Aspen Plus

Rate-Based Model of the CO$_2$ Capture Process by K$_2$CO$_3$ using Aspen Plus

Contents

Introduction

This file describes an Aspen Plus rate-based model of the CO_2 capture process by K_2CO_3 (Potassium Carbonate) from a gas mixture of N_2, H_2O, CO_2, and H_2S. The model consists of an absorber and a stripper. The operation data from a pilot plant at TU Berlin[1] were used to specify feed conditions and unit operation block specifications in the model. Thermophysical property models and reaction kinetic models are based on the works of Aspen Technology(2007)[2] and Pinsent(1956)[3]. Transport property models and model parameters have been validated against experimental data from open literature.

The model presented here includes the following key features:

- True species including ions
- Electrolyte NRTL method for liquid phase properties and RK equation of state for vapor phase properties
- Concentration-based reaction kinetics
- Electrolyte transport property models
- Rate-based models for absorber and stripper with packing

1 Components

The following components represent the chemical species present in the process:

Table 1. Components Used in the Model

ID	Type	Name	Formula
N2	Conventional	NITROGEN	N2
H2O	Conventional	WATER	H2O
CO2	Conventional	CARBON-DIOXIDE	CO2
KOH	Conventional	POTASSIUM-HYDROXIDE	KOH
H3O+	Conventional	H3O+	H3O+
OH-	Conventional	OH-	OH-
HCO3-	Conventional	HCO3-	HCO3-
CO3-2	Conventional	CO3--	CO3-2
K+	Conventional	K+	K+
H2S	Conventional	HYDROGEN-SULFIDE	H2S
HS-	Conventional	HS-	HS-
S-2	Conventional	S--	S-2
K2CO3	Conventional	POTASSIUM-CARBONATE	K2CO3

2 Process Description

The flowsheet for the pilot plant at TU Berlin[1] for CO_2 capture by K_2CO_3 includes an absorber and a stripper. Table 2 represents typical operation data:

Table 2. Data of the TU Berlin pilot plant

Absorber	
Diameter	100 mm
Packing Type and Size	SULZER Mellapak 350Y
Packing Height	2568 mm
Stripper	
Diameter	100 mm
Packing Type and Size	SULZER Mellapak 350Y
Packing Height	2568 mm
Feeds and Products	
Sour Gas to Absorber	47.58 Nm^3/hr
Lean KOH solution to Absorber	70.00 l/hr
Rich KOH solution to Stripper	99.98 l/hr
CO_2 in Feed (Gas)	2.335(Vol %)
H_2S in Feed (Gas)	0.404(Vol %)
CO_2 in Outlet (Gas)	2.323(Vol %)
H_2S in Outlet (Gas)	0.0035(Vol %)

3 Physical Properties

The electrolyte NRTL method is used for computing liquid phase properties while RK equation of state is used for computing vapor phase properties in this Rate-based K_2CO_3 model. The model parameters were taken from the works of Aspen Technology(1983)[2] and Jou et al.[4,5,6].

CO_2, H_2S, and N_2 are selected as Henry-components to which Henry's law is applied and the Henry's constants are retrieved from Aspen Plus databanks for these components with water. In the reactions calculations, the activity coefficient basis for the Henry's components is chosen to be Aqueous. Therefore, in calculating the unsymmetric activity coefficients (GAMUS) of the solutes, the infinite dilution activity coefficients will be calculated based on infinite-dilution condition in pure water, instead of in mixed solvents.

The liquid molar volume model and transport property models have been updated and model parameters regressed from literature experimental data. Specifications of the transport property models include:

- For liquid molar volume, the Clarke model, called VAQCLK in Aspen Plus, is used with option code of 1 to use the quadratic mixing rule for solvents. The Aspen Plus built-in databank values for the Clarke model parameter VLCLK/1 of some main electrolytes (K+, OH^-), (K+, HCO_3^-) and (K+, CO_3^{-2}) are used.

- For liquid viscosity, the Jones-Dole electrolyte correction model, called MUL2JONS in Aspen Plus, is used with the mass fraction based ASPEN liquid mixture viscosity model for the solvent. There are three models for electrolyte correction and the K_2CO_3 model always uses the Jones-Dole correction model. The three option codes for MUL2JONS are set to 1 (mixture viscosity weighted by mass fraction), 1 (always use Jones and Dole equation when the parameters are available), and 2 (ASPEN liquid mixture viscosity model), respectively. The Jones-Dole model parameters, IONMUB, for HCO_3^- is regressed against $KHCO_3$-H_2O viscosity data from Palaty(1992)[13]; and that of CO_3^{-2} is regressed against K_2CO_3-H_2O viscosity data from Pac(1984)[8]. For K^+ and the other ions, Aspen Plus built-in databank values for Jones-Dole model parameters are used.

- For liquid surface tension, the Onsager-Samaras model, called SIG2ONSG in Aspen Plus, is used with its option codes being -9 (exponent in mixing rule) and 1 (electrolyte system), respectively.

- For thermal conductivity, the Riedel electrolyte correction model, called KL2RDL in Aspen Plus, is used.
- For binary diffusivity, the Nernst-Hartley model, called DL0NST in Aspen Plus, is used with option code of 1 (mixture viscosity weighted by mass fraction).

In addition to the updates with the above transport properties, the heat capacity at infinite dilution (CPAQ0) for CO_3^{-2} and HCO_3^- are adjusted to keep constant with the rate-based amines models.

The estimation results of the transport and thermal properties are summarized in Figures 1-6:
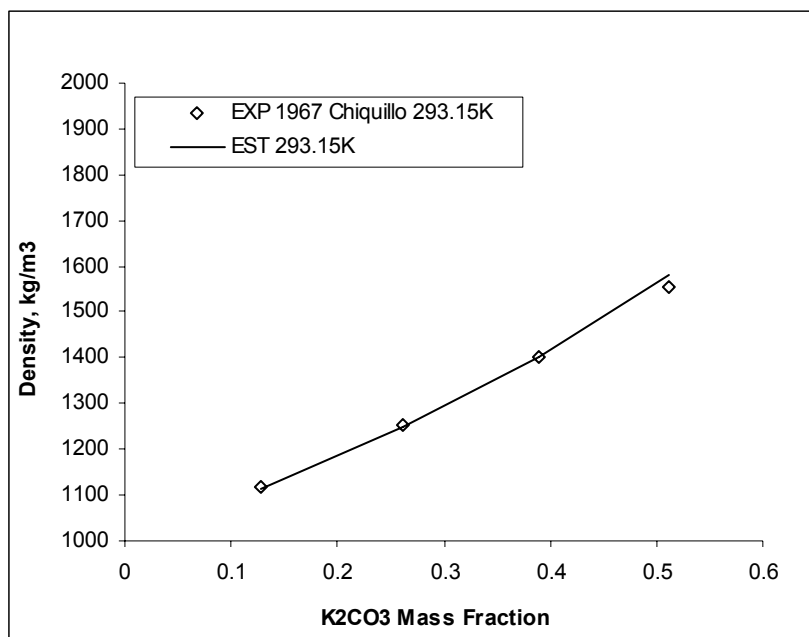

Figure 1. Liquid Density of K_2CO_3-H_2O at 293.15K, experimental data from Chiquillo (1967)[7]
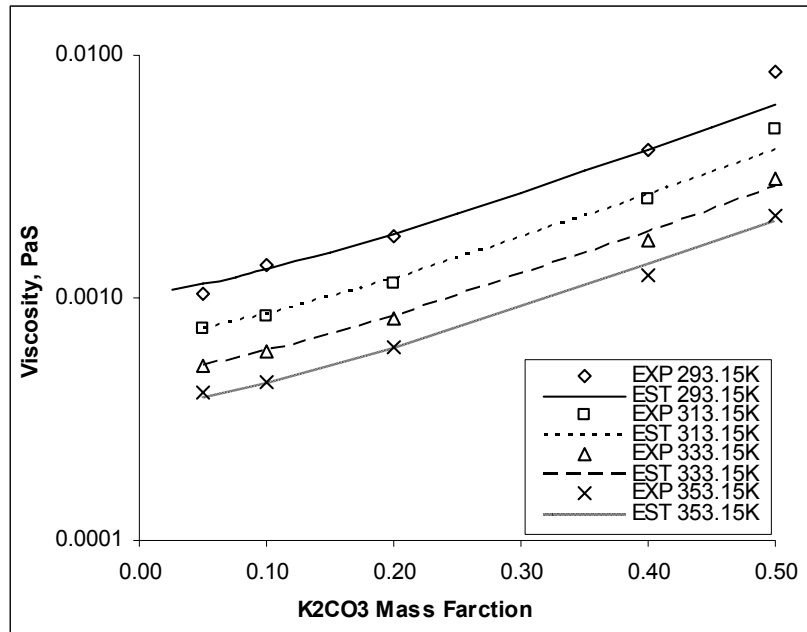
Figure 2. Liquid Viscosity of K_2CO_3-H_2O, experimental data from Pac (1984)[8]
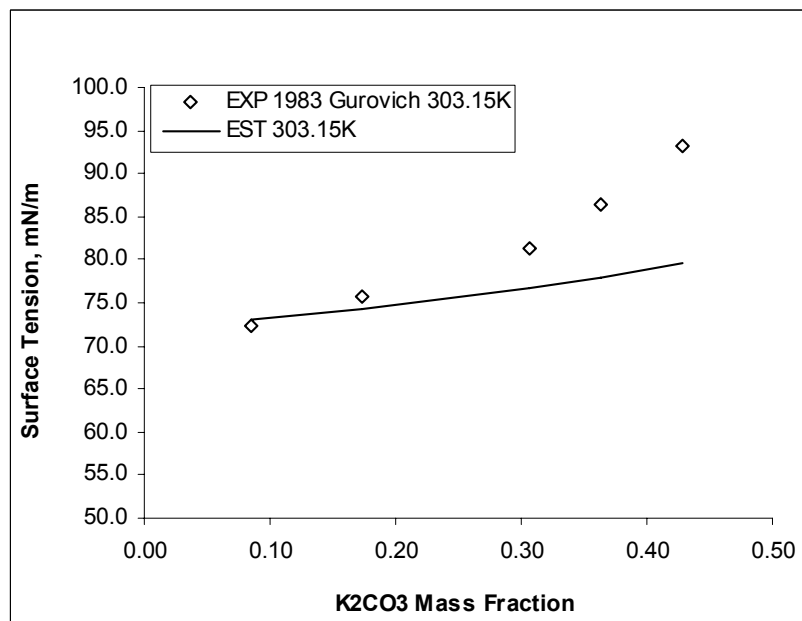

Figure 3. Surface Tension of K_2CO_3-H_2O at 303.15K, experimental data from Gurovic (1983)[9]
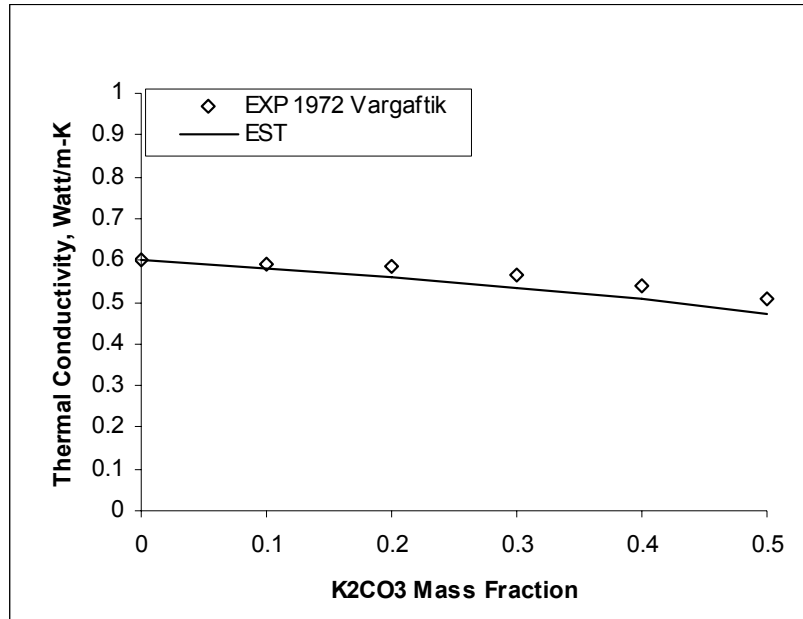
Figure 4. Liquid Thermal Conductivity of K_2CO_3-H_2O at 298.15K, experimental data from Vargaftik (1972)[10]

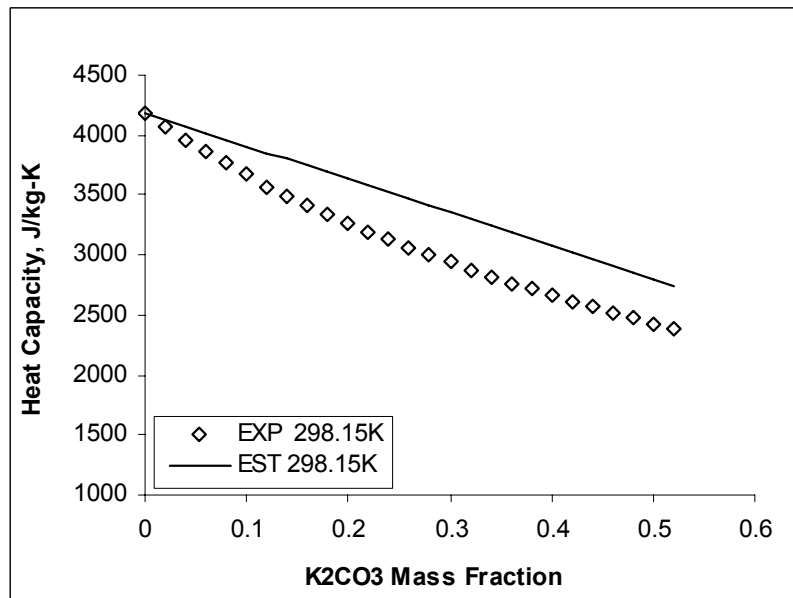**Figure 5. Liquid Heat Capacity of K_2CO_3-H_2O at 298.15K, experimental data from Puchkov (1978)[11]**
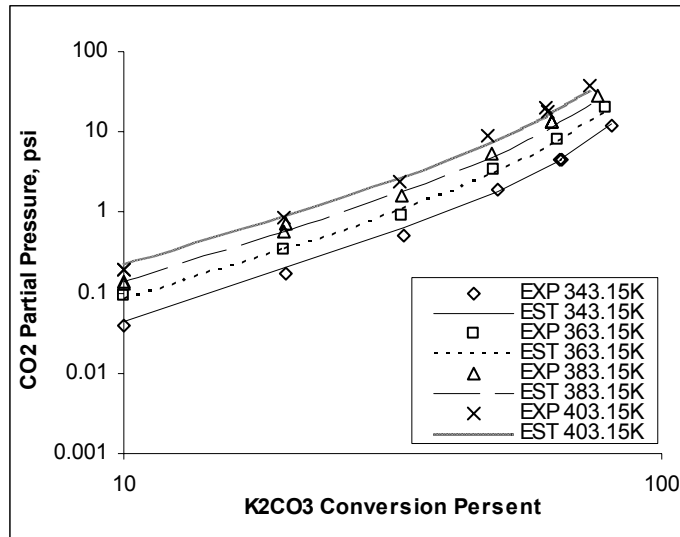
Figure 6. CO$_2$ partial pressure of K$_2$CO$_3$-CO$_2$-H$_2$O (K$_2$CO$_3$ mass fraction = 0.30), experimental data from Tosh (1959)[12]

4 Reactions

The electrolyte solution chemistry has been modeled with a CHEMISTRY model with CHEMISTRY ID of K2CO3, which is used as a global electrolyte calculation option in the simulation by specifying it on the **Global** sheet of the **Properties | Specifications** form. Chemical equilibrium is assumed with all the ionic reactions in CHEMISTRY K2CO3. In addition, a kinetic REACTION model named K2CO3-R has been created, which is used in calculations of the absorber and stripper by specifying it in the **Reaction** part of the absorber and stripper specifications. In K2CO3-R, all reactions are assumed to be in chemical equilibrium except the reactions of CO_2 with OH^-.

A. Chemistry ID: K2CO3

1	Equilibrium	$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^-$
2	Equilibrium	$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{-2}$
3	Equilibrium	$2H_2O \leftrightarrow H_3O^+ + OH^-$
4	Equilibrium	$H_2O + H_2S \leftrightarrow HS^- + H_3O^+$
5	Equilibrium	$H_2O + HS^- \leftrightarrow S^{-2} + H_3O^+$
6	Dissociation	$KOH \rightarrow K^+ + OH^-$
7	Dissociation	$K_2CO_3 \rightarrow 2K^+ + CO_3^{-2}$

B. Reaction ID: K2CO3-R

1	Equilibrium	$2H_2O \leftrightarrow H_3O^+ + OH^-$
2	Kinetic	$CO_2 + OH^- \rightarrow HCO_3^-$
3	Kinetic	$HCO_3^- \rightarrow CO_2 + OH^-$
4	Equilibrium	$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{-2}$
5	Equilibrium	$H_2O + H_2S \leftrightarrow HS^- + H_3O^+$
6	Equilibrium	$H_2O + HS^- \leftrightarrow S^{-2} + H_3O^+$

The equilibrium expressions for the reactions are taken from the work of Aspen Technology(1983)[2] and Jou et al.[4,5,6]. In addition, the power law expressions are used for the rate-controlled reactions (reactions 2-3 in K2CO3-R) and the general power law expression is:

$$r = k\left(T/T_0\right)^n \exp\left[\left(\frac{-E}{R}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]\prod_{i=1}^{N} C_i^{a_i} \tag{1}$$

Where:

r = Rate of reaction;

k = Pre-exponential factor;

T = Absolute temperature;

T_0 = Reference temperature;

n = Temperature exponent;

E = Activation energy;

R = Gas low constant;

N = Number of components in the reaction;

C_i = Concentration of component i;

a_i = The stoichiometric number of component i in the reaction equation.

If T_0 is not specified, the reduced power law expression is used:

$$r = kT^n \exp\left(-\frac{E}{RT}\right)\prod_{i=1}^{N} C_i^{a_i} \tag{2}$$

In this file, the reduced expressions are used. In equation (2), the concentration basis is Molarity, the factor n is zero, k and E are given in Table 3. The kinetic parameters for reaction 2 are taken from the work of Pinsent et al.(1956)[3], and the kinetic parameters for reaction 3 are calculated by using the kinetic parameters of reaction 2 and the equilibrium constants of the reversible reactions 2 and 3.

Table 3. Parameters k and E in Equation (2)

Reaction No.	k	E (cal/mol)
2	4.32e+13	13249
3	2.38e+17	29451

5 Simulation Approaches

Case 5 for the absorber and case 1 for the stripper of the TU Berlin pilot plant[1] for CO_2 capture by K_2CO_3 are used in this study.

Simulation Flowsheet – The TU Berlin pilot plant has been modeled with the following simulation flowsheet in Aspen Plus, shown in Figure 7.
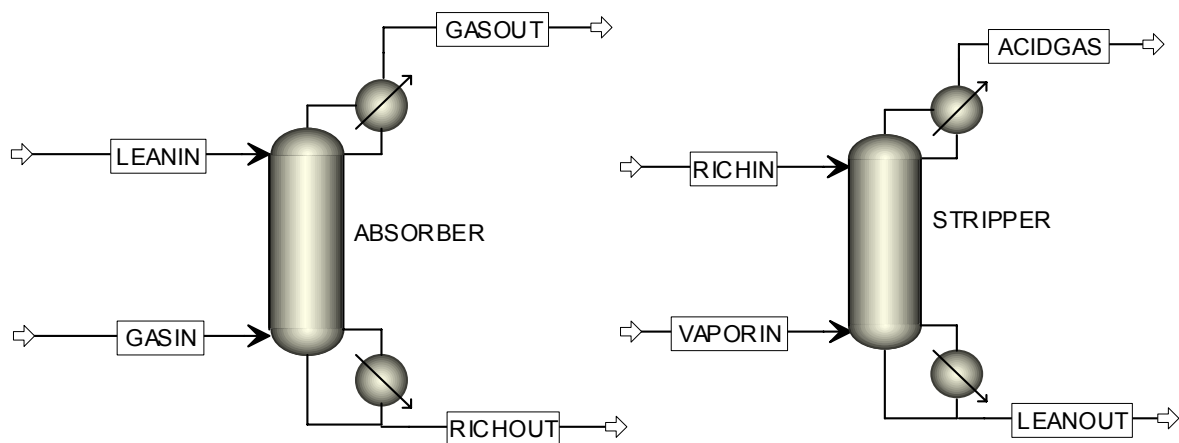

Figure 7. Rate-Based K_2CO_3 Simulation Flowsheet in Aspen Plus

Unit Operations - Major unit operations in this model have been represented by Aspen Plus Blocks as outlined in Table 4.

Table 4. Aspen Plus Unit Operation Blocks Used in the Rate-Based K2CO3 Model

Unit Operation	Aspen Plus Block	Comments / Specifications
Absorber	RadFrac	1. Calculation type: Rate-Based 2. 10 Stages 3. Top Pressure: 1094 mbar, and column pressure drop is 6.45 mbar 4. Reaction: Reaction ID is K2CO3-R for all stages; when calculation type is equilibrium stages, Residence Times is used, and in this file, the liquid Residence time = 0.001s 5. Packing Type: SULZER, 350Y, STANDARD Mellapak 6. Packing height: 2.568 m and Section diameter: 0.1m 7. Mass transfer coefficient method: Bravo et al (1985) 8. Interfacial area method: Bravo et al (1985) 9. Interfacial area factor: 0.6 10. Heat transfer coefficient method: Chilton and Colburn 11. Holdup correlation: Billet and Schultes (1993) 12. Film resistance options: Discrxn for liquid film, and Film for vapor film 13. Additional discretization points for liquid film: 0.0001, 0.001, 0.01, 0.1 and 0.5 14. Flow model: Mixed

Unit Operation	Aspen Plus Block	Comments / Specifications
Stripper	RadFrac	1. Calculation type: Rate-Based
		2. 10 Stages
		3. Partial vapor condenser
		4. Bottom rates: 102.96kg/hr
		5. Top Pressure: 148.8 mbar, and column pressure drop is 9.7 mbar
		6. Reaction: Reaction ID is K2CO3-R for all stages; when calculation type is equilibrium stages, Residence Times is used, and in this file, liquid residence time = 0.001s
		7. Packing Type: SULZER, 350Y, STANDARD Mellapak
		8. Packing height: 2.568 m and Section diameter: 0.1m
		9. Mass transfer coefficient method: Bravo et al (1985)
		10. Interfacial area method: Bravo et al (1985)
		11. Interfacial area factor: 0.6
		12. Heat transfer coefficient method: Chilton and Colburn
		13. Holdup correlation: Billet and Schultes (1993)
		14. Film resistance: Discrxn for liquid film, and Film for vapor film
		15. Additional discretization points for liquid film: 0.0001, 0.001, 0.01, 0.1 and 0.5
		16. Flow model: Mixed

Streams - Feeds to the absorber are gas stream GASIN containing N_2, H_2O, CO_2 and H_2S and liquid solvent stream LEANIN containing aqueous KOH solution. Feeds to the stripper are rich solvent stream RICHIN taking aqueous KOH solutions with absorbed CO_2 and the vapor stream VAPORIN for acid gas stripping. Feed conditions are summarized in Table 5.

Table 5. Feed specifications

Stream ID	GASIN	LEANIN	RICHIN	VAPORIN
Substream: MIXED				
Temperature: C	25.06	25.02	45.04	56.87
Pressure: mbar	1100.45	1300	148.8	Dew point
Total flow		70 l/hr	99.98 l/hr	20 kg/hr
Composition	Mole-Frac	Mass-Conc, kg/cum	Mass-Conc, kg/cum	
N2	0.94161	0	0	0
H2O	0.031	Solvent	Solvent	1
CO2	0.02335	12.38	27.52	0
KOH	0	28.58	35.73	0
H2S	0.00404	0.25	0	0

6 Simulation Results

The simulation was performed using Aspen Plus version 2006.5. The measured versus caculated absorber and stripper liquid temperature and concentration profiles are presented in Figures 8-11.
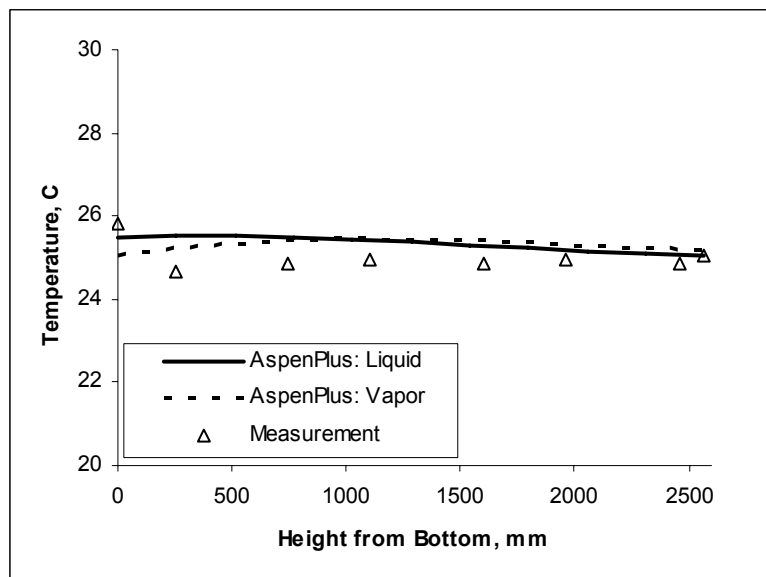

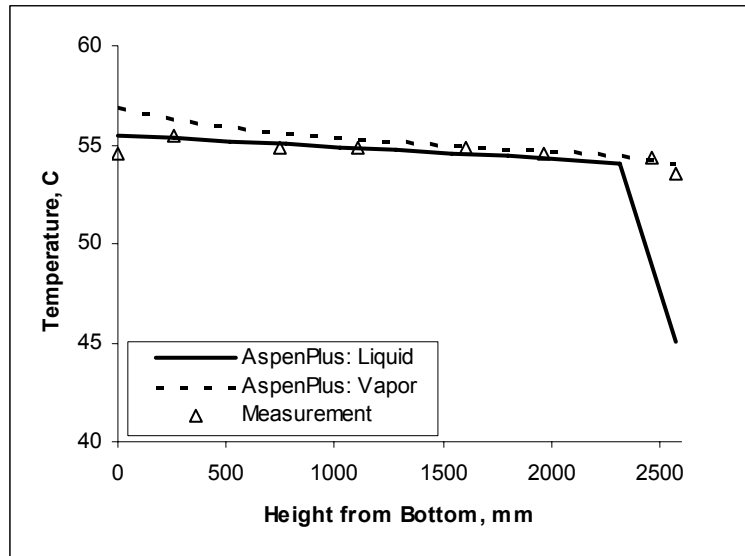*Figure 8. The Absorber Temperature Profile*
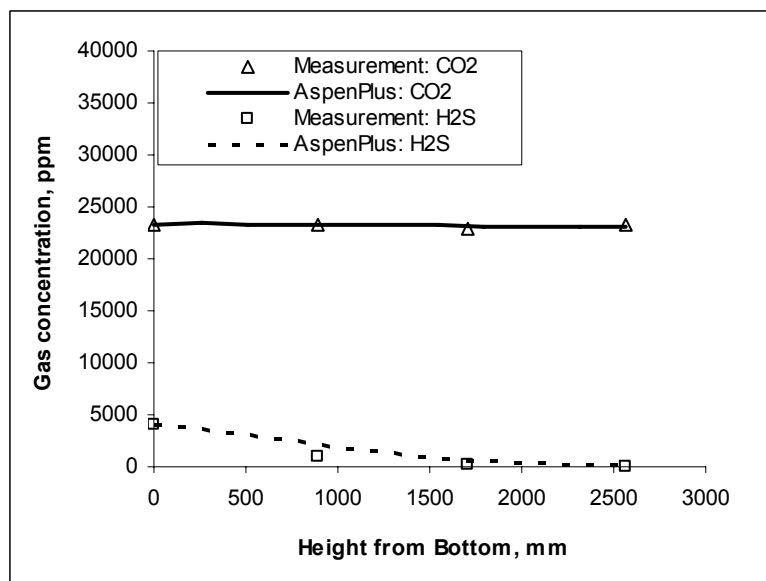
Figure 9. The Stripper Temperature Profile

Figure 10. The Absorber CO$_2$ and H$_2$S Concentration Profiles in Vapor Phase
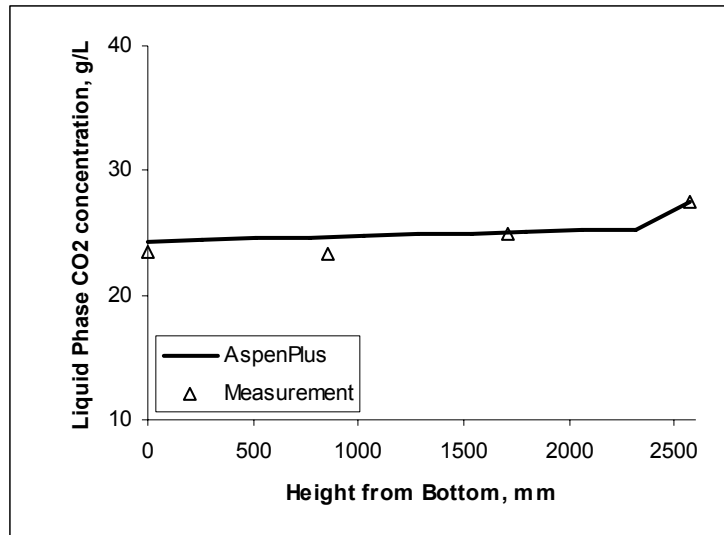
Figure 11. The Stripper CO₂ Concentration Profile in Liquid Phase

7 Conclusions

The Rate-Based K_2CO_3 model provides a rate-based rigorous simulation of the process. Key features of this rigorous simulation include electrolyte thermodynamics and solution chemistry, reaction kinetics for the liquid phase reactions, rigorous transport property modeling, rate-based multi-stage simulation with Aspen Rate-Based Distillation which incorporates heat and mass transfer correlations accounting for columns specifics and hydraulics.

The model is meant to be used as a guide for modeling the CO_2 capture process with K2CO3. Users may use it as a starting point for more sophisticated models for process development, debottlenecking, plant and equipment design, among others.

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