A COMPREHENSIVE STUDY OF THE DEGRADATION OF AQUEOUS MONOETHANOLAMINE SOLUTION DURING CO_2 CAPTURE FROM POWER PLANT FLUE GASES: ANALYTICAL TECHNIQUES, DEGRADATION KINETCS AND DEGRADATION PREVENTION TECHNIQUES

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ABSTRACT

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Mr. Teeradet Supap: A Comprehensive Study of the Degradation of Aqueous Monoethanolamine Solution during CO_2 Capture from Power Plant Flue Gases: Analytical Techniques, Degradation Kinetics, and Degradation Prevent Techniques.
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This study involved the evaluation of the factors that affect the degradation of aqueous monoethanolamine solution during CO_2 capture from power plant flue gas streams. Specific achievements involved the development of analytical techniques for analysis of MEA and its oxidative degradation products, the elucidation of the roles played by SO_2, O_2, MEA and CO_2 in MEA degradation, the formulation and development of mechanism based O_2-SO_2 induced MEA degradation kinetics, and the investigation of degradation prevention techniques based on both the use of degradation inhibitors and suitable operating procedures for amine based CO_2 capture. GC-MS with different column arrangements, HPLC-RID with nucleosil column/KH_2PO_4 mobile phase, CE-DAD using phosphate and borate electrolytes were all capable of analyzing MEA and its degradation products in MEA-O_2 systems with/without CO_2. A total of four kinetic models for MEA-O_2-SO_2-CO_2 degradation system were developed. It was only the combined mechanism based model that best characterized the MEA degradation system in terms of acceptable accuracy, no limitations in predicting MEA degradation rate, and the capability in providing the degradation mechanistic details. Some of the degradation inhibitor chemical such as UR-A were found to minimize the degradation of MEA in the presence of O_2 and SO_2 when used at their optimum concentrations.

บทคัดย่อ

ธีรเดช สุภาพ : การศึกษาเพื่อความเข้าใจอย่างชัดแจ้งของการแตกสลายของ โมโนเอทานอลามีนในสารละลายน้ำ ระหว่างการจับก๊าซคาร์บอนไดออกไซด์จากปล่องก๊าซของโรงไฟฟ้าพลังงาน: วิธีวิเคราะห์ จลนศาสตร์ของการแตกสลาย และวิธีป้องกันการแตกสลายโดยใช้สารยับยั้ง (A Comprehensive Study of the Degradation of Aqueous Monoethanolamine Solution during CO_2 Capture from Power Plant Flue Gases: Analytical Techniques, Degradation Kinetics, and Degradation Prevention Techniques) อ. ที่ปรึกษา: รศ.ดร. จินตนา สายวรรณ์ ศ.ดร. ไพฑูรย์ ตันติเวชวุฒิกุล และ ศ. ดร. ราฟาเอล ไอเด็ม 157 หน้า

งานวิจัยนี้ศึกษาปัจจัยที่เกี่ยวข้องกับผลกระทบต่อการแตกสลายโมโนเอทานอลามีน (เอ็มอีเอ) ในสารละลายที่เป็นน้ำระหว่างการจับก๊าซคาร์บอนไดออกไซด์ จากสายธารก๊าซจากปล่องโรงไฟฟ้าพลังงาน ความสำเร็จของการศึกษาคือ การพัฒนาวิธีวิเคราะห์สารเอ็มอีเอ และผลิตภัณฑ์จากออกซิเดชัน การอธิบายอย่างแจ่มแจ้งถึงบทบาทของซัลเฟอร์ไดออกไซด์ ออกซิเจน เอ็มอีเอและคาร์บอนไดออกไซด์ที่มีต่อการแตกสลายของเอ็มอีเอ การสร้างสมการและการพัฒนากลไกทางจลนศาสตร์ของออกซิเจน-ซัลเฟอร์ไดออกไซด์ที่เหนี่ยวนำให้เกิดการแตกสลาย และการค้นหาวิธีป้องกันการแตกสลายโดยใช้ตัวยับยั้งการแตกสลายและหาวิธีใช้เอมีนอย่างเหมาะสม เพื่อจับคาร์บอนไดออกไซด์ การวิเคราะห์ด้วยจีซี-เอ็มเอสต่อกับคอลัมน์ต่างชนิด เอชพีแอลซี-อาร์ไอดีต่อกับคอลัมน์นูคลีโอซิลและเฟสเคลื่อนที่เป็นโปแตสเซียมไดไฮโดรเจนฟอสเฟต และซีอี-ดีเอดีกับอิเล็กโตรไลท์ฟอสเฟตและบอเรท วิเคราะห์หาเอ็มอีเอและผลิตภัณฑ์ที่ได้จากการแตกสลายในระบบของเอ็มอีเอ-ออกซิเจน ทั้งที่มีและไม่มีคาร์บอนไดออกไซด์อยู่ด้วย สมการทางจลนศาสตร์ที่ใช้รวม 4 สมการ ถูกพัฒนาขึ้นมาใช้อธิบายการแตกสลายของเอ็มอีเอในระบบที่มีออกซิเจน-ซัลเฟอร์ไดออกไซด์-คาร์บอนไดออกไซด์ โมเดลที่พัฒนาขึ้นมาใช้กลไกร่วมบอกลักษณะการแตกสลายของเอ็มอีเอในระบบได้ดีที่สุด ในแง่ของความแม่นยำไม่มีขีดจำกัดของการใช้ทำนายอัตราการแตกสลายและสามารถอธิบายกลไกได้อย่างละเอียด งานวิจัยนี้ยังพบว่าสารยับยั้งยูอาร์-เอสามารถลดอัตราการเกิดปฏิกิริยาแตกสลายของโมโนเอทานอลามีนในระบบที่มีออกซิเจนและซัลเฟอร์ไดออกไซด์เมื่อใช้ที่ความเข้มข้นที่เหมาะสมที่ 0.05 กิโลโมลต่อลูกบาศก์เมตร

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TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	xii
List of Figures	xv
Abbreviations	xx
List of Symbols	xxi

CHAPTER

I	**INTRODUCTION**	1
	1.1 Enhanced Greenhouse Effect and Coal-induced CO_2 Emission	2
	1.2 CO_2 Absorption Process	5
	1.2.1 Alkanolamine Solutions	5
	1.3 Research Motivation	8
	1.3.1 Research Objectives	11
	1.3.1.1 Analysis of MEA and Its Oxidative Degradation Products During CO_2 Absorption from Flue Gases: A Comparative Study of GC-MS, HPLC-RID and CE-DAD Analytical Techniques and Possible Optimum Combinations	11

CHAPTER **PAGE**

I

1.3.1.2 Studies of SO_2 and O_2 Induced Degradation of Aqueous MEA Solution During CO_2 Absorption from Power Plant Flue Gas Streams 12

1.3.1.3 Preliminary Study of Degradation Prevention Techniques Using Degradation Inhibitor for MEA Based CO_2 Absorption from Power Plant Flue Gases 12

II **BACKGROUND OF ALKANOLAMINE DEGRADATION** 14

2.1 Analytical Techniques for Determination of Alkanolamines and Their Degradation Products 14

2.1.1 Gas Chromatography (GC) 14

2.1.2 Liquid Chromatography (LC) 17

2.1.3 Capillary Electrophoresis (CE) 19

2.1.4 Infrared Spectroscopy (IR) and Nuclear Magnetic Resonance Spectroscopy (NMR) 20

2.2 Kinetics and Mechanism of Oxidative Degradation of Alkanolamines 21

2.3 Degradation Inhibitor 29

2.4 Sulfur Induced Degradation of Alkanolamines 32

CHAPTER **PAGE**

III EXPERIMENTALS 35

3.1 Development of Analytical Techniques for MEA Oxidative Degradation 35

3.1.1 Equipment and Chemicals 35

3.1.2 Typical Experimental Runs 36

3.1.2.1 MEA-H_2O-O_2 Degradation System 36

3.1.2.2 MEA-H_2O-O_2-CO_2 Degradation System 37

3.1.3 Analysis of Degradation Products 39

3.1.3.1 Gas Chromatography/Mass Spectrometric Technique (GC-MS) 39

3.1.3.2 High Performance Liquid Chromatographic Technique (HPLC) 49

3.1.3.3 Capillary Electrophoresis Technique (CE) 50

3.2 Degradation Kinetics 51

3.2.1 Equipment and Chemicals 51

3.2.2 Typical Experimental Runs 52

3.2.3 Determination of MEA Concentration in Degraded Samples 52

3.3 Degradation Prevention Techniques using Degradation Inhibitors 53

3.3.1 Equipment and Chemicals 53

3.3.2 Experimental Procedures 53

CHAPTER		PAGE
IV	**ANALYSIS OF MEA AND ITS OXIDTIVE DEGRADATION PRODUCTS DURING CO_2 ABSORPTION FROM FLUE GASES: A COMPREHENSIVE STUDY OF GC-MS, HPLC-RID, AND CE-DAD ANALYTICAL TECHNIQUES AND POSSIBLE OPTIMUM COMBINATIONS**	54
	4.1 Research Objectives	54
	4.2 Results and Discussion	56
	4.2.1 MEA Degradation at 393 K	56
	4.2.1.1 GC-MS Analysis	56
	4.2.1.2 HPLC-RID Analysis	70
	4.2.1.3 CE-DAD Analysis	78
	4.2.2 MEA Degradation at 328 K	86
	4.3 Comparison of GC-MS, HPLC-RID and CE-DAD	88
	4.4 Conclusions	90
V	**STUDIES OF SO_2 AND O_2 INDUCED DEGRADATION OF AQUEOUS MEA SOLUTION DURING CO_2 ABSORPTION FROM POWER PLANT FLUE GAS STREAMS**	92
	5.1 Research Objectives	92
	5.2 Theory	93
	5.2.1 Power Law Model	93
	5.2.2 Modified Power Law Model	94
	5.2.3 Mechanistic-Based Split Model	95
	5.2.3.1 O_2 Pathway	95
	5.2.3.2 SO_2 Pathway	98
	5.2.4 Mechanistic Based-Combined Model	100

CHAPTER **PAGE**

5.3 Results and Discussion 101

5.3.1 Evaluation of the Roles of Temperature and the Concentrations of MEA, O_2, SO_2 and CO_2 101

5.3.2 Degradation Kinetics: Estimation of the Parameters of the Kinetic Models 108

5.3.2.1 Power Law Model 108

5.3.2.2 Modified Power Law Model 109

5.3.2.3 Split Model 112

5.3.2.4 Combined Model 115

5.3.3 Analysis of Kinetic Models 115

5.3.3.1 Model Limitation in Predicting the Degradation Rate 115

5.3.3.2 Model Accuracy 116

5.3.3.3 Model Usability in Describing the Degradation Mechanism 116

5.4 Conclusions 117

VI PRELIMINARY STUDIES OF DEGRADATION PREVENTION TECHNIQUES USING DEGRADATION INHIBITORS FOR MEA BASED CO_2 ABSORPTION FROM POWER PLANT FLUE GASES 118

6.1 Research Objectives 118

6.2 Results and Discussion 120

6.2.1 Determination of Optimum Concentration of Inhibitor UR-A using MEA-O_2 Degradation System 120

6.2.2 Effect of Inhibitor UR-A in MEA-O_2-SO_2 Degradation System 123

CHAPTER		PAGE
	6.2.3 Inhibition Effect of CO_2 in MEA-O_2-SO_2 Degradation System	125
	6.3 Conclusions	127
VII	**INDUSTRIAL APPLICATIONS AND RECOMMENDATIONS FOR FUTURE WORK**	128
	7.1 Industrial Applications	128
	7.1.1 Degradation Analytical Techniques	128
	7.1.2 O_2-SO_2 Induced Degradation Kinetic Rate Model	128
	7.1.3 Preliminary Inhibitor Study	129
	7.2 Recommendations for Future Work	129
	REFERENCES	132
	APPENDICES	139
	Appendix A Concentration Time Data of MEA Oxidative Degradation Experiments	139
	Appendix B Experimental Rates and Model Predicted Rates using Power Law Model	152
	Appendix C Experimental Rates and Model Predicted Rates using Modified Power Law Model	153
	Appendix D Experimental Rates and Model Predicted Rates using Split Model	154
	Appendix E Experimental Rates and Model Predicted Rates using Combined Model	155
	CURRICULUM VITAE	156

LIST OF TABLES

TABLE		PAGE
1.1	CO_2 clean-up target for various industrial processes (Astarita, 1983)	4
1.2	Gaseous compositions of a typical coal-fired flue gas (Chakma et al.,1995)	9
3.1	Degradation conditions for kinetic experiments	52
4.1	Summary of analytical techniques previously used for analysis of alkanolamines and their degradation products	55
4.2	Summary of degradation products suggested by the GC-MS technique and previously reported in the literature	60
4.3	Comparative details of GC-MS, HPLC-RID, and CE-DAD techniques for analysis of MEA oxidative degradation	89
5.1	Summary of kinetic estimates	110
7.1	Isotopic labeled MEA, O_2, SO_2, and CO_2	130
A1	Run No.1: 5 kmol/m^3 MEA, 100% O_2, 0.55 CO_2 loading and 393 K	139
A2	Run No.2: 5.13 kmol/m^3 MEA, 100% O_2, and 393 K	139
A3	Run No.3: 5.06 kmol/m^3 MEA, 100% O_2, and 328 K	140
A4	Run No.4: 4.95 kmol/m^3 MEA, 100% O_2, and 373 K	140
A5	Run No.5: 7 kmol/m^3 MEA, 100% O_2, 0.22 CO_2 loading and 328 K	141
A6	Run No.6: 3.2 kmol/m^3 MEA, 100% O_2, 0.22 CO_2 loading and 373 K	141
A7	Run No.7: 3.18 kmol/m^3 MEA, 100% O_2, 0.42 CO_2 loading and 373 K	142
A8	Run No.8: 6.85 kmol/m^3 MEA, 100% O_2, and 393 K	142
A9	Run No.9: 5.1 kmol/m^3 MEA, 6% O_2, and 393 K	142

TABLE **PAGE**

A10	Run No.10: 5.1 kmol/m^3 MEA, 21% O_2, and 393 K	143
A11	Run No.11: 3 kmol/m^3 MEA, 6% O_2, 0.43 CO_2 loading and 373 K	143
A12	Run No.12: 7.05 kmol/m^3 MEA, 21% O_2, and 393 K	143
A13	Run No.13: 3.25 kmol/m^3 MEA, 100% O_2, 0.52 CO_2 loading and 373 K	144
A14	Run No.14: 3.15 kmol/m^3 MEA, 21% O_2, 0.28 CO_2 loading and 393 K	144
A15	Run No.15: 4.95 kmol/m^3 MEA, 6 % O_2, 6 ppm SO_2, and 393 K	144
A16	Run No.16: 5.88 kmol/m^3 MEA, 6 % O_2, 6 ppm SO_2, and 373 K	145
A17	Run No.17: 6.9 kmol/m^3 MEA, 6 % O_2, 11 ppm SO_2, and 373 K	145
A18	Run No.18: 6.95 kmol/m^3 MEA, 6 % O_2, 11 ppm SO_2, and 393 K	145
A19	Run No.19: 6.91 kmol/m^3 MEA, 6 % O_2, 196 ppm SO_2, and 328 K	146
A20	Run No.20: 5 kmol/m^3 MEA, 6 % O_2, 196 ppm SO_2, 0.17 CO_2 loading, and 328 K	146
A21	Run No.21: 3 kmol/m^3 MEA, 6 % O_2, 196 ppm SO_2, 0.47 CO_2 loading, and 373 K	146
A22	Run No.22: 5 kmol/m^3 MEA, 6 % O_2, 6 ppm SO_2, 0.33 CO_2 loading, and 393 K	147
A23	Run No.23: 6.8 kmol/m^3 MEA, 6 % O_2, 11 ppm SO_2, 0.24 CO_2 loading, and 393 K	147

TABLE **PAGE**

A24	Run No.24: 6.8 kmol/m^3 MEA, 6 % O_2, 196 ppm SO_2, 0.27 CO_2 loading, and 393 K	148
A25	Run No.25: 3.15 kmol/m^3 MEA, 6 % O_2, 11 ppm SO_2, 0.28 CO_2 loading, and 393 K	148
A26	Run No.26: 5 kmol/m^3 MEA, 6 % O_2, 0.05 kmol/m^3 Inhibitor UR-A and 393 K	149
A27	Run No.27: 5 kmol/m^3 MEA, 6 % O_2, 0.1 kmol/m^3 Inhibitor UR-A and 393 K	149
A28	Run No.28: 5 kmol/m^3 MEA, 6 % O_2, 0.3 kmol/m^3 Inhibitor UR-A and 393 K	150
A29	Run No.29: 7 kmol/m^3 MEA, 100 % O_2, 0.1 kmol/m^3 Inhibitor A and 393 K	150
A30	Run No.30: 5 kmol/m^3 MEA, 6 % O_2, 6 ppm SO_2, 0.05 kmol/m^3 Inhibitor UR-A and 393 K	151
A31	Run No.31: 5 kmol/m^3 MEA, 6 % O_2, 196 ppm SO_2, 0.05 kmol/m^3 Inhibitor UR-A and 393 K	151
B1	Kinetic Data for Power Law Model	152
C1	Kinetic Data for Modified Power Law Model	153
D1	Kinetic Data for Modified Split Model	154
E1	Kinetic Data for Combined Model	155

LIST OF FIGURES

FIGURE		PAGE
1.1	Distribution of world's energy supply (Speight, 1994)	1
1.2	CO_2 emission from fossil fuel use (Davison, 2007)	3
1.3	Simplified alkanolamine-based CO_2 capture process	6
1.4	Chemical structures of conventional alkanolamines	7
2.1	One of the first oxidation mechanisms of MEA	22
2.2	Oxidative degradation of MEA with formation pathways of formic and acetic acid (Rooney, Dupart, and Bacon, 1998)	23
2.3	DIPA oxidation mechanism (Smit, Van Heeringen, and Van Grinsven, 2002)	25
2.4	MEA oxidation mechanism (Chi and Rochelle, 2002)	27
3.1	Schematic of MEA oxidative degradation experiments: Experimental set-up and analysis	38
3.2	A sketch of the internals of the reactor	39
3.3	Mass spectra of imidazole: (a) In degraded MEA sample; (b) NIST database; (c) Standard imidazole	42
3.4	Mass spectra of formic acid: (a) In degraded MEA sample; (b) NIST database; (c) Standard formic acid	43
3.5	Mass spectra of N-(2-hydroxyethyl) acetamide: (a) In degraded MEA sample; (b) NIST database; (c) Standard N-(2-hydroxyethyl) acetamide	44
3.6	Mass spectra of 1-(2-hydroxyethyl)-2-imidazolidinone: (a) In degraded MEA sample; (b) NIST database; (c) Standard 1-(2-hydroxyethyl)-Imidazolidinone	45
3.7	Mass spectra of 18-crown-6: (a) In degraded MEA sample; (b) NIST database; (c) Standard 18-crown-6	46

FIGURE **PAGE**

3.8	Chromatogram of standard 4 kmol/m^3 MEA	47
3.9	Chromatogram of standard 1 kmol/m^3 imidazole	48
4.1	GC-MS chromatograms of degraded MEA solution in MEA-H_2O-O_2 system, 5.13 kmol/m^3 initial MEA concentration, 393 K, 250 kPa O_2 pressure, and 220 hour-reaction time: (a) HP-Innowax column-high polarity; (b) HP-35MS column-intermediate polarity; (c) HP-5MS column-non polarity	58
4.2	GC-MS chromatograms of degraded MEA solution in MEA-H_2O-O_2-CO_2 system, 5.03 kmol/m^3 initial MEA concentration, 393 K, 250 kPa O_2 pressure, 0.51 mole CO_2/mole MEA, and 216 h degradation time: (a) HP-Innowax column-high polarity; (b) HP-35MS column-polarity; (c) HP-5MS column-non polarity	59
4.3(a)	GC-MS degradation product distribution of MEA-H_2O-O_2 system at 393 K: HP-Innowax column-high polarity	62
4.3(b)	GC-MS degradation product distribution of MEA-H_2O-O_2 system at 393 K: HP-35MS column-intermediate polarity	63
4.3(c)	GC-MS degradation product distribution of MEA-H_2O-O_2 system at 393 K: HP-5MS column-non polarity	64
4.4(a)	GC-MS degradation product distribution of MEA-H_2O-O_2-CO_2 system at 393 K: HP-Innowax column-high polarity	65
4.4(b)	GC-MS degradation product distribution of MEA-H_2O-O_2-CO_2 system at 393 K: HP-35MS column-intermediate polarity	66

FIGURE **PAGE**

4.4(c)	GC-MS degradation product distribution of MEA-H_2O-O_2-CO_2 system at 393 K: HP-5MS column-non polarity	67
4.5(a)	HPLC-RID chromatograms using nucleosil column at 393 K: mobile phase of 0.05 kmol/m^3 potassium dihydrogen phosphate: MEA-H_2O-O_2 system	71
4.5(b)	HPLC-RID chromatograms using nucleosil column at 393 K: mobile phase of 0.05 kmol/m^3 potassium dihydrogen phosphate: MEA-H_2O-O_2-CO_2 system	71
4.5(c)	HPLC-RID chromatograms using nucleosil column at 393 K: mobile phase of mixture of 0.005 kmol/m^3 L-tartaric acid, 0.001 kmol/m^3 2, 6-pyridinecarboxylic acid, and 0.024 kmol/m^3 boric acid: fresh MEA solution	71
4.6(a)	HPLC-RID chromatograms of MEA-H_2O-O_2 system at 393 K using shodex YK-421: mobile phase of 0.05 kmol/m^3 potassium dihydrogen phosphate	72
4.6(b)	HPLC-RID chromatograms of MEA-H_2O-O_2 system at 393 K using shodex YK-421: mobile phase of mixture of 0.005 kmol/m^3 L-tartaric acid, 0.001 kmol/m^3 2, 6-pyridinecarboxylic acid, and 0.024 kmol/m^3 boric acid	72
4.7(a)	HPLC-RID degradation product distribution at 393 K using nucleosil column and phosphate mobile phase: MEA-H_2O-O_2	74
4.7(b)	HPLC-RID degradation product distribution at 393 K using nucleosil column and phosphate mobile phase: MEA-H_2O-O_2-CO_2	75
4.8	Identification using standard imidazole: (a) MEA-H_2O-O_2; (b) MEA-H_2O-O_2-CO_2	77

FIGURE **PAGE**

4.9	CE chromatogram of fresh MEA solution using combination of imidazole, 18-crown-6, and HIBA electrolyte	78
4.10	Typical CE chromatograms for analysis of basic products of Degraded MEA solution at approximately 200 h: (a) MEA-H_2O-O_2; (b) MEA-H_2O-O_2-CO_2	80
4.11	Typical CE chromatograms for analysis of acidic products of degraded MEA solution at approximately 400 h: (a) MEA-H_2O-O_2; (b) MEA-H_2O-O_2-CO_2	81
4.12(a)	CE-DAD basic degradation product distribution: MEA-H_2O-O_2	82
4.12(b)	CE-DAD basic degradation product distribution:MEA-H_2O-O_2-CO_2	83
4.13(a)	CE-DAD acidic degradation product distribution: MEA-H_2O-O_2	84
4.13(b)	CE-DAD acidic degradation product distribution: MEA-H_2O-O_2-CO_2	85
4.14	MEA concentration as a function of degradation time at 328 K using GC-MS and HPLC-RID techniques	87
5.1	Effect of temperature in MEA-O_2 degradation system (5 kmol/m^3 MEA and 100% O_2)	103
5.2	Effect of temperature in MEA-O_2-SO_2 degradation system (7 kmol/m^3 MEA, 6% O_2, and 11 ppm SO_2)	104
5.3	Effect of MEA concentration (100% O_2 and 393 K)	105
5.4	Effect O_2 concentration (5 kmol/m^3 MEA and 393 K)	106
5.5	Effect of SO_2 concentration (6% O_2 and 393 K)	107
5.6	Effect of CO_2 concentration (3 kmol/m^3 MEA, 100% O_2, and 373 K)	108

FIGURE **PAGE**

5.7	Verification and comparison of kinetic models using logarithmic plots of experimental and model predicted rates	111
5.8	Verification of $k_1^{'}$ and $k_2^{'}$ for split model	114
6.1	Effect of concentration of Inhibitor UR-A on MEA-6%O_2 degradation system (5 kmol/m^3 MEA, 6% O_2, 393 K)	121
6.2	Adverse effect of excess Inhibitor UR-A on MEA-100% O_2 degradation system (7 kmol/m^3 MEA, 100% O_2, 393 K)	122
6.3	Degradation rate-time plots of MEA-O_2-SO_2-H_2O system with 0.05 kmol/m^3 Inhibitor UR-A (5 kmol/m^3 MEA,6%O_2, 393 K)	124
6.4	Inhibition effect of CO_2 in Degradation of MEA-O_2-SO_2 system (6% O_2 and 393 K)	126

ABBREVIATIONS

OECD	organisation for economic co-operation and development
NIST	national institute for standards and technology
LNG	liquid natural gas
MEA	monoethanolamine
DEA	diethanolamine
MDEA	methyldiethanolamine
TEA	tirethanolamine
DIPA	diisopropanolamine
DGA	diglycolamine
EDTA	ethylenediaminetetraacetic acid
GC-MS	gas chromatography-mass spectrometry
HPLC-RID	high performance liquid chromatography-refractive index detector
CE-DAD	capillary electrophoresis-diode array detector
IR	infrared spectroscopy
NMR	nuclear magnetic resonance spectroscopy
TCD	thermal conductivity detector
FID	flame ionization detector
AED	atomic emission detector
%AAD	averaged absolute deviation percentage

LIST OF SYMBOLS

CO_2	carbon dioxide
O_2	oxygen
SO_2	sulfur dioxide
CO	carbon monoxide
H_2O	water
N_2	nitrogen
H_2	hydrogen
Ar	argon
OH	hydroxyl group
NH_2	amino group
COS	carbonyl sulphide
CS_2	carbon disulfide
NaOH	sodium hydroxide
Na_2CO_3	sodium carbonate
$NaHCO_3$	sodium bicarbonate
$Na_2B_4O_7.10H_2O$	sodium tetraborate decahydrate
H_3BO_4	boric acid
H_2SO_4	sulphuric acid
H_3PO_4	phosphoric acid
KNO_3	potassium nitrate
KH_2PO_4	potassium dihydrogen phosphate
NaH_2PO_4	sodium dihydrogen phosphate
$OH^{\cdot}$	hydroxyl radical
$[MEA]$	MEA concentration (kmol/m^3)
$[O_2]$	O_2 concentration (kmol/m^3)
$[SO_2]$	SO_2 concentration (ppm or kmol/m^3)
$[CO_2]$	CO_2 concentration (kmol/m^3)
a	reaction order with respect to MEA in Eq.(5.3), (5.4), (5.41), and (5.56)

a'	reaction order of MEA in Eq.(5.41)
b	reaction order with respect to O_2 in Eq.(5.3), (5.4), (5.41), and (5.56)
c	reaction order with respect to SO_2 in Eq.(5.3), (5.4), (5.41), and (5.56)
d	reaction order with respect to CO_2 in Eq.(5.3), (5.4), (5.41), and (5.56)
d'	reaction order of CO_2 in Eq.(5.41)
k_0	preexponential constant in Eq.(5.3), (5.4), and (5.56)
k_{01}	Preexponential constant in Eq.(5.41)
k_{02}	Preexponential constant in Eq. (5.41)
k_1'	rate constant in Eq.(5.41)
k_2'	rate constant in Eq.(5.41) and (5.56)
E_a	activation energy (J/mol) in Eq.(5.3), (5.4), and (5.56)
E_{a1}	activation energy (J/mol) in Eq.(5.41)
E_{a2}	activation energy (J/mol) in Eq.(5.41)
R	gas constant
T	temperature (K)