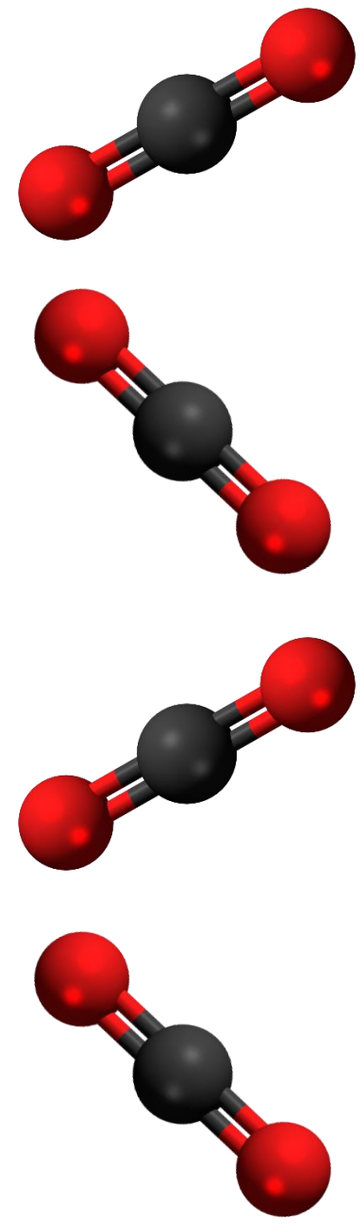
Regeneration of Non-Aqueous Precipitating Amine Solvents

KARLSSON H.K. & SVENSSON H.

Outline

- **Introduction**
  - Project
  - Absorption System
- **Experimental Method**
- **Results**
- **Conclusion & Future work**



Introduction - Project

Energy efficient CO_2 Removal

-mainly funded by the Swedish energy agency

Includes:

- Absorption studies
- Crystallization studies
- Regeneration studies
- Separation studies
- Design and modelling
- Lab scale Demonstration

Swedish Energy Agency

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Presentation by Meher Sanku

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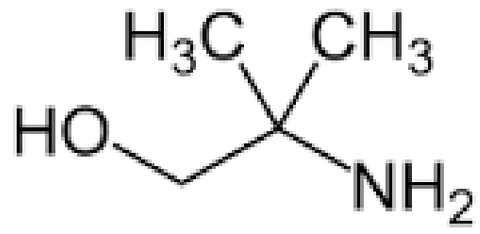
Absorption System

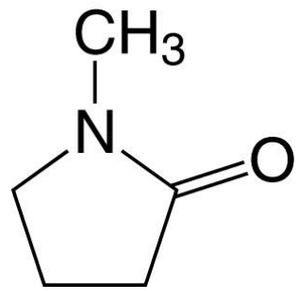
Amine:



AMP
(2-amino-2-methyl-1-propanol)

Solvents:

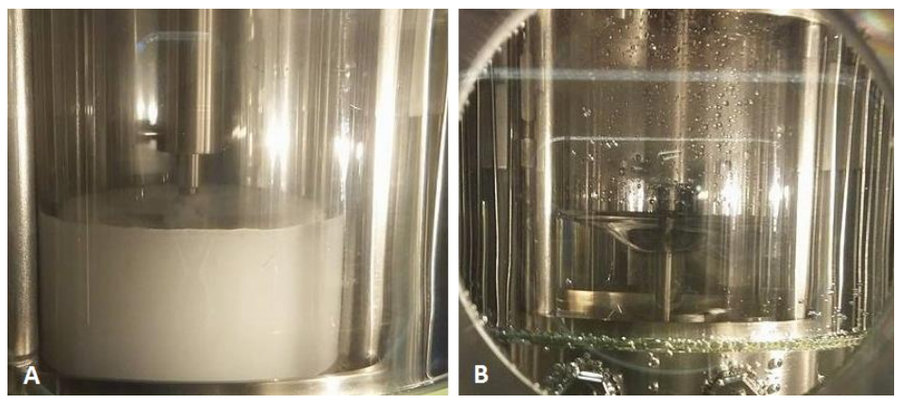
TEGDME
(Triethylene glycol dimethyl ether)

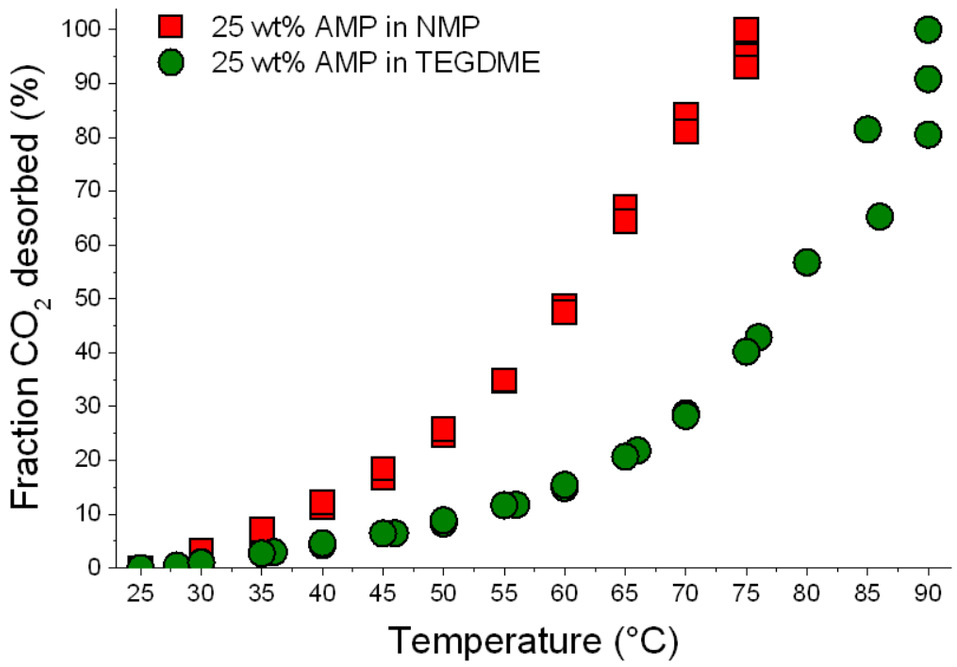


NMP
(*N*-methyl-2-pyrrolidone)

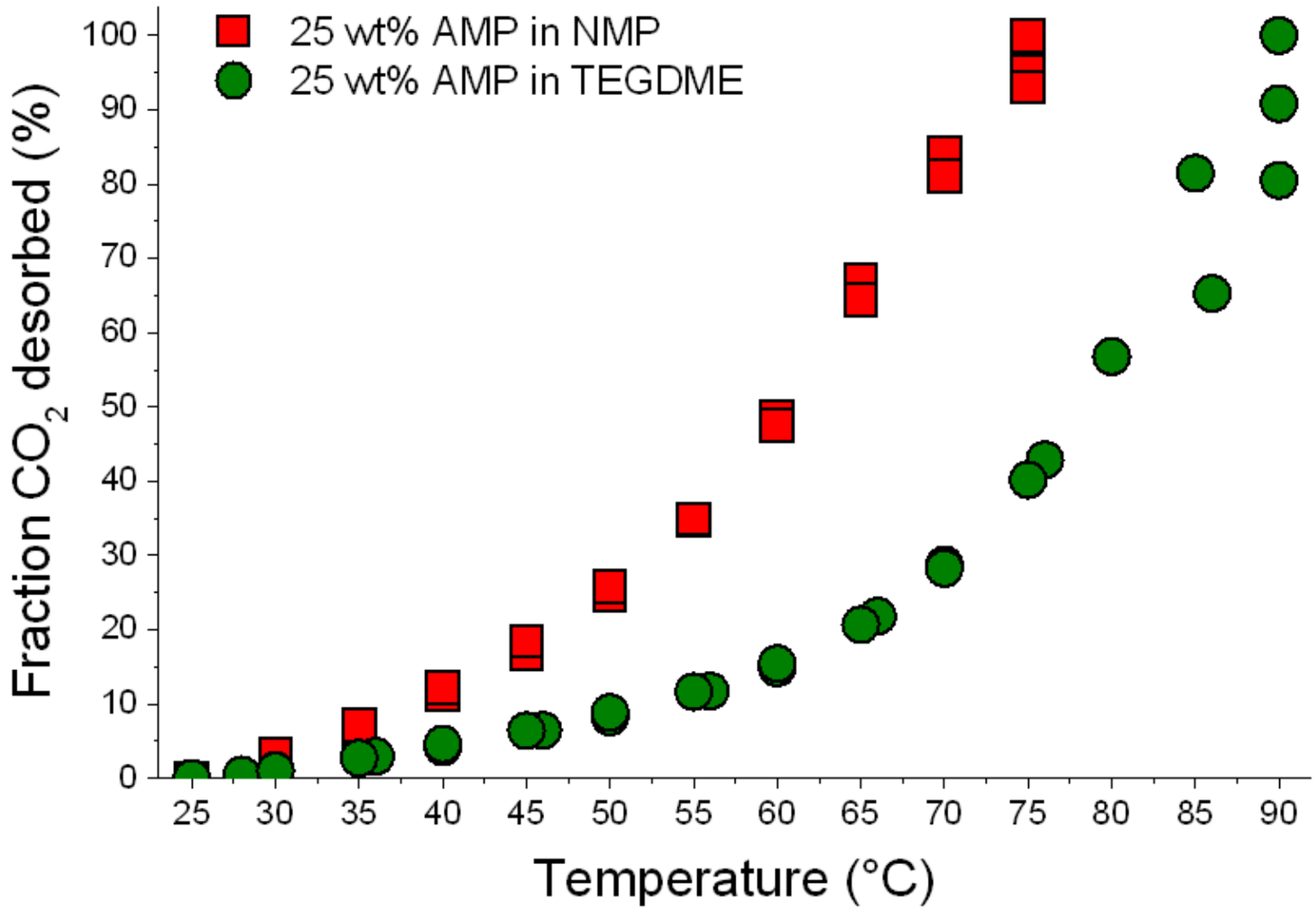
Introduction - Project

- Non-aqueous two phased system
  - Liquid which precipitates when reacted with CO_2
  - Only part of the stream heated for regeneration
- Regenerates at temperatures 70-90 °C
- Possibility to use low grade heat



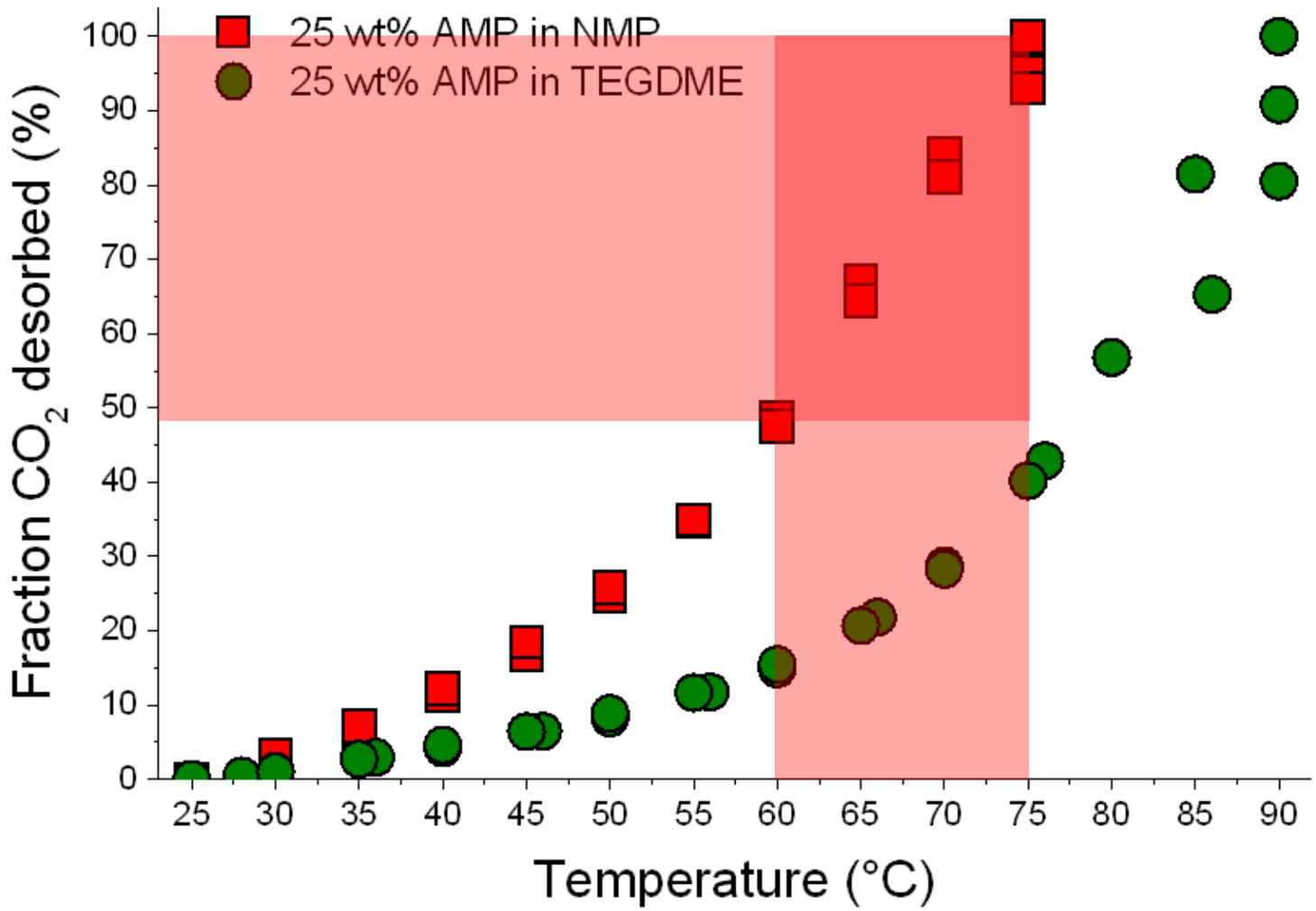


Introduction - Project



H. Svensson, Lund University, 2014.

Introduction - Project



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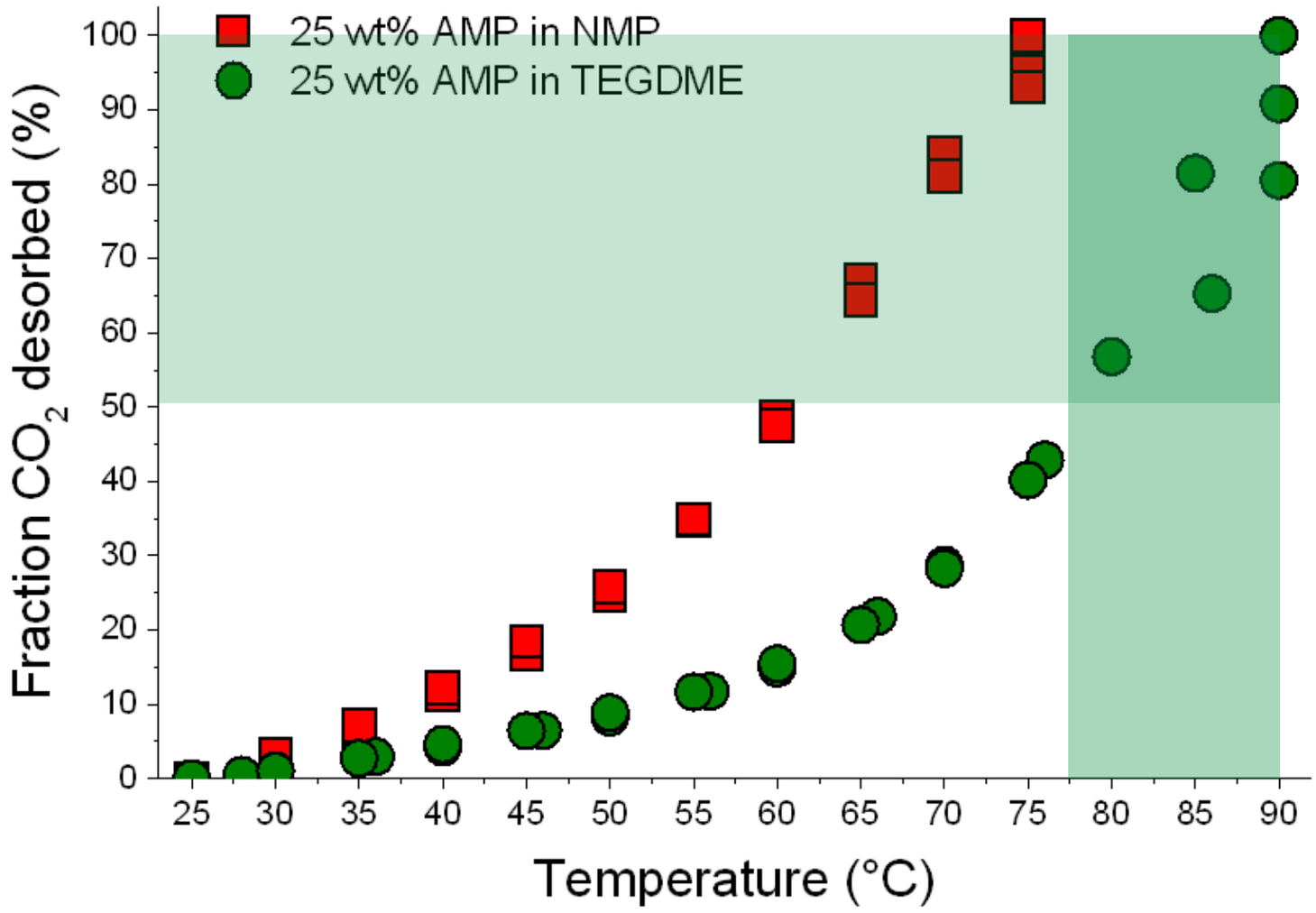

H. Svensson, Lund University, 2014.

Reaction mechanism

$CO_2(g) \leftrightarrow CO_2(sol)$

(1) Dissolution

H. Svensson, C. Hulteberg, H.T. Karlsson Energy Procedia 2014, 63, 750–757.
H. Svensson, V. Zejnullahu Velasco, C. Hulteberg, H.T. Karlsson Int. J. Greenh. Gas Control 2014, 30, 1–8.

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$CO_2(g) \leftrightarrow CO_2(sol)$ (1) Dissolution

$CO_2(sol) + RNH_2(sol) \leftrightarrow RNH_2^+COO^-(sol)$ (2) Zwitter ion formation

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$RNH_2^+COO^-(sol) + RNH_2(sol) \leftrightarrow RNH_3^+(sol) + RNHCOO^-(sol)$

(3) Carbamate formation

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$RNH_3^+(sol) + RNHCOO^-(sol) \leftrightarrow RNH_3^+RNHCOO^-(s)$

(4) Carbamate precipitation

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Maximum loading due to chemical reaction : 0.5 n_{CO2}/n_{Amine}

H. Svensson, C. Hulteberg, H.T. Karlsson Energy Procedia 2014, 63, 750–757.
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Crystal structures – Precipitate

Different CO_2 solubility for NMP and TEGDME

- Precipitation at different amount of CO_2 injected

Two types of crystal structures have been identified for the solid precipitate:

- One monoclinic
- One unidentified

Observed both with NMR and XRD analysis

Both structures observed in both solvents

H. Svensson, C. Hulteberg, H.T. Karlsson Energy Procedia 2014, 63, 750–757.

Aim

To Investigate what CO_2 partial pressures that can be obtained from regeneration of CO_2 absorbed by AMP dissolved in either NMP or TEGDME, at different temperatures.

- Part of evaluation of optimal regeneration temperatures

Experimental Conditions

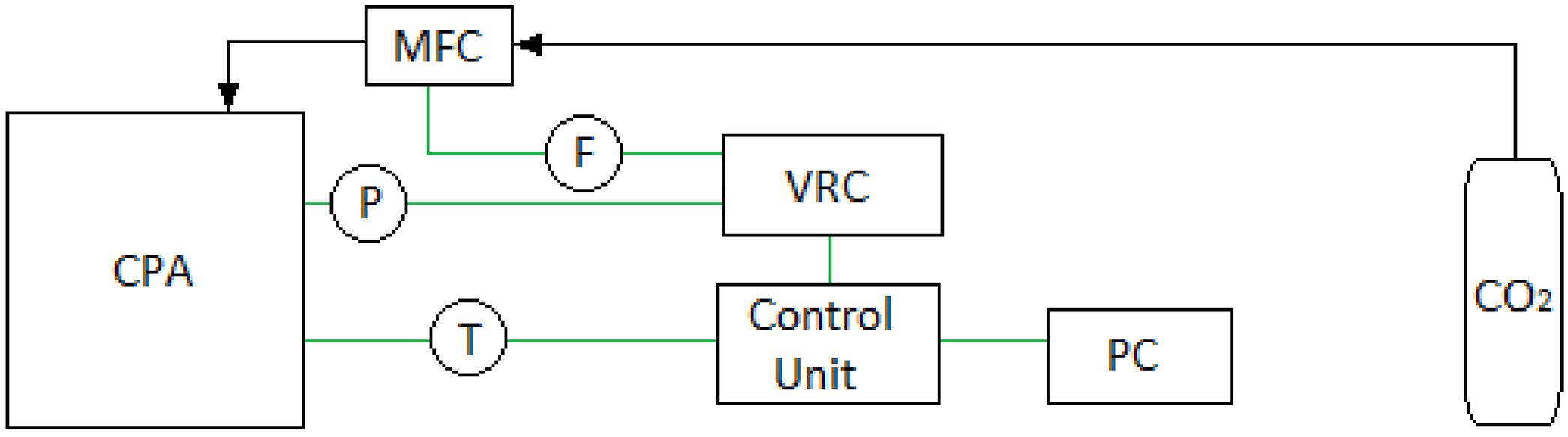
- Two absorption systems
- Two amine concentrations
- Varying initial theoretical loadings

Loading:

$$\alpha = \frac{(n_{CO2})_{abs}}{(n_{amine})_0}$$

Amine	Solvent	C_{amine} (wt%)	Loading Aim (n_{CO2}/n_{Amine})	Theoretical Loading (n_{CO2}/n_{Amine})	Temperature (°C)
AMP	NMP	15	0, 0.2, 0.5	0, 0.20, 0.48	25-85
AMP	NMP	25	0, 0.2, 0.5	0, 0.20, 0.49	25-85
AMP	TEGDME	15	0, 0.2, 0.5	0, 0.20, 0.49/0.51	25-85
AMP	TEGDME	25	0, 0.2, 0.3, 0.5	0, 0.20, 0.31, -	25-85

Experimental Set-up



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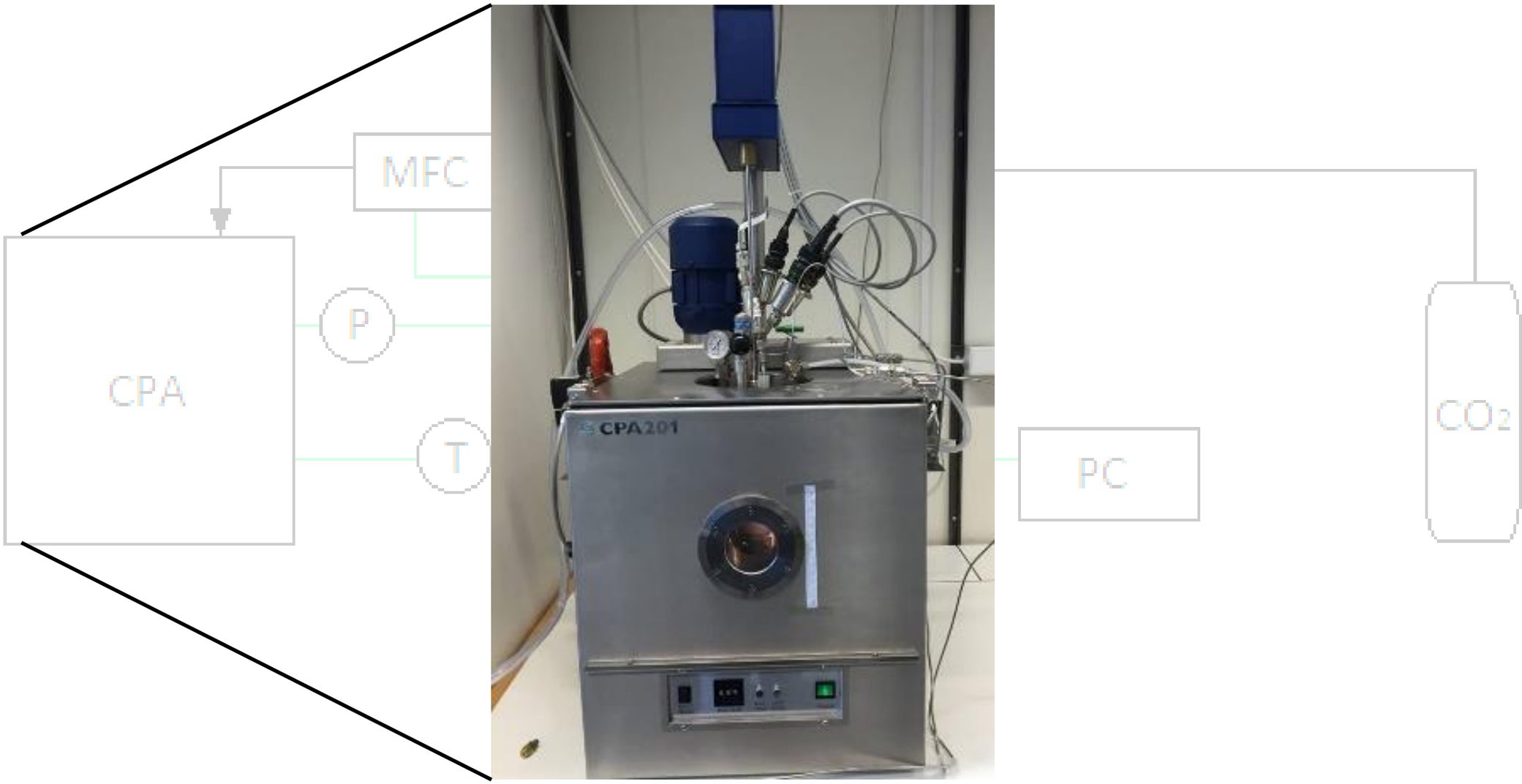
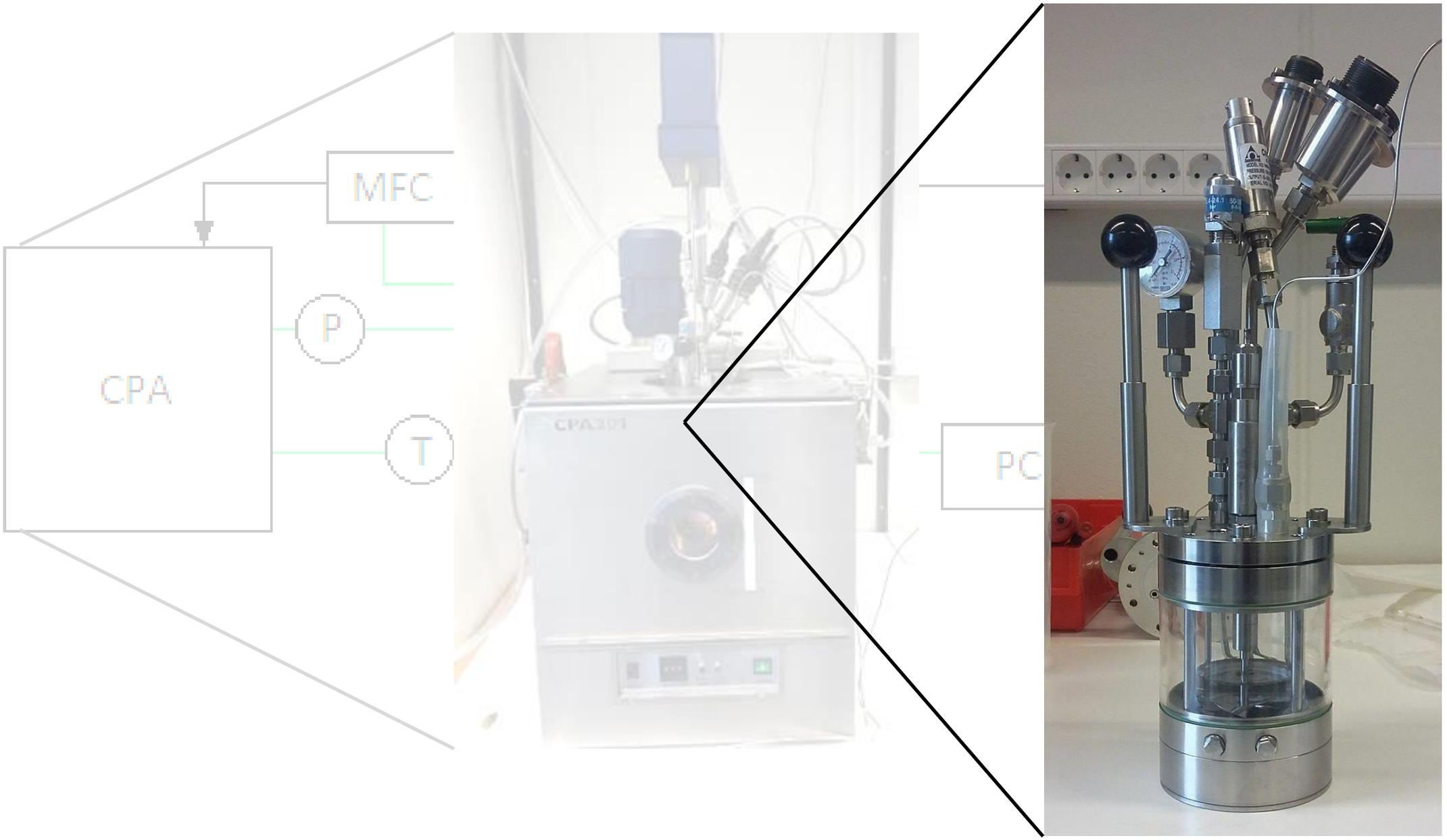


ChemiSens AB true heat-flow CPA201

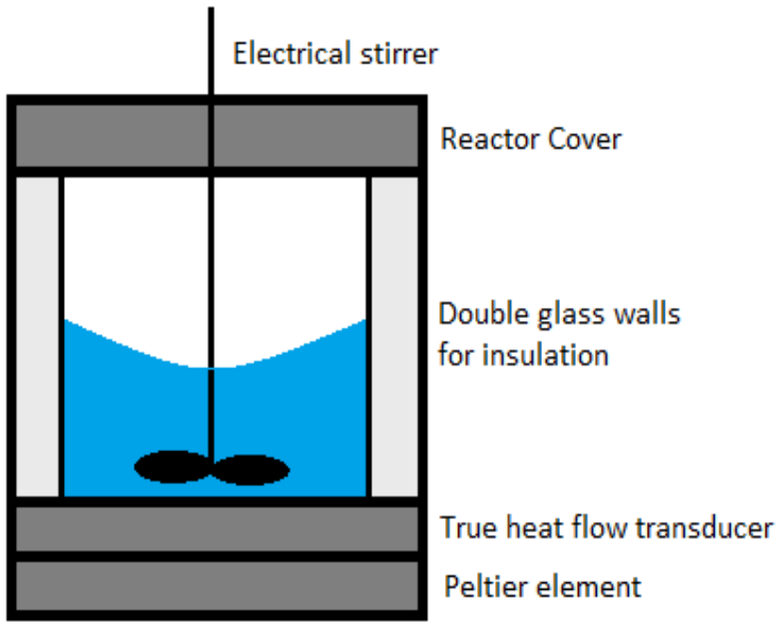
Experimental Set-up



Experimental Procedure

- Thermostat-controlled water-bath

- Batch Reactor
  - 250 cm^3
  - Glass and Stainless steel
  - Electrical Stirrer 300 rpm

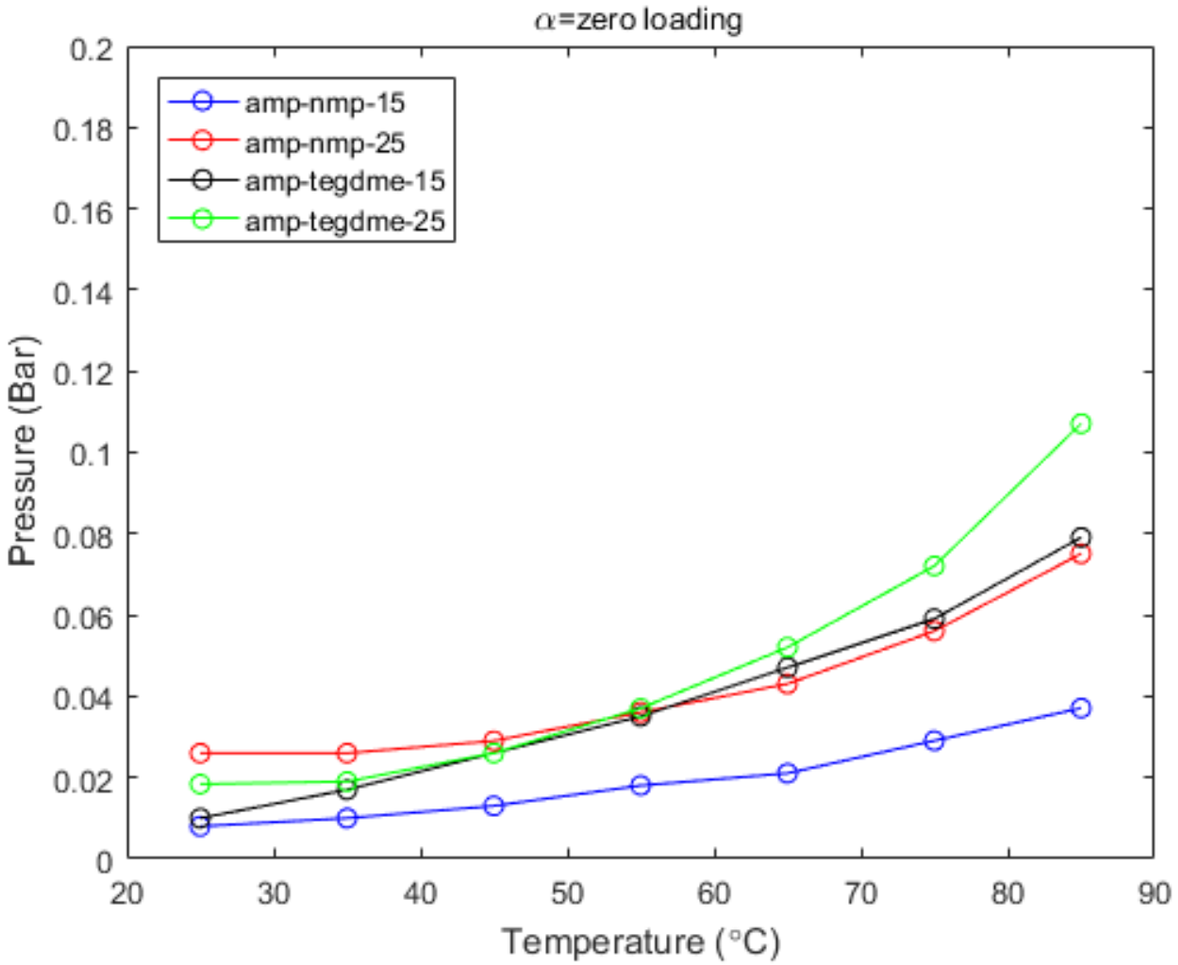


Experimental Procedure

- Approx. 100 g sample
- CO_2 were dosed at 25 °C
- Temperature were ramped between 25-85 °C with pauses to reach equilibrium every 10 °C
- Equilibrium was defined as max deviation of 0.005 bar and heat flow 0.02 W for 500s.
- Experiments performed at elevated pressures.

Results volatility of Solvent mixtures

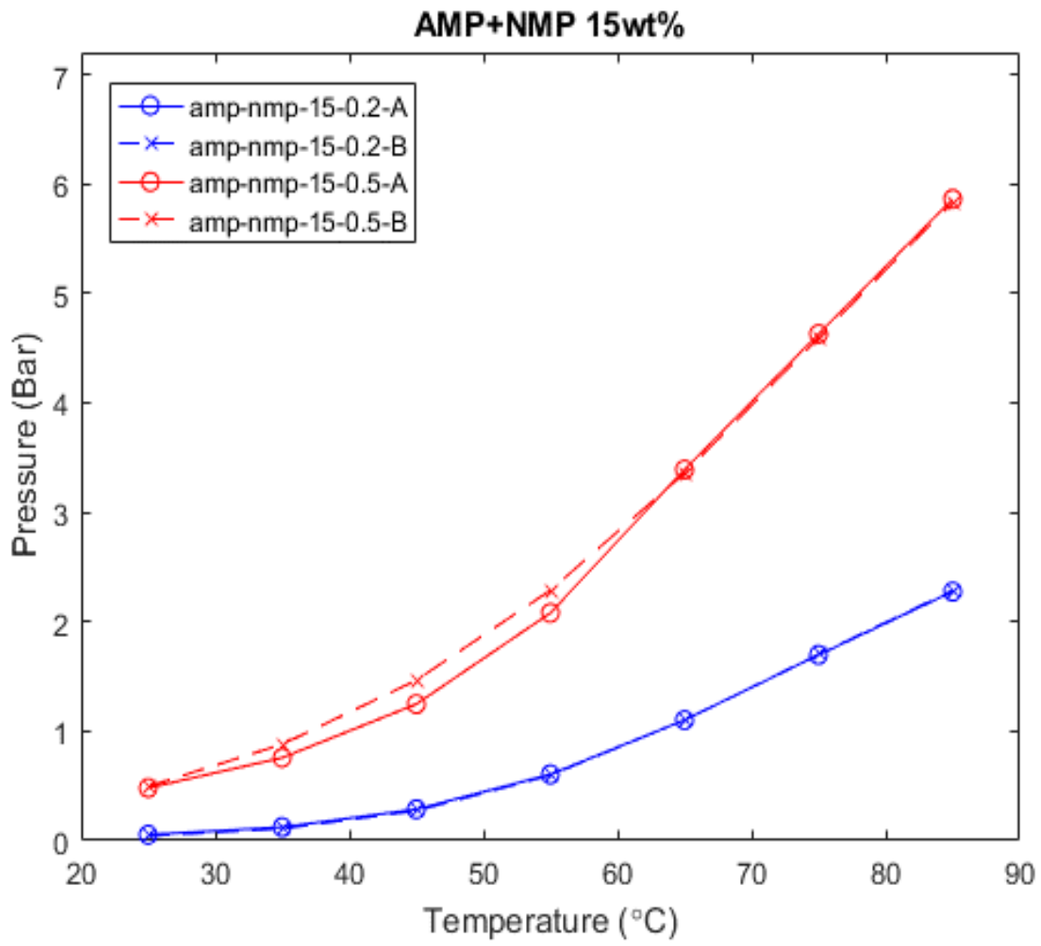
The solvent vapor pressure at zero loading



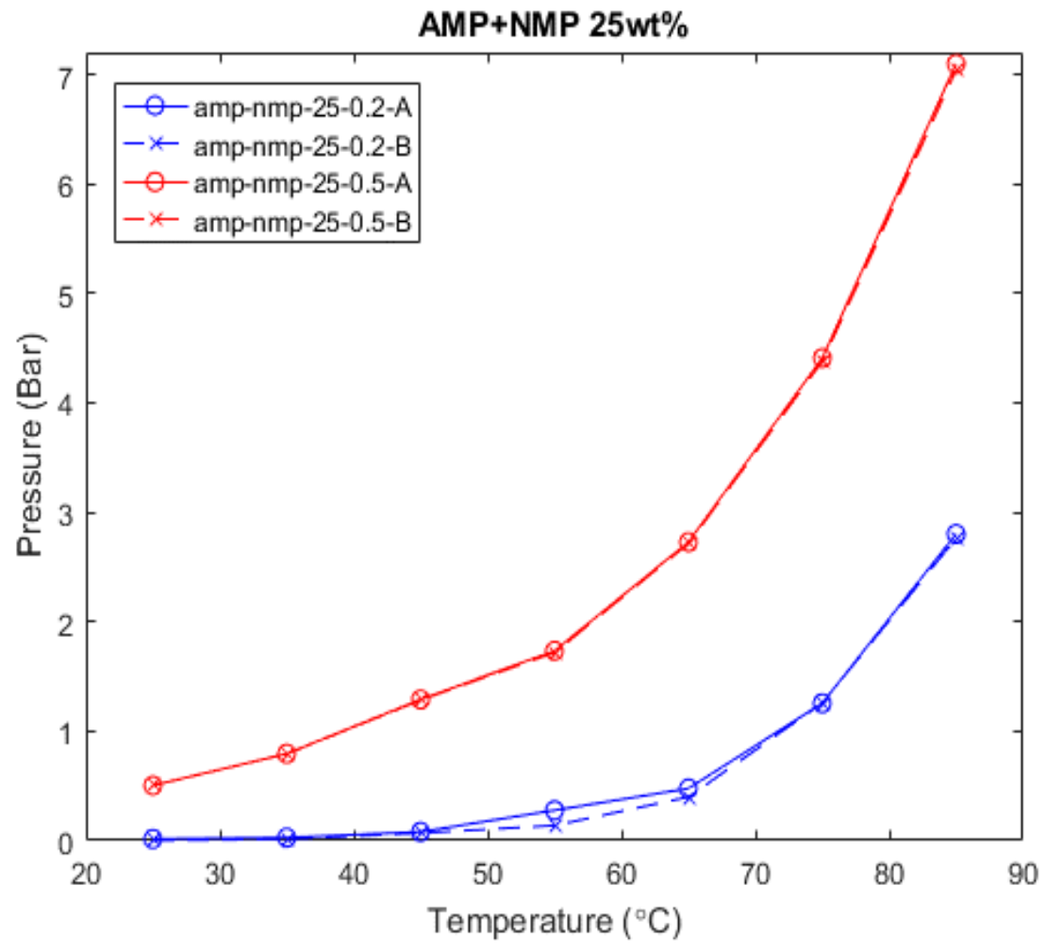
Absorption System	Max. pressure (85°C) (bar)
15wt% AMP in NMP	0.037
25wt% AMP in NMP	0.075
15wt% AMP in TEGDME	0.079
25wt% AMP in TEGDME	0.11

T_b(AMP) = 165 °C
T_b(NMP) = 202 °C
T_b(TEGDME) = 216 °C

Results AMP/NMP

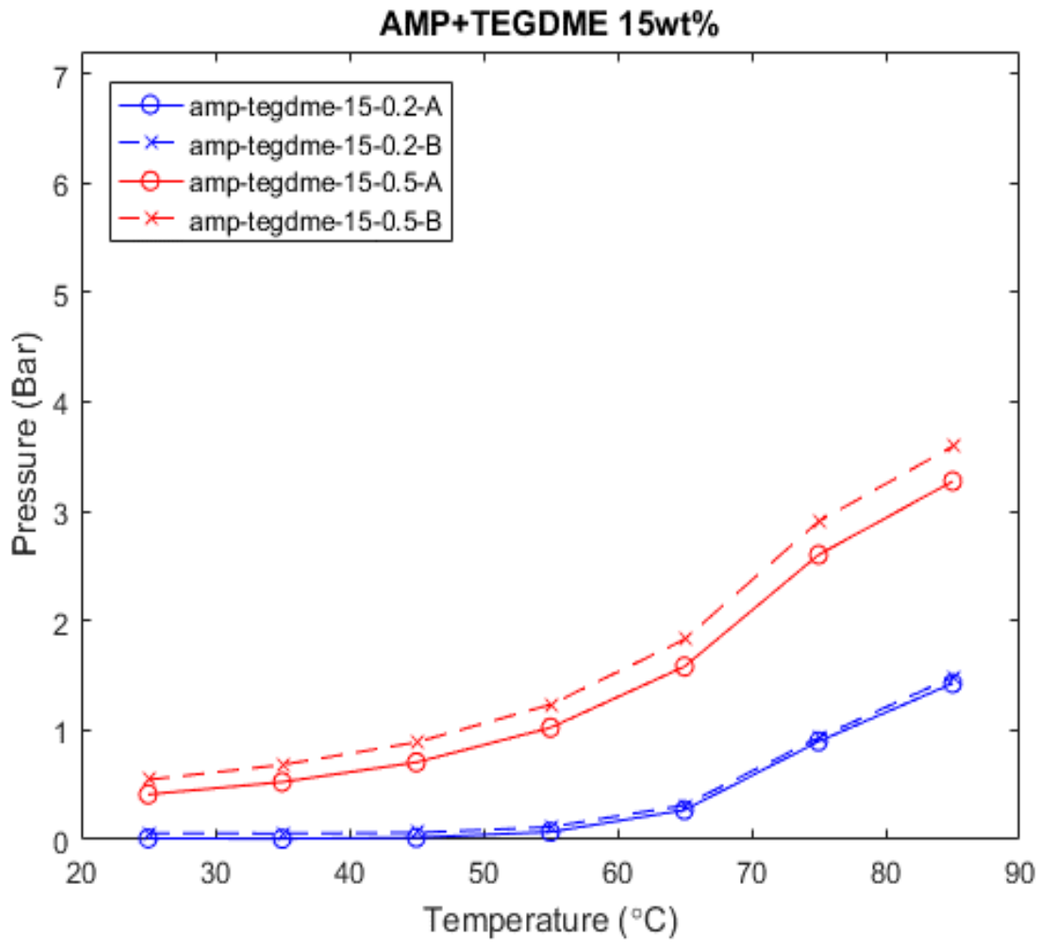


Initial loading (mol_{CO2}/mol_{amine})	P1 (85°C) (bar)	P2 (85°C) (bar)	Devation (%)
0.2	2.28	2.29	0.31
0.5	5.86	5.83	0.36

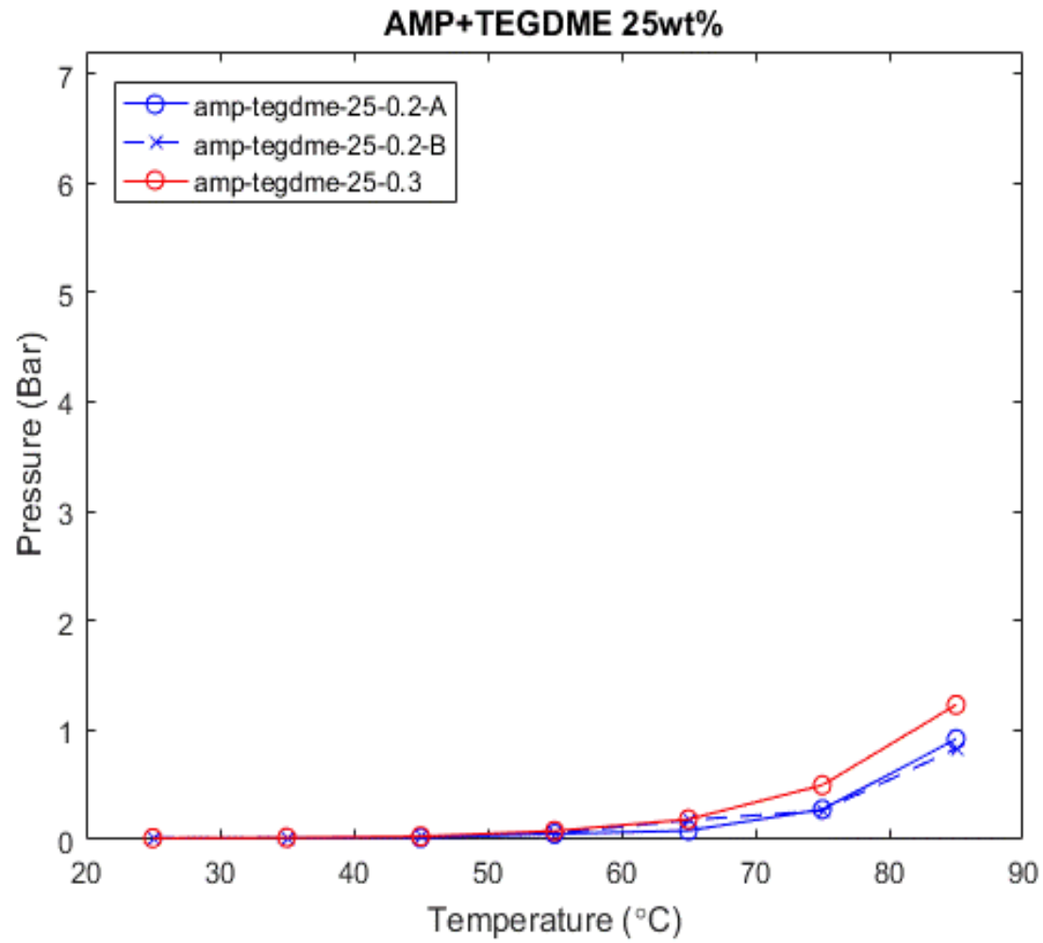


Initial loading (mol_{CO2}/mol_{amine})	P1 (85°C) (bar)	P2 (85°C) (bar)	Devation (%)
0.2	2.80	2.76	1.02
0.5	7.10	7.04	0.60

Results AMP/TEGDME



Initial loading (mol_{CO2}/mol_{amine})	P1 (85°C) (bar)	P2 (85°C) (bar)	Devation (%)
0.2	1.43	1.49	2.91
0.5	3.27	3.59	-

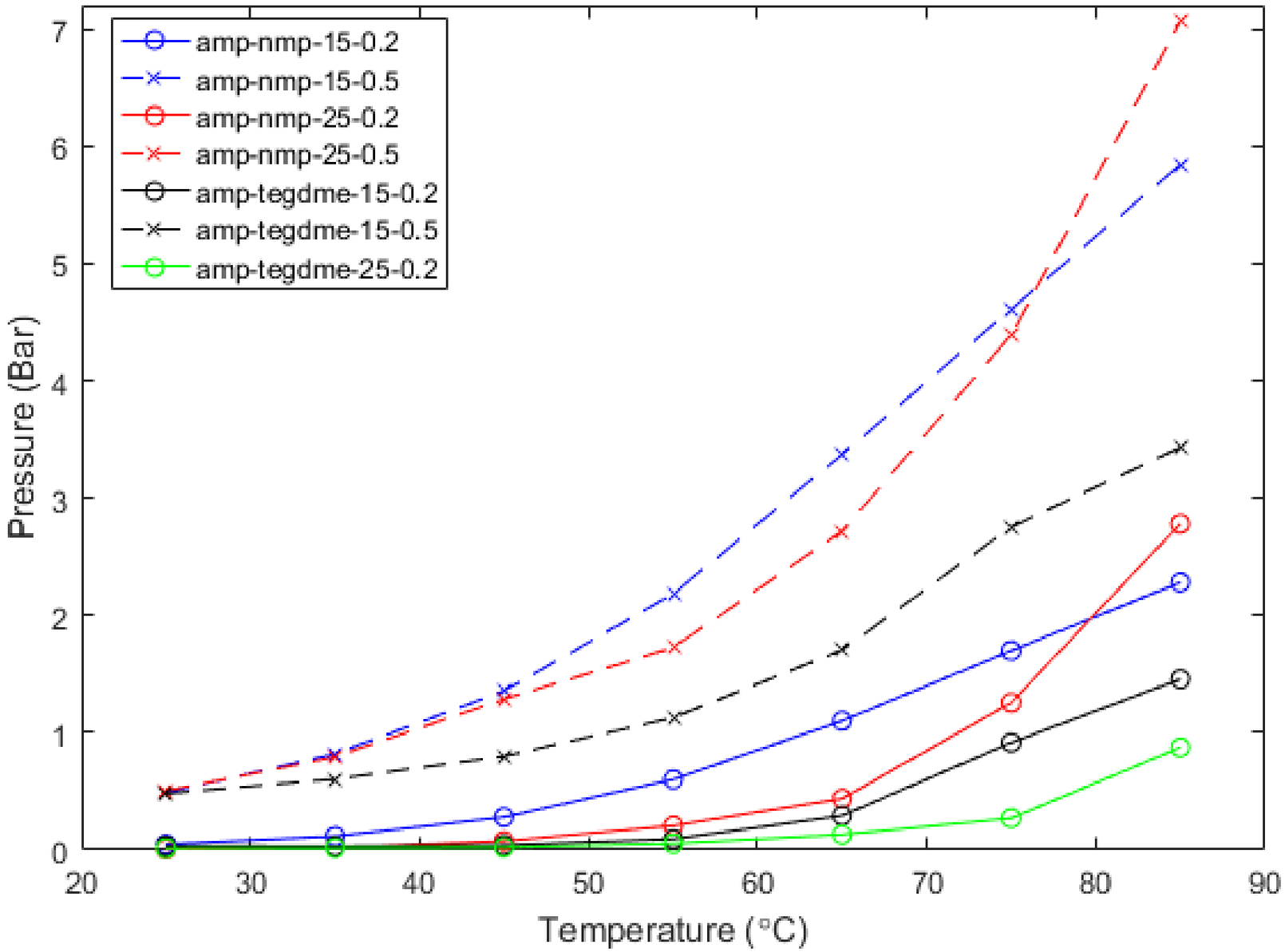


Initial loading (mol_{CO2}/mol_{amine})	P1 (85°C) (bar)	P2 (85°C) (bar)	Devation (%)
0.2	0.92	0.83	7.27
0.3	1.23	-	-

Results AMP/TEGDME 25

Experiments with 25 wt% AMP in TEGDME were cancelled because of severe precipitation and separation

Results Pressure vs. Temp



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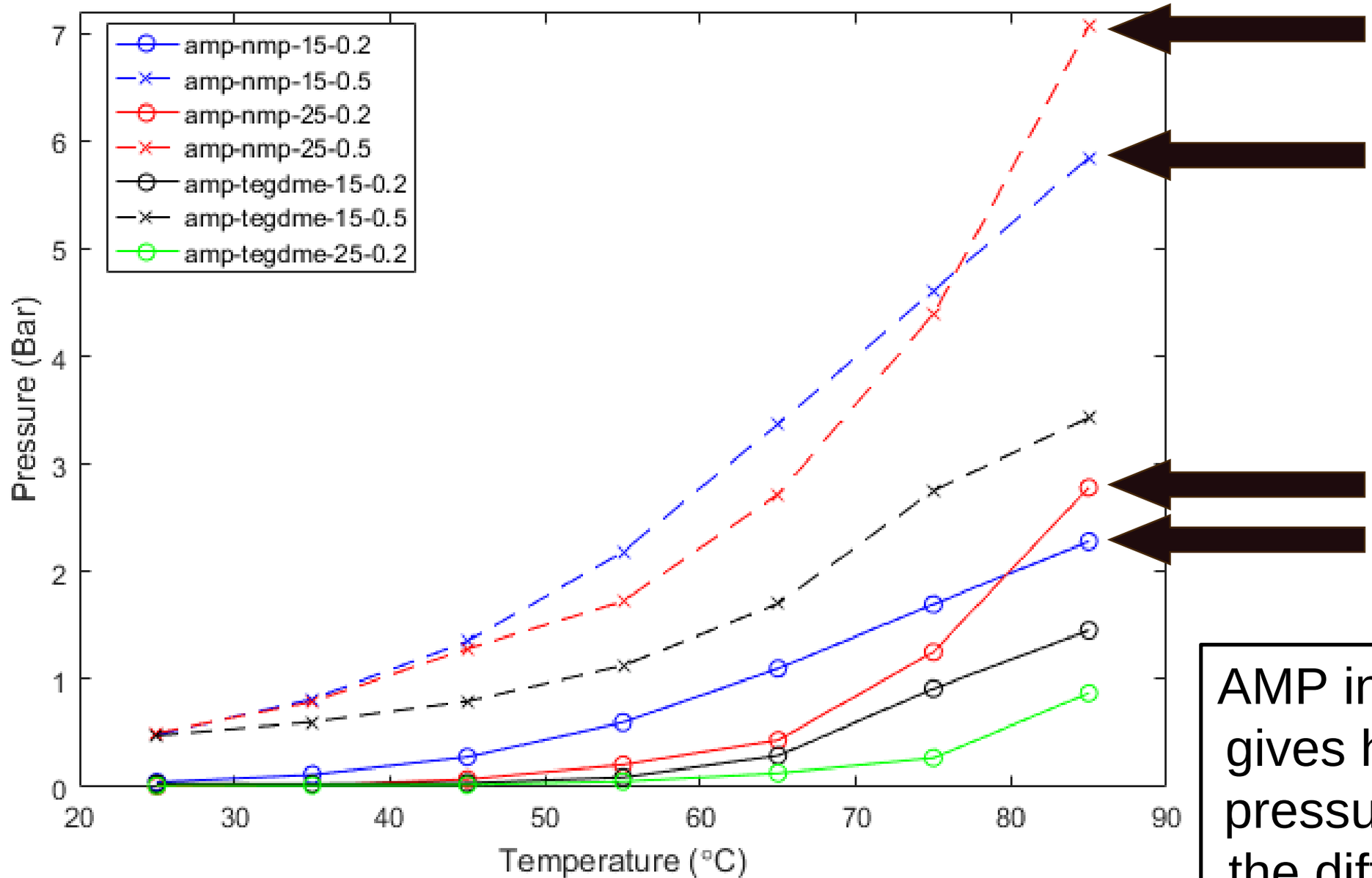
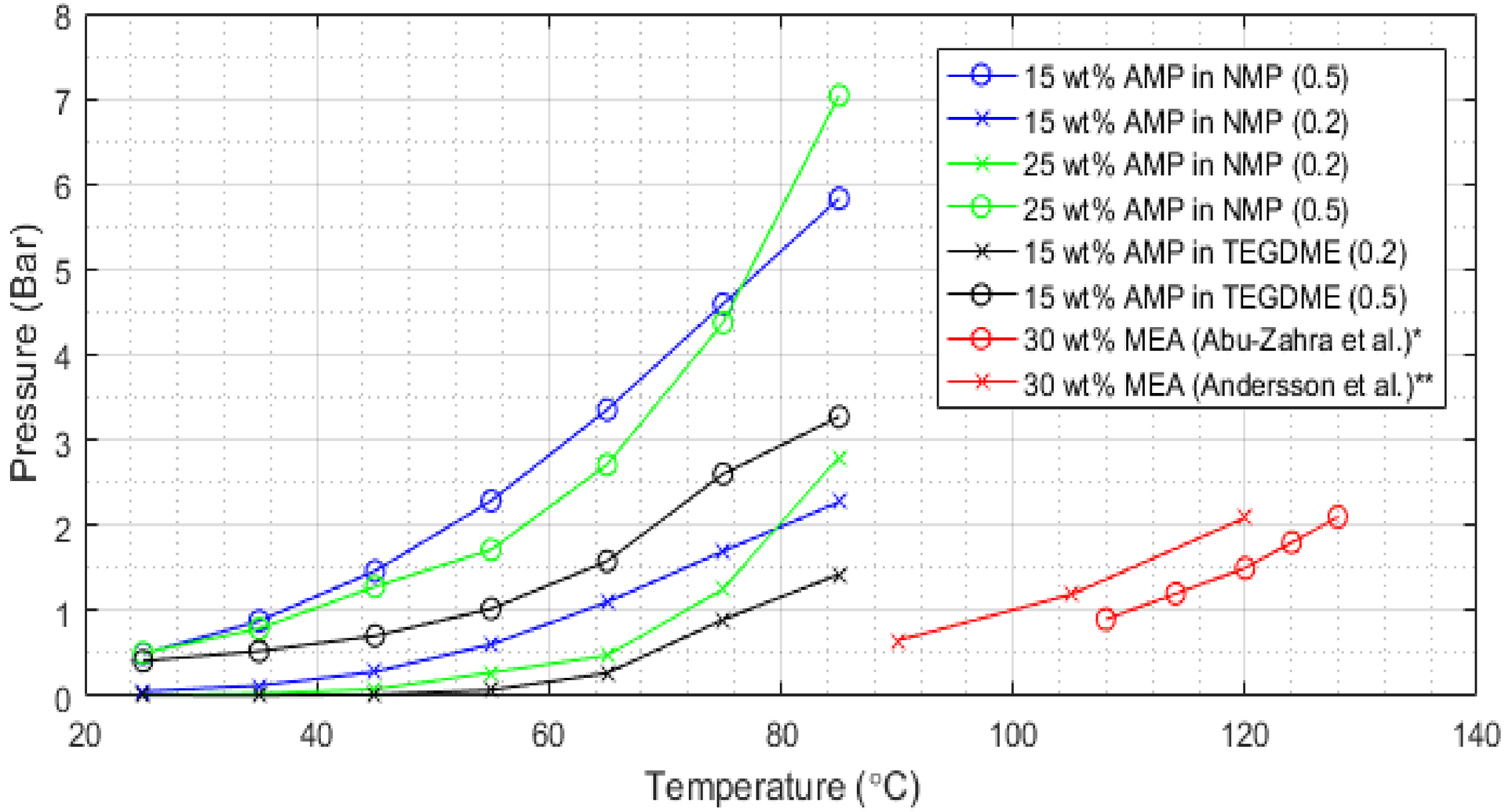


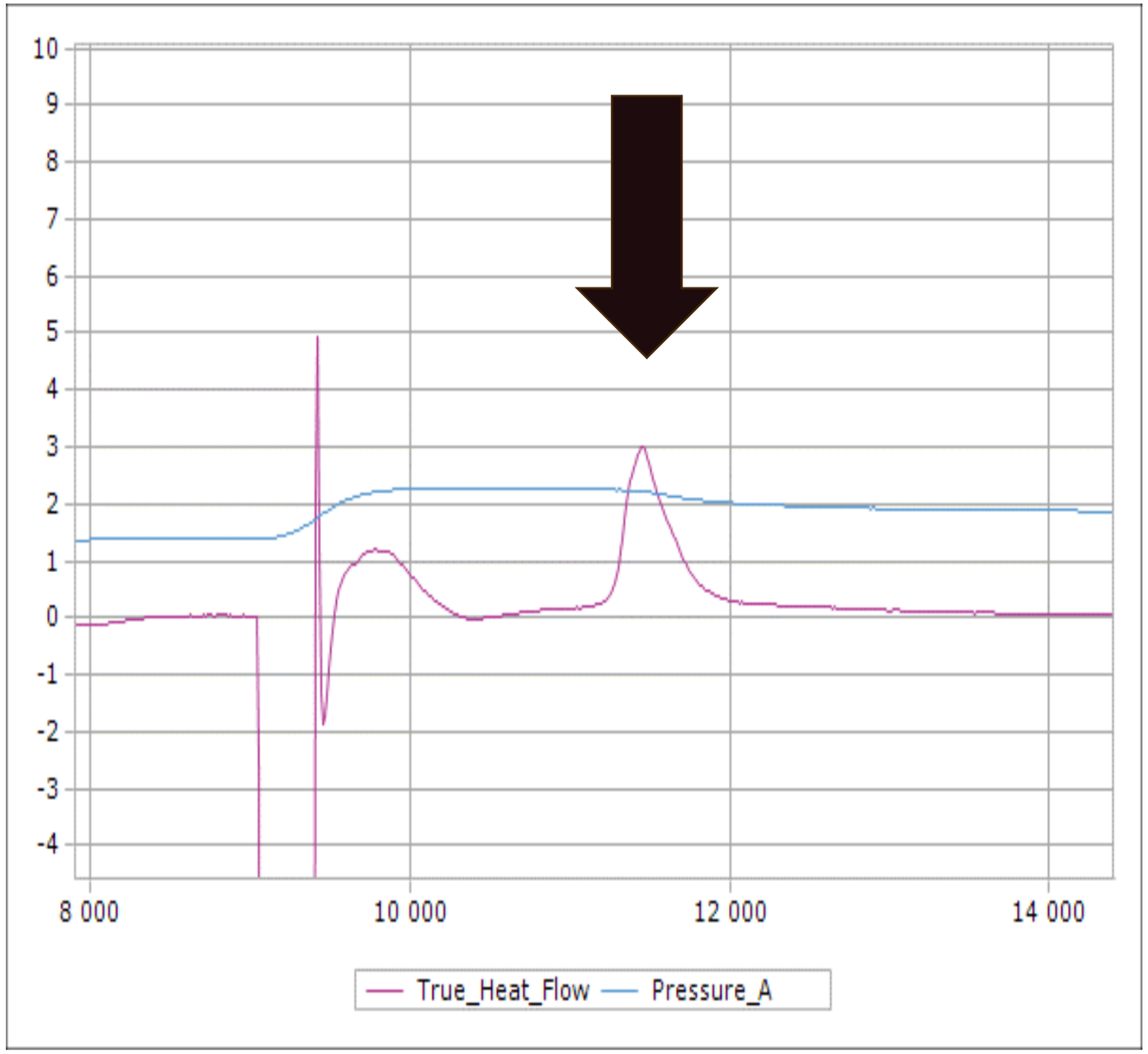
AMP in NMP gives higher pressures in the different categories

Comparison with MEA



*M. R. M. Abu-Zahra et al. *Int. J.Greenh. Gas Control*, vol. 1, pp. 37–46, 2007.
** V. Andersson et al. *Int. J. Greenh. Gas Control*, vol. 21, pp. 1–10, 2014.

Secondary Precipitation



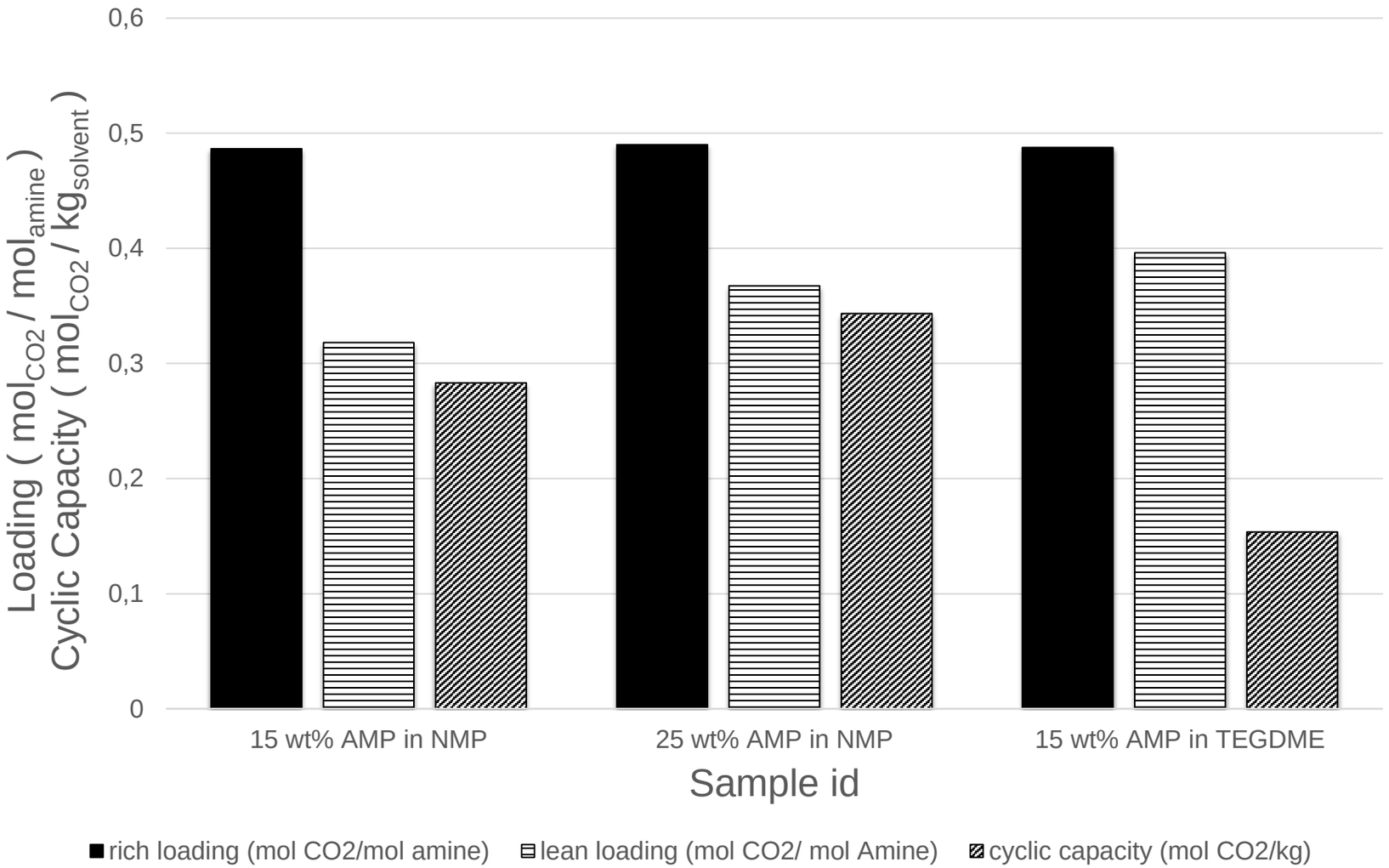
During the experiments a secondary precipitation occurred at elevated temperatures.
Seen as a decrease in pressure and peak in heat flow.

Secondary Precipitation

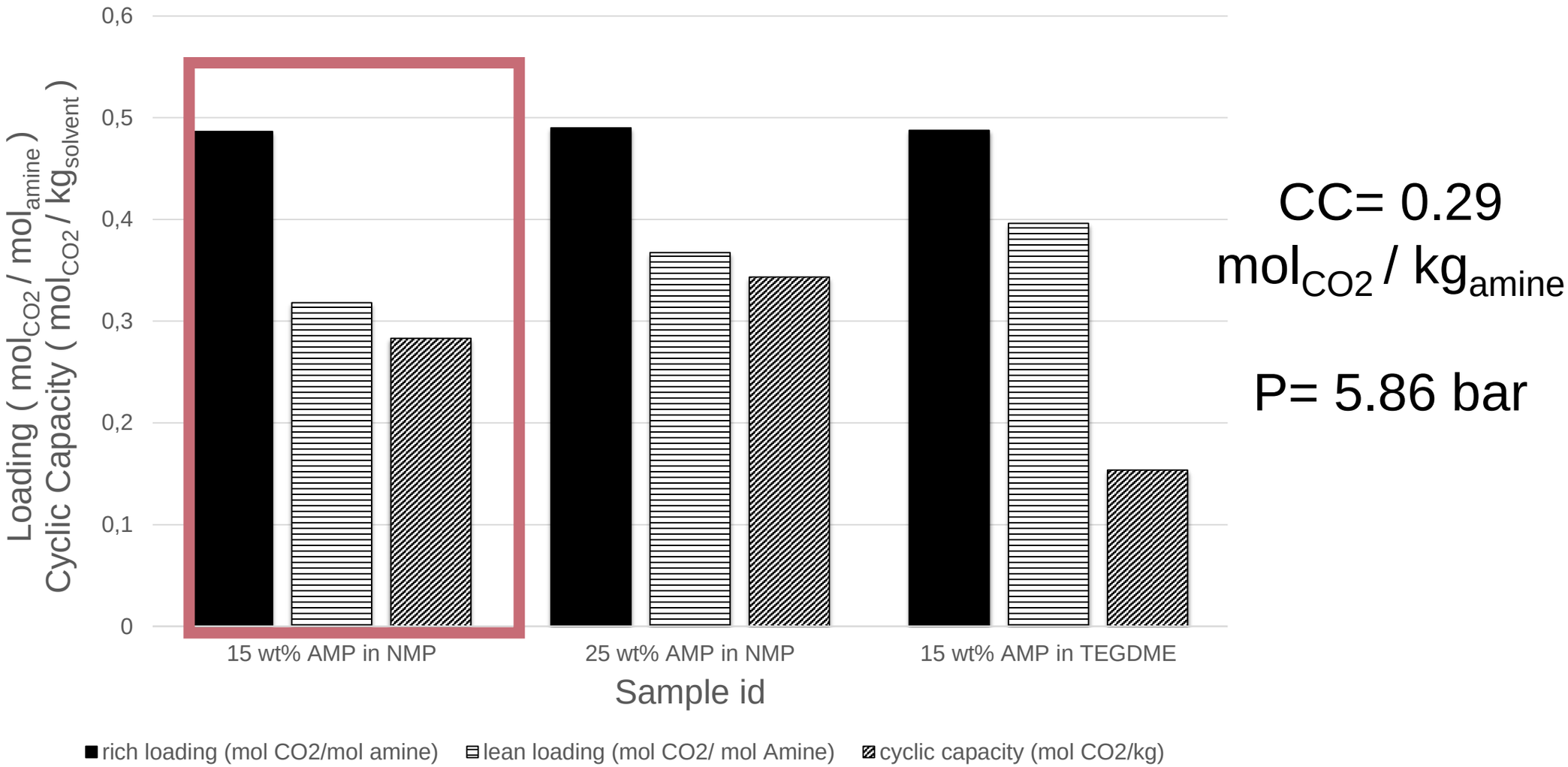
Loading (mol_{CO2}/mol_{amine})	**amine**	**solvent**	**C-amine** (wt%)	**T** (°C)
0.2	AMP	NMP	15	x
0.2	AMP	TEGDME	15	85/85
0.5	AMP	NMP	15	X
0.5	AMP	TEGDME	15	85/85
0.2	AMP	NMP	25	55/65
0.2	AMP	TEGDME	25	65/75
0.5	AMP	NMP	25	55/55
0.3	AMP	TEGDME	25	65

In all experimentns except 15 wt% AMP in NMP

Cyclic capacity



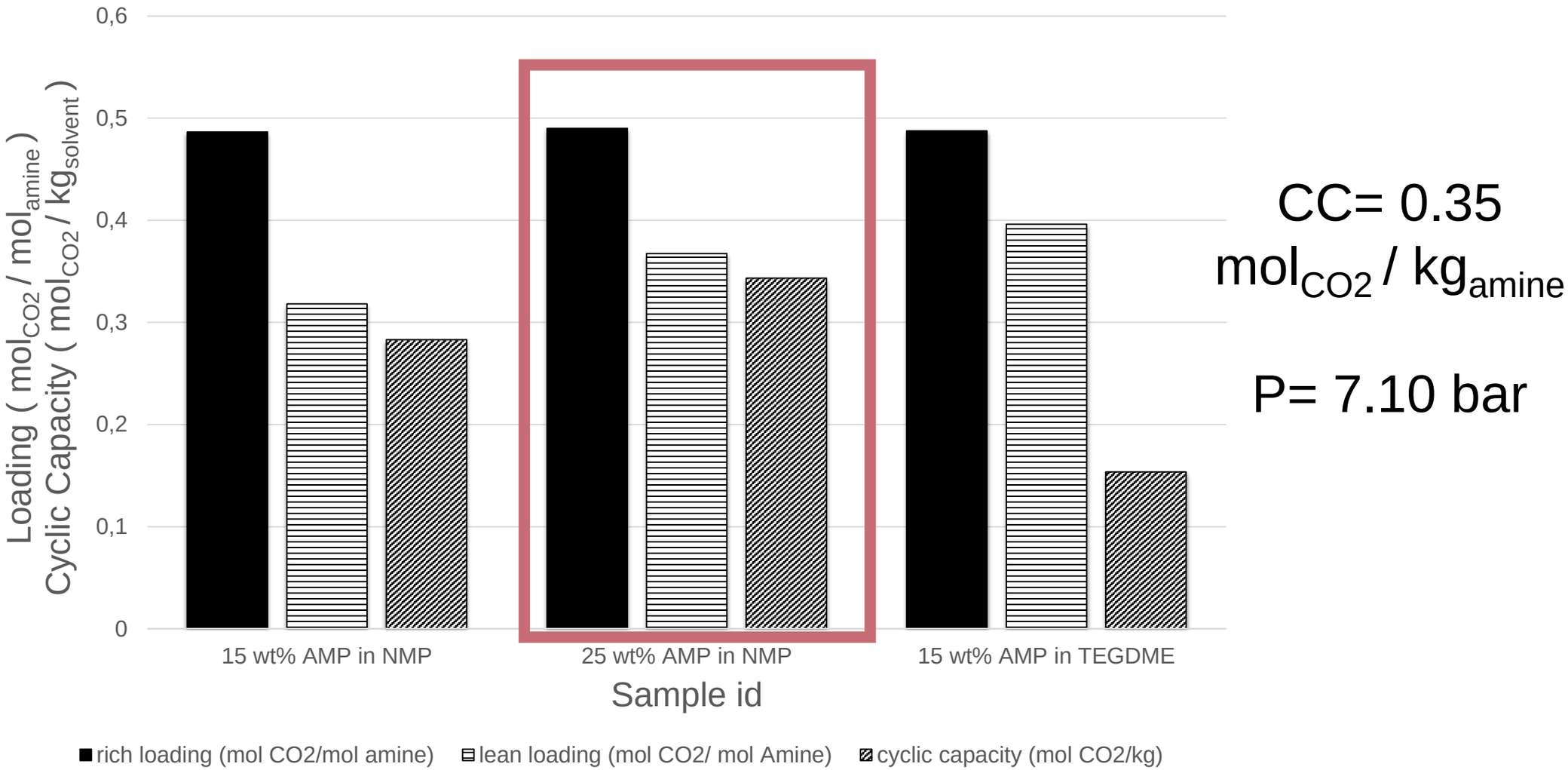
Cyclic capacity



CC= 0.29 mol$_{CO2}$ / kg$_{amine}$

P= 5.86 bar

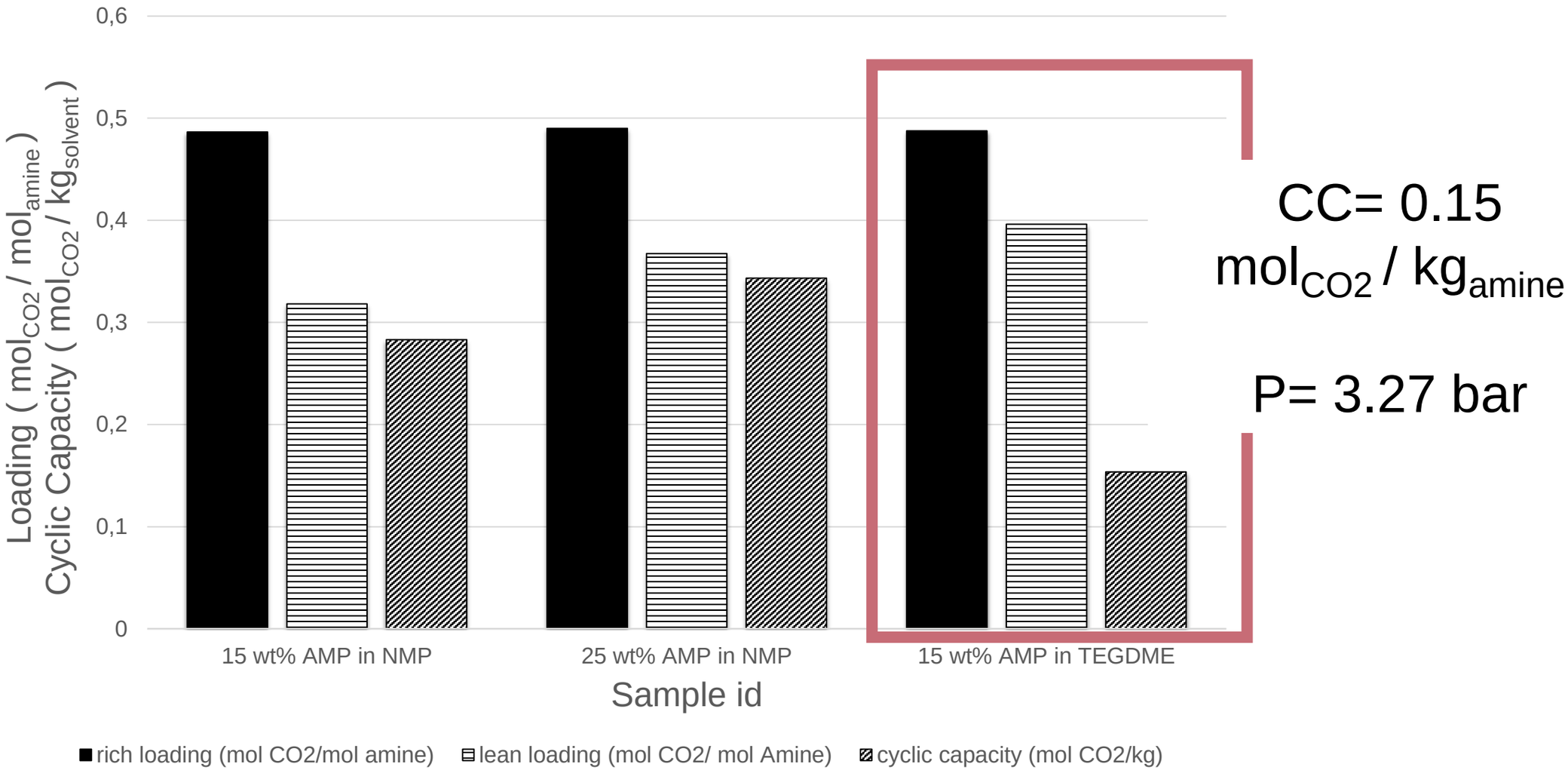
Cyclic capacity



CC= 0.35 mol_{CO2} / kg_{amine}

P= 7.10 bar

Cyclic capacity



Conclusion

- Possibility for pressurized CO_2 from regeneration
- Higher pressures obtained when NMP is used as solvent than when TEGDME is used
- Secondary precipitation (all but 15 wt% AMP in NMP)
  - For 15 wt% AMP regeneration starts at 55 °C
  - Higher for the others (still precipitate left et 85 °C)
- Extensive precipitation for 25 wt% AMP in TEGDME – Not optimal solution – mixing issues

Future work

- Regeneration experiments at atmospheric pressure
  - Rich and lean loadings
  - Cyclic capacities
- Further studies of the crystal precipitate
- Physical properties of amine solutions

Acknowledgements

Acknowledgements

Swedish Energy Agency

Thank you for your attention!

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