

Development and Demonstration of a New Non-Equilibrium Rate-Based Process Model for the Hot Potassium Carbonate Process

by

Su Ming Pamela Ooi

Thesis submitted for the degree of
Doctor of Philosophy

in

The University of Adelaide
School of Chemical Engineering
July 2008

Summary

Chemical absorption and desorption processes are two fundamental operations in the process industry. Due to the rate-controlled nature of these processes, classical equilibrium stage models are usually inadequate for describing the behaviour of chemical absorption and desorption processes. A more effective modelling method is the non-equilibrium rate-based approach, which considers the effects of the various driving forces across the vapour-liquid interface.

In this thesis, a new non-equilibrium rate-based model for chemical absorption and desorption is developed and applied to the hot potassium carbonate process CO₂ Removal Trains at the Santos Moomba Processing Facility. The rate-based process models incorporate rigorous thermodynamic and mass transfer relations for the system and detailed hydrodynamic calculations for the column internals. The enhancement factor approach was used to represent the effects of the chemical reactions.

The non-equilibrium rate-based CO₂ Removal Train process models were implemented in the Aspen Custom Modeler® simulation environment, which enabled rigorous thermodynamic and physical property calculations via the Aspen Properties® software. Literature data were used to determine the parameters for the Aspen Properties® property models and to develop empirical correlations when the default Aspen Properties® models were inadequate. Preliminary simulations indicated the need for adjustments to the absorber column models, and a sensitivity analysis identified the effective interfacial area as a suitable model parameter for adjustment. Following the application of adjustment factors to the absorber column models, the CO₂ Removal Train process models were successfully validated against steady-state plant data.

The success of the Aspen Custom Modeler® process models demonstrated the suitability of the non-equilibrium rate-based approach for modelling the hot potassium carbonate process. Unfortunately, the hot potassium carbonate process could not be modelled as such in HYSYS®, Santos's preferred simulation environment, due to the absence of electrolyte components and property models and the limitations of the HYSYS® column operations in accommodating chemical reactions and non-equilibrium column behaviour. While importation of the Aspen Custom Modeler® process models into HYSYS® was possible, it was considered impractical due to the significant associated computation time.

To overcome this problem, a novel approach involving the HYSYS® column stage efficiencies and hypothetical HYSYS® components was developed. Stage efficiency correlations, relating various operating parameters to the column performance, were derived from parametric studies performed in Aspen Custom Modeler®. Preliminary simulations indicated that the efficiency correlations were only necessary for the absorber columns; the regenerator columns were adequately represented by the default equilibrium stage models. Hypothetical components were created for the hot potassium carbonate system and the standard Peng-Robinson property package model in HYSYS® was

modified to include tabular physical property models to accommodate the hot potassium carbonate system. Relevant model parameters were determined from literature data. As for the Aspen Custom Modeler® process models, the HYSYS® CO₂ Removal Train process models were successfully validated against steady-state plant data.

To demonstrate a potential application of the HYSYS® process models, dynamic simulations of the two most dissimilarly configured trains, CO₂ Removal Trains #1 and #7, were performed. Simple first-order plus dead time (FOPDT) process transfer function models, relating the key process variables, were derived to develop a diagonal control structure for each CO₂ Removal Train. The FOPDT model is the standard process engineering approximation to higher order systems, and it effectively described most of the process response curves for the two CO₂ Removal Trains. Although a few response curves were distinctly underdamped, the quality of the validating data for the CO₂ Removal Trains did not justify the use of more complex models than the FOPDT model.

While diagonal control structures are a well established form of control for multivariable systems, their application to the hot potassium carbonate process has not been documented in literature. Using a number of controllability analysis methods, the two CO₂ Removal Trains were found to share the same optimal diagonal control structure, which suggested that the identified control scheme was independent of the CO₂ Removal Train configurations. The optimal diagonal control structure was tested in dynamic simulations using the MATLAB® numerical computing environment and was found to provide effective control. This finding confirmed the results of the controllability analyses and demonstrated how the HYSYS® process model could be used to facilitate the development of a control strategy for the Moomba CO₂ Removal Trains.

In conclusion, this work addressed the development of a new non-equilibrium rate-based model for the hot potassium carbonate process and its application to the Moomba CO₂ Removal Trains. Further work is recommended to extend the model validity over a wider range of operating conditions and to expand the dynamic HYSYS® simulations to incorporate the diagonal control structures and/or more complex control schemes.

Statement

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

I give consent to this copy of my thesis, when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

Su Ming Pamela Ooi
Adelaide, 16/07/2008

Acknowledgements

I wish to express my sincere appreciation to all organisations and persons who have contributed council and assistance during this work.

In particular, I would like to thank Santos for providing funding and technical support for this project. Special thanks are extended to Keith Humphris, Len Cowen, Ian Smith, Ross Mullner, Claire Barber, Randall Yeates and Mark Moss for their advice and assistance with providing technical data.

I would also like to thank my academic supervisors, Associate Professor Brian O'Neill, Dr Chris Colby and Professor Keith King, for their encouragement, advice and guidance. Special thanks are extended to Dr Robin Thiele who provided invaluable advice regarding rate-based modelling.

Finally, I would like to express my deepest gratitude to my boyfriend Simon and to my parents for providing endless support and encouragement, without which I could not have completed this thesis.

Table of Contents

Nomenclature	xvii
Chapter 1: Introduction	1
1.1 Project Objectives	2
1.2 Thesis Structure	2
Chapter 2: Literature Review	4
2.1 The Hot Potassium Carbonate Process	5
2.2 The Non-Equilibrium Rate-Based Approach	18
2.3 Electrolyte Thermodynamics	30
2.4 Process Simulation Platform	32
2.5 Multivariable Process Control	34
2.6 Summary	45
Chapter 3: Thermodynamic and Physical Properties of the Hot Potassium Carbonate System	46
3.1 Summary of Property Models	47
3.2 The Electrolyte NRTL Model	50
3.3 Summary	58
Chapter 4: Aspen Custom Modeler® Process Model Development	59
4.1 Process Model Equations	60
4.2 Preliminary CO ₂ Train Simulations	69
4.3 Column Model Adjustments	73
4.4 CO ₂ Train Model Validation	83
4.5 Summary	91
Chapter 5: Aspen Custom Modeler® CO ₂ Removal Train Parametric Studies	92
5.1 Solution Operating Parameters	93
5.2 Raw Gas Operating Parameters	97
5.3 Column Operating Parameters	100
5.4 Summary	107
Chapter 6: Modelling the Hot Potassium Carbonate System in HYSYS®	108
6.1 The Modelling Approach	109
6.2 Thermodynamic and Physical Property Models	115
6.3 Summary	120
Chapter 7: The Absorber and Regenerator Column Models	121
7.1 Absorber Column Models	122
7.2 Regenerator Column Models	124
7.3 Preliminary Column Model Simulations	127
7.4 Column Stage Efficiency Correlations	135

7.5 Summary	141
Chapter 8: HYSYS® CO ₂ Removal Train Process Model Development	142
8.1 Ancillary Operation Models	143
8.2 Steady-State CO ₂ Train Models	147
8.3 Model Validation	151
8.4 Summary	158
Chapter 9: Dynamic HYSYS® Simulations of CO ₂ Removal Trains #1 and #7	159
9.1 Dynamic CO ₂ Train Models	160
9.2 Process Case Studies	169
9.3 Summary	175
Chapter 10: Process Control Studies for CO ₂ Trains #1 and #7	176
10.1 Selection of Diagonal Control Structure	177
10.2 Selection of Diagonal Control Structure Configuration	184
10.3 Analysis of Diagonal Control Structure Performance	187
10.4 BLT Tuning	190
10.5 Diagonal Control Structure Dynamic Simulations	192
10.6 Summary	198
Chapter 11: Conclusions and Recommendations	199
11.1 Conclusions	200
11.2 Recommendations	203
References	204
Appendix A: Thermodynamic Model Equations	A-1
A.1 Reference States	A-2
A.2 The Electrolyte NRTL Model	A-3
A.3 Cubic Equations of State	A-8
Appendix B: Property Models for Aspen Custom Modeler®	A-10
B.1 Thermodynamic Property Models	A-11
B.2 Physical and Transport Property Models	A-17
Appendix C: Electrolyte NRTL Adjustable Parameters	A-38
C.1 Parameter Values	A-39
C.2 Data Regression Procedure	A-41
C.3 Data Regression Results	A-44
Appendix D: Aspen Custom Modeler® Simulation Results	A-49
D.1 The Different Modelling Approaches	A-50
D.2 Model Adjustments	A-52
D.3 CO ₂ Train Model Validation	A-56
Appendix E: Hypothetical K ₂ CO ₃ * HYSYS® Component Properties	A-62

E.1 Base Properties	A-63
E.2 Additional Point Properties	A-66
E.3 Temperature Dependent Properties	A-67
Appendix F: Property Models for HYSYS®	A-70
F.1 Thermodynamic Property Models	A-71
F.2 Physical and Transport Property Models	A-72
Appendix G: Enhanced PR Binary Interaction Parameters	A-84
G.1 Data Regression Procedure	A-85
G.2 Data Regression Results	A-87
Appendix H: HYSYS® Simulation Results	A-88
H.1 Preliminary Column Model Simulations	A-89
H.2 Steady-State CO ₂ Train Models	A-95
H.3 CO ₂ Train Model Validation	A-101
Appendix I: Process Control Studies of the CO ₂ Trains	A-107
I.1 Selection of Diagonal Control Structure	A-108
I.2 Selection of Diagonal Control Structure Configuration	A-111
I.3 Analysis of Diagonal Control Structure Performance	A-114
I.4 BLT Tuning	A-115
I.5 Diagonal Control Structure Dynamic Simulations	A-117

List of Figures

Figure 2.1.1:	A simple form of the hot potassium carbonate process.	5
Figure 2.1.2:	Basic CO ₂ train process flow diagrams.	7
Figure 2.1.3:	Reaction flow scheme for the hot potassium carbonate process.	10
Figure 2.2.1:	The two-film model for simultaneous mass and energy transfer.	20
Figure 3.2.1:	Comparison between the Electrolyte NRTL predictions and the experimental data.	54
Figure 3.2.2:	CO ₂ partial pressure over K ₂ CO ₃ solution as a function of CO ₂ loading.	54
Figure 3.2.3:	Comparison between the Electrolyte NRTL predictions and the experimental data.	57
Figure 3.2.4:	H ₂ S partial pressure over K ₂ CO ₃ solution as a function of equivalent H ₂ S content.	57
Figure 4.1.1:	Equilibrium stage for Model 1 (adapted from Thiele (2007)).	62
Figure 4.1.2:	Non-equilibrium stage for Model 2 (adapted from Thiele (2007)).	63
Figure 4.1.3:	Non-equilibrium stage for Model 3 (adapted from Thiele (2007)).	64
Figure 4.2.1:	Preliminary Aspen Custom Modeler® simulation column configurations.	69
Figure 4.2.2:	Results of the absorber discretisation simulation runs for CO ₂ train #1.	70
Figure 4.2.3:	Results of the regenerator discretisation simulation runs for CO ₂ train #1.	70
Figure 4.2.4:	Results of the different modelling approaches for CO ₂ trains #1 and #7.	72
Figure 4.3.1:	Temperature profiles for CO ₂ trains #1 and #7.	74
Figure 4.3.2:	Effect of the liquid phase enthalpy correction on the absorber profiles.	75
Figure 4.3.3:	Sensitivity analysis results for the absorber column model (Model 2).	79
Figure 4.3.4:	Sensitivity analysis results for the regenerator column model (Model 2).	80
Figure 4.3.5:	Effect of the solution reboiler steam flow on the regenerator column model (Model 2).	81
Figure 4.3.6:	Effect of the effective interfacial area adjustment factor on the absorber CO ₂ and H ₂ S vapour phase profiles.	82
Figure 4.4.1:	Simplified CO ₂ train configurations for the Aspen Custom Modeler® simulations.	83
Figure 4.4.2:	CO ₂ and H ₂ S vapour and liquid phase profiles for the first set of plant data.	88
Figure 4.4.3:	CO ₂ and H ₂ S vapour and liquid phase profiles for the second set of plant data.	87
Figure 4.4.4:	Vapour and liquid phase temperature profiles for the two sets of plant data.	88
Figure 5.1.1:	Effect of the solution flow rate on the performance of the CO ₂ trains.	94

Figure 5.1.2:	Effect of the solution strength on the performance of the CO ₂ trains.	95
Figure 5.1.3:	Effect of the solution CO ₂ loading on the performance of the CO ₂ trains.	96
Figure 5.2.1:	Effect of the raw gas flow rate on the performance of the CO ₂ trains.	98
Figure 5.2.2:	Effect of the raw gas CO ₂ content on the performance of the CO ₂ trains.	99
Figure 5.3.1:	Effect of the absorber temperature on the performance of the CO ₂ trains.	101
Figure 5.3.2:	Effect of the regenerator temperature on the performance of the CO ₂ trains.	102
Figure 5.3.3:	Effect of pressure on the performance of the CO ₂ trains.	104
Figure 5.3.4:	Effect of the steam flow rate to the regenerator solution reboilers on the performance of the CO ₂ trains.	105
Figure 5.3.5:	Effect of the makeup water flow rate to the regenerator overhead catchpots on the performance of the CO ₂ trains.	106
Figure 6.1.1:	The different definitions of the column stage efficiency η in HYSYS®.	114
Figure 6.2.1:	Comparison between the enhanced PR predictions and the experimental data.	118
Figure 6.2.2:	Comparison between the enhanced PR predictions and the experimental data.	119
Figure 7.1.1:	Process flow diagram of an absorber column model in HYSYS®.	122
Figure 7.2.1:	Process flow diagrams of the two most dissimilar regenerator column models in HYSYS®.	126
Figure 7.3.1:	Equilibrium stage simulation results for the absorber and regenerator columns.	128
Figure 7.3.2:	Sensitivity analysis results for the absorber models.	130
Figure 7.3.3:	Effect of the column stage efficiencies on the absorber composition and temperature profiles.	131
Figure 7.3.4:	Sensitivity analysis results for the regenerator models.	132
Figure 7.3.5:	Effect of the column stage efficiencies on the regenerator composition and temperature profiles.	133
Figure 7.3.6:	Effect of the reboiler steam flow on the regenerator column performance.	134
Figure 7.4.1:	Effect of the correlated overall stage efficiencies on the steady-state absorber columns.	137
Figure 7.4.2:	Effect of the correlated overall stage efficiencies on the steady-state behaviour of the dynamic absorber columns.	137
Figure 7.4.3:	An example HYSYS® spreadsheet for calculating the absorber overall stage efficiencies.	139
Figure 8.1.1:	HYSYS® process flow diagram of the CO ₂ train absorption circuits.	143
Figure 8.1.2:	HYSYS® process flow diagram of the solution pumpset model.	144
Figure 8.1.3:	HYSYS® spreadsheet for the pumpset calculations.	145

Figure 8.2.1:	Process flow diagram for the steady-state HYSYS® model of CO ₂ train #1.	149
Figure 8.2.2:	Process flow diagram for the steady-state HYSYS® model of CO ₂ train #7.	150
Figure 8.3.1:	CO ₂ and H ₂ S vapour and liquid phase profiles for the first set of data.	153
Figure 8.3.2:	CO ₂ and H ₂ S vapour and liquid phase profiles for the second set of data.	154
Figure 8.3.3:	Vapour and liquid phase temperature profiles for the two sets of plant data.	155
Figure 9.1.1:	Process flow diagram of the simplified dynamic HYSYS® model for CO ₂ train #1.	163
Figure 9.1.2:	Process flow diagram of the simplified dynamic HYSYS® model for CO ₂ train #7.	164
Figure 9.1.3:	Flow control loop responses.	166
Figure 9.1.4:	Temperature control loop responses.	167
Figure 9.1.5:	Liquid level control loop responses.	168
Figure 9.2.1:	Process response curves for a 2% magnitude step change in the raw gas flow rate at 0 min.	171
Figure 9.2.2:	Process response curves for a 2% magnitude step change in the lean solution flow rate at 0 min.	171
Figure 9.2.3:	Process response curves for a 2% magnitude step change in the reboiler steam flow rate at 0 min.	172
Figure 9.2.4:	Process response curves for a 2% magnitude step change in the regenerator liquid level at 0 min.	172
Figure 9.2.5:	Process response curves for a 2% magnitude step change in the raw gas CO ₂ content at 0 min.	173
Figure 10.1.1:	Frequency plots of the MRI and CN.	181
Figure 10.1.2:	Frequency plots of DCN and DC for CO ₂ train #1.	182
Figure 10.1.3:	Frequency plots of DCN and DC for CO ₂ train #7.	183
Figure 10.2.1:	Frequency plots for the RGA elements.	185
Figure 10.3.1:	Frequency plots for $ \mathbf{PRGA}_{ij} $ and $ \mathbf{CLDG}_{ij} $	189
Figure 10.4.1:	Plots of the scalar function W	191
Figure 10.5.1:	Frequency plots of $ 1+\mathbf{G}_{OL,i}(s) $ and $ \mathbf{PRGA}_{ij} $	195
Figure 10.5.2:	CO ₂ train #1 closed-loop step response curves at the high gas throughput conditions.	196
Figure 10.5.3:	CO ₂ train #7 closed-loop step response curves at the high gas throughput conditions.	197
Figure B.1.1:	Comparison between the predicted and experimental solution heat capacities.	A-16
Figure B.2.1:	Comparison between the predicted and experimental solution mass densities.	A-20
Figure B.2.2:	Comparison between the predicted and experimental solution viscosities.	A-25
Figure B.2.3:	Comparison between the predicted and experimental solution surface tensions.	A-28

Figure B.2.4:	Comparison between the predicted and experimental solution thermal conductivities.	A-33
Figure D.1.1:	Results of the different modelling approaches for CO ₂ trains #2 to #4.	A-50
Figure D.1.2:	Results of the different modelling approaches for CO ₂ trains #5 and #6.	A-51
Figure D.2.1:	Temperature profiles for CO ₂ trains #2 to #4.	A-52
Figure D.2.2:	Temperature profiles for CO ₂ trains #5 and #6.	A-53
Figure D.2.3:	Effect of the effective interfacial area adjustment factor on the absorber CO ₂ and H ₂ S vapour phase profiles.	A-55
Figure D.3.1:	CO ₂ and H ₂ S vapour and liquid phase column profiles for the first set of plant data.	A-56
Figure D.3.2:	CO ₂ and H ₂ S vapour and liquid phase column profiles for the first set of plant data.	A-57
Figure D.3.3:	CO ₂ and H ₂ S vapour and liquid phase column profiles for the second set of plant data.	A-58
Figure D.3.4:	CO ₂ and H ₂ S vapour and liquid phase column profiles for the second set of plant data.	A-59
Figure D.3.5:	Column temperature profiles for the first set of plant data.	A-60
Figure D.3.6:	Column temperature profiles for the second set of plant data.	A-61
Figure F.2.1:	Comparison between the predicted and experimental solution mass densities.	A-74
Figure F.2.2:	Comparison between the predicted and experimental solution viscosities.	A-77
Figure F.2.3:	Comparison between the solution surface tensions predicted by the tabular model and the empirical correlation.	A-79
Figure F.2.4:	Comparison between the solution thermal conductivities predicted by the tabular model and the empirical correlation.	A-83
Figure H.1.1:	Equilibrium stage simulation results for the absorber and regenerator columns.	A-89
Figure H.1.2:	Equilibrium stage simulation results for the absorber and regenerator columns.	A-90
Figure H.1.3:	Effect of the correlated overall stage efficiencies on the steady-state absorber columns.	A-91
Figure H.1.4:	Effect of the correlated overall stage efficiencies on the steady-state absorber columns.	A-92
Figure H.1.5:	Effect of the correlated overall stage efficiencies on the steady-state behaviour of the dynamic absorber columns.	A-93
Figure H.1.6:	Effect of the correlated overall stage efficiencies on the steady-state behaviour of the dynamic absorber columns.	A-94
Figure H.2.1:	Process flow diagram for the steady-state model of CO ₂ train #2.	A-96
Figure H.2.2:	Process flow diagram for the steady-state model of CO ₂ train #3.	A-97
Figure H.2.3:	Process flow diagram for the steady-state model of CO ₂ train #4.	A-98
Figure H.2.4:	Process flow diagram for the steady-state model of CO ₂ train #5.	A-99
Figure H.2.5:	Process flow diagram for the steady-state model of CO ₂ train #6.	A-100

Figure H.3.1:	CO ₂ and H ₂ S vapour and liquid phase column profiles for the first set of plant data.	A-101
Figure H.3.2:	CO ₂ and H ₂ S vapour and liquid phase column profiles for the first set of plant data.	A-102
Figure H.3.3:	CO ₂ and H ₂ S vapour and liquid phase column profiles for the second set of plant data.	A-103
Figure H.3.4:	CO ₂ and H ₂ S vapour and liquid phase column profiles for the second set of plant data.	A-104
Figure H.3.5:	Column temperature profiles for the first set of plant data.	A-105
Figure H.3.6:	Column temperature profiles for the second set of plant data.	A-106
Figure I.5.1:	CO ₂ train #1 closed-loop step response curves at the medium gas throughput conditions.	A-121
Figure I.5.2:	CO ₂ train #7 closed-loop step response curves at the medium gas throughput conditions.	A-122
Figure I.5.3:	CO ₂ train #1 closed-loop step response curves at the low gas throughput conditions.	A-123
Figure I.5.4:	CO ₂ train #7 closed-loop step response curves at the low gas throughput conditions.	A-124

List of Tables

Table 2.1.1:	Nameplate capacity of the CO ₂ trains.	8
Table 2.1.2:	Typical operating data for the CO ₂ trains from 2002.	9
Table 2.1.3:	Acid gas absorption reactions in the hot potassium carbonate process.	10
Table 2.1.4:	Ion contribution factors (Pohorecki and Moniuk, 1988).	13
Table 2.1.5:	Acid gas desorption reactions in the hot potassium carbonate process.	13
Table 2.1.6:	CO ₂ -H ₂ S-K ₂ CO ₃ -KHCO ₃ -KHS-K ₂ S-H ₂ O system equilibria.	15
Table 2.1.7:	Temperature dependence of the equilibrium and Henry's Law constants.	16
Table 2.1.8:	Liquid phase relations and vapour-liquid equilibria expressions.	16
Table 2.2.1:	The MESH equations for a stage i and $j = 1 \dots NC$ components.	19
Table 2.2.2:	Mass transfer relations (Taylor and Krishna, 1993).	21
Table 2.2.3:	Mass transfer coefficient and effective interfacial area correlations (Onda et al., 1968ab).	27
Table 2.2.4:	Hydrodynamic relations (Stichlmair et al., 1989).	29
Table 2.2.5:	Packing characteristics and constants for metal random packings.	29
Table 2.5.1:	Common dynamic process behaviour (Stephanopoulos, 1984; Wade, 2004).	35
Table 2.5.2:	Ziegler-Nichols and Tyreus-Luyben controller tuning rules.	37
Table 2.5.3:	Liquid level PID controller tuning rules (Wade, 2004).	37
Table 3.1.1:	Vapour phase thermodynamic and physical property models.	47
Table 3.1.2:	Liquid phase thermodynamic and physical property models.	48
Table 3.1.3:	Property data sources for the hot potassium carbonate system.	49
Table 3.2.1:	Adjustable binary parameters for the Electrolyte NRTL model.	50
Table 3.2.2:	Electrolyte NRTL parameters for the CO ₂ -K ₂ CO ₃ -KHCO ₃ -H ₂ O system.	53
Table 3.2.3:	Electrolyte NRTL parameters for the CO ₂ -H ₂ S-K ₂ CO ₃ -KHCO ₃ -KHS-K ₂ S-H ₂ O system.	56
Table 4.3.1:	The average variation associated with the model parameter values for the CO ₂ train absorbers and regenerators.	77
Table 4.3.2:	Effective interfacial area adjustment factor values and their effect on the CO ₂ train absorbers.	82
Table 4.4.1:	CO ₂ train simulation results for the first set of plant data in Table 2.1.2.	89
Table 4.4.2:	CO ₂ train simulation results for the second set of plant data in Table 2.1.2.	90
Table 6.1.1:	Property estimation methods for the Miscellaneous class of hypothetical components.	110
Table 6.2.1:	Thermodynamic and physical property models.	115

Table 6.2.2:	Enhanced PR parameter values for the CO ₂ -K ₂ CO ₃ -H ₂ O system.	117
Table 6.2.3:	Enhanced PR parameter values for the CO ₂ -H ₂ S-K ₂ CO ₃ -H ₂ O system.	119
Table 7.4.1:	Coefficients for the steady-state column stage efficiency correlations.	136
Table 7.4.2:	Coefficients for the dynamic column stage efficiency correlations.	136
Table 7.4.3:	An example HYSYS® macro for updating the absorber overall stage efficiencies.	140
Table 8.3.1:	CO ₂ train simulation results for the first set of plant data in Table 2.1.2.	156
Table 8.3.2:	CO ₂ train simulation results for the second set of plant data in Table 2.1.2.	157
Table 9.1.1:	Flow control loop characteristics and controller settings for CO ₂ trains #1 and #7.	166
Table 9.1.2:	Temperature control loop characteristics and controller settings for CO ₂ trains #1 and #7.	167
Table 9.1.3:	Liquid level controller settings for CO ₂ trains #1 and #7.	167
Table 9.2.1:	Process transfer functions for CO ₂ train #1.	173
Table 9.2.2:	Process transfer functions for CO ₂ train #7.	174
Table 10.1.1:	Process transfer function matrices for the diagonal control structures.	179
Table 10.1.2:	Sensitivity analysis indices at steady-state.	180
Table 10.2.1:	Steady-state results for the interaction and stability analyses for the RGF-RSF control structure.	185
Table 10.2.2:	Reordered process transfer function matrices for the RGF-RSF diagonal control structure.	186
Table 10.3.1:	Steady-state values for the PRGA and CLDG for the selected configuration for the RGF-RSF diagonal control structure.	188
Table 10.4.1:	BLT tuning parameters for the RGF-RSF diagonal control structures for CO ₂ trains #1 and #7.	191
Table B.1.1:	Component critical properties (Poling et al., 2001).	A-11
Table B.1.2:	Ideal gas heat capacity coefficients and enthalpies of formation (Poling et al., 2001).	A-12
Table B.1.3:	Ionic species thermodynamic properties (Zemaitis et al., 1986).	A-15
Table B.1.4:	Temperature dependence of Henry's Law constants.	A-15
Table B.1.5:	Criss-Cobble entropy parameters (Criss and Cobble, 1964ab).	A-16
Table B.1.6:	Atmospheric solution heat capacity data.	A-16
Table B.1.7:	Parameter values for the Aspen Properties® heat capacity polynomial.	A-16
Table B.2.1:	Antoine equation coefficients (Rowley et al., 1998).	A-17
Table B.2.2:	Parameter values for the modified Rackett equation (Spencer and Danner, 1972).	A-19
Table B.2.3:	Atmospheric solution mass density data.	A-19

Table B.2.4:	Pair parameter values for the Clarke Aqueous Electrolyte Volume model.	A-19
Table B.2.5:	Component characteristic volumes.	A-21
Table B.2.6:	Coefficients for the DIPPR vapour viscosity model (Rowley et al., 1998).	A-23
Table B.2.7:	Coefficients for the Andrade liquid viscosity equation (Reid et al., 1977).	A-24
Table B.2.8:	Atmospheric solution viscosity data.	A-25
Table B.2.9:	Parameter values for the Jones-Dole viscosity equation.	A-25
Table B.2.10:	Coefficients for the DIPPR surface tension equation (Rowley et al., 1998).	A-27
Table B.2.11:	Atmospheric solution surface tension data.	A-28
Table B.2.12:	Surface tension correlation coefficients.	A-28
Table B.2.13:	Coefficients for the DIPPR vapour thermal conductivity model (Rowley et al., 1998).	A-30
Table B.2.14:	Coefficients for the DIPPR liquid thermal conductivity equation (Rowley et al., 1998).	A-32
Table B.2.15:	Atmospheric solution thermal conductivity data.	A-32
Table B.2.16:	Liquid phase thermal conductivity correlation coefficients.	A-32
Table B.2.17:	Normal boiling points and the corresponding liquid molar volumes (Poling et al., 2001).	A-35
Table B.2.18:	Ionic conductivities at infinite dilution.	A-37
Table B.2.19:	Diffusivities in water at 25°C.	A-37
Table C.1.1:	The Electrolyte NRTL adjustable parameters used in this work.	A-39
Table C.1.2:	The Electrolyte NRTL adjustable parameters used in this work.	A-40
Table C.3.1:	Statistical results for the CO ₂ -K ₂ CO ₃ -KHCO ₃ -H ₂ O system data regression runs.	A-45
Table C.3.2:	Suitable parameter value sets for the CO ₂ -K ₂ CO ₃ -KHCO ₃ -H ₂ O system.	A-46
Table C.3.3:	Statistical results for the CO ₂ -H ₂ S-K ₂ CO ₃ -KHCO ₃ -KHS-K ₂ S-H ₂ O system data regression runs.	A-47
Table C.3.4:	Suitable parameter value sets for the CO ₂ -H ₂ S-K ₂ CO ₃ -KHCO ₃ -KHS-K ₂ S-H ₂ O system.	A-48
Table D.2.1:	Alternative mass transfer coefficient and effective interfacial area correlations.	A-54
Table E.3.1:	Temperature dependent property correlation coefficients.	A-67
Table F.2.1:	Coefficient values for the HYSYS® liquid density tabular model.	A-73
Table F.2.2:	Coefficient values for the HYSYS® liquid viscosity tabular model.	A-77
Table F.2.3:	Coefficient values for the HYSYS® liquid surface tension tabular model.	A-79
Table F.2.4:	Coefficient values for the HYSYS® liquid thermal conductivity tabular model.	A-83
Table G.2.1:	Statistical results for the CO ₂ -K ₂ CO ₃ -H ₂ O system data regression runs.	A-87

List of Tables

Table G.2.2:	Statistical results for the CO ₂ -H ₂ S-K ₂ CO ₃ -H ₂ O system data regression runs.	A-87
Table I.2.1:	System poles and zeros for the SGC-RSF control structure.	A-111

Nomenclature

Latin Letters

A	–	Step size or amplitude of limit cycle
A^*	–	Latini component parameter
A_{ca}	$m^3/kmol$	Clarke Aqueous Electrolyte Volume parameter
A_ϕ	–	Debye-Hückel parameter
AAD	%	Average absolute deviation
a	–	Activity
a	$m^6 \cdot bar/kmol^2$	Cubic equation of state mixture parameter
a	m^2/m^3	Specific surface area
a_a	$W \cdot m^2/K \cdot kmol$	Riedel anion parameter
a_c	$W \cdot m^2/K \cdot kmol$	Riedel cation parameter
a_l	m^2/m^3	Effective interfacial area
a_j	$m^6 \cdot bar/kmol^2$	Cubic equation of state parameter for species j
$a_{T,j}$	$kJ/kmol \cdot K$	Criss-Cobble entropy parameter
B_{ca}	L/mol	Breslau-Miller electrolyte parameter
b	$m^3/kmol$	Cubic equation of state mixture parameter
b	$m^3/kmol$	Ion contribution factor
$b_{a,1}$	$m^3/kmol$	Breslau-Miller anion parameter
$b_{a,2}$	$m^3/kmol \cdot K$	Breslau-Miller anion parameter
$b_{c,1}$	$m^3/kmol$	Breslau-Miller cation parameter
$b_{c,2}$	$m^3/kmol \cdot K$	Breslau-Miller cation parameter
b_j	$m^3/kmol$	Cubic equation of state parameter for species j
$b_{T,j}$	–	Criss-Cobble entropy parameter
C	$kmol/m^3$ mol/cm^3	Molar concentration or molar density
\hat{C}_{H_2S}	mol/m^3	Equivalent H_2S content
C_j	–	Electrolyte NRTL parameter (z_j for ions and 1 for molecular species)
C_{jw}°	–	Reduced volume integral of species j at infinite dilution in water
C_p	$kJ/kmol \cdot K$ $cal/mol \cdot K$ $kJ/kg \cdot K$ $Btu/lbmol \cdot ^\circ R$	Heat capacity
\hat{C}_p	$kJ/kg \cdot K$	Mass heat capacity
$C_p _{25}^T$	$kJ/kmol \cdot K$	Average value of C_p between $25^\circ C$ and temperature T
C_R	–	Reduced molar density
C_v	$J/mol \cdot K$	Heat capacity at constant volume
CLDG	–	Closed-loop disturbance gain matrix
CN	–	Condition number
c_t	$kmol/m^3$	Total mole concentration
D	m	Diameter
D	cm^2/s m^2/s	Effective diffusion coefficient or diffusivity

Nomenclature

D_{jk}	m^2/s	Binary diffusion coefficient for species pair j-k
D_w	cm^2/s	Diffusion coefficient in water
\mathcal{D}_{jk}	m^2/s	Maxwell-Stefan diffusivity for the binary species pair j-k
DC	–	Disturbance cost
DCN	–	Disturbance condition number
DR	–	Decay ratio
DRGA	–	Dynamic relative gain array
d	–	Height of first overshoot
d	–	Process load or disturbance
$\mathbf{d}(s)$	–	Vector of process disturbances
d_h	m	Hydraulic diameter
d_N	m	Nominal packing size
d_p	m	Particle diameter
df	–	Degrees of freedom
E	kW/m^2	Energy flux across the vapour-liquid interface
E_{stage}	–	HYSYS® column overall stage efficiency
E_{Murph}	–	Murphree vapour efficiency
EF	–	Enhancement factor
e	C	Charge of an electron (1.60219×10^{-19} C)
F	C/mol	Faraday's constant (96 485 C/mol)
F	kmol/s	Feed molar flow
F	kmol/s	Flow rate
F	–	F-Test result
F	–	BLT detuning factor
F_1, F_2, F_3	–	Chung functions
F_c	–	Fractional conversion of K_2CO_3 to $KHCO_3$ and KHS
F_{CO_2}	–	CO_2 loading
F_j	–	Fractional conversion of CO_3^{2-} to HCO_3^- due to species j absorption
F_{max}	m^3/min	Maximum flow through control valve
ΔF_{in}	%	Maximum percentage step change in inflow
f	atm bar Pa	Fugacity
f_o	–	Particle friction factor
f_T	–	Twu function at temperature T
$f_{x,0}$	–	Ely-Hanley function
G	–	Electrolyte NRTL parameter
G	kmol/s	Vapour phase molar flow
G	–	Transfer function
$\mathbf{G}(s)$	–	Transfer function matrix
\hat{G}	sm^3/h	Vapour phase standard volumetric flow
$\underline{\mathbf{G}}(s)$	–	Transfer function matrix with paired elements along the diagonal
G^E	$kJ/kmol$	Symmetric excess Gibbs energy
G^{E^*}	$kJ/kmol$	Un-symmetric excess Gibbs energy
$G(s)$	–	Process transfer function

Nomenclature

g	m/s ²	Gravitational acceleration (9.81m/s ²)
H	m	Height
H _j	bar·m ³ /kmol	Henry's Law constant for species j in solution
H _j	bar	Henry's Law constant for species j in pure water
H _j ^w	bar·m ³ /kmol	Henry's Law constant for species j in water
Ha	–	Hatta number
HETP	m	Height of packing equivalent to a theoretical plate
h	kJ/kmol kJ/kg	Enthalpy
h	–	Height of relay
h	–	Two function
h _{x,0}	–	Ely-Hanley function
Δh ^f	kJ/kmol kJ/mol	Enthalpy or heat of formation
Δh ^{vap}	kJ/kmol	Enthalpy of vaporisation
Δh _{fk}	kJ/mol	Joback contribution for group k to the enthalpy of formation
I	–	Identity matrix
I _c	kmol/m ³	Molar concentration based ionic strength
I _x	–	Mole fraction based ionic strength
IAE	–	Integral of the absolute error
J	–	Objective function for the linear quadratic regulator problem
J	kmol/m ² ·s	Diffusion flux
K	– kmol/m ³ kmol ² /m ⁶	Chemical equilibrium constant
K	–	Gain
K'	–	Pseudo-equilibrium constant
K' _p	–	Integrator gain
k	J/K erg/K	Boltzmann constant (1.38066×10 ⁻²³ J/K or 1.38066×10 ⁻¹⁶ erg/K)
k	m/s	Mass transfer coefficient
k	1/s m ³ /kmol·s m ⁶ /kmol ² ·s	Reaction rate constant
k _{jk}	–	Cubic equation of state binary interaction parameter for species pair j-k
k'	1/s	Pseudo-first-order reaction rate constant
k''	1/s	Kinetic coefficient
L	kmol/s	Liquid phase molar flow
L _c	–	Closed-loop log modulus
ΔL _{max}	%	Maximum allowable percentage deviation from setpoint
\hat{L}	m ³ /h	Liquid phase volumetric flow
Le	–	Lewis number
M	kmol	Material holdup
MAD	%	Maximum absolute deviation
MIC	–	Morari index of integral controllability
MRI	–	Morari Resiliency Index

Nomenclature

MW	kg/kmol g/mol	Molecular weight
m	–	Manipulated variable
m	kmol/m ³	Solution molarity (total K ₂ CO ₃ concentration)
N	kmol/m ² ·s	Molar flux across the vapour-liquid interface
N	–	Number
N	–	Order of multivariable system
N _{eqm}	–	Number of equilibrium stages
N _k	–	Number of UNIFAC groups of type k for Joback method
N _o	1/mol	Avogadro's number (6.02205×10 ²³ 1/mol)
NC	–	Number of components
ND	–	Number of data points
NI	–	Niederlinski index
n	kmol	Number of moles
n	–	Number of species in the system
P	atm bar Pa psia	Pressure or partial pressure
P ^s	bar	Vapour pressure
P _o	min	Period of oscillation
P _u	min	Ultimate period or limit cycle period
ΔP	Pa kPa	Pressure drop
PRGA	–	Performance relative gain array
p	–	Pitzer-Debye-Hückel closest approach parameter (14.9)
p	–	p-value
Q	–	Objective function for the data regression runs
Q	kJ/s kW	Heat flow or duty
QDR	–	Quarter decay ratio
R	kJ/kmol·K m ³ ·bar/K·kmol atm·cm ³ /mol·K	Gas constant (8.3144 kJ/kmol·K or 0.0831447 m ³ ·bar/K·kmol or 82.06 atm·cm ³ /mol·K)
R	kmol/m ³ ·s	Molar reaction rate
R _{SP}	–	Ratio setpoint
RGA	–	Relative gain array
RRMSQE	–	Residual root mean square error
Re	–	Reynolds number
r _j	m	Born radius of species j
S ₂₅ [∞]	kJ/kmol·K	Infinite dilution entropy at 25°C
S _T [∞]	kJ/kmol·K	Infinite dilution entropy at temperature T
SG	–	Specific gravity
SSQ	–	Sum of squared errors
ΔSG	–	Change in specific gravity
s	–	Laplace transform variable (s = i·ω)

Nomenclature

T	K °C °R °F	Temperature
T _{ref}	K	Reference temperature (298.15 K)
T*	–	Dimensionless temperature
t	min	Time
U	kJ	Energy holdup
U(s)	–	Process input transfer function
u	–	Process input
V	m ³	Volume
V	cm ³ /mol m ³ /kmol	Molar volume
V _{ca} [∞]	m ³ /kmol	Clarke Aqueous Electrolyte Volume parameter
V _e	L/mol	Breslau-Miller effective volume
V _R ^o , V _R ^δ	–	COSTALD reduced volumes
v	m/s	Velocity
v*	cm ³ /mol	Characteristic volume
\tilde{v}	–	Reduced molar volume
\bar{v}^{∞}	cm ³ /mol m ³ /kmol	Partial molar volume at infinite dilution in pure water
W	–	Scalar BLT function
W _i	–	Weight of data group i
WSSQ	–	Weighted sum of squares
wf	–	Weight fraction
wf _{K₂CO₃}	–	Equivalent weight fraction of K ₂ CO ₃
X	–	Effective local mole fraction
x	–	Liquid phase mole fraction
x	–	Component mole fraction
Y(s)	–	Process output transfer function
y	–	Vapour phase mole fraction
y	–	Component mass fraction
y	–	Process output or response
Z	–	Compressibility
Z	–	Chung parameter
Z	cSt	Two kinematic viscosity parameter
Z ^o	1/atm	Isothermal compressibility at infinite dilution in water
Z ⁽⁰⁾	–	Pitzer compressibility function for spherical molecules
Z ⁽¹⁾	–	Pitzer compressibility deviation function
Z _{RA}	–	Rackett parameter
z	–	Charge number
z	–	Feed mole fraction
z	–	Ionic charge
z	–	Secondary process variable

Greek Letters

α	–	Chung parameter
α	–	Electrolyte NRTL non-randomness factor
α	–	Latini component parameter
α	kW/m ² ·K	Heat transfer coefficient
α_c	–	Riedel critical point parameter
α_j	–	Cubic equation of state alpha function for species j
β	–	Chung parameter
β	–	Latini component parameter
β	–	Packing specific constant
β_{CO_2}	m ³ /kmol	Contribution factor for CO ₂ absorption
δ	m	Film thickness
δ	Debye	Dipole moment
δ_p	–	Chapman-Enskog-Brokaw polar parameter
ε	–	Error
ε	C ² /J·m	Dielectric constant
ε	erg	Characteristic energy
ϕ	°	Phase lag
	rad	
ϕ	m ³ /m ³	Phase volumetric holdup
ϕ	m ³ /m ³	Packing voidage
ϕ_{jk}	–	Wilke viscosity function for species pair j-k
Γ	m·K/W	Stiel-Thodos parameter
γ	–	Activity coefficient
γ	–	Latini component parameter
γ	–	Symmetric activity coefficient
γ^*	–	Un-symmetric activity coefficient
η	–	Dimensionless film coordinate
η	–	Column stage efficiency
φ	kV	Electrical potential
φ	–	Fugacity coefficient
κ	–	Chung association factor
λ	–	Relative gain
λ	–	Eigenvalue
λ	min	IMC tuning parameter
λ	W/m·K	Thermal conductivity
λ	–	Vector of eigenvalues
λ'	W/m·K	Ely-Hanley translational thermal conductivity contribution
λ''	W/m·K	Ely-Hanley internal thermal conductivity contribution
λ^∞	m ² /Ω·kmol	Ionic conductivity at infinite dilution in water
μ	kJ·m/kmol	Chemical potential

Nomenclature

μ	cP kg/m·s Pa·s	Dynamic viscosity
$\Delta\mu_{ca}$	cP	Jones-Dole viscosity contribution term for electrolyte ca
ν	cSt m ² /s	Kinematic viscosity
θ	min	Dead time
ρ	g/m ³ kg/m ³	Mass density
σ	–	Standard error associated with a data point
$\sigma(s)$	–	Singular value
σ	Å	Characteristic length
σ_c	N/m	Critical surface tension parameter
$\Delta\sigma_{ca}$	N/m	Onsager-Samaras surface tension contribution term for electrolyte ca
σ_L	N/m dyne/cm	Surface tension
τ	–	Electrolyte NRTL binary interaction energy parameter
τ	min	Natural period of oscillation
τ	min	Time constant
ν	–	Stoichiometric coefficient
$\Omega_{D,jk}$	–	Diffusion coefficient integral for species pair j-k
ω	–	Acentricity
ω	rad/min	Frequency
ξ	K ^{1/6} ·kmol ^{1/2} /kg ^{1/2} ·atm ^{2/3}	Dean-Stiel parameter
Ψ	–	Chung function
ψ_b	–	Riedel parameter
ζ	–	Damping factor

Subscripts

∞	Final or at infinity or at steady-state
0	Reference fluid
Abs	Absorber
a, a'	Anion
aq	Aqueous
av	Average
B	Bandwidth
b	Normal boiling point
CL	Closed-loop
CLR	Closed-loop regulator
CLS	Closed-loop servo
Cond	Condenser
c	Column
c	Controller
c	Critical
c, c'	Cation
ca	Electrolyte consisting of cation c and anion a
co	Cross-over
D	Derivative
d	Disturbance
diag	Diagonal matrix
dry	Dry packing
eq	Equilibrium
est	Estimated
expt	Experimental
F	Feed
f	Film
f	Forward reaction
G	Vapour phase
H	High gas throughput
H ₂ O	Water
I	Integral
I	Vapour-liquid interface
IG	Ideal gas
i	Stage
irr	Irrigated packing
j	Component or species
j	Data point
jk	Component or species pair j-k
K ₂ CO ₃	Potassium carbonate
k	Component or species
L	Liquid phase
L	Low gas throughput

LS	Lean solution
lc	Local composition
M	Medium gas throughput
m, m'	Molecular species
m	Measured
max	Maximum
min	Minimum
OL	Open-loop
o	Pre-loading
PV	Process variable or measured process variable
p	Process
R	Reaction
Reb	Reboiler
RG	Raw gas
r	Reverse reaction
ref	Reference
SP	Setpoint
s	Solvent
T	Temperature
T	Total or mixture
t	Total or mixture
u	Ultimate
vap	Vapour
w	Water
x	Fluid of interest

Superscripts

∞	At infinite dilution in water or in solvent
*	Un-symmetric convention
+	Adjusted matrix with positive diagonal elements
-1	Inverse
Born	Born model
Chem	Chemical
c	Molar concentration basis
E	Excess
eq	Chemical equilibrium
ex	Excess
f	Formation
H	Conjugate transpose
LP	Low pressure or atmospheric pressure
o	Reference
NRTL	Non-Random Two-Liquid model
PDH	Pitzer-Debye-Hückel model
Phys	Physical
res	Residual
s	Saturation or at vapour pressure P^s
T	Transpose
w	Water
ZN	Ziegler-Nichols