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

by

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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 CO_2 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 CO_2 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 CO_2 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® CO_2 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, CO_2 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 CO_2 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 CO_2 Removal Trains. Although a few response curves were distinctly underdamped, the quality of the validating data for the CO_2 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 CO_2 Removal Trains were found to share the same optimal diagonal control structure, which suggested that the identified control scheme was independent of the CO_2 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 CO_2 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 CO_2 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.

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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.

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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·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·K	Breslau-Miller anion parameter
$b_{c,1}$	m^3/kmol	Breslau-Miller cation parameter
$b_{c,2}$	m^3/kmol·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·K cal/mol·K kJ/kg·K Btu/lbmol·°R	Heat capacity
$\hat{C}_p$	kJ/kg·K	Mass heat capacity
$C_p\big|_{25}^T$	kJ/kmol·K	Average value of C_p between 25°C and temperature T
C_R	–	Reduced molar density
C_v	J/mol·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

D_{jk}	m^2/s	Binary diffusion coefficient for species pair j-k
D_w	cm^2/s	Diffusion coefficient in water
$Ð_{jk}$	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
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
G(s)	–	Transfer function matrix
$\hat{G}$	sm^3/h	Vapour phase standard volumetric flow
G̲(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

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	–	Twu 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
Δhfk	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

MW	kg/kmol g/mol	Molecular weight
m	–	Manipulated variable
m	kmol/m^3	Solution molarity (total K_2CO_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)

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
$\bar{v}^{\infty}$	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
$wf_{K_2CO_3}$	–	Equivalent weight fraction of K_2CO_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	Twu kinematic viscosity parameter
Z°	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	$kW/m^2 \cdot K$	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	$C^2/J \cdot m$	Dielectric constant
ε	erg	Characteristic energy
ϕ	° rad	Phase lag
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	$m \cdot K/W$	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	$W/m \cdot K$	Thermal conductivity
$\boldsymbol{\lambda}$	–	Vector of eigenvalues
λ'	$W/m \cdot K$	Ely-Hanley translational thermal conductivity contribution
λ''	$W/m \cdot K$	Ely-Hanley internal thermal conductivity contribution
λ^∞	$m^2/\Omega \cdot kmol$	Ionic conductivity at infinite dilution in water
μ	$kJ \cdot m/kmol$	Chemical potential

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
υ	–	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_2O	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_2CO_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