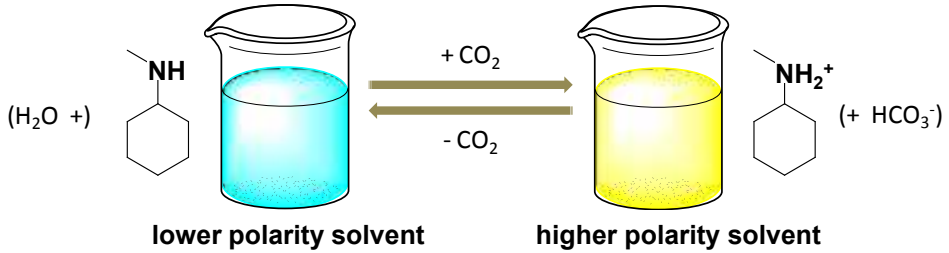


Generally

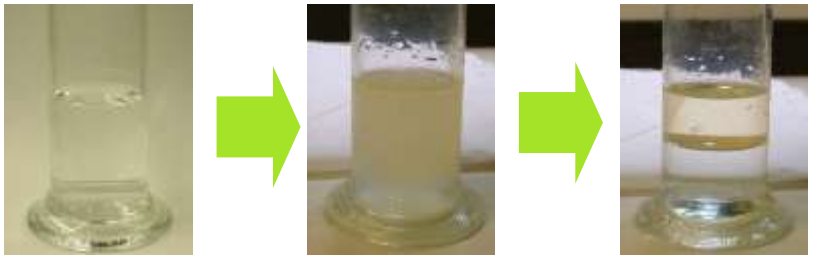
- Primary/secondary amine: low
- Tertiary/hindered amine: high

Alkanolamine vs.	Alkylamine
120+ °C	80-90 °C
MEA (55%)	MCA (90%)
MDEA (90+%)	DMCA (95+%)

Liquid-liquid phase separation →



Switchable-polarity solvents

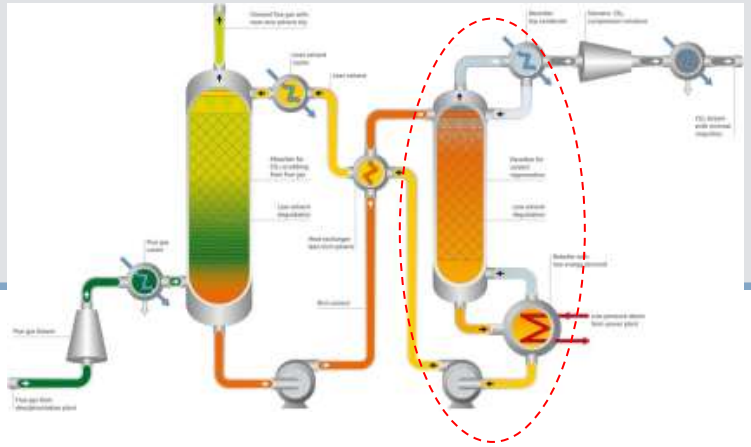


Before regeneration

During regeneration

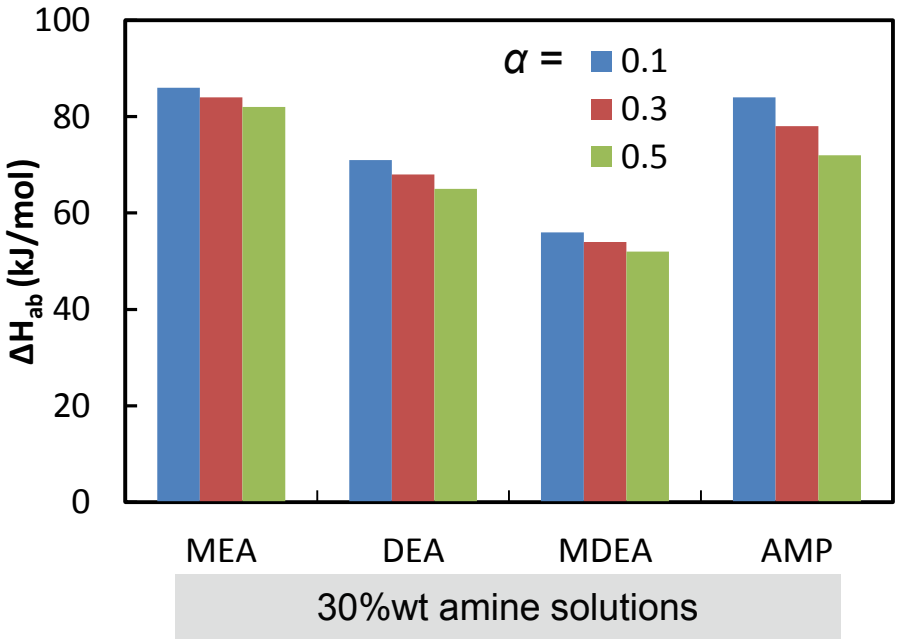
After regeneration

Heat of absorption



Absorption enthalpy

- Primary > secondary > tertiary amine
- Increase α → decrease ΔH_{ab}



	Q_{sen}	Q_r	Q_{str}	Q_{los}	Q_{sum}
MEA	0.9	1.8	1.1	0.2	4.0
DMAE+ PZ	0.6	1.4	1.0	0.2	3.2
Target	0.5	1.2	0.6	0.1	2.4

$$Q_{los} = \phi \cdot \Delta T \cdot A$$

$$Q_{str} = F_{steam} \cdot L_v$$

$$Q_r = F_{CO_2} \cdot \Delta_r H$$

$$Q_{sen} = F_{sol} \cdot C_p \cdot \Delta T$$

Degradation

Generally

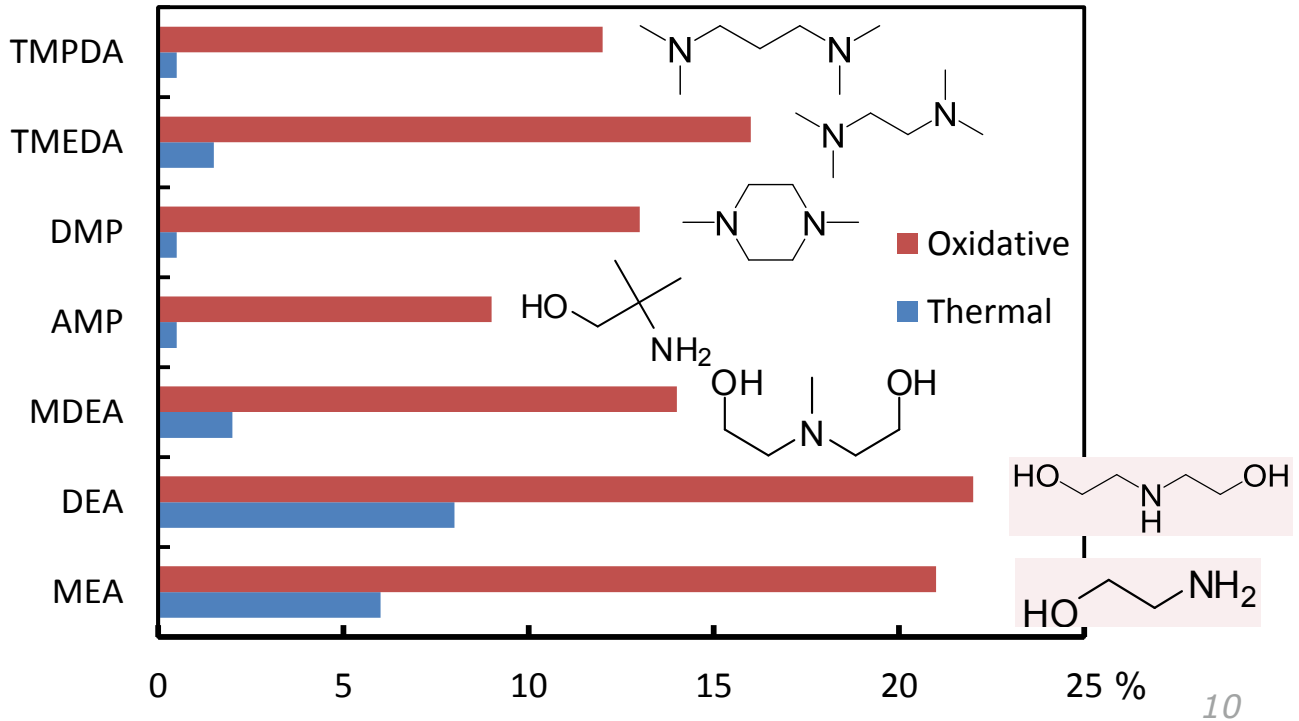
- Primary/secondary amine: reactive
- Tertiary/hindered amine: stable

IFP (Lepaumier)

II > I > III > hindered

Rochelle

- Cyclic amine:
  - e.g. PZ
  - Stable (<180°C)



Data Source: Lepaumier, 2010

Degradation

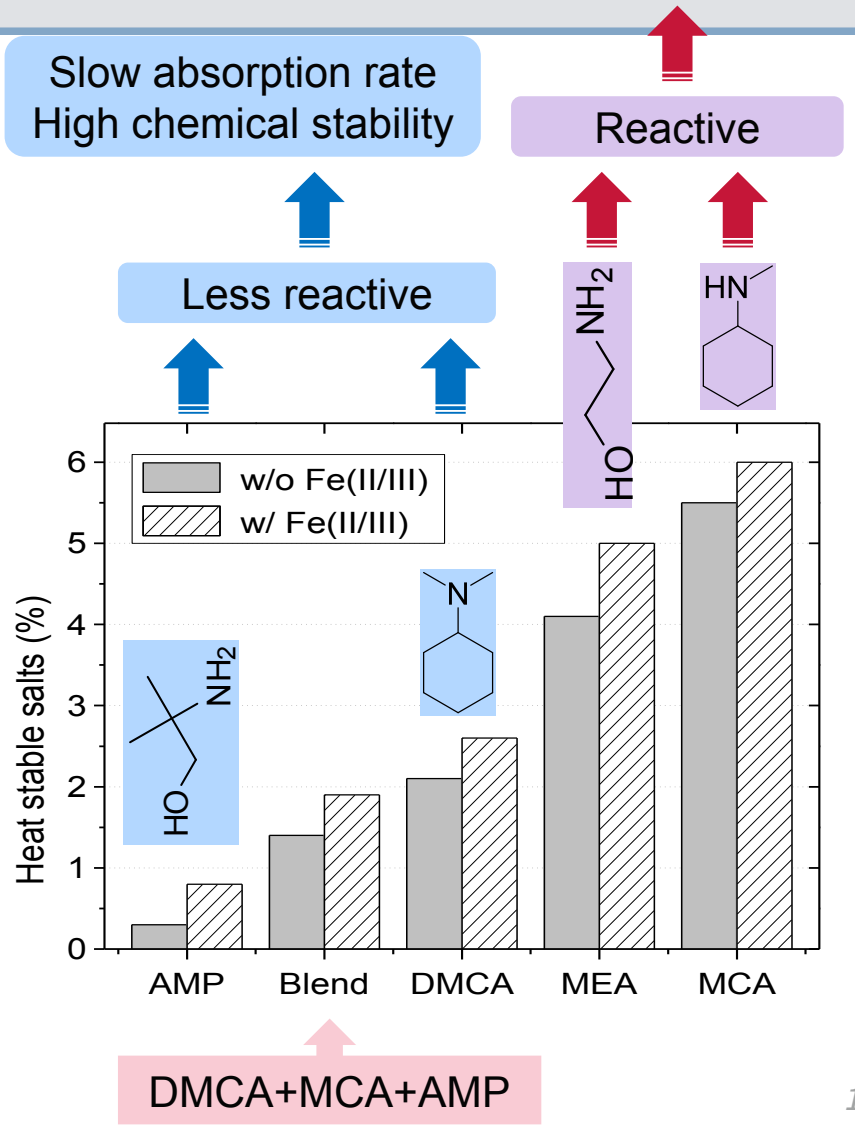
Generally
- Primary/secondary amine: reactive
- Tertiary/hindered amine: stable

IFP (Lepaumier)

II > I > III > hindered

Relations between
- Chemical stability
- Reaction kinetics

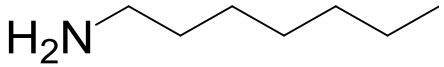
Solvent losses
- Vaporisation → Environment
- Degradation → Irreversible

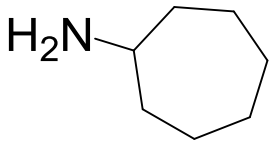


Viscosity

Influence of η

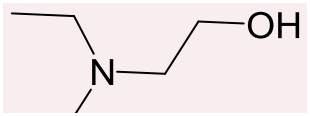
- Substituent: chain length
  - Linear ☹
  - Branched/cyclic ☺
  - e.g.

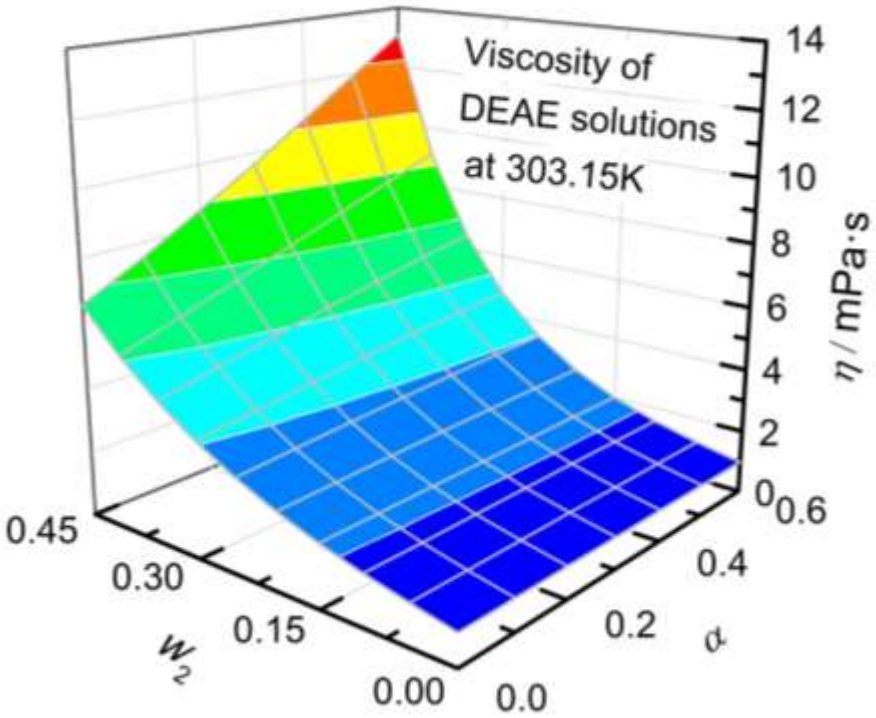


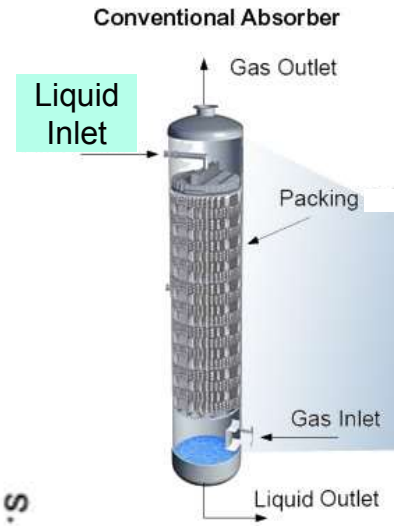


- *T* ↘
- *w* ↗
- *α* ↗

Electrical energy
Pressure drop
Mass transfer





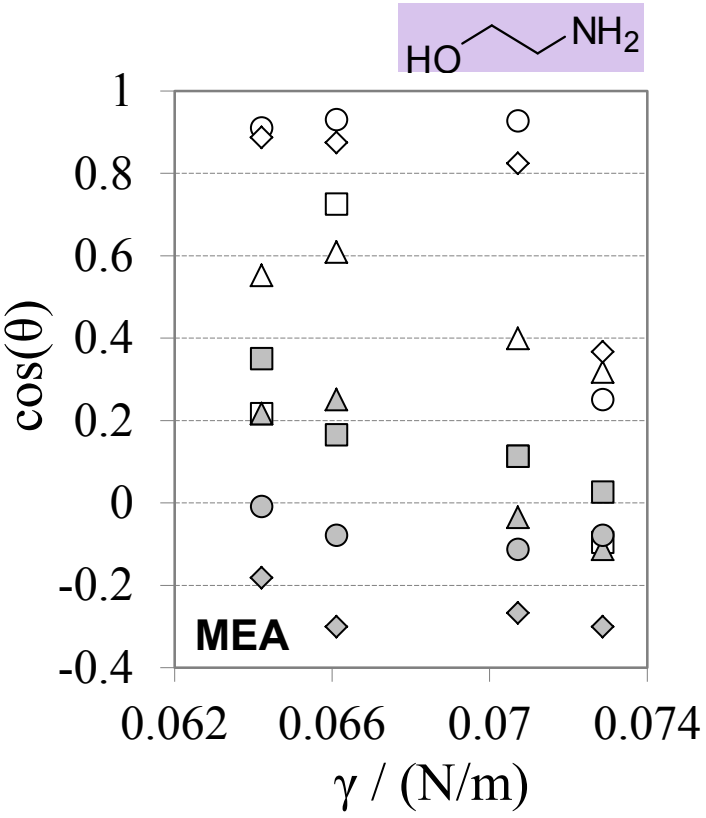


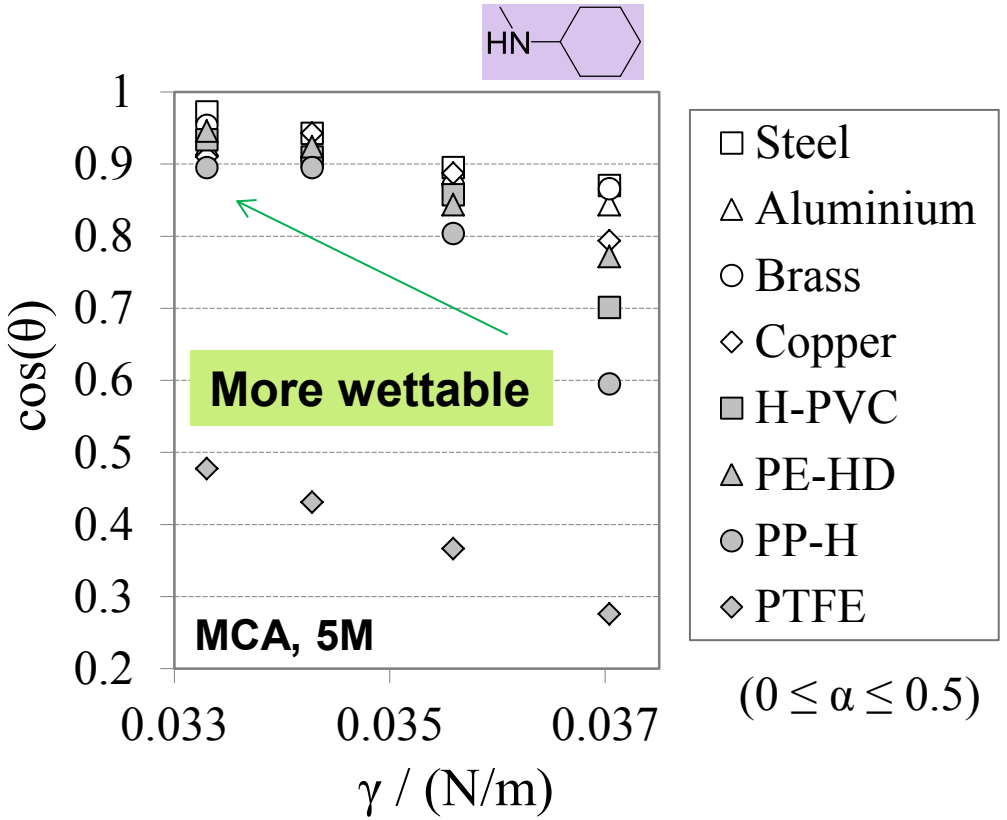
Wettability

Various packing materials

- Surface tension (γ)
- Contact angle

(Alkanolamine vs. Alkylamine)





Summary

Primary/Secondary amine:

- Fast reaction kinetics, high degradability, high absorption enthalpy
- Sterical hindrance: slower absorption rate & degradation, enhance CO_2 loading
- Secondary amine has a high potential to achieve both rapid absorption rate and high CO_2 capacity (with minor sterically hindered effect)

Tertiary amine:

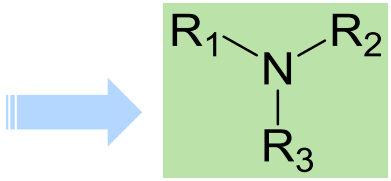
- Slow reaction kinetics, low degradability, low absorption enthalpy

Alkylamine with its

- switchable polarity → liquid-liquid phase separation behaviour upon heating

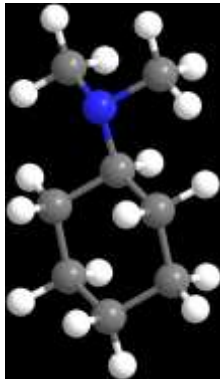
Structural effects of substituents

- hindered amine and cyclic amine (ring structure) typically exhibit a good chemical stability against thermal and oxidative degradations
- a branch at *α*-carbon position → enhance CO_2 capacity
- a branch at *β*-carbon position → enhance absorption rate



Ideal structure?

Acknowledgement



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