Dynamic Modeling and Analysis of Amine-based Carbon Capture Systems

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Abstract: Carbon capture technologies are studied widely to curb the rising trend in the atmospheric concentration of CO_2 causing global warming. The post-combustion carbon capture technology using amine solvents is one of the mature technologies that can be deployed to existing power plants. Chemical absorption based on an amine solvent has a fast reaction rate with a high capacity to capture CO_2 . However, a large amount of energy is needed to regenerate the CO_2 rich solvent after the absorption. Flexible operation with a properly chosen control structure is a way to alleviate this problem and developing a simple, yet accurate dynamic model is a key to finding stable operation conditions while maximizing the flexibility of the process. In this research, chemical absorption process based on the most widely used amine solvent, monoethanolamine (MEA), is developed using the commercial software of *gPROMS*. The Kent-Eisenberg model and a rigorous rate-based approach are used to develop a dynamic column model. The process model is consistent with the experimental data within about 10% error. The model was used to compare two control strategies. As a result, the control strategy that control CO_2 capture with the lean solvent flow showed faster settling time than with the regeneration heat.

Keywords: Process modeling and identification; Process control applications; CO₂ capture

1. INTRODUCTION

Most energy used today is generated through fossil fuel based combustion, using sources such as natural gas, coal, and petroleum. To decrease the dependency on the fossil fuel, renewable energy sources are being investigated vigorously, but fossil fuels are expected to play the role of main energy resrouce for the foreseeable future, considering their favourable economics and availabilities (Mac Dowell et al., 2013). At the same time, CO_2 emission caused by the combustion of fossil fuels accounts for the majority of the anthropogenic emission (Wang et al., 2015). As the continued use of fossil fuels appears inevitable, the CO_2 emission and associated climate change have become a major challenge.

Post Combustion Carbon Capture (PCC) via chemical absorption is known to be the most immediately applicable technique for reducing the CO_2 emission in coal-based power plants, because it can be applied to existing plants without significant modifications. However, a large amount of heat energy is required to strip out CO_2 from the rich solvent, which results in high operating cost. Thus, several researchers have studied the amine-based PCC with the objective of reducing the regeneration energy (Koronaki et al, 2015).

Flexible operation and a suitable control strategy can help alleviate the disadvantage associated with the large energy requirement of the amine-based process. Establishing an economically feasible operation strategy, such as doing more capture when energy costs are low, can be an effective strategy for reducing the operation cost. Development of a dynamic model is needed to analyze various operational scenarios and construct proper control structures. For the last few years, dynamic modeling and simulation have been actively performed to help investigate various operational scenarios and design control strategies.

Among the several process units of the amine-based capture process, the packed absorption column is the most important one that determines performance of the overall process. Thus, various types of column models have been proposed, from the simplest models assuming vapour-liquid and reaction equilibria, to more general and complex models considering mass and heat transfer and kinetics. Among them, the ratebased model employing the mass transfer enhancement factor may be the most widely used (Kvamsdal et al., 2009, Biliyok et al., 2012, Harun et al., 2012, Gaspar et al., 2012). This model, which describes the reaction-enhanced mass transfer using the enhancement factor, represents a good balance between accuracy and computational complexity as it can represent the film reaction and mass transfer phenomena in a relatively simple way. However, since the use of enhancement factor does not account for some phenomena like the reversion of carbamate, it can show limited accuracies in the high loading region (Tobiessen, 2006).

In the present work, a rate-based column model with the Kent-Eisenberg thermodynamic model is developed in $gPROMS^{TM}$ platform. The column model is validated using experimental data and is used to construct an overall process model. Dynamic responses for some scenarios are analysed with different control strategies. The analysis shows that

different dynamic behaviours can result for a same disturbance depending on the control strategy. The present analysis also provides insight on the influence of control strategy in closed-loop dynamic behaviours.

2. MODEL DEVELOPMENT

2.1. Thermodynamic and chemical reaction

For an accurate dynamic simulation of an industrial scale absorption process, it is important to make the model as simple as possible without missing those aspects that strongly affect the dynamics of the process. The use of the Kent-Eisenberg (KE) model (Kent and Eigenberg, 1976) is one simple choice to represent the thermodynamics of aminewater- CO_2 system (Jayarathna et al, 2013). This model assumes the ideal solution and the non-ideality due to electrolytes is lumped into the fitted parameters of the equilibrium constants. Since there is no need to calculate the activity coefficient, it has the advantage of greatly reducing the model's complexity and computation load. On the other hand, the range of validity for such a fitted thermodynamic model may be limited.

The model describes a possible set of reaction in the CO_2 -H₂O-MEA system as follow:

$$2H_2O \longleftrightarrow^{K_1} OH^- + H_3O^+ \tag{1}$$

$$CO_2 + 2H_2O \longleftrightarrow^{K_2} HCO_3^- + H_3O^+$$
⁽²⁾

$$HCO_{3}^{-} \xleftarrow{K_{3}} CO_{3}^{2-} + H_{3}O^{+}$$
(3)

 $MEACOO^{-} + H_{2}O \xleftarrow{K_{4}} MEA + HCO_{3}^{-}$ (4)

$$MEAH^{+} + H_{2}O \xleftarrow{K_{5}} MEA + H_{3}O^{+}$$
(5)

In the KE model, the reaction constants and Henry constant for the equilibrium condition are given in the following form:

$$\ln K_r \quad \text{or} \quad \ln H_{CO} = a + b / T + c \cdot \ln(T) + d \cdot T \tag{6}$$

The parameters used in the model are obtain from the Kent et al (1976) and Aboudheir et al (2003).

2.2. Packed column model

The model equations are similar to those by Mac Dowell et al. (2013) and Taylor and Krishna (1993). The column model connects multiples of a stage model wherein a rate-based approach is used. Conservation equations, transfer rate equations, and equilibrium relations are developed for each stage. The equations for the transfer phenomena between the liquid and vapor phases are based on the two-film theory, which is a widely used mass transfer model.

The following assumptions are used in the column model.

1) The bulk phases are well-mixed.

2) Reactions occur only in the liquid film and liquid bulk phase.

3) Heat loss to the atmosphere is negligible.

4) Degradation of the solvent is not significant.

The mass balance is constructed on a molar basis, which is described as follows:

$$\frac{dM_{i,j}^{L}}{dt} = L_{j,l} x_{j,l} - L_{j} x_{j} + N_{i,j}^{L} + r_{i,j}^{bulk}$$

$$\frac{dM_{i,j}^{V}}{dt} = V_{j+l} y_{j+l} - V_{j} y_{j} + N_{i,j}^{V}$$
(7)

i indicates component, and j is the index for column stage. r represents the generation or consumption by reaction. Since the reaction is assumed to take place only in the liquid phase, the reaction term appears only in the mass balance for the liquid phase. The reaction rate is calculated from the reaction rate equations or the KE model to satisfy the reaction equilibrium condition.

The energy balances for the bulk phases are shown below:

$$\frac{dU_{j}^{L}}{dt} = L_{j-1}H_{j-1}^{L} - L_{j}H_{j}^{L} + q_{j}^{L}$$

$$\frac{dU_{j}^{V}}{dt} = V_{j+1}H_{j+1}^{V} - V_{j}H_{j}^{V} + q_{j}^{V}$$
(8)

The molar flux in the liquid phase is different from that in the vapor phase because electrolytes exist in the liquid phase. Ionic components are generated by reactions in the liquid film and transferred to the liquid bulk. In the case of energy balance in the film region, total heat flux is conserved since there is no accumulation or heat loss. Therefore, the mass and energy balance in the film appears as the following formulae:

$$N_{i,j}^{L} + r_{i,j}^{film} - N_{i,j}^{V} = 0$$
⁽⁹⁾

$$q_j^L - q_j^V = 0 \tag{10}$$

A rigorous mass transfer model is used to describe the transport phenomena. To calculate the molar flux in the multi-component system, the Maxwell-Stefan(MS) equation is used. A detailed set of equations for the MS equation can be found in Taylor and Krishna (1993).

For the calculation of the rate-based model, correlations representing the transfer phenomena and hydraulics in the packing column are required. Major correlations used in the model are summarized in Table 1.

Table 1. Summary of the correlations used in the model

Correlations	Symbols	Reference
Effective surface area	al	Bravo et al (1985)
	u j	
Mass transfer coefficient	IL LV	Bravo et al (1985)
muss transfer esemetent	$\kappa_{i,j}$ $\kappa_{i,j}$	
Heat transfer coefficient	. /	Chilton & Colburn method
ficat transfer coefficient	h_i^-	Clinton & Colourn Inculou
		(Taylor, 1993)
Liquid holdun fraction	L	Billet et al (1999)
Elquid holdup haction	η_j	Diffet et al (1999)
Pressure drop		Billet et al (1000)
r ressure urop	ΔP_{j}	Dilici ci al (1999)

2.3. Utility models

Dynamics conservation equations are constructed only for the energy balance since there is no mass transfer or accumulation in a heat exchanger. In the mass balance, only the reactions due to a temperature change are considered. The conservation equations are as follows:

$$0 = L_{in} x_{in} - L x_i + r_i$$
 (11)

$$\frac{dU}{dt} = L_{in}H_{in}^{L} - LH^{L} + Q_{LMTD}$$
(12)

To calculate the heat transfer rate, the Logarithm Mean Temperature Difference (LMTD) method is used:

$$Q_{LMTD} = UA\Delta T_{mean} \tag{13}$$

$$\Delta T_{mean} = \frac{\Delta T_1 - \Delta T_2}{\ln(\Delta T_1 / \Delta T_2)} \tag{14}$$

where ΔT represents the temperature difference between hot and cold streams in the inlet and outlet side of the heat exchanger.

The flash drum model used as a reboiler or a condenser is same as the one stage equilibrium model. Thus, the MESH equations are simply appended as the flash drum model.

$$\frac{dM}{dt} = L_{in} x_{i,in} + V_{in} y_{i,in} - L x_i - V y_i$$
(15)
$$\frac{dU}{dt} = L_{in} H_{in}^{L} + V_{in} H_{in}^{V} - L H^{L} - V H^{V} + Q$$
(16)

If any unit has a large holdup, it results in a slow response time and the dynamic behavior becomes important. A static model is acceptable if the holdup of the flash drum is negligible compared to the sump and the buffer tank. Since the holdup in the condenser is negligible compared to the other units, the dynamics of condenser is not considered.

2.4. Model Validation

Steady-state validation of the developed model was carried out in pilot plant scale and industrial scale. Since the validation of the model in the industrial scale is limited by the lack of available data, Aspen plus simulation results are used to validate the model in large scale.

2.4.1. Pilot plant scale

The developed model is validated with steady-state pilot plant data provided in the literature. Detailed design specifications and operation condition can be found in Notz et al (2012). The flue gas used in the experiment contains a small amount of O_2 . Since the developed model does not take O_2 into account, the composition of N_2 is adjusted to match the mole balance in the simulation. The data from Experiment 1 and 2 in the literature are used for the model validation. The L/G ratio of operating condition 1 and 2 are 2.78 and 2.76, respectively. Table 2 presents the solvent loading and CO2 removal in both the pilot plant data and simulation results.

For the two operating conditions, it can be found that the developed model predicts the CO_2 capture rate and rich CO_2 loading very well. It is confirmed that the simulation results of the CO_2 capture rate and CO_2 loading deviate 12.5% and

4.4% respectively from the pilot plant data. The temperature profile along the absorber is also shown in Fig. 1.

Table 2. Comparison of the pilot plant and simulation data

Case	Condition 1		Condition 2	
	Pilot	Simulation	Pilot	Simulation
Lean loading	0.265	0.265	0.308	0.308
Rich loading	0.384	0.401	0.456	0.468
CO ₂ Capture rate	75.9	84.4	51.3	58.8



Fig 1. Absorber liquid temperature profile for the condition 1

3. DYNAMIC SIMULATION

3.1. Base process condition

A coal-fired power plant with a 300MWe load was selected to apply the capture process. The composition and flow rate of flue gas from the plant were estimated with a method given by Mac Dowell, 2013. Table 3 shows detailed information about the flue gas inlet condition.

Table 3. Flue gas inlet condition

Specification	Value
Mass flow rate (kg/s)	322
CO ₂ content (mol%)	15.5
H ₂ O content (mol%)	5.7
Temperature (K)	313.15
Pressure (kPa)	130

Since the detailed operating conditions and data for the industrial scale plant are scarce in the literature, the condition obtained from the Aspen plus simulation was used. In the case of Aspen plus simulation, rigorous Electrolyte NRTL model was used as a thermodynamic model. The operating condition and simulation results from the Aspen plus simulation and the developed model are compared in Table 4.

The settling time of the CO_2 capture process is strongly influenced by the size of the sump and buffer tank (var Hann et al, 2016). Therefore, reasonable sizing of the units is one of the important factors in dynamic response analysis. In this study, the size and solvent inventory of each unit were determined based on residence time provided in Flo et al (2016). It is assumed that the reboiler acts as a sump of the stripper. Table 5 shows the solvent inventory and estimated residence time of each unit.

Table 4. Comparison of the models with operating condition

	Developed	Aspen plus
Solvent mass flow rate (kg/s)	1256	1229
L/G ratio (kg/kg)	3.89	3.81
Lean loading (mol/mol)	0.250	0.250
Rich loading (mol/mol)	0.500	0.505
Capture level (%)	90	90
Absorber pressure (kPa)	101.35	101.35
Stripper pressure (kPa)	170.3	170.3
Reboiler duty (MW)	235	241

Table 5. Residence time and solvent inventory of each unit

	Residence time (min)	Solvent inventory (m ³)
Absorber	4	257
Absorber sump	5	398
Stripper	1	54
Reboiler and stripper sump	8	597
Buffer tank	16	1148
Total	34	2454

The solvent flow rate and holdup in the condenser are negligible compared to the other units. So, the dynamics of condenser is not considered. Also, it is assumed that the condenser pressure and temperature are perfectly controlled. In this configuration, the variables to be controlled to ensure a stable operation of the CO_2 capture process are the inventory level, reboiler pressure, MEA concentration, and water balance.

Since amine loss occurs at the top of the absorber and stripper sections, the MEA concentration in the buffer tank is controlled with MEA makeup. Also, water balance is achieved by controlling the buffer tank level. Detailed process scheme is shown in Fig 2.



Fig 2. CO₂ capture process scheme in gPROMS

3.2. Control strategy

In this study, two control strategies were compared for given dynamic scenarios. When a CO_2 capture process is operated, it is important to maintain the CO_2 capture rate to a desired value. The CO_2 capture rate is dependent on the lean solvent flow rate and lean CO_2 loading. Therefore, control strategies that use these variables as manipulate variables (MV) are introduced here. Table 6 shows the two evaluated control strategies.

Table 6. Compared control strategy (CV-MV pair)

	Loop1	Loop2
Strategy A	CV : CO_2 capture rate MV : lean solvent flow	CV : reboiler temperature MV : regeneration heat
Strategy B	CV : CO_2 capture rate MV : regeneration heat	CV : reboiler temperature MV : lean solvent flow

Proportional-Integral (PI) controllers are used to control the desired variables. To find the proper tuning parameters for the controllers, the S-IMC (Simple internal model control) method given by Skogetad et al (2012) is used. Performance of each control strategy is evaluated in Section 4.

3.3. Dynamic scenario

Gas flow rate change is one of the obvious dynamic scenarios that can be considered. These scenarios can occur frequently under a flexible operation like in a load change of power plant or a decrease in the CO_2 capture rate through by-passing. So, the performances of control structures A and B are evaluated based on the two dynamic scenarios: *Gas flow rate ramp up* and *ramp down*. In the ramp down scenario, the flue gas flow to the absorber is reduced to 60% of the initial value during the first 5 minutes. In the other scenario, gas flow increased from 60% to 100% during a period of 5 minutes in the ramp up scenario. The operation condition presented in Section 3.1 is used as the initial point.

In the dynamic simulation, each control strategy is evaluated in terms of the 99.9% settling time and ISE(Integratedsquared-error) of the CV. The ISE of CO_2 capture rate(CC) can be calculated with the following equation:

$$(ISE) = \sum_{sumple}^{t_{sumple}} (\% CC_{measure} - \% CC_{setpoint})^2$$
(17)

where sampling time is 2 min.

4. REULSTS AND DISCUSSION

4.1. Gas flow ramp down (100% → 60%, 10-15 min)

Fig 3. shows the dynamic responses of the main CV, CO_2 capture rate and reboiler temperature, for the 40% gas flow decrease scenario. The CO_2 capture rate increases rapidly as the gas flow decreases initially. When the gas flow change

ends (at the 15min mark), it begins to decrease and gradually reaches the set point. Finally, both control strategies bring the CV to the desired set point over time.

It is observed that the CO₂ capture rate in Structure A returns to the set-point more quickly as the CVs are affected directly. It can be seen that the CO₂ capture rate reached its set point in 24 mins after the disturbance is finished. On the other hands, Structure B responds relatively slowly to the disturbance. It took about 83 mins before the CO₂ capture rate reaches the steady state. The CO₂ capture rate and regeneration heat reach a steady state smoothly without overshoots. Similar results can be seen in the study of Nittaya (2014). The slow response in strategy B may occur because the process units between the reboiler and the absorber act as the buffer. The increase of the total unit holdup and response time of the control loop1 causes the increase in the settling time of CO₂ capture rate. Especially in this process configuration, the change in regeneration heat must go through a buffer tank to affect the main CV, CO₂ capture rate.



Fig 3. Dynamic behaviours of CVs under gas flow decrease

Since the buffer tank has the longest response time in the overall process, the dynamic response appears to be rather delayed in strategy B.

4.2. Gas flow ramp up (60% \rightarrow 100%, 10-15 min)

The dynamic response to gas flow reduction can be seen in Fig 4. It should be noted that the change in the CO_2 capture rate is very large compared to the previous case. Since the gas flow increases to 1.7 times the initial value, the difference between the two strategies can be seen more clearly.

Strategy A shows a relatively aggressive response while Strategy B shows a more moderate dynamic response. For A, the CO_2 capture rate drops to 82%, but quickly reaches to the set point within 23mins. In the case of Strategy B, hwoever, the CO_2 capture rate gets reduced by 70% and it takes about 103 mins to return to the set point.



Fig 4. Dynamic behaviours of CVs under gas flow increase

4.3. Result Summary

Two control strategies were compared in this section, and each key evaluation index is shown in Table 7.

Table 7. ISE and settling time for each control strategies

	Strategy	ISE (%CC)	99.9% settling time
Gas flow decrease	А	158.8	24 min
$(100\% \rightarrow \ 60\%)$	В	886.4	83 min
Gas flow increase	А	164.9	23 min
$(60\% \rightarrow \ 100\%)$	В	1290.0	103 min

For large-scale gas flow rate changes that can occur during a power plant load change (i.e., a gas flow increase or decrease), strategy A shows better performance in terms of the ISE and settling time. This is due to the fact that strategy B involves more process units in closed-loop control, which leads to a larger solvent holdup and residence time.

5. CONCLUSION

In this paper, a dynamic model for an amine-based process is developed using the Kent-Eisenberg model and rigorous ratebased approach. The developed model was compared with experimental data and it was confirmed that the model can predict the performance of CO_2 capture process with reasonable accuracy.

The capture process model for the 300MWe-scale power plant is constructed and compared with the simulation result by Aspen Plus with the eNRTL thermodynamic mdoel. Using the steady state simulation result as an initial state of the dynamic simulation, the dynamic process model is simulated. It is analysed which manipulate variables have significant effects on the major controlled variables, CO2 removal and reboiler temperature. Two different control strategy A (CO₂ capture rate control with lean solvent flow) and B (CO₂ capture rate control with regeneration heat) are simulated and compared with gas flow rate change scenarios. Each strategy was evaluated with ISE and 99.9% settling time. As a result, Strategy A showed less deviation and faster closed-loop response time than Strategy B. It is explained by the increase in the solvent holdup and residence time as the number of process units in the control loop increases.

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