Volume of Appendices

for

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

Table of Contents

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_2CO_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 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_2S vapour phase profiles.	.....	A-55
Figure D.3.1:	CO_2 and H_2S vapour and liquid phase column profiles for the first set of plant data.	.....	A-56
Figure D.3.2:	CO_2 and H_2S vapour and liquid phase column profiles for the first set of plant data.	.....	A-57
Figure D.3.3:	CO_2 and H_2S vapour and liquid phase column profiles for the second set of plant data.	.....	A-58
Figure D.3.4:	CO_2 and H_2S 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_2S vapour and liquid phase column profiles for the first set of plant data.	.....	A-101
Figure H.3.2:	CO_2 and H_2S vapour and liquid phase column profiles for the first set of plant data.	.....	A-102
Figure H.3.3:	CO_2 and H_2S vapour and liquid phase column profiles for the second set of plant data.	.....	A-103
Figure H.3.4:	CO_2 and H_2S 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 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_2CO_3-$KHCO_3$-H_2O system data regression runs.	.....	A-45
Table C.3.2:	Suitable parameter value sets for the CO_2-K_2CO_3-$KHCO_3$-H_2O system.	.....	A-46

Table C.3.3:	Statistical results for the CO_2-H_2S-K_2CO_3-$KHCO_3$-KHS-K_2S-H_2O system data regression runs.	.....	A-47
Table C.3.4:	Suitable parameter value sets for the CO_2-H_2S-K_2CO_3-$KHCO_3$-KHS-K_2S-H_2O 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_2CO_3-H_2O system data regression runs.	.....	A-87
Table G.2.2:	Statistical results for the CO_2-H_2S-K_2CO_3-H_2O system data regression runs.	.....	A-87
Table I.2.1:	System poles and zeros for the SGC-RSF control structure.	.....	A-111