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Computational fluid dynamics study of the atomic layer deposition process around cylindrical and planar configurations



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ABSTRACT

Computational fluid dynamics (CFD) simulations were used to model atomic layer deposition (ALD) coating processes in the continuum flow regime. CFD model was validated for non-reactive and reactive flows. In ALD CFD simulations, surfaces in various test cases were considered as non-porous aluminum oxide. The effect of trimethylaluminium precursor partial pressure, initial condition, and Reynolds number (Re) on coating timescale were analyzed. The CFD model accurately captured the surface coverage solution for all cases when the domain was initially filled with the precursor. The absence of initial precursor delayed coating time during the surface concentration level development process. As Re increased, coating time significantly decreased due to reduced diffusion limitations and promoted convection swiftly transporting precursors to the surfaces. The provided example showed that 2D polydisperse fixed cylinder bed is fully coated within approximately one flow time through the bed. The benefits of CFD in understanding ALD processes were discussed.

1. Introduction

Atomic layer deposition (ALD) is an advanced technique that can produce thin, uniform, and conformal films in complex structures, such as those with high aspect ratios (van Ommen et al., 2000; Johnson et al., 2014). The ALD process involves a series of self-limiting reactions between reactants and the surface, resulting in a coated layer of adsorbed species, remaining gasses, and the production of heat as a byproduct (van Ommen et al., 2000; Johnson et al., 2014). The reaction is exothermic, as described in various studies (Lownsbury et al., 2017; Gakis et al., 2019; Widjaja and Musgrave, 2002). Each full ALD cycle includes four steps: introducing a first reactant, reaction, purging (halfcycle ALD) (Johnson et al., 2014; Richey et al., 2020; Puurunen, 2005), introducing a second reactant and another purge. These cycles can be repeated as many times as needed to achieve the desired film thickness. ALD is of increasing interest due to its ability to produce ultra-thin, highly uniform, and conformal layers on a wide range of substrate sizes from nanometers to centimeters (Liu et al., 2017; Gakis et al., 2018; Cremers et al., 2019).

ALD processes involve multiscale, reactive flows, whose regimes depend on the Knudsen number (Kn), and the simulation approach for modeling such complex flow is extensively discussed in the review by

Aidun and Clausen (2010). According to Karniadakis et al. (2006), four flow regimes can be distinguished. For $Kn \leq 0.001$, the flow is in continuum regime with zero velocity at the solid surface ('no slip' condition). Between 0.001 < Kn < 0.1 the flow can still be considered as a continuum but now the flow does not fully attach to the wall ('slip' condition). When 0.1 < Kn < 10, the flow is in a transition regime and continuum assumption is not valid and, finally, for $Kn \ge 10$, the flow is in the free molecular flow regime. Cremers et al. (2019) presented a detailed review on the conformality of ALD processes along with multiscale modeling aspects. Previous studies have investigated microkinetics reaction aspects of ALD processes at molecular scales (~ 10^{-9} m) for $Kn \ge 10$, using a variety of methods such as Monte Carlo models (Poodt et al., 2017), density functional theory (DFT) (Pan et al., 2015), Lattice Boltzmann method (Zhang et al., 2019; Pan et al., 2014), and molecular dynamics simulations (Hu et al., 2009). In contrast, this study utilizes a continuum approach, using the computational fluid dynamics (CFD) method, to investigate the surface coating process in ALD on macroscopic scales (above 10^{-5} m, Kn < 0.001).

There are various important process parameters affecting ALD processes including the process pressure, mass flow rates, pulse time, purge time, and temperature (van Ommen et al., 2000; Gakis et al., 2019; Søn-

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Nomenclature

c _i	Molar concentration of the species $i \pmod{m^3}$	P_{∞}	Static pressure in the freestream (Pa)
c_{TMA}	Molar concentration of TMA (mol/m ³)	q	Adsorption density of precursor A at saturation $(1/m^2)$
C _{T M A.in}	Molar concentration of TMA at the inlet (mol/m^3)	R	Gas constant (J/(Kmol))
C_d	Drag coefficient (-)	Re	Reynolds number (-)
C_{p}	Pressure coefficient (-)	<i>s</i> ₀	Average surface area of a reactive adsorption site (m ²)
d_A^P	Molecular diameter of precursor gas A (m)	Sc	Schmidt number (-)
d_B	Molecular diameter of carrier gas B (m)	St	Strouhal number (-)
D^{-}	Diameter of the cylinder (m)	t	Simulation time (s)
D_{bed}	Diameter range of polydisperse cylinder fixed bed (m)	t _{ac}	Actual surface coating time (s)
Da_{II}	Second Damköhler number (-)	t _c	Characteristic reaction timescale (s)
D_i	Mass diffusivity of precursor <i>i</i> in carrier gas (m^2/s)	t_{tc}	Total surface coating time (s)
f	Frequency of vortex shedding (1/s)	t_p	Duration of the precursor pulse (s)
H_{LHAR}	Height of the LHAR structure (m)	t _{ftb}	Flow time through the cylinder bed (s)
J_i	Surface flux of the precursor species to the surface	ī	Normalized time (-)
	$(1/(m^2s))$	Т	Temperature (K)
Κ	Adsorption equilibrium constant (1/Pa)	T_s	Cylinder surface temperature for 2D flow validation (K)
Kn	Knudsen number (-)	T_{∞}	Freestream temperature for 2D flow validation (K)
K_b	Boltzmann constant (J/K)	и	Velocity of the carrier gas (m/s)
L	Half perimeter of the cylinder (m)	v_{th}	Mean thermal velocity of the precursor (m/s)
L_{bed}	Length of the polydisperse cylinder fixed bed (m)	W_{LHAR}	Width of the LHAR structure (m)
L_{LHAR}	Length of the LHAR structure (m)	\bar{x}	normalized molar concentration, $c_{TMA}/c_{TMA,in}$ ($0 \le x \le 1$)
ṁ	Mass flow rate (kg/s)	z_A	Collision rate of the precursor molecule (1/s)
M_B	Molar mass of carrier gas B (kg/mol)	ρ	Density of the carrier gas (kg/m^3)
M_A	Molar mass of precursor gas A (kg/mol)	ν	Kinematic viscosity of the carrier gas (m^2/s)
n	Wall normal (-)	μ	Dynamic viscosity of the carrier gas (kg/ms)
N_0	Avogadro Number (1/mol)	β	Sticking coefficient (-)
Nu	Nusselt number (-)	Θ	Surface coverage $(0 \le \Theta \le 1)$
P_A	Partial pressure of precursor A (Pa)	$\bar{\Theta}$	Integrated surface coverage ($0 \le \overline{\Theta} \le 1$)
P_B	Partial pressure of carrier gas B (Pa)	α	Angular coordinate ($0^{\circ} \le \alpha \le 180^{\circ}$)
P_i	Pressure of species i (Pa)	τ_{Diff}	Diffusion timescale (s)
$P_{TMA,in}$	Partial pressure of TMA at the inlet (Pa)	δ_{ac}	Length scale of the cylinder half perimeter
$P_{N_2,in}$	Partial pressure of N_2 at the inlet (Pa)	δ_{tot}	Length scale from inlet to downwind side of the cylinder

steby et al., 2020). Non-optimal setting of these parameters can result in wasted precursor, longer ALD cycles, and increased costs (Oviroh et al., 2019). Numerical methods can be used to optimize ALD processes. Several CFD studies have been conducted in the past focusing on the gas flow within ALD reactors under different process parameters. Nonreactive CFD studies, such as Gakis et al. (2018) and Peltonen et al. (2018), used CFD simulations to investigate the mixing process of precursor and carrier gas, the effect of reactor geometry, gas flow rate (e.g. Reynolds number) and temperature. These studies concluded that CFD is a useful tool in ALD reactor design to understand gas transport phenomena. Deng et al. (2016) proposed an optimized CFD model that found that higher temperature increases the growth rate of the surface, but has less impact on precursor distribution. Additionally, for faster precursor diffusion and more homogeneous distribution, the process should occur under low pressure and high mass flow rate conditions.

Several studies have employed CFD to investigate the gas flow and surface reactions together in an ALD process. Pan et al. (2015) presented a combined experimental-numerical study on the flow and surface reactions on a wafer using DFT methods for surface reaction kinetics and CFD for material deposition process. They found that increasing the carrier gas flow rate resulted in faster purging but also in lower deposition rate due to shortened collision time of precursor molecules with surface species. Similarly, Zhang et al. (2019) used CFD combined with microkinetics based on Monte Carlo methods to investigate the gas phase development and film growth on a wafer, proposing an optimized reactor geometry. Gakis et al. (2019) emphasized the importance of combining surface kinetics with CFD to better understand gas-solid reactions in ALD process.

The fluid dynamics in fixed bed ALD reactors, in which powders are used, are complex and differ from those observed in flat wafer surfaces. According to Dixon et al. (2006), understanding fluid flow through particle arrays is crucial for optimizing reactor design. Aspects such as flow patterns, heat and mass transport rates, and particle bed arrangement (e.g. size, shape, and configuration) must be taken into account. These flows involve time- and space-dependent surface reactions, and CFD methods can be used to model them (Dixon and Partopour, 2020). Experimentally, coating processes of powders and particles have been investigated, including fixed-bed reactors (Strempel et al., 2017; Voigt et al., 2019) and fluidized-bed reactors (Li et al., 2022; Lu et al., 2022; King et al., 2007; Beetstra et al., 2009). Reactive flows in porous media have also been investigated using CFD in the context of particle shape and arrangement effects (Nijemeisland et al., 2004) as well as methanol synthesis processes (Izbassarov et al., 2021, 2022). A general overview on usage of CFD in fixed bed reactors has been provided by Jurtz et al. (2019). Specifically, ALD processes in fluidized bed reactors were investigated Duan et al. (2017) using CFD by simulating microscopic precursor transport on the reactor scale, and it was found that the minimum pulse time and precursor waste are inversely proportional to the increase in the precursor mass fraction.

Based on the literature study, CFD simulation of reactive ALD processes has not been investigated in the past for single cylinder/particle and fixed cylinder bed reactors. Currently, further research is still needed to fully understand the role of fluid dynamics in ALD processes in various canonical flow setups including planar and cylindrical configurations, such as single particle and fixed particle beds. More study is required to gain a better understanding on the interplay between transport mechanisms, i.e. convection and diffusion, as well as surface coating processes, which are affected by various parameters. It is essential to understand how transport processes affect the coating timescale in different flow setups.

The current study utilizes trimethylaluminium (TMA) as the precursor and nitrogen (N_2) as the carrier gas. Based on the previous literature, the efficiency of the surface coating process is expected to be highly influenced by the pressure and temperature of the carrier and precursor gases as well as fluid dynamics within the bed. The coating time is known to be dependent on the partial pressure (Poodt et al., 2017) and mass transport of the precursor gases close to the solid surfaces (Yanguas-Gil et al., 2021). The irreversible Langmuir adsorption model is used in combination with CFD methods to account for the surface reactions. Additionally, heat transfer at the gas-solid boundary may also play a role in the process but this aspect is not considered in the present study.

The overall goal of this paper is to gain a deeper understanding on the benefits of 2D CFD modeling of the convective and diffusive mass transport and surface coating phenomena in ALD processes. Planar and cylindrical surfaces were considered herein. The main objectives of this study are as follows. First, we validated a 2D flow solver for both steady and unsteady flow conditions. Second, we thoroughly evaluated the CFD model performance and ALD coating process details in various flow configurations. Emphasis was put on exploring the influence of precursor partial pressure, initial conditions, and the Reynolds number (Re) on coating efficiency.

2. Mathematical formulation

2.1. Governing equations

ALD processes involve both chemical and fluid dynamical phenomena. Here, the governing equations for non-reacting flow and reacting flow with species are presented. Here, we assume that the flow is incompressible i.e. density is a constant. This is a common assumption when the flow velocity is low (here: Mach number $Ma \ll 0.3$) and when the flow is nearly isothermal. Flow incompressibility is also the underlying assumption in the aldFoam solver utilized herein (Yanguas-Gil et al., 2021). Here, the flow velocity evolves according to the incompressible Navier-Stokes equation as follows:

$$\frac{\partial \mathbf{u}}{\partial t} + \nabla \cdot (\mathbf{u}\mathbf{u}) = -\frac{1}{\rho}\nabla P + \nu \nabla^2 \mathbf{u},\tag{1}$$

where **u** (m/s) is the velocity, *P* (Pa) is the pressure which is used to enforce mass conservation via the pressure gradient, ρ (kg/m³) is the density, and ν (m²/s) is the kinematic viscosity of the carrier gas. Since the flow is incompressible, conservation of mass is guaranteed by the continuity equation where

$$\nabla \cdot \mathbf{u} = 0. \tag{2}$$

Here, the vectors are denoted by bold symbols. The vector differential operator ∇ is defined as $\nabla = \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z}$, where \hat{i} , \hat{j} , \hat{k} are unit vectors (Fleisch, 2008), " ∇ ·" represents divergence, " $\nabla^2 = \nabla \cdot \nabla$ " represents the laplacian operator, and " ∇P " represents the pressure gradient. The PIMPLE algorithm was used in OpenFOAM (Weller et al., 1998) to solve the Navier-Stokes equations using the finite-volume method. In addition, an additional scalar transport equation was solved for the mass transport of the species in terms of its molar concentration c_i (mol/m³), depending on the precursor partial pressure P_i (Pa) with the gas constant R (J/(Kmol)) and the temperature T (K). As implemented in the aldFoam (Yanguas-Gil et al., 2021), the precursor gas is assumed to behave as a passive scalar so its effect (i.e. consumption) on density variations can be neglected.

$$c_i = \frac{P_i}{RT},\tag{3}$$

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (\mathbf{u}c_i) = \nabla \cdot (D_i \nabla c_i).$$
(4)

Here D_i (m²/s) is the mass diffusivity of species *i* in the carrier gas. In the present study (see Sec. 3.4 and 3.5), the stationary velocity field **u** that was obtained from Eq. (1), is used as an input for the molar concentration Eq. (4) in order to avoid repetitive calculation of the same velocity field multiple times. We assume that the precursor species occur in relatively small concentrations in the carrier gas flow. Therefore, the fluid properties of the carrier/precursor gas blend are assumed to correspond to the well known carrier gas properties of N₂.

The governing equations are solved using the <code>OpenFOAM CFD</code> code using second-order temporal (backward) and second-order spatial discretization methods for the velocity (Gauss linearUpwind) and concentration (Gauss limitedLinear 1) fields. In the aldFoam simulations focusing on the diffusive (low *Re*) flow regime, we target at maintaining the timestep (Δt) small enough so that the maximum Courant-Friedrichs-Lewy (CFL= $\frac{\Delta t D_l}{\Delta x^2}$) number CFL < 1. In the flow solver validation part, the maximum Courant ($\frac{u\Delta t}{\Delta x}$) number Co < 0.5.

2.2. Modeling of boundary conditions and surface coating

As a boundary condition, while modeling the irreversible reactions on the wall, the mass balance equation can be locally written as (Yanguas-Gil et al., 2021):

$$-D_i \frac{\partial c_i}{\partial n} = \beta \frac{1}{4} v_{th} c_i, \tag{5}$$

where the derivation refers to the wall normal derivative, β is the reaction probability and v_{ih} (m/s) is the mean thermal velocity of the precursors. For the inlet boundary conditions, a proper ALD precursor pulse time is set. In the present study, the simulation time is equivalent to the pulse time.

Gas-solid surface reactions in the ALD process were modeled with an open source code called aldFoam (Yanguas-Gil et al., 2021) within the open source CFD package OpenFOAM (Weller et al., 1998). This model corresponds to the irreversible Langmuir adsorption kinetics and the surface coverage (Θ) evaluation depends on time as follows:

$$\frac{\partial \Theta}{\partial t} = s_0 \beta J_i (1 - \Theta), \tag{6}$$

where J_i (1/(m²s)) represents the surface flux of precursor species to the surface, s_0 (m²) is the average surface area of a reactive adsorption site for the precursor, and K_b (J/K) is the Boltzmann constant. In practice Eq. (6) is solved using the explicit Euler method. The surface flux J_i depends on the precursor partial pressure as follows:

$$J_i = \frac{1}{4} \upsilon_{ih} \frac{P_i}{K_b T}.$$
(7)

Based on Yanguas-Gil et al. (2021), to model irreversible surface reactions on the wall, the mass diffusivity of the precursor D_i is needed and it can be calculated as follows (Ylilammi et al., 2018):

$$D_i = \frac{3\pi v_{ih}^2}{16z_A}.$$
(8)

In this study, trimethylaluminium (TMA) is chosen as the precursor gas for surface reaction modeling. Here, the mean thermal velocity of the precursor v_{th} , and the collision rate of the precursor molecule z_A (1/s) are shown as follows:

$$v_{th} = \left(\frac{8RT}{\pi M_A}\right)^{(1/2)},$$

$$z_A = N_0 \left(\frac{\pi}{4}(d_A + d_B)^2 \left[\frac{8RT}{4}\left(\frac{1}{M_A} + \frac{1}{M_A}\right)\right]^{(1/2)} \frac{P_B}{RT}$$
(9)

$$N_{0}\left(\frac{\pi}{4}(d_{A}+d_{B})^{2}\left[\frac{\pi}{\pi}\left(\frac{\pi}{M_{A}}+\frac{\pi}{M_{B}}\right)\right] = \frac{D}{RT} + \pi(d_{A})^{2}\left[\frac{16RT}{\pi M_{A}}\right]^{(1/2)}\frac{P_{A}}{RT}\right),$$
(10)

where M_A (kg/mol) is the precursor molar mass, M_B (kg/mol) is the carrier gas molar mass, d_A (m) is the diameter of the precursor



Fig. 1. Validation cases. (a) Flow over cylinder for the fluid dynamical flow solver pimpleFoam (D = 0.02 m). (b) ALD deposition in LHAR channel for the gas-solid surface reaction solver aldFoam (H = 500 nm).

molecule, d_B (m) is the diameter of the carrier gas molecule, and N_0 (1/mol) is the Avogadro number. As a remark, as the present study focuses on macroscale effects ($Kn \ll 0.001$), the Knudsen diffusion effects (Yanguas-Gil et al., 2021) are considered to be negligible. From equation (6), assuming a fixed P_i , the surface coverage (Θ) can be solved analytically as:

$$\Theta = 1 - e^{-s_0 \beta \frac{1}{4} v_{th}} \frac{r_i}{k_b T} t = 1 - e^{-t/t_c}$$
(11)

$$t_{c} = \frac{1}{s_{0}\beta \frac{1}{4}v_{th}\frac{P_{i}}{K_{c}T}}$$
(12)

From the theoretical considerations above, the characteristic reaction timescale t_c (s) is identified. Under the made assumptions (fixed P_i), t_c is the timescale required for $1 - e^{-1} \approx 63\%$ of the surface reactions to occur. In order to fully coat the surface, several of such timescales would be required. As a remark, we note that t_c depends strongly on the partial pressure of the precursor which is directly related to the normalized molar concentration (Eq. (5)). In a transient situation, when the precursor is being transported to the object in question, the concentration levels will start to build up around the object along with the increase of precursor partial pressure. Hence, since t_c depends on the partial pressure, the actual time to coat 63% of the surface will be affected by the convection/diffusion processes around the object. This aspect will be further explored in the present paper.

2.3. Simulation details

In this paper, non-reacting (pimpleFoam) and reacting (aldFoam (Yanguas-Gil et al., 2021)) flow solvers are studied and validated. Two validation cases, i.e. flow over a cylinder and lateral high-aspect ratio (LHAR) structure, are investigated. Additionally, two other cases, i.e. flat plate and polydisperse fixed cylinder bed, are investigated herein. The computational domains for the two validation cases are provided in Fig. 1. Here, D represents the diameter of the cylinder. For the LHAR structure, the aspect ratio (L/H) of the elongated channel is 400. For non-reacting 2D flow over a cylinder, in Fig. 1a, the cylinder is located 15D from the inlet with symmetry boundary conditions at the upper and bottom boundaries. More details of the boundary conditions are given in Table 1. The validation cases for the 2D flow solver are carried out with different flow Reynolds numbers $\left(Re = \frac{uD}{v}\right)$ controlled by the flow velocity while the diameter of the cylinder (D) is maintained constant (here D = 0.02 m). The input parameters are shown in Table 2 to model the non-reacting carrier gas flow. The density ρ of the carrier gas is calculated from the ideal gas equation as $P_{N_2} = \rho \frac{R}{M_p} T$ at T = 500 K for different pressure levels. The dynamic viscosity for nitrogen (N₂) is calculated from the Sutherland's law which is given as $\mu = \mu_0 \left(\frac{T}{T_0}\right)^{3/2} \frac{T_0 + S}{T + S}$. Here, $T_0 = 273$ K is the reference temperature, $\mu_0 = 1.66 \times 10^{-5}$ (kg/(ms)) is the reference value and S = 107 K is the effective temperature for N2 (White and Majdalani, 2006). Then, the kinematic viscosity is obtained as $v = \mu/\rho$. In the present study, since the viscosity of the TMA gas is not well defined, we assume that the gas mixture viscosity corresponds to the carrier gas viscosity N2.

Table 1	
Summary of boundary conditions for the 2D flow field variables.	

Fluid dynamical boundary conditions for pimpleFoam. Here, temperature is needed to calculate the Nusselt number.						
	Inlet Outlet Wall					
Р	$\frac{\partial P}{\partial n} = 0$	fixed value	$\frac{\partial P}{\partial n} = 0$			
u	fixed value	$\frac{\partial \mathbf{u}}{\partial n} = 0$	fixed value (0)			
Т	fixed value (290 K)	$\frac{\partial T}{\partial n} = 0$	fixed value (350 K)			
Surface coating process boundary conditions for aldFoam. In aldFoam simulations, temperature is assumed to be constant ($T = 500K$).						
	Inlet	Outlet	Wall			
$\bar{x} = \frac{c_{TMA}}{c_{TMA}}$	fixed value (1)	$\frac{\partial \bar{x}}{\partial n} = 0$	see Eq. (5)			

The LHAR structure shown in Fig. 1b is studied to validate the ald-Foam transport equation solver with gas-solid surface reactions. Here, surface coating were studied for a single reaction step of ALD where TMA precursor molecules attach to the active surface sites of aluminum oxide (Al₂O₃). The incoming gas mixture consists of TMA and the carrier gas N₂. The used parameters for the surface coating modeling are presented in Table 3. Here, the surface site area s_0 is defined as the inverse of the adsorption density of the molecules in saturation q (m⁻²) which is determined for the specific ALD reaction in questions. Here, we defined $s_0 = 2 \times 10^{-19}$ m² which is specific to the reactions between TMA and Al₂O₃ (Ylilammi et al., 2018) and the sticking probability is defined as $\beta = 0.01$ (Ylilammi et al., 2018).

In the aldFoam simulations, we solved for the precursor concentration c_i (i.e. precursor density) which is normalized by the inlet precursor concentration in the domain i.e. $\bar{x} = c_{TMA}/c_{TMA,in}$. From this point on, the variable \bar{x} is called the normalized molar concentration. When $c_{TMA,in}$ is known, the partial pressure of precursor (needed in Eq. (7)) can be simply recovered from Eq. (3) when the inlet pressure is known i.e. $P_{TMA} = \bar{x} \times P_{TMA,in}$. At the inlet, the normalized molar concentration \bar{x} of the precursor is set to 1 during the simulation. One of the important aspects of ALD coating processes is to understand the effect of Re and pressure on the surface coating. Here we studied two different initial conditions, i.e., $\bar{x} = 0$ and 1. For $\bar{x} = 1$, the domain is homogeneously filled with precursors. On the other hand, for $\bar{x} = 0$, precursors are not present inside the domain, and once the pulse starts, precursors enter the domain along with the carrier gas. We acknowledge that the former initial condition ($\bar{x} = 1$) is a rather theoretical one but it offers a numerical way to avoid the initial transients for the precursors to reach the surfaces.

The 2D simulation domains, i.e. a single cylinder and a randomly packed fixed cylinder bed, are illustrated in Fig. 2. The two meshes are generated using the snappyHexMesh utility, which is a built-in mesh generator in OpenFOAM. Hexahedral cells form the base of the mesh, and a body-conforming boundary layer mesh is employed at the cylinder surfaces. As shown in the flow solver validation part, the fluid dynamical solutions, in particular the single cylinder case, are considered to be consistent with the reference data. The mesh used for the single cylinder case has approximately 195000 cells while for the polydisperse

Table 2

The input parameters for modeling non-reacting carrier gas flow for 2D flow over a single cylinder and polydisperse fixed cylinder bed cases.

$P_{N_2,in}$ (Pa)	T (K)	ρ (kg/m ³)	μ (Pa s)	$v (m^2/s)$	Re = 2	Re = 10
1000	500	6.74×10^{-3}	2.58×10^{-5}	3.83×10^{-3}	u=0.38 m/s	u=1.92 m/s
10000	500	6.74×10^{-2}	2.58×10^{-5}	3.83×10^{-4}	u = 0.04 m/s	u = 0.19 m/s

Table	3
Iavie	Э.

The parameters needed in Eqs. (10), (11) and (12) for modeling surface coating processes.

M _{TMA} (kg/mol)	M_{N_2} (kg/mol)	d_{TMA} (m)	d_{N_2} (m)	N_0 (1/mol)	K (1/Pa)
0.0749	0.0280	5.91×10^{-10}	3.74×10^{-10}	6.022×10^{23}	100
R (J/Kmol)	T (K)	<i>v_{th}</i> (m/s)	$s_0 = 1/q \ (m^2)$	β(-)	K_B (J/K)
8.3145	500	375.951	2×10^{-19}	0.01	1.38×10^{-23}



Fig. 2. 2D simulation domains to investigate surface coating: a) a single cylinder (D = 0.02 m) and b) a polydisperse fixed cylinder bed ($L_{bed} = 0.22$ m, $0.01 < D_{bed} < 0.04$ m).

case the mesh has approximately 570000 cells. The grid spacing normal to the cylinder wall on the cylinder surface is 0.0008D and 0.0001D respectively. These meshes are used in the respective aldFoam simulations. In the fixed cylinder bed, the fluid dynamics effects on the space-time-dependent surface coverage effect area of interest. The dimensions of the cylinders in the fixed polydisperse bed vary between 0.01 m $< D_{hed} < 0.04$ m. The total length of the bed (L_{hed}) is defined in the x-direction as 0.22 m and while the domain is assumed to be periodic in the v-direction. The solution of the ALD process consists of two phases. In the first phase, the non-reacting flow solver (pimpleFoam) is used to obtain a steady-state solution for the carrier gas velocity. Then, the ALD process can be relatively efficiently solved using the aldFoam which requires the steady state flow velocity as input i.e. the flow solution and the precursor transport equations are not solved in the same simulation. The simulated reactive flow conditions for the flat plate, single cylinder and polydisperse fixed cylinder bed configurations are shown in Table 4.

3. Results and discussion

In this part, the validation results for the flow solver are presented in laminar flow conditions. Additionally, ALD simulation cases are shown in 2D problems with increasing level of complexity.

3.1. Flow solver validation (2D)

The non-reacting flow solver is validated for the 2D flow over a cylinder case from Fig. 1a in terms of the standard dimensionless parameters such as the local pressure coefficient (C_p), the Nusselt number (Nu), the drag coefficient (C_d), and the Strouhal number (St). We investigated the steady and laminar unsteady flow cases at Re = 10, 20, 40, and 100. The values $Re \le 40$ correspond to steady flow state with either no vortices (Re = 0) or a fixed pair of vortices ($5 \le Re \le 40$) while Re > 40 corresponds to unsteady conditions where vortex shedding is expected (Lienhard et al., 1966). While C_p and C_d are standard metrics

Table 4

The simulated reactive flow conditions for the flat plate, single cylinder and polydisperse fixed cylinder bed configurations. Here, \bar{x} corresponds to initial condition while $P_{TMA,in}$ (Pa), $P_{N_2,in}$ (Pa), and Re are inlet conditions. Flat plate with one initial condition and four pressure levels = 1x4 simulations. Single cylinder in cross flow with two initial condition x two pressure levels x three Re numbers = 12 simulations. Polydisperse fixed cylinder bed in cross-flow with two initial conditions and one pressure level = 2 simulations.

	Re	\bar{x}	$P_{TMA,in}$	$P_{N_2,in}$	t _c
Flat plate	0	1	$10 \\ 10^{2} \\ 10^{3} \\ 10^{4}$	$50 \\ 50^2 \\ 50^3 \\ 50^4$	3.67×10^{-3} 3.67×10^{-4} 3.67×10^{-5} 3.67×10^{-6}
Single cylinder in cross-flow	0 2 10	0 and 1	2×10^2 2×10^3	10^{3} 10^{4}	1.84×10 ⁻⁴ 1.84×10 ⁻⁵
Polydisperse fixed cylinder bed in cross-flow	10	0 and 1	2×10^{2}	10 ³	1.84×10^{-4}

for predicting the aerodynamic performance of bluff bodies, Nu quantifies the heat transfer coefficient while St indicates the vortex shedding frequency for Re > 40. The values $C_p = 2(P - P_\infty)/\rho u^2$ and the local $Nu = \frac{\frac{\partial (T_s - T)}{D}|_{n=0}}{\frac{\partial (T_s - T_\infty)}{D}}$ are compared with the reference data from the literature. Fig. 3 shows the local profiles C_p and Nu as a function of the angular coordinate α along the half-cylinder surface (in Fig. 2a). Here, $\alpha = 0^\circ$ corresponds to the upstream impingement point while $\alpha = 180^\circ$ corresponds to the downstream location along the cylinder surface. As can be seen, simulation results are in excellent agreement with the literature.

Furthermore, the performance of the solver is also investigated in terms of St = f D/u for cases Re = 80,100 and in terms of $C_d = 2F_d/\rho u^2 D$ for Re = 20,40,80,100, as can be seen in Fig. 4a and b respectively. Here, the vortex shedding frequency f is calculated based on the periodic oscillation of the lift coefficient. Since vortex shedding starts for Re > 40, St was only compared with Re = 80 and Re = 100 with the literature.



Fig. 3. Validation of non-reacting flow over single cylinder case using pimpleFoam. Comparison of C_p at a) Re = 10, b) Re = 20, c) Re = 40 and d) Re = 100 with the present study, De Vanna et al. (2020) and Izbassarov et al. (2021). Comparison of Nu at e) Re = 10, f) Re = 20, g) Re = 40 and h) Re = 100 with the present study, Bharti et al. (2007), Lo and Su (2012) and Izbassarov et al. (2021). For parametric values and domain dimensions, please see Table 2, and Fig. 1a. Additionally, Nu calculation requires information on the following temperature levels: $T_s = 350$ K and $T_{cos} = 290$ K.



Fig. 4. Validation of non-reacting flow over a single cylinder using pimpleFoam. a) Comparison of *St* at Re = 80 and 100 with the present work, Henderson (1995), Posdziech and Grundmann (2001), Williamson (1989), Sahin and Owens (2004), Wang and Zhang (2011), Ren et al. (2013) and Izbassarov et al. (2021). b) Comparison of C_d at Re = 20, 40, 80 and 100 with the present work, Henderson (1995), Posdziech and Grundmann (2001), Sahin and Owens (2004), De Vanna et al. (2020), Ren et al. (2013), Guo et al. (2019) and Izbassarov et al. (2021). For parametric values and domain dimensions, please see Table 2, and Fig. 1a.

The qualitative difference between the steady flow and vortex shedding mode is depicted in the passive scalar fields (here temperature) in the inset of Fig. 4b. Once again, the simulation results are noted to be consistent with the literature. Hence the present non-reacting flow solver can be considered to be fluid dynamically validated in terms of fundamental metrics justifying usage of the solver in the present flow conditions.

3.2. ALD solver validation: lateral high aspect ratio (LHAR) structure (1D)

The section 3.1 was related to the validation of the flow solver. In this section, the surface coating process was studied using the precursor concentration Eq. (4) and the surface coverage Eq. (6) based on the irreversible Langmuir adsorption model in a 1D LHAR, which is illustrated in Fig. 1b.

The surface coverage profiles $\Theta = \Theta(x, t)$ and reactant pressure profiles $P_{TMA,in}$ on the wall inside the channel are shown in Fig. 5 at different pulse times $t_p = 0.01$, 0.02, 0.05, and 0.1 s. The normalized molar concentration value \bar{x} is fixed to unity at the inlet of the LHAR structure and this value is directly related to pressure via Eq. (3). Starting from the inlet, the precursor partial pressure in the channel starts to decrease due to the surface reactions which consume the precursor molecules in the system. The longer the pulse time, the more precursor molecules are introduced into the system and the deeper the surface coating extends in the LHAR structure.

To compare the numerical results of the surface coverage between different numerical approaches, we utilized aldFoam (2D) (Yanguas-Gil et al., 2021), the full diffusion model (1D) (Ylilammi et al., 2018), and the simplified model (1D) (Ylilammi et al., 2018) in the LHAR structure case. The first model is the aldFoam, developed by Yanguas-Gil et al. (2021), that is based on a full 2D solution of Eqs. (4) and (6) neglecting the velocity field. The second model is the 1D full diffusion model. We implemented the model (Eqs. (4) and (6)) into Matlab and solved them by the finite difference method assuming a purely diffusion dominated problem (velocity vanishes). The third model is the 1D simplified model developed by Ylilammi et al. (2018) for the gas concentration equation for the LHAR structure. This model was also implemented and numerically investigated in Matlab. Under the conditions studied, the simplified model is fast and easy to implement. Therefore, this model is often utilized in the literature (Yim et al., 2022, 2020). Out of the three models, the aldFoam approach can be considered to be the most sophisticated one. In fact, one of the benefits of combining 2D CFD simulations with time-space dependent convection-diffusionreaction equation is to get a more realistic concentration distribution in the system in arbitrary geometries. In case of the LHAR structure, once \bar{x} has been updated from Eq. (4), the Θ profile along the channel walls



Fig. 5. Comparison of three numerical approaches for the LHAR structure validation case: simplified model (Ylilammi et al., 2018), full diffusion model (Ylilammi et al., 2018) and aldFoam (Yanguas-Gil et al., 2021). The development of a) the surface coverage (Θ) profiles and b) the precursor partial pressure profiles are shown for increasing pulse times. For parametric values and domain dimensions, please see Table 3, and Fig. 1b. Additionally, Θ calculation requires information on the following simulation parameters: $H_{LHAR} = 5 \times 10^{-7}$ m, $L_{LHAR} = 2 \times 10^{-4}$ m, $W_{LHAR} = 1 \times 10^{-4}$ m, $P_{TMA} = 100$ Pa, and $P_{N_s} = 300$ Pa.



Fig. 6. Time evolution of 1D normalized molar concentration \bar{x} fields for two different partial pressure levels a) $P_{TMA,in} = 10$ Pa, and b) $P_{TMA,in} = 100$ Pa. Three time snapshots are shown for each pressure level marked with the corresponding Θ values. For parametric values and domain dimensions, please see Table 3. The width and height of the simulation domain are 0.1 m and 0.25 m respectively.

can be numerically updated at different locations as well based on the irreversible Langmuir adsorption model (Eq. (6)).

As seen from Fig. 5, increasing the pulse time (i.e. duration of the pulse) increases the length of the coated part of the wall along with the partial pressure distribution of the gas (also referred to as molar concentration in Eq. (4)). Clearly, aldFoam predictions are consistent with the other numerical approaches. Importantly, aldFoam can also be applied in complex structures of general shape and will thus be further explored and utilized here as well.

3.3. Flat plate (1D)

Next, we investigate the surface coating process of a simple flat plate. The gas volume outside the surface is initially at concentration $\bar{x} = 1$ and the partial pressure of the precursor gas starts to decrease in the system when the precursor molecules adsorb on the flat surface. As a remark, through-out the present paper, walls are assumed to be non-porous.

The development of the reactant gas concentration is investigated at $P_{TMA,in} = 10$ and 10^2 Pa as a function of time in Fig. 6. Initially, the

precursor is homogeneously distributed inside the domain i.e. $\bar{x} = 1$. At a higher pressure, the near-wall concentration boundary layer is very thin as compared to the lower pressure case. The concentration gradient at the wall is essential since it relates to the rate at which the precursor attaches to the surface (see Eq. (5)). Once the surface reaches a saturation state, it is considered to be fully coated ($\Theta = 0.999$). In the present simulations, such a situation is reached for both pressure levels when the near-wall $\bar{x} \approx 0.92$ at the latest considered time. First, this number is of interest because in order to use Eq. (5) the near-wall concentration value during the coating process is required as the near-wall value should be less than unity due to precursor consumption. Second, as seen in Fig. 6, the development of the near-wall concentration level will swiftly reach values above 0.85. Eventually, the near-wall concentration value would reach unity when the coating process is fully completed. As seen also later on in the paper, the value $\bar{x}\approx\!0.92$ is commonly considered to be a representative, effective value for the near-wall concentration level during the transient coating process for the simulated cases. We acknowledge that, at different temperature levels, the exact value of \bar{x} may depend on the precursor partial pressure, mean thermal velocity, and sticking coefficient. However, we did not



Fig. 7. a) The evaluation of the surface coverage Θ vs. non-dimensional time \overline{t} (2D CFD) and b) sensitivity of the characteristic reaction timescale (t_c) and the estimated near-wall normalized molar concentration \overline{x} . The transient variation of \overline{x} due to transport processes may strongly affect the t_c value. For parametric values and domain dimensions, please see Table 3. The width and height of the simulation domain are 0.1 m and 0.25 m respectively.



Fig. 8. Analytical and numerical comparison of integrated surface coverage $\bar{\Theta}$ at $P_{TMA,in} = 200, 2000$ Pa, $P_{N_2,in} = 1000, 10000$ Pa, and Re = 0, 2, and 10. For parametric values and domain dimensions, please see Tables 2, 3, and Fig. 2a.

investigate this topic further in the present study. Once the surface is fully coated and the concentration flux to the surface approaches zero, the average precursor concentration in the domain starts to increase (constant supply of precursor from the top boundary of the domain), until the domain is again completely filled with the precursor.

The analytical time evolution of the surface coverage Θ is provided in Eq. (11) under the given assumptions. Fig. 7a shows the comparison of the simulated surface coverage with the analytical solution at different pressures. Here, the time was normalized as $\bar{t} = t/t_c$. As noted from the earlier simulations, the value $\bar{x} = 0.92$ can be considered as a representative value for a fully coated state $\Theta = 0.999$ and that value is used to evaluate Eq. (11). Using the value $\bar{x} = 0.92$, i.e. calculating t_c using the partial pressure level $0.92P_{TMA}$, the simulated time profile is noted to offer a very good agreement with the analytical one. As a theoretical remark from Fig. 7b, we note that the near-wall precursor concentration may strongly affect the characteristic reaction timescale t_c . Hence, it is important to consider the detailed concentration levels near the surfaces.

3.4. Cylinder in cross-flow (2D)

To investigate surface coating process on the outer wall of a smooth (non-porous) cylinder, a cylinder was placed in a 2D channel. The channel is initially uniformly filled with the precursors ($\bar{x} = 1$) and more precursors flow into the channel constantly along with the carrier gas as represented on the right side of Fig. 8. *Re* effects and the partial pressure effect on the coating process are demonstrated considering the normalized time (\bar{i}). We note that the analytical Eq. (11) predicts well the surface coverage for all the considered Reynolds numbers and partial pressures. It can be said that the total coating time to reach $\bar{\Theta} = 0.999$ is approximately $10t_c$ for the considered values Re = 0, 2 and 10. For this

particular simulation set-up and initial condition ($\bar{x} = 1$), no significant *Re* sensitivity to the surface coating time could be observed. This can be mostly explained by a relatively uniform supply of precursor to the cylinder surface from the ambient initial conditions and the inlet.

In contrast to the previous case, we also investigated the surface coverage process when the initial precursor concentration inside the simulation domain is $\bar{x} = 0$. In such a case the precursor is initially not in direct contact with the surface. Fig. 9 indicates the local surface coverage on the outer surface of the cylinder at Re = 0, 2, and 10 with $P_{TMA,in} = 200$, 2000 Pa, and $P_{N_2,in} = 1000$, 10000 Pa. In this particular case ($\bar{x} = 0$), the total coating time (t_{tot}) consists of two parts: 1) the time for the precursor to reach the cylinder from the inlet, and 2) the time for actual coating (t_{ac}) that starts when the precursor reaches the cylinder.

Fig. 9 shows that, at a fixed pressure level, the coating occurs faster for the higher Reynolds number because the precursor reaches the entire substrate surface faster. As mentioned, according to Eq. (12), t_c decreases when the precursor partial pressure increases. As a remark, Eq. (12) as such does not take transient convection and diffusion phenomena directly into account. However, at a fixed $Re \leq 10$, it is noted that the coating time increases when the pressure increases. Such behavior is expected and can be explained as follows. The collision rate z_A (see Eq. (10)) is directly proportional to the pressure, leading to the decrease of the diffusion coefficient with increasing pressure (see Eq. (8)). When pressure increases, the diffusion timescale (τ_{diff}) over a given length scale δ subsequently increases.

In the present cases ($Re \le 10$) precursor diffusion over the length scale of the cylinder will limit the process. Here, $\tau_{diff} = \frac{\delta^2}{(2\pi)^2 D_i}$. As seen in Table 5, the surface is coated rapidly at $P_{TMA,in} = 200$ Pa in contrast to $P_{TMA,in} = 2000$ Pa. It is noted that when Re = 10 at both pressure



Fig. 9. Simulated surface coverage as a function of the angular coordinate $0^{\circ} \le \alpha \le 180^{\circ}$ along the half surface of the cylinder in Fig. 2. Top row: $P_{TMA} = 200$ Pa and $P_{N_2} = 1000$ Pa. Bottom row: $P_{TMA} = 2000$ Pa and $P_{N_2} = 10000$ Pa. Left column: Re = 0 Middle column: Re = 2 Right column: Re = 10. The shown four time instances are chosen in order to reflect the times when the surface is approximately 10, 20, 90, and 100% coated. For parametric values and domain dimensions, please see Tables 2, 3, and Fig. 2a.

Table 5

The actual coating time t_{ac} and the total coating time t_{tot} at different *Re* and pressures for 2D flow over a single cylinder case for the initial condition $\bar{x} = 0$. Here, δ_{tot} is the length scale from inlet to downwind side of the cylinder and δ_{ac} the length scale of the cylinder half perimeter. This is a summary of Fig. 9.

	$\begin{split} P_{TMA,in} &= 200 \text{ Pa} \\ Da_{II} &= 1.5 \times 10^2 \\ D_i &= 8.93 \times 10^{-4} \text{ m}^2/s \\ t_c &= 1.84 \times 10^{-4} \text{ s} \end{split}$	$\begin{split} P_{TMA,in} &= 2000 \text{ Pa} \\ Da_{II} &= 1.5 \times 10^4 \\ D_i &= 8.93 \times 10^{-5} \text{ m}^2/s \\ t_c &= 1.84 \times 10^{-5} \text{ s} \end{split}$
$\begin{split} \delta_{ac} &= \pi \frac{D}{2} \\ \delta_{tot} &= 15D + \frac{D}{2} (\pi - 1) \end{split}$	$\begin{aligned} \tau_{diff_{ac}} &= 0.028 \text{ s} \\ \tau_{diff_{iot}} &= 2.93 \text{ s} \end{aligned}$	$\tau_{diff_{ac}} = 0.28 \text{ s}$ $\tau_{diff_{tot}} = 29.31 \text{ s}$
Re=0	$t_{ac} = 4.30 \text{ s}$ $t_{tot} = 8.0 \text{ s}$	$t_{ac} = 22.0 \text{ s}$ $t_{tot} = 50.0 \text{ s}$
Re=2	$t_{ac} = 0.23 \text{ s}$ $t_{tot} = 0.85 \text{ s}$	$t_{ac} = 2.10 \text{ s}$ $t_{tot} = 7.50 \text{ s}$
Re=10	$t_{ac} = 0.07 \text{ s}$ $t_{tot} = 0.21 \text{ s}$	$t_{ac} = 0.47 \text{ s}$ $t_{tot} = 1.85 \text{ s}$

levels, $\tau_{diff_{ac}} \sim t_{ac}$ i.e. the two timescales become in the same order of magnitude. Here, we chose the length scale δ to be the half perimeter of the cylinder in order to reflect the dimensions of the system. Hence, the total coating time increases when the pressure increases because of the increased diffusion timescale i.e. the present CFD model works consistently (see objective 2).

The discrepancy in coating times can also be understood in terms of the dimensionless number $Da_{II} = \frac{reaction rate}{diffusion rate}$ (Catchpole and Fulford, 1966) which can also be written as a time scale ratio $Da_{II} = \frac{\tau_{diff}}{t_c}$. Fig. 10 shows a plot of Da_{II} as a function of P_{TMA} . In the cases considered above ($P_{TMA} = 200/2000$ Pa), when $Da_{II} \gg 1$ the reaction time is much shorter than the diffusion time. Hence, the diffusion timescale dominates the situation. At $P_{TMA,in} = 2000$ Pa, the relative importance of diffusion effects becomes more dominant, resulting in longer coating times for each *Re*. Based on the results, in the present setup where the system size is kept constant, at a fixed pressure the total coating time can be reduced by increasing *Re* i.e. by increasing the mass flow

Fig. 10. Damköhler number Da_{II} vs P_{TMA} . Here, τ_{diff} is defined based on the cylinder half perimeter. It is seen that for higher pressure levels the relative importance of diffusion becomes more dominant. In the present study we fixed the ratio $P_{TMA}/P_{N_2} = 5$.

rate. The increased velocity transports the precursor molecules to the surface faster. As a remark, at Re = 0, t_{ac} and τ_{diffac} differ by two orders of magnitude because in this case, the concentration build-up time around the cylinder is limited by the diffusion time from the inlet to the cylinder surface i.e. convection does not support in building up the near-wall concentration levels. In addition, to achieve a faster diffusion, lower pressure with higher *Re*, would lead to reduce the total coating time. Our observations are consistent with those by Deng et al. (2016) who emphasized that an optimized ALD process may be implemented at low pressure and high mass flow rate. Such conditions will reduce the Damköhler number so that diffusion limits the process less.

Our observations above highlight the importance of convection and diffusion modeling in ALD surface coating processes. The surface coating time not only depends on the partial pressure (Eq. (12)) but also on the fluid dynamical processes affecting the time to transport the precursor into contact with the surface. We note that the present observations are consistent with the findings of Blomberg (2013) who emphasize that, along with the reaction rate, the precursor flow rate is an important aspect limiting the coating process and affecting the minimum pulse time.

Fig. 11. 2D polydisperse fixed cylinder bed initially at $\bar{x} = 1$ at Re = 10 (u = 1.92 m/s), $P_{TMA} = 200$ Pa and $P_{N_2,in} = 1000$ Pa. a) Integrated surface coverage $\bar{\Theta}$ in the entire bed. b) Integrated surface coverage $\bar{\Theta}$ for the bed divided into six bins. For parametric values and domain dimensions, please see Tables 2, 3, and Fig. 2b.

3.5. Polydisperse fixed cylinder bed in cross flow (2D)

Next, the complexity of the problem is further increased by adding randomly located cylinders into the system in order to emulate a fixed particle bed configuration. The boundary conditions are periodic in the spanwise direction to represent an infinite particle bed array. For consistency, the surface coating was investigated by again considering two different initial conditions ($\bar{x} = 1$ and 0). For a single cylinder case, a relatively fast occurring coating process was observed at Re = 10 (u = 1.92m/s), $P_{TMA,in} = 200$ Pa, and $P_{N_2,in} = 1000$ Pa. Such a situation is further explored in what follows.

Consistent with the single cylinder case, in Fig. 11a, the surface coating simulation results for the unity initial concentration case ($\bar{x} = 1$) are noted to be in agreement with the analytical results. It is noted that the coating time to reach $\overline{\Theta} = 0.999$ is again $\approx 10t_{\odot}$ for the considered set-up. In order to analyze the propagation of the coating in the streamwise direction, the polydisperse cylinder bed was divided into six bins. Fig. 11b indicates the surface coverage at the location of the bin centers. Since the precursor was initially homogeneously distributed inside the domain, the coating process occurs similarly for each bin regardless of its location inside the cylinder bed. Hence, the transport processes (convection/diffusion) do not essentially affect the total coating time when $\bar{x} = 1$ in the studied situation where the precursor supply in the system is guaranteed from the inlet. However, as noted earlier for the flat plate case, such observations may change for different parametric conditions. For example, at lower pressures the existing precursor may be consumed faster in the bed than new precursor is introduced into the bed. Also, for high porosity surfaces or high aspect ratio structures, the consumption rate may exceed the supply rate.

Fig. 12a illustrates the domain ($\bar{x} = 0$) representing the surface coverage as a function of the normalized time t/t_{ftb} . Here, $t_{ftb} = L_{bed}/u$ (see Fig. 2b) is the timescale for the flow to travel over the cylinder bed (from the first to the last cylinder) and $t_{ftb} = 0.115$ s. Using this information, it can be found how many t_{ftb} timescales are required to coat all the cylinders. Fig. 12b indicates that, on average, the first bin row starts to coat before the other bins deeper in the bed. However, the random structure of the cylinder bed may introduce local flow phenomena which will be explored next.

In order to better understand the flow character within the bed $(\bar{x} = 0)$, the velocity field in Fig. 13 is discussed. The flow naturally chooses the easiest path to travel which commonly involve unobstructed parts of the bed and wider gaps. As noted in Fig. 13a, the

velocity field inside the bed is highly non-uniform. Consistent with the Bernoulli law, peak velocity values $u \approx 10$ m/s are observed at the narrowest gaps. In contrast, the flow may be nearly stagnant at certain other locations. In such low-speed zones, precursors are not efficiently transported to the cylinder surfaces by convection and those stagnation zones would mainly be characterized by precursor diffusion. Additionally, the normalized molar concentration field at different time levels was shown as time snapshots in Fig. 13b. The polydisperse fixed cylinder bed from a 3D view angle is represented in Fig. 13c to show the surface coating qualitatively (red: fully coated, blue: uncoated).

A close-up to the 2D polydisperse fixed cylinder bed is shown in Fig. 14a along with a zoom into the downstream part of the bed to further understand fluid dynamical effects on the spatial variation in the coating process. The zoomed area consists of a low speed stagnation zone surrounded by higher speed flow regions. The following aspects were observed. In zone I, relatively weak convection into the system was identified. Similarly, in zone II, a low-speed flow region appears with almost stagnant flow. On the other hand in zones III and IV, there are high speed flow parts outside the stagnation region. Cylinders A, B, C, and E are located such that they experience versatile flow conditions from four different zones. On the other hand, cylinder D is mostly exposed to the low-speed zones II and I.

The instantaneous surface coverage (Θ) distribution at t = 0.19 and 0.21 s was presented in Fig. 14b. At t = 0.19 s, it can be clearly seen that regions with high velocities (zones III and IV) are coated faster than the cylinders of zone II. In particular, it is clearly seen that regions with high coverage align with zones III and IV for cylinders A, B, C, and E. Moreover, the whole surface of cylinder D and zone II of cylinders A, B, and E are closer to the inlet than cylinder C. Therefore, one would expect that cylinder C would become coated after cylinders A, B, D and E. However, a detailed inspection reveals that cylinder C is covered before the other cylinders due to high speed region in its vicinity. As time progresses (t = 0.21 s), overall surface coverage increases, fully coating the far downstream cylinder C, while the remaining four cylinders are still not fully coated. Finally, all cylinders in the bed were coated by the time $t \approx 0.27$ s as shown in previous Fig. 13c. We note that $t_{fth} = 0.115$ s, the diffusion timescale over a representative single cylinder half perimeter is $\tau_{diff_{ac}} = 0.028$ s and $t_c = 1.84 \times 10^{-4}$ s at $P_{TMA,in} = 200$ Pa and $P_{N_2,in} = 1000$ Pa. As a remark, the diffusion time scale over the bed would be 1.37 s for the investigated pressure level. Hence, since the coating time is in the order of t_{ftb} , the flow through bed timescale is concluded to characterize and limit the coating process in the present

Fig. 12. 2D polydisperse fixed cylinder bed initially at $\bar{x} = 0$ inside the flow system at Re = 10 (u = 1.92 m/s), $P_{TMA} = 200$ Pa and $P_{N_2,in} = 1000$ Pa. a) Integrated surface coverage $\bar{\Theta}$ in the entire bed. b) Integrated surface coverage $\bar{\Theta}$ for the bed divided into six bins. For parametric values and domain dimensions, please see Tables 2, 3, and Fig. 2b.

Fig. 13. Surface coverage process investigation (initial condition: $\bar{x} = 0$, $P_{TMA,in} = 200$ Pa and $P_{N_2,in} = 1000$ Pa). The precursors enter the channel from the left inlet as $\bar{x} = 1$ with the carrier gas flow. a) Velocity field of the carrier gas flow at Re = 10 (u = 1.92 m/s) and $P_{N_2,in} = 1000$ Pa. b) Normalized molar concentration field at different time levels. c) Integrated surface coverage at different times. Red: surface fully coated (1). Blue: surface uncoated (0).

0.4 0.5

0.0

0.195

Fig. 14. Zoom into the 2D polydisperse cylinder bed. a) Velocity magnitude. b) Surface coverage on the finest zoom level at t = 0.19 and 0.21 s. The figure shows that the last cylinders can be coated before some of the cylinders inside the bed indicating spatial variation in local coating process.

b

configuration (Re = 10). However, the observations herein should be revisited for other particle shapes and arrangements in future studies. For lower Reynolds numbers, the diffusion time scale over the bed would certainly become more dominant in limiting the coating process.

4. Conclusions

Here, we investigated ALD coating processes using CFD and the irreversible Langmuir surface kinetics. First, the non-reacting CFD flow solver was validated. Then, the reacting aldFoam (Yanguas-Gil et al., 2021) solver (2D/OpenFOAM) was validated with the full diffusion model (Ylilammi et al., 2018) (1D/Matlab) and the simplified model (Ylilammi et al., 2018) (1D/Matlab). Next, surface coating processes were studied on a simple flat plate (1D), single cylinder (2D), and polydisperse fixed cylinder bed (2D) configurations. Sensitivity to the pressure level, initial conditions, and Reynolds number was explored and the CFD model was noted to be consistent with the given modeling assumptions.

Regarding the overall objective of the study, we noted that CFD simulations may offer deeper insight to the space-time variation of ALD coating processes in complex geometries. The main findings of the study can be summarized as follows:

- 1. In the studied setups, the corrected analytical solution for surface coverage predicts well the CFD simulation results for an idealized initial condition ($\bar{x} = 1$). In such situations, fluid dynamical transport effects were found to be less important.
- 2. Regarding objective 1, the 2D flow solver was validated in laminar non-reactive and reactive flow conditions. The results indicated excellent agreement for e.g. flow over a cylinder (non-reacting) and the observed coating process of the LHAR structure (reacting).
- 3. Regarding objective 2, we investigated the coating process for a few reacting flow situations. CFD simulations indicated that convection and diffusion effects may become most obvious in the single cylinder, and polydisperse fixed cylinder bed configurations with initial condition $\bar{x} = 0$. At a fixed *Re* and the studied conditions (*Kn* < 0.001 and diffusion limited regime), increasing pressure resulted in an increased total coating time. For the polydisperse fixed cylinder bed the total coating time was noted to be related to the flow-through bed timescale. In higher velocity regions convection

tion may enable faster surface coating. In contrast, in the observed stagnation regions, diffusion becomes more important and, consequently, surface coating occurs more slowly. Additionally, CFD offered numerical evidence from a situation where particles deeper in the bed can be coated before particles that are closer to the upstream side. Particle beds may pose strong, non-trivial velocity variation inside the bed affecting the transport rates to the surfaces.

In general, the numerical results support the view that ALD coating processes may occur the fastest at low pressures and high mass flow rates. CFD methods may be useful in future optimizing ALD processes with minimal precursor consumption and coating duration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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