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Piperazine as a Solvent for Post-combustion Carbon Capture using Rotating Packed Bed Technology through Modelling and Simulation

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Abstract— *United nation report suggest that countries are planning to produced more than double the amount of fossil fuels in 2030, which implies more amount of greenhouse emission will be generated. CO_2 emission more especially from power plants is largest emission among the greenhouse gasses. Capture of CO_2 from the large source emitters is necessary in dealing with the current global warming concerns. This paper presents process analysis of standalone intensified absorber for post-combustion CO_2 capture using piperazine solvent in Aspen Plus® and Intel visual FORTRAN. Standalone steady state model for intensified absorber was done by linking Aspen Plus with visual FORTRAN and the model developed was validated with experimental data from National Tsing Hua University Taiwan. Process analysis on the effect of liquid to gas (L/G) ratio, lean solvent temperature and lean solvent concentration on the CO_2 capture efficiency was done. The study shows that as the lean solvent temperature increases there is an increase in CO_2 capture efficiency. Finally, the study will help process plant operators to determine safe operating point for an RPB absorber.*

Keywords— *Post-combustion CO_2 capture, PZ solvent, Process Intensification (PI), Rotating Packed Bed (RPB), Process Modelling, Process simulation.*

I. INTRODUCTION

1.1 Background

The 21st Conference of Parties (COP21) in Paris in December 2015 has reached an agreement to "*hold the increase in the global average temperature to well below 2°C above pre-industrial levels and to pursue efforts to limit the temperature increase to 1.5 °C above pre-industrial levels*" by 2050[1]. To achieve this target, decarbonisation of world's energy system is necessary. Carbon capture and storage (CCS) which is targeted to contribute around one-fifth of total emissions reductions by 2050 is the most cost effective option[2]. Post-combustion capture is the most mature CO_2 abatement option but its present's challenge of high capital and operating cost[3]. Rotating packed bed as a typical process intensification equipment was invented by Ramshaw and Mallison[4] for enhancing gas – liquid mass transfer in distillation and absorption processes. RPB achieved intensification of mass transfer by rotation of the packed bed leading more of the droplet and film flow in the unit[5]. This will mean increase in interfacial surface area which will results in enhance mass transfer. Typical RPB absorber is shown in Figure 1. Joel *et al.* [6–9] found that intensified absorber and stripper are smaller in size compared to conventional packed bed (PB) absorber and stripper by 12 times and 9.63 times respectively. Low solvent residence time in the intensified absorber will lead to low CO_2 capture efficiency this will require that solvent with high reactivity be used in the intensified absorber. Compared with 1-ethanolamine (MEA), PZ has a greater CO_2 absorption rate, capacity, and thermal stability[10]. These properties should reduce the overall energy requirements of a CO_2 capture facility operating with PZ solvent compared to one operating with MEA.

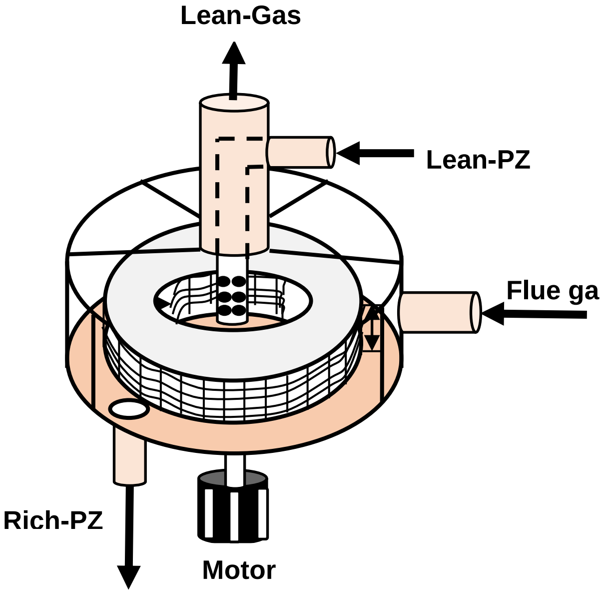

Figure 1. Schematic diagram of RPB absorber[23]

1.2 Motivation

Typical 500 Megawatt electrical (MWe) supercritical coal fired power plant operating at 46% efficiency (LHV basis) will be releasing 8,000 tons of CO_2 per day[11]. This huge volume of flue gas will result in the use of high amount of solvent and big size packed columns if conventional technology is to be applied. Lawal *et al.* [12] reported dynamic modelling study of a 500 MWe sub-critical coal-fired power plant using the conventional packed column. From the analysis, two absorbers of 17 m in packing height and 9 m in diameter will be needed to separate CO_2 from the flue gas and one regenerator of 17 m in packing height and 9 m in diameter will be needed for regeneration of rich-MEA solvent. Also, Agbonghae *et al.*[13] showed that two absorbers (with packing height of 19.06 m and 11.93 m in diameter) and a stripper (with packing height of 28.15 m and 6.75 m in diameter) are required to process flue gas from 400 MWe gas fired combined cycle gas turbine (CCGT) power plant. These huge conventional packed columns will mean higher capital and operating costs. A reasonable amount of steam will be needed from the power plant for solvent regeneration this could increase electricity costs by over 50% and has been a major obstacle to commercializing the technology[14].

II. MODEL DEVELOPMENT

Model for intensified absorber using RPB does not exist in any commercially available model library (including Aspen Plus®). To model intensified absorber using RPB, the default mass/heat transfer correlations in the Aspen Plus® rate-based model were replaced with subroutines written in Intel® visual FORTRAN. The new model now represents an intensified absorber using RPB. The correlations include: liquid phase mass transfer coefficient given by Chen et al. [15], gas-phase mass transfer coefficient given by Chen [16], interfacial area correlation estimated by Luo et al. [17] and liquid hold-up correlation given by Burns et al.[5]. Dry pressure drop expression was used since it accounts in an additive manner of the drag and centrifugal forces, the gas-solid slip and radial acceleration effect [18].

2.1 *Governing Modelling Equations*

2.1.1 Gas and liquid material balances

Assuming steady state conditions, material balances for gas and liquid phase in the RPB is described by Equations 1 and 2. Due to flow directions in RPB, the equations are based on numerical discretisation in the radial direction. Also, the term $2\pi rZ$ is described preferably as tangential area to differentiate it from cross sectional area as it varies from section to section along the radial direction.

Material balances for gas phase:

$$0 = \frac{1}{2\pi rZ}\frac{\partial(G^m y_i)}{\partial r} - aN_i \tag{1}$$

Material balances for liquid phase:

$$0 = -\frac{1}{2\pi rZ}\frac{\partial(L^m x_i)}{\partial r} + aN_i + \in_L rxn_i \tag{2}$$

The equation includes component molar flow balances (represented by the derivative terms) across each radial segment per tangential area, interfacial molar fluxes (aN_i) and liquid phase reaction rate ($\in_L rxn_i$). By this, reactions are deemed to occur only in the liquid phase and ionic components therefore only exist in the liquid phase.

2.1.2 Gas and liquid energy balances

Energy balances for gas and liquid phase is given by Equations 3 and 4 respectively [19]

Energy balances for gas phase:

$$0 = \frac{1}{2\pi rZ}\frac{\partial(G^m h_G)}{\partial r} - ah_{\frac{g}{l}}\left(T_l - T_g\right) - Q_G^{Loss} \tag{3}$$

Energy balances for liquid phase:

$$0 = -\frac{1}{2\pi rZ}\frac{\partial(L^m h_L)}{\partial r} - a\left(h_{g/l}\left(T_l - T_g\right) - \Delta H_r N_{CO_2} - \Delta H_{vap} N_{H_2O}\right) - Q_L^{Loss} \tag{4}$$

The equations include interfacial heat transfer, $h_{g/l}\left(T_l - T_g\right)$, heat released due to CO_2 desorption from the loaded PZ solvent, $\Delta H_r N_{CO_2}$ and heat released or absorbed due to H_2O condensation or vaporization, $\Delta H_{vap} N_{H_2O}$[19]. Due to the relatively higher temperature of the absorber compared to ambient condition, heat losses (Q_G^{Loss} and Q_L^{Loss}) are also taken into account.

2.2 *Physical Property*

Electrolyte Non-Random-Two-Liquid (ElecNRTL) activity coefficient model in Aspen Plus® was used to describe the vapour–liquid equilibrium, the chemical equilibrium and the physical properties of the system. The equilibrium constants for reactions 5-9 are calculated from the standard Gibbs free energy change, the equilibrium reactions are assumed to occur in the liquid film and kinetic reactions equations and parameters are obtained from AspenTech[20]. The electrolyte solution chemistry which is used in property calculation is modelled with chemistry model and all the ionic reactions are assumed to be in chemical equilibrium as shown in Equations 5-8[20].

Equilibrium $\mathrm{2H_2O \leftrightarrow H_3O^+ + OH^-}$ (5)
Equilibrium $\mathrm{HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+}$ (6)
Equilibrium $\mathrm{PZ}H^+ + \mathrm{H_2O \leftrightarrow PZ + H_3O^+}$ (7)
Equilibrium $HPZCOO + \mathrm{H_2O \leftrightarrow PZCO}O^- + \mathrm{H_3O^+}$ (8)

Kinetic reactions used for the intensified absorber calculation is specified by Equations 9 – 14 in the reaction part of the regenerator model in the Aspen Plus.

Kinetic $\mathrm{CO_2 + OH^- \rightarrow HCO_3^-}$ (9)
Kinetic $\mathrm{HCO_3^- \rightarrow CO_2 + OH^-}$ (10)
Kinetic $\mathrm{PZ + CO_2 + H_2O \rightarrow PZCOO^- + H_3O^+}$ (11)
Kinetic $\mathrm{PZCOO^- + H_3O^+ \rightarrow PZ + CO_2 + H_2O}$ (12)
Kinetic $\mathrm{PZCOO^- + CO_2 + H_2O \rightarrow PZCO}O^{-2} + \mathrm{H_3O^+}$ (13)
Kinetic $\mathrm{PZCOO^{-2} + H_3O^+ \rightarrow PZCO}O^- + \mathrm{CO_2 + H_2O}$ (14)

Power law expression Equation 15 is used for the rate-controlled reactions. The kinetic parameters for reactions in Equations 9 – 14 were listed in Table 1

$$r_j = k_j^o exp\left(-\frac{E_j}{R_c}\left[\frac{1}{T} - \frac{1}{298.15}\right]\right) \prod_{i=1}^{N} a_i^{\alpha_{ij}} \tag{15}$$

TABLE 1. Constants for power law expressions for the absorption of CO_2 by MEA[19]

Reaction No.	k_j^o (kmol/m^3.s)	E_j, J/kmol
9	4.32e+13	5.54709e+07
10	2.38e+17	1.23305e+08
11	4.14e+10	3.36548e+07
12	7.94e+21	6.59756e+07
13	3.62e+10	3.36548e+07
14	5.56e+25	7.69199e+07

2.3 *Implementation Procedure*

The procedure used in this paper for modelling and simulation of the RPB absorber is shown in Fig. 2

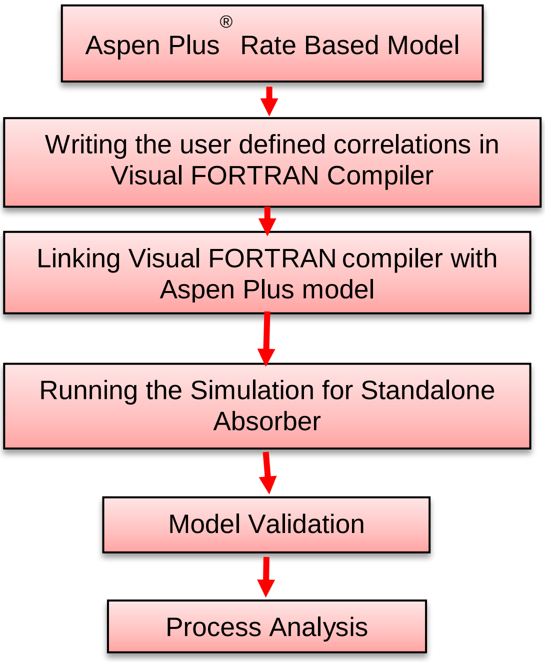

Figure 2. Methodology used in this paper[23]

III. MODEL VALIDATION OF STANDALONE RPB ABSORBER

Experimental data for the validation of the model was obtained from Yu and Tan[21]. The experiment has the following RPB absorber geometry: Packing internal diameter (ID) = 2.5 cm, RPB outer diameter (OD) = 12.5 cm, Height of the packing = 2.3 cm. Stainless steel wire mesh with surface area of 887.6 m^2/m^3 and a void fraction of 0.96 was used. Table 2 shows the process input conditions used for the validation.

CO_2 capture efficiency as an output parameter was used for the validation of the developed model of the intensified absorber using PZ as a solvent. Based on the input condition given in Table 2, percentage error of 5.09 % was obtained as shown in Table 3. The error is good enough for the model to be used to carryout process analysis so as to study effect of some process variables on the performance of the RPB model.

TABLE 2. Input process conditions for validation[21]

Variable	Value
Rotor Speed (RPM)	1300
Lean Temperature (K)	323
Lean Pressure (atm)	1
Flue gas flow rate (L/min)	30
Lean-PZ flow rate (mL/min)	100
Lean-PZ composition (%)	
PZ	40.8
H_2O	59.2

TABLE 3. Simulation results compared to experimental result

Variable	Exp.	Model	Relative Error (%)
CO_2 Capture efficiency (%)	85.00	80.67	5.09

IV. PROCESS ANALYSIS

To have full insight into the system behaviour, process analysis of the intensified absorber is necessary. Experimental data for validation of intensified absorber is from National Tsing Hua University Taiwan. Model prediction percentage error is 5.09 % which is reasonably good to proceed for process analysis to understand the system behaviour. The RPB absorber used for this analysis have the following packing geometry: Outer radius = 12.5 cm; Inner radius = 2.5 cm; axial depth of packing = 2.3 cm; Packing void fraction = 0.96; packing specific surface area = 887.6 m^2/m^3.

4.1 *Effect of Lean Solvent Temperature on CO_2 Capture Efficiency*

Understanding how the RPB absorber behave when lean solvent temperature changes is important, because of the benefit of saving costs needed for cooling the solvent before it enters the absorber and also the challenges of drop in CO_2 capture efficiency because of temperature bulge as reported in Kvamsdal and Rochelle [22].

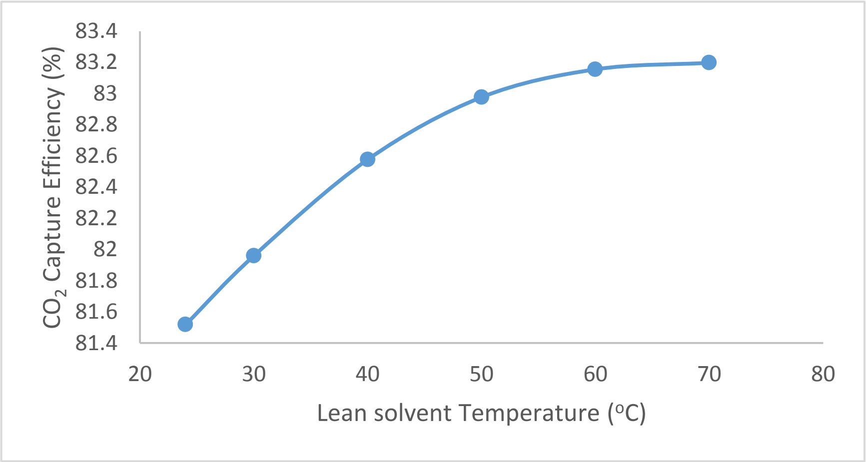

Figure 3. Effect of Lean solvent temperature on CO_2 capture efficiency

Figure 3 shows that as the lean solvent temperature increases the CO_2 capture efficiency also increases this is associated to increase in the rate of reaction[9]. As the lean solvent temperature exceed 50 °C the rate of increase in CO_2 capture efficiency decreases this is associated to the presence of temperature bulge which reduces the rate of CO_2 absorption since the reaction between CO_2 and the solvent is exothermic.

4.2 Effect of L/G Ratio on CO_2 Capture Efficiency

Energy for regeneration increases with increase in liquid to gas ratio for closed loop capture unit due to high amount of solvent to be regenerated in the stripper. Study on the suitable L/G ratio is necessary so as to get point for high capture with less regeneration energy implication in the stripper.

Figure 4 shows that as the L/G ratio increases the CO_2 capture efficiency increases, this is due to high amount of solvent available for CO_2 capture. Figure 4 shows that the rate of increase in the CO_2 capture efficiency increases rapidly from 2.2 kg/kg to 10 kg/kg L/G ratio, but increasing the L/G ratio beyond 10 kg/kg there is no significant increase in the rate of CO_2 absorption, this is due to the fact that the solvent is sufficient to capture most of the CO_2.

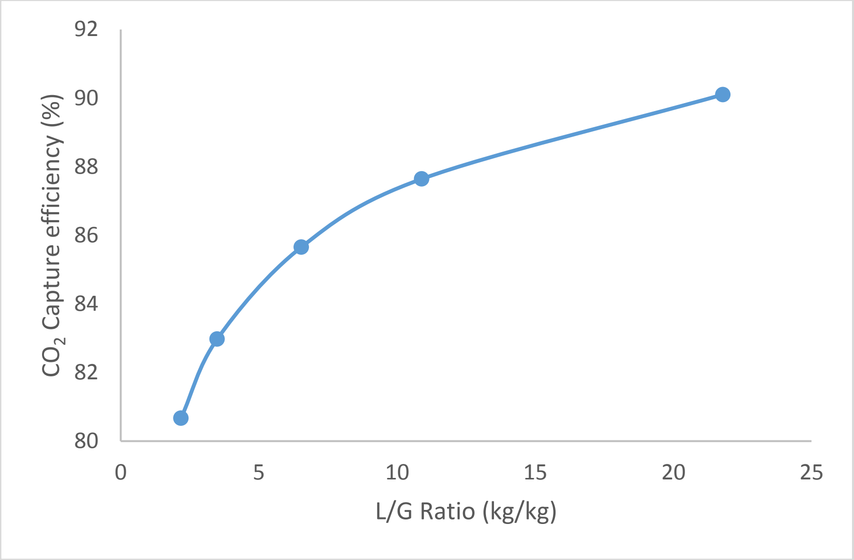

Figure 3. Effect of Liquid to Gas (L/G) ratio on CO_2 capture efficiency

V. CONCLUSIONS

Model of intensified absorber using PZ solvent was developed from first principle using Aspen Plus® and Intel® visual fortran software. The RPB model developed was validated with experimental results from National Tsing Hua University Taiwan[21] with percentage error on CO_2 capture efficiency of 5.09% which was reasonably good to carry out process analysis. The effect of lean solvent temperature on CO_2 capture efficiency shows that as the temperature increases the capture efficiency also increases this is due increase in rate of chemical reaction and also decrease in the solvent viscosity which will lead to increase in film and droplet flows in the RPB[7]. CO_2 capture efficiency increases with increase Liquid to gas (L/G) ratio this is due increase in sited available for CO_2 capture. Finally, this study will help operators to takes decision on the operating point for CO_2 capture RPB absorber.

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