# Effects of Heat Exchanger Tubes on Hydrodynamics and $CO_2$ Capture of a Sorbent-based Fluidized Bed Reactor

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## Abstract

In virtual design and scale up of pilot-scale carbon capture systems, the coupled reactive multiphase flow problem must be solved to predict the adsorber's performance and capture efficiency under various operation conditions. This paper focuses on the detailed computational fluid dynamics (CFD) modeling of a pilot-scale fluidized bed adsorber equipped with vertical cooling tubes. Multiphase Flow with Interphase eXchanges (MFiX), an open-source multiphase flow CFD solver, is used for the simulations with custom code to simulate the chemical reactions and filtered sub-grid models to capture the effect of the unresolved details in the coarser mesh for simulations with reasonable accuracy and manageable computational effort. Previously developed filtered models for horizontal cylinder drag, heat transfer, and reaction kinetics have been modified to derive the 2D filtered models representing vertical cylinders in the coarse-grid CFD simulations. The effects of the heat exchanger configurations (i.e., horizontal or vertical tubes) on the adsorber's hydrodynamics and $CO_2$ capture performance are then examined. A one-dimensional three-region process model is briefly introduced for comparison purpose. The CFD model matches reasonably well with the process model while provides additional information about the flow field that is not available with the process model.

**Keywords**

Computational fluid dynamics, bubbling bed, carbon capture, model validation, multiphase reactive flow, filtered models

# 1 Introduction

In the United States, power generation accounts for about 37% of the total carbon dioxide ($CO_2$) emissions, the main culprit attributed to global warming. Within the electric power sector, coal-fired power plants are responsible for 71% of the overall $CO_2$ emissions. As stated in [1], "achieving substantial reductions in temperatures relative to the coal-based systems will depend on rapid and massive deployment of some mix of conservation, wind, solar, and nuclear, and possibly carbon capture and storage." Carbon capture and storage methods can afford continued use of fossil fuels while substantially reducing the amount of $CO_2$ emissions, which also could be part of an integrated strategy to stabilize global climate change. Most $CO_2$ capture processes involve absorbent (solvent), adsorbent (solid sorbent), and membrane-based technologies. Scientists at the National Energy Technology Laboratory (NETL) have developed amine-based solid sorbents [2] to capture $CO_2$ from post-combustion flue gas with reduced energy penalty, minimal water usage, negligible corrosion, and fewer anticipated operational issues [3].

For different capture technologies to be practically and effectively applied in reducing $CO_2$ emissions, the associated development-to-deployment cycle must be shortened and implementation costs decreased. In practical terms, technological improvements during the scale up process are critical for commercial viability within the power generation sector [4, 5]. To accelerate development and deployment of post-combustion carbon capture technology, the Carbon Capture Simulation Initiative (CCSI), a partnership between U.S. Department of Energy (DOE) national laboratories, industry, and universities, was created to improve state-of-the-art computational modeling and simulation tools that can be employed for efficient carbon capture [6].

Because typical solid sorbent-based capture devices are inherently complex chemical engineering systems that involve multiphase reacting flows, high-fidelity computational fluid dynamics (CFD) models have been developed and used by CCSI to simulate the coupled physical and chemical processes associated with sorbent-based carbon capture. In the current effort, the open-source code Multiphase Flow with Interphase eXchanges (MFiX: https://mfix.netl.doe.gov) is used to gain more insights into the flow field and reaction behaviors in the bubbling fluidized bed reactor. Because MFiX has been independently verified for various simple and small-scale multiphase reactive flow problems [7-9], the intention here is to use the computational framework to virtually scale up the reactor design to pilot scale to inform system-level designs and decision-making.

For a pilot-scale design, the physical size of the adsorber means that only coarse-grid MFiX simulations are possible at the device level. However, to accurately resolve the fine-scale particle clusters, grid sizes smaller than 10 particle diameters are necessary [10]. This would translate to more than six billion cells for a three-dimensional (3D) device-scale model or six million cells for a two-dimensional (2D) one, neither of which is computationally feasible for the desired time scales with the current software and hardware infrastructure. Alternatively, filtered sub-grid models have been introduced in coarse-grid CFD simulations to consider the effects of unresolved fine-scale flow heterogeneity and other characteristics [11-17]. For fluidized beds, the correction to gas-particle drag is especially significant [18].

The filtered gas-particle drag force generally is expressed as a correction to the microscopic drag model [19, 20], and the correction itself typically is a function of the solid fraction [17, 21] and gas-particle slip velocity [16]. Other hydrodynamic filtered corrections also are applied to the solids pressure and viscosity.

For a pilot-scale design, various cooling strategies must be implemented to negate the reaction-generated heat in the sorbent-based adsorber and regulate the bed temperature to ensure forward reaction. Typically, heat exchanger tubes in either horizontal or vertical configurations are employed, which add more computational difficulties to the device-scale CFD simulations. In the CCSI 1 MWe conceptual design, vertical cooling tubes have been selected because of better resistance to equipment corrosion and erosion compared to the horizontal design [22]. Although these tubes occupy a small overall volume (e.g., 0.64%), they have significant impact on the flow hydrodynamics as they exert direct drag on the suspension. Because cooling tubes (e.g., ~10 mm diameter) are too small to be resolved explicitly by the CFD grid resolution (e.g., ~18.5 mm), coarse-graining *filtered* models need to be developed to approximate the effective constitutive behaviors of the fine and unresolved flow characteristics [17, 21]. The filtered models for horizontal cooling tubes on hydrodynamics [17] and heat transfer [21] have been developed and implemented in the coarse-grid MFiX simulations to consider the detailed influences of these tubes on the adsorber performance.

In this study, we first develop filtered models for vertical cooling tubes called out in the CCSI 1 MWe conceptual design by quantitatively scaling down the filtered drag closure models previously developed for horizontal tubes. Second, we examine the effects of vertical heat exchanger tube configurations on the bed hydrodynamics and associated $CO_2$ capture efficiency via the improved filtered models. The CFD-predicted capture efficiencies at various flow rates then are compared and contrasted with results from the one-dimensional (1D) process model developed by CCSI's process modeling team.

The paper is organized as follows: Section 2 briefly describes the computational framework, which includes the 1 MWe pilot-scale adsorber conceptual design, open-source MFiX code, and associated carbon capture chemical reactions for the specific sorbent of interest. The section then focuses on improvements made to the horizontal cylinder filtered models in order to approximate the vertical tubes in the 1 MWe system. In Section 3, numerical implementation is briefly described, and the result comparisons from different tube configurations and operating conditions are presented, focusing mainly on hydrodynamics characteristics and the predicted $CO_2$ capture efficiency. Finally, the result comparisons between the CFD model and the CCSI-developed process model for a bubbling fluidized bed are presented. Section 4 features concluding remarks.

# 2 Computational Framework

## 2.1 1 MWe Pilot-scale Adsorber Conceptual Design

The details about the adsorber geometry and operating conditions have been fully described in [23] but will be briefly explained here. Figure 1(a) shows the schematic geometry and dimensions of the bubbling fluidized bed adsorber. Fresh sorbent particles enter the adsorber column from the top of the downcomer section and exit from the outlet on the right side, while hot $CO_2$-rich flue gas enters from the bottom of the adsorber and lean gas exits from the top ( Figure 1(b)). The simulation domain of the current study focuses on the lower stage (tray), which has a height of 6.88 m with the lower 5.88 m occupied by vertical heat exchanger tubes to improve $CO_2$ adsorption by cooling the flue gas and effectively removing the heat generated by the exothermic adsorption reactions. These tubes extend well above the bed's top surface (~1 m) into the freeboard area. As illustrated in Figure 1(b), the cooling tubes have a diameter of 0.01 m, and their spacing is 0.111 m. The overall volume fraction of the cooling tubes is about 0.64%.

## 2.2 CFD Formulations of Reactive Multiphase Flow

The open-source two-fluid model (TFM) of MFiX was used to conduct all simulations in this study (https://mfix.netl.doe.gov/). The TFM framework is an Eulerian-Eulerian formulation where the gas and solid phases are treated as interpenetrating continua. Interphase momentum, energy, and mass transfer are achieved through empirical and theoretical models. Constitutive relations for the solid phase are formulated such that any flow regime, from dilute to dense granular flows, can be accurately simulated. While a Lagrangian particle-based approach can offer a more physically accurate representation of multiphase systems, the TFM was preferred for this study because of its superior computational efficiency and existing filtered models for large-scale simulations [14, 17, 21].

The full set of governing equations solved in MFiX [24], as well as the additional details about multiphase flow theory and the associated numerical techniques employed in MFiX [25] will not be repeated here. Instead, because custom filtered models are also being employed, the modified filtered governing equations are listed here. Continuity equations for gas phase and solid phase m are

$$\frac{\boldsymbol{\partial}}{\boldsymbol{\partial t}}\left(\bar{\Phi}_g \boldsymbol{\rho}_{\boldsymbol{g}}\right) + \boldsymbol{\nabla} \cdot \left(\bar{\Phi}_g \boldsymbol{\rho}_{\boldsymbol{g}} \widetilde{\boldsymbol{V}}_{\boldsymbol{g}}\right) = \sum_{n=1}^{N_g} R_{gn} \tag{1}$$

$$\frac{\partial}{\partial t}(\bar{\Phi}_m \rho_m) + \nabla \cdot (\bar{\Phi}_m \rho_m \tilde{\boldsymbol{V}}_m) = \sum_{n=1}^{N_m} R_{mn} \tag{2}$$

where $\rho$ is density, $\bar{\Phi}$ is filtered phase-fraction, $\tilde{\boldsymbol{V}}$ is filtered phase-velocity, $R_n$ is the generation rate for species $n$, and $g$ and $m$ are subscripts denoting gas or $m^{\text{th}}$ solid phase, respectively. The filtered phase-fraction is defined in terms of the microscopic phase-fraction $\bar{\phi}$ and the cylinder volume-fraction $\bar{\Phi}_c$ [17]

$$\bar{\Phi}_g = (1 - \bar{\Phi}_c)\bar{\phi}_g \,, \qquad \bar{\Phi}_m = (1 - \bar{\Phi}_c)\bar{\phi}_m \tag{3}$$

Similar to the continuity equations, the momentum (Eq. 4-5) and energy (Eq. 6-7) governing equations are re-written with filtered variables

$$\frac{\partial}{\partial t}(\bar{\Phi}_g \rho_g \tilde{\boldsymbol{V}}_g) + \nabla \cdot (\bar{\Phi}_g \rho_g \tilde{\boldsymbol{V}}_g \tilde{\boldsymbol{V}}_g) = -\bar{\Phi}_g \nabla \cdot \bar{\boldsymbol{\Sigma}}_g - \bar{\boldsymbol{\mathcal{F}}}_{g.m} + \bar{\Phi}_g \rho_g \boldsymbol{g} \tag{4}$$

$$\frac{\partial}{\partial t}(\bar{\Phi}_m \rho_m \tilde{\boldsymbol{V}}_m) + \nabla \cdot (\bar{\Phi}_m \rho_m \tilde{\boldsymbol{V}}_m \tilde{\boldsymbol{V}}_m)$$
$$= -\bar{\Phi}_m \nabla \cdot \bar{\boldsymbol{\Sigma}}_g - \nabla \cdot \bar{\boldsymbol{\Sigma}}_m + \bar{\boldsymbol{\mathcal{F}}}_{g.m} + \bar{\boldsymbol{\mathcal{F}}}_{c.gm} + \bar{\Phi}_m \rho_m \boldsymbol{g} \tag{5}$$

$$\frac{\partial}{\partial t}(\bar{\Phi}_g \rho_g C_{p,g} \tilde{\Theta}_g) + \nabla \cdot (\bar{\Phi}_g \rho_g C_{p,g} \tilde{\boldsymbol{V}}_g \tilde{\Theta}_g) = \nabla \cdot (\bar{\Phi}_g k_g \nabla \tilde{\Theta}_g) + H_{gs} + \bar{Q}_{cg} \tag{6}$$

$$\frac{\partial}{\partial t}(\bar{\Phi}_g \rho_g \tilde{\boldsymbol{V}}_g) + \nabla \cdot (\bar{\Phi}_g \rho_g \tilde{\boldsymbol{V}}_g \tilde{\boldsymbol{V}}_g) = -\bar{\Phi}_g \nabla \cdot \bar{\boldsymbol{\Sigma}}_g - \bar{\boldsymbol{\mathcal{F}}}_{g.m} + \bar{\Phi}_g \rho_g \boldsymbol{g} \tag{7}$$

$$\frac{\partial}{\partial t}\left(\bar{\Phi}_m \rho_m C_{p,m} \tilde{\Theta}_m\right) + \nabla \cdot \left(\bar{\Phi}_m \rho_m C_{p,m} \tilde{\boldsymbol{V}}_m \tilde{\Theta}_m\right)$$ (8)

$$= \nabla \cdot \left(\bar{\Phi}_m k_m \nabla \tilde{\Theta}_m\right) - \sum_{m=1}^{M} H_{gm} + \bar{Q}_{cm}$$

where $\bar{\boldsymbol{\Sigma}}$ is the filtered phase-stress, $\bar{\boldsymbol{\mathcal{F}}}_{g.m}$ is Igci's interphase drag model [14], $\bar{\boldsymbol{\mathcal{F}}}_{c.gm}$ is Sarkar's cylinder-suspension drag model [17], $C_p$ is specific heat capacity, $\tilde{\Theta}$ is the filtered temperature, $k$ is thermal conductivity, $H_{gm}$ is the interphase heat transfer given by the Gunn correlation [26], and $\bar{Q}_{cg}$ and $\bar{Q}_{cm}$ are Lane's cylinder-gas and cylinder-suspension heat transfer models, respectively [21]. Because there are no existing TFM filtered models for the species transfer, the default microscopic MFiX equations were used [24],

$$\frac{\partial}{\partial t}\left(\phi_g \rho_g X_{gn}\right) + \nabla \cdot \left(\phi_g \rho_g \tilde{\boldsymbol{V}}_g X_{gn}\right) = \nabla \cdot \left(\boldsymbol{D}_{gn} \nabla X_{gn}\right) + R_{gn}$$ (9)

$$\frac{\partial}{\partial t}\left(\phi_m \rho_m X_{mn}\right) + \nabla \cdot \left(\bar{\phi}_m \rho_m \tilde{\boldsymbol{V}}_{\boldsymbol{m}} X_{mn}\right) = \nabla \cdot \left(\boldsymbol{D}_{mn} \nabla X_{mn}\right) + R_{mn}$$ (10)

where $X_n$ is species-fraction for species $n$ and $\boldsymbol{D}_n$ is the diffusion tensor. Kinetic theory requires an additional governing equation for each solid phase to quantify the energy of the solid particles: the granular energy (or temperature) [27]. Instead of solving the full conservative PDE for granular energy, the algebraic approximation by Syamlal, Rogers, and O'Brien [24] was used to further reduce computation time,

$$\mathbf{\Theta}_m = \left\{ -\frac{K_{1m}\phi_m \mathrm{tr}(\boldsymbol{D}_m) + \sqrt{K_{1m}^2 \mathrm{tr}(\boldsymbol{D}_m)^2 \phi_m^2} + 4K_{4m}\phi_m \left[K_{2m}\mathrm{tr}(\boldsymbol{D}_m)^2 + 2K_{3m}\mathrm{tr}\left(\boldsymbol{D}_m^2\right)\right]}{2\phi_m K_{4m}} \right\} \tag{11}$$

where $\mathbf{\Theta}_\mathrm{m}$ is granular energy, $K_{1m}$-$K_{4m}$ are granular stress constants [24], and $\boldsymbol{D}_m$ is the rate of strain tensor. The modified Princeton model [28] provides constitutive equations for kinetic theory (e.g., solids stresses, pressure, and viscosity). Frictional stresses are calculating using the Schaeffer model [29] and the Yu-Standish correlation [30] is used to calculate maximum packing of the solids.

The simulations were run using a variable time-step algorithm to maximize step size while maintaining stability. The time-step was limited to $10^{-8}$–$10^{-2}$ s and a maximum of 50 iterations. The algebraic turbulence model [31] was enabled with a length scale of 0.13 m and a maximum turbulent viscosity of 50 kg/ms. All governing equations were discretized using a first-order upwinding scheme and solved using the biconjugate gradient stabilized method. Default under-relaxation factors described in MFiX Users Guide [32] were used except to overcome convergence and stability problems.

A first-order chemistry model for chemical kinetics is used to model the adsorption and desorption of $CO_2$ and water vapor onto amine-based sorbent particles of type NETL-32D, developed at NETL [33]. The reactive model is integrated with MFiX through custom code following the specification outlined in the MFiX User Guide [32]. The chemical reactions considered in the current kinetics model include [34, 35]:

1) Reaction of $CO_2$ with the impregnated amine to form carbamate, i.e., dry adsorption
2) Reaction of $CO_2$, physisorbed $H_2O$, and amine to form bicarbonate, i.e., wet adsorption
3) Physical adsorption of $H_2O$ to the sorbent, i.e., water physisorption.

Equations for the three respective reactions are written as:

$$2\mathrm{R}_2NH + CO_2(g) \leftrightarrow R_2NCO_2^- + R_2NH_2^+ \tag{12}$$

$$\mathrm{R}_2NH + H_2O(phys) + CO_2(g) \leftrightarrow HCO_3^- + R_2NH_2^+ \tag{13}$$

$$H_2O(g) \leftrightarrow H_2O(phys) \tag{14}$$

In each of the preceding equations, the reaction rates and equilibrium constants are represented by four parameters, rendering a total of 12 parameters obtained from thermogravimetric analysis (TGA) [33] — all of which have been obtained with a probabilistic distribution (described in [36]). In the current study, only the mean values of those 12 parameters will be used. It should be pointed out that due to sorbent deactivation and degradation [37, 38], the actual chemical reactions of the amine base sorbent are more complicated than the above equations and the parameters for the reaction rate and equilibrium can describe. However, this is beyond the scope and will not be discussed further in this paper.

## 2.3 Filtered Models for Vertical Heat Exchanger Tubes

The application of filtered models for drag in coarse-grid device-scale CFD simulations has proven to be critical for accurately capturing the bed expansion and other hydrodynamic characteristics of a fluidized bed reactor [13,14,17]. Filtered models for drag and heat transfer have been developed for horizontal exchanger tubes, which is chronicled in the literature [17, 21]. In the 1 MWe pilot-scale adsorber design, the presence of vertical heat exchanger tubes adds more complexity to the development of filtered models. Filtered models for vertical heat exchanger tubes are not yet available because of the difficulties in creating a numerical simulation volume representing the arrays of vertical tubes and the computational intensity of the associated highly resolved 3D simulations. This section discusses the development of filtered models for vertical tubes created by modifying the literature-reported filtered models for horizontal tubes.

The effect of heat exchanger tubes on gas-solid flow was mainly accounted for through the filtered cylinder suspension drag and filtered gas-solid drag. The cylinder suspension drag characterizes the hindrance from heat exchanger tubes, while the filtered gas-solid drag stems mainly from the presence of internal structures affecting the relative motion between gas and particles. A recent computational study with highly resolved 3D simulations of vertical tubes [39] suggests that the suspension drag exerted on the flow by the vertical cylinders is much lower than that of horizontal cylinders as the gas-particle flow moves parallel to the vertical cylinders. This is primarily due to the fact that clustering of particles and bubbles tends to rise along the vertical tubes, allowing gas to bypass and encouraging further gas-particle separation. As suggested in [22], vertical tubes tend to divide the bed into a number of parallel longitudinal compartments standing side by side, making it easy for channeling and gushing to occur due to the inability to break down bubbles. Therefore, the presence of vertical cylinders should lead to gas-solid drag reduction when compared to that in the same reactor with horizontal cylinders.

The results in Figure 2 [39] indicate that the filtered drag coefficient with vertical heat exchanger tubes (black symbols) is considerably lower than those developed earlier for gas-particle flow with horizontal tubes (pink curve) because of their differences in particle clustering. Significant reduction in drag is observed for vertical tubes, particularly at high solids fraction, which stems from the formation and splitting of bubbles rising along the tube length that allow gas to bypass. Based on the results in Figure 2, a solid fraction ($\Phi_s$)-dependent correction factor $H$ is introduced to the previously reported horizontal cylinder filtered model [17] to quantitatively scale down the drag between gas and particles, and the value of $H$ is numerically obtained with the results shown in Figure 2. This is expected to change the predicted fluidized bed behavior and yield a less-well-mixed pattern in the bubbling bed.

Similar filtered models have been developed in [21] to account for the cooling effect of the horizontal heat exchanger tubes through additional source terms in the governing energy equations solved by coarse-grid simulations. The model takes the form of a Nusselt correlation, which is analogous to single-phase flow, but includes the effects of the solids phase, such as density, particle diameter, thermal conductivity, specific heat capacity, solids fraction, and velocity. Without specific filtered models for heat transfer with vertical cylinders, this filtered model is used in the current simulations.

In addition to the filtered drag and heat transfer with the presence of heat exchanger tubes, filtered models with scaled transport are also needed in the coarse-grid simulations to account for the effect of unresolved flow structures, i.e., small bubbles and particle clusters [40, 41]. The filtered models, including diffusivity and interphase heat/mass transfer coefficients, developed in [41] have been adopted in the current study. Specifically, the filtered model for the mass transfer coefficient is directly applied to the reaction rate calculation as the current reaction kinetics for $CO_2$ capture lumps everything together. It should be noted that the filtered models for interphase heat and mass transfer were developed from high-resolution simulations of gas-solid flow without internals. Hence, it is possible that the presence of internals may have certain impacts on these quantities. Further studies are needed to quantify the effect of vertical tubes to develop better filtered models but are beyond the scope of the current study.

## 2.4 MFIX Model Setup, Boundary, and Initial Conditions

A 2D MFiX model similar to those described in [23] is developed for the 1.33 m × 6.88 m adsorber column. The entire domain is discretized into 72 × 372 grids. As shown in Figure 1(c), the solids inlet is modeled as a mass flow inlet at the top-left corner of the adsorber column. The gas that occupies the interstices between the entering solid particles is assigned an inlet velocity comparable to that of the solids. The corresponding solids outlet on the right side is specified as a constant pressure/temperature mass outflow outlet in MFiX.

The flue gas inlet is located at the bottom of the adsorber column and described with a mass inflow boundary condition, where the flow rate is a controllable parameter. The gas exits the adsorber from the top of the column, where a constant pressure outlet is used. To prevent sorbents from leaving the top outlet, a semi-permeable membrane is applied to allow only the gas phase to pass through. Figure 1(b) summarizes the solid and gas inlets and outlets in the conceptual design. Sorbent particles enter through the downcomer to the fluidized bed region, where most chemical reactions and heat transfer occur, and exit from the solid outlet at a height of 4.773 m (shown as B.C. 4 in Figure 1(d)). The flue gas flows into the fluidized bed from the bottom distributor plate and exits from the gas outlet at the top of the adsorber.

In the MFiX model, the regions with heat exchanger cylinders are modeled by a porous media, an additional solid phase (besides the solid phase for sorbent particles) with the equivalent volume fraction as the vertical tubes as shown in Figure 1(c). Different filtered models for drag are used in separate regions of the model. For the upper region without cooling tubes, the standard gas-particle filtered model [21] is used. For the lower region with vertical cooling tubes, the *H*-factor corrected drag (discussed earlier) is used. The cylinder-suspension heat transfer in this region is modeled with the filtered heat transfer relationships developed in [21], which accounts for the cooling effects of the tubes in the region that is modeled as a porous solids phase. Note that in the 2D cylinder drag and heat transfer filtered models, the tube configuration is reduced into one single variable—the volume fraction of the tubes—that accounts for the integrated effect of the tube size and number of tubes.

Figure 1(c) and 1(d) illustrate the initial and boundary conditions in the MFiX simulation. Two internal surfaces at the top and bottom are used to mimic the distributor plate and the membrane to prevent the sorbent outflow, respectively. A mixture of gases initially fills the adsorber column with all field variables (pressure, temperature, and composition) specified for the gas phase for all three regions labeled as "initial conditions." The only difference among the three regions is the void fraction due to the presence of the heat exchanger tubes. It has been observed that the initial conditions do not have any impact on the final steady-state results, although they do have some influence on how the simulation reaches steady state.

Operating conditions needed for the boundary conditions include the gas phase parameters (flow rate, pressure, temperature, and composition) for the gas inlet (B.C. 1 in Figure 1(d)) and solid phase parameters (flow rate, temperature, and composition) for the solid inlet (B.C. 2 in Figure 1(d)). Detailed initial and boundary conditions have been presented in detail as part of our earlier work [23] and will not be repeated here.

# 3 Numerical Implementation, Results, and Discussions

## 3.1 Details of Numerical Implementation

Custom MFiX CFD simulations of the 1 MWe system have been performed at five different gas flow rates: 0.36, 0.48, 0.60, 0.72, and 0.84 kg/s. Each simulation is run for at least 100 additional seconds after a statistical steady state is reached. In this highly dynamic fluidized bed simulation, a statistical steady state is considered achieved if the fluctuation of moving averages of the key quantities of interest (QOIs) does not exceed 10% when different averaging windows are used. Ample time (100 seconds in this case) after reaching the maximum bed height is necessary to confirm stability and to provide adequate time windows to obtain the moving averages for key QOIs. A typical parallel simulation with 20 processors takes three to five days to complete the 450-second simulation on PNNL's Institutional Computing (PIC) high-performance computer clusters, and the actual time for each case depends on the flow rate and other conditions. As discussed in [23], the computational cost is heavily influenced by the chemical reaction parameters, and the computational cost can be quite high when the combination of parameters makes the reactive system stiff. In the current study with the mean values of the chemical reaction parameters, extremely stiff chemistry has not been encountered.

The posterior mean values of the 12 parameters for chemical reactions obtained earlier in [36] are used in the simulations, because the same amine-based sorbent is used. Similarly amine molar fraction and particle size are set to their posterior means of 0.1438 and 117.90

μm, respectively. The nominal simulations represent the adsorber behavior under typical operating conditions.

The QOIs pertinent to a $CO_2$-capturing fluidized bed include voidage, temperature, pressure, and species compositions of gas and solid. Figure 3 depicts the spatial distribution of voidage, gas phase temperature, and $CO_2$ mass fraction at t = 600 seconds for flow rate 0.60 kg/s. The abrupt increase in void fraction in Figure 3(a) indicates the fluidized bed's range with chemical adsorption of $CO_2$ mostly occurring at the bottom of the adsorber with little $CO_2$ in the freeboard region. In particular, the void fraction distribution, or equivalently, the volume fraction of sorbent particles, can be used to compute the fluidized bed height. For example, the bed height is determined at the location where void fraction reaches a critical value of 0.95 in the current study. Figure 3(b) plots the gas phase temperature distribution, where the bottom of the fluidized bed has a relatively higher temperature because of the heat generated from the exothermic adsorption reaction. Figure 3(c) presents the distribution of $CO_2$ mass fraction, where most $CO_2$ adsorption occurs at the bottom of the adsorber column at the given gas flow rate of 0.60 kg/s.

The most important QOI for any carbon capture device is its overall capture efficiency. The capture efficiency is calculated as the ratio of the total amount adsorbed over the total $CO_2$ flow rate. Because the inlet gas flow rate and $CO_2$ mass fraction are fixed, the total $CO_2$ captured at steady state can be calculated by subtracting the inlet amount with the sum of the $CO_2$ leaving the fluidized bed from the two exits. Alternatively, the $CO_2$ captured can also be indirectly calculated by the sorbent composition and flow rate leaving the exits. Our post-processing calculations indicate that the total $CO_2$ captured computed with these different methods yields the same value when the moving average is used for each calculation. However, the details will not be shown here.

## 3.2 Effects of Tube Configurations on Hydrodynamics and Associated $CO_2$ Capture

Along with the filtered models for horizontal tubes featured in the literature [17, 21] and the filtered models for vertical tubes discussed in Section 2.3, we examine the effects of heat exchanger tube configurations, i.e., horizontal or vertical, on the flow and $CO_2$ capture of the 1 MWe adsorber. The QOIs studied include voidage, gas and particle vertical velocities, and temperature distributions in the fluidized bed.

Figure 4(a) and (b) show the snapshots of voidage contours in fluidized beds at a gas flow rate of 0.84 kg/s for the two different tube configurations, respectively. On the left of the horizontal tubes, the voidage contours in Figure 4(a) illustrate a well-mixed fluidized bed, while on the right in Figure 4(b), the bed with the vertical tubes shows much higher degrees of flow heterogeneity. The alignment of regions with high void fractions suggests that gas may go through the fluidized bed with more channeling. On the other hand, more isolated dark blue regions are also observed in the contours on the right with vertical tubes, suggesting higher degrees of solid clustering. Note that the application of the gas-solid drag closures in the Eulerian-Eulerian TFM in MFiX means that actual bubbles cannot be explicitly resolved. This is fundamentally different from the “bubbles” used in the process model to simulate the reduction of capture efficiency due to actual large gas bubbles or gas channeling. Section 3.4 will examine the details regarding such comparison.

Figure 5(a) and (b) show the gas phase vertical velocity, and Figure 5(c) and (d) show slip velocity contours between the gas and solid phase for the two tube configurations, respectively. The comparisons of vertical velocity contours shown in Figure 5(a) and (b) provide more insights on the fundamental differences in the flow characteristics between the two tube configurations—a key factor limiting fluidized bed performance that cannot be captured by process models. On the left of the horizontal tubes, the gas velocity distribution for the fluidized bed looks more even with the maximum upward gas velocity around 3.4 m/s. On the right, the maximum upward gas velocity reaches 4.3 m/s for the bed with vertical tubes. In addition to higher gas velocity, Figure 5(b) also shows a larger connected red region with relatively high gas upward velocity, indicating possible gas channeling and gushing with the vertical tubes. The predicted downward gas velocity near the adsorber wall also is higher for the bed with vertical tubes. Note that at the gas flow rate of 0.84 kg/s, the average inlet gas velocity is around 0.43 m/s. Figure 5(c) and (d) show the contours of vertical slip velocity, or the difference between the vertical velocities of the gas and solid phases at the same location. With the vertical tubes, the solid particles experience more extreme vertical velocity, and the velocity difference between solid and gas, or slip velocity, also shows more disparity. This means that considering the distributions of both voidage and gas velocity, the fluidized bed with the vertical tubes will experience higher degrees of flow heterogeneity and less gas-solid contact compared to the bed with horizontal tubes.

It is well established that flow heterogeneity leads to poor interphase mass transfer and chemical reactions. As shown in Figure 6, the overall adsorber $CO_2$ mass fraction contour for the vertical tube is higher compared to the case on the left with horizontal tubes because more $CO_2$-rich gas channels through the bed with higher velocity, leaving less time for reaction and mass transfer. Figure 7 depicts the corresponding temperature contours in the fluidized beds for the two tube configurations. Because the bed with horizontal tubes has better mixing and a lower degree of gas channeling, a higher gas temperature profile is predicted as additional heat is generated when more $CO_2$ is captured. A similar comparison has been observed for other gas flow rates: 0.36, 0.48, 0.60, and 0.72 kg/s. Those details will not be repeated here.

## 3.3 Effects of Gas Flow Rates

This section describes the quantitative examination of the effects of gas flow rate on the degree of flow heterogeneity for the adsorber with vertical heat exchanger tubes. As the gas flow rate increases, the average gas velocity increases proportionally.

Figure 8 compares the voidage distributions for flow rates of 0.60 kg/s and 0.84 kg/s. As expected, a lower gas flow rate yields more evenly distributed void and solid clustering with less tendency for large bubble formation and gas channeling. For illustrative purposes and more direct comparisons, Figure 9 shows the pseudo bubble distribution for three different gas flow rates. Here, a *pseudo bubble* is defined as the region with voidage fraction (EP_g)>0.83 in the predicted void fraction contours. As expected, a higher flow rate increases both the number and size of the pseudo bubbles. Figure 10 compares the gas vertical velocity profiles for the two flow rates. At the higher flow rate, higher gas vertical velocity is predicted, indicating more channeling and gushing. Higher gas velocity and channeling through the bed lead to a shorter resident time, resulting in fewer opportunities for the gas to be mixed well and react with the sorbent and leading to a lower overall $CO_2$ capture efficiency (refer to the green curve in Figure 11). The blue curve in Figure 11 depicts the overall $CO_2$ captured by the fluidized bed as a function of flow rate. For a higher gas flow rate, although the $CO_2$ capture efficiency decreases, the overall amount of $CO_2$ captured in molar rate increases. This is because more $CO_2$-rich gas is available for the same amount of sorbent to react, and the solids leaving the adsorber from the side exit are expected to be more amine-depleted.

### 3.4 Comparison with Process Model

Currently, no available experimental data for a pilot-scale device similar to the 1 MWe system studied here are available in the literature for model validation. Instead, the results generated by the CCSI process modeling team on the same system [42] are used to compare and contrast with the CFD modeling results. Because the process modeling results also depend on the parameters used in the model, the goal here is to offer some insights on the key parameters that influence bed behaviors and $CO_2$ capture.

When the gas velocity continuously increases beyond the minimum fluidization velocity, the bed falls into different fluidized bed regimes: uniform expansion bed, bubbling bed, turbulent fluidization, and fast fluidization. The 1D three-region process model [42] focuses solely on the bubbling and turbulent regions, i.e., between the onset of bubble formation and the transition to fast fluidization, based on the work in [43]. Three distinct regions are considered in the bubbling bed: bubble region, cloud-wake region, and the emulsion region. The bubble region represents rising, mostly solid free voids that pass through the bed. Each bubble carries with it a wake of solids that are drawn up behind the bubble, and has a surrounding "cloud" of gas-solids suspension with which it interacts. The remained of the bed is represented by the emulsion region, which contains a relatively dense suspension of gas and solids and near-minimum fluidization conditions.

The mass and energy balances for the gas and solid species within the bed were modeled using a system of partial differential-algebraic equations, with variation considered only in the axial (vertical) direction. In order to simplify the model equations, it was assumed that the axial flow of gas occurred predominantly through the bubble region and that axial gas flow through the cloud-wake and emulsion regions could be neglected. It was also assumed that the presence of solids within the bubbles was negligible, thus the reaction between gas and solids occurs only in the cloud-wake and emulsion regions. This resulted in the following set of mass balances for the gas phase.

$$0 = -\frac{\partial}{\partial x} y_{b,j,x} G_{b,x} - \delta_x A_X K_{bc,j,x} \left( C_{b,j,x} - C_{c,j,x} \right) + K_{g,bulk,j,x} \tag{15}$$

$$0 = \delta_x A_X K_{bc,j,x} \left( C_{b,j,x} - C_{c,j,x} \right) - \delta_x A_X K_{ce,j,x} \left( C_{c,j,x} - C_{e,j,x} \right) + \alpha_x \delta_x \left( 1 - \varepsilon_{d,x} \right) A_X r_{g,c,j,x} \tag{16}$$

$$0 = \delta_x A_X K_{ce,j,x} \left( C_{c,j,x} - C_{e,j,x} \right) - K_{g,bulk,j,x} + \left( 1 - \alpha_x \delta_x - \delta_x \right) \left( 1 - \varepsilon_{d,x} \right) A_X r_{g,e,j,x} \tag{17}$$

Here $G_{b,x}$ is the total axial molar flow rate of gas via the bubble region at height $x$, $y_{b,j,x}$ is the mole fraction of gaseous species $j$ in the bubble region at height $x$, $C_{r,j,x}$ is the molar concentration of species $j$ in region $r$ (b = bubble, c = cloud-wake, e = emulsion), $A_X$ is the cross-sectional area of the fluidized bed, $\delta_x$ is the volume fraction of the bed occupied by the bubble region and $\alpha_x$ is the volume ratio of the cloud-wake to bubble regions at height $x$, $\varepsilon_{d,x}$ is the voidage of the dense emulsion, $K_{bc,j,x}$ and $K_{ce,j,x}$ are mass transfer coefficients for species $j$ between regions, $K_{g,bulk,j,x}$ is the bulk transfer of species $j$ between the emulsion and bubble regions due to pressure differences and $r_{g,r,j,x}$ is the rate of reaction of gaseous species $j$ in region $r$. Similar equations can be developed for the gas phase energy balances, however these will not be reproduced here. Readers are directed to [42] for further details. As each bubble rises through the bed it carries with it a significant wake of solids, resulting in an upward flux of solids throughout the bed in the cloud-wake region, thus a corresponding downward flux of solids must occur in the emulsion region. For this system, it was assumed that the solid sorbent consisted of an inert substrate plus adsorbed gaseous species, which resulted in the following set of mass balances for the solid phase.

$$\frac{\partial J_{c,x}}{\partial x} = \frac{\partial J_{e,x}}{\partial x} \tag{18}$$

$$0 = -\frac{A_X}{\rho_s}\frac{\partial}{\partial x} J_{c,x} n_{c,i,x} - K_{s,bulk,x} - A_X \delta_x K_{ce,bs,x}\left(n_{c,i,x} - n_{e,i,x}\right) + A_X \alpha_x \delta_x \left(1-\varepsilon_{d,x}\right) r_{s,c,i,x} \tag{19}$$

$$0 = -\frac{A_X}{\rho_s}\frac{\partial}{\partial x} J_{e,x} n_{e,i,x} + K_{s,bulk,x} + A_X \delta_x K_{ce,bs,x}\left(n_{c,i,x} - n_{e,i,x}\right) + A_X \left(1-\alpha_x\delta_x - \delta_x\right)\left(1-\varepsilon_{d,x}\right) r_{s,e,i,x} \tag{20}$$

Here $J_{c,x}$ and $J_{e,x}$ are the superficial mass flux of the inert substrate material at height $x$ (note that $J_{e,x}$ is defined as being downwards), $n_{r,i,x}$ is the loading (mol species per kg inerts) of adsorbed species $i$ in region $r$, $\rho_s$ is the density of the solid particles, $K_{ce,bs,x}$ is a mass transfer coefficient relating to mixing of solids between the cloud-wake and emulsion regions, $K_{s,bulk,x}$ is the bulk transfer of solids between the cloud-wake and emulsion regions due to changes in cloud-wake volume and $r_{s,r,i,x}$ is the rate of reaction of adsorbed species $i$ in region $r$ at height $x$. Again, a similar set of energy balances can be developed but will not be reproduced here. Transfer and mixing of gas and solids between the different regions was modeled using theoretical predictions based on the interaction of the rising bubbles with the emulsion and gas phase diffusion.

The predicted behavior and performance of the model is primarily dependent of the hydrodynamics of the rising bubbles, which stems from the correlations used to predict the bubble size and velocity. The correlations for the bubble size were drawn from the work of Horio and Nonaka [43], which were used to predict the bubble velocity based on correlations proposed by Kunii and Levenspiel [44] based on the bench scale experimental observations of Hilligardt and Werther [45].

As these correlations were developed from experimental data from small bench scale apparatus (diameters of less than 1m), there is significant uncertainty associated with scaling up these correlations to larger industrial scale beds. In order to examine the effects of these correlations on the behavior of the model, a scaling parameter, *sf*, was added to the correlation for bubble diameter, which scales the bubble diameter proportionally. For the current example, at the top of the fluidized bed the predicted bubble diameter is *0.15m* for *sf=0.6*, *0.20m* for *sf=0.8*, and *0.25m* for *sf=1.0*. Because bubble velocity increases with bubble diameter, intuitively, the larger the bubble size, the lower the overall capture efficiency, as evidenced in Figure 12.

It should be pointed out that the process model differs from the MFiX-based CFD model in many aspects. One of the most important differences stems from the fact that in the process model, all of the axial transport of the $CO_2$-rich gas through the bed occurs via the bubbles, which have very poor contact with the solids. The gas in contact with the solids is only renewed through mass transfer phenomena between the bubbles and the emulsion due to a mix of bubble motion and diffusion. This means that the gas in contact with the solids ends up being depleted of $CO_2$, which greatly reduces the rate of reaction. In the MFiX-based reactive multiphase flow CFD model, the sorbent and gas mixing and associated adsorption reaction equations are solved in a coupled manner, and the results are the spatial and temporal distributions of the voidage and solid fractions throughout the bed. Because the gas and solid phases are treated as two interpenetrated phases, no bubbles with the strict numerical definition of void fraction=1 exist in the CFD results which is more consistent with the experimental evidences. Rather, gas-rich pseudo bubble regions can be illustrated, like those in Figure 9. The dynamic distributions of voidage, as well as the gas and sorbent particle velocities, define the fluidized bed's overall behavior.

The temperature distributions shown in Figure 13 illustrate a major difference in the two modeling approaches. In the CFD model, the gas and solid mix relatively well, despite the existence of large slip velocity shown indicated by in the velocity distributions shown in Figure 5, and the temperatures for the gas and solid phases remain fairly close for any given point with no visible difference, as shown in the figure for three different gas flow rates. This is usually expected for fluidized bed reactors with vigorous solid mixing. However, because three distinct regions are considered in the process model with limited heat and mass transfer between them, the temperature in the gas bubbles differs substantially from that of the solids in the emulsion region, and thus two distinct temperature distributions are shown in the figure for one gas flow rate.

Despite the differences in modeling approaches between the CFD and process models, a comparison of overall $CO_2$ capture rates (Figure 12) illustrates the CFD result (solid black line) is quantitatively similar to that of the process models (dashed lines) with *sf* between 0.6 and 0.8. Meanwhile, the process model result with *sf=1.0* (much larger bubble size) predicts a rather steep decrease in $CO_2$ capture rate with a flow rate increase. This would tend to suggest that the correlations used in the process model for the bubble diameter and velocity are over-predicting the size and velocity of the bubbles, and thus the axial flowrate of gas, which is limiting the gas-solids contacting in the system. Figure 12 also includes data from the earlier CFD simulations with horizontal tubes (solid blue line) [23]. As expected, the $CO_2$ capture rate is significant higher than those with vertical tubes.

# 4 Conclusion

In this paper, we present the CFD modeling results from predicting the hydrodynamics and $CO_2$ capture efficiency of a 1 MWe pilot-scale bubbling fluidized bed reactor equipped with vertical cooling tubes. A fully coupled multiphase reactive flow CFD model with chemical reaction, energy, and species transport has been developed to solve the spatial and temporal distributions of flow, temperature, and species composition. The device's overall performance in $CO_2$ capture also is predicted. Previously developed filtered models for drag and heat transfer for horizontal cooling tubes are modified and implemented in the MFiX model to represent the vertical cooling tubes. One focus point has been on drag reduction to account for the fact that the vertical tubes produce less drag than the horizontal tubes. Effect on the kinetics rate has been introduced to account for the mass transfer rate difference in different tube configurations. With the new filtered models, the effects of heat exchanger tube configurations on the hydrodynamics and $CO_2$ capture efficiency of the 1 MWe conceptually designed adsorber are closely studied. Effects of gas flow rate on bed behaviors also are examined. For comparison purpose, a 1D process model is then introduced to compute the performance of the 1 MWe reactor. Finally, the overall $CO_2$ capture efficiency predicted by the CFD model is compared and contrasted with that of the 1D process model, and reasonable comparisons have been obtained.

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