Absorption and desorption kinetics of catalyst-aided CO_2 capture in blended solutions of butyl (amino) ethanolamine and 2-amino-2-methyl-1-propanol (BEA-AMP), monoethanolamine and methyl diethanolamine (MEA-MDEA), and monoethanolamine (MEA)

Daniel B. Afari

James Coker[1], Jessica Narku-Tetteh[1] and Raphael Idem[1]*

[1]*Clean Energy Technologies Institute, Faculty of Engineering and Applied Science,*

University of Regina

4th Post Combustion Capture Conference (PCCC4), 2017 September 05 - 08

Presentation Outline

- Introduction
- Objective
- Theory and Experimental
- Results and Discussion
- Conclusion
- Acknowledgement

Introduction

Amine-based Post-combustion capture (PCC) of CO_2 from flue gases is considered a part of mature technologies in Carbon Capture and Sequestration (Shi et al, 2014)

Solvent improvement and **process optimization** are currently the main areas being understudied to improve the Post-Combustion capture technology (Narku-Tetteh et al, 2017).

Narku-Tetteh et al used some criteria to develop a novel solvent which can be better than MEA and MEA-MDEA in kinetic performance

Kinetic studies has been done for MEA and MEA-MDEA on incorporation of solid acid catalyst into the desorption column and it showed an improvement over the conventional desorber. (Akachuku, 2016)

Objectives

- To obtain experimental kinetic data for the novel solvent blend 2-butylethanol amine and 2-amino-2-methyl-1-propanol (BEA-AMP) and compare with blended monoethanolamine and methyl diethanolamine (MEA-MDEA) and single monoethanolamine (MEA) in a pilot plant

- To compare their kinetic performance with the addition of solid acid catalyst in the desorption column on a pilot plant basis

Theory

Some typical desorption reactions occurring in the CO_2 - aqueous amine solutions studied

$$MEAH^{+}/BEAH^{+} + H_2O \leftrightarrow MEA/BEA + H_3O^{+}$$

$$MEACOO^{-}/BEACOO^{-} + H_3O^{+} \leftrightarrow MEA/BEA + CO_2 + H_2O$$

Carbamate-forming amines

$$AMPCOO^{-} + H_2O \leftrightarrow AMP + HCO_3^{-}$$

$$AMPH^{+} + H_2O \leftrightarrow AMP + H_3O^{+}$$

$$HCO_3^{-} + H_3O^{+} \leftrightarrow CO_2 + 2H_2O$$

Sterically-hindered amines

$$MDEA + CO_2 + H_2O \leftrightarrow MDEAH^{+} + HCO_3^{-}$$

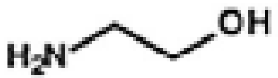
$$MDEAH^{+} + H_2O \leftrightarrow MDEA + H_3O^{+}$$

$$HCO_3^{-} + H_3O^{+} \leftrightarrow CO_2 + 2H_2O$$

Bicarbonate-forming amines

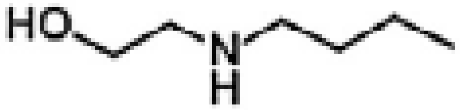
Experimental

Chemical structure of amines studied

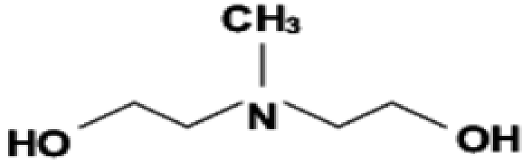


Monoethanolamine (MEA)

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

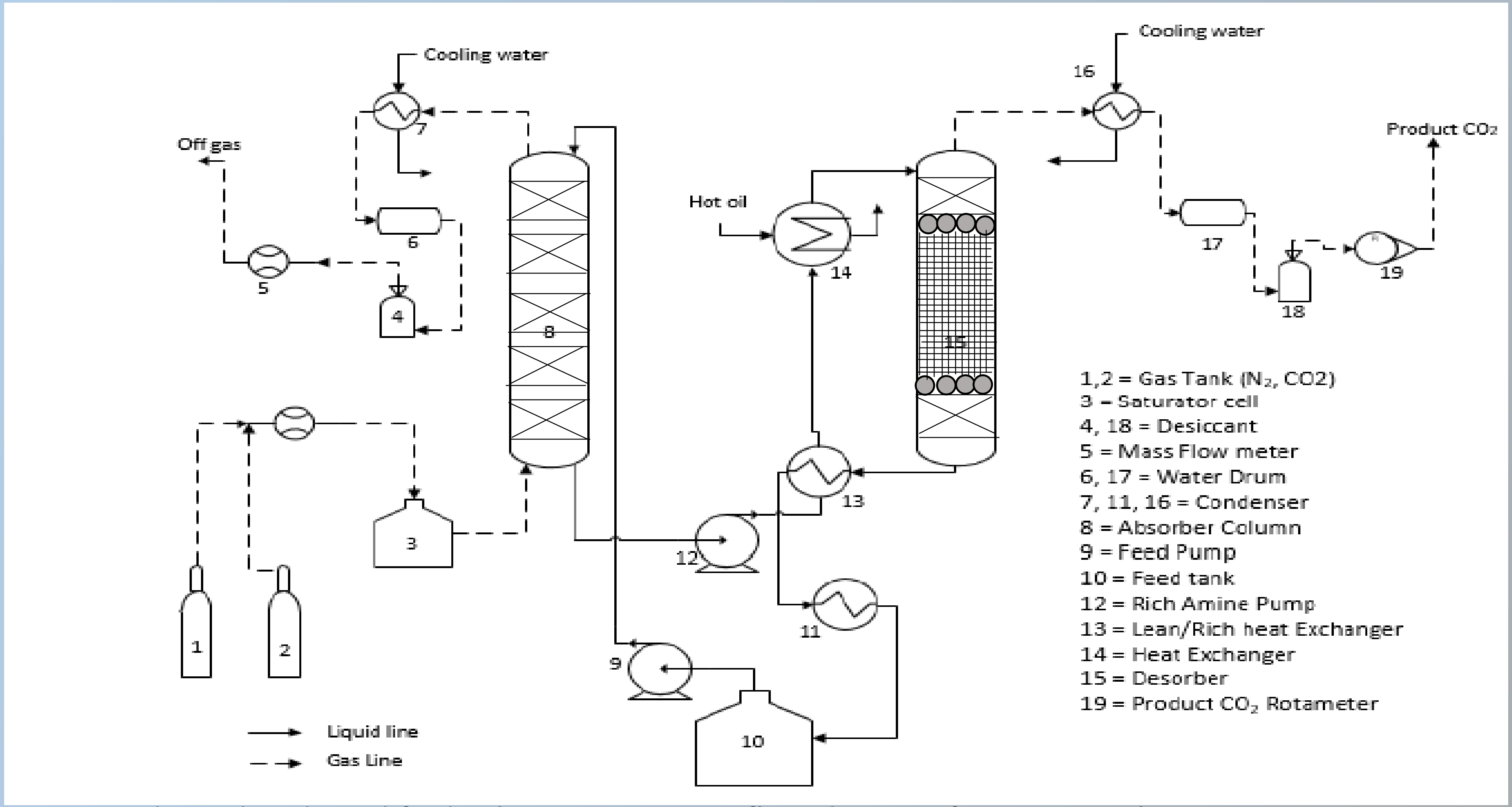


Butylethanolamine (BEA)



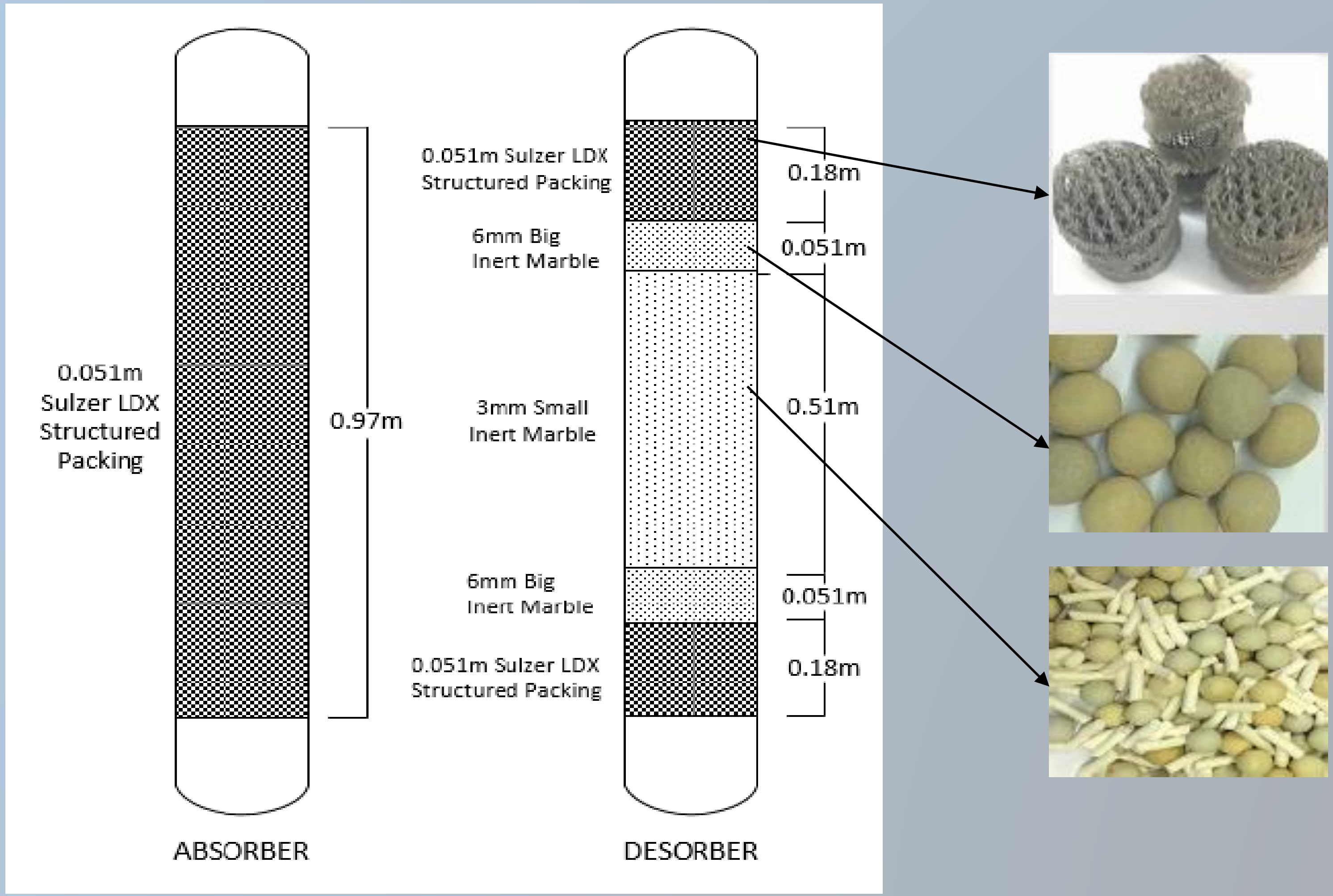
Methyldiethanolamine (MDEA)

Experimental



Adapted and Modified Schematic process flow diagram for post-combustion CO_2 capture from (Osei P.A., 2016)

Experimental



Column Packing and catalyst bed arrangement (Osei P. A., 2016)

Experimental

Plug flow condition

- Applying Froment and Bischoff et al (1990) criterion:

$$\frac{\text{Catalyst bed height}}{\text{Catalyst particle size}} = \frac{L}{d_p} \geq 50$$ **This work (L/d_p = 170)**

$$\frac{\text{Catalyst bed diameter}}{\text{Catalyst particle size}} = \frac{D}{d_p} \geq 10$$ **This work (D/d_p = 17)**

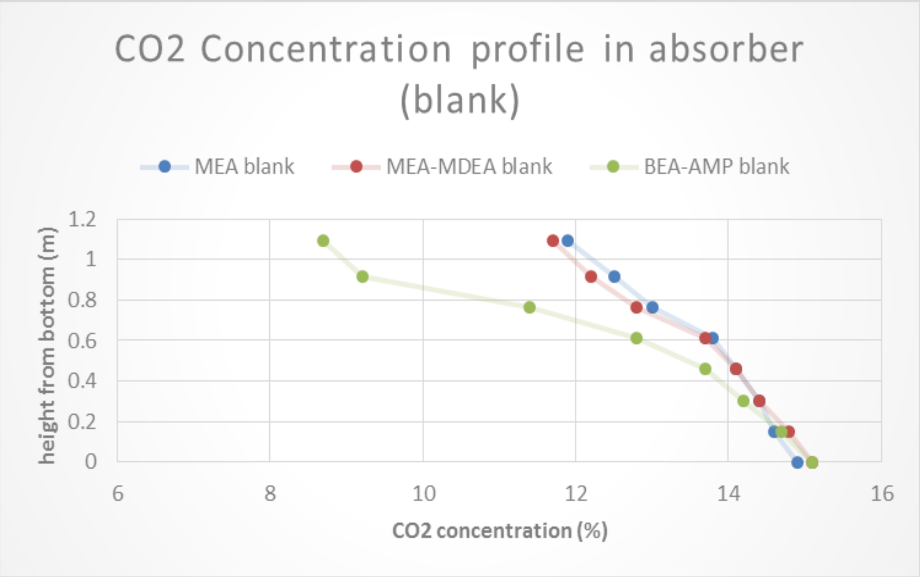
Experimental

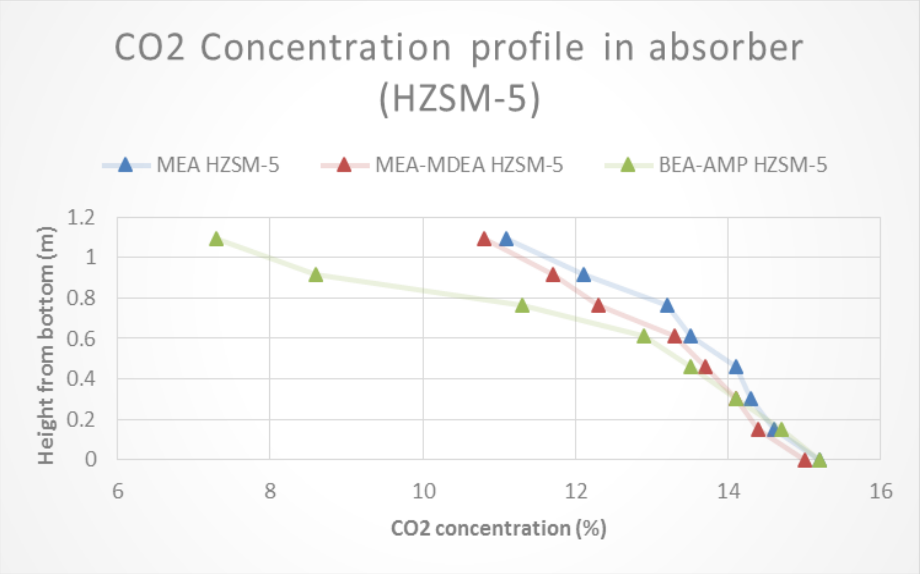
Process Parameters

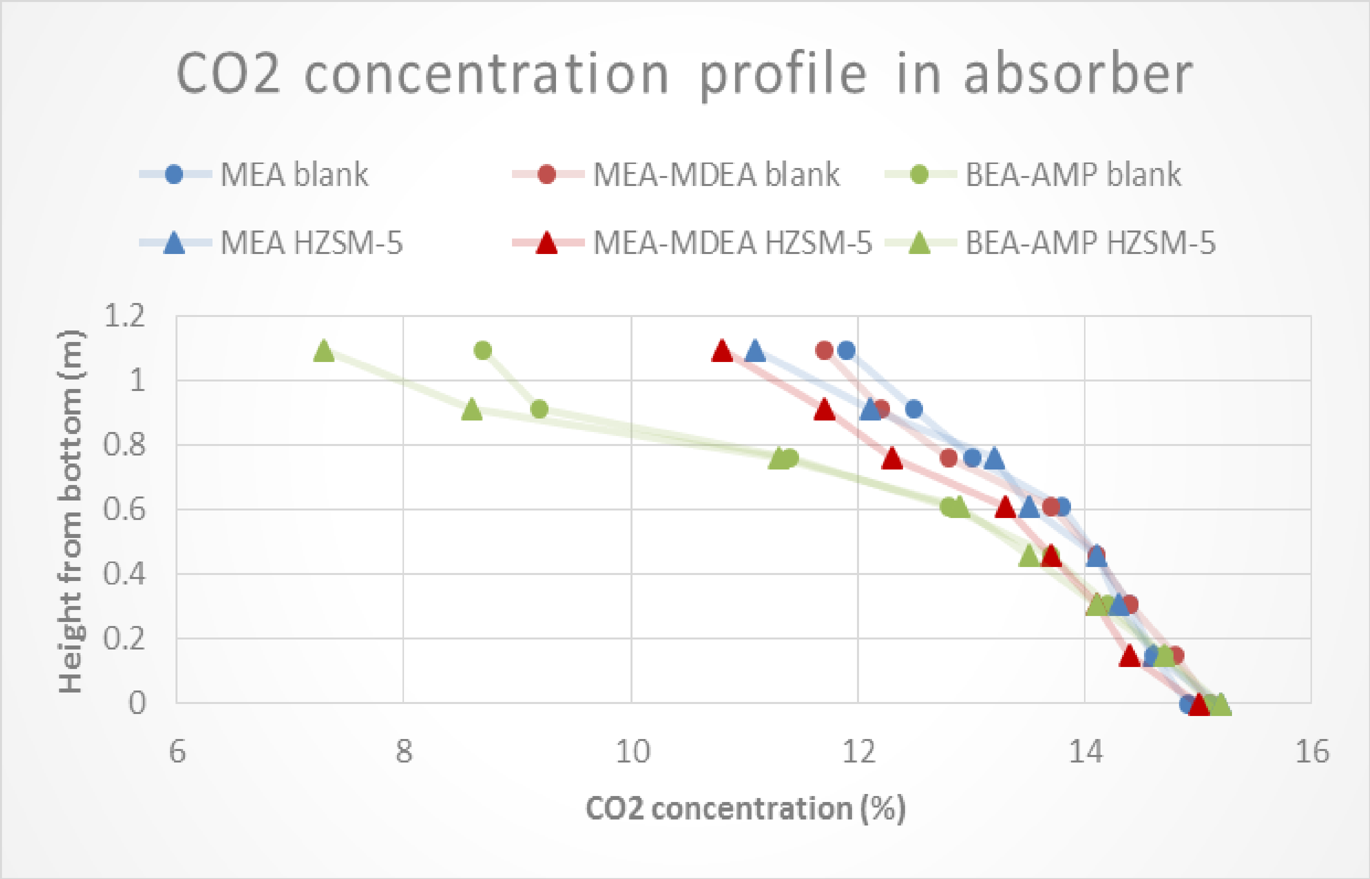
Parameters	
Gas flowrate	15 slpm
Liquid flowrate	60 ml/min
CO_2 concentration in feed gas	15%
liquid concentration	5M MEA, 7M MEA-MDEA, 4M BEA-AMP
Absorber inlet temperature	28^{o}C
Desorber inlet temperature	87^{o}C
Absorber operating pressure	101.325 KPa
Desorber catalyst and weight	HZSM-5 (150g)

Results and Discussion

CO_2 concentration profile in absorber for both blank and catalytic systems

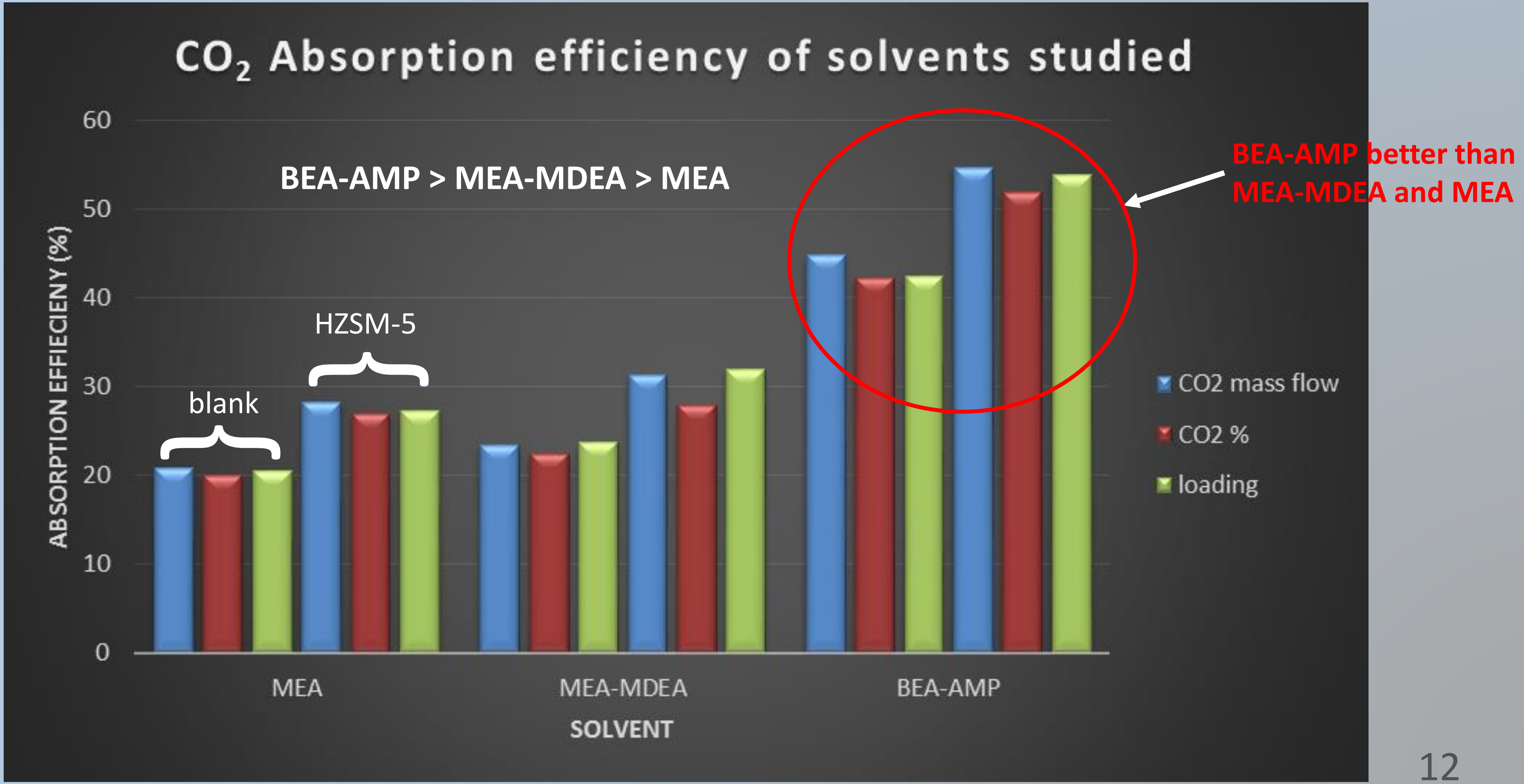






BEA-AMP > MEA-MDEA > MEA

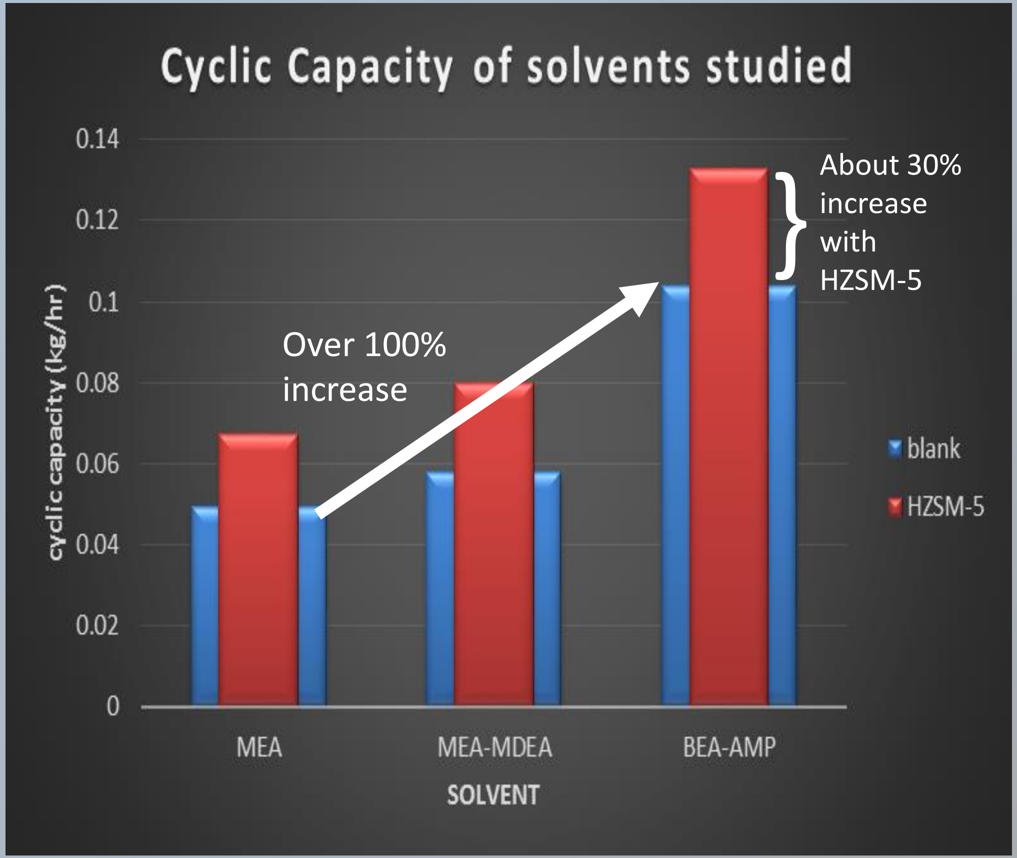
Results and Discussion



Results and Discussion

Lean loadings of solvents in plant run

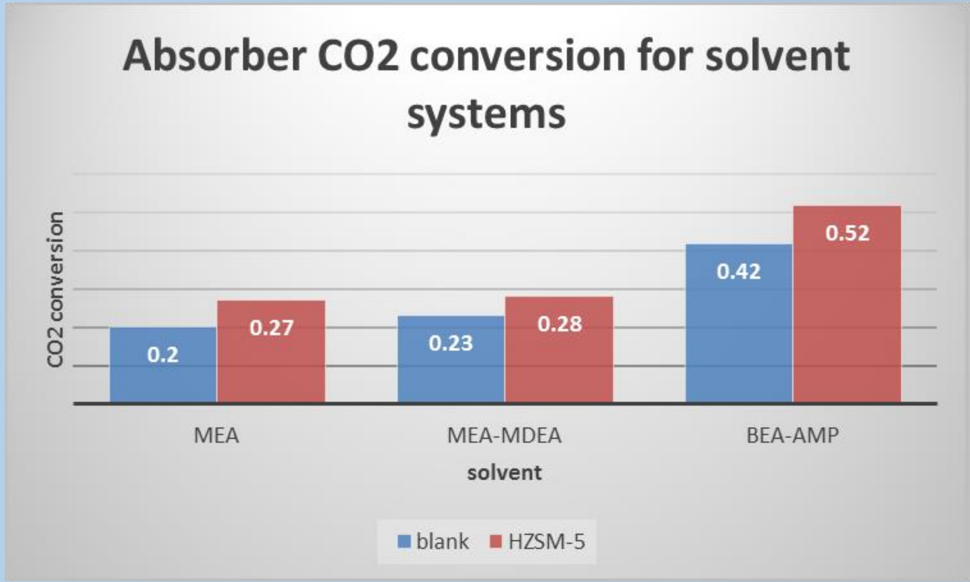
Lean loading (mol CO_2/mol amine)	5M MEA	5/2M MEA-MDEA	2/2M BEA-AMP
no catalyst (blank)	0.42	0.35	0.33
HZSM-5 catalyst (Si/Al = 19)	0.41	0.32	0.30

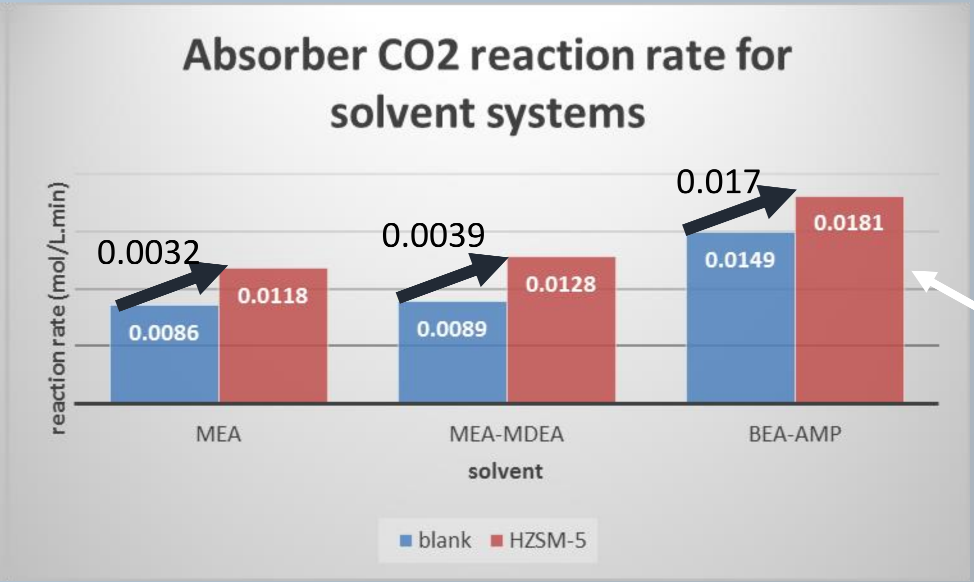


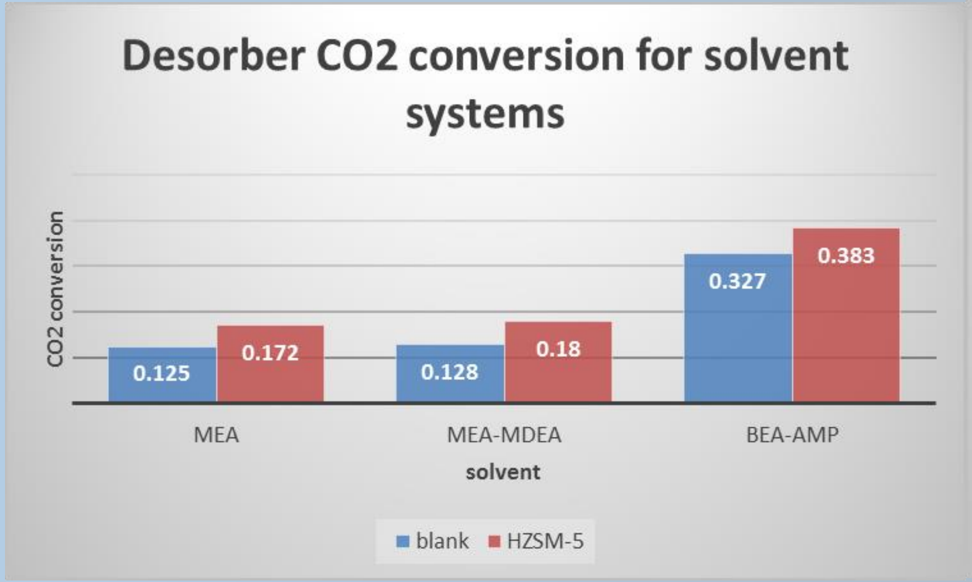
Percentage (%) increase in cyclic capacity using MEA (blank) as base case

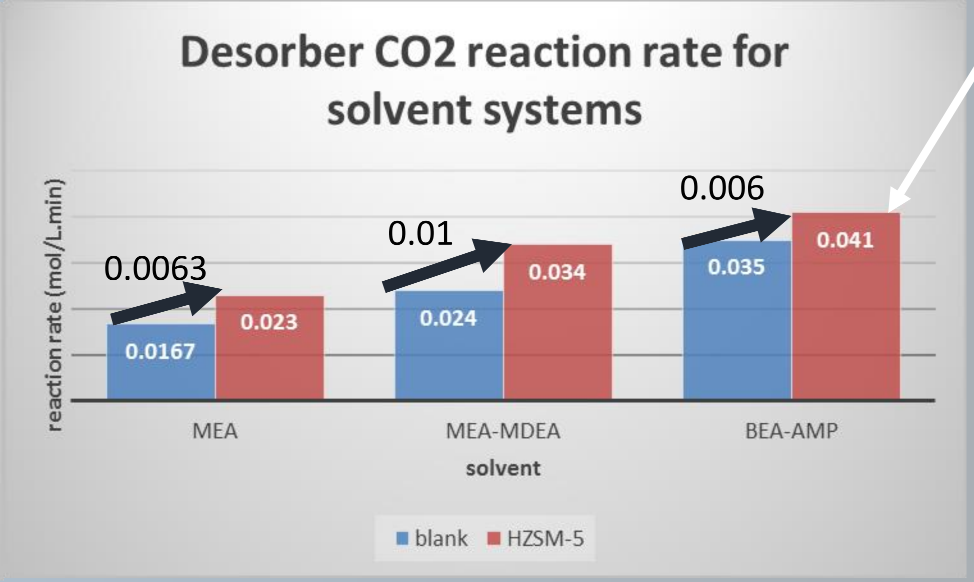
	MEA	MEA-MDEA	BEA-AMP
Blank	0%	17%	**110%**
HZSM-5	36%	62%	**169%**

Results and Discussion









BEA-AMP better than MEA-MDEA and MEA

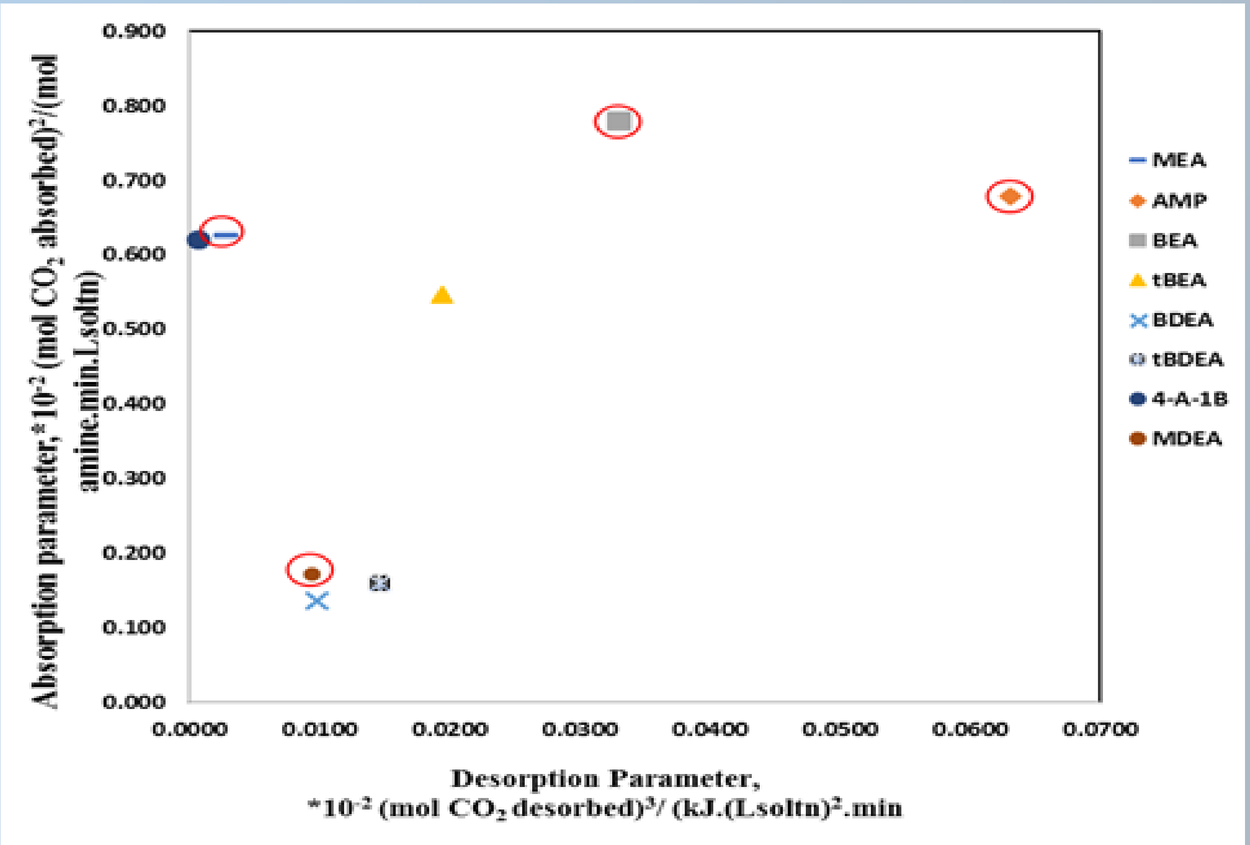
- **Solvent Structural properties**
- **Lean loading**

Results and Discussion

Percentage (%) increase in reaction rate using MEA (blank) as base case

Absorber	MEA	MEA-MDEA	BEA-AMP
Blank	0%	5%	**73%**
HZSM-5	37%	49%	**110%**

Desorber	MEA	MEA-MDEA	BEA-AMP
Blank	0%	44%	**110%**
HZSM-5	38%	103%	**146%**



Amine Selection Chart (Narku-Tetteh et al., 2017)

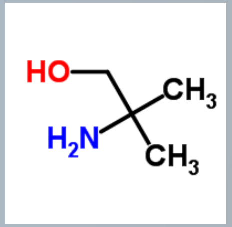
Absorption parameter =

$$\text{initial absorption rate} \times \text{equilibrium loading} \times \text{pka}$$

Desorption parameter = $\dfrac{\text{initial desorption rate} \times \text{cyclic capacity}}{\text{heat duty}}$

$$AMPCOO^- + H_2O \leftrightarrow AMP + HCO_3^-$$

Highly unstable carbamate



Conclusions

- The novel blend BEA-AMP had the fastest absorption and desorption rates followed by MEA-MDEA blend with single MEA being the slowest

- The solvent structural properties (alkyl, H and OH^- groups) greatly contributes to their kinetic performance

- It confirms the results obtained by Narku-Tetteh et al., (2017) on a pilot plant scale. The 4 M bi-solvent blend consisting of equimolar concentration of BEA and AMP was found to be the best solvent because it displayed the best desorption performance and a very good absorption parameter

- The lower lean loading of MEA-MDEA provided a greater driving force (more free amines) for its reactivity towards CO_2 as compared to single MEA

- The addition of a solid acid catalyst, HZSM-5 increased desorption rates by transferring its available protons to bicarbonate. This provided an alternative pathway resulting in the faster release of CO_2

- It is economically feasible to use the novel blend BEA-AMP in industrial applications as it outperformed the other solvents greatly.

Future Work

- Studies on selection and addition of solid base catalyst in absorber for novel solvent blend BEA-AMP system.
- Effect of solid base catalyst weight, temperature, solvent concentration and flowrate on the BEA-AMP-CO_2 system
- Development of empirical power law and mechanistic models for blended solvent BEA-AMP reaction with CO_2

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Acknowledgement

Clean Energy Technology Research Institute

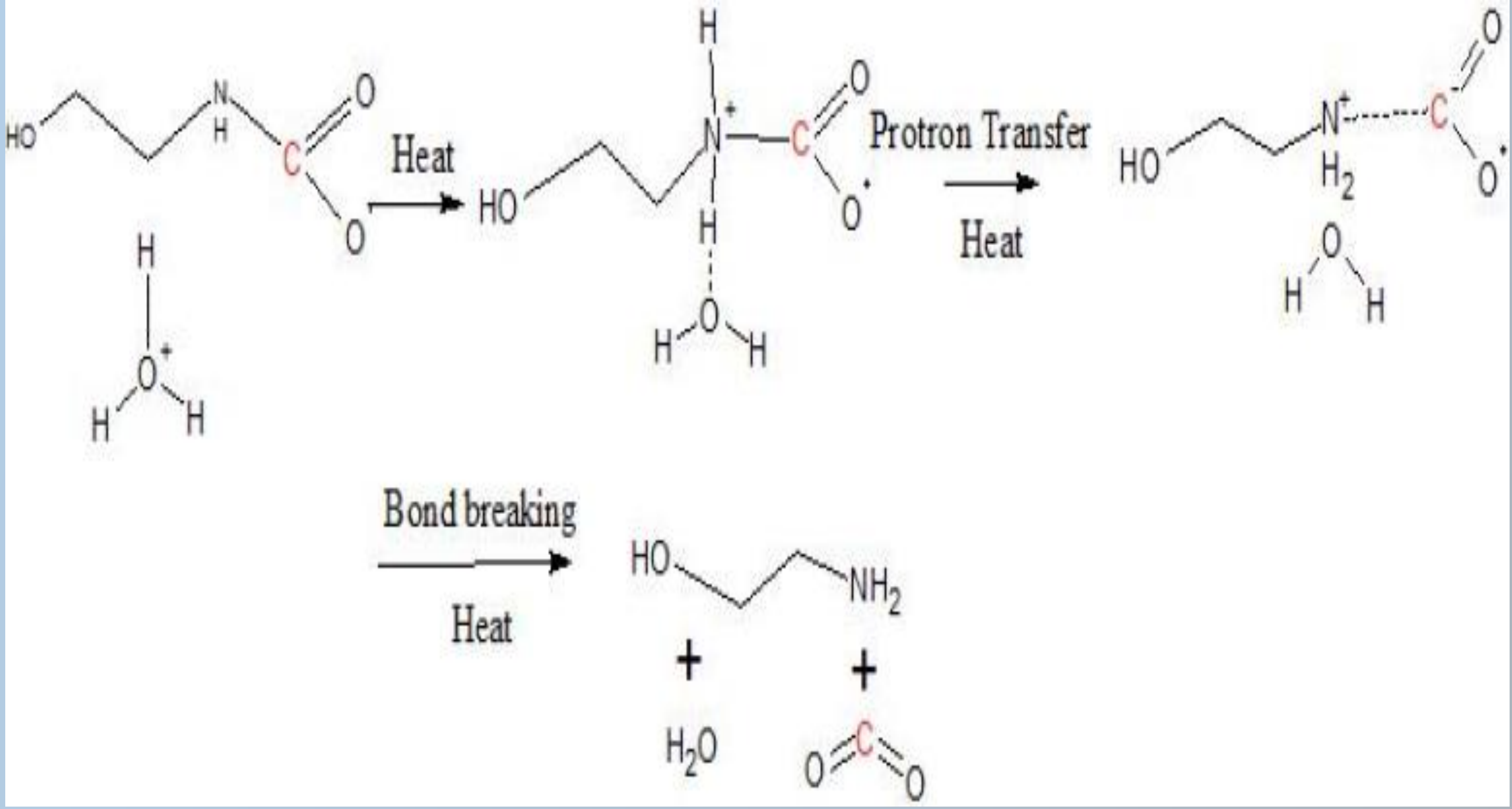
Natural Sciences and Engineering Research Council of Canada

Faculty of Graduate Studies and Research (FGSR), University of Regina

THANK YOU

Appendix

Non-catalytic CO_2 desorption mechanism

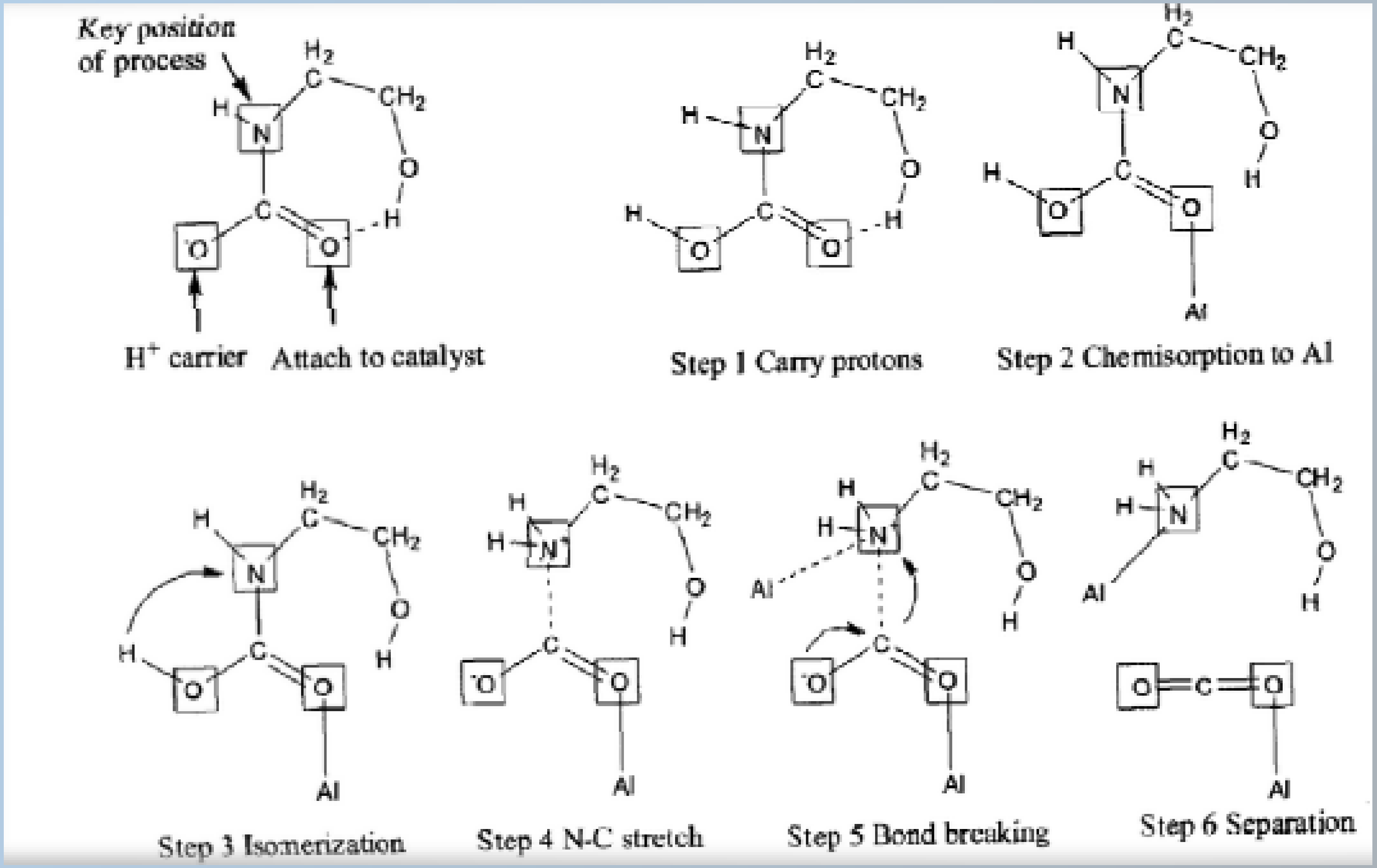


(Akachuku et al, 2016)

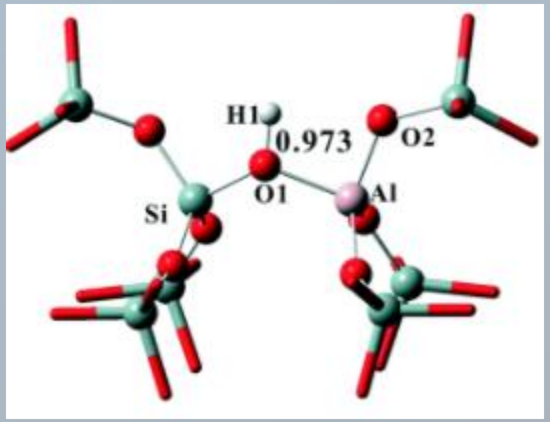
- Regeneration heat weakens hydrogen bond of Hydrozonium ion (H_3O^+)
- Attack of nitrogen in carbamate ion by H^+ weakens N-C bond
- N-C bond breaks forming free CO_2 and amine

Appendix

Catalytic CO_2 desorption mechanism (Action of HZSM-5)



(Akachuku et al, 2016)



HZSM-5 structure

- Proton (H^+) donation by catalyst
- Conversion of carbamate ion to carbamic acid
- Chemisorption on Al site
- N-C bond breaks forming free CO_2 and amine

Appendix

- **Solvent Structural properties**
- **Lean loading**

OH-

(Hydroxyl)

Electron withdrawing

Electron donating

$CH_3CH_2CH_2CH_2$-

(n-butyl)

BULKY

H-

(Hydrogen)

$$AMPCOO^{-} + H_2O \leftrightarrow AMP + HCO_3^{-}$$

Highly unstable carbamate