Enzyme catalyzed CO_2 absorption

November 2015

PROCEDE

Outline

General introduction
Experiments – general information
Results of absorption in MDEA
Results in relation to pKa effect
Results in relation to temperature effect
Simulations: MDEA+CA vs. MEA
Conclusions

Reactions

- **during CO_2 absorption into aqueous tertiary amine solutions:**

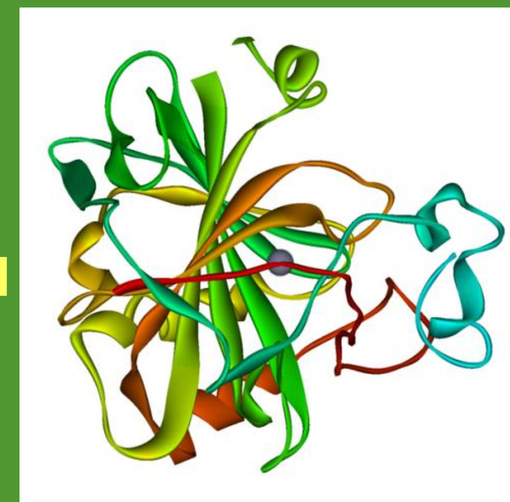
- **R1: $CO_2 + R_3N + H_2O \xrightarrow{k_{Am}} HCO_3^- + R_3NH^+$**
  - $R_{CO2} = k_{Am} \cdot c_{Am} \cdot c_{CO2} = k_{Am}' \cdot c_{CO2}$

- **R2: $CO_2 + OH^- \xrightarrow{k_{OH}} HCO_3^-$**
  - $R_{CO2} = k_{OH} \cdot c_{OH} \cdot c_{CO2} = k_{OH}' \cdot c_{CO2}$

- **R3: $CO_2 + 2\ H_2O \xrightarrow{k_{H2O}} HCO_3^- + H_3O+$**
  - $R_{CO2} = k_{H2O} \cdot c_{CO2}$

- **$k_{OV} = k_{Am}' + k_{OH}' + k_{H2O}$**

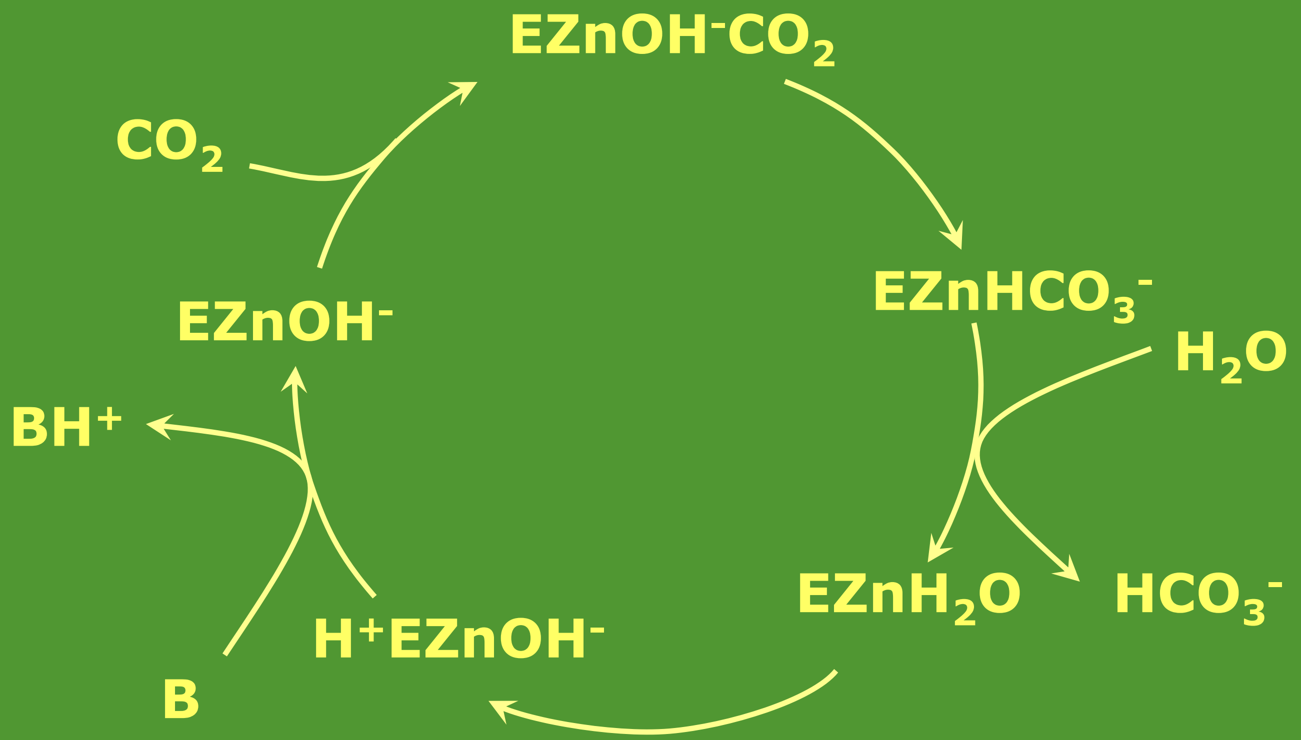
Carbonic anhydrase (CA)



- Is a group of zinc-metalloenzymes
- Is found in almost all living organisms
- Catalysis CO_2 hydration at high pH
- Catalysis HCO_3^- dehydration at low pH
- Has a pKa value of approx. 7.1
- Molecular weight ca 30 000 g/mol

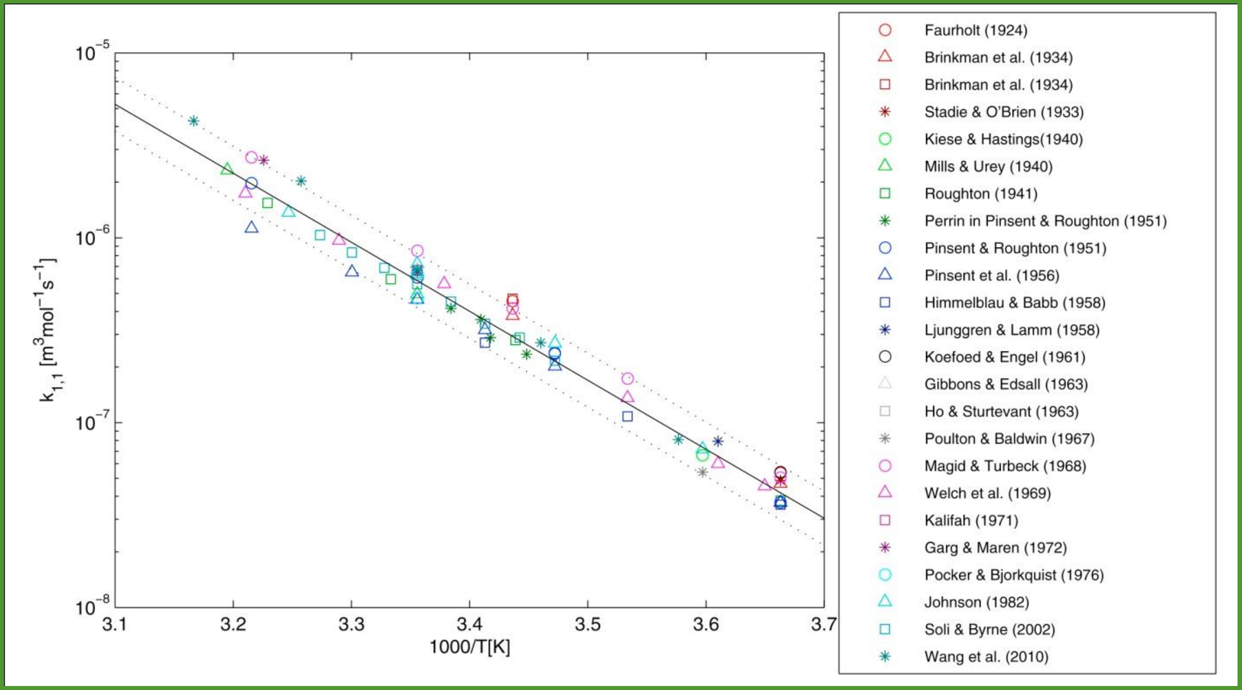
- CA II is most fast of all CA variants
- CA II is found in red blood cells
- CA II facilitates respiration

Mechanism of CO_2 hydration with CA



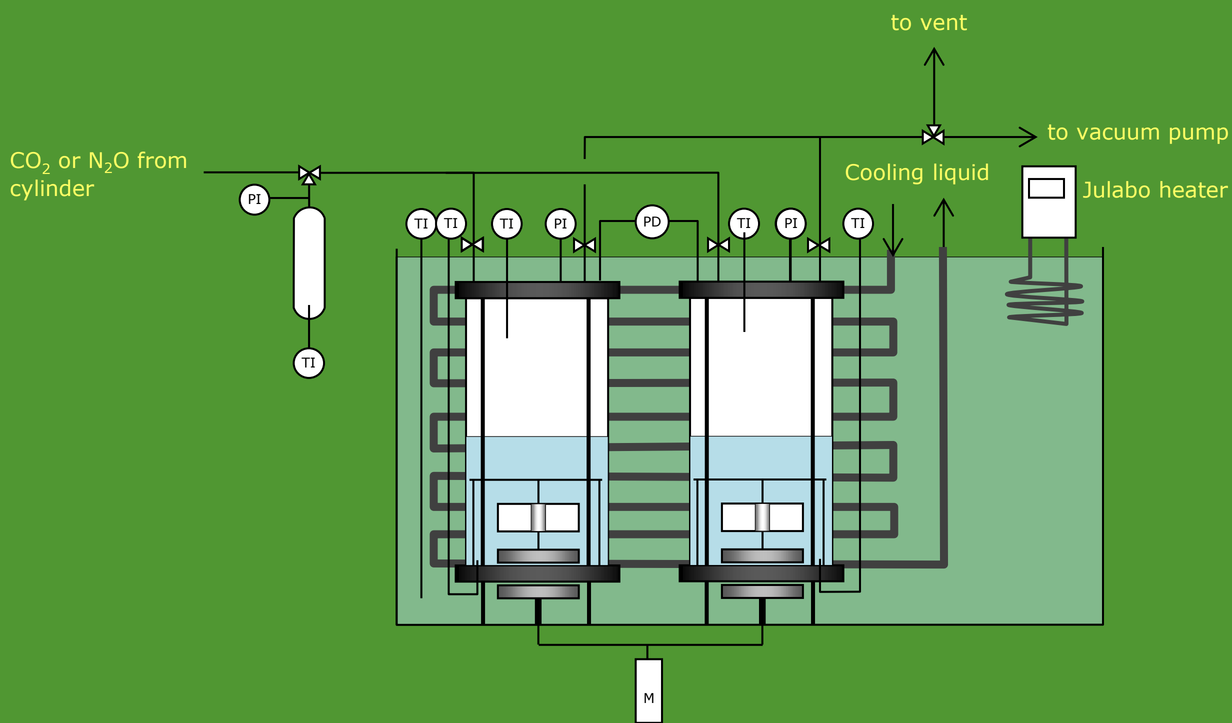
Uncatalysed CO_2 hydration

- CO_2 hydration actually 1st order in CO_2 <u>and</u> H_2O with: $k_{H2O} = 1.94 \cdot 10^6 \cdot \exp\left(\frac{-8590}{T}\right)$ (T< 318 K)



Set-up

- **Stirred Cell Contactor**



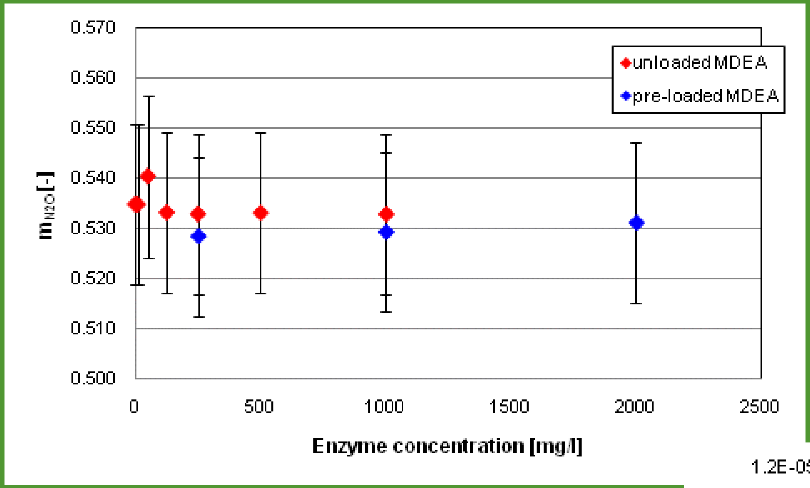
Features :

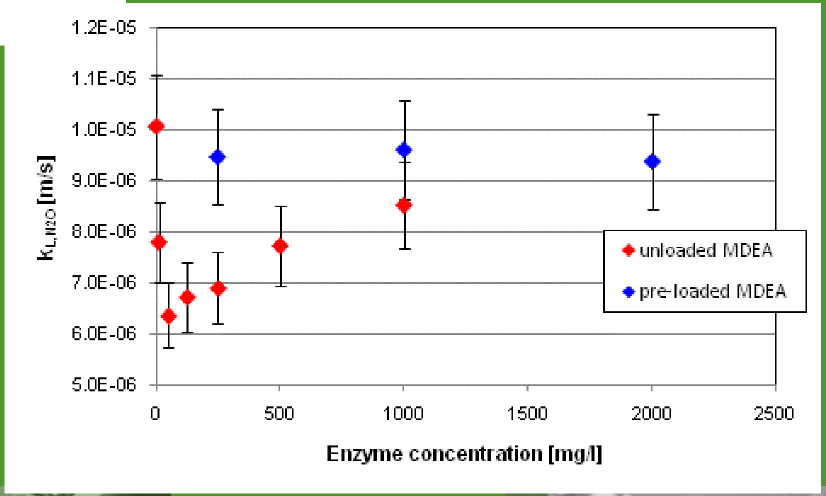
- Pressure readout
- Temperature readout
- Temperature control

- Liquid phase stirring
- Flat gas-liquid interface

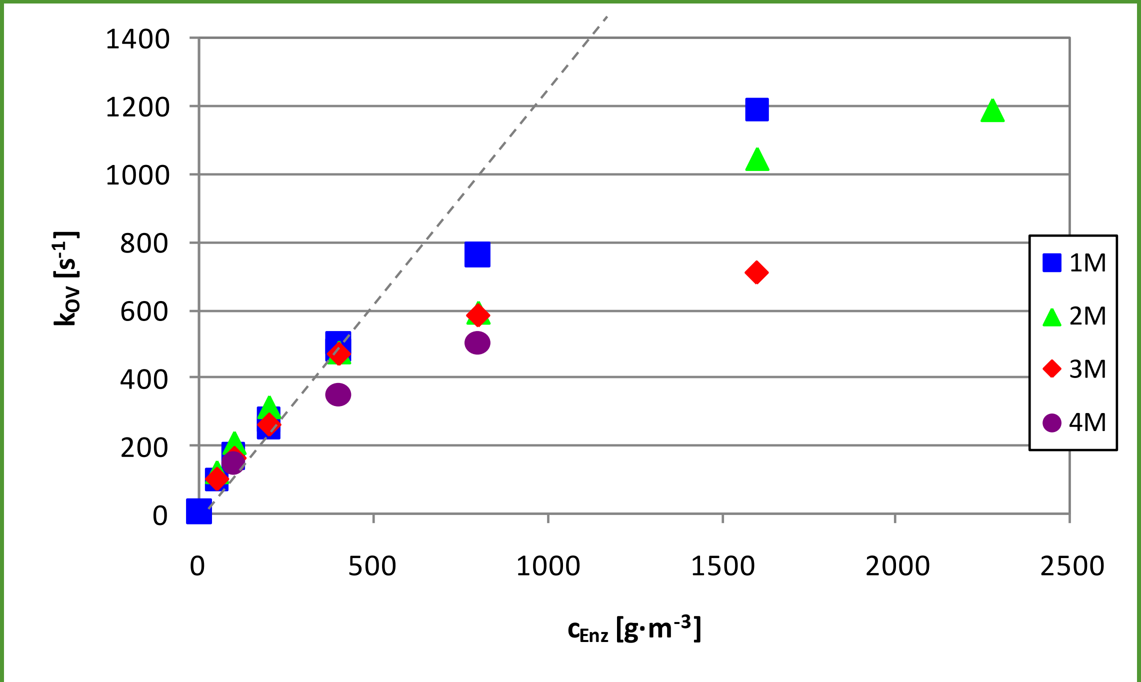
- Vacuum connection
- CO_2 / N_2O connection

Physical absorption





Absorption rate experiments

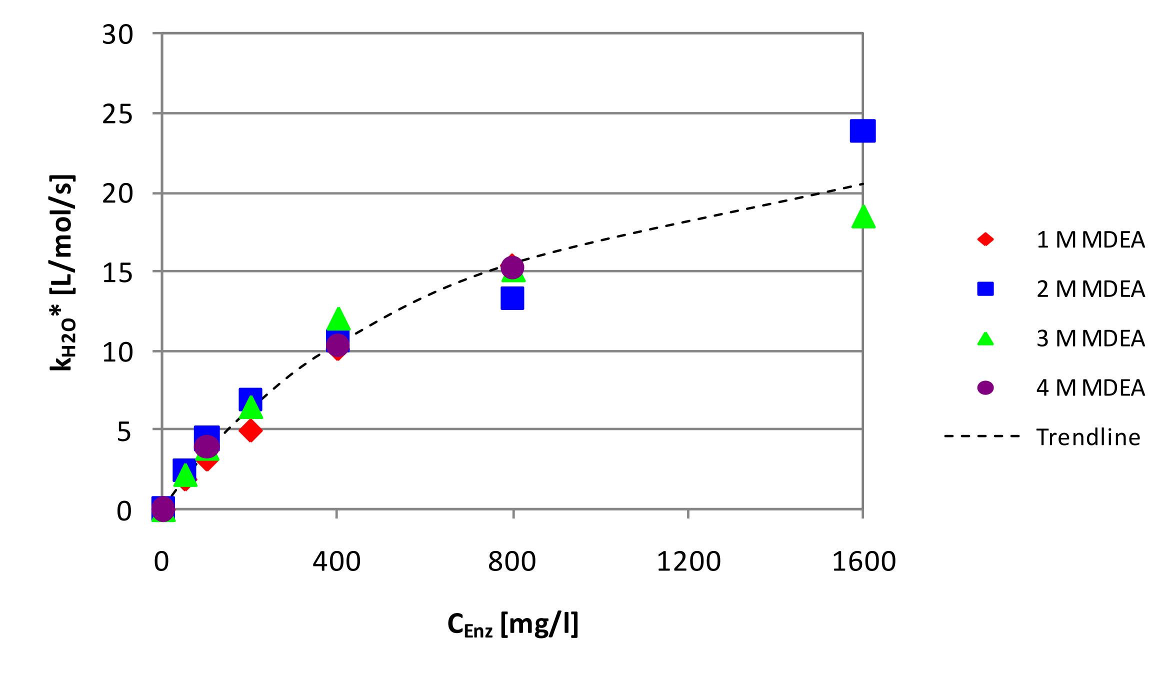


- Overall reaction rate increases with increasing enzyme concentration
  - At low enzyme concentration reaction rate linear dependent on enzyme concentration
  - At higher enzyme concentration rate increase levels off

Absorption rate experiments

- k_{H2O}* is calculated as:

$$k^*_{H2O} = \frac{k_{OV,with\ CA} - k_{OV,without\ CA}}{C_{H2O}}$$

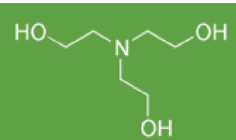
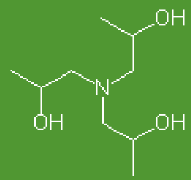
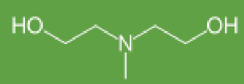


$$k^*_{H2O} = \frac{k^*_3 C_{Enzyme}}{1 + k^*_4 C_{Enzyme}}$$

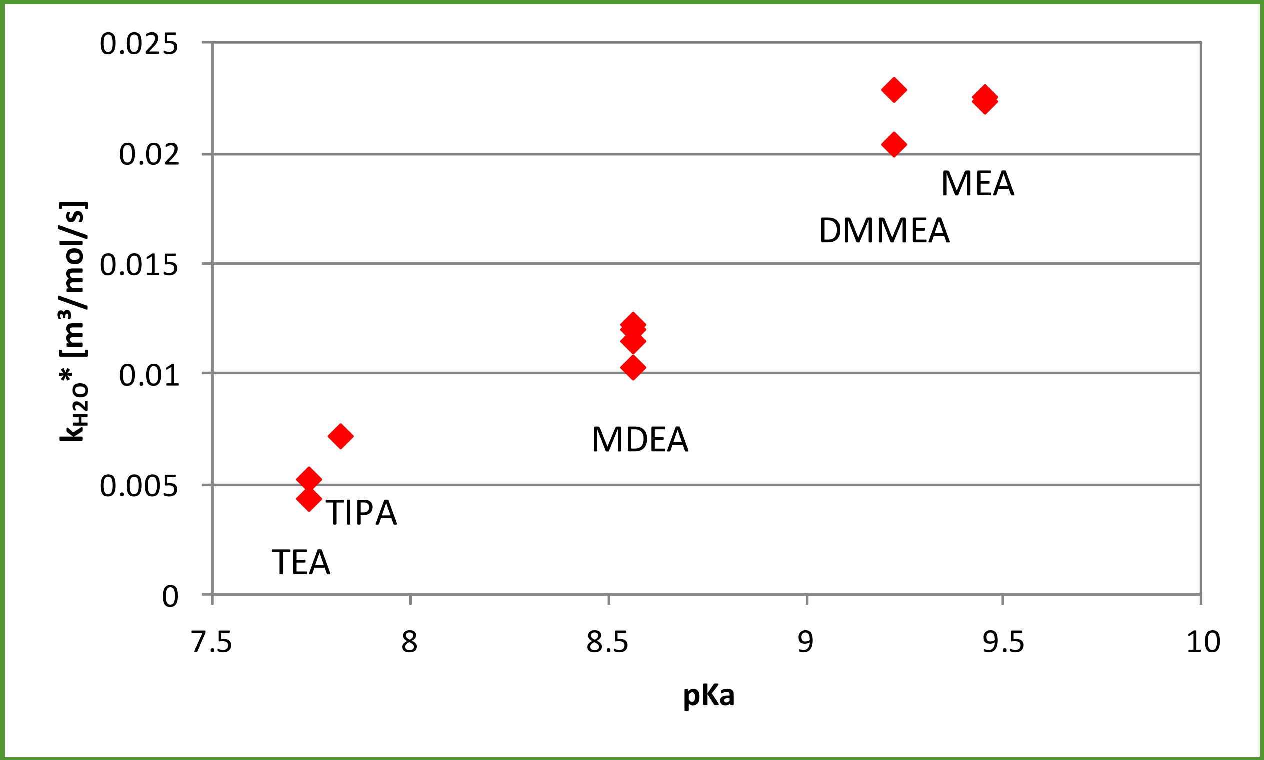
- Catalyzed reaction is independent of MDEA concentration
- Catalyzed reaction is first order in water

⇨ Reaction 3 is enhanced by enzyme

pKa effect

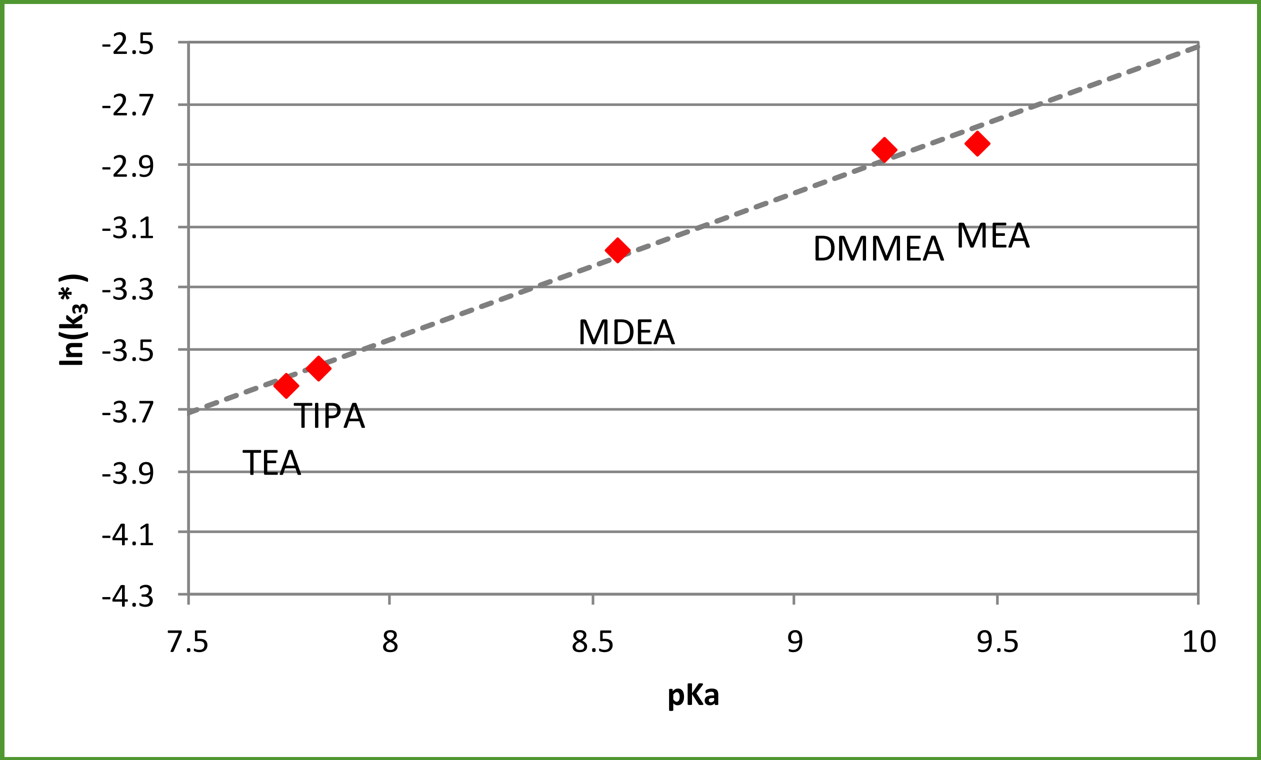
Amine	Structure	MW [g/mol]	C_{H2O} @ 1 M Am [kmol/m³]	pKa
TEA		149.19	48.3	7.74
TIPA		191.27	45.5	7.82
MDEA		119.16	49.3	8.56
DMMEA		89.14	50.1	9.22
MEA		61.08	52.1	9.45

pKa effect



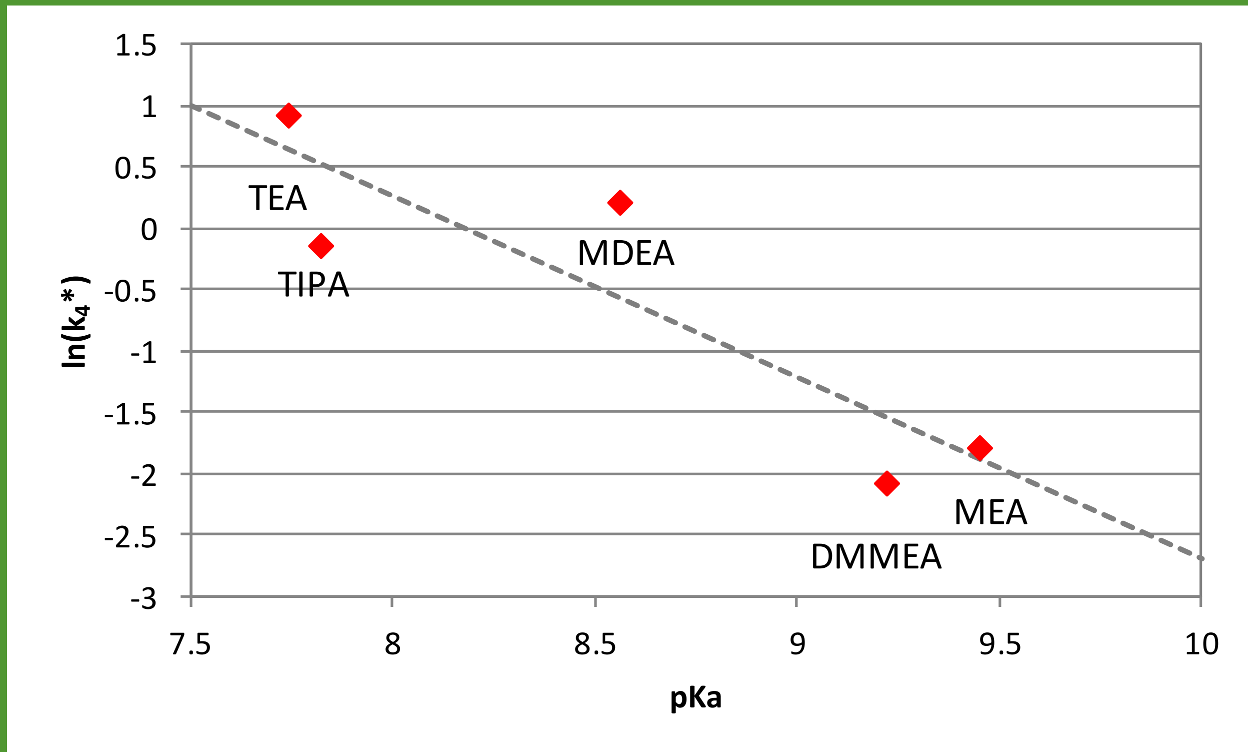
pKa value of amine has large influence on k_{H2O}*

pKa effect



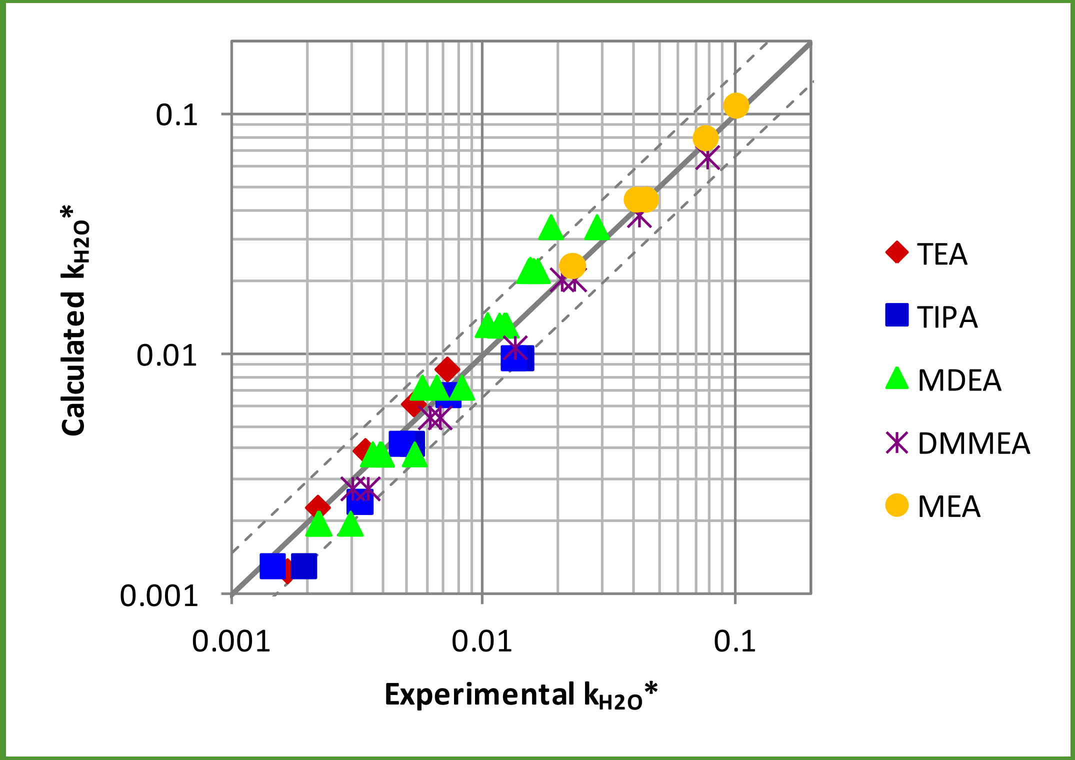
$$k_3^* = 6.7 \cdot 10^{-4} \exp(0.48 \cdot pKa) \quad [m^6 kg^{-1} mol^{-1} s^{-1}]$$

pKa effect



$$k_4^* = 1.8 \cdot 10^5 \exp(-1.5 \cdot pKa) \quad [m^3 kg^{-1}]$$

pKa effect



$$k_{H2O}^* = \frac{6.7 \cdot 10^{-4} \exp(0.48 \cdot pKa) \cdot C_{Enzyme}}{1 + 1.8 \cdot 10^{5} \exp(-1.5 \cdot pKa) \cdot C_{Enzyme}}$$

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Temperature effect

Amine	278	283	288	298	308	313
TEA				7.74	7.55	
TIPA	8.18		7.99	7.82	7.62	
MDEA	8.98		8.76	8.56	8.36	
DMMEA	9.65	9.54		9.22	9.02	8.92
AMP		10.1		9.69		9.25
Na_2CO_3 K_2CO_3		10.5		10.3		10.2

Temperature effect

- **Temperature dependent Brønsted relation:**

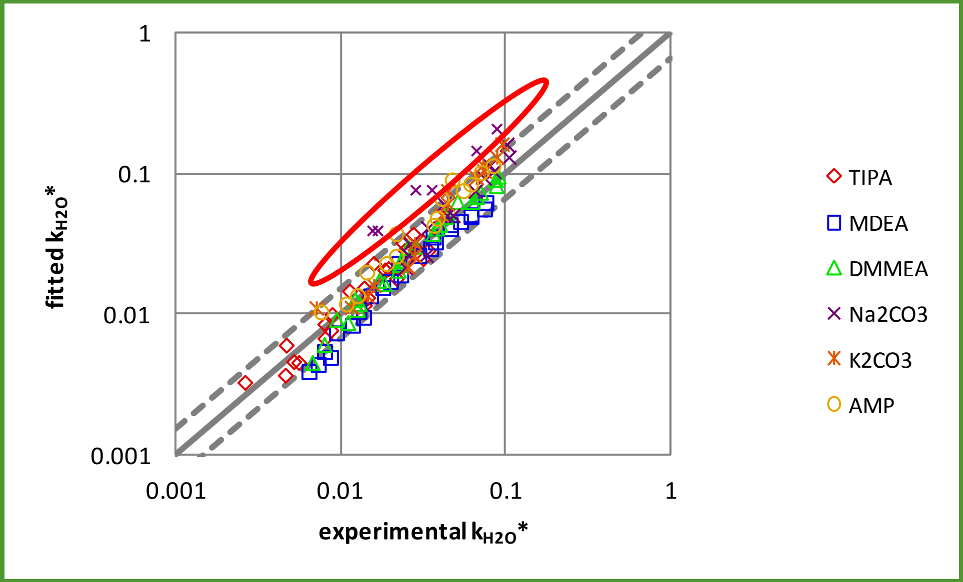
$$\ln(k) = A \cdot pKa + B + \frac{C}{T}$$

- **Fit on only data tertiary amines:**

	A	**B**	**C**
k_3*	0.16	-0.20	-1240
k_4*	-0.88	1.00	1740

Temperature effect

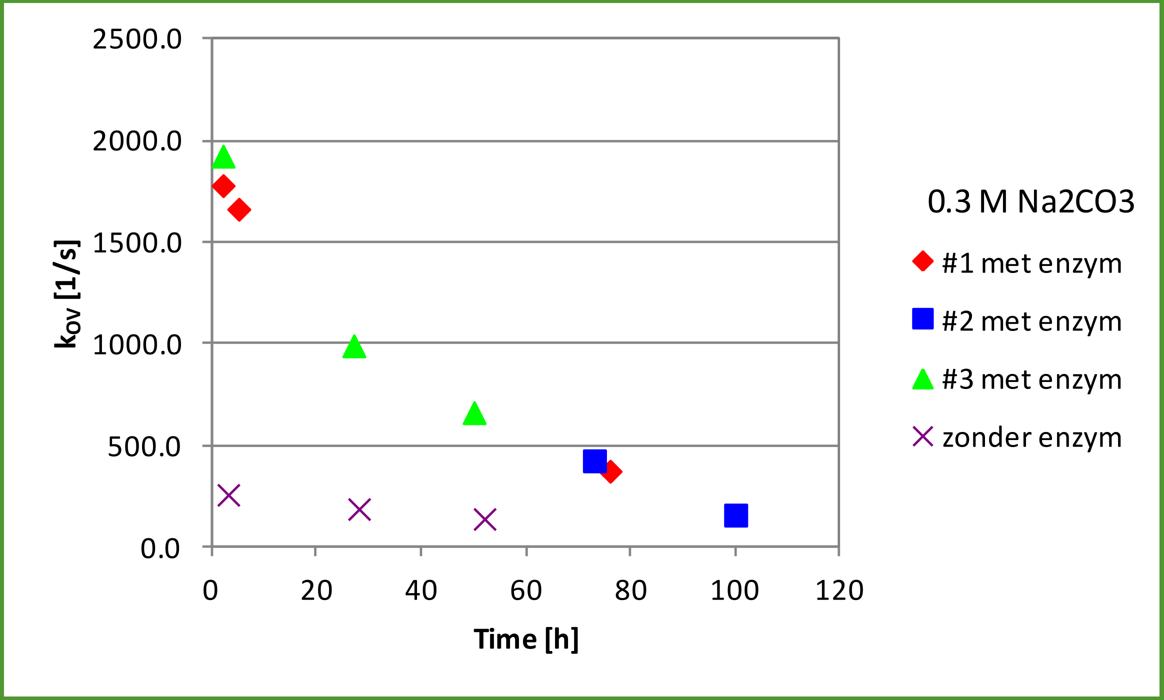
- **Fit compared to data all examined solvents:**



- **Data Na_2CO_3 at 333 K deviates from fit due to deactivation of CA**

Carbonate solutions – Na_2CO_3

- **Enzyme stability at 333 K**

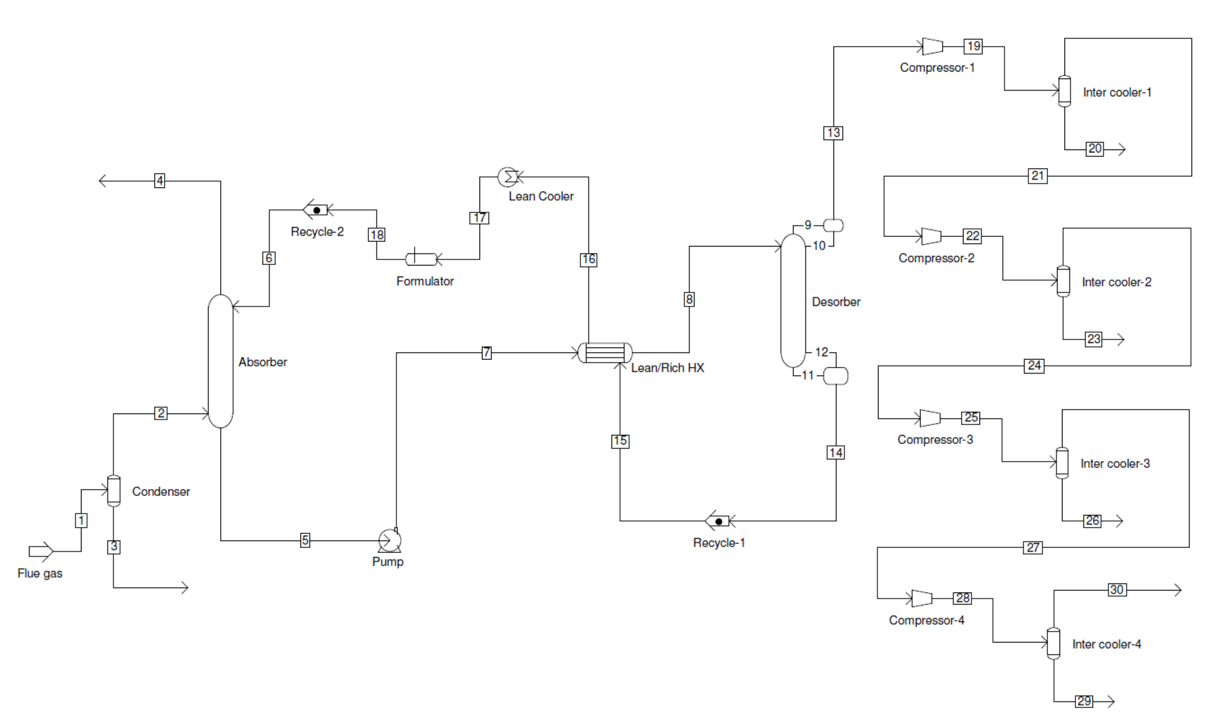


P R O C E D E

Base case

- **NETL report case 12**
  - Gerder et al. (2010) 'Cost and performance baseline for fossil energy plants – volume 1: Bituminous coal and natural gas to electricity' Revision 2, Technical report DOE/NETL-2010/1397, National Energy Technology Laboratory

- **PPS flowsheet:**

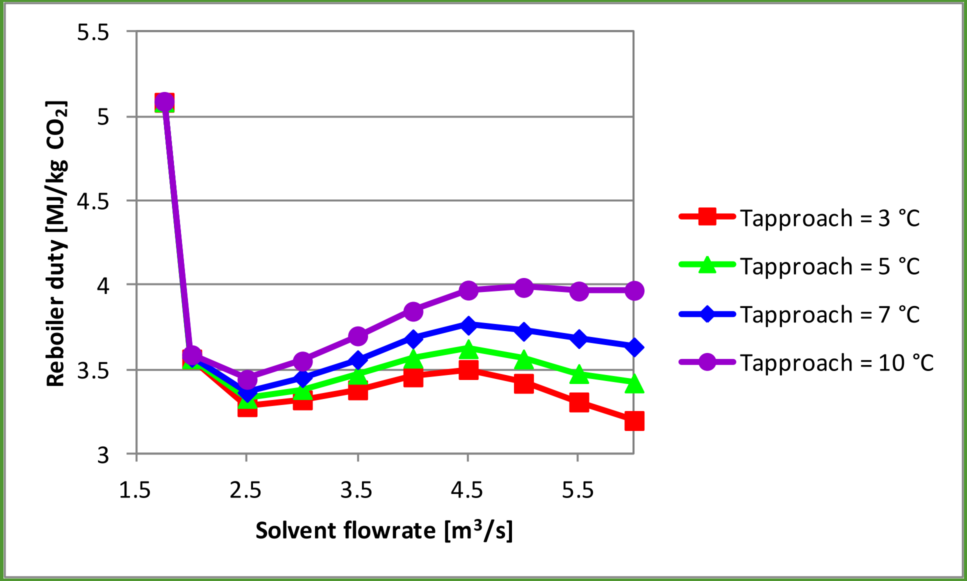


Base case - input

Solvent	30 wt% MEA	
Flue gas	Temperature Pressure Flow (mass)	331 K 1 bar 821.18 kg/s
	Composition:	
	CO_2 H_2O Ar N_2 O_2	13.50 mol% 15.37 mol% 0.81 mol% 67.94 mol% 2.38 mol%
Absorber parameters	Diameter Height Packing type CO_2 capture efficiency	20 m 30 m Sulzer Metal BX 90 %
Stripper parameters	Diameter Height Packing type Condensor temperature Stripper pressure	20 m 10 m Sulzer Metal BX 313 K 2 bar
Lean solvent cooler	Temperature	313 K

Base case - results

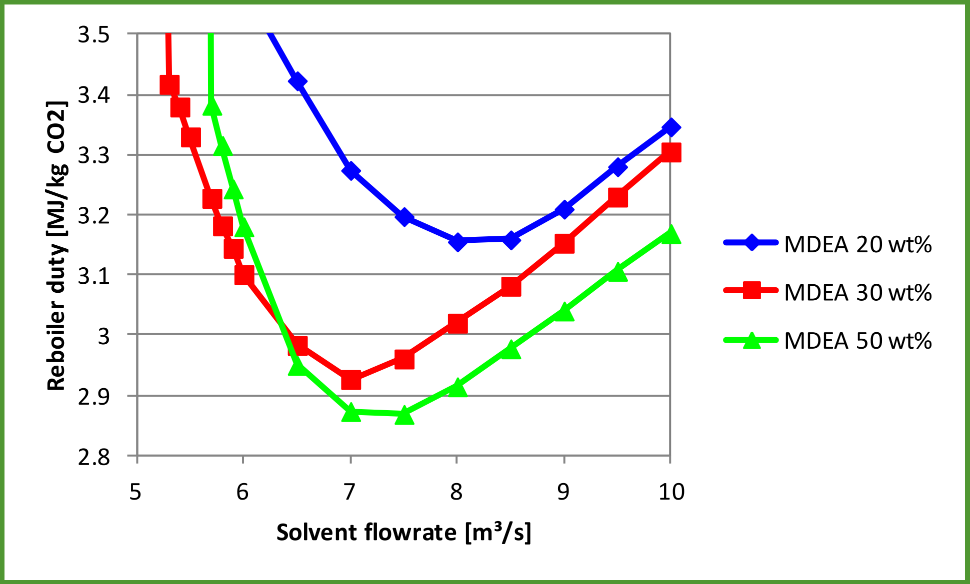
- **NETL-report case 12: reboiler duty = 3.56 MJ/kg CO_2**



- **Reboiler duty 3.57 MJ/kg CO_2 if:**
  - Temperature approach = 5 K and
  - Solvent flowrate = 4 m^3/s

MDEA with enzymes

- **Reboiler duty vs. solvent flow**



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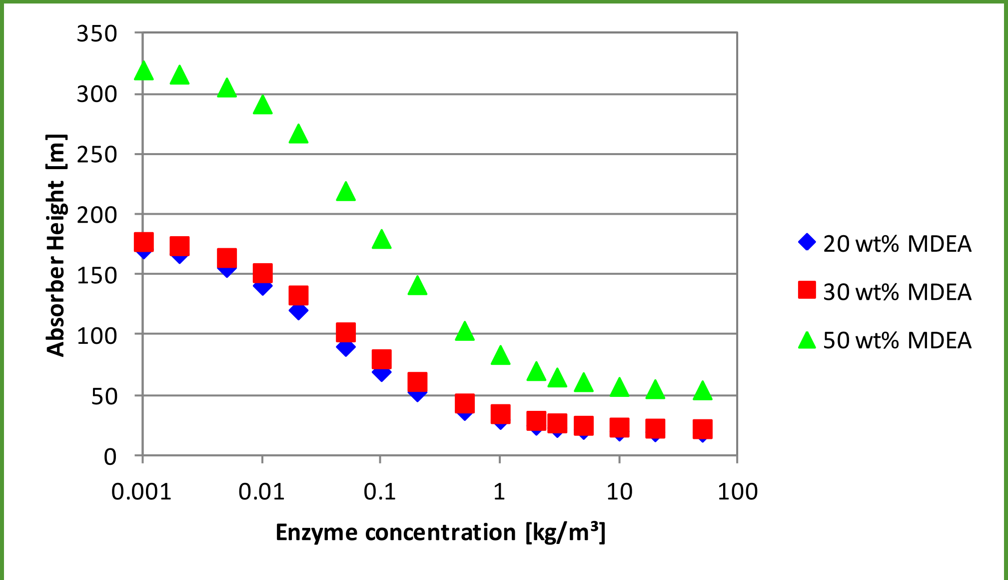
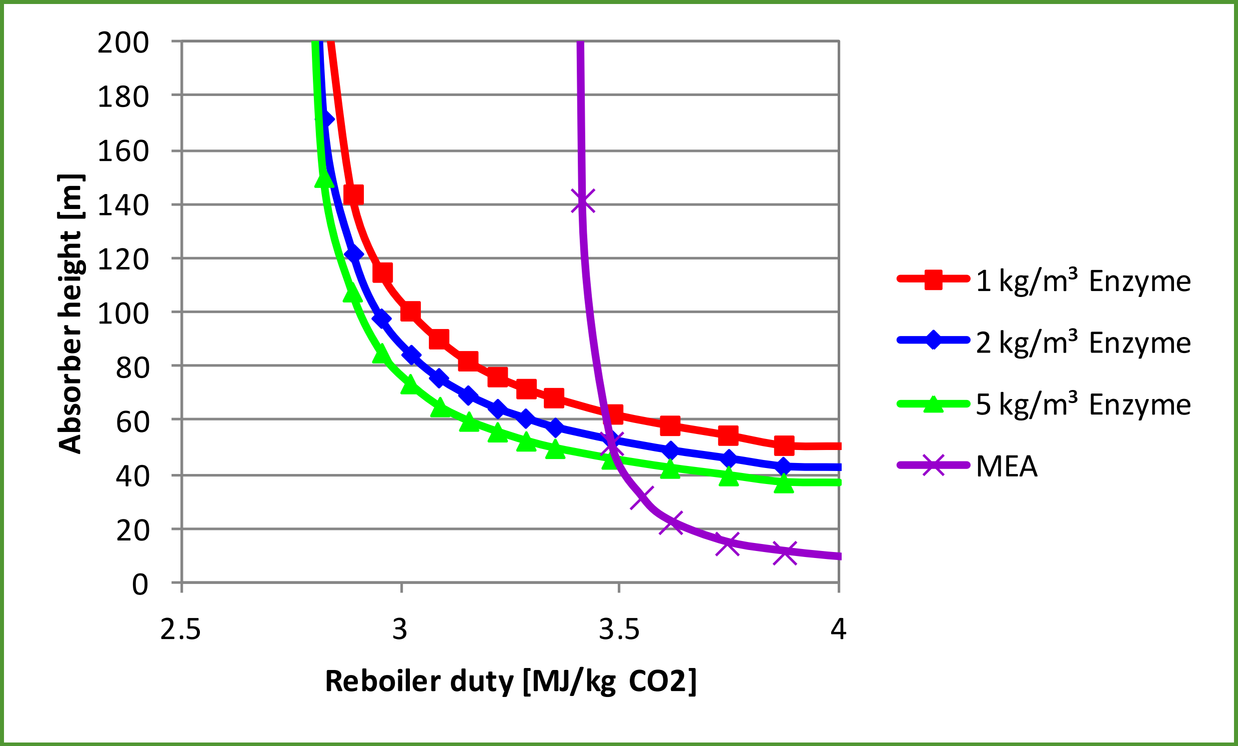
MDEA with enzymes

- **Absorber height vs. enzyme concentration**



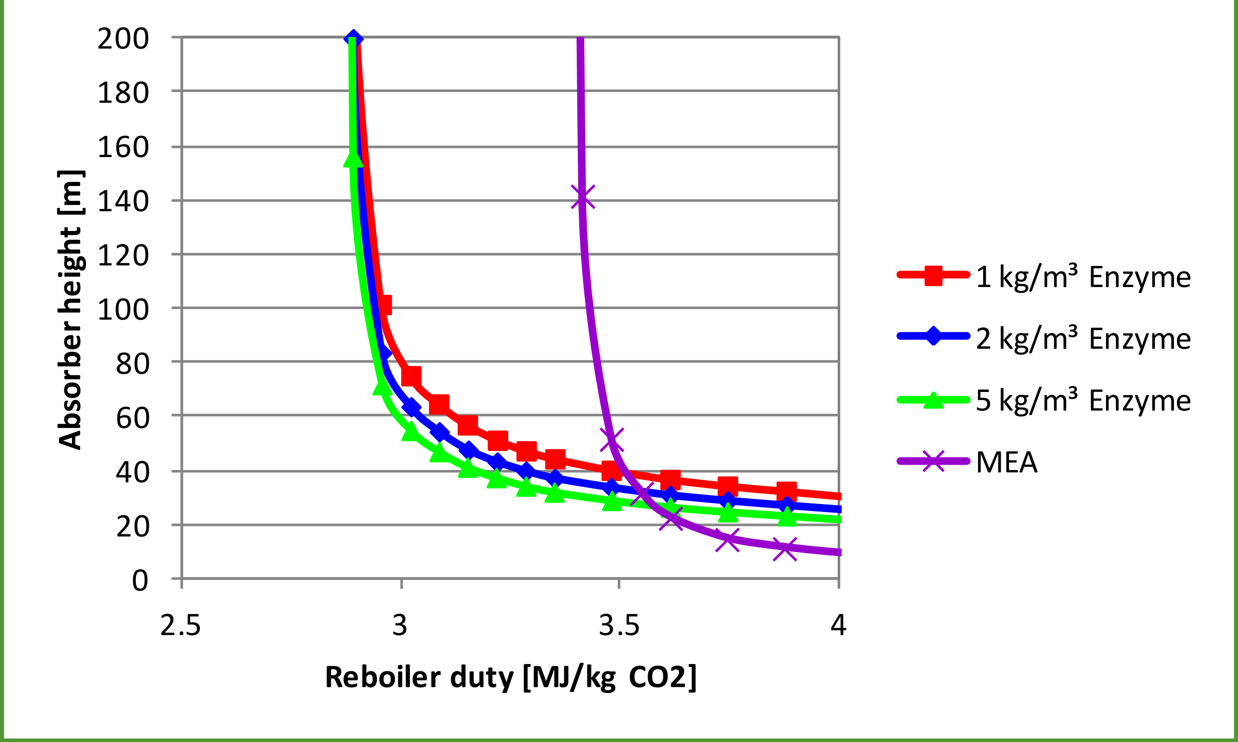
MDEA with enzymes vs. MEA

- **Absorber height vs. reboiler duty**
  - For 50 wt% MDEA



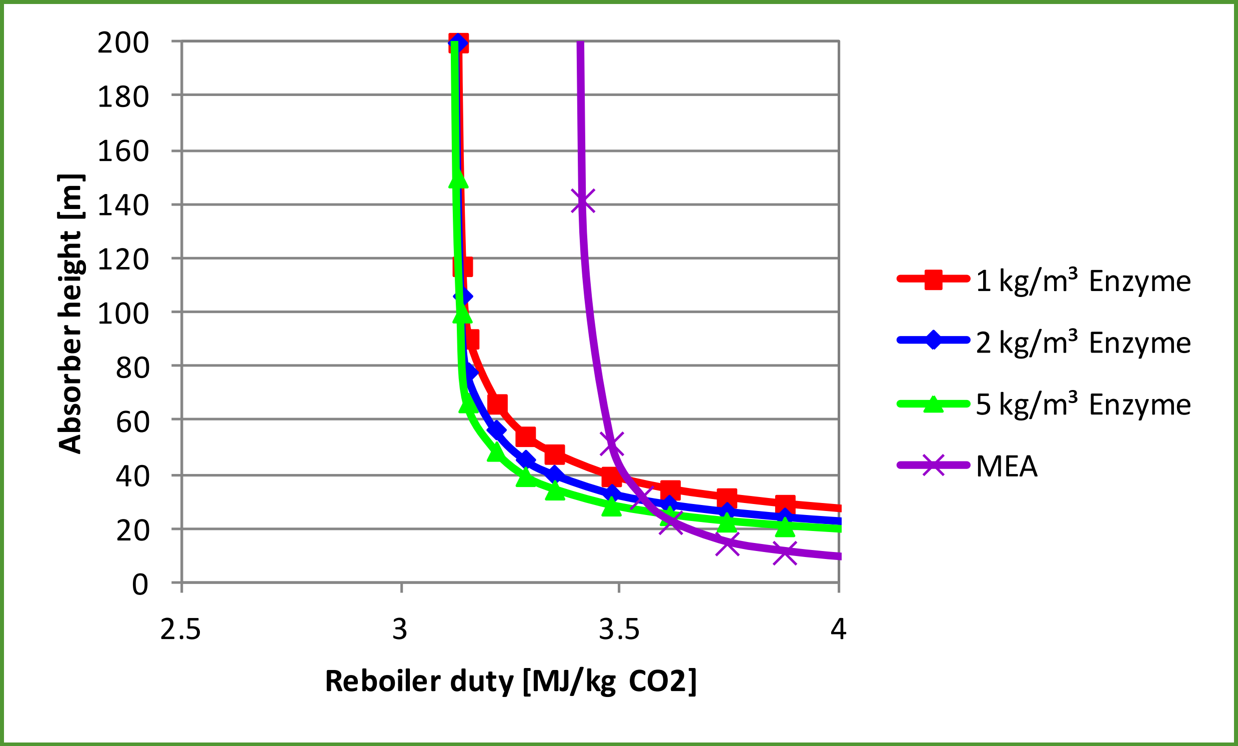
MDEA with enzymes vs. MEA

- **Absorber height vs. reboiler duty**
  - For 30 wt% MDEA



MDEA with enzymes vs. MEA

- **Absorber height vs. reboiler duty**
  - For 20 wt% MDEA



Conclusions

- **Physical absorption:**
  - Enzyme has no effect on m_{N2O}
  - Enzyme decreases k_L of unloaded solutions. This effect is less significant when the solution is partially loaded

- **Absorption rate experiments:**
  - Enzyme has no effect on k_{Am}'
  - k_{H2O}^* is mainly determined by the enzyme concentration; amine and water concentration seem to have little effect on reaction rate
  - pKa value proton acceptor has a large effect on reaction rate
  - Enzyme decreases activation temperature significantly
  - At temperatures higher than 40 °C the enzyme activity decreases

Conclusions

- **Simulations:**
  - Combination MDEA+CA reduces reboiler duty significantly compared to MEA
  - More active enzymes required to reduce both reboiler duty and absorber height