Thermodynamics and ANN models for correlation and predication of the equilibrium CO_2 solubility of seven tertiary amine solvents

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University of Regina, CANADA
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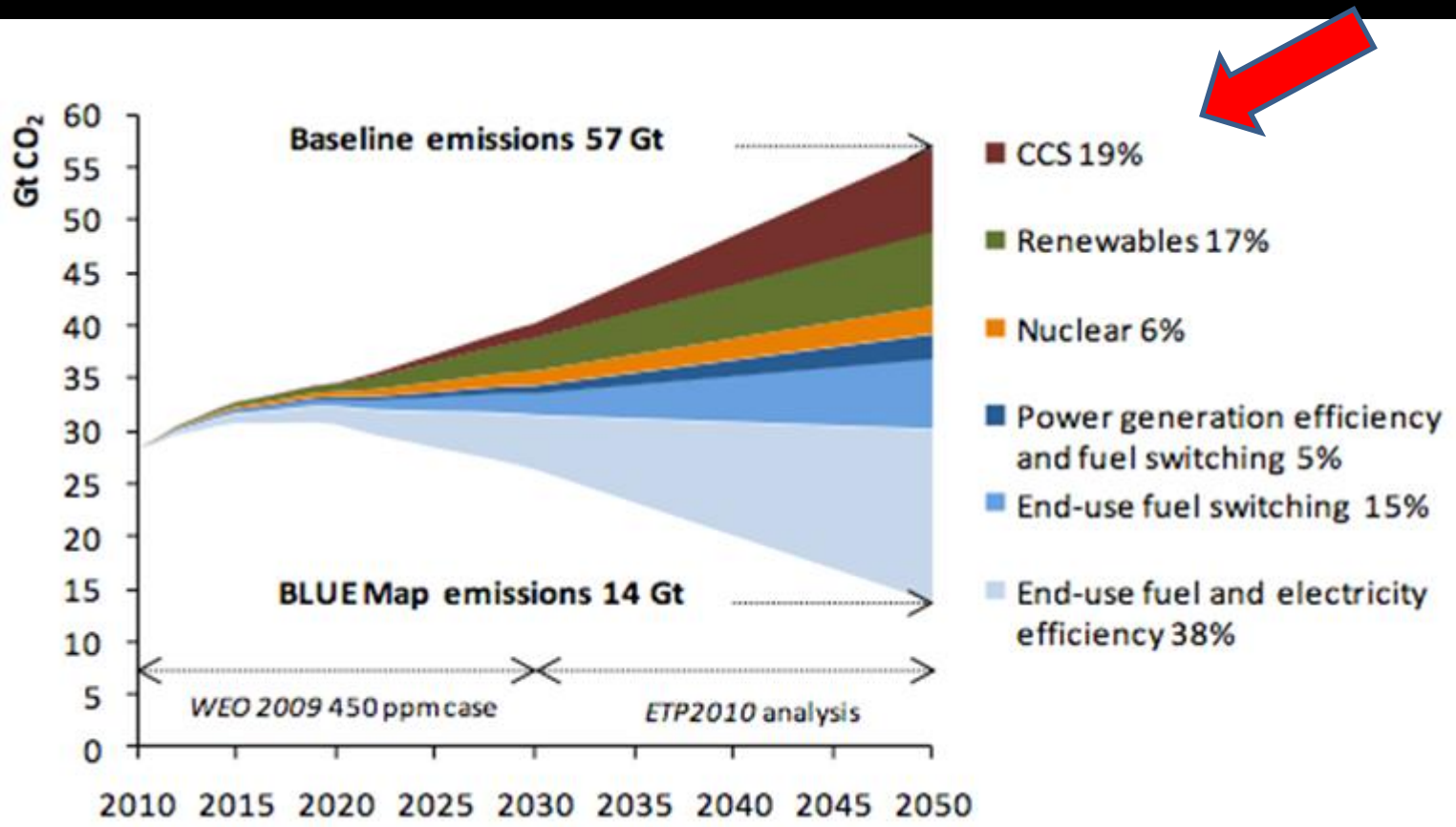
Hunan University, China

Outline

1. Introduction
2. Theory
3. Experiment
4. Results and discussion
5. Conclusion
6. Acknowledgements

CCS Research ?

Key technologies for reducing global CO_2 emissions under Blue Map scenario

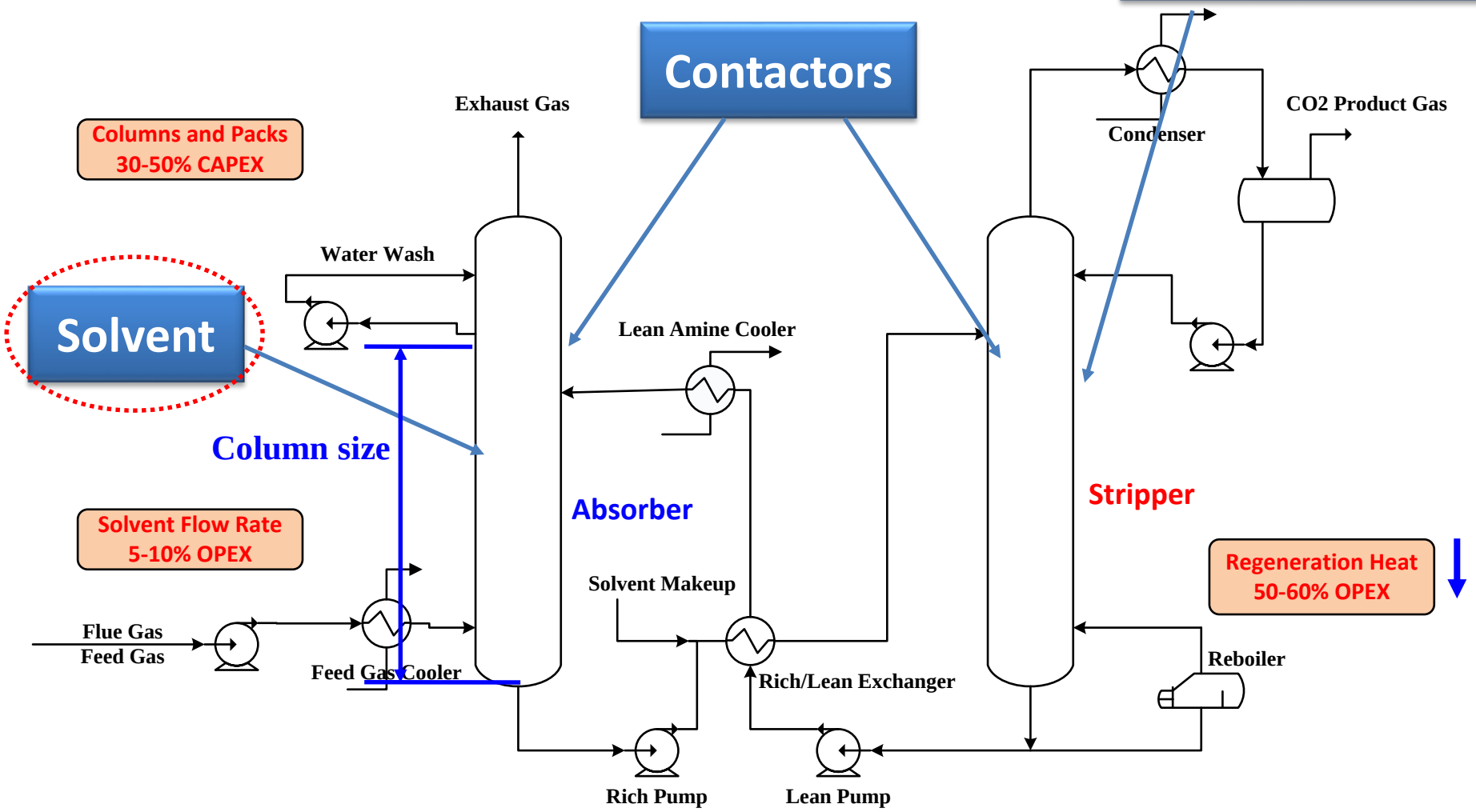


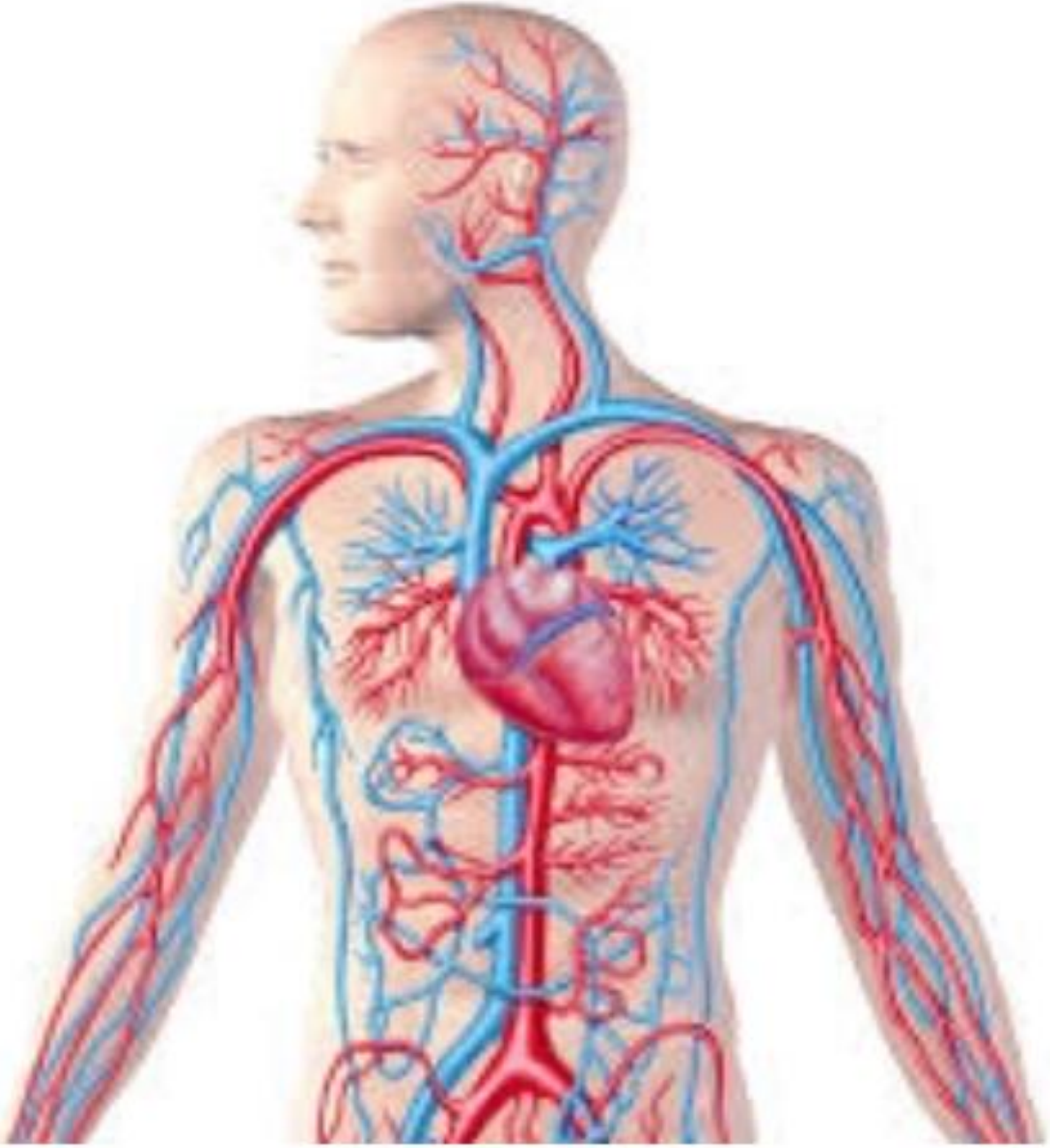
A wide range of technologies will be necessary to reduce energy-related CO_2 emissions substantially.

Introduction

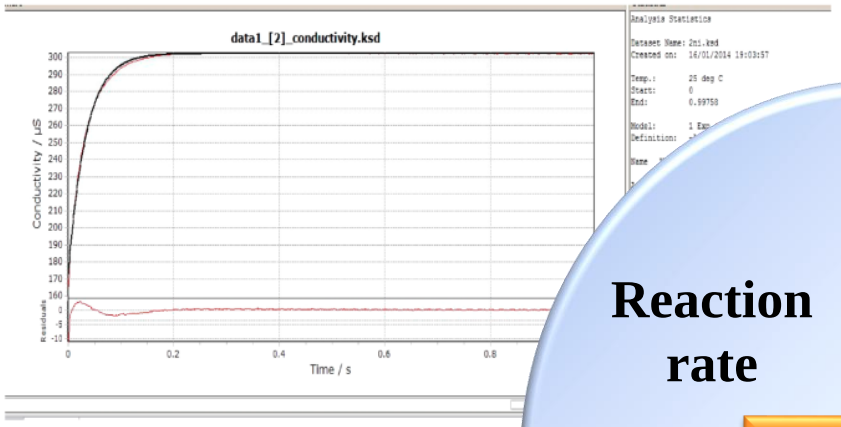
Post-combustion Carbon Capture

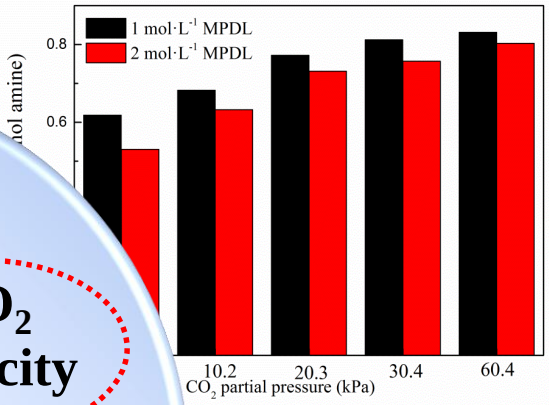
Optimization of process





Introduction





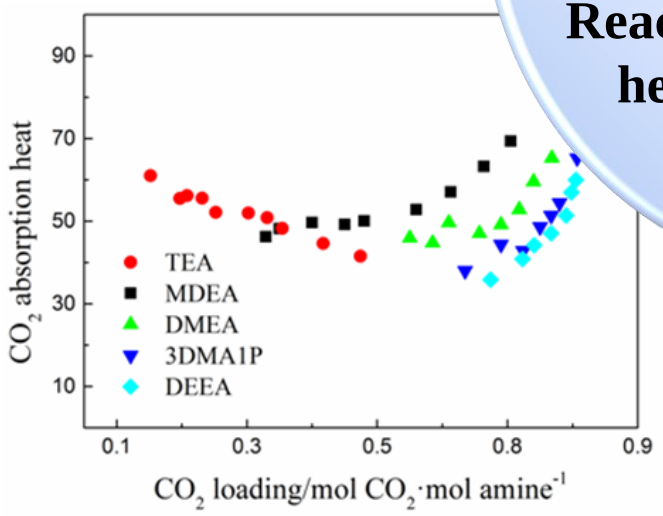
Reaction rate

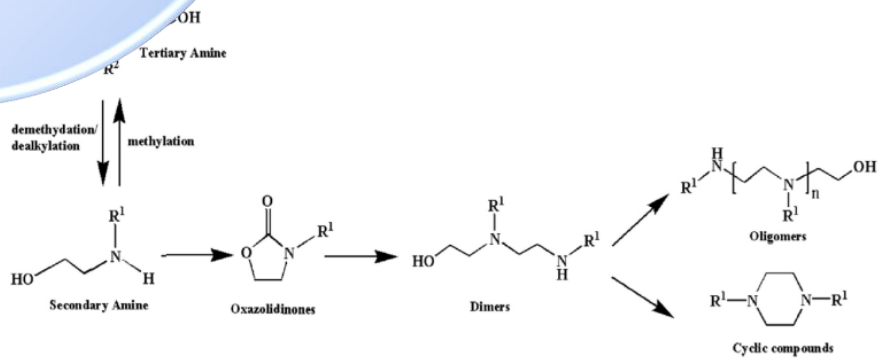
CO_2 capacity

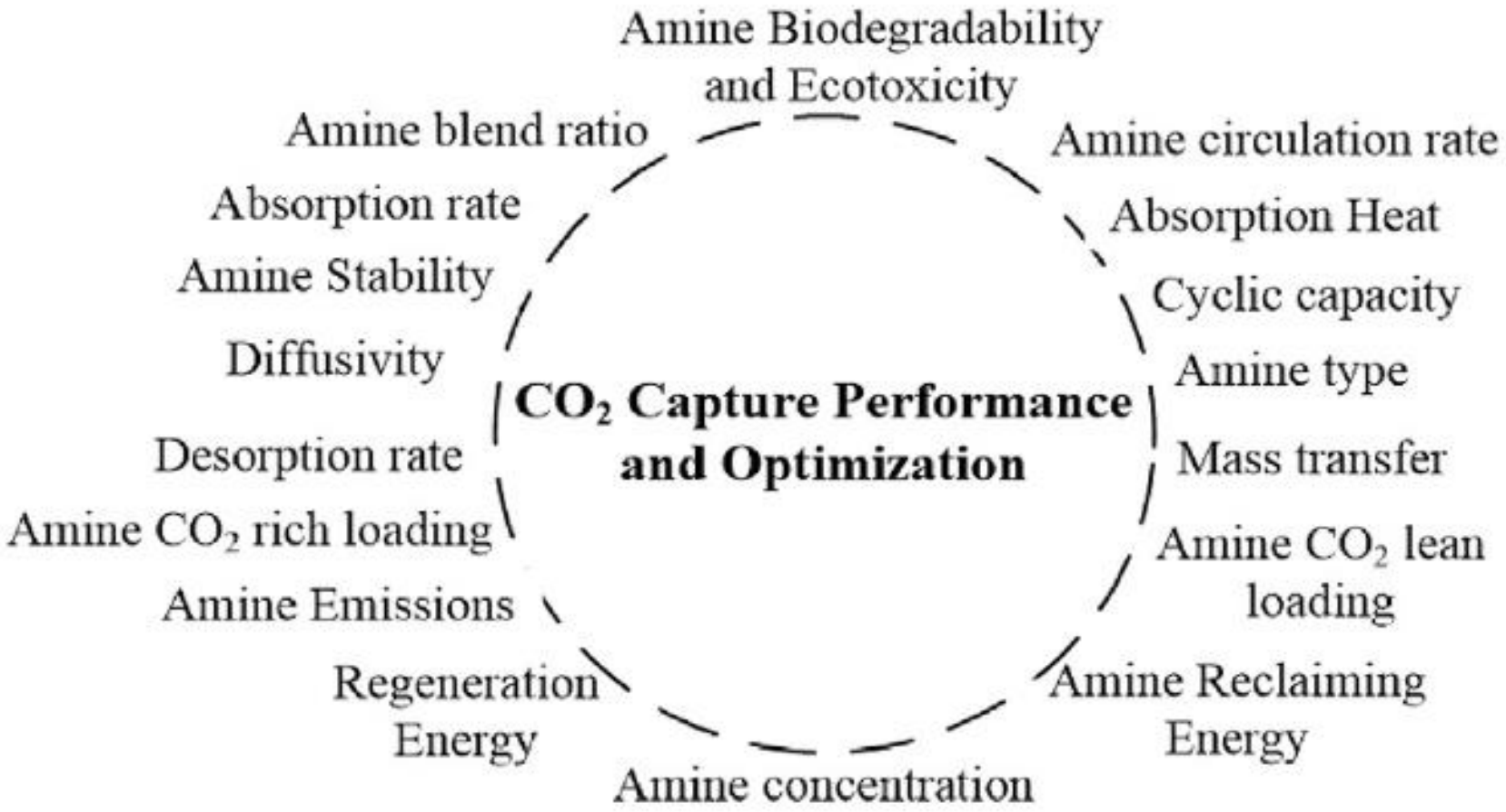
Solvent

Reaction heat

Physical property







Several performance criteria's of an optimized amine solution.

History of Solvent Development

Use of Amine Solvents

- ***CCS Applications and ….***
  - ❖***Gas Processing***
  - ❖***Refinery gas***
  - ❖***Landfill gas***
  - ❖***Bio gas***
  - ❖***Solution gas***
  - ❖***EOR gas***
  - ❖***Etc.***

In the 1960's and 1970's

Gas-Liquid Reactions

P. V. Danckwerts, F.R.S.

Shell Professor of Chemical Engineering
University of Cambridge

In the 1980's

GAS TREATING WITH CHEMICAL SOLVENTS

GIANNI ASTARITA
University of Naples and University of Delaware

DAVID W. SAVAGE
Exxon Research and Engineering Company

ATTILIO BISIO
Exxon Research and Engineering Company

Ind. Eng. Chem. Fundam. **1983**, *22*, 239–249

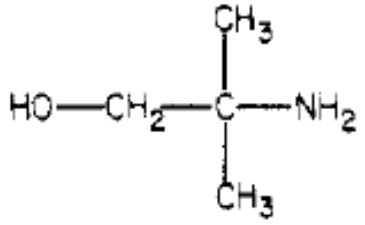
Sterically Hindered Amines for CO_2 Removal from Gases

Guido Sartori* and David W. Savage

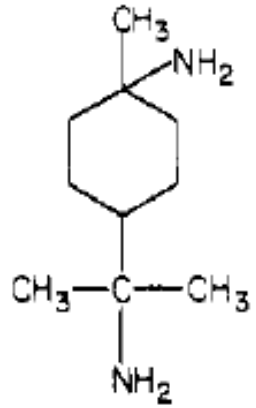
Corporate Research, Exxon Research and Engineering Company, Linden, New Jersey 07036

Steric hindrance and basicity are shown to control CO_2–amine reactions. In aqueous amino alcohols, steric hindrance is the dominant factor giving high thermodynamic capacity and fast absorption rates at high CO_2 loadings. Introducing steric hindrance by a bulky substituent adjacent to the amino group lowers the stability of the carbamate formed by CO_2–amine reaction. Reduced carbamate stability allows thermodynamic CO_2 loadings to exceed those attainable with conventional, stable-carbamate amines. Lowering carbamate stability also leads to high free-amine concentration in solution; therefore fast amine–CO_2 reaction rates are obtained despite some reduction of the rate constant owing to steric interference. Hindered amines show capacity and absorption rate advantages over conventional amines for CO_2 removal from gases by absorption in aqueous amine solutions and amine-promoted hot potassium carbonate. Cyclic capacity broadening of 20–40% and absorption rate increases up to 100% or more are possible with certain hindered amines.

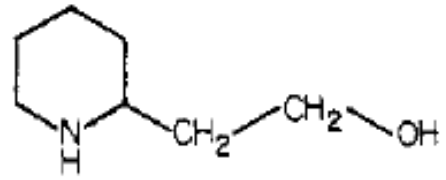
Table II. Examples of Sterically Hindered Amines



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



1,8-*p*-menthanediamine (MDA)



2-piperidineethanol (PE)

In 2000's to now

- ***PCCC Conferences***
- **GHGT Conferences**
- **and much more ….**

US007910078B2

(12) **United States Patent**
Tontiwachwuthikul et al.

(10) **Patent No.: US 7,910,078 B2**
(45) **Date of Patent: Mar. 22, 2011**

(54) **METHOD OF CAPTURING CARBON DIOXIDE FROM GAS STREAMS**

(75) Inventors: **Paitoon Tontiwachwuthikul**, Regina (CA); **Andrew G. H. Wee**, Regina (CA); **Raphael Idem**, Regina (CA); **Kreangkrai Maneeintr**, Regina (CA); **Gao-jun Fan**, Regina (CA); **Amornvadee Veawab**, Regina (CA); **Amr Henni**, Regina (CA); **Adisorn Aroonwilas**, Regina (CA); **Amit Chakma**, Waterloo (CA)

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35

C07D 211/02 (2006.01)
C07D 211/00 (2006.01)
C07D 295/00 (2006.01)

(52) **U.S. Cl.** **423/228**; 423/230; 423/238; 544/170; 546/184; 546/248; 564/503

(58) **Field of Classification Search** 410/210, 410/226, 228, 229; 423/228, 230, 238; 544/170; 546/248; 564/503

See application file for complete search history.

(56) **References Cited**

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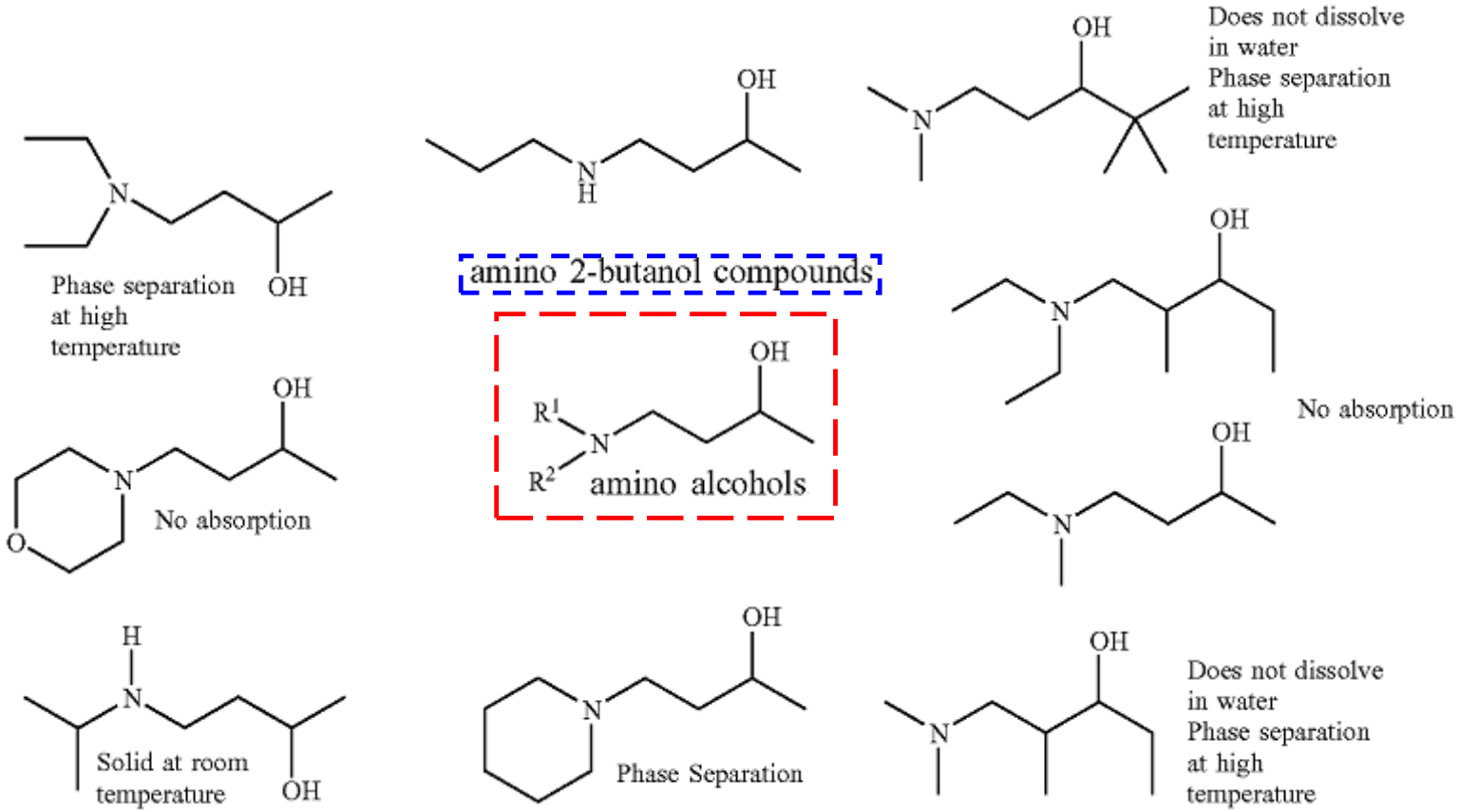
4,112,052	A	9/1978	Sartori et al.
4,372,925	A	2/1983	Carnelissa



"Developed based on a systematic modification of the structure of amino alcohols by an appropriate placement of the substituent, especially hydroxyl function and relative position of amino group" **(US Patent 7,910,078 – B2)**

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Synthesis of new amines for enhanced carbon dioxide (CO_2) capture performance: The effect of chemical structure on equilibrium solubility, cyclic capacity, kinetics of absorption and regeneration, and heats of absorption and regeneration

Sudkanueng Singto [a], Teeradet Supap [b,*], Raphael Idem [b,*], Paitoon Tontiwachwuthikul [b,*], Supawan Tantayanon [a,c,*], Mohammed J. Al-Marri [d], Abdelbaki Benamor [d]

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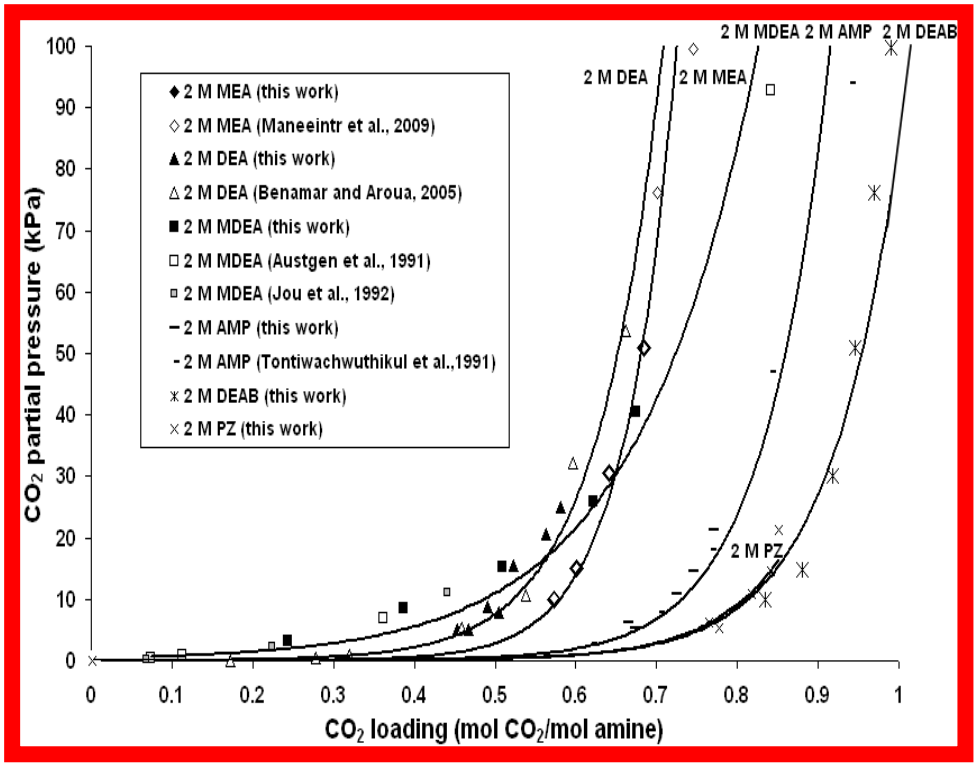
[d] *Gas Processing Center, Qatar University, Doha, Qatar*

*** Equilibrium Solubility – One of the key parameters

Equilibrium Solubility of CO_2

DEAB~PZ>AMP>MDEA>MEA >DEA



Math model for Equilibrium Solubility of CO_2

(AAD=7.3%)

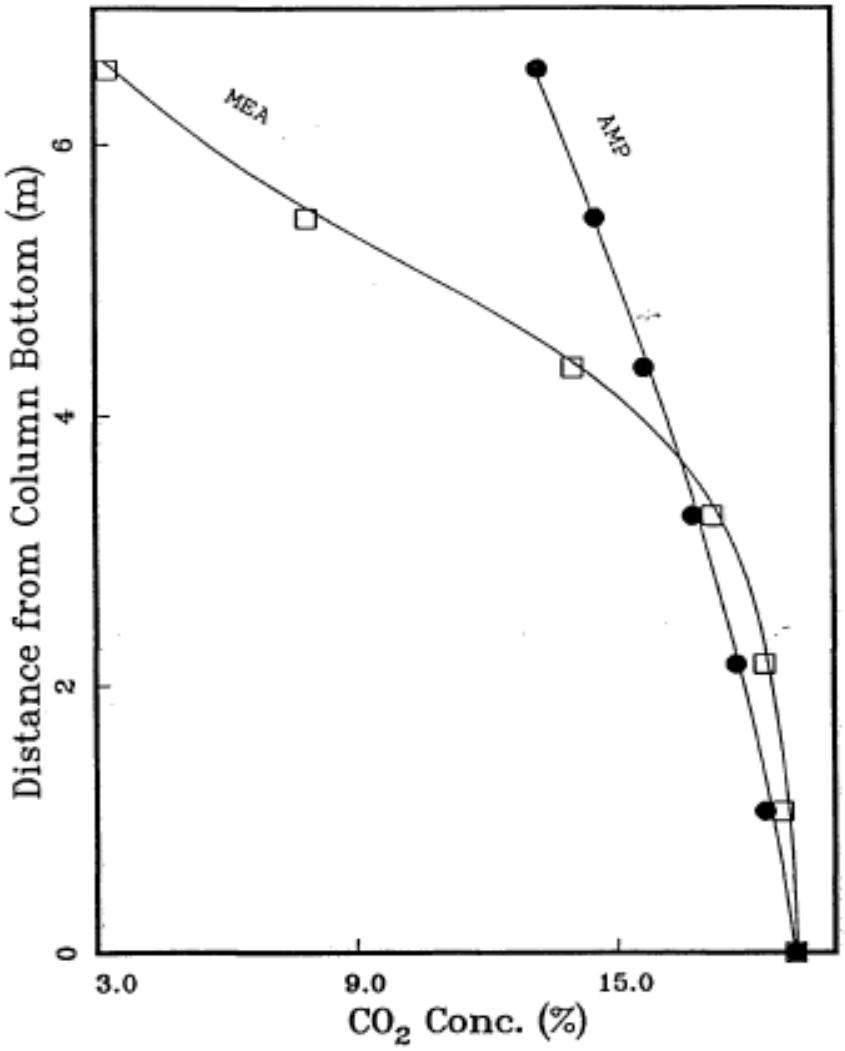
Equilibrium constant

$$CO_2 + RR_2'N + H_2O \xleftrightarrow{K_i} RR_2'NH^+ + HCO_3^-$$

$$K_2 = \frac{\left[RR_2'NH^+\right]\left[HCO_3^-\right]}{\left[CO_2\right]\left[RR_2'N\right]}$$

$$K_i = \exp\left[-193 + \frac{(-1.685\times10^4)}{T} + 67.85\ln T - 0.4325T\right]$$

*(Sema et al., **Ind. Eng. Chem. Res.** 2011, 50, 14008-14015)*



Column performance at high loading. **AMP** (Run T28 - solid circles) vs **MEA** (Run T18 - open squares). Operating conditions: gas flow rate = 14.8 mol/m^2 s; liquid flow rate = 9.5 m^3/m^2 hr; total amine concentration = 2.0 kmol/m^2; inlet gas CO_2 concentration = 19.15%; outlet CO_2 loading = 0.583 moles of CO_2 / mole of amine. The lines represent smoothed experimental values.

Why do we need this information ?

Kent, R. L.; Eisenberg, B. *Hydrocarbon Process*. **1976**, *55* (2), 87.

$$RNH_3^+ = H^+ + RNH_2 \quad (1)$$

$$RNHCOO^- + H_2O = RNH_2 + HCO_3^- \quad (2)$$

$$H_2O + CO_2 = H^+ + HCO_3^- \quad (3)$$

$$H_2O = H^+ + OH^- \quad (4)$$

$$HCO_3^- = H^+ + CO_3^{2-} \quad (5)$$

Classical Model of CO2-Amines Solubility

$$K_1 = [H^+][RNH_2]/[RNH_3^+] \quad (6)$$

$$K_3 = [H^+][HCO_3^-]/[CO_2] \quad (7)$$

$$K_4 = [H^+][OH^-] \quad (8)$$

$$K_5 = [H^+][CO_3^{2-}]/[HCO_3^-] \quad (9)$$

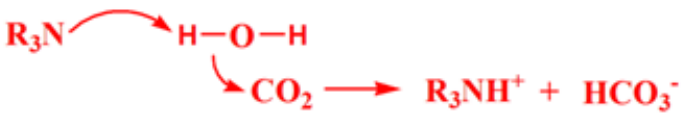
$$[AMP] = [RNH_2] + [RNH_3^+] \quad (10)$$

$$\alpha[AMP] = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \quad (11)$$

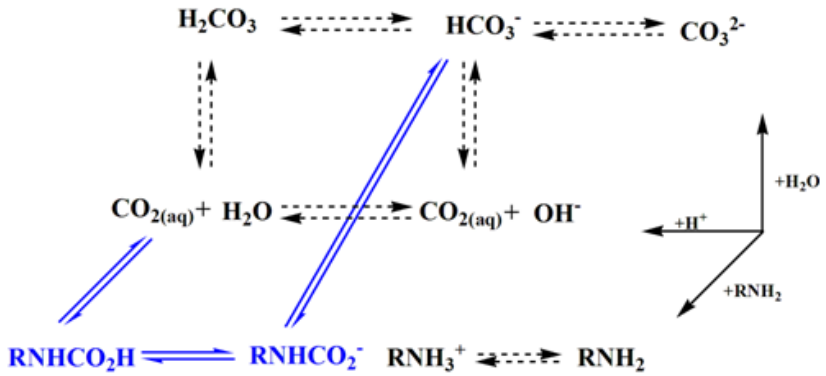
$$[RNH_3^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \quad (12)$$

Theory-thermodynamic model

➢**Tertiary amine and steric hindrance amine**



➢**Primary and secondary amine**



Liquid phase

Chemical Reactions

$$R_1R_2R_3H^+ \xleftrightarrow{K_1} R_1R_2R_3N + H^+$$

$$CO_2 + R_1R_2R_3 + H_2O \xleftrightarrow{K_2,k_2,k_{-2}} R_1R_2R_3H^+ + HCO_3^-$$

$$H_2O + CO_2 \xleftrightarrow{K_3} H^+ + HCO_3^-$$

$$CO_2 + OH^- \xleftrightarrow{K_4} HCO_3^-$$

$$HCO_3^- \xleftrightarrow{K_5} H^+ + CO_3^{2-}$$

$$H_2O \xleftrightarrow{K_6} H^+ + OH^-$$

Balance equation

$$[R_1R_2R_3N]_0 = [R_1R_2R_3NH^+] + [R_1R_2R_3N]$$

$$\alpha[R_1R_2R_3N]_0 = [CO_{2(aq)}] + [HCO_3^-] + [CO_3^{2-}]$$

$$[R_1R_2R_3NH^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

--where α denotes CO_2 loading

Gas-Liquid phase

Henry's Law

$$P_{CO_2} = He_{CO_2}[CO_{2(aq)}]$$

Gas phase

CO_2, N_2

Theory-thermodynamic model

Expressions of K_i (i=3,5,6) and H_{CO2}

$$K_i \text{ or } H^0_{CO_2} = exp\left(a + \frac{b}{T} + \frac{c}{T^2} + \frac{d}{T^3} + \frac{e}{T^4}\right) \qquad H_{CO_2} = \frac{H^0_{CO_2}}{7.50061}$$

	a	b	c	d	e
K_3	-248.818	298.253E3	-148.528E6	332.648E8	-282.394E10
K_5	-294.74	364.385E3	-184.158E6	415.793E8	-354.291E10
K_6	39.5554	-987.9E2	568.828E5	146.4561E8	136.146E10
H_{CO2}^0	22.2819	-138.306E2	691.346E4	-155.895E7	120.037E9

Dominate reaction

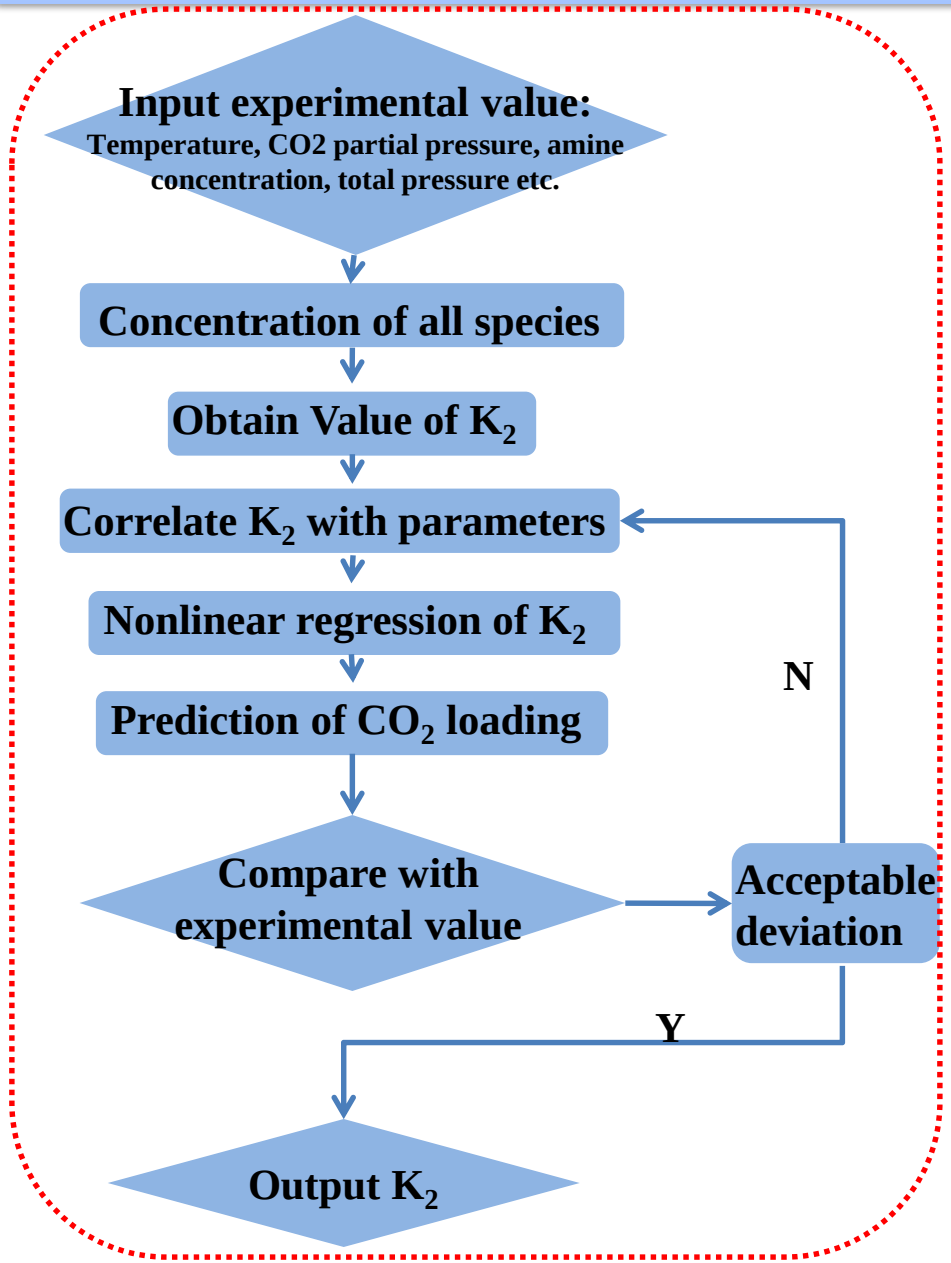
$$CO_2 + R_1R_2R_3 + H_2O \xleftrightarrow{K_2, k_2, k_{-2}} R_1R_2R_3H^+ + HCO_3^-$$

Equilibrium Constant K_2

- ➢Temperature
- ➢CO2 partial pressure
- ➢Amine concentration
- ➢Total pressure

Data source: Kent and Elsenberg, *Hydrocarbon processing*, 1976

Theory-thermodynamic model



Expression of K2

KE model

$$K_i = \exp(A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} + \frac{E}{T^4})$$

Heli-Liu model

$$K_i = \exp(B_1 + \frac{B_2}{T} + B_3 \ln T + B_4 T)$$

Hu-Chakma

$$K_i = \exp(D_1 + D_2 T + D_3[CO_{2aq}] + D_4 \ln[A\min e])$$

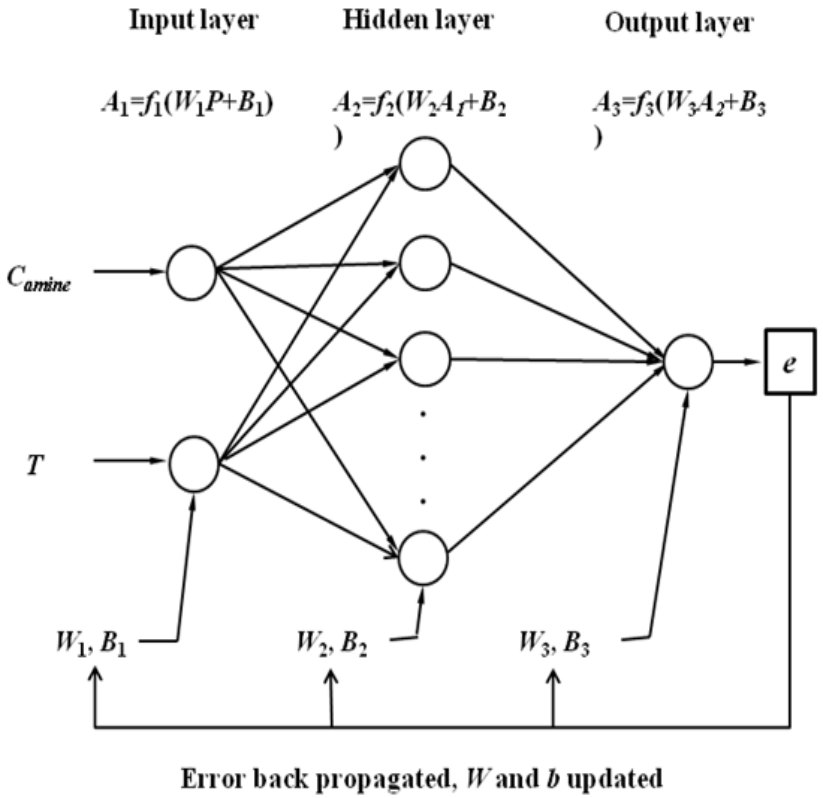
Li-Shen model

$$K_i = \exp(A_1 + \frac{A_2}{T} + \frac{A_3}{T} + C_1\alpha + \frac{C_2}{\alpha} + \frac{C_3}{\alpha} + C_4 \ln[A\min e])$$

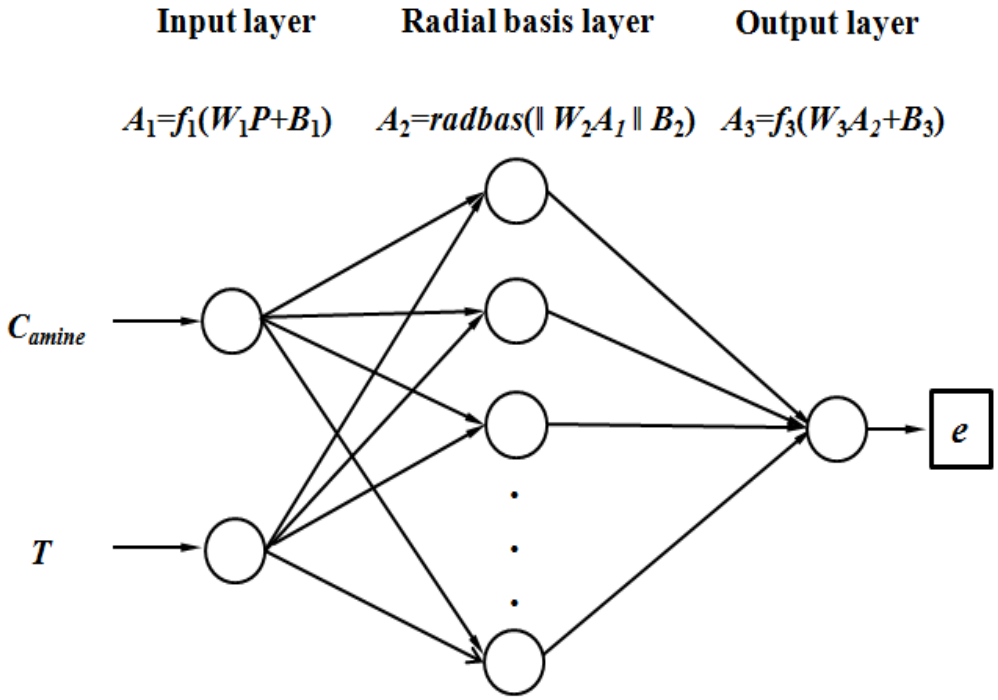
Liu et.al model

$$K_2 = \exp(E_1 + E_2 T + E_3[CO_{2aq}] + E_4 \ln[A\min e] + \frac{E_5}{P_{total}})$$

Theory-ANN model

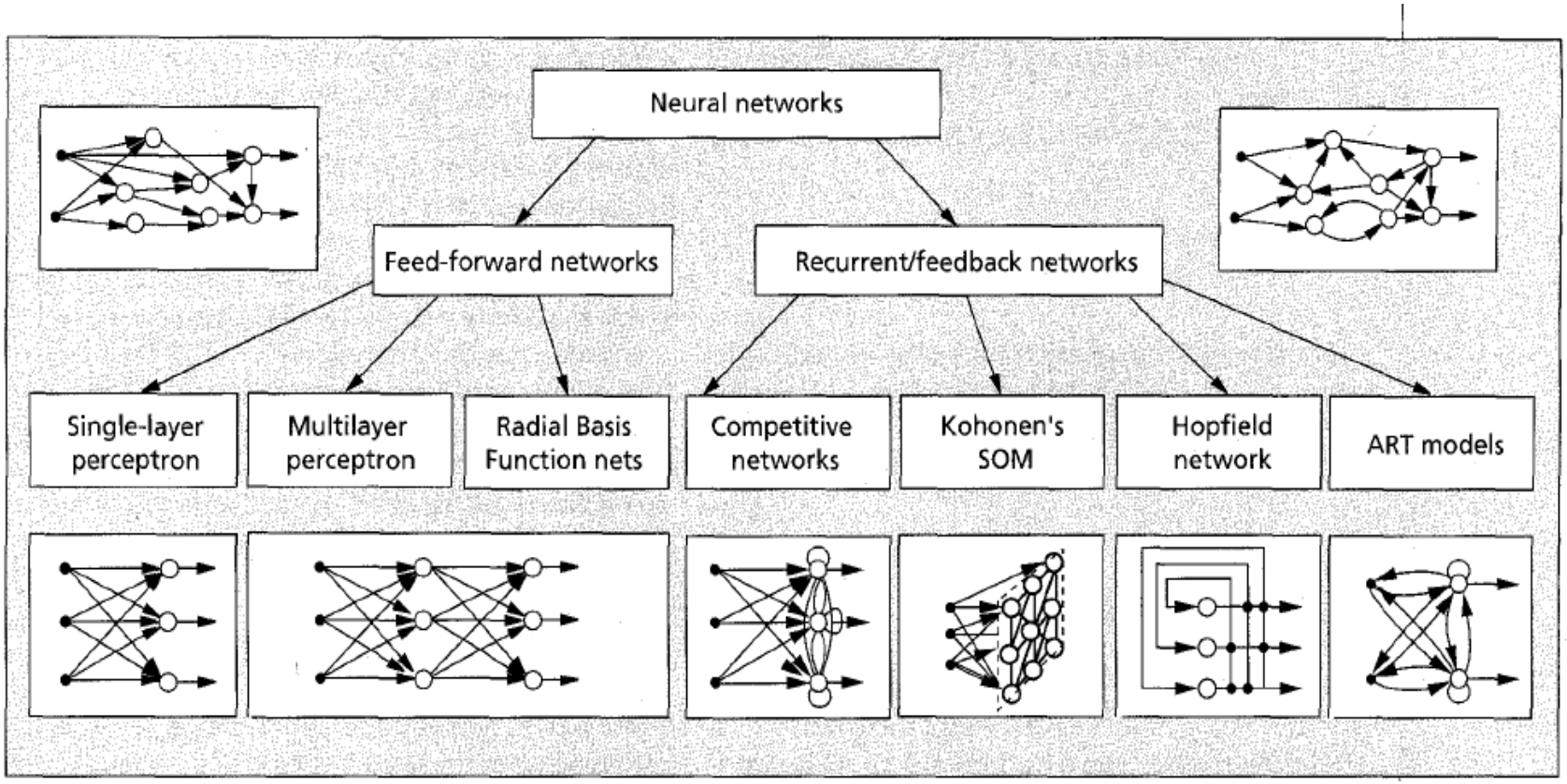


(a) The basic structure of RBFNN with multi-input parameters



(b) the basic structure of BPNN

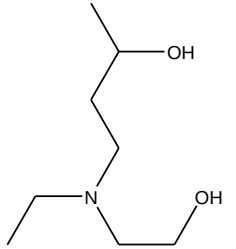
Topologies/Architectures of ANNs



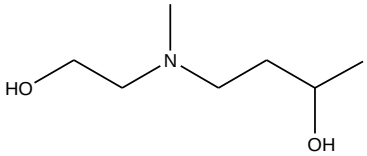
A taxonomy of feed-forward and recurrent/feedback network architecture (Jain & Mao, 1996)

Experiment

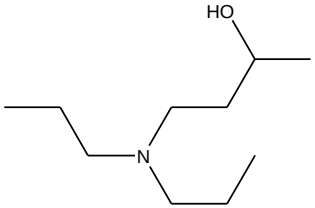
Structure and abbreviation



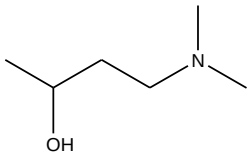
4-((2-hydroxyethyl)(ethyl)amino)-2-butanol
HEEAB



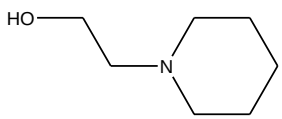
4-((2-hydroxyethyl)(methyl)amino)-2-butanol
HEMAB



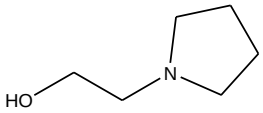
4-(dipropylamino)-2-butanol
DPAB



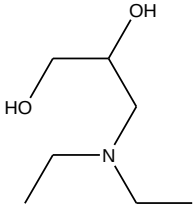
4-(dimethylamino)-2-butanol
DMAB



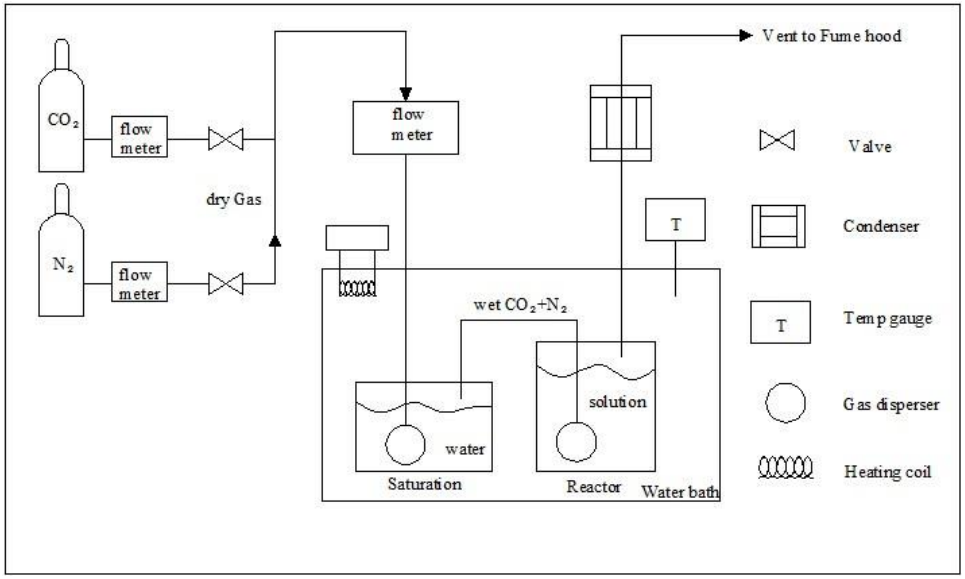
1-(2-Hydroxyethyl)-piperidine
1-(2-HE)PP



1-(2-Hydroxyethyl)pyrrolidine
1-(2-HE)PRLD



3-diethylamino-1,2-propanediol
DE-1,2-PD



Schematic diagram of the experimental setup for CO_2 loading measurement

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Synthesis of new amines for enhanced carbon dioxide (CO_2) capture performance: The effect of chemical structure on equilibrium solubility, cyclic capacity, kinetics of absorption and regeneration, and heats of absorption and regeneration

Sudkanueng Singto [a], Teeradet Supap [b,*], Raphael Idem [b,*], Paitoon Tontiwachwuthikul [b,*], Supawan Tantayanon [a,c,*], Mohammed J. Al-Marri [d], Abdelbaki Benamor [d]

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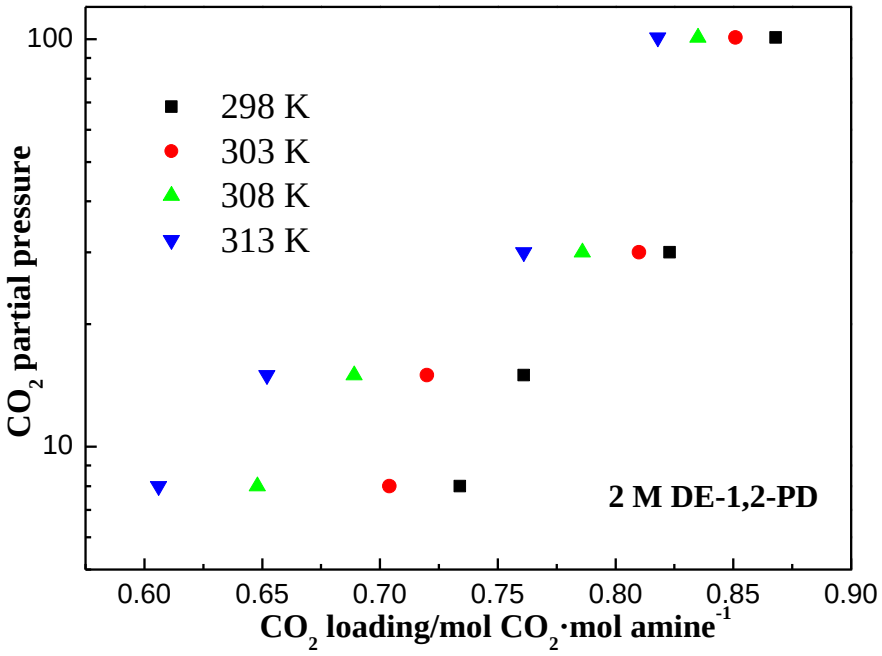
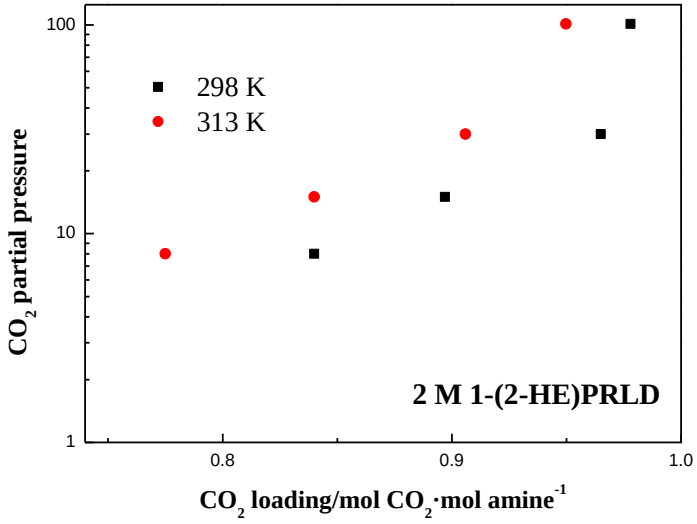
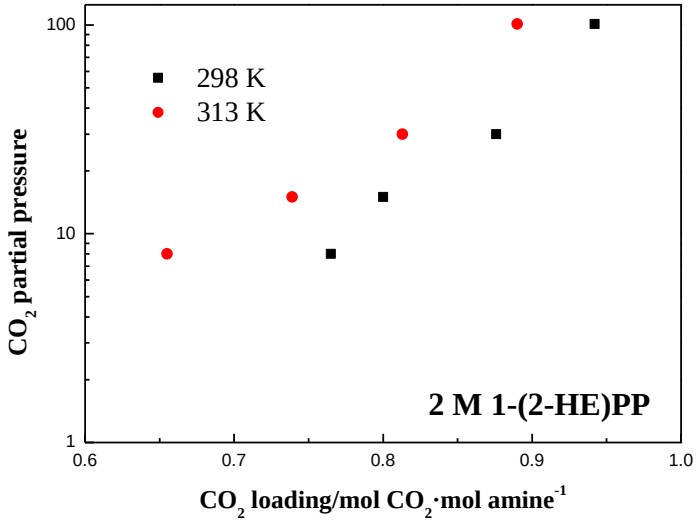
[b] Clean Energy Technologies Research Institute (CETRI), Faculty of Engineering and Applied Science, University of Regina, Regina, Saskatchewan S4S 0A2, Canada
[c] Green Chemistry Research Lab, Faculty of Science, Department of Chemistry, Chulalongkorn University, Bangkok 10330, Thailand
[d] Gas Processing Center, Qatar University, Doha, Qatar

Results and discussions



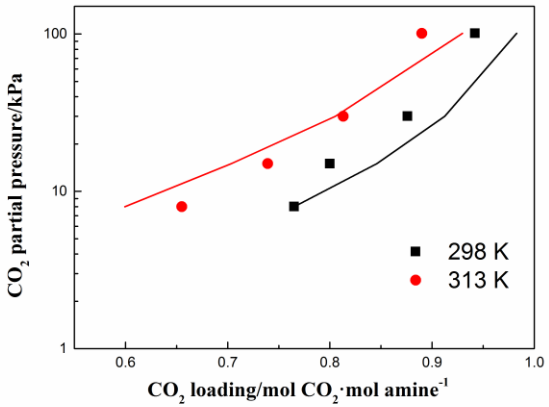




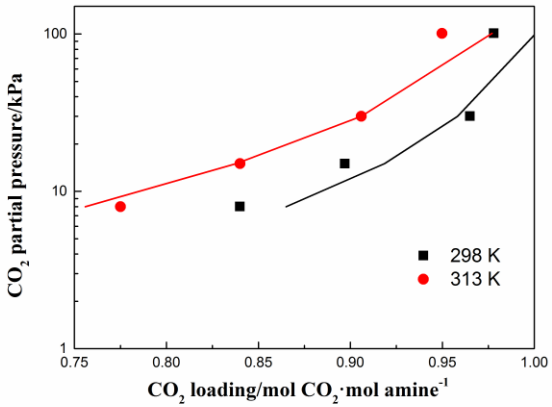
Higher temperature —decrease→ **CO_2 loading**

Higher CO_2 partial pressure —increase→ **CO_2 loading**

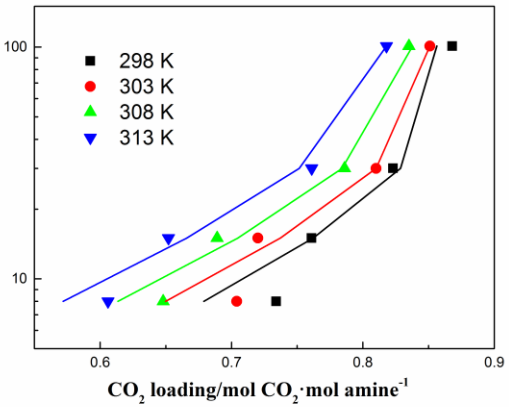
Results and discussions



1-(2-HE)PP (1.7%)



1-(2-HE)PRLD (4.1%)

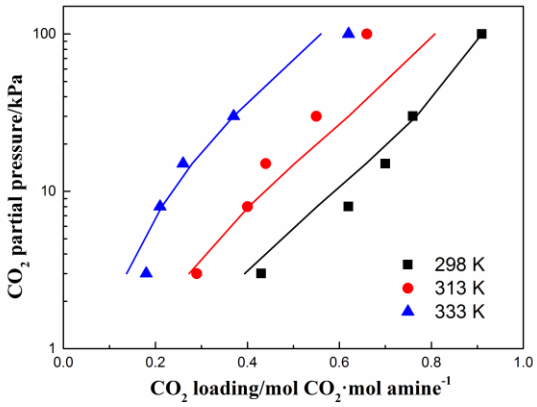


DE-1,2-PD (2.3%)

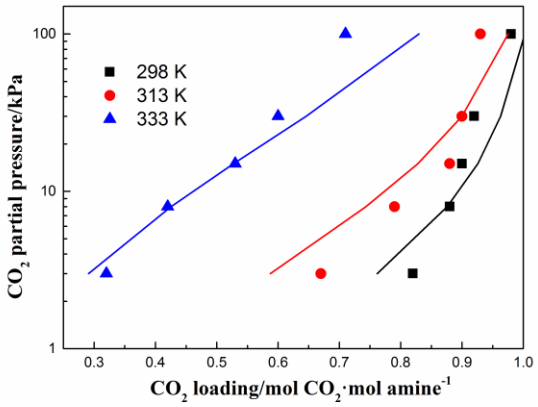
$$K_2 = \exp(E_1 + E_2 T + E_3[CO_{2aq}] + E_4 \ln[Amine] + \frac{E_5}{P_{total}})$$

Parameters	Values		
	1-(2-HE)PP	*1-(2-HE)PRLD*	*DE-1,2-PD*
E_1	-40.4898	-40.56	-35.7233
E_2	0.076937	0.073686	0.048486
E_3	4.300501	4.258291	48.42123
E_4	-27.8278	-27.8767	-21.974
E_5	0.453665	0.463335	-0.97328

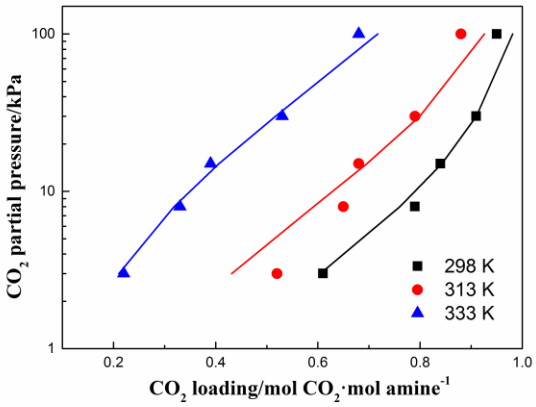
Results and discussions



HEMAB (8.3%)



DMAB (5.4%)



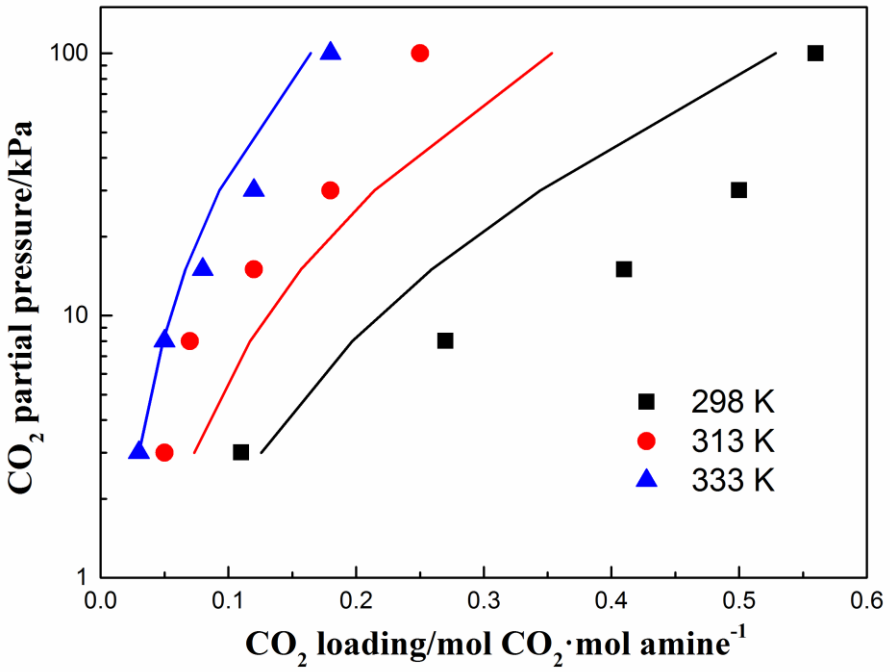
HEEAB (4.2%)

$$K_2 = \exp(E_1 + E_2 T + E_3[CO_{2aq}] + E_4 \ln[Amine] + \frac{E_5}{P_{total}})$$

Parameters	Values		
	HEMAB	*DMAB*	*HEEAB*
E_1	-37.1862	-44.3071	-40.637
E_2	0.065151	0.092229	0.077803
E_3	3.809235	2.00779	4.223386
E_4	-25.5374	-30.6291	-27.9302
E_5	0.036432	0.667424	0.473955

Data source: Singto et al., *Separation and Purification Technology*, 2016

Results and discussions



DPAB → **24.7%**

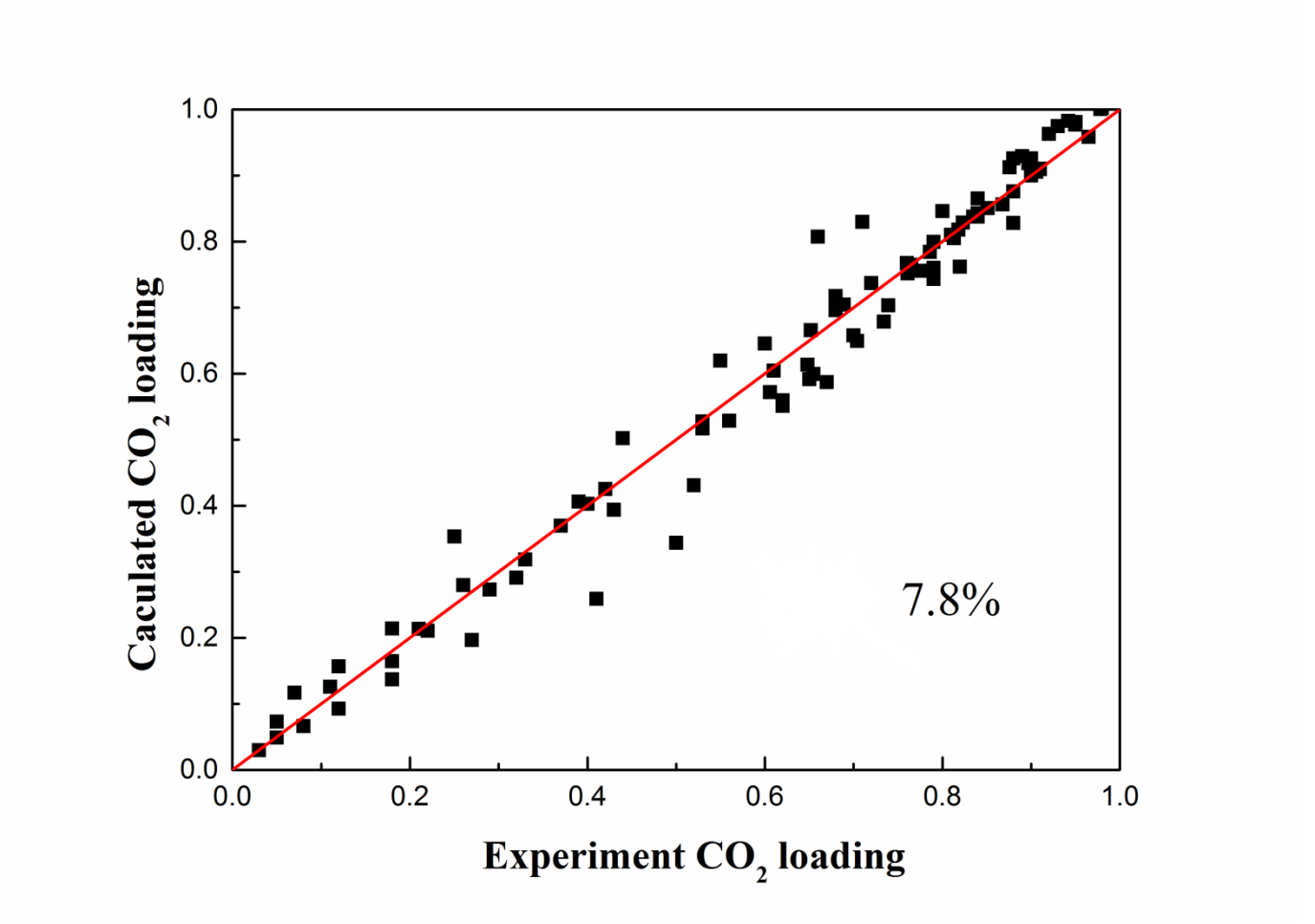
Fail to give reasonable result

- **The expression of K_2 is not suitable at low CO_2 loading region**
- **The absolute deviation is small although the relative deviation is large**

$$K_2 = \exp(E_1 + E_2 T + E_3[CO_{2aq}] + E_4 \ln[A\,min\,e] + \frac{E_5}{P_{total}})$$

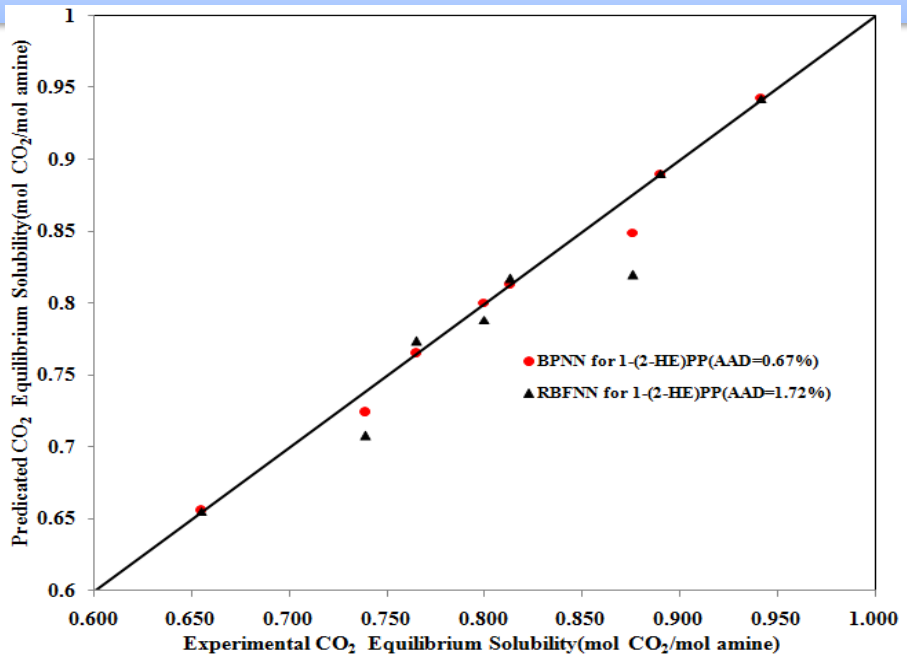
Parameters	Values
	DPAB
E_1	-37.8501
E_2	0.07901
E_3	3.365714
E_4	-26.4749
E_5	0.978131

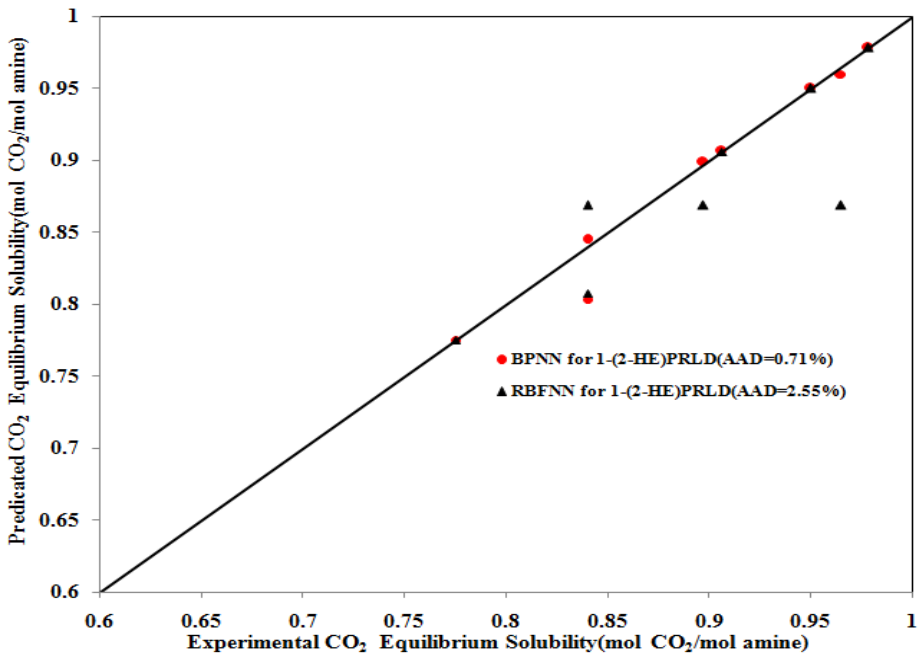
Results and discussions

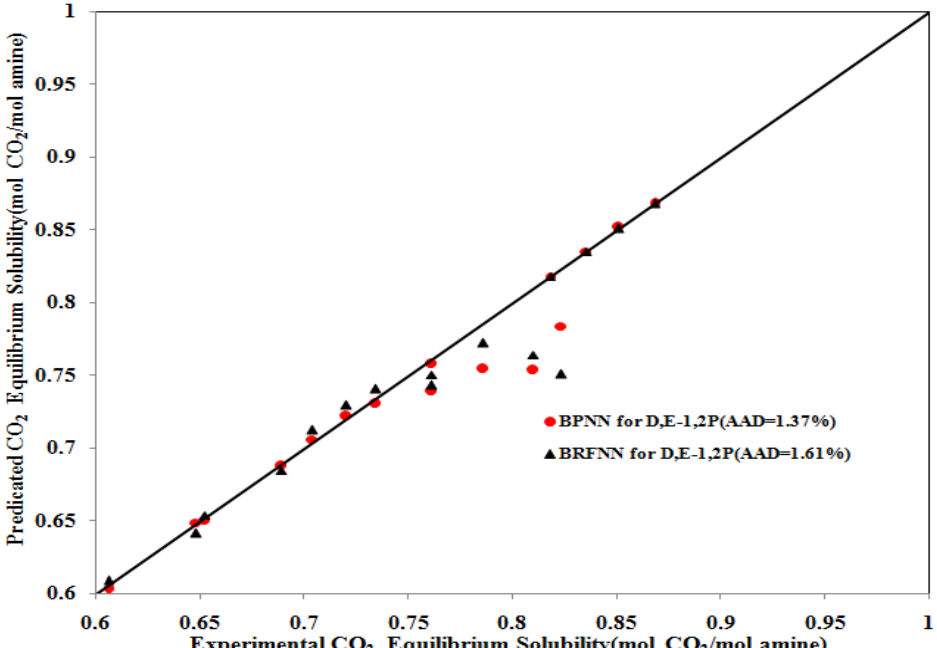


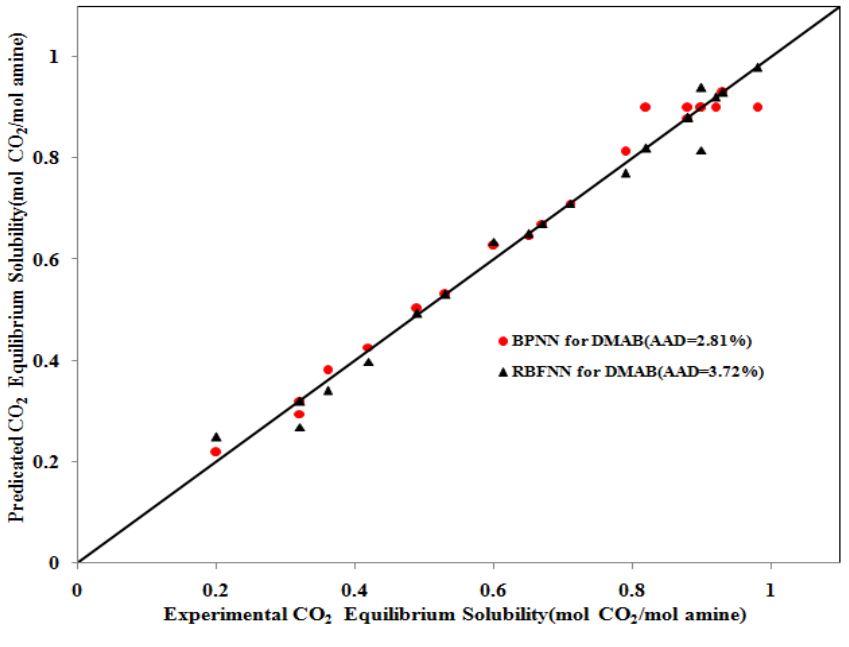
The summarize of all prediction results for investigated amines

Results and discussions-ANN

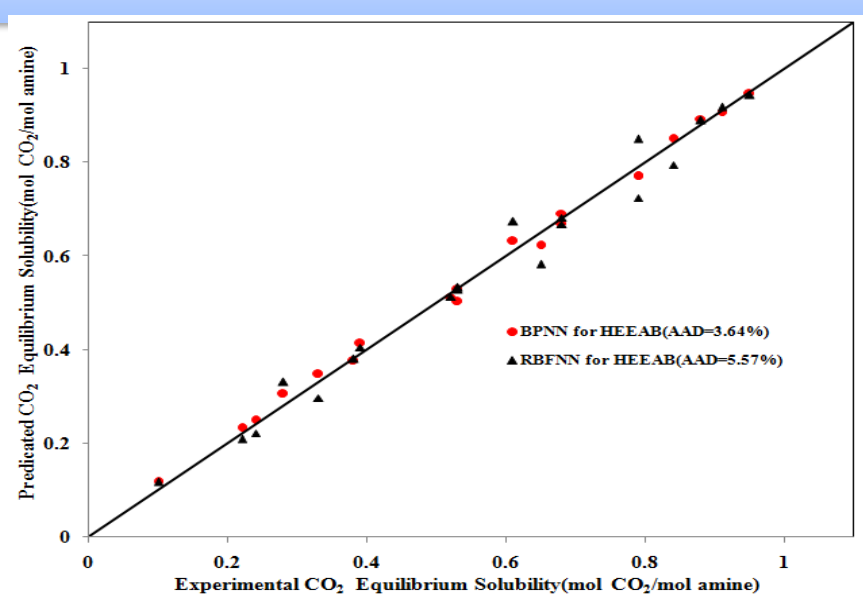


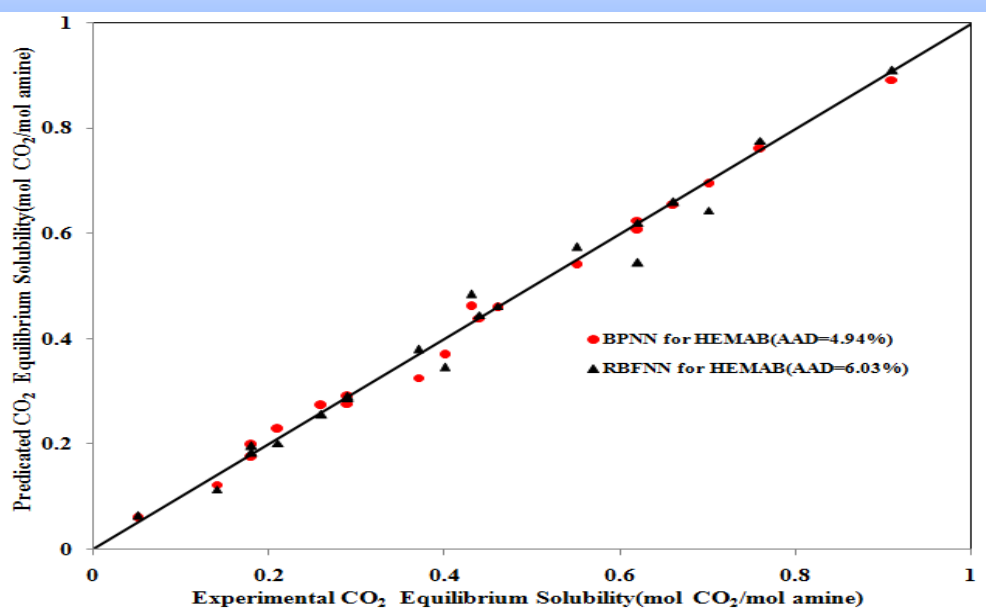


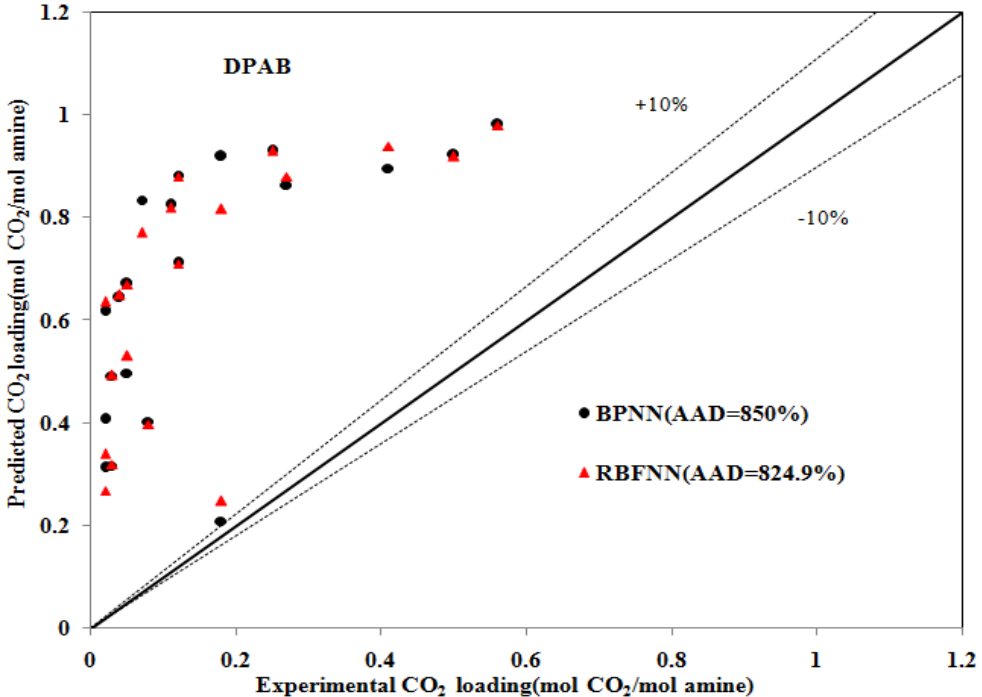




Results and discussions-ANN







Results and discussions

Amines	AAD(%)							
	Kent-Eisenberg model	*Austgen Model*	*Liu-Helei model*	*Li-Shen model*	*Hu-Chakma model*	*Liu et al model*	*BPNN model*	*RBFNN model*
DMAB	6.5	5.2	6.2	15.3	5.4	5.4	2.8	3.7
DPAB	28.5	24.8	25.6	23.3	25.8	24.7	850	824.9
HEMAB	8.5	9.3	8.7	66.4	8.4	8.3	4.9	6.0
HEEAB	4.6	4.7	4.9	32.7	4.2	4.2	3.6	5.6
1-(2-HE)PP	2.1	2.1	2.5	6.6	4.1	4.1	0.7	1.7
1-(2-HE)PRLD	2.6	2.6	2.1	3.2	1.7	1.7	0.7	2.6
D,E-1,2-AP	8.3	8.3	7.6	8.9	2.3	2.3	1.4	1.6

Conclusion

- **The CO_2 loading of some tertiary amine solvents was measured at various temperature and CO_2 partial pressure.**
- **A novel model was developed for predicting CO_2 loading. It was found that the model was able to give reasonable predictions for most of investigating amines.**
- **ANN models were developed for predicting CO_2 loading with the excellent AADs**
- **The solvents presented need to be used with other mixtures to get good results for CO2 capture.**

Good solvents need more than one ingredients !

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Advancement and new perspectives of using formulated reactive amine blends for post-combustion carbon dioxide (CO_2) capture technologies

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ARTICLE INFO

ABSTRACT

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Thank you