

Rate-Based Modelling of CO₂ Capture Process by Reactive Absorption with MEA

Bao-Hong Li^{*a}, Nan Zhang^b, Robin Smith^b

^aDepartment of Chemical Engineering, Dalian Nationalities University, Dalian 116600, China

^bCentre for Process Integration, School of Chemical Engineering and Analytical Science, The University of Manchester, Manchester M13 9PL, UK
 libh@dlnu.edu.cn

A rate-based model of CO₂ capture process by MEA is built within Aspen Plus V8.0 software in this study. The model is built on the basis of an example model coming along with Aspen Plus V8.0, thermodynamic model of ENRTL-RK is adopted and both absorption and desorption columns are modelled by rate-based model. Important improvements have been achieved for its accuracy. To be specific, the washing section of the absorption column is strictly modelled and the error on mass balance of MEA is greatly reduced. In addition, the model is validated using the recently published pilot-scale experiment results of the absorption of CO₂ by MEA and structured packing Sulzer of Mellapak is employed for both absorption and desorption columns in the process. It predicts the experimental profiles of the temperature and the concentration of CO₂ in the liquid phase with an accuracy of $\pm 4\%$, and obviously much better than recently reported model of $\pm 8\%$.

1. Introduction

Carbon Capture and Storage (CCS) is known as a promising route for controlling the global warming (Kale et al., 2013). Amine scrubbing is probably the only technology for Post-Combustion Capture (PCC) for CO₂ that is available to existing power plants (Rochelle, 2009), and most commonly used amine is MEA (an aqueous solution of monoethanolamine). The challenges on the way in implementing the process for treating the entire flue gas of a full size power plant are: how to scale up the amine scrubbing process and how to reduce obviously the exceeding high energy requirement for solvent regeneration (Notz et al., 2012). A recent review of the research work carried out PCC by chemical absorption is given by Wang et al. (2011). To deal with the second challenge, Anantharaman and Berstad (2012) considered those energy integration options in Natural Gas Combined Cycle (NGCC) with PCC, and application of their methodology resulted an improvement in efficiency of the overall process by 0.4 % points. Also, Neveux et al. (2013) considered the interaction between process design and the adopted solvent since the energy efficiency of process modifications depends on the considered solvent. This work focus will be on a reliable and rigorous model which is badly needed to face up to those challenges.

Hassan (2005) built an equilibrium-stage type model of the CO₂ capture process with MEA using Aspen Plus software. The flue gas data from a cement plant was used and the recommended MEA solvent concentration is 30% by weight to reduce the energy requirement of solvent regeneration to its minimum, the washing section of the absorber column has been neglected in his model to reduce its complexity (Hassan, 2005). Zhang et al. (2009) built a rate-based absorber model for CO₂ absorption with MEA and demonstrate the superiority of the rate-based models over the traditional equilibrium-stage models for the pilot plant data from University of Texas at Austin.

A rate-based model of CO₂ capture process by MEA is built in this study, which is based on an example model within Aspen Plus software (Aspen Technology, 2012). Important improvements have been achieved in accuracy. Specifically, the washing section of the absorption column is strictly modelled by a separate column. In addition, the model is validated using the recently published pilot-scale experiment results of the absorption of CO₂ by MEA (Notz et al., 2012). It accurately predicts the experimental profiles

of the temperature and the concentration of CO₂ in the liquid phase, and obviously much better than recently reported model of ±8 % (Kale et al., 2013). Furthermore, this study shows that accuracy rate-based model can be built by selecting suitable unit models and providing proper optional estimates without relying on equation-oriented Aspen Custom Modeler (Kale et al., 2013) and much labour work can be saved.

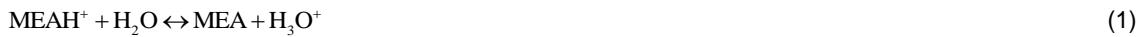
2. Chemical system and physical properties

Since the aim of this work is to demonstrate the rate-based model improvements of a rigorous process model for the reactive absorption CO₂ with MEA solvent, the updated electrolyte solution chemistry model coming along with Aspen Plus V8.0 is adopted in this study (Aspen Technology, 2012). Furthermore, NO_x and SO_x are supposed to be removed completely before they enter the CO₂ capture process. A summary of the chemistry model is provided below for completeness and further information can be found in the cited reference (Aspen Technology, 2012).

A chemistry model named as MEA is used as the global electrolyte calculation option in the simulation, and the chemical equilibrium is assumed with all the ionic reaction in the MEA chemistry. In addition, two reaction models called Absorber and Stripper have been created. In the Absorber/Stripper models, all reactions are assumed to be in chemical equilibrium except those of CO₂ with OH⁻ and CO₂ with MEA (Aspen Technology, 2012).

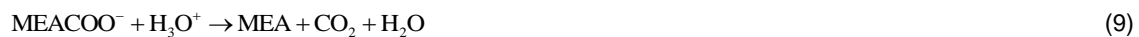
2.1 Chemistry: MEA

The chemistry of MEA consists of the following instantaneous reactions:



2.2 Reaction: Absorber/Stripper

The reaction models of Absorber/ Stripper consist of instantaneous reactions (1, 3, 5) and the following finite rate reactions:



The equilibrium constants for reactions 1-5 in MEA chemistry are calculated from the standard Gibbs free energy change. Power law expressions are used for the Rate-controlled reactions (reactions 6-9 in Absorber/ Stripper). Note that Absorber and Stripper share all kinetic parameters except those of reaction 9, those parameters can be found in the reference (Aspen Technology, 2012).

The unsymmetric electrolyte NRTL property method (ENRTL-RK) and PC-SAFT equations of state are used to computer liquid and vapour properties, respectively, in this work. CO₂, N₂ and O₂ are selected as Henry-components (solutes) to which Henry's law are applied.

3. The experiment data

The flow diagram of a pilot plant (Notz et al., 2012) is shown in Figure 1. In the process, flue gas is contacted with MEA at ambient pressure in an absorption column and the amine loaded with acidic gases is regenerated in a desorber column. Treated flue gas leaves the absorber column, lean in acid gases. For reducing amine losses, a washing section is installed at the top of the absorber above the lean solvent feed. In the washing section, water is recycled from the liquid collector to the top of the section.

The rich solvent leaving the absorber is pumped through a heat exchanger (so called rich-lean heat exchanger) in which it is heated up by the hot lean solvent from the desorber bottom. Then, it is directly distributed on the top of the desorber packing sections. A stripping steam is generated in the desorber bottom by partial evaporation of liquid solvent with electrical heating elements. Above the desorber packing, a washing section similar to that in the absorber is installed to retain amines. Condensate is used as washing water.

4. Previous reported simulation

4.1 The simulation model by Kale et al. (2013)

The model presented by Kale et al. (2013) consists of a system of differential and algebraic equations, which was implemented in the equation-oriented Aspen Custom Modeler(ACM) simulation environment. To validate the model, the experimental data (Notz et al., 2012) was used, and the comparison of the simulation result with the experimental measurements validates the rate-based model of reactive absorption. The model predicts the experimental profiles of the temperature and the concentration of CO₂ in the liquid phase with an accuracy of $\pm 8\%$. However, simulation flowsheet is not provided in Kale et al. (2013)'s work and how to simulate the washing section is not explained too. Only the absorption column rather than the absorption-desorption cycle is modeled, the interactions of these two columns have not been explored.

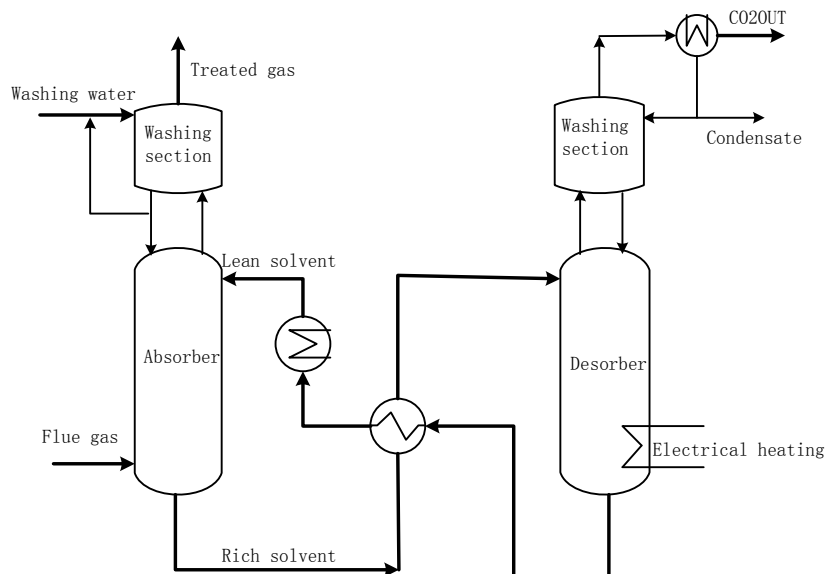


Figure 1: Process flow diagram of absorption-desorption pilot plant

4.2 The simulation model by Aspen Technology, Inc. (2012)

Coming with Aspen Plus V8.0, an example rate-based model of CO₂ capture process by MEA (Named as Model 1) is developed by Aspen Technology, Inc. in 2012. This example model was just to closely simulate Case 1 of the pilot plant cited in Notz et al. (2012) which incorporates an absorption and a stripper columns, heat exchange between the two columns, and water and amine recycles. The operating conditions of the model were chosen to be as close to those used in Case 1 as possible. An amine makeup stream was not present in the Case 1, but was added to the simulation to maintain mass balance and to aid convergence. The simulation flowsheet of the example model is not provided here because of limited space and can be provided on demand.

In this model, the absorber and its washing section are modelled as a complex absorption column of the rate-based type. The whole packing height including the wash section height of 0.42 m and absorber section of 4.2 m is corresponding to 20 stages for simulation, and the washing section is corresponding to stages 1-2 while the absorber section to stages 3-20.

The desorber and its washing section are modelled as one column with two packed sections in it. Also, the rate-based model is adopted and 20 stages are specified for the column, Stage 1 represents the condenser at the top, Stage 2 represents the washing section, Stages 3-19 represent the desorber section. And Stage 20 is corresponding to the electrical boiler at the bottom.

The simulation results are summarized and compared with those data of the pilot plant in Tables 1-3. Note that a heat exchanger of HX2 is added to change the temperature of the rich solvent to its measured temperature of 112.85 °C before it enters the desorber column. Its heat duty is 262 W, and can be explained as the heat loss during the rich solvent flows from the exchanger HX1 to the stripper column.

4.3 The improved rate-based simulation model

The simulation flowsheet of the proposed rate-based simulation model (Named as Model 2) is given in Figure 2, it inherits those chemical and reaction models embedded in Model 1 and the following improvements are introduced:

(1) The absorber column and its washing section are modelled by two separated columns, one is the absorber of the rate-based type, and the other is the abs-wash of the equilibrium type. The washing section adopts the equilibrium model because there is no obvious benefit when a rate-based one is used. The advantage of this modification is that the function of the washing section can be easily analyzed.

(2) Heat loss of the rich solvent after it leaves the absorber column is also considered in Figure 2. The lost heat duty of 389 W reduces its temperature to be 51.66 °C (the same as the measured temperature). Such treatment will make the operating conditions of its subsequent process units closely approach those cited in Notz et al.(2012).

Table 1: Comparison of experimental and simulation result- Absorber

		Experimental	Model 1		Model 2	
		value	value	error	value	error
Treated gas	N ₂ (g/g)	0.797	0.7980	0.1 %	0.8008	0.5 %
	O ₂ (g/g)	0.109	0.1085	0.5 %	0.1088	0.2 %
	H ₂ O (g/g)	0.072	0.0743	3.2 %	0.0752	4.4 %
	CO ₂ (g/g)	0.022	0.0191	13 %	0.0151	31.3 %
	F (kg/h)	66.6	67.03	0.6 %	66.80	0.3 %
	T (°C)	47.13	48.21	2.3 %	47.86	1.5 %
	P (mbar)	977.08	977.08	0	977.08	0
Rich solvent	H ₂ O (g/g)	0.661	0.6606	0.1 %	0.6596	0.2 %
	MEA (g/g)	0.265	0.2658	0.3 %	0.2655	0.2 %
	CO ₂ (g/g)	0.074	0.0736	0.5 %	0.0749	1.2 %
	F (kg/h)	206.5	207.01	0.2 %	207.26	0.4 %
	T (°C)	51.66	53.35	3.3 %	53.96	4.5 %
	P (mbar)	1,065.05	987.08	7.3 %	988.2	7.3 %
Washing water(in)	F (kg/h)	30.48(30.87*)	30.48	0	30.48	0
	T (°C)	43.87	43.87	0	43.87	0
	Q (W)	-61.7	-75	21.6 %	-94	52.4 %

Note: * marks the original value of 30.87 kg/h is not correct because it does not satisfy the mass balance.

5. Model validation

To validate the improved rate-based model, case 1 of pilot plant experiment of the absorption of CO₂ with MEA reported by Notz et al. (2012) was used. The main results are summarized and compared in Tables 1-3. In addition, the temperature profile of liquid in the absorber section and the desorber column are provided in Figure 3. From the Figure 3, it is obviously that Model 2 can properly predict the temperature profiles of liquid except the first temperature point of 64.62 °C in the absorber section. Further comparison of Tables 1-3 shows that Model 2 is more closely to the experimental data than Model 1. Note that errors of heat duty are usually larger than 10 %. It can be attributed to heat loss to the environment.

6. Conclusions

An improved rate-based model of CO₂ capture process is developed in this study. It is validated by the reported pilot plant and compared with an existing example model within Aspen Plus V8.0. Comparison shows that the new model can properly predict Case 1 of the pilot plant and is much more accurate than the example model. Especially, the error on whole MEA mass balance has been reduced from 0.007 kg/h to 0.001 kg/h, and the washing section of the absorber column has been modelled successfully by a separate column. This work shows that accuracy rate-based model can be built by selecting suitable unit models and providing proper optional estimates with Aspen Plus V8.0 software and much labour work can be saved.

7. Acknowledgements

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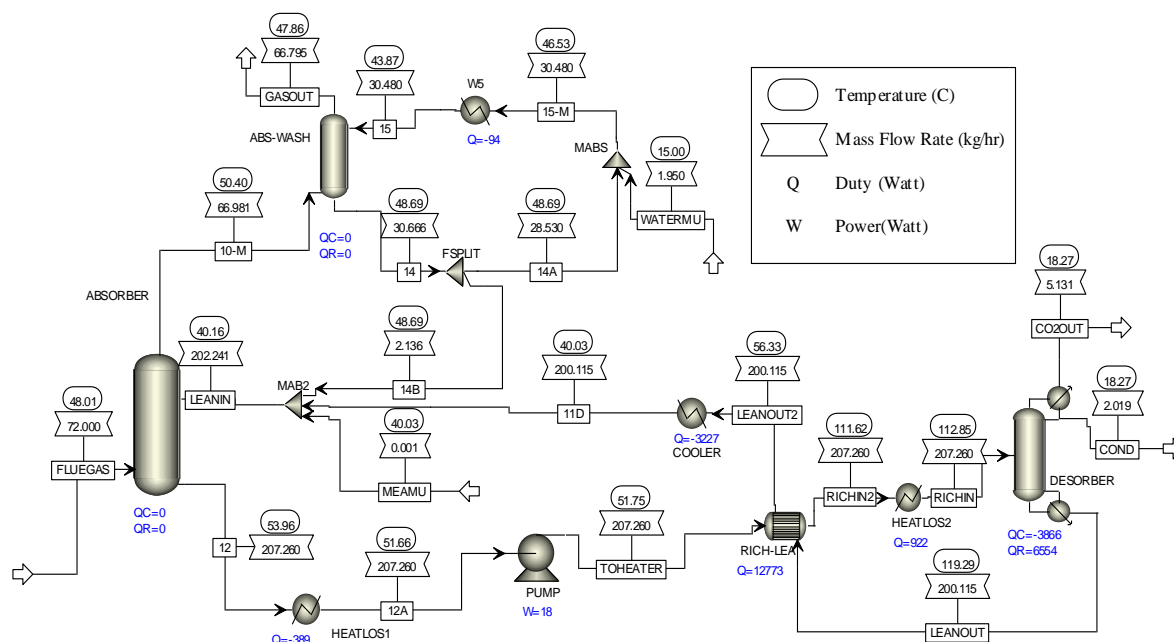


Figure 2: The improved simulation flowsheet of CO₂ capture process with MEA

Table 2: Comparison of experimental and simulation result- Desorber

		Experimental	Model 1		Model 2	
		value	value	error	value	error
CO ₂ out	H ₂ O (g/g)	0.004	0.0043	7.5 %	0.0044	10 %
	CO ₂ (g/g)	0.996	0.9943	0.2 %	0.9942	0.2 %
	N ₂ (g/g)	0	0.0011	-	0.0011	-
	O ₂ (g/g)	0	0.0003	-	0.0003	-
	F (kg/h)	4.67*	4.86	-	5.131	-
	T (°C)	18.27	18	1.5 %	18.27	0
	P (mbar)	2,000	2,000	0	2,000	0
Lean solvent	H ₂ O (g/g)	0.673	0.6731	0	0.6731	0
	MEA (g/g)	0.275	0.2750	0	0.2749	0
	CO ₂ (g/g)	0.052	0.0520	0	0.0520	0
	F (kg/h)	200.1	200.09	0	200.11	0
	T (°C)	120.8	119.36	1.2 %	119.29	1.2 %
	P (mbar)	-	2,009.1	-	2,005	-
Condensate	H ₂ O (g/g)	1.0	0.995	0.5 %	0.9930	0.7 %
	MEA (g/g)	0	0.009	-	0.0006	-
	CO ₂ (g/g)	0	0.0041	-	0.0020	-
	F (kg/h)	2.04	2.07	1.5 %	2.02	1 %
	T (°C)	16.02	18	11.1 %	18.27	14 %
	P (mbar)	-	1,999.1	-	2,000	-
Condenser duty (W)	-2,773.6	-3,257	17.4 %	-3,866	39.4 %	
Reboiler duty (W)	7,951.5	7,050	11.3 %	6,554	17.6 %	

Note: * marks the value should be questioned because the whole mass balance is not satisfied if the flowrate of other input and output streams are corrected. Specifically, for water balance in Figure 2, the inlet streams are Watermu and Fluegas while the outlet streams are Gasout, CO₂out and Cond.

Table 3: Comparison of experimental and simulation result- key process parameters

		Experimental	Model 1		Model 2	
		value	value	Error(abs)	value	Error(abs)
Water makeup	F (kg/h)	1.95	1.949	0.001	1.950	0
MEA makeup	F (kg/h)	0	0.007	0.007	0.001	0.001
Rich-Lean Exchanger	duty (W)	13,524	12,424	1,100	12,773	751
Cooler on lean solvent	duty (W)	-2,866.9	-3,593	726.1	-3,364	497.1
Fluegas	F (kg/h)	72.0	72.0	0	72.0	0

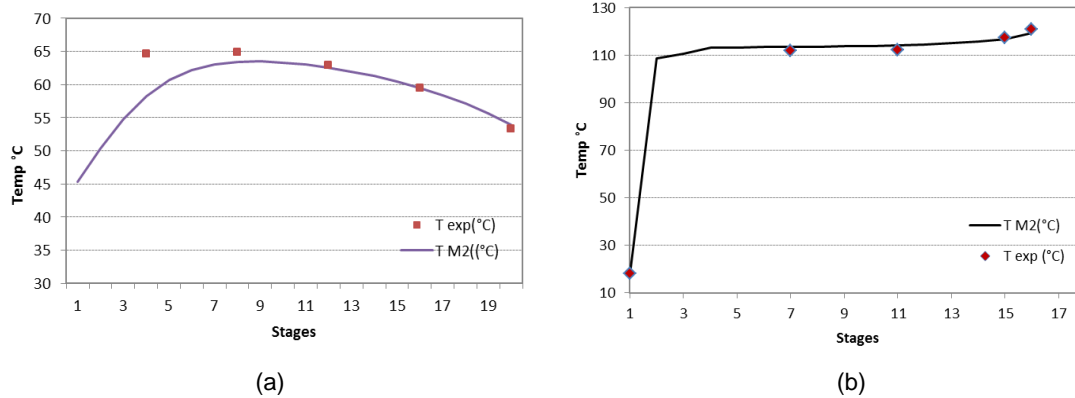


Figure 3: The temperature profile of liquid in (a) the absorber section, (b) the desorber column(x axis represents stages while y axis represents temperature)

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