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## Novel Analytical Mass Transfer Model for CO<sub>2</sub> Capture using Sprays

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### Abstract

The capture of carbon dioxide from the earth's atmosphere has become very important in order to fight the climate crisis and meet the Paris agreement by 2050. Basic solutions such as amines, NaOH, etc., are used as absorbent liquids to capture CO<sub>2</sub> from flue gas or atmospheric air. The goal of such carbon capture plants is to obtain the utmost CO<sub>2</sub> removal rate, which is limited by the overall effective area between the absorbent and gas flow. Spray systems are expected to increase the mass transfer between the sprayed liquid and its surrounding gas environment by increasing the overall effective area between the liquid and the gas. The mass transfer in a spray-based channel is strongly dependent on design parameters such as nozzle specifications, channel specifications, gas flow rate, solvent flow rate, temperature, pressure, and thermophysical parameters of the solvent and the gas. The overall mass transfer ( $K_G A_v$ ) is a crucial design indicator to evaluate the system's effectiveness. This study develops a novel analytical model to predict mass transfer in spray-based systems for CO<sub>2</sub> capture by evaluating  $K_G A_v$  and capture efficiency. The model considers the Sauter Mean Diameter (SMD) as the uniform droplet diameter of the spray across the entire channel height, solvent properties of 30 wt% monoethanolamine (MEA), channel dimensions, nozzle orifice diameter, temperature, total gas pressure, CO<sub>2</sub> partial pressure, liquid flow rate, and gas flow rate as input parameters. The model predictions are then validated across different experimental studies for a range of design parameters, such as the liquid flow rate, inlet solvent loading, etc. The relative importance of the incorporation of equilibrium partial pressure of CO<sub>2</sub> ( $P^*$ ) into amine with respect to CO<sub>2</sub> partial pressure is also investigated. It is found that its effect on  $K_G A_v$  is prominent in high liquid flow rate and low inlet solvent loading regimes where the overall CO<sub>2</sub> capture is high. Lastly, the variation of key parameters such as  $K_G A_v$ ,  $K_G$ ,  $A_v$ ,  $\alpha$ ,  $X_{CO_2}$  along the channel height is studied, which gives insights towards the optimization of the channel height for a new CO<sub>2</sub> capture system at given operating conditions.

**Keywords:** Carbon capture; overall mass transfer; absorbents; capture efficiency; solvent loading; flue gas; effective surface area.

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### Nomenclature

|            |                                                                                |
|------------|--------------------------------------------------------------------------------|
| $A_d$      | Area of single droplet (m <sup>2</sup> )                                       |
| $A_v$      | Effective mass transfer cross-sectional area (m <sup>2</sup> /m <sup>3</sup> ) |
| $C_{init}$ | Initial concentration of MEA (kmol/m <sup>3</sup> )                            |
| $d$        | Droplet diameter (μm)                                                          |
| $D$        | Diameter of the channel (m)                                                    |

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|                  |                                                                                               |
|------------------|-----------------------------------------------------------------------------------------------|
| $D_{CO_2,g}$     | Diffusivity of CO <sub>2</sub> in gas phase (m <sup>2</sup> /s)                               |
| $D_{CO_2,MEA}$   | Diffusivity of CO <sub>2</sub> in liquid phase (m <sup>2</sup> /s)                            |
| $G_I$            | Inert gas flow rate (m <sup>3</sup> /m <sup>2</sup> -h)                                       |
| $H_{CO_2,MEA}$   | Henry's constant for solubility of CO <sub>2</sub> in amine (kPa-m <sup>3</sup> /kmol)        |
| $H$              | Height of the channel (m)                                                                     |
| $J$              | Flux of CO <sub>2</sub> absorption (kmol/m <sup>2</sup> -h)                                   |
| $K_G$            | Total mass transfer coefficient (kmol/m <sup>2</sup> -h-kPa)                                  |
| $k_g$            | Mass transfer coefficient of gas phase (kmol/m <sup>2</sup> -h-kPa)                           |
| $k_L$            | Reactive mass transfer coefficient of liquid phase (kmol/m <sup>2</sup> -h-kPa)               |
| $k_2$            | Second-order reaction rate constant (m <sup>3</sup> /mol-s)                                   |
| $\dot{n}_{CO_2}$ | Mole flow rate of CO <sub>2</sub> consumed (mol/s)                                            |
| $n_{MEA,free}$   | Moles of free amine in solvent                                                                |
| $n_{CO_2,cons}$  | Moles of CO <sub>2</sub> consumed                                                             |
| $\dot{n}_{tot}$  | Total mole flow rate of gas (mol/s)                                                           |
| $N$              | Number of droplets per unit length (m <sup>-1</sup> )                                         |
| $n_d$            | Number of droplets                                                                            |
| $P_{CO_2}$       | Partial pressure of CO <sub>2</sub> in gas phase (kPa)                                        |
| $P^*$            | Equilibrium CO <sub>2</sub> partial pressure at given CO <sub>2</sub> loading and temperature |
| $P_{tot}$        | Total operating pressure (kPa)                                                                |
| $\dot{Q}_G$      | Gas flow rate (m <sup>3</sup> /s)                                                             |
| $\dot{Q}_G''$    | Flux of gas flow rate (m <sup>3</sup> /m <sup>2</sup> -h)                                     |
| $\dot{Q}_L$      | Liquid flow rate (m <sup>3</sup> /s)                                                          |
| $\dot{Q}_L''$    | Flux of liquid flow rate (m <sup>3</sup> /m <sup>2</sup> -h)                                  |
| $R$              | Universal gas constant (= 8.314 kJ/kmol-K)                                                    |
| $T$              | Temperature (K)                                                                               |
| $U$              | Velocity of single droplet (m/s)                                                              |
| $V_d$            | Volume of single droplet (m <sup>3</sup> )                                                    |
| $X_{CO_2}$       | Mole fraction of CO <sub>2</sub> in gas stream                                                |
| $X_{CO_2,in}$    | Mole fraction of CO <sub>2</sub> in gas stream at inlet                                       |
| $X_{CO_2,out}$   | Mole fraction of CO <sub>2</sub> in gas stream at exit                                        |
| $Y_{CO_2}$       | Mole ratio of CO <sub>2</sub> to N <sub>2</sub> in gas stream                                 |
| $z$              | Distance along channel (m)                                                                    |

### Greek Characters

|               |                                                                              |
|---------------|------------------------------------------------------------------------------|
| $\alpha$      | Solvent loading (mole CO <sub>2</sub> / mole solvent)                        |
| $\alpha_{in}$ | Solvent loading at liquid inlet                                              |
| $\nu_g$       | Gas dynamic viscosity (kg/m-s)                                               |
| $\eta$        | Capture efficiency (%)                                                       |
| $\xi$         | Parameter defined for simplification of equations (= $\alpha/(1 + \alpha)$ ) |

## 1. Introduction

As per the World Health Organization, the biggest threat to humanity has been climate change. The increased release of CO<sub>2</sub> into the environment by burning of fossil fuels to generate electricity is the primary source of anthropogenic climate change [1]. To tackle this challenge, the United Nations formed the Paris agreement which aims for net-zero CO<sub>2</sub> emission by the year 2050. The current operational Carbon Capture and Storage (CCS) capacity

is around 40Mt per annum which must increase at last 100-fold by 2050 to meet the Paris agreement. Thus, the need for CCS has become imminent. Such a technology would need to be adapted at the power plants where CO<sub>2</sub> is emitted, also called as point-source capture. In order to achieve net-zero CO<sub>2</sub> emissions, there would also be a need to capture CO<sub>2</sub> directly from air, also called as Direct Air Capture (DAC) [2].

A typical CO<sub>2</sub> capture plant, whether it be from a point-source capture or direct air capture, comprises of an absorber, and a stripper [2, 3]. The absorber allows for CO<sub>2</sub> capture using solid or liquid sorbents and convert it into salts. Monoethanolamine (MEA), methyldiethanolamine (MDEA), diethanolamine (DEA), sodium-hydroxide (NaOH), Calcium oxide (CaO), etc. are some of the materials used for CO<sub>2</sub> capture [4-8]. Gas absorption from an aqueous alkanolamine solution is the most well-established technology for CO<sub>2</sub> capture [9]. The CO<sub>2</sub> loaded solvents are passed into the stripper where they are heated to remove CO<sub>2</sub> and the solvent can be reused. The absorber is designed to attain maximum CO<sub>2</sub> capture by enhancing contact area and thus mass transfer between the liquid solvent and CO<sub>2</sub> rich gas stream. This can be attained by packed beds or spray-based system [7, 10, 11]. A packed bed allows solvent breakdown into thin films as it hits the packing bead material, which leads to increased contact area. The packing arrangement can be randomly arranged, structured, or be a hybrid. The material can be metal, ceramic, or plastic. Three primary mass transfer properties, the effective area ( $a_e$ ), gas mass transfer coefficient ( $k_g$ ), and liquid mass transfer coefficient ( $k_L$ ) were studied for random and structured packing [12]. The effective area was found to increase with liquid flow rate until it hits an asymptote at the packing material surface area which is generally around 100-300 m<sup>2</sup>/m<sup>3</sup>. The gas and liquid side mass transfer coefficients were strong functions of gas and liquid velocities respectively. Several models have been developed to obtain these three parameters for a packed bed, some of which have been reviewed in [13].

A typical spray-based capture system consists of a nozzle at the top of the reactor which allows for atomization of liquid solvent into smaller droplets. This causes an increase in effective contact area between the liquid and gas streams. The gas stream can be co-current or counter-current. The inlet conditions of both liquid and gas streams are known, and the outlet conditions are experimentally or numerically obtained. A spray system removes the need of extra material that a packing bed would require. Furthermore, a spray system also allows for visualization of the absorber better which wouldn't be as easily possible on a packed bed. However, there are only limited studies on CO<sub>2</sub> capture using spray-based systems [10]. Some such studies are outlined in Table 1.

Table 1. A summary of studies on spray-based CO<sub>2</sub> capture.

| Reference | Inlet CO <sub>2</sub> Composition | Solvent Used         | Key Finding                                                                        |
|-----------|-----------------------------------|----------------------|------------------------------------------------------------------------------------|
| [7, 8]    | 5-15 vol%                         | MEA                  | Performance of spray found to be 2-7 times higher than packing                     |
| [2]       | Air                               | NaOH                 | The cost of CO <sub>2</sub> capture ranges between 53-127 \$/ton-CO <sub>2</sub> . |
| [14]      | 2.5 vol%                          | NaOH                 | Swirling inlet gas flow increases $K_G A_v$ by 31-49%                              |
| [6]       | 12 mol%                           | NaOH                 | $K_G A_v$ was obtained at two different height within the channel                  |
| [15]      | 10-20 kPa                         | NH <sub>3</sub>      | Highest $K_G A_v$ appears for 15kPa and gas temperature 30-40 °C                   |
| [16]      | 15 vol%                           | MEA                  | Variation along column height was studied                                          |
| [17]      | 8-18 vol%                         | MEA                  | Diameter varying reactor used for experiments and simulations                      |
| [18]      | 15 vol%                           | NH <sub>3</sub> + PZ | Upward and downward liquid injection was compared                                  |

An experimental study was conducted using MEA to compare the two methods of area enhancement [7, 8]. A spray-based reactor using three different nozzles was compared with Mellapak 500Y packing. They found that the system's performance was heavily dependent on the liquid flow rate and the spray system was 2-7 times higher in performance than packing. A technoeconomic analysis for different channel height and liquid flow rates to ascertain the feasibility of using NaOH to capture CO<sub>2</sub> from air using sprays was conducted [2]. The cost of CO<sub>2</sub> capture in absorber was in the range 53-127 \$/ton-CO<sub>2</sub>. This excluded costs in the stripper for solvent recovery and CO<sub>2</sub> sequestration. It was found that the equivalence ratio of NaOH to CO<sub>2</sub> is the key parameter affecting CO<sub>2</sub> removal

efficiency [5]. The effect of a swirling inlet gas flow on the overall mass transfer coefficient ( $K_G A_v$ ) was also studied and a 31-49% enhancement with respect to axial inlet gas flow was observed [14]. A roughly 30% variation in the Sauter Mean Diameter (SMD) along radial distance within the channel was reported [19]. Parameters such as  $K_G A_v$ , SMD and planar surface area were experimentally evaluated at two different heights within the channel and along radial distance, for different flow rates and inlet loading conditions [6]. It was found that the inlet loading did not affect planar surface area significantly, but the  $K_G A_v$  was heavily dependent on the inlet loading. A numerical study was conducted to study the flow within a single droplet and a vortex was found within the droplet enhancing mixing between fresh solvent and solvent that has captured  $\text{CO}_2$  [20]. An experimental study with  $\text{NH}_3$  was conducted and  $K_G A_v$  was observed to increase with  $\text{NH}_3$  concentration, liquid to gas flow rate, and gas flow rate [15]. The highest  $K_G A_v$  was found for inlet gas flow condition of 15kPa  $\text{CO}_2$  partial pressure and temperature of 30-40°C. Another experimental study using three spray columns connected in series was conducted to obtain the variation of solvent loading and  $\text{CO}_2$  concentration along channel height [16]. They also studied the effect of solvent loading and temperature on solvent properties and overall  $\text{CO}_2$  removal rate of the system. A diameter varying reactor along with dual nozzle impinging MEA from two sides was studied using both experiments and ANSYS simulations [17]. They found the system to have doubled the overall effective area when compared to the traditional single nozzle spray tower. An air-blast atomizing column using MEA and NaOH as solvents was studied and MEA was found to obtain better overall performance [21]. Thermophysical properties of solvent blends of  $\text{NH}_3$  and piperazine (PZ) blends were experimentally evaluated [18]. This was utilized in an ANSYS model and the upward and downward liquid injection was compared. It was found that upward injection increased droplet residence time thus improving overall mass transfer and  $\text{CO}_2$  capture.

It should be noted that the solvent used for the studies listed in Table 1 is limited to MEA, NaOH and  $\text{NH}_3$ . There is a need to conduct more experimental studies with other solvents and solvent blends to get a better understanding of spray-based  $\text{CO}_2$  capture. Furthermore, all of the previously reported modeling work validates with experiments conducted by the same group. No study exists till date that develops a model that validates spray-based  $\text{CO}_2$  capture systems from different studies, and can thus be used for the development of a new  $\text{CO}_2$  capture plant. The previous modeling works are either completely empirical in nature which requires experimentation, or are ANSYS simulations which require high computing power. This work focusses on an analytical model that is validated with experiments on 30wt% MEA used in a spray-based  $\text{CO}_2$  capture absorber from [6] and [8]. The presented model can be numerically solved much faster than an ANSYS simulation. The work outlines a novel approach to modelling, thus creating a good baseline for future development of the model. It provides key insights into the system's performance within the channel, which gives information on the performance at a given operating condition and a given reactor size. This information can be used to obtain ideal operating conditions and reactor design. This also helps with developing a new capture plant as the techno-economic analysis to develop a plant would be heavily dependent on the size of the reactor.

## 2. Mathematical Model

A typical spray-based capture plant is shown in Figure 1. Lean solvent is introduced from the top ( $z = 0$ ) via a spray. The lean solvent can be fresh ( $a_{in} = 0$ ) or  $\text{CO}_2$  loaded ( $a_{in} > 0$ ). After capturing  $\text{CO}_2$ , the rich solvent exits from the bottom of the channel ( $z = H$ ). The  $\text{CO}_2$  rich gas stream ( $Y_{\text{CO}_2, in}$ ) is introduced from the bottom and the  $\text{CO}_2$  lean gas stream exits the top ( $Y_{\text{CO}_2, out}$ ). Any system is operated at a known inlet gas stream and solvent loading conditions, along with other operating parameters like  $\dot{Q}_L$ ,  $\dot{Q}_G$ ,  $P_{tot}$ ,  $T$ , etc. Using these operating parameters, the variation of  $Y_{\text{CO}_2}$  and  $\alpha$  within the reactor has been evaluated. Equation 1 can be used to estimate flux of  $\text{CO}_2$  absorption [14].

$$J = K_G (P_{\text{CO}_2} - P^*) \quad (1)$$

Here,  $P_{\text{CO}_2}$  is partial pressure of  $\text{CO}_2$  in gas stream and  $P^*$  is equilibrium partial pressure of  $\text{CO}_2$  for a given amine loading and temperature which can be obtained from equation 2 [22].  $K_G$  is the overall mass transfer coefficient which

is obtained according to the two-film theory from both gas-side and liquid-side mass transfer coefficient as described in equation 3 below [23]. The gas side mass transfer coefficient ( $k_g$ ) is obtained from Sherwood number correlation for a falling droplet in countercurrent flow. The reactive liquid side mass transfer coefficient ( $k_L$ ) incorporates both reaction kinetics and mass transfer boundary layer.

$$P^* = \exp(39.3 - 12155 / T - 19\alpha^2 + 1105\alpha / T + 12800\alpha^2 / T) \quad (2)$$

$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{1}{k_L} \quad (3)$$

The two mass transfer coefficients can be obtained from the equations below [23], where  $C_{init}$  is the concentration of amine at the inlet,  $D_{CO_2,MEA}$  is the diffusivity of  $CO_2$  in the amine solution,  $D_{CO_2,g}$  is the diffusivity of  $CO_2$  in the gas stream, and  $H_{CO_2}$  is the Henry's constant for solubility of  $CO_2$  in amine solution.

$$k_g = \left( \frac{D_{CO_2,g}}{RTd} \right) \left( 2 + 0.552 * \left( \frac{Ud}{\nu_g} \right)^{0.5} \left( \frac{\nu_g}{D_{CO_2,g}} \right)^{1/3} \right) \quad (4)$$

$$k_L = \frac{\sqrt{k_2 C_{init} (1 - 2\alpha) D_{CO_2,MEA}}}{H_{CO_2}} \quad (5)$$

Here,  $k_2$  is second-order reaction rate constant for 30wt% MEA solution which can be obtained from empirical relations provided in [24].

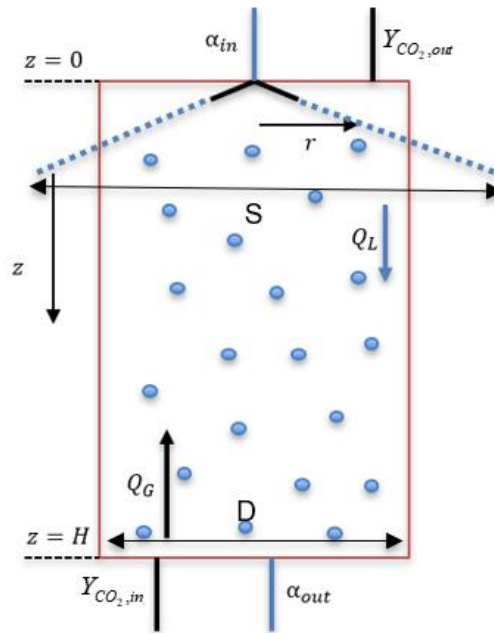


Fig. 1. Schematic of a typical spray-based  $CO_2$  absorber.

Next, a parameter  $N$  is defined as the number of droplets per unit length as shown below in equation 6. This parameter describes droplet density and can be evaluated in terms of droplet size, velocity and liquid flow rate as described in equation 7 where the factor  $f$  estimates the fraction of liquid in the form of droplets. It is considered to be equal to 1 when the spread associated with the spray ( $S$ ) is smaller than the channel diameter ( $D$ ), and is equal to  $D/S$  when  $D < S$ . The spread of the spray ( $S$ ) is obtained from correlations provided in [25].

$$N = \frac{dn_d}{dz} \quad (6)$$

$$N = \frac{\dot{Q}_L}{v_d V_d} f \quad (7)$$

This gives the rate of moles of  $\text{CO}_2$  captured per unit distance as shown in equation 8.

$$\frac{d\dot{n}_{\text{CO}_2}}{dz} = JN A_d \quad (8)$$

The rate of moles of  $\text{CO}_2$  captured can also be expressed as  $d\dot{n}_{\text{CO}_2} = \dot{n}_{N_2} dY_{\text{CO}_2}$  where  $\dot{n}_{N_2} = \dot{Q}_{N_2} / P_{\text{tot}} RT$ . Substituting into equation 8, and rearranging, the variation of mole ratio of  $\text{CO}_2$  along column height can be expressed as shown in equation 9 below.

$$\frac{dY_{\text{CO}_2}}{dz} = K_G RT \frac{\dot{Q}_L}{\dot{Q}_{N_2}} \frac{A_d}{UV_d} \left( \frac{Y_{\text{CO}_2}}{1 + Y_{\text{CO}_2}} - \frac{P^*}{P_{\text{tot}}} \right) \quad (9)$$

For the liquid side, the change in loading of solvent can be described by equation 10. The rate of absorption of  $\text{CO}_2$  into the liquid is the same as the rate at which  $\text{CO}_2$  is removed from the gas phase as shown in equation 11.

$$\alpha = \frac{n_{\text{CO}_2, \text{init}} + n_{\text{CO}_2, \text{cons}}}{n_{\text{MEA}, \text{init}}} = \alpha_{\text{in}} + \frac{n_{\text{CO}_2, \text{cons}}}{n_{\text{MEA}, \text{init}}} \quad (10)$$

$$\frac{d\dot{n}_{\text{CO}_2} |_{\text{in}, \text{liq}}}{dz} = \frac{d\dot{n}_{\text{CO}_2} |_{\text{out}, \text{gas}}}{dz} \quad (11)$$

The rate of moles of  $\text{CO}_2$  consumed in the liquid phase can also be expressed as  $d\dot{n}_{\text{CO}_2} |_{\text{liq}} = \dot{Q}_L C_{\text{init}} d\alpha$ . Upon applying this relation with equations 8 and 9, and rearranging, the variation of amine loading along distance can be obtained as described in equation 12 below.

$$\frac{d\alpha}{dz} = \frac{P_{\text{tot}}}{C_{\text{init}}} \frac{6}{Ud} K_G \left( \frac{Y_{\text{CO}_2}}{1 + Y_{\text{CO}_2}} - \frac{P^*}{P_{\text{tot}}} \right) \quad (12)$$

To solve the given set of differential equations for  $Y_{\text{CO}_2}$  and  $\alpha$ , the gas properties are obtained for flue gas with given inlet  $\text{CO}_2$  concentration. The liquid properties such as  $D_{\text{CO}_2, \text{MEA}}$  and  $H_{\text{CO}_2, \text{MEA}}$  are obtained using the  $N_2O$

analogy wherein the properties are measured for CO<sub>2</sub> and N<sub>2</sub>O in water, and then for N<sub>2</sub>O in amine. The ratio of property values for CO<sub>2</sub> and N<sub>2</sub>O in water, along with those of N<sub>2</sub>O in amine is used to obtain the properties of CO<sub>2</sub> in amine as directly measuring the properties of CO<sub>2</sub> in amine becomes challenging due to its reactivity. The detailed procedure for the same is described in [26], which provides these relations as functions of temperature. The velocity of the droplet was evaluated using stokes flow for a droplet with initial velocity obtained from jet velocity, and gas properties from given inlet CO<sub>2</sub> concentration of gas. The velocity was found to reach terminal velocity within first 20% of the channel height.

Equations 9 and 12 can be used to evaluate  $\alpha$  and  $Y_{CO_2}$  along column height. For a given operating condition,  $\alpha_{in}$  and  $Y_{CO_2,in}$  are known. The two equations were solved as initial value problems (IVP) with solve\_ivp function of the scipy library in Python using a relative tolerance of  $10^{-6}$ . The predictor-corrector method was used to solve the two IVPs. At first, an initial guess of  $Y_{CO_2,out}$  was used along with the given inlet loading. The velocity profile, liquid flow rate, gas flow rate, and temperature was used to obtain the parameter  $K_G(z)$  in equations 9 and 12. The final solution of the IVP evaluated  $Y_{CO_2}(@z = H) = Y_{CO_2,in,pred}$  which is also given for any operating system. The iterated  $Y_{CO_2,in}$  was compared with the given  $Y_{CO_2,in}$  and the residual was minimized to  $10^{-5}$  using the minimize function in scipy library. Once the residual was minimized, the final profiles for  $K_G(z)$ ,  $Y_{CO_2}(z)$  and  $\alpha(z)$  was obtained. These were used to obtain overall volumetric mass transfer performance and capture efficiency of the system as-

$$K_G A_v = \left( \frac{G_I}{P_{tot} X_{CO_2} - P^*} \right) \left( \frac{dY_{CO_2}}{dz} \right) \quad (13)$$

$$\eta(\%) = \frac{X_{CO_2,in} - X_{CO_2,out}}{X_{CO_2,in}} 100 \quad (14)$$

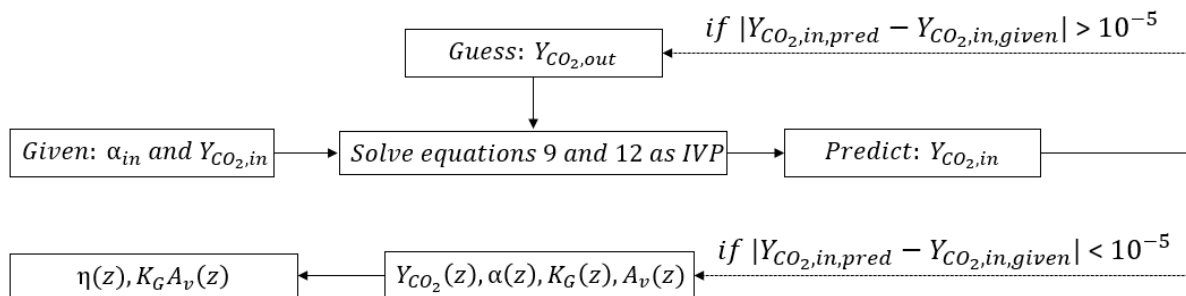


Fig. 2. Block diagram outlining the procedure for solving the system of equations in the model.

The model can be used to study the effect of all relevant design parameters on the overall performance of the system. It also allows us to understand the variation of performance parameters such as  $K_G$  and  $A_v$  along the channel height. Furthermore, it can be used to understand the effect of  $P^*$  on a given system by neglecting it or not. However, it should be noted that the methodology adapted for the model has the following assumptions-

- The droplet-droplet interaction was neglected. The liquid flow was assumed to be spread out into equally sized droplets with the diameter equal to the Sauter mean diameter that was obtained from the manufacturer's data for a given nozzle. Due to the lack of manufacturer's data about nozzle specifications, the droplet-droplet interaction could not be modeled.
- The temperature variation along column height was neglected. The temperature was assumed to be a

constant equal to the temperature at inlet conditions. This was to simplify the model and an extension to this study would be to incorporate the energy equation to the current model and has been left as an exercise for future work.

- The evaporation of amine and water was ignored. The incorporation of evaporation to the model is also left as scope of future work.
- Only variation in axial direction was considered and the model was lumped in the radial direction since  $D \ll H$ .

### 3. Results and Discussion

#### 3.1. Validation of the Model

The analytical model was validated with the experimental data from [6] and [8]. Both the studies utilize 30 wt% MEA in a spray column at atmospheric pressure with a nozzle on top of the column and gas stream flowing counter-current to the liquid flow. The variation in overall performance of the system ( $K_G A_v$ ) was studied with varying liquid flow rates, inlet solvent loading, and inlet partial pressure of  $\text{CO}_2$ . The key experimental parameters for the two studies are listed in Table 2 below.

Table 2. Relevant parameters for experiments conducted in [6] and [8].

| Reference | Channel Diameter | Channel Height | Nozzle used     | Inlet $\text{CO}_2$ Composition | Temperature | Gas Flow Rate ( $\text{m}^3/\text{m}^2\text{-h}$ ) | Liquid Flow Rate ( $\text{m}^3/\text{m}^2\text{-h}$ ) | Inlet solvent loading |
|-----------|------------------|----------------|-----------------|---------------------------------|-------------|----------------------------------------------------|-------------------------------------------------------|-----------------------|
| [6]       | 0.2 m            | 3.7 m          | BETE MPL 0.30N  | 12 mol%                         | 30 °C       | 609.8                                              | 1.41, 2.12                                            | 0 - 0.38              |
| [8]       | 0.1 m            | 0.55 m         | BETE P-20, P-28 | 5-15 kPa                        | 25 °C       | 382 - 764                                          | 1.9 – 10.3                                            | 0 – 0.45              |

The purely analytical model was validated with the results in [6] and it was observed that the trends in  $K_G A_v$  with inlet loading were well-predicted as shown in figure 3. Model was found to perform well for the higher liquid flow rate and was found to underpredict for lower liquid flow rate. This was attributed to the fact that for lower liquid flow rate, the droplet residence time was also low since the Sauter mean diameter was high. Since the droplet-droplet interaction was neglected, the further breakdown of droplets was not considered, thus limiting the predicted  $K_G A_v$ . The analytical model also underpredicts for lower inlet loading conditions. This was because any formation of liquid films on the channel walls was neglected, and its contribution to  $K_G A_v$  would be much more prominent in lower solvent loading conditions. To circumvent these limitations, slope and bias correction fitting factors were added to the analytical model as described in equation 15 below. Upon the addition of fitting parameters, the trends were in much more agreement with the experiments.

$$K_G A_v |_{fit} = m * K_G A_v |_{analytical} + c \quad (15)$$

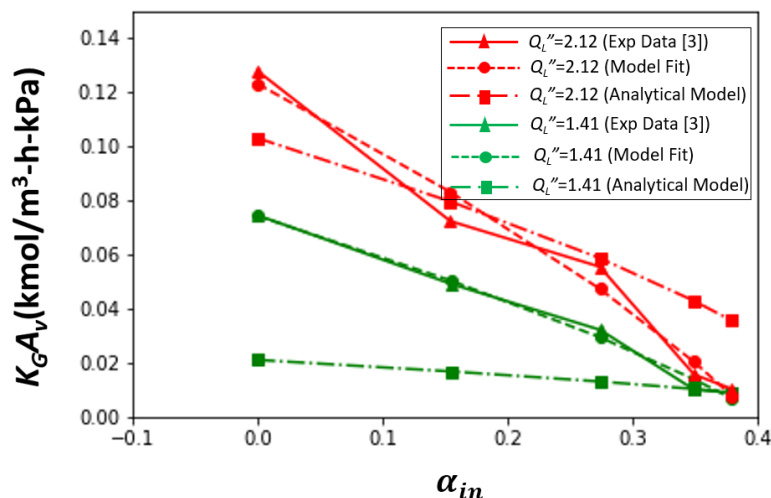


Fig. 3: Model validation across variation in  $\alpha_{in}$  for MPL 0.30 N nozzle and two different liquid flow rates used in [6]

Next, the variation with liquid flow rate was studied and the model's performance for experiments in [8] is depicted in figure 4. For the corresponding experiments, inlet  $\text{CO}_2$  partial pressure of 15kPa was used along with the P-28 nozzle. It was found to validate within 15% error margin with the experimental data, with significant errors only in region of high liquid flow rate and low solvent loading due to the same reasons mentioned before. Using the model's fit, the optimal operating conditions can be evaluated for P-28 nozzle, given inlet  $\text{CO}_2$  partial pressure, and design parameters.

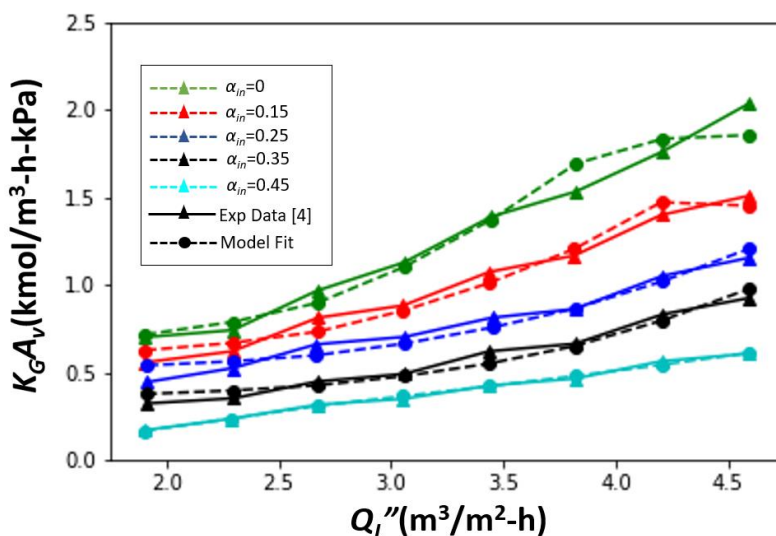


Fig. 4: Validation across variation in  $Q_L''$  for P-28 nozzle and range of inlet loading used in [8]

Lastly, the model was validated with a range of inlet  $\text{CO}_2$  partial pressures and solvent loading conditions from data in [8]. The corresponding experiments were conducted with P-20 nozzle, liquid flow rate of  $1.53 \text{ m}^3/\text{m}^2\text{-h}$ , and gas flow rate of  $382\text{-}764 \text{ m}^3/\text{m}^2\text{-h}$ . The model predicted the trends extremely well as can be seen in figure 5. This means that the model predictions can be extrapolated to estimate the system's performance at other operating

conditions such as those in Direct Air Capture where the  $\text{CO}_2$  partial pressures are much lower. This also helps identify the ideal operating conditions for the given system.

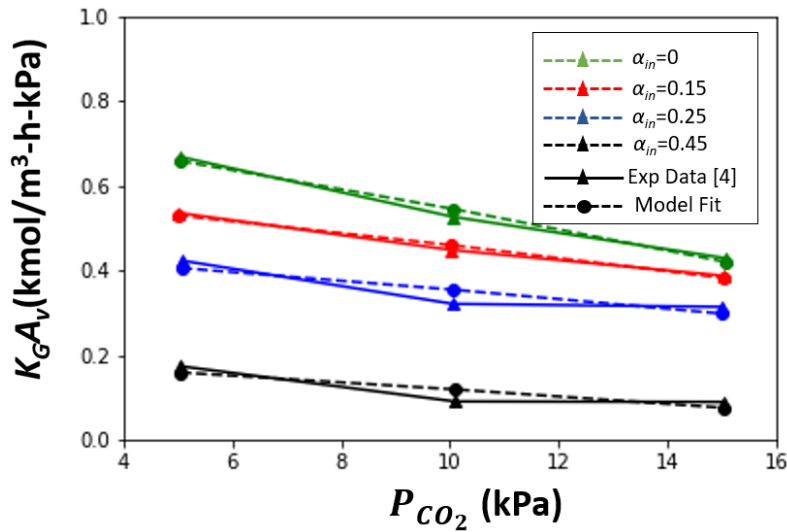
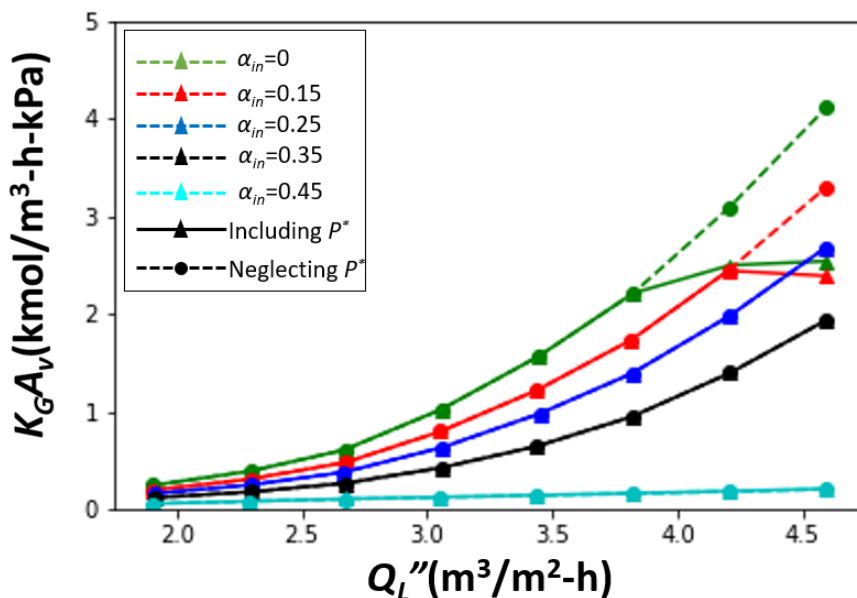


Fig. 5: Validation across variation in  $P_{\text{CO}_2}$  (kPa) for P-20 nozzle and range of inlet loading used in [8]

### 3.2. Inferences obtained from the Model

The effect of considering the equilibrium partial pressure of  $\text{CO}_2$  on the overall mass transfer has been shown in Figure 6. The purely analytical results were considered with the inclusion and exclusion of  $P^*$  to understand its relative importance for a range of inlet loading and liquid flow rates. It was observed that the effect is prominent only for higher flowrates and at lower  $\text{CO}_2$  loading, where the overall mass transfer coefficient is high. This was because the driving force  $P_{\text{CO}_2} - P^*$  is small enough only when the overall removal is high causing  $P_{\text{CO}_2}$  to be comparable to  $P^*$ . In the scenario when overall removal is low due to lower overall mass transfer coefficient, then  $P_{\text{CO}_2} \gg P^*$  and thus the effect of  $P^*$  is negligible, which was observed with low liquid flow rates and high  $\text{CO}_2$  loading.

Fig. 6. Effect of inclusion/exclusion of  $P^*$  on the model

To obtain further insights from the model, two sets of cases were studied in greater detail. For the first case, the experimental data from [6] and the model's validation was considered. This was corresponding to an inlet loading of 0, 0.15, and a flux of liquid flow rate equal to 1.41 and 2.12  $\text{m}^3/\text{m}^2\text{-h}$ . The other case studied was the model's validation for experimental data of [8] for P-28 nozzle, flux of liquid flow rate of 3.05  $\text{m}^3/\text{m}^2\text{-h}$ , and flux of gas flow rate of 382  $\text{m}^3/\text{m}^2\text{-h}$ . The model was used to obtain variation of mole fraction ( $X_{\text{CO}_2}$ ),  $\text{CO}_2$  loading ( $\alpha$ ), volumetric overall mass transfer coefficient ( $K_G A_v$ ), total mass transfer coefficient ( $K_G$ ), and volumetric effective area ( $A_v$ ), along channel height. The results for the same are depicted in figures 7-9, with subfigures (a) and (b) corresponding to the two cases respectively. From figure 7a, it can be shown from the flat lines until the middle of the reactor that the majority of  $\text{CO}_2$  consumption takes place in the second half of the reactor for all the four conditions shown. This is not true for the other case when the channel height is only 0.55 m compared to 3.7 m. For the smaller reactor, the consumption takes place throughout the channel. This implies that for the given parametric space in operating conditions, the channel in case b could use an addition to its height while the one in case a is already beyond what's needed. Fig 8a describes the very low  $K_G A_v$  in the first half of the reactor followed by a peak around the middle of the channel, while figure 8b shows a steady decrease in the  $K_G A_v$  with a peak only at the beginning of the reactor. The overall  $K_G A_v$  and  $K_G$  were used to obtain  $A_v$  along channel height and the results are described in figure 9. It is found that the  $K_G$  plateaus in second half of the reactor for the first case with a maximum at the middle of the channel, and  $A_v$  reduces along the channel height. For case b, the  $K_G$  follows similar trends as  $K_G A_v$  and the effective area was again found to behave similar to case a. Figure 9 also shows that the effective area changes significantly with increase in liquid flow rate. It is also found to change only slightly with loading, but this can be attributed to the fact that the way it is evaluated is using  $K_G A_v$  and  $K_G$  which vary significantly along channel height and inlet loading. The volumetric effective area was found to be in the range 225-425  $\text{m}^2/\text{m}^3$ , which was found to be close to the range of 100-300  $\text{m}^2/\text{m}^3$  reported in [7].

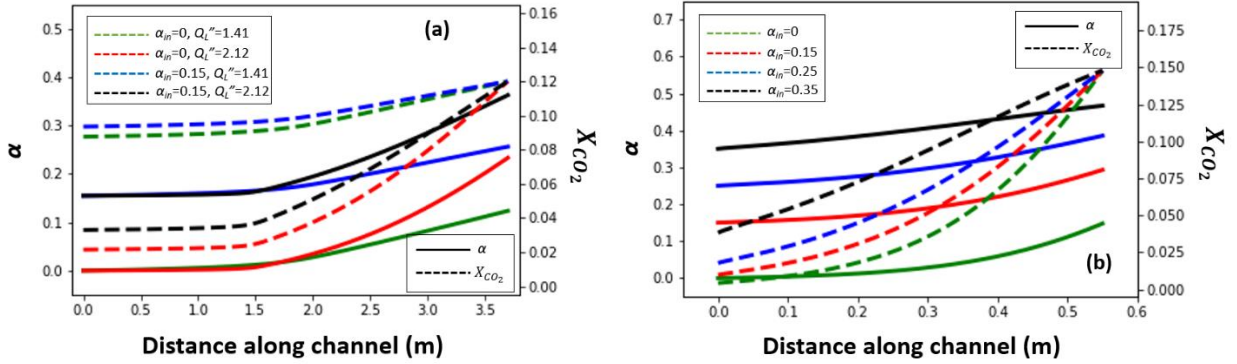


Fig. 7. Variation of  $\alpha$  (solid line, left axis) and  $X_{CO_2}$  (dashed line, right axis) along channel height using model's validation for (a) [6] and (b) [8]

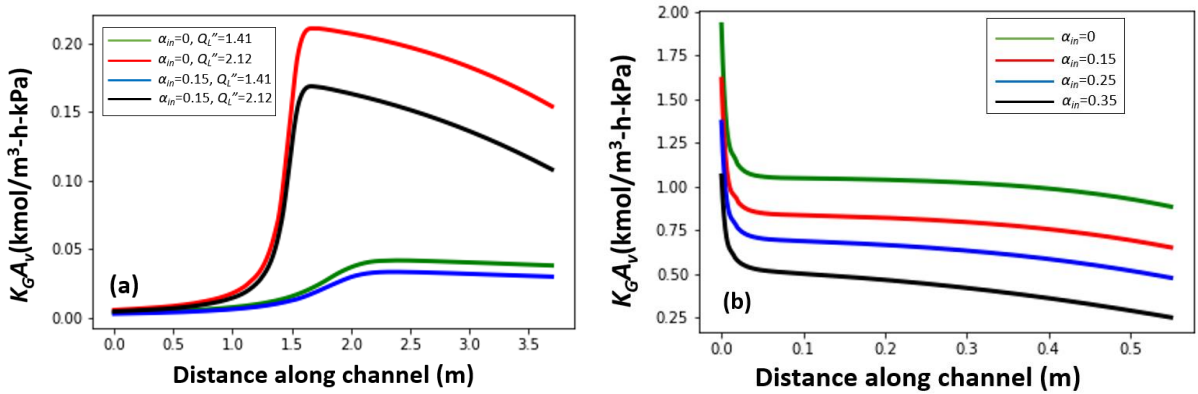


Fig. 8. Variation of  $K_G A_v$  along channel height using model's validation for (a) [6] and (b) [8]

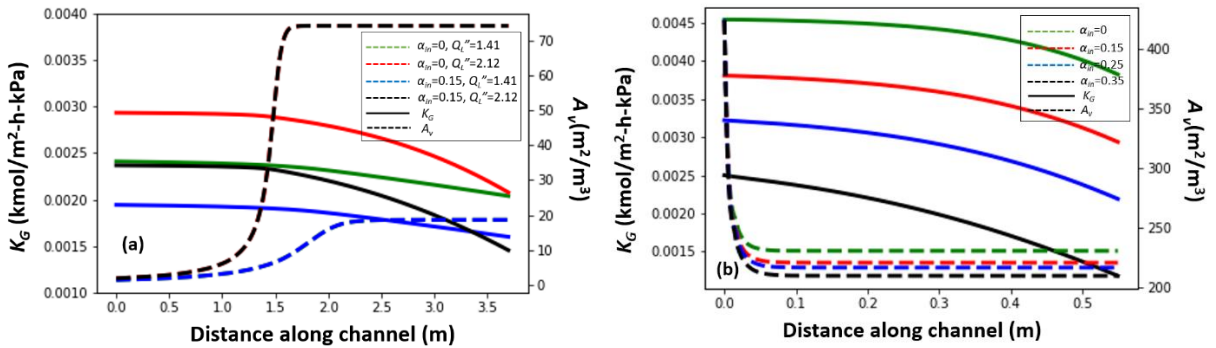


Fig. 9. Variation of  $K_G$  (solid line, left axis) and  $A_v$  (dashed line, right axis) along channel height using model's validation for (a) [6] and (b) [7, 8]

#### 4. Conclusions

The present work developed a novel analytical model for spray-based CO<sub>2</sub> capture systems. The model was validated for a range of design parameters with experimental data from previous studies. The effect of inclusion of  $P^*$

on the computed performance ( $K_G A_v$ ) was also studied and was found to be significant only at high liquid flow rate and low solvent loading, which correspond to high overall CO<sub>2</sub> capture. The variation of key parameters such as  $K_G A_v$ ,  $K_G$ ,  $A_v$ ,  $\alpha$ ,  $X_{CO_2}$  along the channel height was studied and it was found that in some cases only parts of the channel are utilized for CO<sub>2</sub> capture. This gives insights into the design of a reactor for given operating conditions. The model can be used to obtain  $K_G A_v$  for operating conditions in a wider range than those conducted in the experiments. This data can then be used to obtain the optimum flow conditions for a given system to optimize parameters like CO<sub>2</sub> capture rate, moles of CO<sub>2</sub> captured per total energy consumed [moles/kW], the amount of CO<sub>2</sub> captured by the amount of solvent used [kg-CO<sub>2</sub>/kg-solvent], and the amount of CO<sub>2</sub> captured per operating cost [kg-CO<sub>2</sub>/\\$], based on the designer's needs. Such a study is left as scope of future work.

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# NOVEL ANALYTICAL MASS TRANSFER MODEL FOR CO<sub>2</sub> CAPTURE USING SPRAYS

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## BACKGROUND AND MOTIVATION

Global pipeline of commercial CCUS facilities operating and in development, 2010-2021

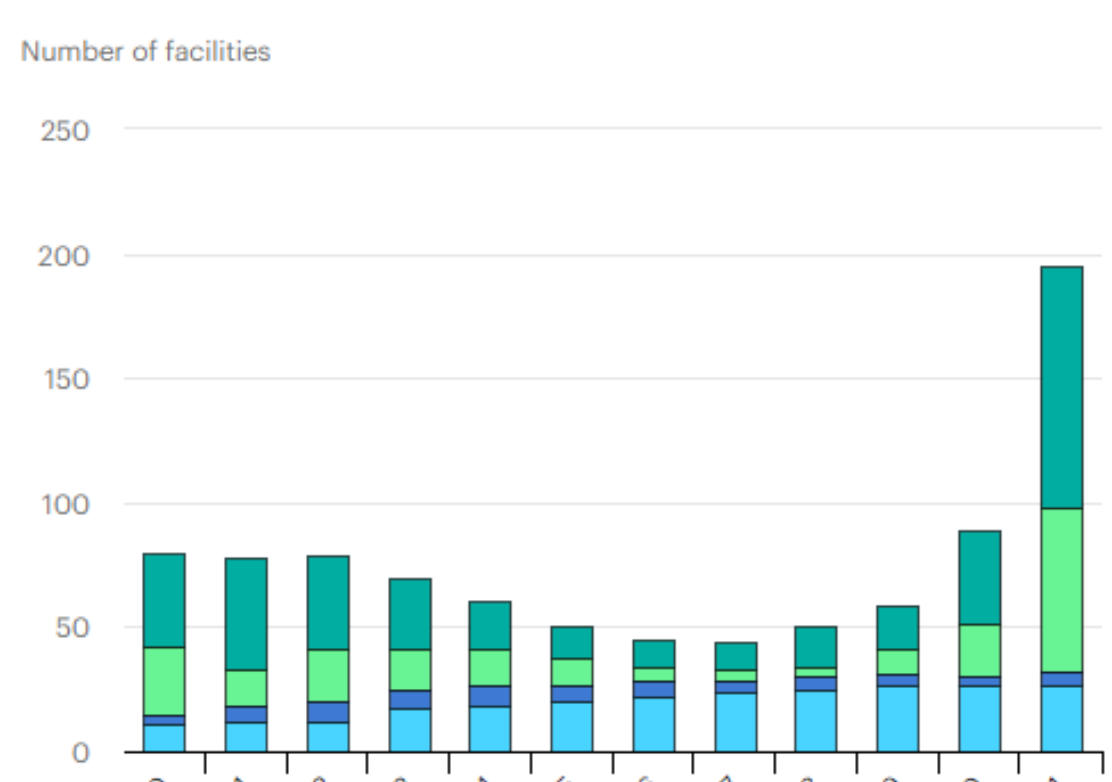


Figure 1: Number of CCUS facilities in last decade [1]

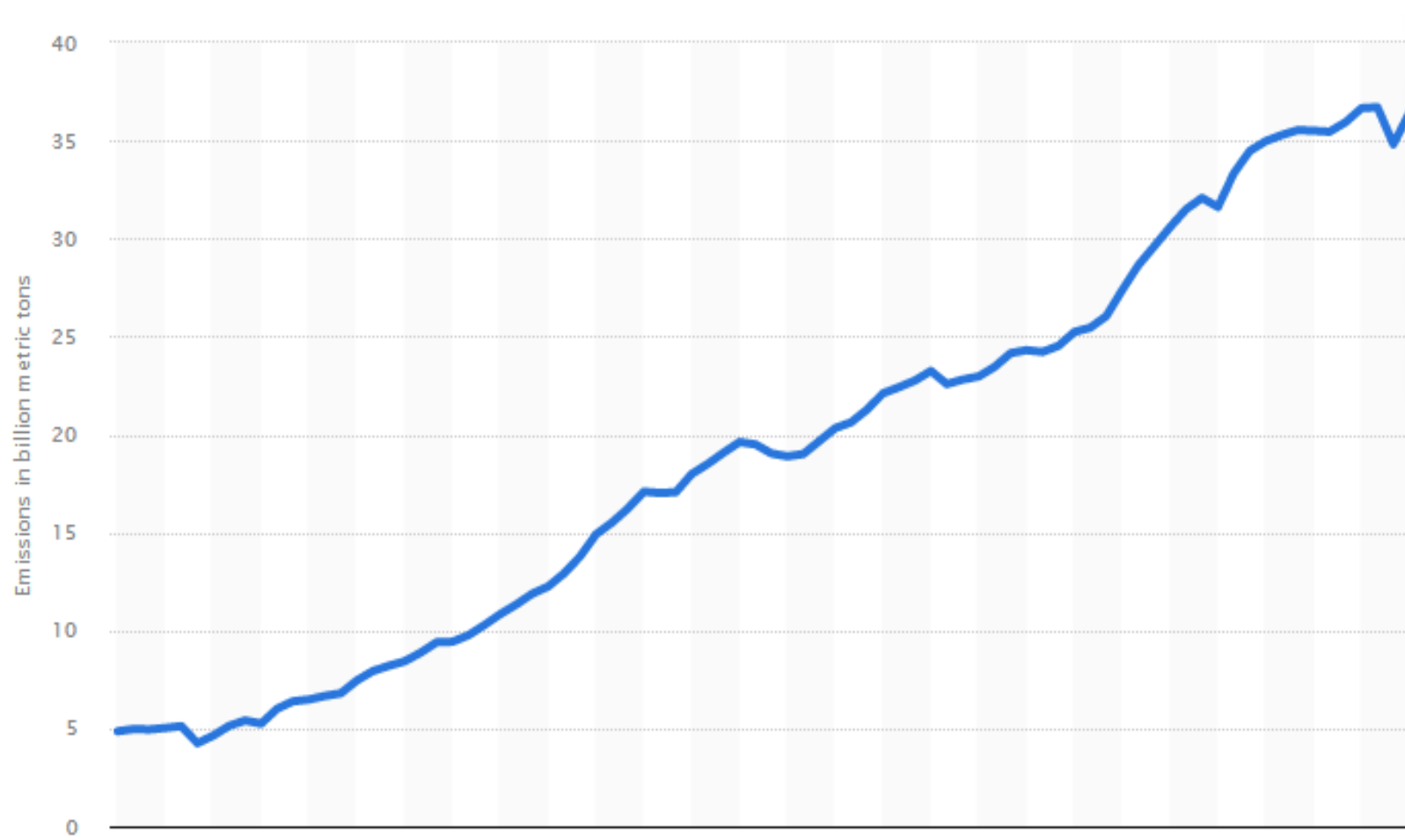


Figure 2: Rising CO<sub>2</sub> emissions per year for the last 80 years [2]

- Paris agreement by UN aims at net-zero CO<sub>2</sub> emission by the year 2050.
- Rapid increase in the deployed CCUS facilities to meet the target.
- CO<sub>2</sub> absorber consists of a packed bed, or a spray-based system, or both.
- Lack of models that predict system's performance to design a new capture system.

## OBJECTIVES OF CURRENT WORK

- Develop an analytical model that can be validated across different studies [3,4].
- Use model to gain insights on behavior within the reactor.
- Study other potential uses of the validated model.

## MATHEMATICAL MODEL

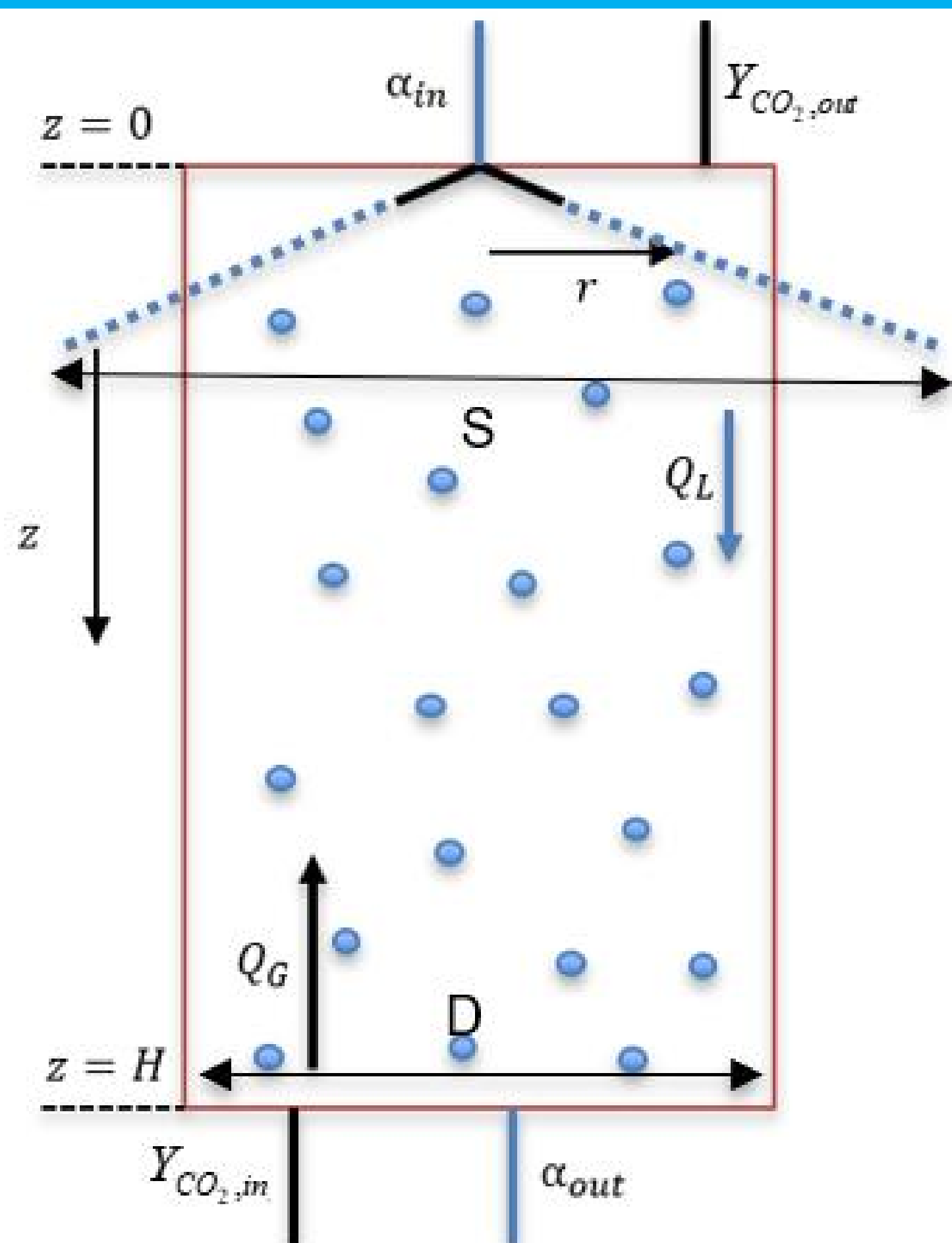


Figure 3: Domain for model describing Spray-based capture plant

### Gas-side Equations

$$J = K_G(P_{CO_2} - P^*)$$

$$N = \frac{dn_d}{dz} = \frac{\dot{Q}_L}{UV_d} f; \quad f = \frac{D}{S} \text{ if } D < S$$

$$\frac{dn_{CO_2}|_{gas}}{dz} = JNA_d$$

$$dn_{CO_2} = \dot{n}_{N_2} dY_{CO_2} = \left( \frac{P_{tot} \dot{Q}_{N_2}}{RT} \right) dY_{CO_2}$$

$$\frac{dY_{CO_2}}{dz} = K_G RT \frac{\dot{Q}_L}{\dot{Q}_{N_2}} \frac{A_d}{UV_d} \left( \frac{Y_{CO_2}}{1 + Y_{CO_2}} - \frac{P^*}{P_{tot}} \right) \quad (A)$$

- Equations A and B were solved as IVP using the predictor corrector method.
- The residual between predicted and given  $Y_{CO_2,in}$  was minimized to  $10^{-5}$ .
- Stokes flow relations were used to obtain velocity profile and thus residence time.
- Liquid properties of 30 wt% MEA were used.
- Analytical model results were fitted with slope and bias correction factors.

$$K_G A_v = \left( \frac{\dot{Q}_{N_2}}{P_{tot} \left( \frac{Y_{CO_2}}{1 + Y_{CO_2}} - P^* \right)} \right) \left( \frac{dY_{CO_2}}{dz} \right)$$

### Liquid-side Equations

$$\frac{dn_{CO_2}|_{liq}}{dz} = \frac{dn_{CO_2}|_{gas}}{dz}$$

$$\alpha = \frac{n_{CO_2,init} + n_{CO_2,cons}}{n_{MEA,init}} = \alpha_{in} + \frac{n_{CO_2,cons}}{n_{MEA,init}}$$

$$dn_{CO_2}|_{liq} = \dot{Q}_L C_{init} d(\alpha)$$

$$\frac{P_{tot} \dot{Q}_{N_2}}{RT \dot{Q}_L C_{init}} \frac{dY_{CO_2}}{dz} = \frac{d\alpha}{dz}$$

$$\frac{d\alpha}{dz} = \frac{P_{tot}}{C_{init} U d} K_G \left( \frac{Y_{CO_2}}{1 + Y_{CO_2}} - \frac{P^*}{P_{tot}} \right) \quad (B)$$

$$K_G A_v|_{fit} = m * K_G A_v|_{analytical} + c$$

### Key assumptions involved in the model:

- The droplet-droplet interaction was neglected.
- Energy equation was not considered, i.e., temperature was assumed a constant.
- The evaporation of amine and water was estimated to be negligible.
- System was lumped in radial direction.

## RESULTS

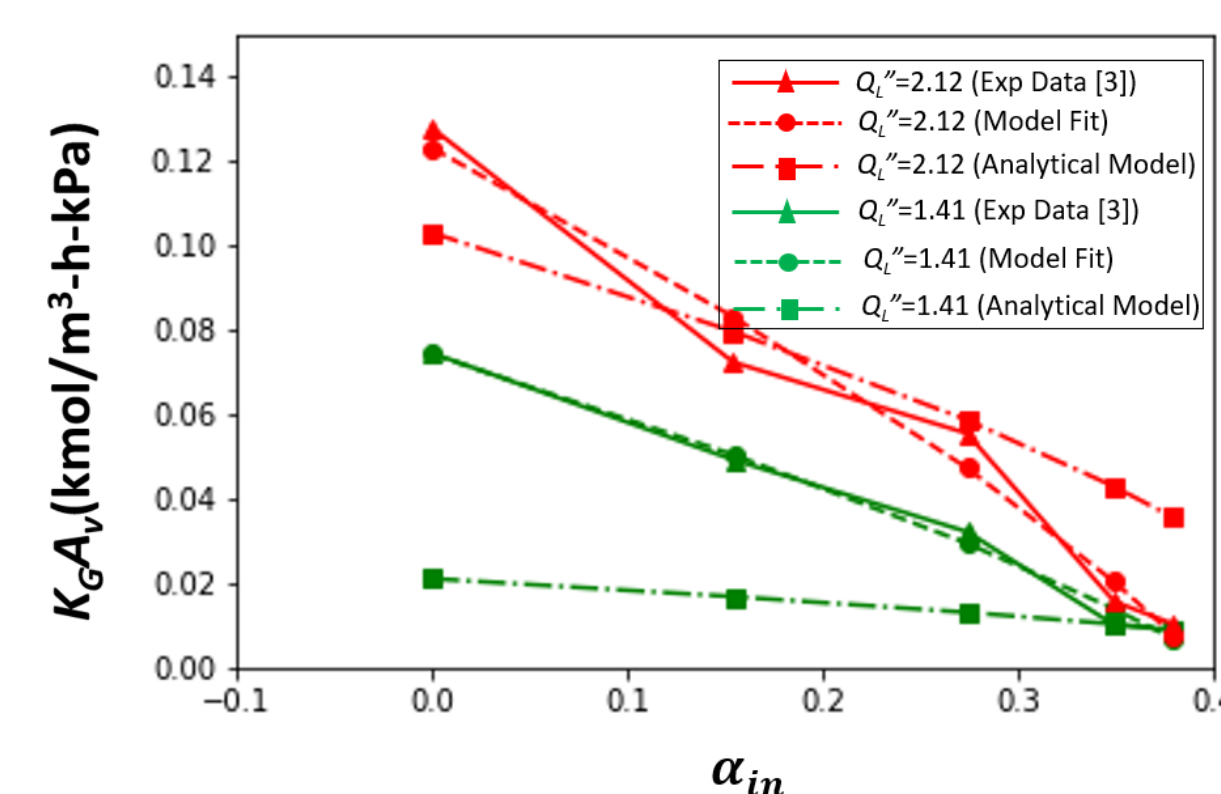


Figure 4: Model validation for variation in  $K_G A_v$  with inlet loading [3]

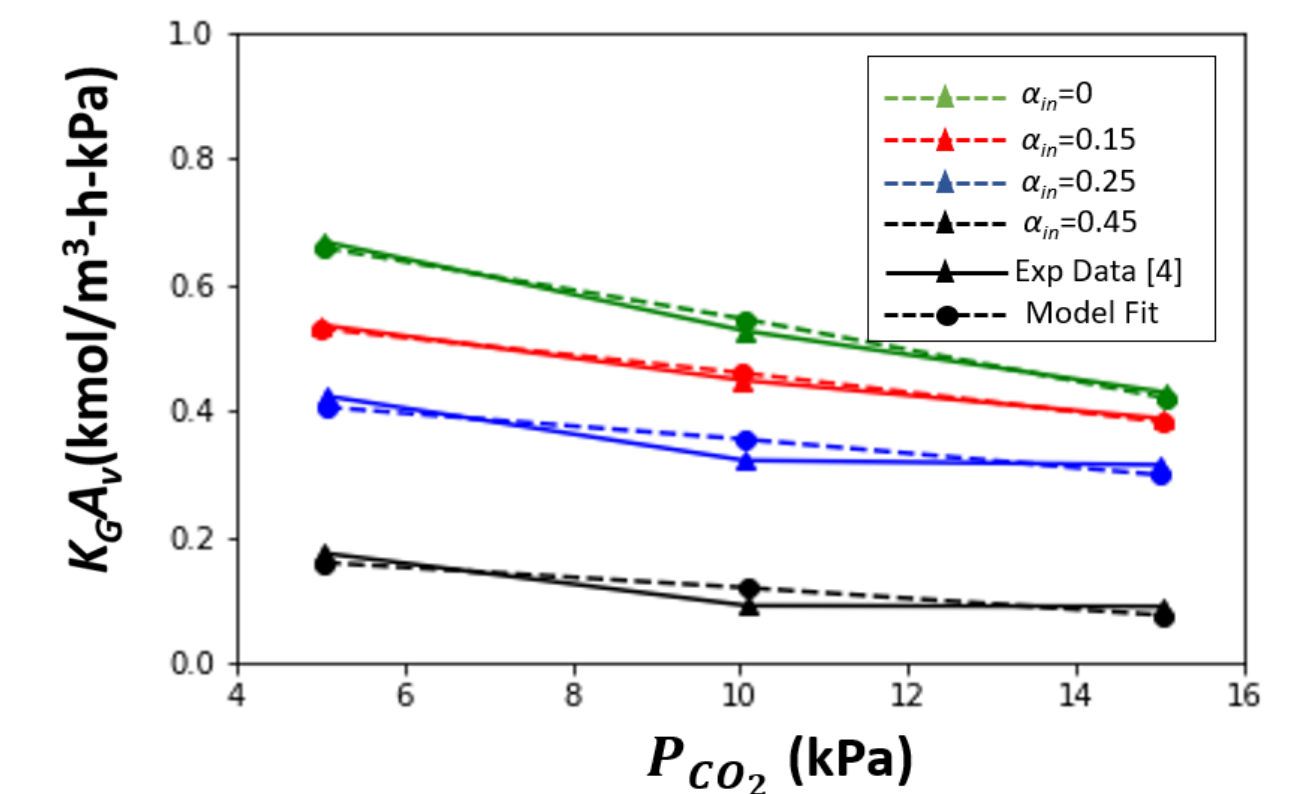


Figure 5: Model validation for variation in  $K_G A_v$  with inlet CO<sub>2</sub> partial pressure [4]

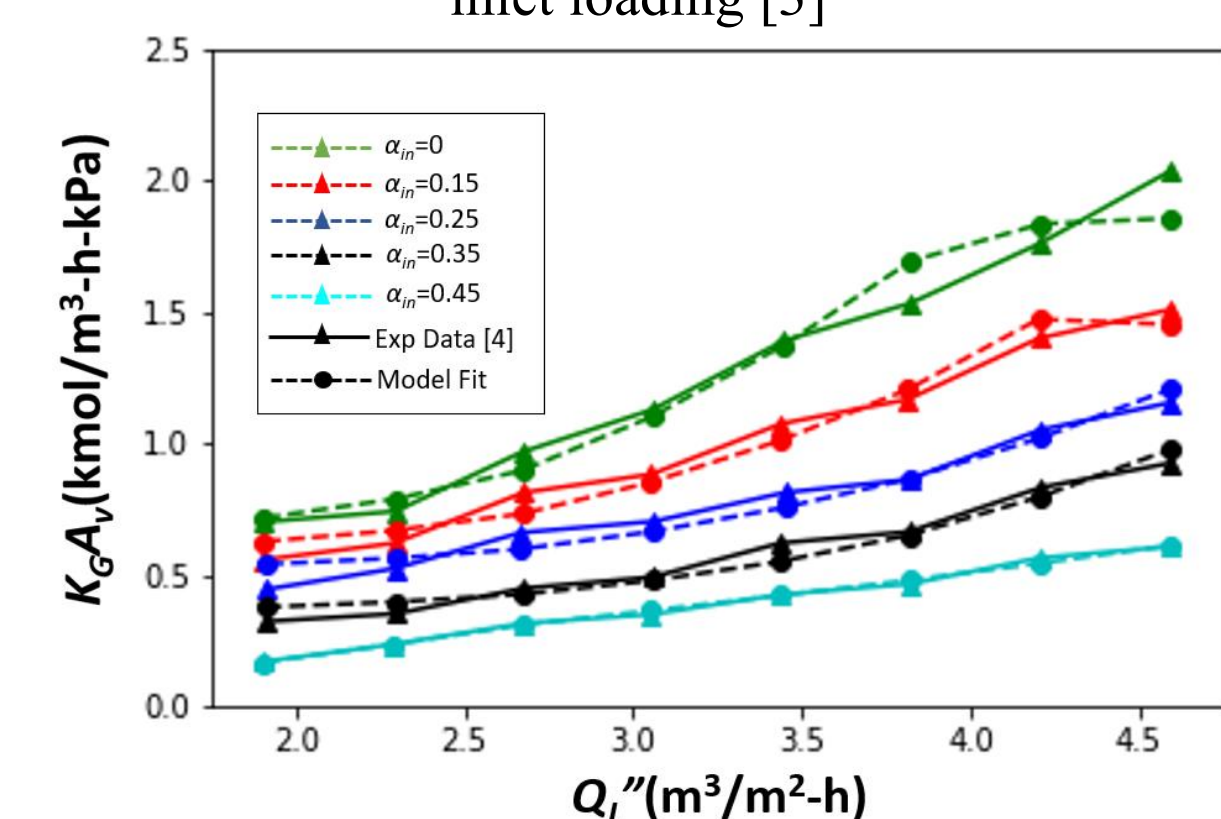


Figure 6: Model validation for variation in  $K_G A_v$  with liquid flow rate [4]

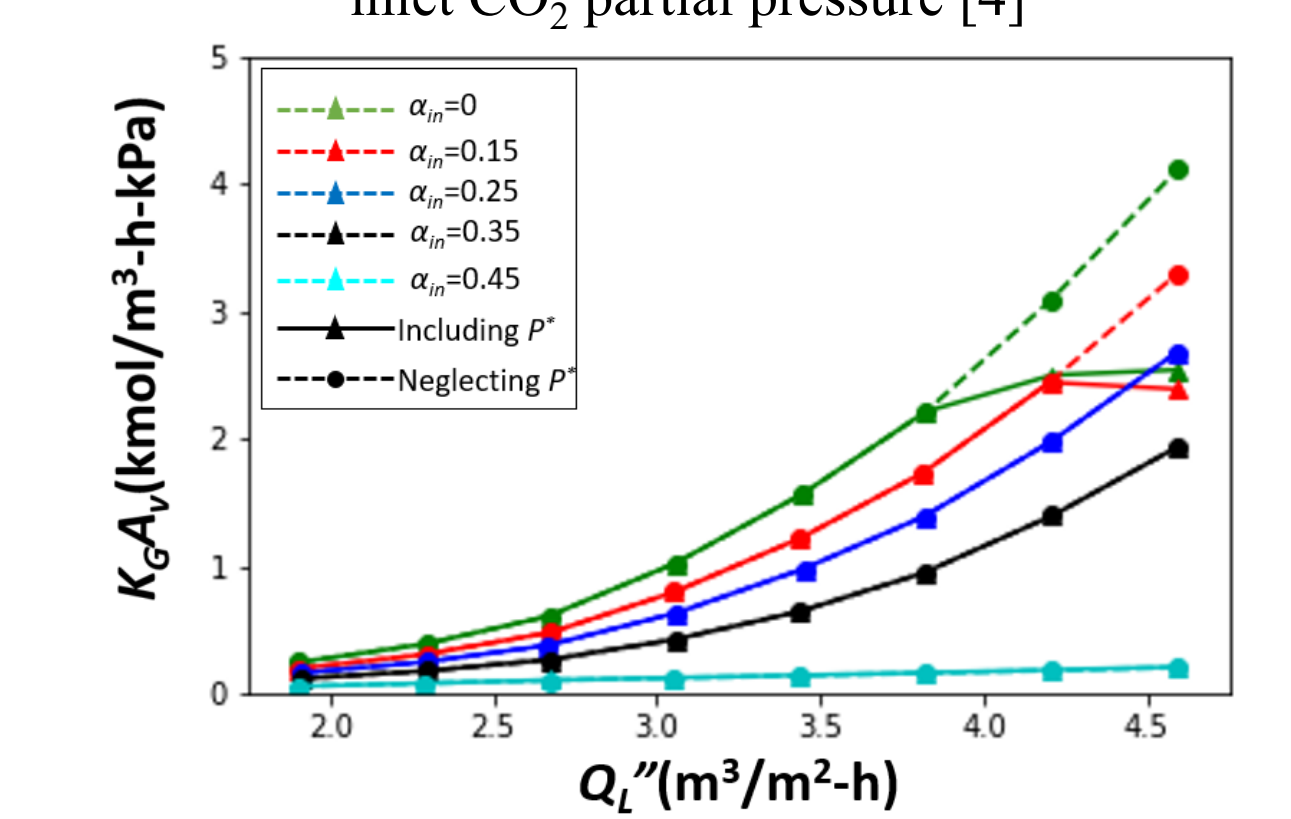


Figure 7: Effect of  $P^*$  on the model predictions

- The purely analytical model predicted trends reasonably well.
- Model underpredicted and overpredicted  $K_G A_v$  at lower and higher liquid flow rates, respectively.
- The model's prediction after fitting is in good agreement with the experimental data.
- Model predictions can be used to estimate the system's performance for application with much lower partial pressure of CO<sub>2</sub>, for example, in the case of direct air capture.
- The model predictions can be used to extrapolate and estimate the ideal operating conditions.
- Enhanced capture for high liquid flow rate and low loading conditions cause the effect of  $P^*$  to be significant in that regime.
- Variation of parameters such as  $X_{CO_2}$ ,  $\alpha$ ,  $K_G A_v$ ,  $K_G$ , and  $A_v$  was studied along channel height.
- Optimal channel height can be estimated for any given operating conditions.

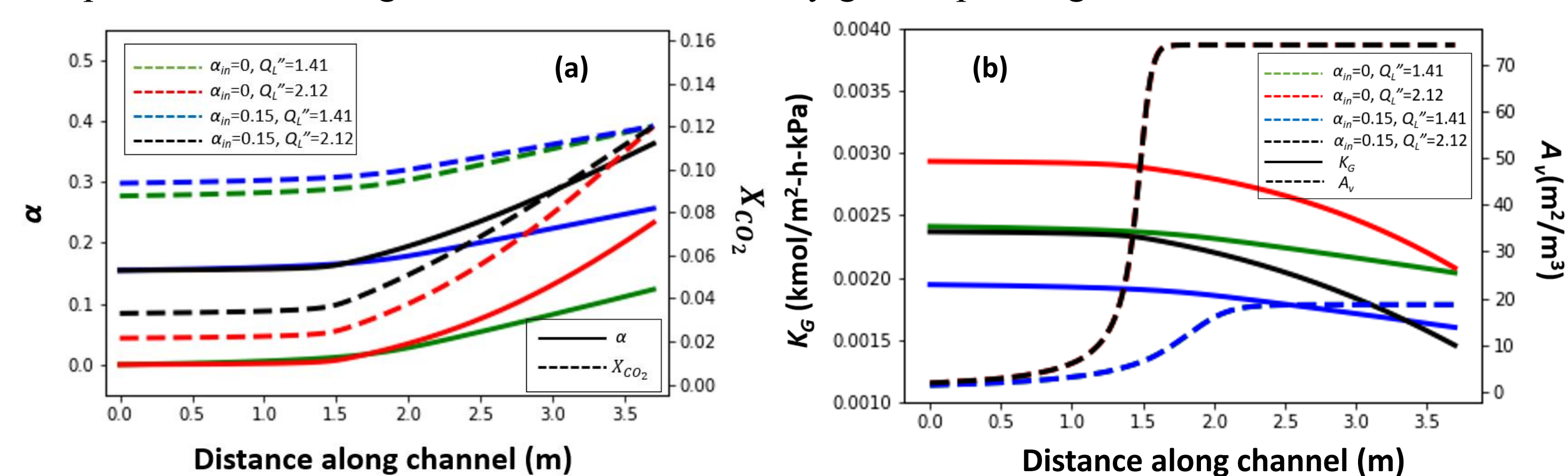


Figure 8: Variation of (a)  $\alpha$  (solid line, left axis),  $X_{CO_2}$  (dashed line, right axis), and (b)  $K_G$  (solid line, left axis),  $A_v$  (dashed line, right axis) along channel height using model validation results for [3]

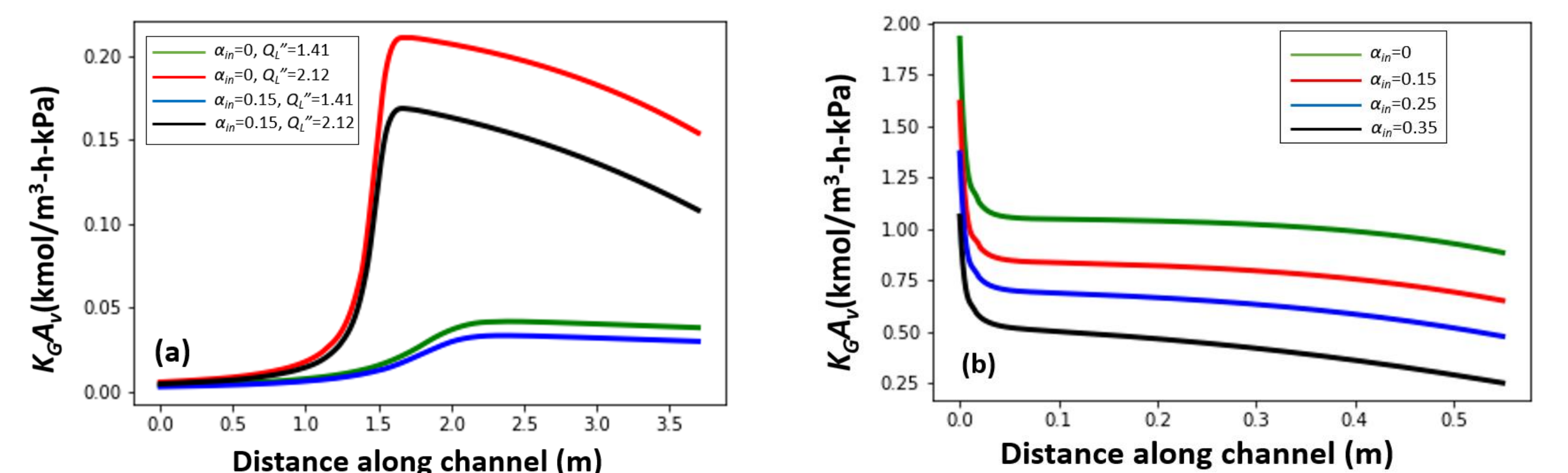


Figure 9: Variation of  $K_G A_v$  along channel height using model validation results for (a) [3] and (b) [4]

## CONCLUSIONS

- Effect of  $P^*$  is found to be significant only for high liquid flow rates, and low solvent loading.
- Model provides insights into performance of each section of the reactor independently.
- Model predictions can be used to get optimal working and design conditions.

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