



CHE 400 TECHNICAL PROJECT

Mathematical Modeling of Flue-Gas Desulfurization via the Seawater Process

Submitted by:

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Nomenclature

β	Liquid holdup	
η	Percent removal SO_2	
\vec{N}	Flux	$\frac{\text{mol}}{\text{m}^2 \cdot \text{s}}$
a	Surface area per liquid volume	m^{-1}
A_{cs}	Cross sectional area of tower	m^2
C_A	Concentration of SO_2 in the liquid phase	$\frac{\text{mol}}{\text{m}^3}$
C_B	Concentration of H^+ in the liquid phase	$\frac{\text{mol}}{\text{m}^3}$
C_C	Concentration of HSO_2^- in the liquid phase	$\frac{\text{mol}}{\text{m}^3}$
C_D	Concentration of SO_3^{2-} in the liquid phase	$\frac{\text{mol}}{\text{m}^3}$
C_E	Concentration of HCO_3^- in the liquid phase	$\frac{\text{mol}}{\text{m}^3}$
C_F	Concentration of CO_2 in the liquid phase	$\frac{\text{mol}}{\text{m}^3}$
d_p	Average droplet radius	m
H	Henry's Law constant for SO_2	$\frac{\text{mol}}{\text{m}^3 \cdot \text{atm}}$
k	Reaction rate coefficient of H^+ neutralization by HCO_3^-	$\frac{\text{mol}}{\text{m}^3 \cdot \text{s}}$
K_1	Equilibrium constant for first dissociation of SO_2	$\frac{\text{mol}}{\text{m}^3}$
K_2	Equilibrium constant for second dissociation of SO_2	$\frac{\text{mol}}{\text{m}^3}$
k_G	Gas film coefficient	$\frac{\text{m}}{\text{s}}$
k_L	Liquid film coefficient	$\frac{\text{m}}{\text{s}}$
K_{MT}	Overall mass transfer coefficient	$\frac{\text{m}}{\text{s}}$
P_A	Partial Pressure of SO_2 in the gas phase	atm
Q_G	Gas flow rate	$\frac{\text{m}^3}{\text{s}}$
Q_L	Liquid flow rate	$\frac{\text{m}^3}{\text{s}}$
R	Gas Constant	$\frac{\text{m}^3 \text{atm}}{\text{mol} \cdot \text{K}}$
T	Temperature	K

1 Introduction and Background

While electric power generation facilities provide electricity to millions across the country, they also produce harmful pollutants like sulfur dioxide. According to the EPA, two thirds of the sulfur dioxide in the atmosphere is produced from electric power generators [8]. When sulfur dioxide rises up in the atmosphere, it reacts with nitrogen dioxide in the presence of oxygen and water to produce acid rain. Thus, it is essential to reduce harmful emissions such as sulfur dioxide. Currently, power plants use flue gas desulfurization (FGD), to limit the release of gaseous sulfur dioxide into the atmosphere [9]. Although most systems utilize limestone slurries to scrub SO_2 , in coastal areas there is an interest in developing seawater-based processes. This report will model a pilot-scale seawater FGD system in both counter and co-current streams.

2 Model Formulation

2.1 Reaction Kinetics

In flue-gas desulfurization, the absorption of SO_2 is enhanced by a liquid-phase reaction with alkaline species. In classical systems, solid limestone particles in an aqueous slurry supply the reagent for this reaction; however, in the seawater process of flue-gas desulfurization, the natural alkalinity of seawater is used to enhance the absorption of SO_2 . The total alkalinity is expressed as the sum of the concentrations of several species that allow seawater to resist changes in pH, but the dominant contribution comes from the bicarbonate ion, HCO_3^{2-} [2]. The reaction of aqueous SO_2 with bicarbonate can be described by the following steps:



In order to simplify the kinetics somewhat, we assumed the dissociation of SO_2 to be fast, which allowed us to describe steps (1) and (2) using the equilibrium step assumption (ESA). The interaction between bicarbonate, carbonic acid, and dissolved carbon dioxide is represented by (3). In reality, carbonate chemistry in seawater is a process involving several chemical species and equilibria; however, for modeling purposes we approximated the neutralization of excess H^+ in seawater as an irreversible reaction. Rather than explicitly modeling the full complexity of seawater's bicarbonate buffer system, we instead aimed to capture the essential behavior by formulating the following simplified rate equation:

$$r = k ([\text{H}^+] - [\text{H}^+]_0) [\text{HCO}_3^-], \quad (4)$$

where $[\text{H}^+]_0$ is the concentration of hydrogen ions found naturally in seawater, which has a pH of 8.0. Following the method used by Schwartz and Freiberg [1], another assumption we make is that a condition of electroneutrality must be satisfied:

$$[\text{H}^+] = [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] \quad (5)$$

By combining (5) with the ESA expression derived for (2), we can express the concentrations of bisulfite and sulfite ions as

$$[\text{SO}_3^{2-}] = \frac{K_2[\text{H}^+]}{2K_2 - [\text{H}^+]} \quad [\text{HSO}_3^-] = \frac{[\text{H}^+]^2}{[\text{H}^+] + 2K_2}$$

Substituting our equation for bisulfite concentration as a function of H^+ into the ESA expression for (1), we can directly relate the concentration of SO_2 dissolved in the liquid to the acidity of the solution.

$$[SO_{2(aq)}] = \frac{[H^+]^3}{K_1[H^+] + 2K_1K_2} \quad (6)$$

By deriving an expression relating the equilibrium concentrations of SO_2 and H^+ , we can now use this relationship to describe how the a change in concentration of either species shifts the concentration of the other.

2.2 Gas-Liquid Mass Transfer

Mass transfer of sulfur dioxide from the gas to liquid phase is described using the two-film theory of mass transfer (Appendix B). This allows us to write the flux of SO_2 across the interface in terms of its partial pressure in the gas stream, concentration in the liquid bulk, and an overall mass-transfer coefficient.

$$\vec{N}_A = -K_{MT}(C_A - HP_A) \quad (7)$$

For simplicity, we assume the only species present in the liquid film is $SO_{2(aq)}$, and that it only dissociates upon reaching the liquid bulk region. Although this is somewhat unphysical given that reaction is likely to occur in the liquid film, describing the interplay between reaction and diffusion at the gas-liquid interface is analytically difficult. The increased rate of absorption due to chemical reaction in the liquid film can be described using an enhancement factor defined as follows:

$$\varepsilon = \frac{\vec{N}_A \text{ in the presence of reaction}}{\vec{N}_A \text{ in absence of reaction}} \quad (8)$$

Determining ε requires the solution of coupled reaction-diffusion equations for each species in the liquid film of the form

$$0 = D\nabla^2 C + R \quad (9)$$

The boundary conditions for (9) are specified by whether or not a given species is allowed to diffuse across the gas-liquid interface, as well as the concentrations in the bulk phases [6]. Analytical solutions exist for only first order or pseudo-first order kinetics; nonlinear rate expressions like the ones in our model require one to numerically solve (9) in order to determine concentration profiles in the liquid film and flux across the gas-liquid interface. Although currently beyond the scope of our project, future efforts could involve modeling this behavior.

2.3 Spray Tower Mass and Species Balances

The actual scrubbing of SO_2 from flue gas with seawater takes place in a spray tower. In order to construct a mathematical model of this system, it was assumed that the tower operates at steady state and that the liquid and gas streams obey plug-flow. By taking mass balances on SO_2 (A), H^+ (B), and HCO_3^- (E), the following equations describing concentration changes with respect to position were obtained.

$$\frac{dP_A}{dz} = \sigma \frac{\beta A_{cs}}{Q_G} [RT K_{MT} a (C_A - HP_A)] \quad (10)$$

$$\frac{dC_A}{dz} = \frac{\beta A_{cs}}{Q_L} \left[-K_{MT} a (C_A - HP_A) - k (C_B - C_{B0}) C_E \left(\frac{\partial C_A}{\partial C_B} \right) \right] \quad (11)$$

$$\frac{dC_B}{dz} = \frac{\beta A_{cs}}{Q_L} \left[-K_{MT} a (C_A - HP_A) \left(\frac{\partial C_B}{\partial C_A} \right) - k (C_B - C_{B0}) C_E \right] \quad (12)$$

$$\frac{dC_E}{dz} = \frac{\beta A_{cs}}{Q_L} [-k (C_B - C_{B0}) C_E] \quad (13)$$

The partial derivative of C_A with respect to C_B describes the equilibrium between dissolved SO_2 and H^+ , and was derived from (6).

$$\frac{\partial C_A}{\partial C_B} = \left(\frac{\partial C_B}{\partial C_A} \right)^{-1} = \frac{2C_B^2 (C_B + 3K_2)}{K_1 (C_B + 2K_2)^2} \quad (14)$$

The variable σ takes a value of either 1 or -1 , and indicates whether the spray tower is operating in a co-current or countercurrent configuration. The variable a describes the interfacial area per liquid volume of uniform spheres. The variable β describes the fraction of a spray tower volume element that is occupied by liquid.

3 Numerical Methodology

All simulations were performed in MATLAB R2018a [7], using the parameter values and code specified in Appendix A.

3.1 Co-current Configuration

In a co-current configuration, both the gas and liquid streams enter the spray tower at the same point. This means that the inlet conditions are fully specified, and concentration profiles can be obtained by numerically integrating equations (10)–(13) along the length of the tower to the outlet.

3.2 Countercurrent Configuration

In a countercurrent configuration, the gas and liquid streams enter the tower from opposite sides; the liquid inlet is the gas outlet. This means that the conditions aren't fully specified at either end, and that equations (10)–(13) can no longer be solved as an initial value problem as was the case in the co-current setup. In order to solve for the concentration profiles in the spray tower, we employ an iterative method outlined in Appendix C.

4 Results and Analysis

The purpose of the FGD process is to remove as much sulfur dioxide from the gas inlet stream. Based on Figure 1, it can be seen that the partial pressure of sulfur dioxide decreased from 7×10^{-4} atm to 9.1×10^{-5} atm for cocurrent and 3.3×10^{-5} atm for countercurrent, or about 87.1% and 95.3% removal, respectively. This significant decrease in concentration of sulfur dioxide in the

gas indicates that this system is very effective in preventing sulfur dioxide from being released to the atmosphere. It can also be seen from Figure 1 that the countercurrent stream was more efficient in terms of sulfur dioxide removal. This is due to the difference in concentrations for the two streams in both systems. In the countercurrent system, there is initially a large concentration gradient, but they quickly reach equilibrium. However, in the co-current stream, the concentration gradient isn't as large, but is maintained for a longer period of time.

As the reaction proceeds, the concentration of H^+ ions increases as explained in the reaction mechanism. This trend is illustrated in Figure 1 as the H^+ ion concentrations reach 1.32 mol/m^3 and 1.86 mol/m^3 for co-current and countercurrent streams, respectively. For both streams, the concentration increases greatly at first but then reaches a more consistent rate of production for the rest of the reactor. This initial accelerated rate is due to mass transfer. When there is no concentration of sulfur dioxide in the liquid stream, it is easy for sulfur dioxide to transfer into the liquid. However, this transfer is quickly limited by the reaction rate as the sulfur dioxide in the liquid cannot be consumed rapidly, leading to an equilibrium between sulfur dioxide in the gas and the liquid streams. The reaction is then limited by the speed of the multistep reaction. This helps explain the changing dynamics seen in the H^+ ion concentration profile.

Figure 2 illustrates the forces driving the removal of SO_2 from the flue gas. Physical absorption occurs due to the concentration difference between liquid and gas. This difference is maintained by a liquid phase reaction that has the long-range effect of shifting the equilibrium described by reaction (1) away from SO_2 . Averaged over the total volume of the spray tower, there is roughly the same amount of reaction occurring in both the co-current and countercurrent setups (this value is analogous to the area under the reaction rate curve). However, when the flux is averaged over the volume of the reactor, it is seen that there is more total SO_2 moving from the gas to the liquid in the countercurrent setup. This makes sense given that the countercurrent system is better at maintaining concentration gradients.

Besides removing the sulfur dioxide from the gaseous stream, it is important to look at what other products are formed and the impact they may have on the environment. As previously discussed, the seawater stream used for the reaction experienced a significant increase of H^+ ions. This greatly increases the acidity of the seawater. Figure 3 models the pH of water and percent removal SO_2 as a function of distance throughout the reactor for both co-current and countercurrent streams. It can clearly be seen that the pH of water drops from 8.0 to less than 3.0 for both systems. This significant drop in pH makes the stream being returned to the ocean very acidic and potentially harmful to the ocean ecosystem. However, it must be noted that this model does not include the complex buffer qualities of seawater. Since seawater has many ions like bicarbonate dissolved within it, seawater is resistant to changes in pH. In a real world environment, it is likely the actual returning seawater stream will not have a pH as low as 3.0. Regardless, the acidification of the ocean is a growing concern and engineers involved in the operation of seawater FGD processes would have to consider the ecological impact of the acidified ocean stream.

5 Conclusions

It is the responsibility of the engineers that create and operate these processes to understand all of consequences of FGD. Seawater FGD provides an easy and efficient way to remove sulfur dioxide for sites that are located close to the sea which prevents harmful pollutants from entering the atmosphere. However, this process can increase the acidity of nearby seawater which could harm local ecosystems. The amount of sulfur dioxide in the atmosphere and the pH of seawater will need to be balanced so that the negative impact to the environment is minimal.

References

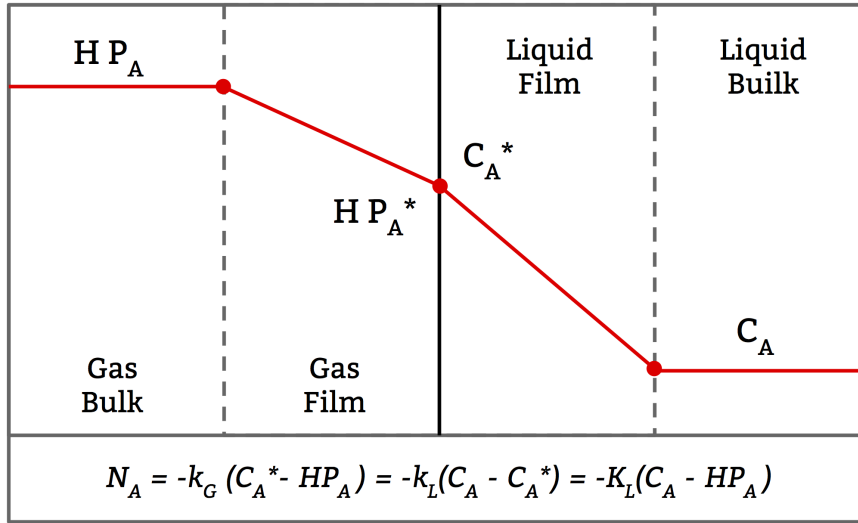
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A Simulation Values

<i>Parameter:</i>	<i>Value:</i>	<i>Source:</i>
β	0.05	n/a
A_{cs}	0.25 m ²	n/a
C_{A0}	0 mol / m ³	n/a
C_{B0}	10 ⁻⁵ mol / m ³ (pH of 8.0)	[2]
C_{E0}	2.3783 mol / m ³	[2]
d_p	1 mm	n/a
H	1260 mol / m ³ · atm	[1]
k	26.7 m ³ / mol · s	[3]
K_1	17.4 mol / m ³	[1]
K_2	6.24 × 10 ⁻⁵ mol / m ³	[1]
k_G	3.217 × 10 ⁻³ m / s	[4]
k_L	7 × 10 ⁻⁴ m / s	[4]
P_{A0}	0.0007 atm	[5]
Q_G	1 m ³ / s	n/a
Q_L	0.1 m ³ / s	n/a
R	8.20573 × 10 ⁻⁵ m ³ atm / mol · K	n/a
T	298.15 K	n/a

All code is available at <https://github.com/KieranFitzmaurice/CHE-400-Technical-Project>

B Two-Film Theory of Mass Transfer



Two-film model of gas-liquid mass transfer

The two-film theory of mass transfer assumes that between the well mixed bulk regions of liquid and gas, there exists stagnant films of thickness δ in where linear concentration profiles exist and no reaction occurs. The interface between the liquid and gas films are assumed to be in equilibrium and obey Henry's Law. From Fick's first law of diffusion, we can obtain the following expression for flux across the film:

$$\vec{N}_A = -k_G(C_A^* - HP_A) = -k_L(C_A - C_A^*)$$

$$k_G = \frac{D_{A(g)}}{\delta_G} \quad k_L = \frac{D_{A(l)}}{\delta_L}$$

By writing C_A^* in terms of bulk concentrations, we can obtain an overall expression for mass transfer

$$\vec{N}_A = -K_{MT}(C_A - HP_A) \quad K_{MT} = \left(\frac{1}{k_G} + \frac{1}{k_L} \right)^{-1}$$

C Countercurrent Iterative Procedure

At the liquid inlet of a countercurrent spray tower, the concentrations of C_A , C_B and C_E are specified; however, P_A is unknown, since the liquid inlet is at the same position as the gas outlet. In order to approximate the value of P_A at the liquid inlet, we provide an initial guess for the percent removal of SO_2 , η . This allows us to calculate a guess for P_A at the liquid inlet as follows:

$$P_A^{\text{guess}} = P_{A0}(1 - \eta^{\text{guess}})$$

where P_{A0} is the partial pressure of SO_2 in flue gas entering the tower. By integrating from the liquid inlet to the liquid outlet using this guess, we will end up with a calculated value of P_{A0} . Our boundary conditions are satisfied when this calculated value matches up with the actual value of P_{A0} . Let us define the following objective function:

$$f(\eta) = (P_{A0} - P_{A0}^{\text{calc}})^2$$

We can solve for the actual value of η by finding where our objective function is equal to zero. In our program, we accomplish this using Newton's method.

$$\eta^{k+1} = \eta^k - \frac{f(\eta^k)}{f'(\eta^k)}$$

The value of $f'(\eta)$ is computed numerically as follows

$$f'(\eta) = \frac{f(\eta + \Delta\eta) - f(\eta)}{\Delta\eta}$$

D Figures

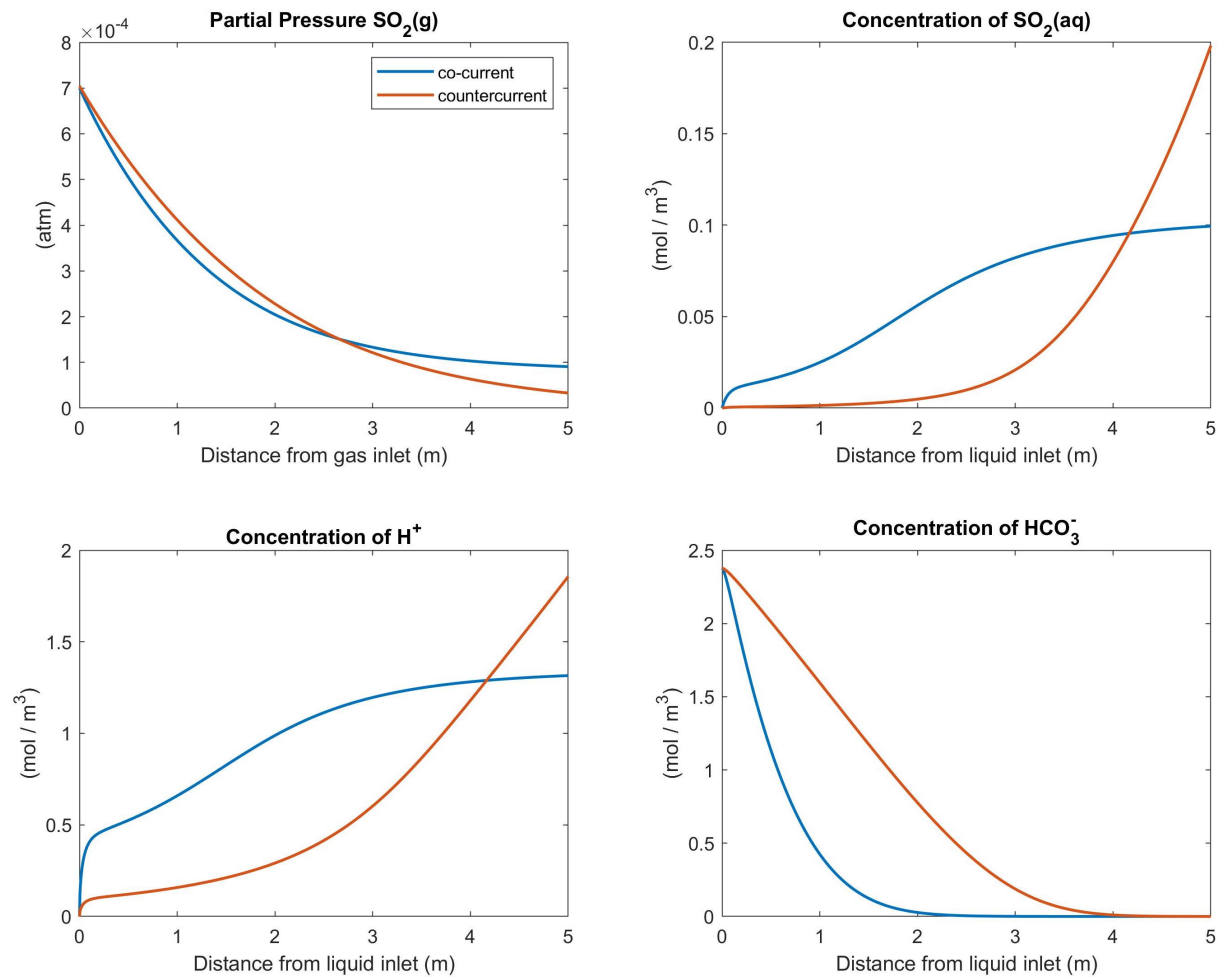


Figure 1: The partial pressure of $\text{SO}_{2(g)}$, and the concentrations of $\text{SO}_{2(aq)}$, H^+ , and HCO_3^- all as a function of distance from the gas or liquid inlet for co-current and countercurrent streams.

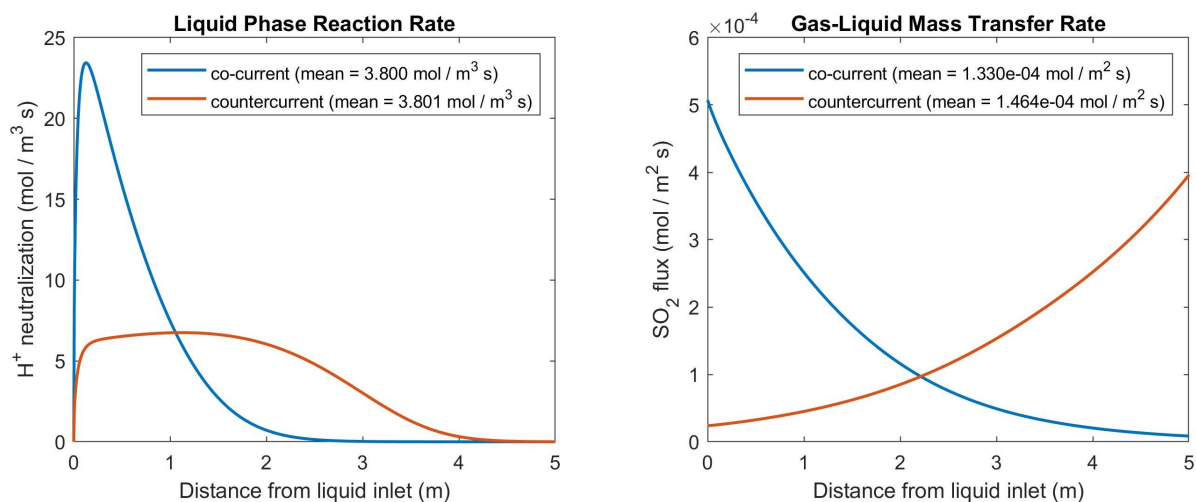


Figure 2: The liquid phase reaction rate and gas-liquid mass transfer rate as functions of distance from the liquid inlet for co-current and countercurrent streams.

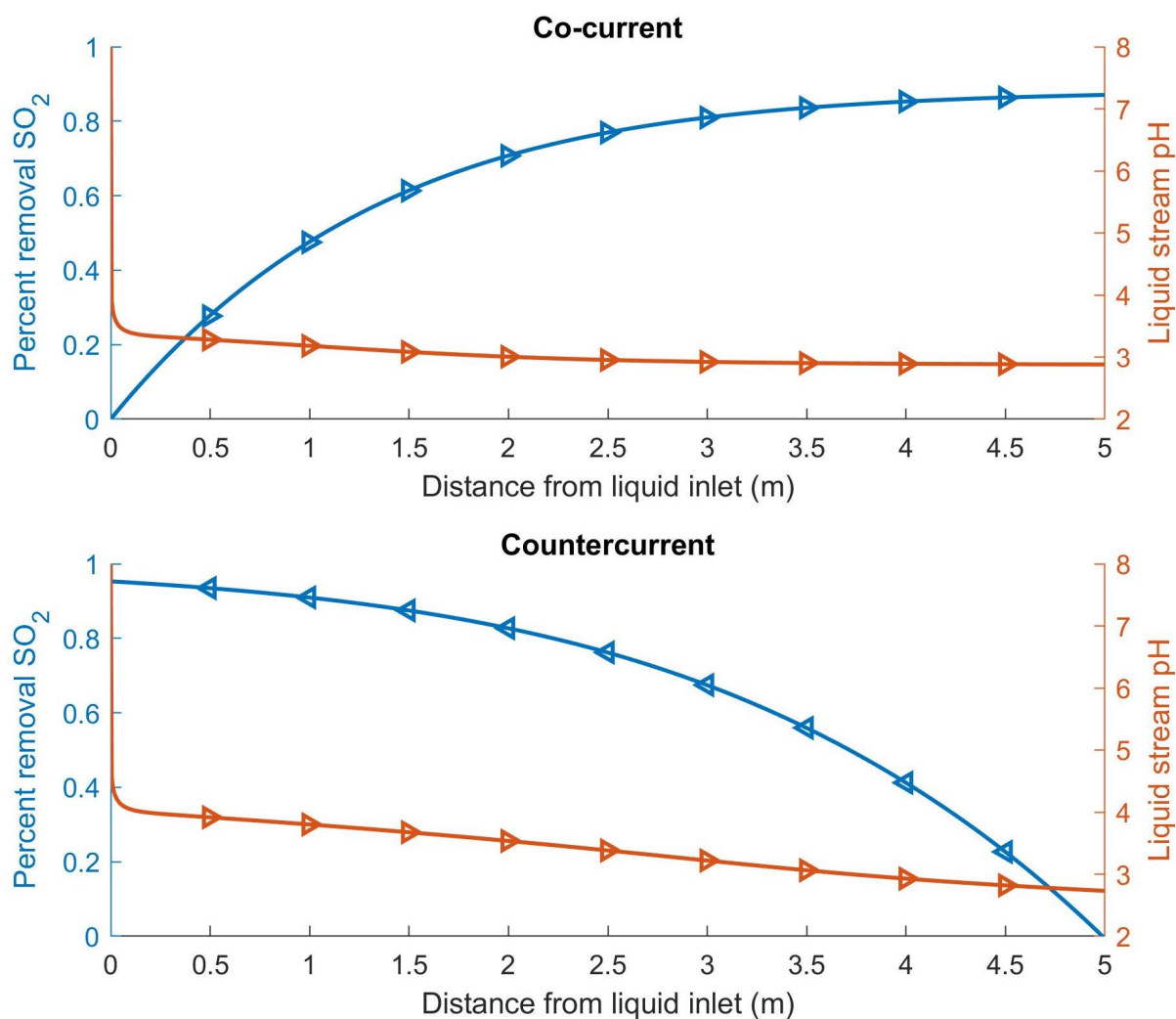


Figure 3: The pH and percent removal SO_2 of the reactors as functions of distance from the liquid inlet for co-current and countercurrent streams.