Mass transfer of CO_2 in Activated MDEA for CO_2 Capture from Natural Gas

PCCC4

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Presentation outline:

- Introduction
- Objectives
- CO_2 pilot plant process diagram
- Operating conditions
- Results and Discussion
- Conclusions

Introduction:

- 85% of energy production comes from fossil fuels.
- Natural gas is one of the fossil fuels.
- Natural gas contains acid gases such as H_2S, CO_2, etc. which need to be removed:

  To protect the environment from gas emissions.

  To satisfy the specification for transporting and selling natural gas.

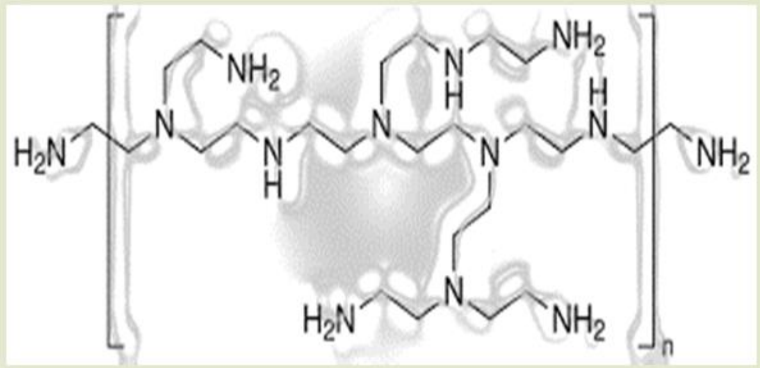
  (Alcheikhhamdon, and Hoorfar, 2016) .
- Absorption process is widely used for gas sweetening using activated MDEA.
- (MDEA is typically blended with MEA, DEA ,PZ).
- MDEA is selective for H_2S.
- PZ is considered to be bad for the environment and need to find better solvent than PZ.

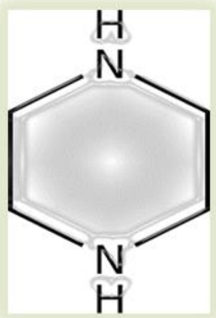
  (Chakravarty et al., 1985).

Activators selected for use in this study:- based on structure

- Polyamines are good activator as they have many amino groups available to react with CO_2:

- Polyethylenimine [PEI] branched
- Tetraethylenepentamine [TEPA] - linear
- Piperazine [PZ] – cyclic
- 3 M MDEA blending with 0.1 and
- 0.3 M activator

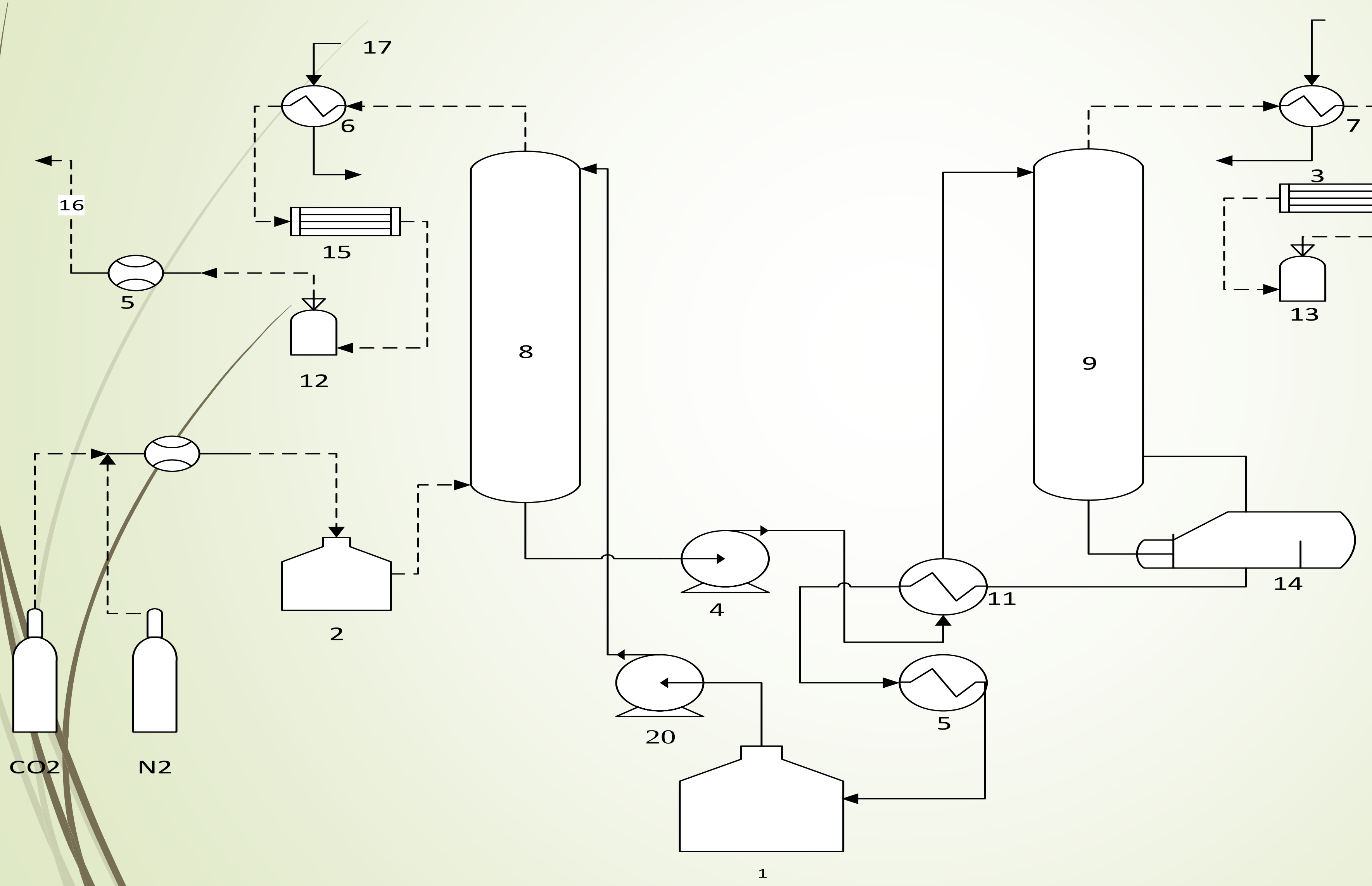




Objectives:

- To evaluate the performance of MDEA activated with PEI-B, TEPA and PZ in terms of:
- - cyclic capacity
- - concentration profile
- - temperature profile
- To evaluate the overall mass transfer coefficient of CO_2 absorption (gas phase) and desorption (liquid phase) in MDEA activated with PEI-B, TEPA and PZ.

CO_2 capture pilot plant process diagram:



1 Feed tank
2 Saturator
12,13 Desiccant
5 Mass Flow meter
16 Off gas
17 , 18 Cooling water
15,3 Condenser
5, 6, 7 Cooler
8 Absorber Column
20 lean Amine Pump
4 Rich Amine Pump
11 heat Exchanger
14 Reboiler
9 Desorber
10 Product CO_2 Rotameter
19 CO_2 product

Operating Conditions:

- Total gas flow rate 25SL/min
- Amine flow rate 60ml/min.
- CO_2 content is 20,50, 100%.
- Total pressure as 101.3 kpa.
- Temperature of absorber in 20 ˚C
- Temperature of the desorber in 120 ˚C
- Absorber packing type in the absorber is structured packing.
- Absorber packing type in the desorber is random packing.
- total height of the column = 1.0668 m

Possible products polyamine (PEI-B) reaction with CO_2

For primary amino groups:

$PEI + CO_2 + H2O \longrightarrow PEI\ (COO)^{-}_{(P)} + H3O^{+}$

$PEI\ (COO)^{-}_{(P)} + CO2 + H2O \longrightarrow PEI\ (COO)_2{}^{2-}{}_{(2P)} + H3O^{+}$

$PEI\ (COO)^{2-}{}_{2(2P)} + CO2 + H2O \longrightarrow PEI\ (COO)^{3-}{}_{3(3P)} + H3O^{+}$

$PEI\ (COO)^{3-}{}_{3(3P)} + CO2 + H2O \longrightarrow PEI\ (COO)^{4-}{}_{4(4P)} + H3O^{+}$

$PEI\ (COO)^{4-}{}_{4(4P)} + CO2 + H2O \longrightarrow PEI\ (COO)^{5-}{}_{5(5P)} + H3O^{+}$

$PEI\ (COO)^{5-}{}_{5(5P)} + CO2 + H2O \longrightarrow PEI\ (COO)^{6-}{}_{6(6P)} + H3O^{+}$

Secondary amino groups:

$PEI + CO_2 + H2O \longrightarrow PEI\ (COO)^{-}_{(s)} + H3O^{+}$

$PEI\ (COO)^{-}_{(s)} + CO2 + H2O \longrightarrow PEI\ (COO)_2{}^{2-}{}_{(2s)} + H3O^{+}$

$PEI\ (COO)^{2-}{}_{2(2s)} + CO2 + H2O \longrightarrow PEI\ (COO)^{3-}{}_{3(3s)} + H3O^{+}$

$PEI\ (COO)^{3-}{}_{3(3s)} + CO2 + H2O \longrightarrow PEI\ (COO)^{4-}{}_{4(4s)} + H3O^{+}$

$PEI\ (COO)^{4-}{}_{4(4s)} + CO2 + H2O \longrightarrow PEI\ (COO)^{5-}{}_{5(5s)} + H3O^{+}$

$PEI\ (COO)^{5-}{}_{5(5s)} + CO2 + H2O \longrightarrow PEI\ (COO)^{6-}{}_{6(6s)} + H3O^{+}$

Primary and secondary amino groups
The possible products

PEI $(COO)_2{}^{2-}{}_{(1p1s)}$, PEI $(COO)_3{}^{3-}{}_{(1p2s)}$, PEI $(COO)_4{}^{4-}{}_{(p3s)}$, PEI $(COO)_5{}^{5-}{}_{(p4s)}$, PEI $(COO)_6{}^{6-}{}_{(p5s)}$, PEI $(COO)_7{}^{7-}{}_{(p6s)}$,

PEI $(COO)_3{}^{3-}{}_{(2p1s)}$, PEI $(COO)_4{}^{4-}{}_{(3p1s)}$, PEI $(COO)_5{}^{5-}{}_{(4p1s)}$, PEI $(COO)_6{}^{6-}{}_{(5p1s)}$, PEI $(COO)_7{}^{7-}{}_{(6p1s)}$,.............................

PEI $(COO)_{12}{}^{12-}{}_{(6p6s)}$

Reaction of Tertiary amino groups and MDEA with CO_2

$MDEA + CO2 + H2O \longrightarrow MDEAH^+ + HCO_3^-$

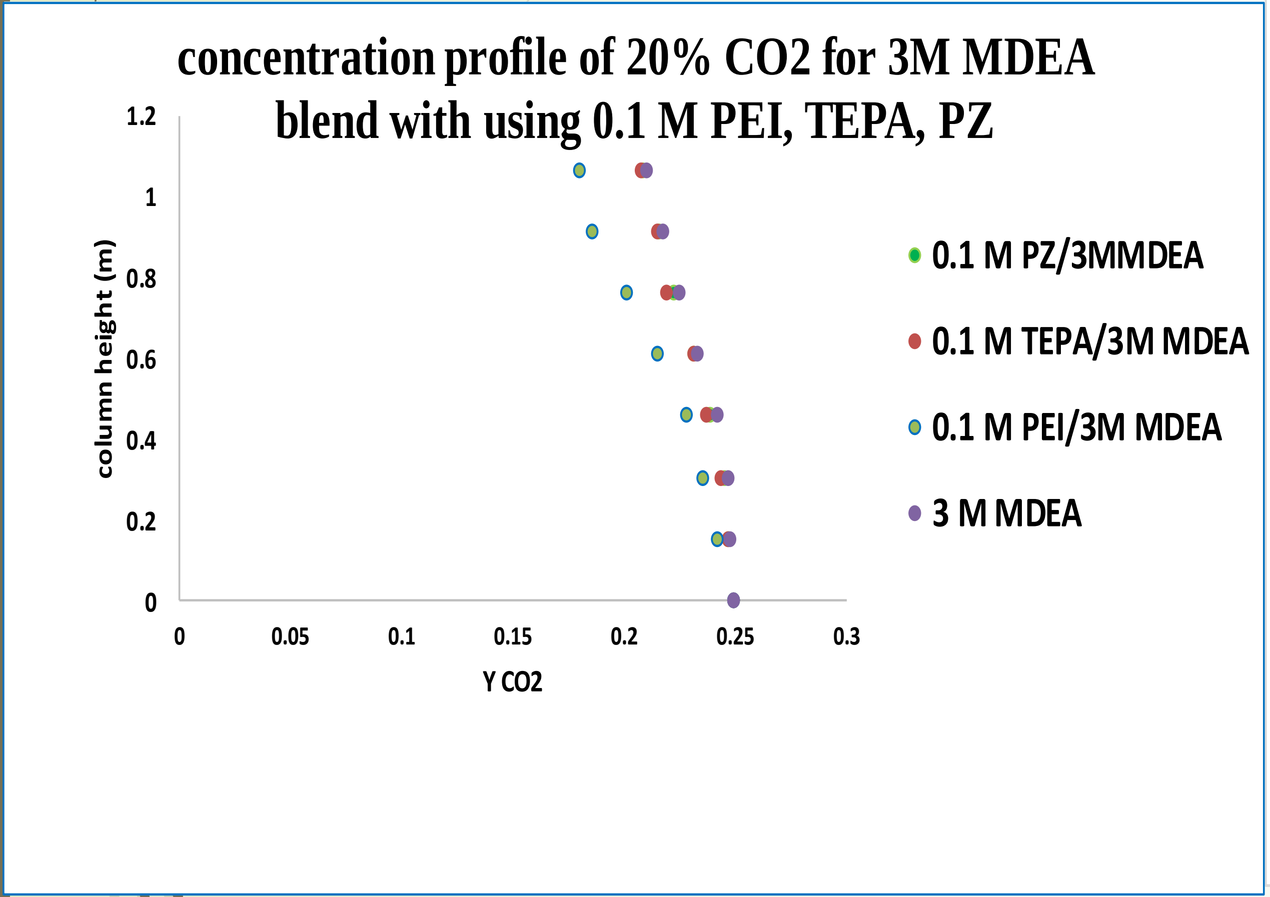
$PEI + CO2 + H2O \longrightarrow PEIH^+ + HCO_3^-$

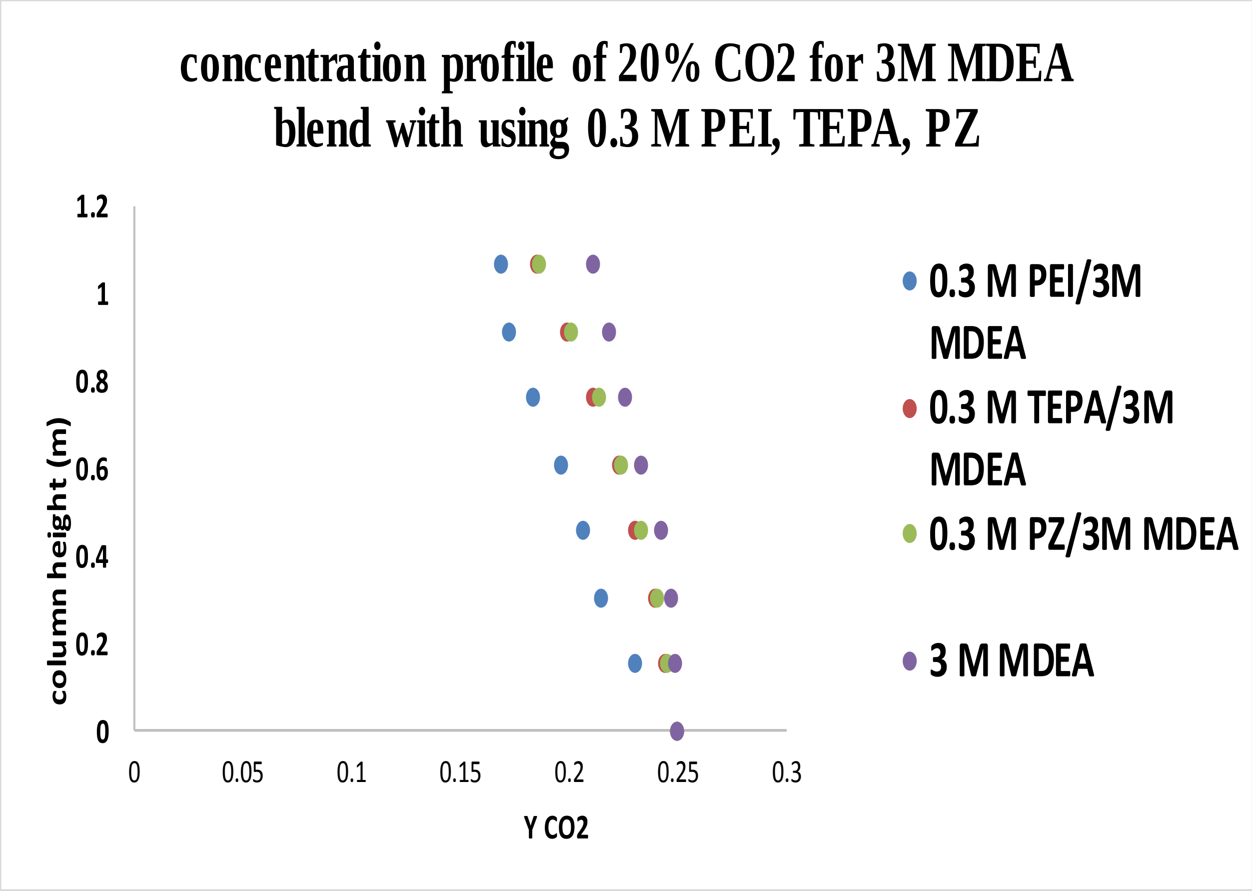
$PEIH^+ + CO2 + H2O \longrightarrow PEIH_2^{2+} + HCO_3^-$

$PEIH_2^{2+} + CO2 + H2O \longrightarrow PEIH_3^{3+} + HCO_3^-$

$PEIH_3^{3+} + CO2 + H2O \longrightarrow PEIH_4^{4+} + HCO^-_3$

Results and discissions: Concentration profile (20% CO_2)

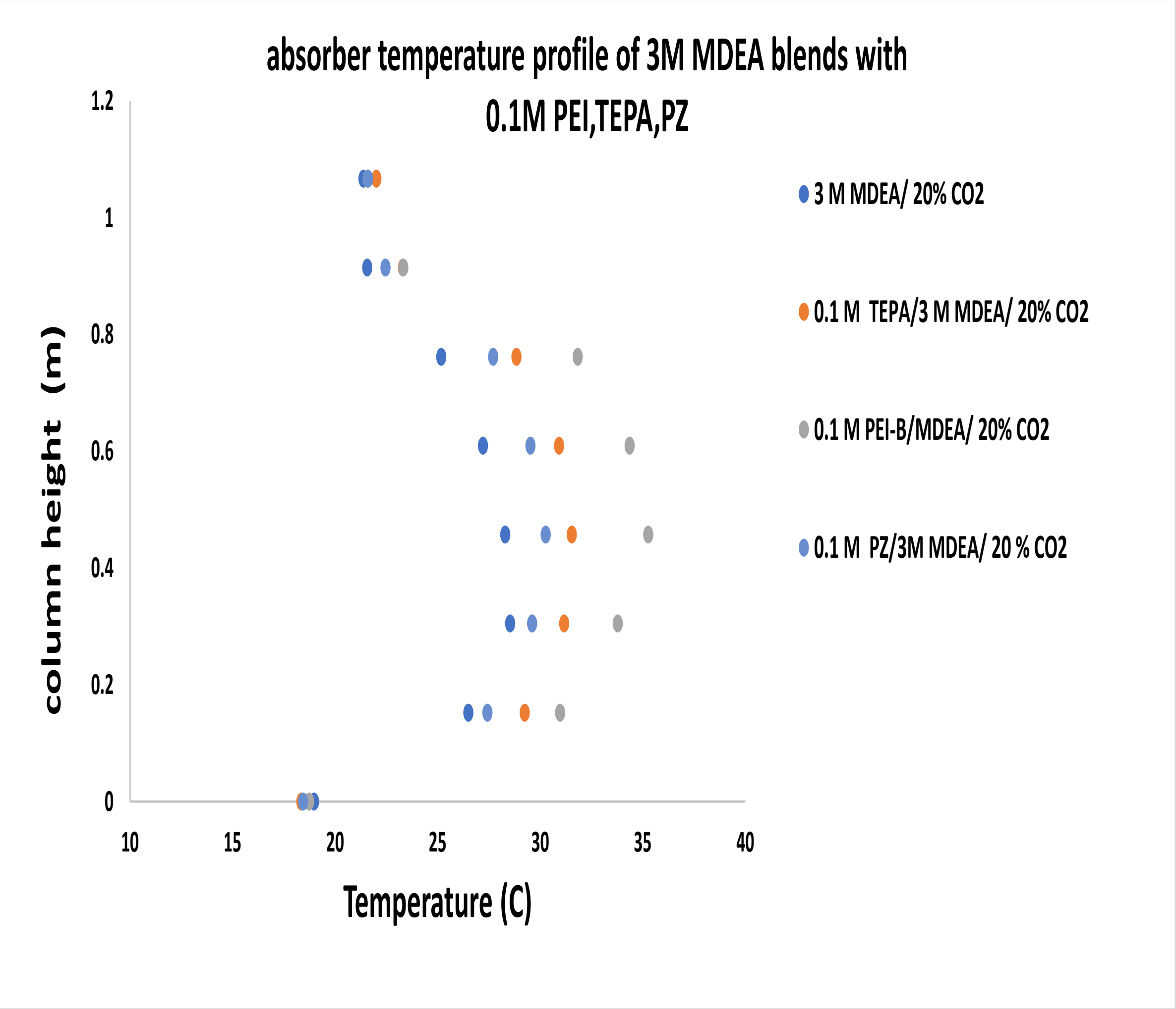


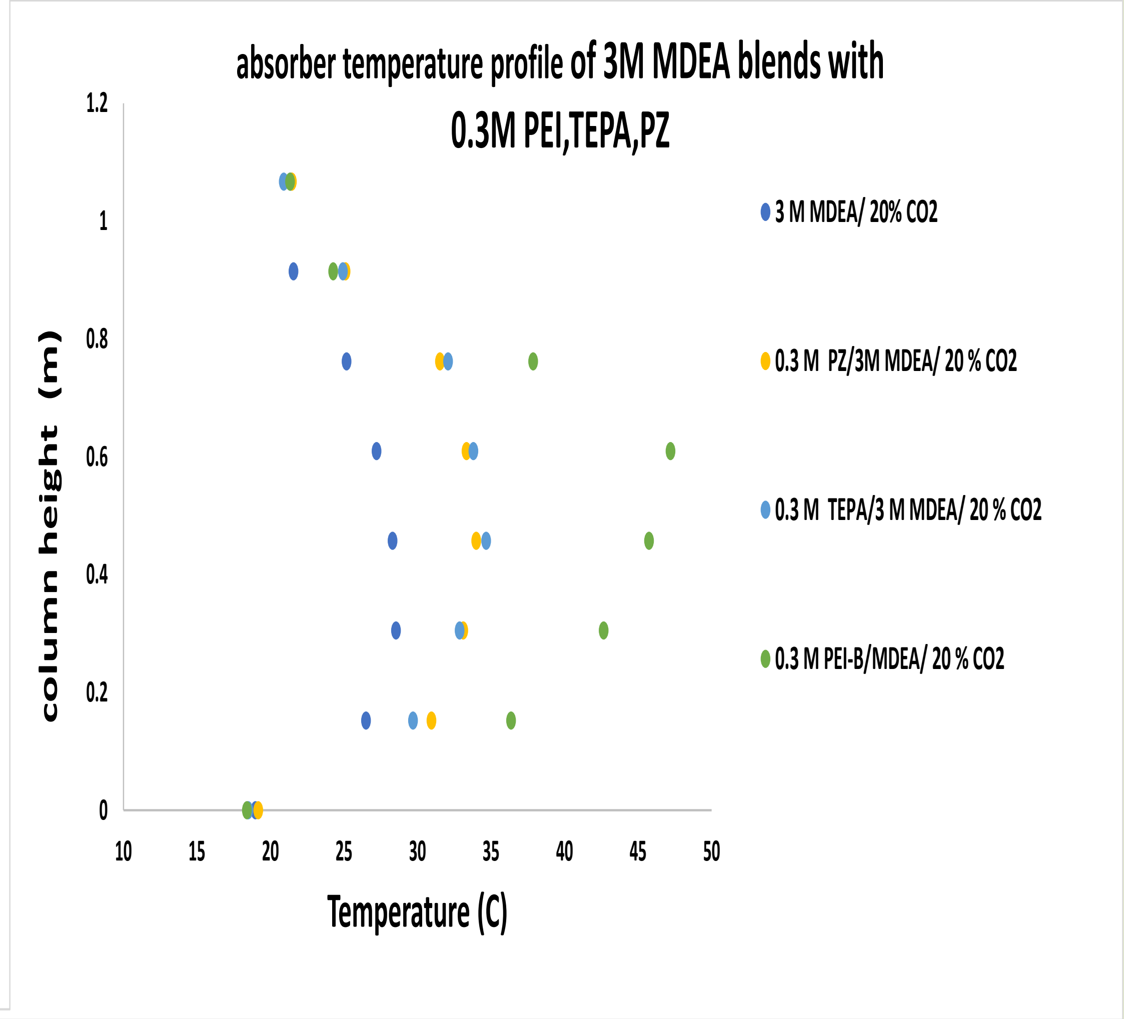


MDEA/PEI-B > MDEA/TEPA >MDEA/PZ > 3 M MDEA.

Results and discussion:

Absorber temperature profile:





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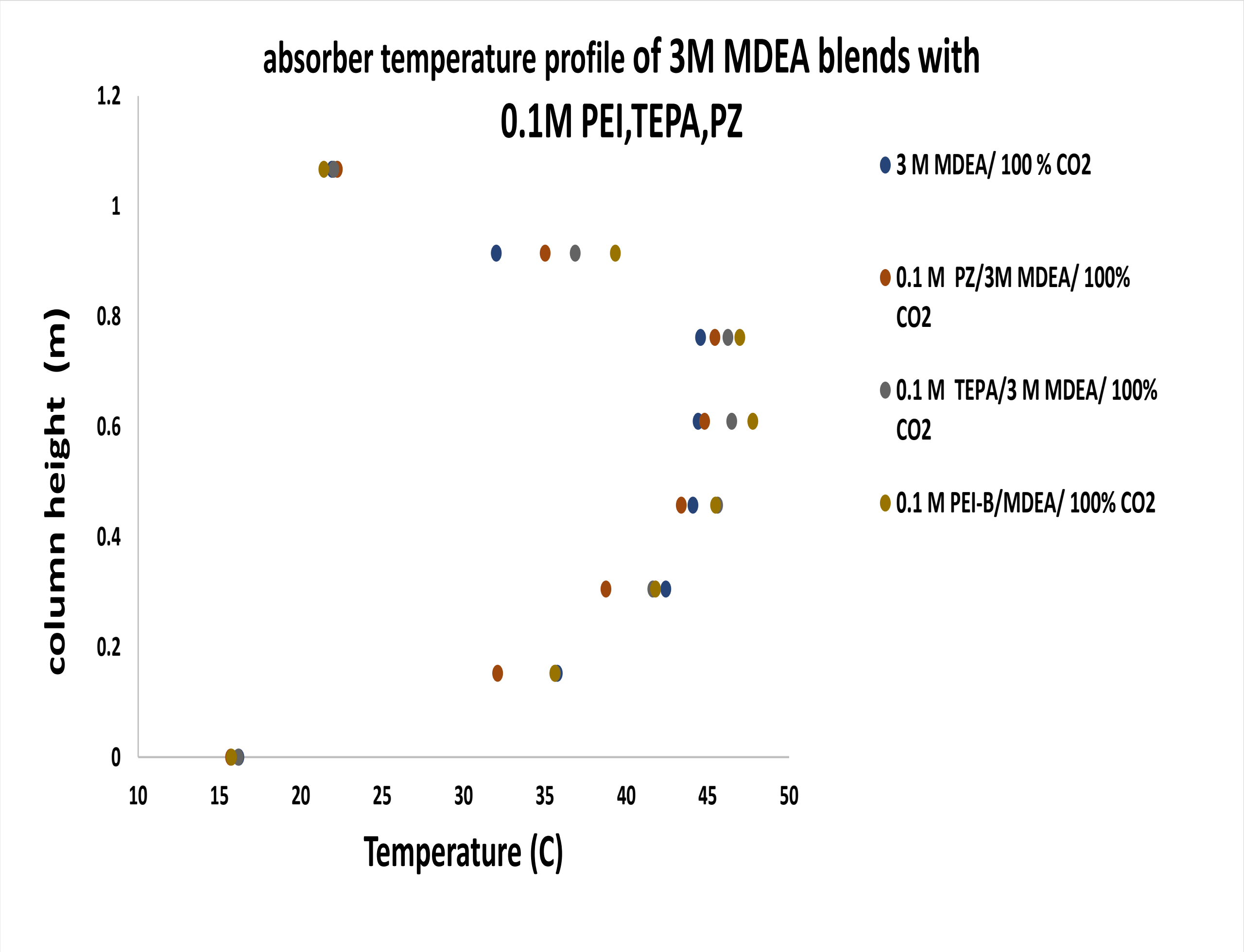
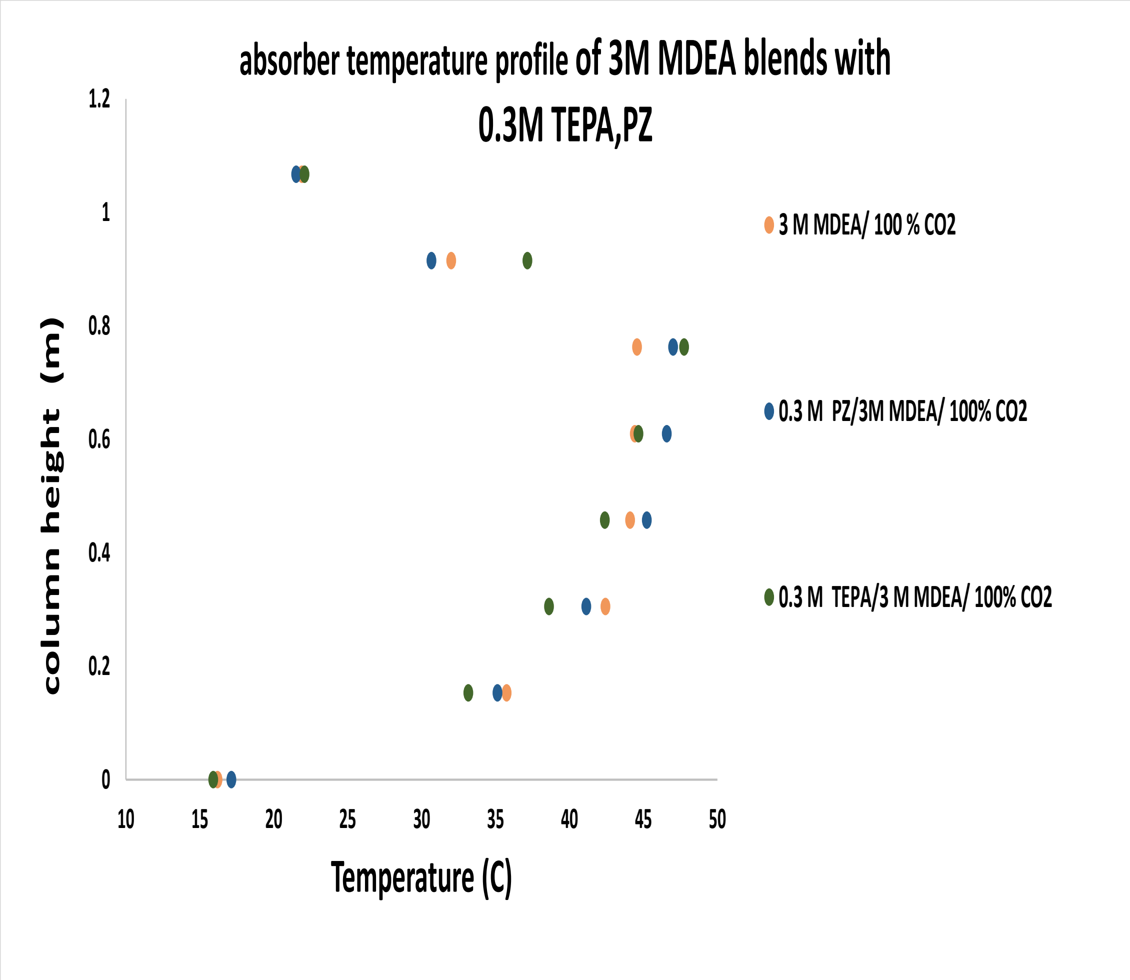
Results and discussion:
Absorber temperature profile:

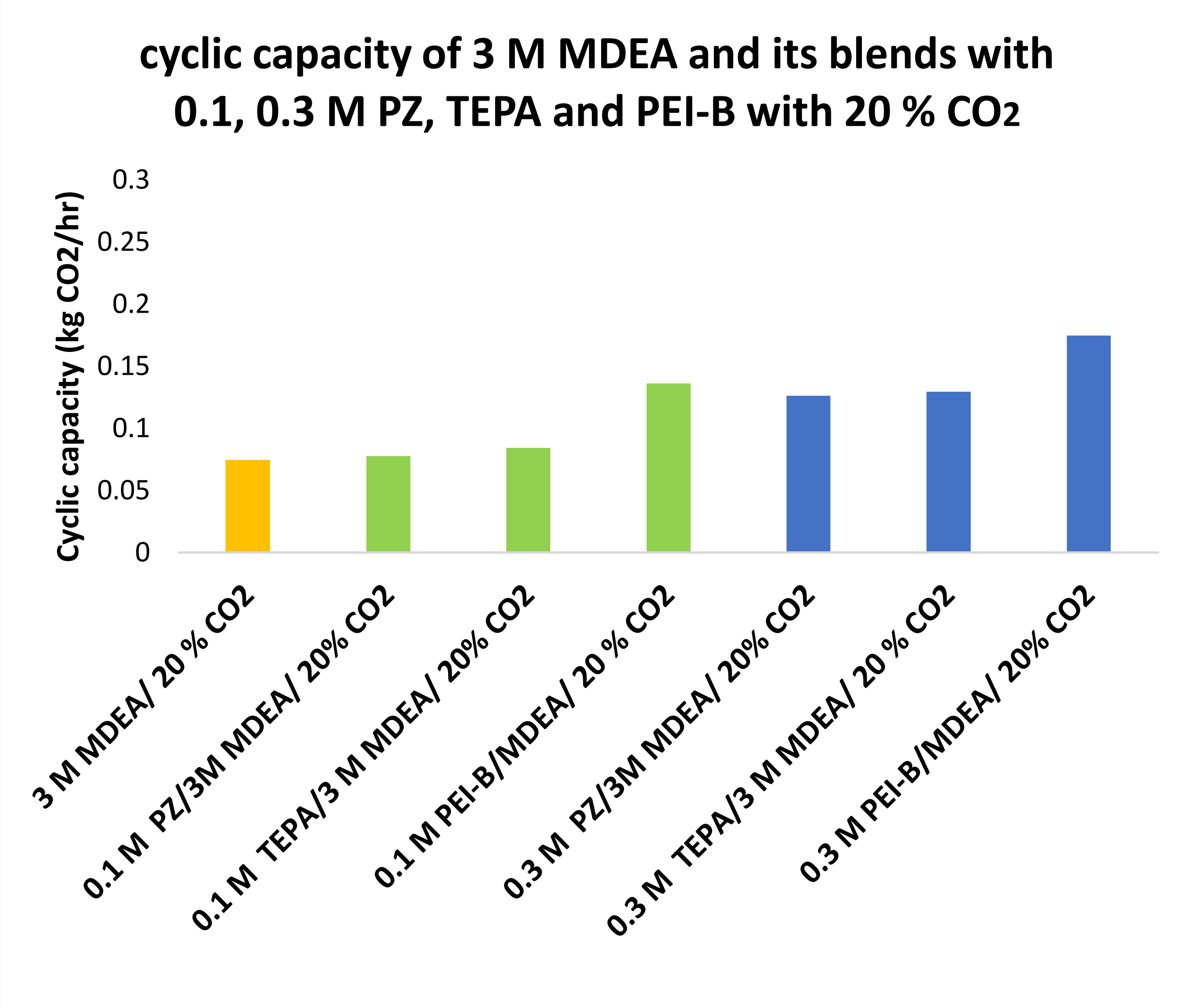


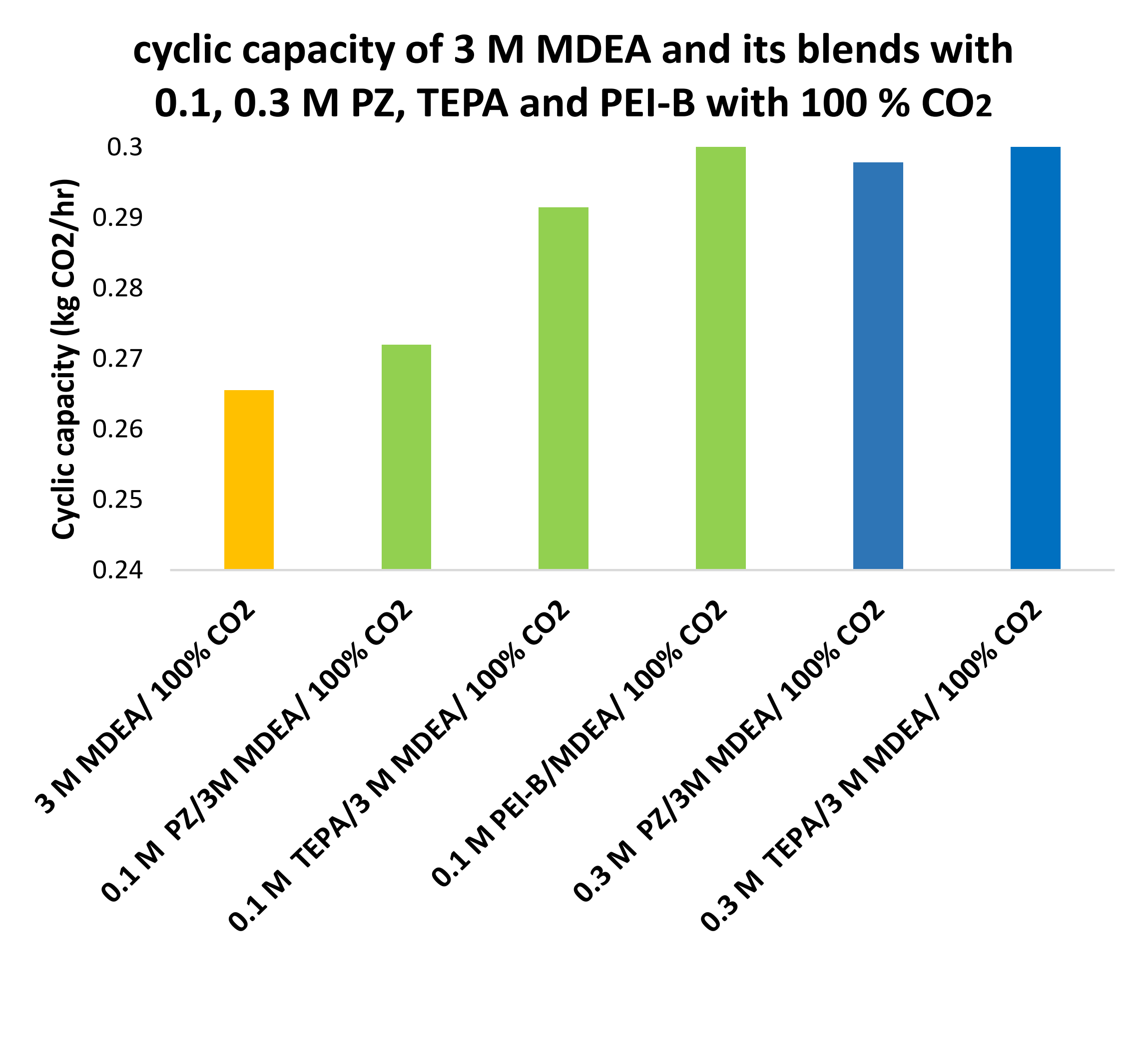


MDEA/PEI-B > MDEA/TEPA >MDEA/PZ > 3 M MDEA.

Results and discussion:

Cyclic capacity





MDEA/PEI-B > MDEA/TEPA >MDEA/PZ > 3 M MDEA.

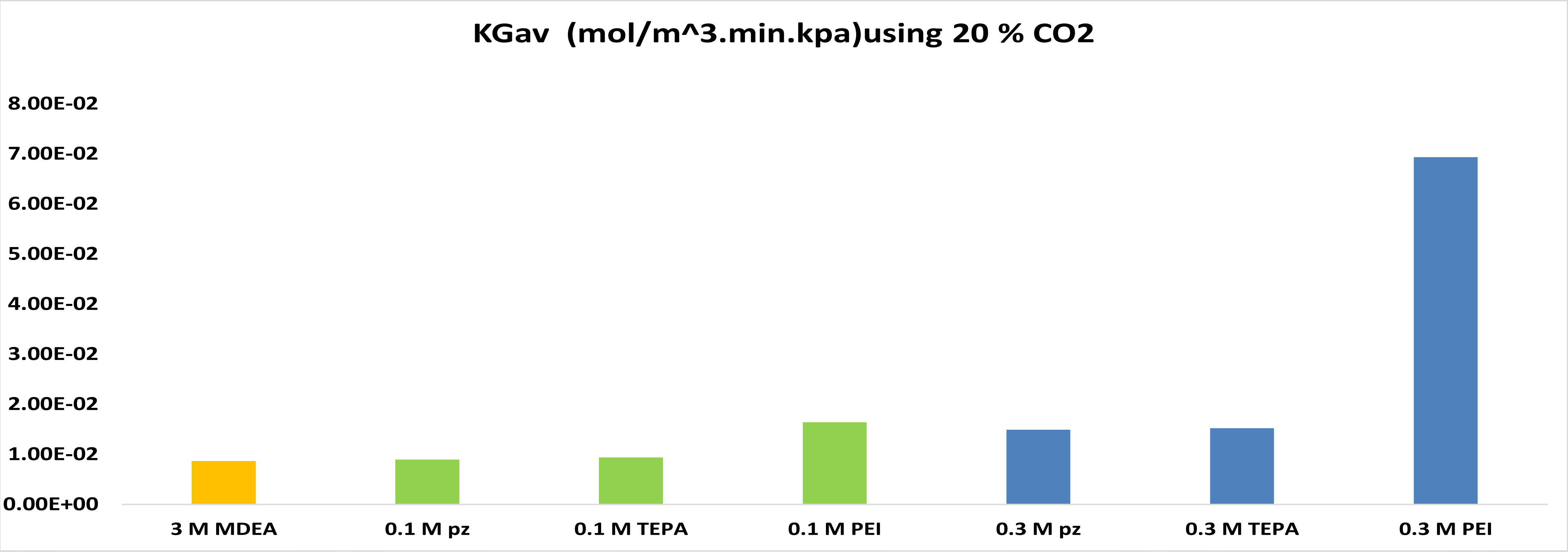
Over all mass transfer coefficient in gas phase

$$K_G a_v = \left[\frac{G_I}{P(y_{A,G} - y_A^*)_{lm}}\right]\left[\frac{dY_{A,G}}{dz}\right]$$

(Naami et al., 2012)

$$(y_{A,G} - y_A^*)_{lm} = \frac{(y_{A,G} - y_A^*)_1 - (y_{A,G} - y_A^*)_2}{\ln\left[\frac{(y_{A,G} - y_A^*)_1}{(y_{A,G} - y_A^*)_2}\right]}$$

Results and discussion: 3 M MDEA blend with 0.1 and 0.3 M activator



MDEA/PEI-B > MDEA/TEPA >MDEA/PZ > 3 M MDEA.

Overall mass transfer coefficient in liquid phase in the desorber

$$K_L a_v = \frac{1}{Z}\sum_{i=1}^{N}\frac{\overline{L_{m,i}}\Delta x_{A,i}}{\overline{\rho_{m,i}}(1-\overline{x_{A,i}})(\overline{x_{A,i}}-\overline{x_{A,i}^{*}})}$$

(Osei, 2016)

Over all mass transfer coefficient in liquid phase in the desorber

- $\Delta X_A = \left(\frac{x\ CO2\ (rich)}{1-x\ CO2\ (rich)}\right)-\left(\frac{x\ CO2\ (lean)}{1-x\ CO2\ (lean)}\right)$

- Density (mol/m^3) = $mol/\ cm^3 * 10^6$
- Density = (ρ rich – ρ lean)/ LN (ρ rich/ ρ lean)

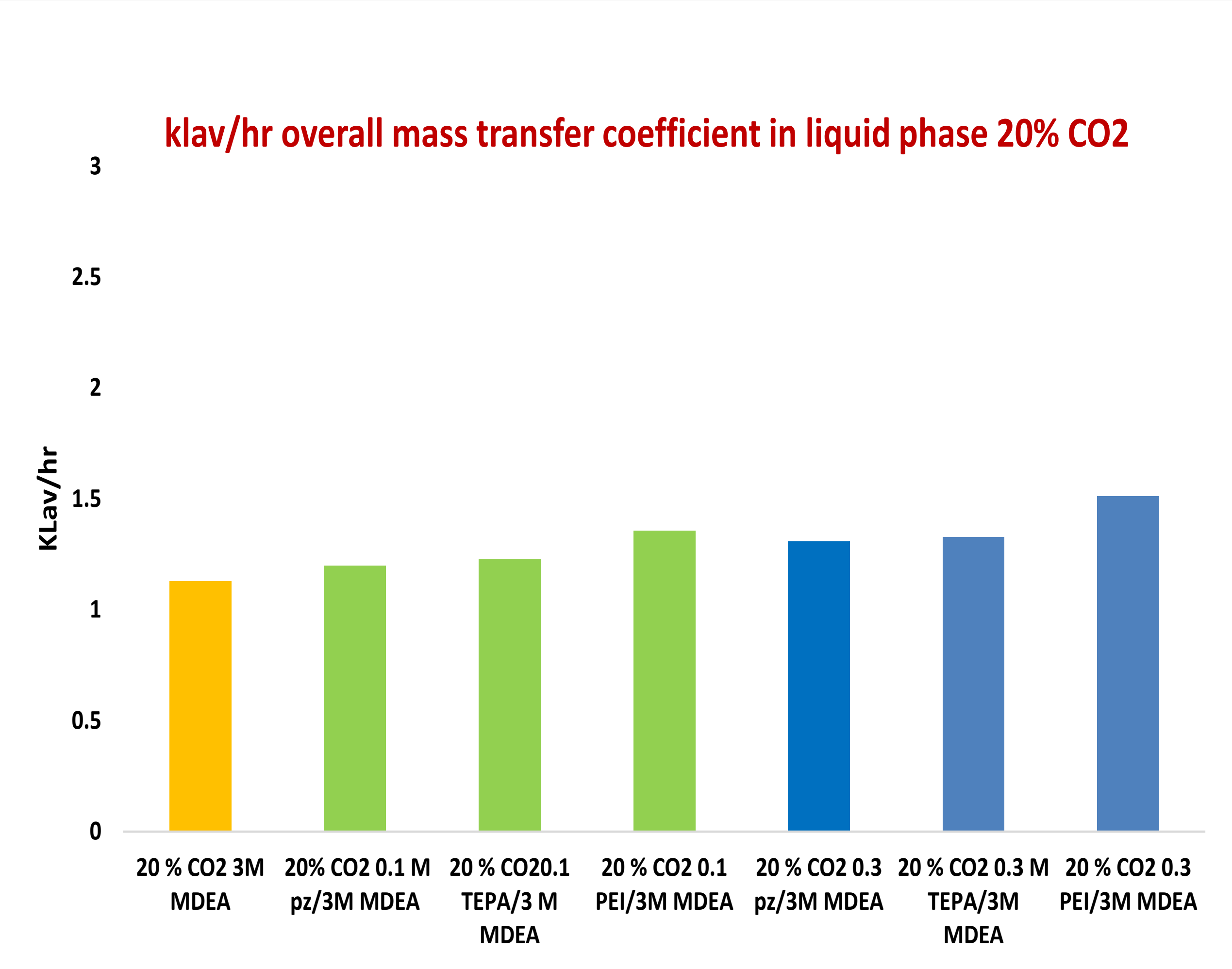
$(x_a - x_a^*)lm = (x_l - x^*) - \ (x_R - x^*)$ /(LN$(x_l - x^*)/\ \ (x_R - x^*)$)

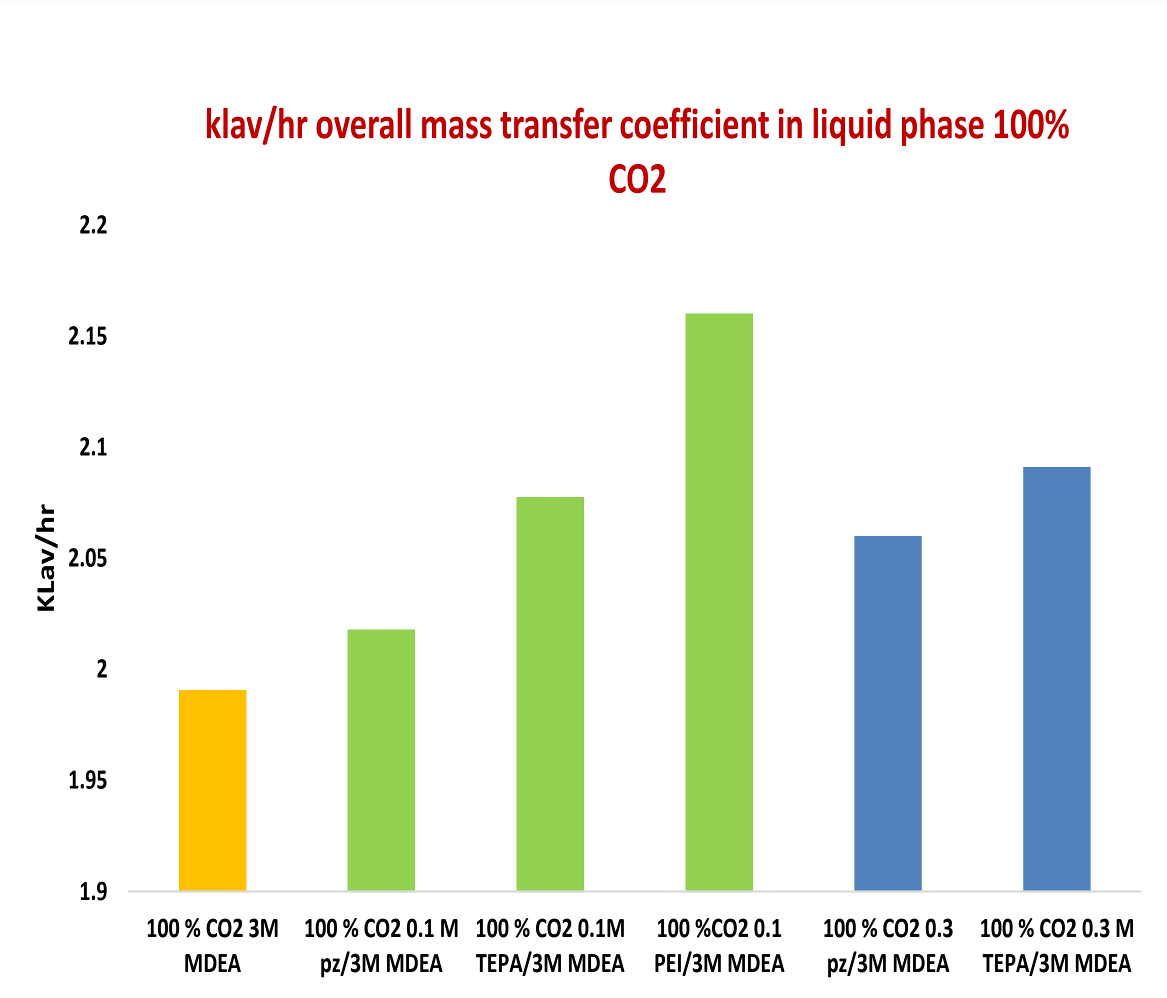
- $l_{m,l}$ molar rate of liquid solution per unit area

- $l_{m,l}$ = solution density $mol/\ cm^3$* (60 ml/min)*60/ A = $mol/m^2 * \mathrm{hr}$

- $l_{m,l}$ = ($l_{m,\ R}$- $l_{m,\ L}$)/ LN($l_{m,\ R}$- $l_{m,\ L}$)

Results and discussion:





MDEA/PEI-B > MDEA/TEPA >MDEA/PZ > 3 M MDEA.

Conclusions

- PEI-B is a better activator for blending with MDEA than TEPA and PZ.
- MDEA/PEI-B system shows higher performance for KGav, Klav, cyclic capacity, temperature profile, and concentration profile.
- The presence of secondary and primary amino groups leads to the formation of multi primary and/or secondary carbamates which are faster to absorb and easier to desorb CO_2 (Choi et al. (2014)).
- The trend is: MDEA/PEI-B > MDEA/TEPA >MDEA/PZ > 3 M MDEA.

References

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Acknowledgements

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