CO_2 ABSORPTION: SOLUBILITY OF CO_2 IN 2–AMINO-2-METHYL-1-PROPANOL SOLVENT PROMOTED BY PIPERAZINE AND MONOETHANOLAMINE BLENDS

Mr. Chikezie Ndubuisi Nwaoha

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University, and Institut Français du Pétrole

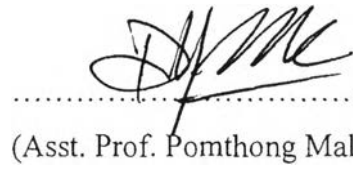
2015

I28368332

580004

Thesis Title:	CO_2 Absorption: Solubility of CO_2 in 2-Amino-2-Methyl-1-Propanol Solvent Promoted by Piperazine and Monoethanolamine Blends
By:	Chikezie Ndubuisi Nwaoha
Program:	Petroleum Technology
Thesis Advisors:	Assoc. Prof. Chintana Saiwan
	Prof. Paitoon Tontiwachwuthikul

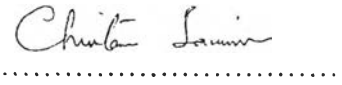
Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfillment of the requirements for the Degree of Master of Science.



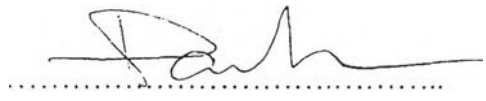
.....College Dean

(Asst. Prof. Pomthong Malakul)

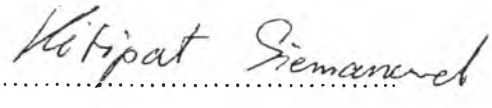
Thesis Committee:



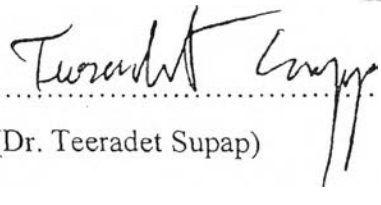
(Assoc. Prof. Chintana Saiwan)



(Prof. Paitoon Tontiwachwuthikul)



(Asst. Prof. Kitipat Siemanond)



(Dr. Teeradet Supap)

ABSTRACT

5673037063: Petroleum Technology Program

Chikezie Ndubuisi Nwaoha: CO_2 Absorption: Solubility of CO_2 in 2-Amino-2-Methyl-1-Propanol Solvent Promoted by Piperazine and Monoethanolamine Blends.

Thesis Advisors: Assoc. Prof. Chintana Saiwan, and Prof. Paitoon Tontiwachwuthikul 147 pp.

Keywords: Carbon dioxide solubility/ 2-amino-2-methyl-1-propanol/ Piperazine/ Absorption working capacity/ Monoethanolamine/ ProMax® 3.2/ Reboiler duty

This research work investigates the solubility data of carbon dioxide (CO_2) in a novel ternary blend of aqueous 2-amino-2-methyl-1-propanol (AMP) promoted by piperazine (PZ) and monoethanolamine (MEA) blends have been experimentally analysed at 20 °C, 40 °C, and 60 °C at CO_2 partial pressures between 2 kPa and 100 kPa. At 40 °C and 93.93 kPa CO_2 partial pressure, the concentrations of PZ and MEA promoters were varied between 0.5 M – 1 M and 2 M – 4 M, respectively, while the AMP concentration was kept at 2 M. The various concentrations of the ternary blend possessed superiority in both the equilibrium CO_2 loading (6.9 % to 19 %) and absorption working capacity (13.8 % to 48.3 %) compared to the conventional 5 M MEA. The effects of MEA and PZ concentrations, and H_2O-Amine molar ratio in terms of H_2O/PZ was also studied, and the solvent combination of 2 M AMP – 0.5 M PZ – 3 M MEA was selected for further equilibrium CO_2 loading analysis considering its very minimal potential of forming solid precipitates. The results were reported as a function of CO_2 partial pressures at the investigated temperatures. In addition, the energy penalty during regeneration was predicted using a validated ProMax® 3.2 CO_2 capture plant simulation. The simulation results indicated that the ternary blend solutions higher than 5 M had energy reductions between 5.3 % - 26.3 % compared to 5 M MEA (at the same condition).

บทคัดย่อ

ชิกเกะซี อัวฮาร์: ค่าการละลายของแก๊สคาร์บอนไดออกไซด์ในตัวทำละลาย 2-อะมิโน-2-เมทิล-1-โพรพานอล กระตุ้นโดยสารผสมระหว่างไพเปอราซีนและมอนอเอทาโนลามีน (CO_2 Absorption: Solubility of CO_2 in 2-Amino-2-Methyl-1-Propanol Solvent Promoted by Piperazine and Monoethanolamine Blends) รศ.ดร. จินตนา สายวรรณ์ และ ศ.ดร. ไพฑูรย์ ตันติเวชวุฒิกุล

ในการวิจัยนี้ได้มีการพิสูจน์ข้อมูลด้านการละลายของแก๊สคาร์บอนไดออกไซด์ ในสารละลาย ผสม 2-อะมิโน-2-เมทิล-1-โพรพานอล กระตุ้นโดยไพเปอราซีนและมอนอเอทาโนลามีน โดยการทดลองการวัดค่าการละลายดังกล่าวได้มีการวิเคราะห์ที่อุณหภูมิ 20 40 และ 60 องศาเซลเซียส ที่ความย่อยระหว่าง 2 กิโลพาสคัล และ 100 กิโลพาสคัล โดยแปรเปลี่ยนค่าความเข้มข้นของไพเปอราซีนที่ 0.5 - 1 โมลาร์ และมอนอเอทาโนลามีนที่ 2 – 4 โมลาร์ ในขณะที่ความเข้มข้นของ 2-อะมิโน-2-เมทิล-1-โพรพานอล อยู่ที่ 2 โมลาร์ ความเข้มข้นที่แปรเปลี่ยนไปของสารผสมทั้งสามทำให้ที่มีสมบัติบางประการที่ดีขึ้น เช่น ในเชิงสมบัติในการดักจับแก๊สคาร์บอนไดออกไซด์ (CO_2 loading) เพิ่มขึ้นจาก 6.9 เป็น 19 เปอร์เซ็นต์ และสมบัติความจุในการดูดซับ (absorption working capacity) เพิ่มขึ้นจาก 13.8 เป็น 48.3 เปอร์เซ็นต์ เมื่อเปรียบเทียบกับมอนอเอทาโนลามีนที่ความเข้มข้น 5 โมลาร์ ในงานวิจัยนี้ได้มีการศึกษาอิทธิพลของความเข้มข้นของมอนอเอทาโนลีนและเพพพาลาซีนในอัตราส่วนระหว่างน้ำต่อไพเปอราซีนและน้ำต่อ 2-อะมิโน-2-เมทิล-1-โพรพานอลที่มีผลต่อการเกิดตะกอนของของแข็ง ซึ่งผลปรากฏว่าความเข้มข้นของสารละลายผสมทั้งสามที่ 2 โมลาของ 2-อะมิโน-2-เมทิล-1-โพรพานอล 0.5 โมลาร์ของไพเปอราซีนและ 3 โมลาร์ของมอนอเอทาโนลามีนถูกใช้เป็นตัวชี้วัดสมบัติในการดักจับแก๊สคาร์บอนไดออกไซด์ (CO_2 loading) เนื่องจาก ณ สภาวะดังกล่าวส่งผลต่อการตกตะกอนของของแข็งในระบบน้อยที่สุด ผลของงานวิจัยนี้ได้เสนอในรูปแบบของความดันย่อยของแก๊สคาร์บอนไดออกไซด์ที่อุณหภูมิที่ต่างๆ โปรแกรมโปรแมกซ์เวอร์ชัน 3.2 (ProMax® 3.2) ใช้ในการจำลองการดักจับแก๊สคาร์บอนไดออกไซด์เพื่อทำนายผลของพลังงานที่ต้องการใช้ในส่วนนำสารละลายผสมกลับมาใช้ใหม่ ผลในแง่ของแบบจำลองระบุว่าสารละลายผสมทั้งสามที่ความเข้มข้นมากกว่า 5 โมลาร์ สามารถลดพลังงานในส่วนของการนำสารละลายกลับใช้ใหม่ได้ 5.3 ถึง 26.3 เปอร์เซ็นต์ เมื่อเปรียบเทียบกับความเข้มข้น 5 โมลาร์ของมอนอเอทาโนลามีนที่สภาวะเดียวกัน

ACKNOWLEDGEMENTS

First of all, I would like to thank my thesis advisors Assoc. Prof. Chintana Saiwan and Prof. Paitoon Tontiwachwuthikul for the great opportunity offered to me as a member of the research group and to learn about CO_2 capture using potential new solvent blends. I am also grateful to Dr. Teeradet Supap who was part of our research meetings for his valuable contributions from the start to finish of my research work. Without their support, it would have been near impossible to achieve all the experimental and simulation results presented in this work. Their follow-up and motivation in this research project is highly appreciated.

I am grateful for the partial scholarship and partial funding of the thesis work provided by the Petroleum and Petrochemical College.

My sincere appreciation also goes to some Engineers of Bryan Research and Engineering, USA (BR&E), licensors of ProMax® for their constant availability and constructive discussions during the period of simulation work: Mr. Martin D. Pieronek, Mr. Peter Krouskop and Mr. Jared Peterson.

I also thank Asst. Prof. Kitipat Siemanond, a member of my thesis committee for his participation and interest in appraising my research work.

I also wish to thank all my colleagues (MSc and PhD students) who contributed in one way or the other towards the achievement of this research work.

I also extend profound gratitude to all the staffs of the Petroleum and Petrochemical College for their entire support during the period of my studies and research.

Finally, my heartfelt thanks goes to my entire family members, my father Chief Edison Nwaoha, my mother Mrs. Josephine Nwaoha and step-mother Dame Eunice Nwaoha, my sisters Mrs. Chioma Nwofor and Mrs. Ijeoma Nwankwo, my brothers Mr. Kelechi Nwaoha and Dr. Iheanyi Nwaoha for their wonderful encouragement, love and prayers which sustained me during the tough periods of my studies and research work. I also extend my appreciation to my in-laws Prof. Okey Nwofor and Mr. Tochukwu Augustine Nwankwo for their backing and assistance.

TABLE OF CONTENTS

		PAGE
Title Page		i
Abstract (in English)		iii
Abstract (in Thai)		iv
Acknowledgements		v
Table of Contents		vi
List of Tables		x
List of Figures		xi
Abbreviations		xv
List of Symbols		xvi
CHAPTER		
I	**INTRODUCTION**	1
II	**THEORETICAL BACKGROUND AND LITERATURE REVIEW**	4
	2.1 Sources of CO_2 Capture	4
	2.1.1 Post-combustion Capture	7
	2.1.2 Pre-combustion Capture	8
	2.1.3 Oxyfuel Combustion	8
	2.1.4 Industrial Separation	8
	2.2 CO_2 Separation and Capture Technologies	10
	2.2.1 Absorption Process	11
	2.2.2 Adsorption Process	12
	2.2.3 Cryogenic Process	12
	2.2.4 Membrane	17
	2.3 Chemical Absorption	15
	2.3.1 Alkanolamine Solutions	16

CHAPTER **PAGE**

2.3.2 Sterically Hindered Amines 24
2.3.3 Polyamines 25
2.3.4 Blended/Mixed Amines 29
2.3.5 Hybrid Solvents 32
2.4 Amine Problems 32
2.4.1 Degradation 32
2.4.2 Vaporization Losses 33
2.4.3 Solvent Reactivity 34
2.4.4 Corrosion 34
2.4.5 Environmental Impact 35
2.4.6 Regeneration Energy 35
2.5 Related Works 37

III EXPERIMENTAL 40
3.1 Materials and Equipment 40
3.1.1 Materials 40
3.1.2 Equipment 40
3.1.3 Software 41
3.2 Experimental Procedures 41
3.2.1 Experimental Set-up 41
3.2.2 Solution Preparation Analysis 43
3.2.3 Solvent Concentration Analysis 45
3.2.4 Hydrochloric Acid Preparation and Standardization 46
3.2.5 CO_2 Loading Analysis αCO_2 47
3.2.6 Displacement Solution Preparation 49

IV RESULTS AND DISCUSSION 51
4.1 Validation of Experimental Set-up 51

CHAPTER **PAGE**

4.2 CO_2 Solubility and Absorption Working Capacity in Single Solvents 52

4.2.1 CO_2 Solubility in AMP 53

4.2.2 CO_2 Solubility in PZ 54

4.2.3 CO_2 Solubility in MEA 55

4.3 CO_2 Solubility in AMP-PZ Binary Blends 57

4.4 AMP-PZ-MEA Ternary Blends 59

4.4.1 Chemical Equilibria of AMP-PZ-MEA 59

4.4.2 CO_2 Solubility in AMP-PZ-MEA Ternary Blends 61

4.5 CO_2 Solubility in Novel 2 M AMP - 0.5 M PZ – 3 M MEA 69

4.6 CO_2 Capture Plant Simulation 71

4.6.1 Simulation using ProMax 3.2 71

4.6.2 The MEA Base Case and Validation 72

4.6.3 AMP – PZ – MEA vs MEA Simulation 76

V **CONCLUSIONS AND RECOMENDATIONS** 80

5.1 Conclusions 80

5.2 Recommendations 82

REFERENCES 84

APPENDICES 102

Appendix A Amine Solution Preparation Calculation 102

Appendix B Hydrochloric (HCl) Acid Preparation and Standardization 105

Appendix C Amine Solution Concentration Calculation 108

Appendix D Carbon Dioxide (CO_2) Loading Calculation 112

Appendix E Carbon Dioxide (CO_2) Partial Pressure Calculation 114

CHAPTER **PAGE**

Appendix F H_2O/PZ Molar Ratio Calculation 116

Appendix G Process Simulation Result Datas of Base Case (5 M MEA) and the Ternary Blends 119

Appendix H Equilibrium Curve and Reproducibility of Experimental Results 135

Appendix I Reducing Sources of Error during Experimental Analysis 138

Appendix J CO_2 Solubility in AMP – PZ – DETA – MEA Quaternary (Quad-Solvent) Blends 142

CURRICULUM VITAE 147

LIST OF TABLES

TABLE		PAGE
2.1	Merits and de-merits of CO_2 capture sources	9
2.2	Comparison of CO_2 separation and capture technologies	14
2.3	Most common types of primary amines	19
2.4	Most common types of secondary amines	20
2.5	Most common types of tertiary amines	21
2.6	Properties of alkanolamines	23
2.7	Sterically hindered amines	25
2.8	Skeletal structure of other polyamines	28
2.9	Several proposed CO_2 capture process configurations	37
3.1	Properties of AMP, PZ and MEA	44
4.1	Visual and tests observations for the different AMP-PZ-MEA concentrations at 40 °C and 93.93 kPa CO_2 partial pressure before and after CO_2 loading	63
4.2	Flue gas composition	73
4.3	Base case validation for 5 M (30 wt %) MEA	75
4.4	Cyclic capacity prediction and comparison of the amine solution using ProMax 3.2	77
A1	Properties of AMP, PZ and MEA	102
B1	Required properties of HCl and Na_2CO_3	105
J1	Skeletal structure of other DETA	142

LIST OF FIGURES

FIGURE		PAGE
2.1	Annual CO_2 emissions by fuel type.	4
2.2	2012 CO_2 emissions by sector.	5
2.3	Schematic of a carbon capture storage and utilization System.	6
2.4	Sources of CO_2 capture.	7
2.5	Schematic of CO_2 separation and capture technologies.	11
2.6	Simplified membrane unit.	13
2.7	Typical process flow diagram of CO_2 chemical absorption.	16
2.8	Several routes to an improved solvent mixture for CO_2 capture.	38
3.1	Diagram of the experimental set-up.	43
3.2	Pure 2-amino-2-methyl-1-propanol, AMP (99 wt%).	45
3.3	Schematic of chittick apparatus.	49
4.1	Results of validation using 5 M (30 wt%) MEA vs Shen & Li, 1992; 3.1 M (30 wt%) DEA vs Seo & Hong, 1996; and 3 M AMP vs Roberts & Mather, 1988 at 40 °C.	51
4.2	Precipitation of rich solution of 4 M AMP after it was cooled to 20 °C for over 200 hours.	53
4.3	CO_2 solubility (mol CO_2/mol amine) and absorption working capacity (aWC, mol CO_2/L of solution) of 2 – 4 M AMP at 40 °C and 93.93 kPa CO_2 partial pressure.	54
4.4	Solubility of CO_2 (mol CO_2/mol amine) and absorption working capacity (aWC, mol CO_2/L amine solution) in different concentrations of PZ at temperature and CO_2 partial pressure of 40 °C and 93.93 kPa respectively.	55

FIGURE **PAGE**

4.5	Non-precipitation of rich solution of 16.5 M MEA (99 wt %) after it was cooled at 20 °C for over 480 hours.	56
4.6	Solubility of CO_2 (mol CO_2/mol amine) and absorption working capacity (aWC, mol CO_2/L amine solution) in different MEA concentrations at temperature and CO_2 partial pressure of 40 °C and 93.93 kPa respectively.	56
4.7	CO_2 Solubility (mol CO_2/mol amine) and absorption working capacity (aWC, mol CO_2/L amine solution) of AMP – PZ blends at 40 °C and 93.93 kPa CO_2 partial pressure.	58
4.8	Rich solution of 3 M AMP – 1.5 M PZ it was cooled at 20 °C for over 480 hours.	58
4.9	CO_2 solubility (mol CO_2/mol amine) and absorption working capacity (aWC, mol CO_2/L amine solution) of different concentrations of ternary AMP-PZ-MEA blends at 40 °C and 93.93 kPa CO_2 partial pressure.	62
4.10	Non-precipitation of rich solution of the highly concentrated (6 – 7 M) ternary blends after they were cooled at 20 °C for over 480 hours.	64
4.11	Water-Amine molar ratios in terms of H_2O/PZ.	66
4.12	Equilibrium CO_2 loading in 2 M AMP – 0.5 M PZ – 3 M MEA.	70
4.13	A typical CO_2 capture process configuration.	73
4.14	Temperature profile of the base case (30 wt% MEA) Simulation.	76
4.15	Reboiler duty comparisons between the base 5 M MEA, 3 M AMP – 1.5 M PZ and the ternary AMP-PZ-MEA blends.	78

FIGURE **PAGE**

5.1	Proposed Individual solvent selection and their concentration in tri-solvent blends.	81
G1	Absorber process data information's for the simulation.	119
G2a	Absorber stage data summary and results for the base case simulation.	120
G2b	Absorber stage data hardware general results for the base case simulation.	121
G2c	Absorber stage data structured hardware results for the base case simulation.	122
G3	Absorber convergence specification.	123
G4	Stripper process data information's for the simulation.	123
G5a	Stripper Stage Data Summary and Results for the base case simulation.	124
G5b	Stripper stage data hardware general results for the base case simulation.	125
G5c	Stripper stage data structured hardware results for the base case simulation.	126
G6	Stripper specifications for the simulations.	127
G7	Stripper convergence specification for the simulations.	127
G8	Simulation results for the base case 5 M MEA.	128
G9	Simulation results for 2 M AMP – 0.5 M PZ – 2.5 M MEA.	129
G10	Simulation results for 2 M AMP – 0.5 M PZ – 3 M MEA.	130
G11	Simulation results for 2 M AMP – 1 M PZ – 2 M MEA.	131
G12	Simulation results for 2 M AMP – 1 M PZ – 2.5 M MEA.	132
G13	Simulation results for 2 M AMP – 1 M PZ – 3 M MEA.	133
G14	Simulation results for 2 M AMP – 1 M PZ – 4 M MEA.	134
H1	CO_2 Equilibrium graph for 2 M AMP – 0.5 M PZ – 3 M MEA at 25 – 60 °C and 100 % CO_2.	135

FIGURE **PAGE**

H2	Reproducibility results of 2 M AMP – 0.5 M PZ – 3 M MEA at 25 – 60 °C and 100 % CO_2.	136
I1	Sources of error during experimental analysis.	138
I2	CO_2 equilibrium graph for 2 M AMP – 0.5 M PZ – 3 M MEA at 25 – 60 °C and 100 % CO_2.	139
J1	CO_2 solubility (mol CO_2/mol amine) and absorption working capacity (aWC, mol CO_2/L amine solution) of different concentrations of quartenary AMP-PZ-DETA-MEA Blends at 40 °C and 93.93 kPa CO_2 partial pressure compared to 5 M MEA, 3 M AMP – 1.5 M PZ and AMP-PZ-MEA ternary blends.	143
J2	Rich solution of 2 M AMP – 0.5 M PZ – 1 M DETA – 1.5 M MEA showing the color change.	139
J3	Rich solution of 1.5 M AMP – 0.5 M PZ – 1.5 M DETA – 1.5 M MEA showing the color change.	145

ABBREVIATIONS

%AAD = Absolute average deviation
AEP = N-2-aminoethyl-piperazine
AMP = 2-amino-2-methyl-1-propanol
aWC = Absorption working capacity
CC = Cyclic capacity
DEA = Diethanolamine
DETA = Diethylenetriamine
DGA = Diglycolamine
DIPA = Diisopropanolamine
EDA = Ethylenediamine
E-ELR = Electrolytic extended long range
E-NRTL = Electrolytic non-random two liquid
HSS = Heat stable salts
L/G = Liquid/gas flow rate ratio
MEA = Monoethanolamine
MAPA = 3-methylaminopropylamine
MDEA = Methyldiethanolamine
MSDS = Material safety data sheet
PE = 2-piperidineethanol
PZ = Piperazine
RE = Regeneration efficiency
TEPA = Tetraethylenepentamine
TETA = Triethylenetetramine

LIST OF SYMBOLS

Ar	=	Argon
CO_2	=	Carbon dioxide
COS	=	Carbonyl sulphide
CS_2	=	Carbon disulphide
H_2O	=	Water
H_2S	=	Hydrogen sulphide
HCl	=	Hydrochloric acid
M	=	mol/L or kmol/m^3
N	=	Amino group
N_2	=	Nitrogen
Na_2CO_3	=	Sodium carbonate
NO_x	=	Nitrogen oxides
O_2	=	Oxygen
OH^-	=	Hydroxyl group
P_{CO2}	=	Partial pressure of CO_2, kPa
Q_{reg}	=	Energy of regeneration
Q_{sen}	=	Sensible heat
Q_{des}	=	Heat of desorption
Q_{vap}	=	Latent heat of vaporization
SO_x	=	Sulphur oxides
SO_2	=	Sulphur dioxide

Greek Letters

αCO_2	=	CO_2 loading, mol CO_2/mol amine