

Simplification of Detailed Rate-based Model of Post-combustion CO₂ Capture for Full Chain CCS Integration Studies

Eni Oko, Meihong Wang*, Akeem K Olaleye

Process and Energy Systems Engineering Group, School of Engineering, University of Hull, HU6 7RX
United Kingdom

*Corresponding Author: Tel.: +44 1482 466688. E-mail address: Meihong.Wang@hull.ac.uk

ABSTRACT

As post-combustion CO₂ capture (PCC) technology nears commercialization, it has become necessary for the full carbon capture and storage (CCS) chain (from power plants, to PCC plant, CO₂ compression, CO₂ transport and CO₂ injection) to be studied for better understanding of its dynamic characteristics. Model-based approach is one option for economically and safely reaching this objective. However, there is a need to ensure that such models are reasonably simple to avoid the requirement for high computational time when carrying out such a study. In this paper, a simplification approach for a detailed rate-based model of post-combustion CO₂ capture with solvents (rate-based mass transfer and reactions assumed to be at equilibrium) is presented. The approach was mainly adopted from Peng et al. (2003), but with improvement in calculating liquid phase mass transfer coefficient. The work was implemented in gPROMS[®], an equation-oriented process modelling and simulation platform. With this approach, we demonstrated significant reduction in CPU time (up to 60%) with reasonable model accuracy retained in comparison with the detailed model under steady state and dynamic conditions. The simplified dynamic model for PCC will be used in model-based control and/or full chain CCS simulation studies.

NOMENCLATURE

a_w	effective interfacial area of packing	m ² /m ³
a	total specific surface area of packing	m ² /m ³
D_L	diffusivity coefficient of liquid phase	m ² /s
D_v	diffusivity coefficient of gas phase	m ² /s
d_p	diameter of packing pore	m
G	gravitational acceleration	m/s ²

g_0	characteristic acceleration value	100 m/s ²
k_G	gas phase mass transfer coefficient	kmol/m ² s Pa
k_L	liquid phase mass transfer coefficient	kmol/m ² s Pa
L_w	superficial mass velocity of liquid	kg/m ² .s
P	Pressure	Pa
Q_L	volumetric flow rate of liquid	m ³ /s
R	Ideal gas constant	Pa m ³ /kmol K
T	temperature	K
V_w	superficial flow velocity	m/s

Greek letters

ρ_L	liquid density	kg/m ³
ρ_v	gas density	kg/m ³
σ_L	Liquid surface tension	N/m
σ_c	critical surface tension	N/m
μ_L	liquid dynamic viscosity	kg/m .s
μ_v	Gas dynamic viscosity	kg/m .s

1 INTRODUCTION

1.1 Background

Post-combustion CO₂ capture (PCC) technology has been proven to have the potentials to be commercially deployed to help achieve CO₂ emission reduction targets from power plants and industries (Wang *et al.*, 2011). Based on this technology, the full chain carbon capture and storage (CCS) network comprises of upstream CO₂ sources (e.g. power station), PCC process and downstream CO₂ compression, transport and underground storage systems (Alhajaj *et al.*, 2013). This technology is expected to be commercially available in the next few years, for instance, E.ON ROAD CCS Project, Rotterdam is planned to be commissioned in 2017 (Uilenreef and Kombrink, 2013).

PCC technology involves CO₂ absorption/stripping with aqueous solvents such as monoethanolamine (MEA) and their blends (See Figure 1). Studies by Lawal *et al.* (2010) among others have shown that the PCC dynamics is critical to effective operation of the entire system. Studies based on pilot plants (Faber *et al.*, 2011) and mathematical modelling

(Lawal *et al.*, 2009a, 2009b, 2010, 2012 and Biliyok *et al.* 2012) have been carried out to properly understand the dynamic behaviour of the PCC technology.

1.2 Motivations

The capture plant is strongly coupled with upstream power generation plants and downstream CO₂ compression, transport and storage systems. Studies so far have shown that it will greatly limit the capability of the power plant to be operated up and down to meet changing load demand (Faber *et al.*, 2011, Lawal *et al.*, 2012). Studying the behaviour of the entire CCS chain, from source to sink, is necessary to understand how the chain can be operated efficiently, safely and economically.

When carried out via model-based approach, there will be significant challenge with the CPU time requirement for simulating the entire CCS chain. The CPU time can be reduced if simplified component models are used. Simplified models are also important for carrying out model-based control of the system.

PCC process with solvents such as MEA is highly complex when modelled using rate-based approach and requires lengthy CPU time when carrying out simulations using the model. Simpler versions of the model obtained using equilibrium approach do not reflect the true dynamics of the PCC process with solvents (Lawal *et al.*, 2009a). Reduced CPU time can be achieved while reasonably representing actual behaviour of the process (Peng *et al.*, 2003). This can be achieved by simplifying certain aspects of the rate-based PCC model. When simplified and integrated with other components of the CCS chain, meaningful reduction in overall CPU time required for simulating the whole chain can be achieved. It is however difficult to simplify the model without greatly compromising its capability.

1.3 Aim of the Paper and Its Novelty

The paper presents a model simplification strategy for a detailed rate-based model of post-combustion CO₂ capture with solvents such as Lawal *et al.* (2010). As noted in previous sections, simplification is necessary to avoid demanding CPU time required for simulating the entire CCS chain when the model is coupled with the upstream and downstream component models. Similar simplification strategy has been reported by Peng *et al.* (2003) and Katariya *et al.* (2006). However, in Peng *et al.* (2003) and Katariya *et al.*(2006), the model simplification strategy was applied to packed reactive distillation column for the

production of tert-amyl methyl ether (TAME). Also, they achieved simplification by adopting constant values for the mass transfer coefficients and the wetted ratio. In this paper, we adopted a similar strategy for packed absorption column used in PCC. The gas phase mass transfer coefficient and the wetted ratio are assumed to be constant. The liquid phase mass transfer coefficient is obtained using a multi-variable linear equation obtained from regression analysis.

2 DEVELOPMENT OF THE DETAILED PCC MODEL

2.1 Process Description

The PCC process involves chemical absorption in an MEA solvent. The process comprise of two packed columns, namely absorber and regenerator (Figure 1). CO₂-rich flue gas stream from a power plant (or industrial process) is fed at the bottom of the absorber at 40-50°C. Lean solvent (about 30 wt% MEA solution) is fed at the top of the absorber and they typically absorbs about 80-100 wt% of CO₂ in the flue gas (Biliyok *et al.*, 2012). Treated gas exits through the top of the absorber while the CO₂-rich solvent is sent to the regenerator where pure CO₂ (about 99 wt %) is recovered from the solvent. Additional details on the PCC process are widely available in literature (i.e. Wang *et al.*, 2011; Lawal *et al.*, 2009a, 2010, 2012; Biliyok *et al.*, 2012).

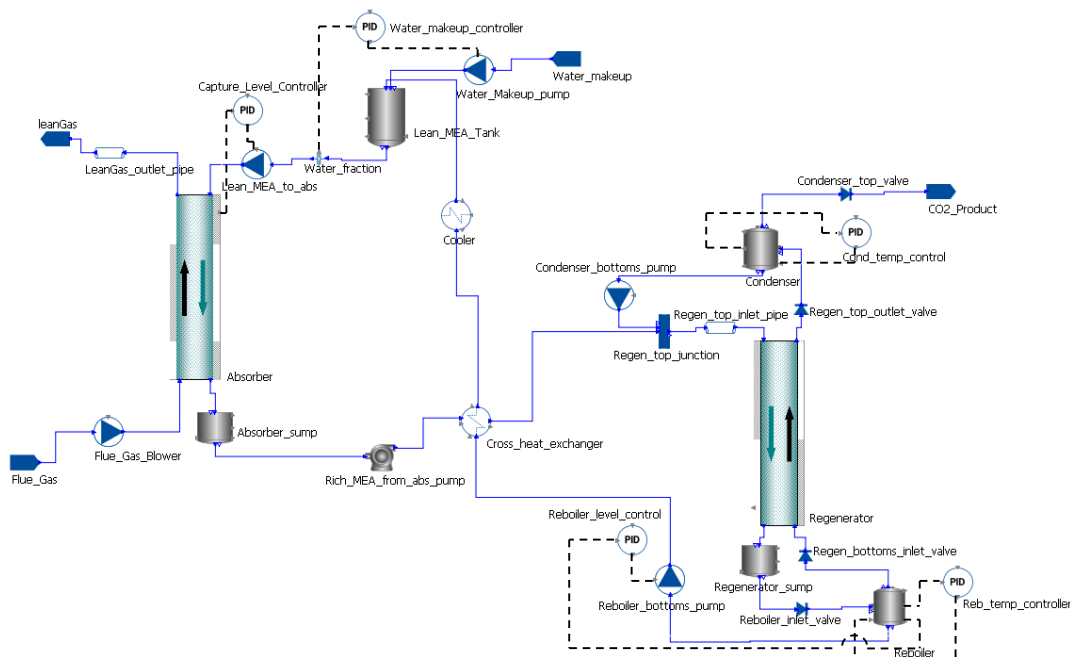


Figure 1: Process Flowsheet in gPROMS[®] for Post-combustion CO₂ Capture Process (Lawal *et al.* 2010)

2.2 Modelling Principle

Different approaches, namely equilibrium and non-equilibrium (rate-based), have been proposed for modelling the PCC process (Wang *et al.*, 2011). The rate-based approach is reported to be more accurate in describing the actual behaviour of the PCC process (Peng *et al.*, 2003, Lawal *et al.*, 2009a, Zhang *et al.* 2009). This is because that heat and mass transfer between the liquid and vapour phases is considered as rate-based, and reactions are assumed to be at equilibrium at the interface.

The modelling follows the well established two-film theory (Lawal *et al.*, 2010). The Maxwell–Stefan formulation was used to determine the mass fluxes of components in both the vapour and the liquid film (Krishna and Wesselingh, 1997). Diffusion coefficients in vapour and liquid phase have been determined using the methods of Fuller *et al.* (1966) and Versteeg and Van Swaaij (1988) respectively. The mass transfer coefficient for both the vapour and the liquid film, in addition to the wetted area of packing was obtained using the method of Onda *et al.* (1968).

The vapour-liquid equilibrium, the chemical equilibrium and the physical properties of the system have been determined using the ElecNRTL model obtained from Aspen Properties® (Biliyok *et al.* 2012). The model was then implemented in gPROMS. The model developed has been described in Lawal *et al.* (2009a, 2009b), Lawal *et al.* (2010) and Biliyok *et al.* (2012). Additional details can therefore be obtained from these publications.

3 MODEL SIMPLIFICATION TECHNIQUE

3.1 Review for Model Simplification

The simplification technique used in this paper was first reported by Peng *et al.* (2003) for a packed reactive distillation column for the production of TAME. Peng *et al.* (2003) showed that this technique can potentially achieve up to two-third reduction in the total model equations of the TAME process with minimal impact on model performance.

The model simplification approach involves simplifying the non-linear algebraic equations to obtain constant mass transfer coefficients. The main governing equations for the detailed model are relatively simple but the constitutive equations, mostly algebraic equations for obtaining heat and mass transfer coefficients, are numerous and numerically unstable. The algebraic equations in detailed model are therefore the targets for simplification. In Peng *et al.*

(2003), the equations for mass transfer coefficients were simplified by assuming that they were invariant. This assumption eliminates the equation and other related equations effectively reducing the complexity of the model. Peng et al. (2003) reported fairly reasonable performance over wide variations in process conditions. In this study, this approach is adapted and improved for simplifying the detailed rate-based model for PCC with solvent.

3.2 Analysis for Model Simplification

The key algebraic equations considered for simplification in the detailed model are as follows:

$$k_L \left(\frac{\rho_L}{\mu_L g} \right)^{1/3} = 0.0051 \left(\frac{L_w}{a_w \mu_L} \right)^{2/3} \left(\frac{\mu_L}{\rho_L D_L} \right)^{-1/2} (ad_p)^{0.4} \quad (1)$$

$$\frac{k_G RT}{a D_v} = 3.6 \left(\frac{V_w}{a \mu_v} \right)^{0.7} \left(\frac{\mu_v}{\rho_v D_v} \right)^{1/3} (ad_p)^{-2.0} \quad (2)$$

$$\frac{a_w}{a} = 1 - \exp \left[-1.45 \left(\frac{\sigma_c}{\sigma_L} \right)^{0.75} \left(\frac{L_w}{a \mu_L} \right)^{0.1} \left(\frac{L_w^2 a}{\rho_L^2 g} \right)^{-0.05} \left(\frac{L_w^2}{\rho_L \sigma_L a} \right)^{0.2} \right] \quad (3)$$

The intention is to either obtain a single value or a simple linear equation for these variables (i.e. k_L , k_G , and a_w/a). To do this, how these variables behave at different input conditions across the packed column was investigated using the detailed model presented in Lawal et al. (2010). The only inputs expected to vary from time to time are the liquid solvent and flue gas flowrate. We assumed that other inputs, namely temperature, pressure and composition are well controlled and do not change significantly. While performing this test, other inputs were therefore kept constant. Also, the liquid solvent and flue gas flowrate were varied in such a way to maintain an L/G ratio of 6. This is expected since the L/G ratio is important for maintaining capture level. The adjustments represented a 100% increase in the gas flowrate. This covers all possible scenarios that can be encountered assuming the PCC plant was integrated with an upstream thermal power plant operated in load-following mode.

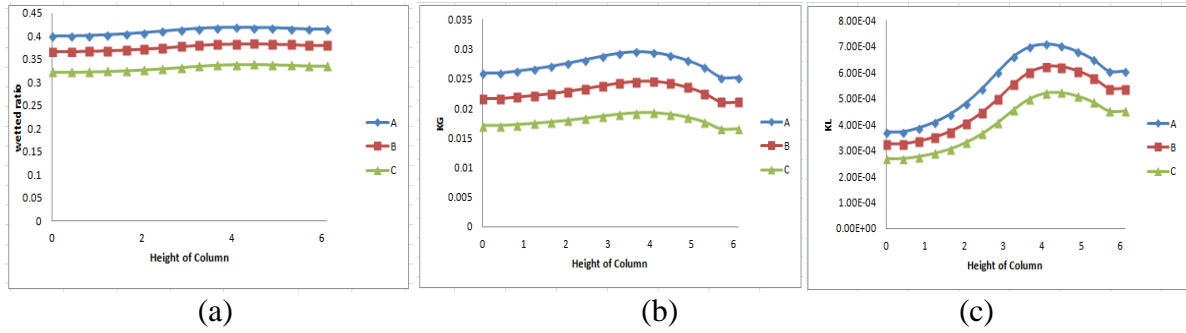


Figure 2: Variation of (a) wetted ratio, (b) gas phase mass transfer and (c) liquid phase mass transfer at different input conditions across the packed column [Condition A: Liquid flowrate = 0.96 kg/s, Gas flowrate = 0.16 kg/s; Condition B: Liquid flowrate = 0.72 kg/s, Gas flowrate = 0.12 kg/s; Condition C: Liquid flowrate = 0.48 kg/s, Gas flowrate = 0.08 kg/s]

The results in Figure 2 show that these variables have strong correlation with input conditions but the trends are similar at different conditions. Also, the variations across the column height reflect variations in temperature, pressure and superficial mass velocity of the respective phases across the column. Gas phase mass transfer coefficient (k_G) and wetted ratio ($\frac{a_w}{a}$) varies slightly across height of the packed column (Figure 2a and 2b), the liquid phase mass transfer coefficient (k_L) shows more visible variation across the height of column (Figure 2c).

3.3 Determination of k_G , k_L and $\frac{a_w}{a}$ for the Simplified Model

Average values of gas phase mass transfer coefficient (k_G) and wetted ratio ($\frac{a_w}{a}$) across the column is obtained based on the detailed model predictions from Lawal et al. (2010). This is because they both vary less than 15% across the height of the column and the average values represents the actual values at all points across the column (Figure 2a and 2b) fairly well. However, the same principle cannot apply to the liquid phase mass transfer coefficient (k_L) due to the wide variation across height of the column. Rather than using average values, linear equation involving multi-variables will be obtained to determine the coefficient.

To avoid calling physical properties from external applications, k_L will be correlated as a function of temperature, pressure and superficial mass velocity as expressed in Equation (4). These variables change across the height of the column.

$$k_L = k + n_1 T + n_2 P + n_3 L_w \quad (4)$$

The values of the constants k , n_1 , n_2 and n_3 are obtained through multi-variable linear regression approach in Microsoft-Excel based on temperature, pressure and superficial mass velocity (liquid phase) data obtained using the detailed model (Lawal et al. 2010) under condition B. Validation of this linear correlation has been carried out under condition C (Figure 3) and the result is reasonable.

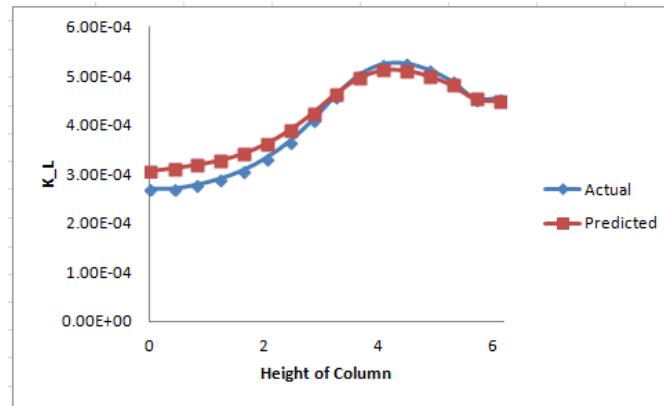


Figure 3: Validation of the linear correlation obtained

3.4 Implementation of Simplified Model in gPROMS®

To implement the simplified model in gPROMS, the average values of the k_G and $\frac{a_w}{a}$ and the linear correlation for k_L obtained from the detailed model analysis substitutes Equations 1, 2 and 3 respectively. The equations and other related ones are therefore eliminated. Also, the number of discretisation intervals for obtaining the solutions of some of the partial differential equations was reduced.

The simplified model in gPROMS was used for simulation study. The simulation results were summarised in **Table 1**. The simulations were carried out with an i5-2400 CPU @3.10 GHz processor and 4 GB RAM machine. The results show significant reduction in the model equations and CPU time.

Table 1: CPU Time of the Simplified Model

	Detailed Model	Simplified Model
Number of equations	24721	11022
Simulation duration (h)	10	10
Average CPU time (sec)	248	98

4 VALIDATION OF THE SIMPLIFIED gPROMS[®] MODEL AND DISCUSSIONS

Validation tests were performed by comparing the predictions of the detailed model (Lawal et al. 2010) and this simplified model at steady state and dynamic conditions. During the validation tests, the lean loading, flue gas flowrate, liquid solvent flowrate and gas inlet composition were kept the same for the detailed and simplified models.

4.1 Steady State Validation

Steady state tests were carried out by comparing the absorber and stripper temperature profile predictions from the detailed and simplified models (Figure 4a and b) across the height of the column. The model predictions are within 5% for the absorber and stripper respectively. Therefore the simplified model can predict the plant behaviour reasonably good.

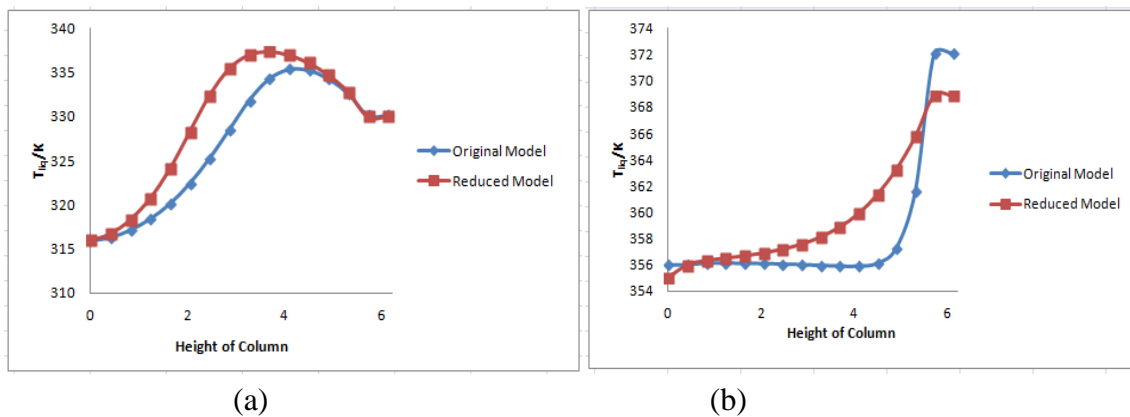


Figure 4: Temperature Profile for absorber and stripper across the height of the column: (a) for absorber and (b) for stripper

4.2 Dynamic Validation

Dynamic test was carried out by investigating the impact of step and ramp change in flue gas flowrate and reboiler temperature on CO₂ capture level. This is the common change expected when a post-combustion capture process is coupled to an upstream power generation plant operated in the load following mode. The simplified model should be able to capture this behaviour reasonably to be considered suitable for use in full chain CCS integration.

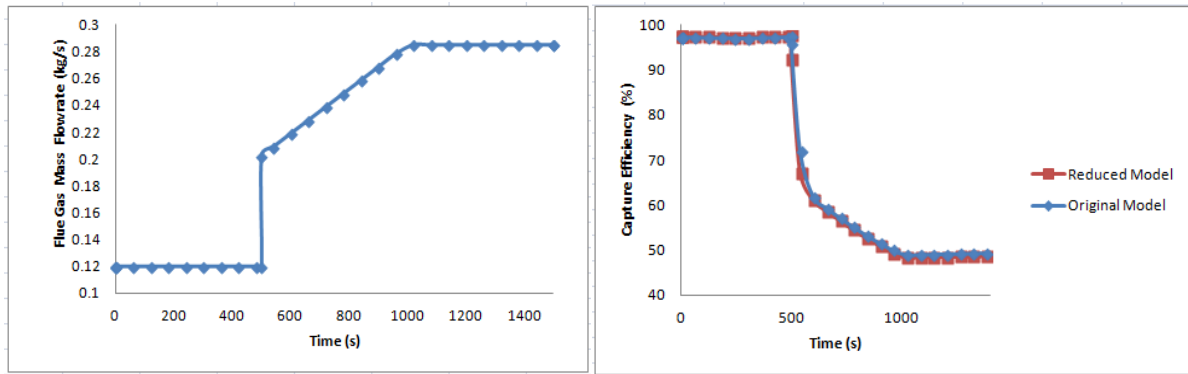


Figure 5: Step/ramp changes in flue gas flowrate (left) and capture level response (right)

Increase in power plant electricity output over a period of time results in increasing flue gas flowrate. Figure 5 shows the response of the CO₂ capture level in detailed rate-based model and the simplified model to a combined step and ramp change in the flue gas flow rate. The flowrate was maintained at 0.12 kg/s for 500 seconds. A step input in the flowrate from 0.12 kg/s to 0.2 kg/s was applied at 500 seconds. The flowrate was then ramped up by 40% (from 0.2 kg/s to 0.28 kg/s) from 500 to 1000 seconds. Finally, the condition was maintained until 1500seconds to achieve steady state. From right part of Figure 5, the CO₂ capture level decreases from 97% to about 50% in response to the step/ramp increase in flue gas flowrate from 0.12 kg/s to 0.28 kg/s (here the lean solvent flow rate was kept constant) over a period of 1500 seconds. Figure 5 shows an excellent agreement of the simplified model with the detailed model.

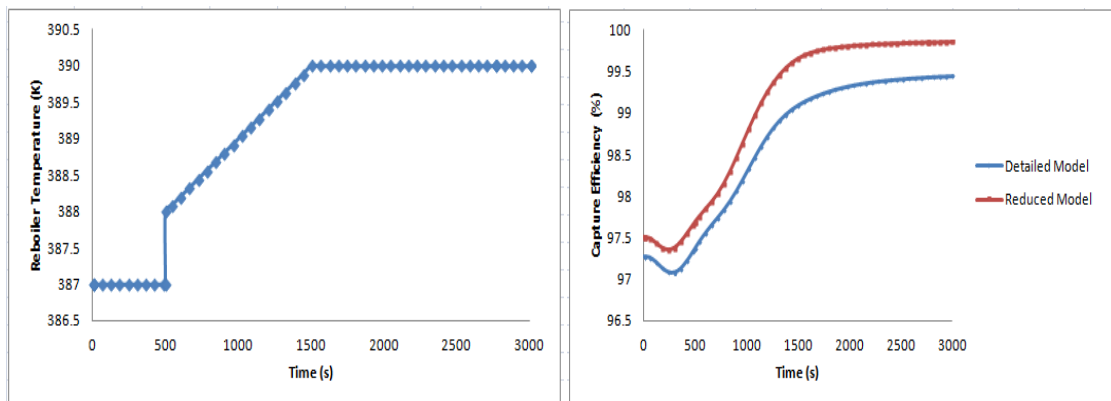


Figure 6: Step/ramp changes in reboiler temperature (left) and capture level response (right)

The required heat duty to maintain the reboiler temperature is supplied by steam from the IP/LP steam turbine crossover pipe in a typical power plant. Hence, an increase in reboiler temperature means a decrease in power generation capacity and vice versa. Figure 6 shows the response of the CO₂ capture level in detailed rate-based model and the simplified model to a step/ramp change in the reboiler temperature. The reboiler temperature was maintained at 387 K for 500 seconds. A unit step input (from 387K to 388K) in the reboiler temperature was then applied at 500 seconds. Then the absorber temperature was ramped up from 388K to

390K from 500 to 1000 seconds. Finally, the reboiler temperature was maintained at 390K until 1500 seconds to achieve steady state. The CO₂ capture level increases from approximately 97% to 99.75% with step/ramp increase in reboiler temperature from 387 K to 390 K over the period. The results in Figure 6 indicates that same trend with response from the detailed model and the simplified model. The relative error between the two responses is always less than 0.75%.

5 CONCLUSIONS AND FUTURE WORK

In this paper, we adopted model simplification technique proposed by Peng *et al.* (2003) and improved it, then applied it to a post-combustion CO₂ capture process with MEA solvent. This resulted in a simplified post-combustion carbon capture rate-based model in terms of number of model equations and CPU time requirement. The work was implemented in gPROMS[®], an equation-oriented process modelling and simulation platform. Steady state and dynamic validation tests performed by comparing the predictions of the detailed and simplified models showed that the simplified model performance was reasonably good. The simplified model will be used for full chain CCS integration studies.

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