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# Evaluation of $CO_2$ Capture Using Aqueous Ammonia Solution in a Flexible Operation Scenario

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Carbon dioxide has the largest contribution to the greenhouse effect among all of the greenhouse gases and its emission levels have become a big concern in the last decades. Carbon Capture and Storage (CCS) technologies aim to curb $CO_2$ emissions not only from the power generation but also from other energy-intensive sectors. Among the various approaches to separate $CO_2$ from flue gas, the absorption-based $CO_2$ capture technology is known to be the most practical method mainly due to its technical maturity and large gas treating capacity. The power plants are required to be operated in dynamic scenario, due to the timely variation of the grid demand. Dynamic simulation is a viable solution to identify any operational issue at transient conditions for the integration of $CO_2$ capture into power plants.
In this paper, a rigorous dynamic rate-based model for $CO_2$ absorption using aqueous ammonia in a packed column has been developed. The main model equations are developed by applying the overall mass, component mass and energy balances for the liquid and vapour phases, respectively. The model also considers mass and heat transfer resistance in the liquid and gas phase, hydrodynamics and column properties of the whole absorption system. The kinetic model has significant impact on the simulation and analysis of absorber. The partial differential equations of model have been solved in Matlab/Simulink, the model has been validated with data collected from pilot plant, published in literature. The developed model is used to analyse the species concentration profile, temperature profile, mass transfer rate and coefficient in the gas and liquid phase along the packing height. In order to analyse the capability of the model to predict the effect of the operating conditions and the disturbances from the up-stream power plant on the $CO_2$ capture plant operation a dynamic simulations were performed. Also, the evaluations of various operation conditions for optimization of technical indicators of $CO_2$ capture were done.

## 1. Introduction

Carbon dioxide is regarded as the largest contribution to the greenhouse effect among all of the greenhouse gases and its emission situation has become severe. Among the various approaches to separate $CO_2$ from flue gas, the absorption-based $CO_2$ capture technology is known to be the most practical method mainly due to its technical maturity and large capacity of gas treating volume. The most representative chemical absorption method is $CO_2$ capture with alkali solution absorption. Its basic principle is neutralization reaction in which alkaline solution is used as absorbent to react with $CO_2$ in the flue gas and then form carbonate and/or bicarbonate. As the commonly absorbent strong alkaline solutions including KOH, NaOH, and weak alkaline solutions including alcohol amine and aqueous ammonia ($NH_3 \cdot H_2O$), are used. Due the strong corrosion to equipment of alkaline solution and poor regeneration of the products the applicability is limited (Zao et al., 2012). The alkanolamines, including monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA) and methyldiethanolamine (MDEA) (Aroonwilas and Veawab, 2004), usually suffer the disadvantages of high energy requirement for regeneration and system corrosion. $CO_2$ capture using aqueous ammonia solution has several technical and economic advantages over conventional amine-based $CO_2$ capture technology including high efficiency, high stability, low corrosiveness, cheap chemical cost, low regeneration energy duty, low investment and convenient

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operation (Zao et al., 2012). In the last decade, post-combustion $CO_2$ capture by aqueous ammonia has made great progress and has become an important method for emission control of $CO_2$ from post-combustion flue gases (Figure 1), and is receiving more attention due to its advantages over other $CO_2$ capture methods and technologies.
The process flow-sheet diagram is shown in Figure 1 (Zao et al., 2012). The flue gas containing $CO_2$ is introduced into the bottom of absorber, where carbon dioxide is absorbed by an ammonia solution and the rich ammonia is regenerated in the stripper.

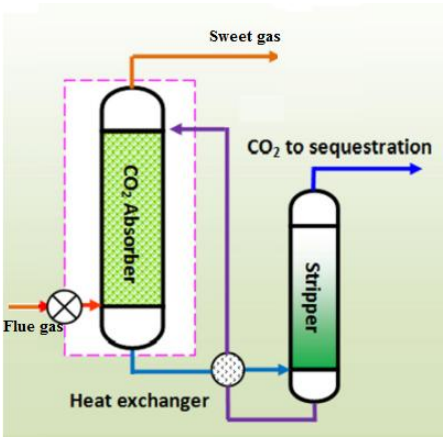


*Figure 1: Schematic flow-sheet of post-combustion $CO_2$ capture by aqueous ammonia (Zao et al.,2012)*

The major chemical absorption reactions for $CO_2$ capture by aqueous ammonia can be described as (Liu et al., 2009):

$$2NH_3 + CO_2 \leftrightarrow NH_2COONH_4 \quad (1)$$

$$NH_2COONH_4 + H_2O \leftrightarrow NH_4HCO_3 + NH_3 \quad (2)$$

$$NH_3 + H_2O \leftrightarrow NH_4OH \quad (3)$$

$$NH_4HCO_3 + NH_4OH \leftrightarrow (NH_4)_2CO_3 + H_2O \quad (4)$$

$$(NH_4)_2CO_3 + CO_2 + H_2O \leftrightarrow 2NH_4HCO_3 \quad (5)$$

The overall reaction of $CO_2$ absorption by aqueous ammonia can be usually expressed as the following equation:

$$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3 \quad (6)$$

The power plants are required to be operated in dynamic scenario, due to the timely variation of the grid demand. Dynamic simulation is a viable solution to identify any operational issue at transient conditions for the integrated power and $CO_2$ capture plants. In the current work, a rigorous dynamic rate-based model for $CO_2$ absorption using aqueous ammonia in a packed column has been developed. The model is extended from already developed models within the group (Gaspar and Cormos, 2011, 2012).

## 2. Mathematical model of ammonia-based carbon capture unit

### 2.1 Balance equations

By applying the total mass, component mass and energy balances for the liquid and gas phases results the main model equations. The present model is based on two film theory. The mathematical model of carbon dioxide absorption includes partial differential equations (PDE) to describe the time and space dependent parameters (concentration, temperature, flow) of the absorption process in a plug flow reactor (Gaspar and Cormos, 2011).
Thermodynamic properties are required to evaluate the performance of the $CO_2$ capture process using aqueous ammonia; the model described the chemical equilibrium, vapour–liquid equilibrium, speciation

and physical properties. The model also considers mass and heat transfer resistance in the liquid and gas phase, hydrodynamics and column properties of the absorption system.
The total mass balance for the gas and liquid phases are:

$$\frac{\partial F^j}{\partial t} = -\frac{\partial\left(U_j F^j\right)}{\partial z} \pm \frac{U_j S a_e}{\rho_j} \sum\left(M_i \cdot N_i\right) \tag{7}$$

where *j* represents gas or liquid phase, *i* is component: $CO_2$, $NH_3$, $H_2O$, $F_j$ is liquid/gas flow, *S* is the cross-sectional area, *j* is phase density, $M_i$ is the molecular mass of component *i* and $N_i$ is the flux of component *i* and $U_j$, the gas/liquid velocity. The sign ± shows the direction of mass transfer in the columns.
The component mass balance for the liquid and gas phase is:

$$\frac{\partial C_i^j}{\partial t} = -\frac{\partial\left(U_j C_i^j\right)}{\partial z} \pm a_e \cdot N_i - N_R \tag{8}$$

where $C_i^j$ is the concentration of component *i* in phase *j*, $a_e$ is the interfacial mass transfer area and $N_R$ is the reaction term is included only in liquid phase.
The heat balance for the liquid and gas phase is:

$$\frac{\partial T^j}{\partial t} = -\frac{\partial\left(U_j T^j\right)}{\partial z} - \frac{N_R \cdot \Delta_R H}{\rho_j \cdot c_{pj}} - a_e \cdot \sum\left(\frac{N_i \cdot \Delta_V^i H}{\rho_j \cdot c_{pj}}\right) \pm \frac{h \cdot a_e}{\rho_j \cdot c_{pj}} \cdot \left(T^G - T^L\right) \tag{9}$$

where $c_{p,j}$ is the heat capacity for gas/liquid, $\Delta_R H$ is the reaction heat, $\Delta_v H$ is the vaporization/condensation heat and *h* is the interfacial heat transfer coefficient.
The second term in equation 9 represents the released/consumed heat from the reaction between $CO_2$ and ammonia and is included only in liquid phase equation. The third term represents the released /absorbed heat at water and $NH_3$ condensation /vaporization (includes only in liquid phase equation) and the fourth term represents the heat change between the two phases due to temperature difference where the sign shows the direction of heat transfer (Gaspar and Cormos, 2012).

### 2.2 Mass transfer model

The mass transfer across the gas-liquid interfaces is described by the two-film theory. Empirical correlations which depend on physical properties, packing type and hydrodynamics are the main base for calculating the mass transfer coefficients
Determinant parts of the absorption mathematical model are the effective interfacial area, the mass transfer coefficient, heat transfer coefficient and liquid hold-up models. In literature, there are published several mass transfer and hydraulic models. A summary of the implemented correlation methods for mass transfer coefficient, mass transfer area, and most important physical and chemical properties of the components are presented in Table 1.

*Table 1. Overview of correlations and model parameters*

| Parameter | |
|---|---|
| Kinetics rate constants | Qin et al. (2010) |
| Henry constant $CO_2$ | Maceiras et al. (2008) |
| Diffusion coefficient of $CO_2$ in ammonia solution | Verstege, et al. (1996) |
| Diffusion coefficient of $CO_2$ in water | Perry, and Green (1999) |
| Viscosity | Maceiras et al. (2008) |
| Specific heat capacity | Perry and Green (1999) |
| Gas/Liquid side mass transfer coefficients | Qin et al. (2010) |
| Effective interfacial area | Billet and Schultes (1999) |

## 3. Results and discussions

All mathematical equations used in this model have been implemented in process simulator Matlab/Simulink after the partial differential equations of model were transformed in ordinary ones, by discretization. The dynamic model of carbon dioxide capture using ammonia solution has been validated with data collected from pilot plant at the Munmorah black coal fired power plant station in Australia, published in literature by Yu et al. (2011).
A summary of the columns characteristics and operating data, used in this work is presented in Table 2.

The reliability of the $CO_2$ absorption model into aqueous ammonia solution was confirmed by comparing the column concentration and temperature data, collected from model with experimental data. Yu et al. (2011) calculated the $CO_2$ removal efficiency based on gas analysis, the calculated value was 84 %. The $CO_2$ removal efficiency found by simulation is 82.5 %, this value is in line with experimental data from pilot plant operation. Most of the power plant designs with carbon capture are considering at least 80 % carbon capture rate (IEA-GHG, 2003). The predicted $K_{G,CO2}$ values and the pilot plant experimental results are in a reasonable agreement with each other. Overall gas phase $CO_2$ mass transfer coefficient $K_{G,CO2}$ values are 0.1-0.4 mmol/(s·m$^2$·kPa) for different $CO_2$ loading in range 0.5 – 0.1 (Yu et al. 2011).
The simulation of the mathematical model of $CO_2$ gas-liquid absorption into aqueous ammonia solution show the evolutions, in time and space, of temperature, and concentration in the liquid/gas phase along the absorption column. The most representative simulation results (variation of reactants concentration vs. column height and gas/liquid temperature vs. column height) are presented in the Figure 2. In figure 2.a, the carbon dioxide concentration (blue line) is in gas phase and the ammonia concentration (green line) refers to liquid phase. The temperature profiles in both gas and liquid phases are presented in figure 2.b showing an increase of the temperature towards the top of the column.

*Table 2: Absorber characteristics and operating data (Yu et al., 2011)*

| **Parameter** | |
|---|---|
| Column inside diameter (m) | 0.6 |
| Height of packing (m) | 5.8 |
| Packing type | Pall rings, 25 mm |
| Gas flow rate (kg/h) | 640-660 |
| Liquid flow rate (L/min) | 134 |
| Lean loading (kmol $CO_2$/kmol $NH_3$) | 0 - 0.6 |
| $NH_3$ inlet concentration (%) | 5 |
| Inlet Liquid temperature - absorber (K) | 288 - 303 |
| Top column pressure - absorber (atm) | 1 |

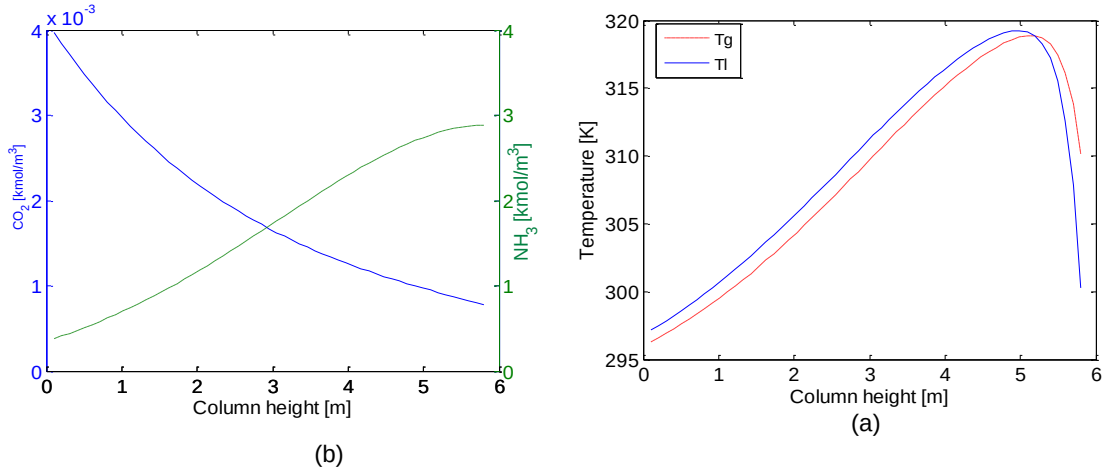


*Figure 2: a) Reactants concentration profile along absorber b) Temperature profile along absorber*

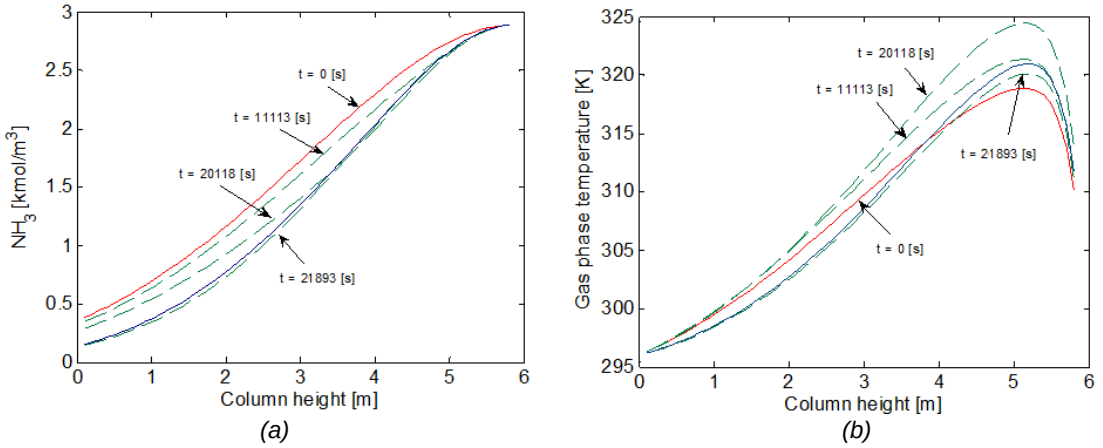


*Figure 3: Dynamic behaviour of absorption column a) Variation of $NH_3$ concentration b) Variation of absorber gas temperature*

In order to analyse the dynamic behaviour and to identify any operational issue at transient conditions for the integrated power and $CO_2$ capture plants, different simulations scenarios have been performed. Figure 3 shows the effect of increasing with 30 % of the absorber gas feed stream's carbon dioxide concentration on the absorber liquid phase composition (Figure 3a) and on the absorber gas temperature (Figure 3b). The liquid's $NH_3$ concentration profile varies from the initial-steady state operating conditions (red line) to new steady state profile (blue line) in about 6 h. The increasing with 30 % of the absorber carbon dioxide concentration cause the decreasing of $NH_3$ concentration in liquid phase from 0.4 to 0.15 kmol/$m^3$ and increasing of the output gas phase temperature with 4 degree. In term of $CO_2$ removal efficiency this is increasing with 3 % showing the potential of dynamic operation scenarios to adjust the overall plant performance indicators. Another important aspect of ammonia-based carbon capture compared to other gas-liquid absorption processes (e.g. alkanolamines) is the lower heat duty for solvent regeneration (around 2.5 MJ/kg $CO_2$ vs. higher than 3 MJ/kg $CO_2$ for alkanolamines). This aspect implies that an ammonia-based carbon capture unit will impose an energy penalty for the carbon capture of about 8.5 net electricity percentage points while the alkanolamine capture has an energy penalty of about 10 percentage points (Valenti et al., 2012). It worth also to be mention here the lower cost of ammonia compared to alkanolamines and the high tolerance of ammonia solution to inlet flue gas sulphur oxides content (a valuable ammonium sulphate is produced). The $SO_x$ tolerance is very problematic for alkanolamines which form non-heat regenerable stable salts (a deep desulphurisation to about 10 ppm sulphur is required prior the carbon capture rate). All these technical improvements of ammonia process have positive effects also on economic performances (e.g. capital and operational costs, cost of electricity, $CO_2$ removal and avoided costs etc).

These dynamic variations of carbon capture unit are of great importance for evaluation of power plant performance and operational scenario in the case of varying the plant load. The capability of the power plants to vary the load is of particular importance in the modern energy sector due to the fact that the increasing integration of highly time irregular renewable energy sources (e.g. wind and solar) put an operational burden to the power plants. As presented in literature, the dynamic operation of fossil fuel power plants could have important technical and economic advantages in grid load following operation (Bui et al.,2014).

## 4. Conclusions

Ammonia-based gas-liquid absorption carbon dioxide capture is a viable and promising option for post-combustion carbon capture to the alkanolamines technology. The main positive aspects of ammonia process compared to amines are the following: the lower energy (heat) consumption for solvent regeneration; the inlet flue gas conditions that are tolerant of acid gases (e.g. sulphur oxides which are converted to valuable ammonium sulphatesulphate by product); a regenerable carbon capture reagent requiring low make-up ratio. A rate-based mathematical model has been developed for all $CO_2$ post-combustion process simulation using aqueous ammonia solutions. The developed model has been validated against experimental data, published in literature. The model predicted well the composition and temperature in the aqueous ammonia absorption column. The developed model is used to analyse the

species concentration profile, temperature profile, mass transfer rate and coefficient in the gas and liquid phase along the packing height. The $CO_2$ removal efficiency found by simulation (82.5 %) is in line with experimental data from pilot plant operation.
Dynamic simulations were performed to analyse the capability of the model to predict the effect of the disturbances from the up-stream power plant and the operating conditions of the $CO_2$ capture plant itself, on the plant operation. In case of perturbation in input flow gas, is needed a long time (6 h) to achieve a new steady state profile. The technical indicators of carbon dioxide capture process, for various operation conditions can be optimized on model based. The simulation results show the promising prospects of ammonia-based technology to be used for $CO_2$ capture process.

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