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A numerical study on concentration polarization in 3D cylindrical fluidized beds with vertically immersed membranes

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Abstract

Concentration polarization is a serious issue for systems in which high-flux, palladium-based, hydrogen perm-selective membranes are used to extract hydrogen, not only for packed-bed reactor systems, but also for fluidized bed membrane reactors. Two-Fluid Model simulations of 3D cylindrical lab-scale fluidized beds with single and multiple vertically immersed cylindrical membranes with state-of-the-art hydrogen permeability were performed to quantify concentration polarization, to study the interaction between concentration polarization zones of multiple vertically immersed membranes and to link these findings to the bed hydrodynamics. Simulations of a fluidized bed consisting of 500 μm particles using a H_2/N_2 mixture as fluidization gas with a single immersed membrane, show that reduced hydrogen concentrations prevail mostly within 1 cm from the membrane surface, and have disappeared beyond about 2 cm distance from the membrane surface. A 3D simulation was compared to a Cartesian 2D simulation that represents a slice of the 3D system, to assess the accuracy of 2D simulations. The 2D simulation did not fully capture the hydrodynamics and radial mass transfer effects of 3D cylindrical fluidized bed membrane reactors and overestimated the severity of concentration polarization and the formation of densified zones near the membrane surface. In particular, the hydrogen fluxes were determined at $0.217 \text{ mol}/(\text{m}^2 \text{ s Pa}^{0.5})$ for the 3D case, and $0.133 \text{ mol}/(\text{m}^2 \text{ s Pa}^{0.5})$ for the 2D case. The severity of densified zones is also affected by the particle size, because for smaller particles (250 μm) the emulsion phase density near the membrane surface is higher than for systems with larger particles (500 μm), which results in increased concentration polarization and a reduced extractive hydrogen flux. Therefore, employing relatively large particles of at least 500 μm in fluidized beds with modern high-flux membranes is advised. In fluidized beds with multiple membranes, interaction between concentration polarization zones of each membrane was observed. The interaction becomes more significant at smaller inter-membrane distances, especially below 2 cm, and decreasing the bed diameter decreases the system performance even more due to hydrogen depletion. Vertically immersed membranes also affect the fluidized bed hydrodynamics by reducing bubble size and increasing the number of small bubbles.

Keywords

Concentration polarization, mass transfer, hydrodynamics, fluidized bed, membranes, Two-Fluid model, CFD.

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Highlights:

- Concentration polarization near 3D vertically immersed membranes was quantified
- Cartesian 2D simulations overpredict the severity of densified zones
- Smaller particles increase densified zones near membranes and reduce performance
- Multiple membranes can compete for H_2 with each other and hereby reduce performance
- Increasing the number of membranes increases the number of small bubbles

Graphical abstract

Bubbles around membranes

Interaction between membranes

H₂ extraction
Concentration polarization

Nomenclature

Symbols

A	Area	m^2
c_1, c_2	Constants in frictional stress model	-
C_d	Drag coefficient	-
D	Dispersion coefficient	m^2/s
d	Diameter	m
e	Coefficient of restitution	-
Fr	Constant in frictional stress model	N m^{-2}
$\mathbf{g}$	Gravitational acceleration	m s^{-2}
g_0	Radial distribution function	-
H	Height	m
$\mathbf{I}$	Unit tensor	-
J	Exchange of fluctuation energy	$\text{kg m}^{-1} \text{s}^{-3}$
L	Length	m
M_w	Molecular weight	kg mol^{-1}
m	Index of summation	-
N	Flux	$\text{mol m}^{-2} \text{s}^{-1}$
n	Power in Sieverts' law	-
P	Partial pressure	Pa
p	Pressure	Pa
Q_m	Permeance of the membrane	$\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-0.5}$
R	Universal gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
Re	Reynolds number	-
r	Radial position	m
$\dot{\mathbf{S}}$	Strain rate	s^{-1}
S	Source term	$\text{kg m}^{-3} \text{s}^{-1}$
t	Time	-
T	Temperature	K
$\mathbf{u}$	Velocity	m s^{-1}
V	Volume	m^3
X	Molar fraction	-
x	x-position	m
Y	Mass fraction	-

Greek letters

α	Volume fraction	-
β	Interphase drag coefficient	$\text{kg m}^{-3} \text{s}^{-1}$
γ	Dissipation of granular energy	$\text{kg m}^{-1} \text{s}^{-3}$
δ	Film layer thickness	m
θ	Granular temperature	$\text{m}^2 \text{s}^{-2}$
κ	Conductivity of granular energy	$\text{kg m}^{-1} \text{s}^{-1}$
λ	Bulk viscosity	$\text{kg m}^{-1} \text{s}^{-1}$
μ	Shear viscosity	$\text{kg m}^{-1} \text{s}^{-1}$
ρ	Density	kg m^{-3}
τ	Shear stress tensor	N m^{-2}
ϕ^{fr}	Angle of internal friction	°

Subscripts & superscripts

<i>c</i>	Cell(s)
<i>FB</i>	Fluidized bed
<i>fr</i>	Frictional/friction
<i>g</i>	Gas
<i>in</i>	inlet
<i>init</i>	Initial
<i>m</i>	Membrane
<i>max</i>	Maximum
<i>mf</i>	Minimum fluidization
<i>min</i>	Minimum
<i>p</i>	Particle
<i>pp</i>	Particle-particle
<i>pw</i>	Particle-wall
<i>perm</i>	Permeate
<i>s</i>	Solid
<i>sim</i>	simulation
<i>T</i>	Transposed

Abbreviations

CFD	Computational Fluid Dynamics
DPM	Discrete Particle Model
FBMR	Fluidized Bed Membrane Reactor
KTGF	Kinetic Theory of Granular Flow
PDE	Partial Differential Equation
PSA	Pressure Swing Adsorption
SMR	Steam Methane Reforming
TFM	Two-Fluid Model
VM	Vertical Membrane
WGS	Water Gas Shift

1. Introduction

Hydrogen is recognized as an important alternative energy carrier to move towards a more sustainable society in the near future, as well as an important feedstock for chemicals. Hydrogen is commonly produced by Steam Methane Reforming (SMR) in (multi-tubular) packed bed reactors. Methane reacts in an equilibrium reaction with steam to form carbon monoxide and hydrogen at temperatures around 900 °C, after which the Water Gas Shift (WGS) reaction occurs in separate reactors; carbon monoxide from the SMR reaction further reacts with steam to form carbon dioxide and hydrogen. To ensure a high methane conversion, high temperatures and low hydrogen concentrations are required. Complex and energy intensive separation units such as pressure swing adsorption columns (PSA) are required to separate the hydrogen from by-products like CO₂, which increases the cost and energy usage, and decreases system performance [1].

Packed bed membrane reactors have previously been suggested for hydrogen production [2,3], however, fluidized beds have better mixing properties than packed beds, resulting in reduced mass transfer limitations towards the membranes. Furthermore, a packed bed can only use relatively large catalytic particles because of pressure drop limitations which reduces the catalyst particle effectiveness. The fluidized bed membrane reactor is a novel reactor concept in which hydrogen is both continuously produced and separated from the reaction mixture with modern high-flux, palladium-based, hydrogen perm-selective membranes. Using a fluidized bed removes the pressure drop limitations from the system and enables usage of small catalytic particles without internal particle mass transfer limitations. Next to obtaining a virtually pure hydrogen stream at the permeate side of the membrane, the hydrogen extraction drives the chemical reaction equilibria towards the product side, increasing the reaction rate and allowing reactor operation at much lower temperatures (around 600 °C) compared to the conventional industrial process, increasing the overall process efficiencies.

In practice, membranes are generally inserted lengthwise in fluidized bed reactors, which is referred to as vertically immersed membranes in this work. In previous research, Helmi et al. [4] have found that when feeding binary H₂/N₂ gas mixtures, the mixing even in fluidized beds with state-of-the-art, high-flux, vertically immersed palladium membranes is still insufficient to completely prevent mass transfer limitations from the bulk of the bed to the membrane surface, also known as concentration polarization [5]. They have quantified the concentration polarization with Cartesian 2D Two-Fluid Model (TFM) simulations and experiments, considering a single membrane in a small fluidized bed. The TFM simulations showed that there is indeed a significant concentration gradient next to the membrane and the permeation flux decreases over the membrane height.

Even though the 2D TFM simulations were found to predict the order of magnitude of concentration polarization quite well, full 3D simulations are required to capture the complex hydrodynamic effects and hereby capture the extent of concentration polarization around a membrane. Because of the increase in area when moving from the center to the outside of a cylindrical grid, the amount of hydrogen that can be supplied to the membrane is larger than in a rectangular domains, so the extent of concentration polarization is expected to be smaller in 3D cylindrical systems than in Cartesian systems. Moreover, the bubbles passing by and around the immersed membrane could have a significant effect on the mass

transfer around the membranes, which cannot be fully captured with 2D simulations. Furthermore, laboratory-scale systems with multiple membranes cannot be simulated with 2D simulations, so ultimately 3D simulations are an important next step in fluidized bed membrane reactor research. By comparing the 2D and 3D simulations, the advantages and shortcomings of 2D simulations can be identified, and the conceptual usefulness of 2D simulations can hereby be assessed.

Most studies on vertical objects immersed in fluidized beds have focused on hydrodynamics [6] or heat transfer between a vertical tube and the emulsion phase [7,8]. Densified zones in fluidized bed membrane reactors and mass transfer phenomena in flat pseudo-2D fluidized beds have already been studied by Tan et al. [9–11] with a Discrete Particle Model (DPM), however, they used flat vertically immersed membranes that were installed in the bed walls, so the effects of using cylindrical systems and possible interaction between multiple membranes were not investigated. Jaso et al. [12] have studied 3D cylindrical fluidized bed membrane reactors for the oxidative coupling of methane, providing some design rules for this system, but they have not investigated concentration polarization in detail, nor the occurrence of densified zones and the possibility of interactions between the concentration polarization zones in case of multiple inserted membranes. Recently, the study by Yang et al. [13] has investigated the concentration polarization coefficient (CPC) in fluidized bed membrane reactors in 3D, using hydrogen selective membranes. They have investigated different immersed membrane configurations as well as an external membrane wall. Their main findings are that eccentric placement of the membranes can lower the concentration polarization. Using the membrane as an external wall promotes mainly the hydrogen separation in the bottom of the reactor.

Despite these studies, research on the positioning of vertical membranes in fluidized beds is very much unexplored. Palladium membranes are expensive, so they should be utilized to their fullest potential. If membranes are placed too close to one another, the reactor performance is aggravated due to the interaction of the concentration polarization zones around each membrane. The membranes will compete for hydrogen with each other, leading to areas in the reactor with strongly reduced hydrogen concentrations, leading to reduced membrane fluxes. Furthermore, if the membranes are placed too far apart, there will be a lot of hydrogen bypassing, which will also lead to reduced system performance. Therefore, the effect of inter-membrane distance on the hydrogen recovery should be investigated.

This work is a numerical study on concentration polarization in 3D cylindrical fluidized bed reactors with vertically immersed membranes. The goal of this work is to identify, describe and explain how concentration polarization manifests itself in fluidized beds with vertically immersed membranes. A Two-Fluid Model (TFM) is used to perform the simulations and to obtain detailed information on the phenomena occurring near the membranes. The OpenFOAM® v.2.3.0 *twoPhaseEulerFoam* solver was used as hydrodynamic framework, which was extended with a species balance equation and a realistic membrane model to simulate selective extraction of hydrogen from the system. The extended TFM has been thoroughly verified and validated. Due to the large number of computational cells, the 3D simulations were run in parallel on the Dutch national supercomputer Cartesius.

This paper will first briefly discuss the model and its most important equations. Also the grid convergence for fluidized beds with horizontal membranes will be discussed. Special attention will be given to the implementation of the species balance, the implementation of the membrane source term and the

membrane boundary condition. Next, the simulation settings and configurations will be presented. Subsequently, the results of this study will be discussed, and finally the main conclusions will be summarized.

2. Model description and validation

2.1. Model description

A Two-Fluid Model (TFM) considers the gas and solids phase as interpenetrating continua. The governing and constitutive equations are presented in Table 1. The gas phase obeys the ideal gas law and the solids phase rheology is modeled with the Kinetic Theory of Granular Flow (KTGF), where the solids packing limit is controlled by the solids pressure and the solids phase momentum transfer is described with a Newtonian stress tensor with a shear and bulk viscosity, augmented with a frictional stress model. The KTGF transport parameters all depend on the granular temperature, a measure of the kinetic energy involved in the random motion of the particles, for which the full granular temperature equation is solved. The KTGF closure equations used in this work are presented in Table 2 [14]. Details on the TFM and KTGF can be found in literature [15–20]. Detailed information on OpenFOAM and its TFM specifically has been published in literature as well [21–26].

The drag between the solids and the gas phase is calculated using Gidaspow’s drag model [20], which combines the drag model of Ergun [27] and Wen & Yu [28], where Ergun’s equation is used for high solids hold-ups (above 20%) and Wen & Yu’s equation is used at lower solids hold-ups (below 20%). The drag coefficient C_d is determined based on the particle Reynolds number.

Mass transfer and membranes

A hydrogen mass balance describes the hydrogen concentration profile in the fluidized bed (see Equation 1), where the extraction of hydrogen via the membrane(s) is accounted for via a sink term S_m in the gas phase continuity equation in the computational cells adjacent to the membrane boundary (the red cells in Figure 1). The sink term, S_m , is calculated by multiplying Sieverts’ law with the boundary cell’s area A_c , divided by the cell volume V_c , as shown in Equation 2 [29]. The dispersion coefficient was kept constant throughout the fluidized bed systems studied in this work.

$$\frac{\partial \alpha_g \rho_g Y_{H_2}}{\partial t} + \nabla \cdot (\alpha_g \rho_g \mathbf{u}_g Y_{H_2}) = \nabla \cdot (\alpha_g \rho_g D_{H_2} \nabla Y_{H_2}) + S_m \quad (1)$$

$$S_m = \frac{A_c}{V_c} Q_m M_{w,H_2} \left[\left(X_{H_2}^{ret} P_{tot} \right)^n - \left(X_{H_2}^{perm} P_{tot} \right)^n \right] \quad (2)$$

Table 1: Summary of all governing and constitutive equations used in the TFM.

Continuity equation of the gas phase

$$\frac{\partial \alpha_g \rho_g}{\partial t} + \nabla \cdot (\alpha_g \rho_g \mathbf{u}_g) = S_m$$

Continuity equation of the solids phase

$$\frac{\partial \alpha_s \rho_s}{\partial t} + \nabla \cdot (\alpha_s \rho_s \mathbf{u}_s) = 0$$

Momentum equation gas phase

$$\frac{\partial \alpha_g \rho_g \mathbf{u}_g}{\partial t} + \nabla \cdot (\alpha_g \rho_g \mathbf{u}_g \mathbf{u}_g) = -\left(\nabla \cdot \alpha_g \overline{\overline{\boldsymbol{\tau}_g}}\right) - \alpha_g \nabla p - \beta(\mathbf{u}_g - \mathbf{u}_s) + \alpha_g \rho_g \mathbf{g}$$

Momentum equation solids phase

$$\frac{\partial \alpha_s \rho_s \mathbf{u}_s}{\partial t} + \nabla \cdot (\alpha_s \rho_s \mathbf{u}_s \mathbf{u}_s) = -\left(\nabla \cdot \alpha_s \overline{\overline{\boldsymbol{\tau}_s}}\right) - \alpha_s \nabla p - \nabla p_s + \beta(\mathbf{u}_g - \mathbf{u}_s) + \alpha_s \rho_s \mathbf{g}$$

Granular temperature equation (non-equilibrium)

$$\frac{3}{2} \left(\frac{\partial (\alpha_s \rho_s \theta)}{\partial t} + \nabla \cdot (\alpha_s \rho_s \mathbf{u}_s \theta) \right) = \left(-p_s \overline{\overline{\mathbf{I}}} + \alpha_s \overline{\overline{\boldsymbol{\tau}_s}} \right) : \nabla \mathbf{u}_s + \nabla \cdot (\kappa_s \nabla \theta) - \gamma_s - J_s$$

Viscous stress tensor gas phase

$$\overline{\overline{\boldsymbol{\tau}_g}} = - \left[\mu_g (\nabla \mathbf{u}_g + (\nabla \mathbf{u}_g)^T) + \frac{2}{3} \mu_g (\nabla \cdot \mathbf{u}_g) \overline{\overline{\mathbf{I}}} \right]$$

Viscous stress tensor solids phase

$$\overline{\overline{\boldsymbol{\tau}_s}} = - \left[\mu_s (\nabla \mathbf{u}_s + (\nabla \mathbf{u}_s)^T) + \left(\lambda_s - \frac{2}{3} \mu_s \right) (\nabla \cdot \mathbf{u}_s) \overline{\overline{\mathbf{I}}} \right]$$

Inter-phase drag coefficient

$$\beta = 150 \frac{\alpha_s^2 \mu_g}{\alpha_g d_p^2} + 1.75 \frac{\alpha_s \rho_g |\mathbf{u}_g - \mathbf{u}_s|}{d_p} \quad \text{for } \alpha_s \geq 0.20$$

$$\beta = \frac{3}{4} C_d \frac{\alpha_g \alpha_s \rho_g}{d_p} |\mathbf{u}_g - \mathbf{u}_s| \alpha_g^{-2.65} \quad \text{for } \alpha_s < 0.20$$

$$C_d = \frac{24}{\text{Re}_p} (1 + 0.15 \text{Re}_p^{0.687}) \quad \text{for } \text{Re}_p \leq 1000$$

$$C_d = 0.44 \quad \text{for } \text{Re}_p > 1000$$

$$\text{Re}_p = \alpha_g \frac{\rho_g d_p |\mathbf{u}_g - \mathbf{u}_s|}{\mu_g}$$

Table 2: Summary of all KTGF closure equations used in this work [14].

Solids shear viscosity

$$\mu_s = 1.016 \frac{5}{96} \pi \rho_s d_p \sqrt{\frac{\theta}{\pi}} \frac{\left(1 + \frac{8(1+e)}{5} \alpha_s g_0\right) \left(1 + \frac{8}{5} \alpha_s g_0\right)}{\alpha_s g_0} + \frac{4}{5} \alpha_s \rho_s d_p g_0 (1+e) \sqrt{\frac{\theta}{\pi}}$$

Solids bulk viscosity

$$\lambda_s = \frac{4}{3} \alpha_s \rho_s d_p g_0 (1+e) \sqrt{\frac{\theta}{\pi}}$$

Solids pressure

$$p_s = \alpha_s \rho_s \theta (1 + 2(1+e) \alpha_s g_0)$$

Frictional pressure

$$p_s^{fr} = Fr \frac{\left[\max\left((\alpha_s - \alpha_s^{\min fr}), 0\right)\right]^{c_1}}{\left[\max\left((\alpha_s^{\max} - \alpha_s), 5 \cdot 10^{-2}\right)\right]^{c_2}} \quad \text{with: } \alpha_s^{\min fr} = 0.50, \quad Fr = 0.05, \quad c_1 = 2, \quad c_2 = 3$$

Frictional shear viscosity

$$\mu_s^{fr} = \frac{p_s^{fr} \sqrt{2} \sin \phi^{fr}}{2 \alpha_s \sqrt{\bar{\mathbf{S}} : \bar{\mathbf{S}} + \frac{\theta}{d_p^2}}} \quad \text{with: } \bar{\mathbf{S}} = \frac{1}{2} \left((\nabla \mathbf{u}_s) + (\nabla \mathbf{u}_s)^T \right) - \frac{1}{3} \nabla \cdot \mathbf{u}_s \bar{\mathbf{I}} \quad \text{and } \phi^{fr} = 28.0^\circ$$

Radial distribution function

$$g_0 = \frac{1 + 2.5 \alpha_s + 4.5904 \alpha_s^2 + 4.515439 \alpha_s^3}{\left[1 - \left(\frac{\alpha_s}{\alpha_s^{\max}}\right)^3\right]^{0.67802}} \quad \text{with: } \alpha_s^{\max} = 0.62$$

Conductivity of granular energy

$$\kappa_s = 1.02513 \frac{75}{384} \pi \rho_s d_p \sqrt{\frac{\theta}{\pi}} \frac{\left(1 + \frac{12(1+e)}{5} \alpha_s g_0\right) \left(1 + \frac{12}{5} \alpha_s g_0\right)}{\alpha_s g_0} + 2 \alpha_s \rho_s d_p g_0 (1+e) \sqrt{\frac{\theta}{\pi}}$$

Dissipation of granular energy

$$\gamma_s = 3(1 - e^2) \alpha_s^2 \rho_s g_0 \theta \left[\frac{4}{d_p} \sqrt{\frac{\theta}{\pi}} - (\nabla \cdot \mathbf{u}_s) \right]$$

Fluctuating velocity/force correlation

$$J_s = 3 \beta \theta$$

The extraction of mass via a membrane also results in momentum extraction from the system. Therefore, a boundary condition was added for the membranes to ensure the corresponding momentum leaves the system. The boundary condition imposes a velocity normal to the membrane surface, based on the magnitude of the extractive flux (see Equation 3). Depending on the gas extraction rate and particle size, momentum extraction could be an important topic for fluidized beds, because it could cause densified zones to form near the membrane surface, which can aggravate concentration polarization. Extracting a large amount of gas from a fluidized bed via porous walls can even alter the flow pattern of the solids, as shown by De Jong et al. [30] and Dang et al. [31]. However, Helmi et al. [4] have shown that selective extraction of hydrogen via a supported palladium-based membrane only has a small effect on the bed hydrodynamics.

$$u_m = \frac{S_m RT}{p M_{w,H_2}} \frac{V_c}{A_c} \quad (3)$$

Figure 1: Schematic representation of how the membrane source term has been implemented.

Boundary conditions

In this work 3D simulations have been performed, with for the gas phase the no-slip boundary condition applied to the surrounding wall of the bed and to the top and bottom of the membrane, a constant velocity at the inlet (fixed value boundary condition), a prescribed pressure condition ($P=1.5$ bar) applied at the outlet and the boundary condition of Equation 3 at the surfaces of the immersed membranes. For the solids velocity and granular temperature, the Johnson & Jackson partial slip boundary condition [32] with a specular coefficient of 0.50 was applied on the surrounding wall and on the membrane surfaces. The mass fraction of hydrogen at the inlet was set to a fixed value and on the walls and outlet it was set to a zero-gradient condition.

Numerical schemes and accuracy

The temporal discretization was done with the second order Crank-Nicolson scheme. All simulations were run with an adjustable time-step, with a maximum time-step of $1 \cdot 10^{-5}$ s. The selected time-step value each iteration was selected based on a maximum Courant number of 0.1. A combination of two second order schemes, the Gauss linear scheme and the Van Leer scheme, were used for the spatial discretization. The numerical tolerances for the residuals were set to $1 \cdot 10^{-11}$ for all quantities.

Verification and validation

The TFM used in the present work has previously already been verified by checking the pressure drop over a packed bed [33], and validated by comparing the hydrogen flux and bubble sizes to experimental results [4,34]. Furthermore, the component mass balances have been verified with the analytical solution of Ogata and Banks [35] and the Fourier solutions for two-sided diffusion.

2.2. Grid sensitivity

To ensure a grid independent solution, a cylindrical fluidized bed, 8 cm in diameter and 24 cm in height, with an initial 55% solids hold-up placed up to 12 cm, with one single vertically immersed membrane in the center was simulated on a coarse, middle and fine grid. An example of various aspects of the grid of the fine case is presented in Figure 2. The number of computational cells of the coarse, middle and fine grid are presented in Table 3. The membrane was added to a cylindrical grid with the OpenFOAM tool snappyHexMesh. The membrane consists of a 7 cm long cylinder which is 1 cm in diameter, with a 1 cm in diameter semi-sphere placed on its top and bottom to ensure that the membrane is rounded and the transition from the membrane boundary to the internal grid is as smooth as possible, in order to avoid any numerical difficulties or grid inconsistencies due to sharp corners in the grid.

To ensure all the flow and mass transfer details near the membrane are captured accurately, the grid is refined at the membrane boundary. In Figure 2, the cell distribution of the cylindrical domain shows that, unlike with cylindrical coordinates, there is no centerline singularity in the grid. Because OpenFOAM uses the Finite Volume Method (FVM) to solve equations, it is possible to combine cylindrical grids with non-hexahedral cells and also have less cell tapering towards the outside of the cylinder, thus making the cells sizes at the center and outside walls of the cylinder more equal than when using cylindrical coordinates only.

Table 3: Number of computational cells for the coarse, middle and fine grid.

Grid refinement level	Number of cells			Total number of cells [-]
	Width (X) [-]	Depth (Y) [-]	Height (Z) [-]	
Coarse	39	39	120	267 234
Middle	48	48	135	385 081
Fine	60	60	150	578 714

The results of the grid dependence study are presented in Figure 3 and Figure 4, in which results are averaged over time and over the azimuth (i.e. over a circle with its center on the central simulation axis) combined with axial (Figure 3) or radial (Figure 4) averaging. The results of each grid have been binned with 30 points because of the irregular shape of the grid cells. The solids hold-up and the hydrogen mole fraction have been time-averaged, and averaged over both the axial and radial positions. The solids hold-up and especially the hydrogen mole fraction show good grid convergence, even at the coarsest grid the results are sufficiently accurate. However, for all the simulations in this work, the fine grid was selected, also to ensure that the membrane shape is as rounded as possible.

Figure 2: Grid of the 3D cylindrical fluidized bed with a single immersed vertically placed membrane; (a) Side view of the bed and membrane; (b) Top view of the membrane; (c) Close-up view of the clipped grid around the membrane; (d) Grid at the inlet (and outlet) of the fluidized bed.

Figure 3: Comparison of the time, azimuthally and axially averaged solids hold-up and hydrogen mole fractions for the single vertically immersed membrane case with a coarse, middle and fine grid.

Figure 4: Comparison of the time, azimuthally and axially averaged gas velocities for the single vertically immersed membrane case with a coarse, middle and fine grid.

2.3. Geometries and settings

Using the fine grid, simulations of fluidized beds with various different vertical membrane configurations were performed. The configurations and their corresponding measurements are presented as front and top view in Figure 6. Only one side view has been presented because most of the measurements of the VM1 case, such as membrane length, height of the solids and diameters, are the same for the cases with multiple membranes. All additionally required data, such as inter-membrane distances and angles, is given in the top view pictures in Figure 6. The number of membranes and the total membrane area per case are provided in Table 4. The simulation settings are presented in Table 5. The simulation domain size is similar to a realistic laboratory scale fluidized bed membrane reactor. The values for the membrane flux data, reactor pressure, hydrogen mole fraction at the inlet, reactor temperature and dispersion coefficient were obtained from the work by Helmi et al. [4]. The membrane permeation flux data was obtained for a 5 μm thick dense Pd/Ag thin film onto a ceramic support. Near vacuum has been assumed at the permeate side, so that the mass transfer resistance in the support can be neglected. The dispersion effects were implemented as an effective dispersion coefficient, which was estimated based on the Tsotsas and Schlünder equation for axial and radial dispersion in a packed bed [27].

All simulations have been performed with 500 μm particles, however, to verify the effect of gas extraction on the formation of densified zones near the membrane, additional simulations with 250 μm particles has been performed with the VM1 geometry. All particle properties for the 250 μm simulation were kept the same as in the 500 μm simulation. The gas inlet velocity for the 250 μm VM1 simulation was 0.27 m/s, which is three times the minimum fluidization velocity. To investigate the influence of the extent of gas extraction for membranes with improved permeability, the coarse grid single membrane case was also simulated with three different permeances: low, standard (as used for all other simulations) and high permeability (see Table 4 for the values).

The single membrane case simulations are significantly faster than multiple membrane cases because they have fewer grid cells, so the single membrane cases will be used to quantify and understand the phenomena occurring in these types of systems, such as concentration polarization. The multiple membrane cases are subsequently used to study the interactions between the membranes. Especially the

VM3 cases, which have been run at three different inter-membrane distances, will show how close the membranes can be stacked together before resulting in reduced system performance. The VM3 close case, with the closest membrane packing, was simulated with three different fluidized bed diameters, viz. 4, 6 and 8 cm, to investigate how the mass transfer limitations are affected by these changes in geometry. The overall hydrogen recovery and the hydrogen recovery per membrane will quantify the possible decrease in performance. Comparison of the VM4, VM5-P and VM5-Q configurations will reveal how much hydrogen bypassing could take place via the center of the bed, and will help determining guidelines for optimal positioning of the membranes in fluidized bed membrane reactors.

Cartesian 2D versus cylindrical 3D simulations:

Previously, concentration polarization has been quantified in fluidized bed membrane reactors with 2D Cartesian TFM simulations, where the left wall boundary was simulated as an immersed membrane [4]. The 2D simulations can qualitatively describe how concentration polarization manifests in fluidized bed membrane reactors, but may over-predict the extent of concentration polarization and the solids hold-up near the membranes. Therefore, the 3D cylindrical simulations will be compared to the 2D Cartesian approach to assess the accuracy of the 2D simulations and thus their usefulness for future research. A schematic picture of the 2D set-up, and how it compares to the single membrane set-up (VM1) is presented in Figure 5. The dimensions and geometry of the 2D simulation were kept as close as possible to the 3D dimensions. The number of cells in the width and height were 80 and 501 cells respectively.

Figure 5: Schematic representation of the 3D fine grid and the 2D fine grid. The red areas are the membranes. All measurements are in cm.

Parallel efficiency:

The number of grid cells of a 3D vertical membrane simulation is significantly larger than a 2D case. The smallest 3D cases in this work employed around 300 000 grid cells, whereas the large cases had around 1.8 million grid cells (compared to 40 000 cells for a 2D simulation). Single core simulations of such cases would take months to finish, which is why all simulations presented in this work were run in parallel on the Surfsara cluster in Amsterdam. The grids were decomposed with the Scotch algorithm, which means no geometric information is required from the user when decomposing the domain into sub-domains. The Scotch algorithm attempts to minimize the number of processor boundaries, which helps improving the parallel efficiency of the simulations. The single membrane simulations were run on 32 cores and the multiple membranes cases were run on 64 cores. To simulate 16 s of real time, the single membrane simulation with a fine grid, containing 0.5 million grid cells, took approximately three weeks and the five membranes quincunx simulation, which has almost 1.8 million grid cells, took about one and a half month. The parallel efficiency of these systems was between 50% and 60% and for our 3D cases where we used approximately 10 000 to 30 000 cells per processor.

Figure 6: Configurations and geometries of the simulated fluidized bed membrane reactor set-ups. The red areas are the membranes. All distances are in cm.

Table 4: Number of membranes and membrane area per simulation.

Membrane configuration	Number of membranes [-]	Membrane area [cm ²]
VM1	1	21.99
VM3 close – 4 cm	3	65.97
VM3 close – 6 cm	3	65.97
VM3 close – 8 cm	3	65.97
VM3 mid	3	65.97
VM3 far	3	65.97
VM4	4	87.96
VM5-P (pentagram)	5	109.96
VM5-Q (quincunx)	5	109.96

Table 5: Simulation settings.

Quantity	Setting	Quantity	Setting
d_{FB}	0.04; 0.06; 0.08 m	u / u_{mf}	3.0
H_{FB}	0.24 m	u_{mf} (500 μ m)	0.21 m/s
d_m	0.01 m	u_{mf} (250 μ m)	0.09 m/s
H_m	0.07 m	D_{H_2}	$1.0 \cdot 10^{-4}$ m ² /s
d_p	500 μ m; 250 μ m	Q_m (std.)	$4.30 \cdot 10^{-3}$ mol/(m ² s)
ρ_p	2500 kg/m ³	Q_m (low)	$2.15 \cdot 10^{-3}$ mol/(m ² s)
e_{pp}	0.97	Q_m (high)	$8.60 \cdot 10^{-3}$ mol/(m ² s)
e_{pw}	0.97	n	0.50
T	405 °C	$X_{H_2, init}$	0.25
Δt_{sim}^{max}	$1 \cdot 10^{-5}$ s	p_{outlet}	$1.5 \cdot 10^5$ Pa
t_{sim}	16 s	p_{perm}	$0.01 \cdot 10^5$ Pa

3. Results and discussion

The results and discussion section will be split into two parts. Firstly, the results of the single membrane cases will be presented, and the prevalent mass transfer and hydrodynamic phenomena will be discussed. The emphasis of the single membrane section is on concentration polarization, a comparison between 2D and 3D simulations, and on the effect of particle size on the formation of densified zones near the membrane. The multiple membrane cases section will first focus on the interaction between multiple membranes and how this affects the system performance, after which the bubble properties and solids hold-up profiles of these systems will be discussed.

3.1. Single membrane

3.1.1. Concentration polarization

In 3D cylindrical simulations of fluidized beds with vertically immersed membranes, concentration polarization occurs under realistic hydrodynamic conditions. The time-averaged solids hold-up, bubbles snapshots and hydrogen mole fractions in Figure 7 show how the solids are distributed in the reactor, how bubbles move around the membrane and how concentration polarization has manifested itself near the membrane. The bubbles have been defined as areas where the solids hold-up is equal to or below 20%. The time averaged solids hold up profiles are as expected; near the walls an increased solids hold up is found due to solids down flow and collisions of particles with the wall. Near the membrane a slight increase in solids hold-up is found, however, it is less pronounced than near the wall because solids can easily move around the membrane. Below the membrane, a small volume with reduced solids hold-up is located. The reduced solids hold-up is caused by the formation of gas pockets, which happens after a bubble has passed, causing solids to fall down again past the membrane. The bubbles move mostly between the wall and the central membrane, but sometimes they pass by through the membrane as well, effectively reducing in size. To be able to draw conclusions from these simulation snapshots, the concentration and solids profiles were quantified as well.

Figure 8 shows a quantitative representation of the average hydrogen concentration and solids hold-up near the membrane, and the concentration profiles at various axial positions. In the left graph of Figure 8, the data has been averaged over time, as well as azimuthally and axially. In the right graph of Figure 8, the data has only been time and azimuthally averaged, and concentration profiles at various axial positions are displayed to show the progression of concentration polarization over the length of the membrane. The graphs show that the concentration gradient is quite high within 5 mm distance from the membrane surface. There is a significant amount of hydrogen bypass, because only a single membrane was used, so the bulk concentration is quite constant beyond about 1.5 cm from the membrane surface, which means the single membrane case can be considered as an ideal case with the maximum possible hydrogen supply for the membrane.

The concentration profiles at various axial positions in Figure 8 show that, around the top of the membrane, most of the concentration polarization has disappeared within about 1 cm distance from the membrane, and near the bottom of the membrane it has already disappeared within about 3 mm distance from the membrane surface. The increase in concentration polarization when going upwards along the membrane should be considered when designing fluidized beds with multiple membranes, because if their inter-membrane distance is too small, the membrane can compete for hydrogen with one another and hereby reduce the overall efficiency of the system. According to this single membrane simulation, an inter-membrane distance of at least 2 cm should be chosen to avoid even further reduction in hydrogen near the membrane. What the effect of inter-membrane distance is on membrane performance will be further investigated with simulations of fluidized beds with multiple membranes.

Appendix A shows how changes in membrane permeance could affect concentration polarization and hydrodynamics. For membranes with high permeances, the hydrogen flux is significantly higher at the bottom of the membrane than for low permeances, but the differences between the hydrogen flux higher up the membrane are fairly small for all cases, indicating that the systems are almost fully dominated by bed-to-membrane mass transfer limitations and not by membrane performance. In comparison with the work due to Yang et al. [13], the hydrogen profile in our simulations shows a more gradual decrease over the reactor height, which may be attributed to both the used dispersion coefficient, membrane permeability and (most likely) the particle size.

Figure 7: Snapshot of the time-averaged solid hold-up, instantaneous bubble contours ($\alpha_s \leq 0.20$) and time-averaged hydrogen molar fraction for the VM1 fine case.

Figure 8: (left) Azimuthally, axially and time-averaged hydrogen mole fraction and solids hold-up versus distance from the membrane surface, and (right) azimuthally and time-averaged hydrogen mole fraction profiles at various axial positions, for the VM1 fine case.

3.1.2. The 2D flat plate versus 3D cylinder approach

This section discusses the most important differences between the hydrodynamics and mass transfer phenomena occurring in a 2D and 3D single membrane simulation. Previously, the symmetry approach of 2D simulations was used by Helmi et al. [4] to render useful qualitative results on concentration polarization in fluidized bed membrane reactors. However, the hydrodynamics of the bed cannot be fully captured in these flat Cartesian 2D systems and the extent of the overprediction of concentration polarization when using a flat plate approach is assessed here.

In Figure 9, Figure 10 and Figure 11 the concentration profiles, hydrogen flux, time-averaged solids hold-up data, instantaneous solids hold-up contours and solid flux profiles are presented for both the 3D cylindrical VM1 fine case and a 2D Cartesian representation of the 3D geometry. Figure 9 shows that the concentration polarization in 2D systems is overestimated compared to 3D systems, but qualitatively the concentration profiles match quite well. In the 2D case, the flux reduces significantly faster axially along the membrane than in the 3D case. The incorrect prediction of the mass transfer phenomena are inherently related to the incorrect predictions of both the solids hold-up and solids flux profiles in 2D Cartesian simulations, which is portrayed in Figure 10 and Figure 11. Figure 10 shows that the Cartesian 2D simulation predicts a significantly higher solids hold-up near the membrane than the 3D simulation. In the 2D simulation, bubbles do not pass by very close to the membrane because in this simulation it is basically an unsurpassable hydrogen-extracting wall, whereas in the 3D case the bubbles closely pass by the immersed membrane, sometimes even passing through it, because the bubble can cross the center of and move to the other side of the bed. Additionally, slugging type behavior is also observed in the 2D simulation, causing less bubbles to form, which reduces the mass transfer in the system. This slugging behavior often occurs when simulating systems with a small width, which is the case for this 2D sliced mesh. Figure 11 shows the time-averaged solids flux and the time-averaged solids velocity vectors near the membrane. The solids flux profiles near the membrane are similar in magnitude, but the direction in which the solids flow is completely different for the 2D and 3D case. In the 2D case there is significant solids down flow near the membrane, whereas in the 3D case the solids move upwards, albeit very slowly. Now the differences between 2D and 3D simulations have been described, the extent of concentration polarization will be quantified.

To quantify the effect of concentration polarization, Helmi et al. [4] have correlated the concentration film layer thickness, δ , assumed constant along the membrane, for a flat plate and cylindrical approach of a membrane. The flat plate and cylindrical approach derived with a continuity equation with Fickian dispersion, including drift flux, are presented in Equation 4 and Equation 5 [4]. The film layer thickness for each approach are calculated with these equations, using the steady flux from the TFM simulations at the top of the membrane, which are $0.217 \text{ mol}/(\text{m}^2 \text{ s Pa}^{0.5})$ for the 3D case and $0.133 \text{ mol}/(\text{m}^2 \text{ s Pa}^{0.5})$ for the 2D case. Table 6 presents the film layer thicknesses for the 2D and 3D TFM simulations calculated with Equation 4 and Equation 5. To show the differences between the film layer thickness values, their representative physical locations in the fluidized bed have also been drawn in the concentration plot in Figure 9. The differences between approaching the 2D system as a flat plate (Equation 4) and cylinder (Equation 5) are not very large in the absolute sense, whereas the relative difference is 26%. However, the difference between the 2D film layer thickness calculated with a cylindrical approach and the 3D film

layer thickness is approximately a factor 3. This shows that, for this case, using Equation 5 to only correct for geometric effects that are missing in the 2D flat plate approach is insufficient to estimate a proper film layer thickness δ . The hydrodynamics have by far the largest influence in this case, which has already been elaborated in the previous paragraph. Moreover, these hydrodynamic effects will not be predicted well by axisymmetric simulations, because the solids down flow and increased solids hold-up near the membrane are also expected in these simulations. We can thus conclude that concentration polarization effects predicted by 2D simulations can only be considered as rough estimates that could be used to obtain fast worst case estimations for a 1D phenomenological fluidized bed membrane reactor model, and that 3D simulations are required for more realistic predictions of the film layer thickness.

$$N_{H_2,plate} = \frac{D_{H_2}}{\delta_{plate}} C_{tot} \ln \left(\frac{1 - X_{H_2,m}}{1 - X_{H_2,bulk}} \right) \quad (4)$$

$$N_{H_2,cylinder} = \frac{D_{H_2}}{(r_m + \delta_{cylinder}) \ln \left(1 + \frac{\delta_{cylinder}}{r_m} \right)} C_{tot} \ln \left(\frac{1 - X_{H_2,m}}{1 - X_{H_2,bulk}} \right) \quad (5)$$

Table 6: Film layer thicknesses for 2D and 3D simulations calculated with a flat plate and cylindrical approach.

	Flat plate	Cylinder
2D	3.95 mm	3.13 mm
3D	-	1.06 mm

Figure 9: Comparison of the hydrogen mole fractions (with physical location of film layer thicknesses δ) and flux for the VM1 fine case (3D) and the 2D case.

Figure 10: (left) Comparison of the solids hold-up for the VM1 fine case (3D) and the 2D case; (right) Snapshots of the instantaneous solids hold-up for the 3d and 3D case, in which a bubble is present.

Figure 11: Time-averaged solids flux and velocity vectors around the membrane for the 3D (slice of the VM1 fine simulation) and the 2D case.

3.1.3. Densified zones and bubble frequency for different particle sizes

The extractive flux of a membrane can cause momentum to flow towards the membrane, possibly causing densified zones to form near the membrane. Densified zones can affect the system performance negatively by hindering hydrogen extraction and thus reducing hydrogen recovery. However, the formation of densified zones also depends on particle properties, such as their density and size. In Figure

12, the solids hold-up and hydrogen fluxes along the membrane are displayed for two different cases with 250 and 500 μm particles at three times their respective minimum fluidization velocities. A clear increase in average solids hold-up is found next to the membrane when using smaller particles. The solids hold-up profiles show that the extraction of momentum affects the smaller particles more than the larger ones, and results in a decrease in the local hydrogen concentration and local hydrogen flux. This is much more in line with the results by Yang et al.[13], whom have used 160 μm particles, especially showing the sharp decrease of the hydrogen profile near the membrane. This effect is expected to worsen for even smaller particles and fine powders, especially with electrostatic forces start playing a role.

Figure 12: (left) Azimuthally, axially and time-averaged solids hold-up versus radial distance along the membrane, and (right) azimuthally and time-averaged hydrogen flux profiles along the axial positions of the membrane, for the VM1 fine case with 250 and 500 μm particles.

To further understand how the membrane affects particles of different size, the effect of the bubble and emulsion phases have been separated by displaying the azimuthally averaged bubble frequency and the average emulsion solids hold-up contour plots in Figure 13. The axial positions between 0.03 and 0.10 m are where the membrane is located, and the radial position is counted from the membrane surface at 0.005 m from the center of the fluidized bed. The bubble frequencies were calculated by counting the number of times a computational cell contains an area that is part of a bubble ($\alpha_s \leq 0.20$), and dividing this number by the total number of times a bubble area has been counted. To calculate the average emulsion solids hold-up, only the solids hold-ups between 0.30 and 0.62 were time-averaged over the entire simulation.

For both cases, most bubbles clearly move through the center in between the membrane and the bed wall. The bubble frequency also is significantly different for both particle size cases, however, this is mostly caused by the small number of bubbles that are counted in these relatively short simulations (only 10 seconds of data is available for averaging and bubble counting), especially at the bottom of the 500 μm case plot. Generally, for both particle sizes, the number of bubbles that occur near the membrane is relatively low, but the 500 μm case has slightly more bubbles near the top of the membrane than the 250

μm case. The average emulsion phase density next to the membrane is higher for the 250 μm case than for the 500 μm case. A significant part of the membrane in the 250 μm case is surrounded with approximately 48% solids, whereas the 500 μm case has at most a very small area with 46% solids but mostly areas with lower solids hold-ups. These results show that, on average, the extractive flux of the membrane increases the emulsion phase density near the membrane, whereas the bubble flow near the membrane is only affected slightly because it is quite low. Additionally, the effect of an increased and decreased membrane performance on 500 μm particles was checked, see Appendix A. The results show that doubling or halving the permeance of the membrane does not show significant changes in the solids hold-up near the membrane surface, so the increased emulsion phase density near the membrane can be attributed mostly to the reduced particle mass of 250 μm particles.

To conclude, it is beneficial for hydrogen extraction to use particles of at least 500 μm to minimize the effect of an increasingly densified emulsion phase near the membrane surface. It should be noted that for reactive systems, because small particles have a higher surface to volume ratio, using small particles can be beneficial for catalytic systems, so a balance between particle size and densified zone formation near the membranes surface should be found when deciding on which particle size to use.

Figure 13: Bubble frequency and average emulsion solids hold-up contour plots for the VM1 fine cases with 250 and 500 μm particles.

3.2. Multiple membranes

3.2.1. Interaction between membranes and hydrogen recoveries

To achieve interesting hydrogen recoveries from a fluidized bed membrane reactor, multiple membranes are required. Even though there have already been experimental hydrodynamic studies on cylindrical fluidized beds with vertically immersed membranes [37], the effect of the membranes on the fluidization behavior remains difficult to be quantified, and simulations are required to visualize and quantify concentration polarization effects. CFD simulations are limited by the number of grid cells in the system, so only cases with a small number of membranes can be simulated. In the present work, three, four and five membrane cases were simulated. Bubble contours and time-averaged hydrogen concentration contours for four cases are displayed in Table 7. The time-averaged results presented in this table have been supplied as an external data set, which can be found and downloaded through reference [38]. The bubbles often travel through the membranes and are often found in the center of the bed, in between the membranes. Most of the cases in Table 7 show only very little interaction between the concentration layers around the membranes, but the VM5-Q case shows some interaction between the center membrane and the four corner ones.

To study the effect of inter-membrane distance on the hydrogen recovery in more detail, the distances between three vertically immersed membranes were varied between 1.732 cm ('close'), 2.595 cm ('middle') and 3.031 cm ('far'). The case with a single membrane serves as a reference case for the recoveries of multiple membrane cases, because the single membrane is optimally supplied with hydrogen without any interaction. The recoveries per membrane for these cases are presented in Figure 14. Once the membranes are placed within a distance less than 2 cm of one another, the recovery decreases strongly. This matches with the approximation of 2 cm inter-membrane distance to avoid overlapping of concentration polarization zones, which was observed from the single membrane simulation data. However, the differences in recoveries for these cases are fairly small. To demonstrate this: if a hypothetical total hydrogen recovery of 80% is required, placing the membranes 1.732 cm from one another will require 3% more membrane area compared to placing them 2.595 cm apart. This increased interaction between more closely positioned membranes is visualized by means of time-averaged hydrogen concentrations in Figure 15. The concentrations were averaged over the slices indicated with the dashed line in the small top view sketch of the bed. The radial positions in these plots always start from the point where the membrane is closest to the wall (0.04 m) and move to the point on the wall furthest from the membrane (-0.04 m). The VM3 close case exhibits significantly lower hydrogen concentrations around the membranes, causing the mass transfer from the bed to the membrane surface to be lower than for the VM3 far case.

Table 7: Overview of bubble and hydrogen concentration contour snapshots for multiple membrane cases. The time-averaged hydrogen mole fraction contours are shown with 3 view points; front view, diagonal/top view and top-down view. For quantitative analysis, see Figures 15, 16 and 17. These data can be explored interactively through reference [38].

Simulation	Bubble contours	Mole fraction hydrogen (XH ₂)		
Legend
VM3 mid
VM4
VM5 Quincunx
VM5 Pentagon

Placing membranes closer to one another could not only result in interaction between the concentration polarization zones, but there is also less volume present between the membranes, so the low hydrogen concentrations near the membranes will be replenished slower. The VM3 close cases on the left side in Figure 14 were performed with a bed diameter of 8 cm, which means there is sufficient hydrogen present to replenish the outer wall-side of the membranes. The VM3 close cases on the right side in Figure 14 show how reducing the bed diameter, thus reducing the amount of hydrogen available to the outer wall-side of the membranes, affects the hydrogen recovery. Again, the differences in hydrogen recovery per membrane are fairly small, but the effect of the close inter-membrane distance combined with the reduction in bed diameter become more apparent. Taking the hypothetical case of a required total hydrogen recovery of 80%, the VM3 close case with the smallest bed diameter would require 6% additional membrane area compared to the VM3 far case and 9% additional membrane area compared to the ideal case where a single membrane is surrounded by large amounts of hydrogen (VM1 fine). Similar results as the cases with a smaller bed diameter are expected for systems with large numbers of closely packed membranes. If the membrane performance would further drop, to for example to 2.7% per membrane, 15% additional membrane area would be required to achieve the same performance as the ideal case of a single immersed membrane.

Figure 14: Comparison of the hydrogen recovery relative to the single membrane case (VM1) (left) for the cases with 3 membranes at different inter-membrane distances; (right) for cases with 3 membranes at closest inter-membrane distance with different fluidized bed diameter.

Figure 15: Time-averaged hydrogen mole fractions, averaged over the indicated slices (dashed lines) for the following cases: (left) VM3 close; (right) VM3 far.

In Figure 16a the effect of interaction is quantified by plotting the hydrogen recoveries per membrane for the simulated cases. All multiple membrane cases perform worse than the single membrane case, because the membranes compete for hydrogen with one another. This trend progresses from the three membrane cases to the five membrane cases. The recoveries are quite low, because only a small number of membranes were simulated due to time limitations, which results in a large hydrogen bypass. The cases with five membranes, especially the ones in a quincunx formation, suffer from the greatest reduction in recovery. This effect further increases if the membranes are positioned closer together, as discussed for the three membrane cases in Figure 14.

Figure 16b-d shows how this interaction between the membranes manifests itself in the reactor over time. The time-averaged hydrogen concentrations over the indicated vertical slices for the VM5-Q case show a pronounced interaction between the center membrane and the corner membranes, whereas the outer side of the corner membranes show significantly less concentration polarization. This interaction is also seen for the VM4 and VM5-P cases, but to a lesser extent than for the VM5-Q case. Furthermore, in the cases with closely packed membranes there is less hydrogen available because there is less volume present. Most of the interaction occurs at the top of the membranes, but some interaction can already be found at the bottom half of the membranes. Considering the VM5-Q case in Figure 16, the interaction already starts below the middle of the membrane. It should be noted that the membranes in this work are relatively short compared to practical applications; in the simulations they are 7 cm long, whereas for experimental work membranes of 10-50 cm are typically used, and for currently constructed pilot plants these membranes are lengthwise connected to arrive at 50-100 cm membrane length. This means that for practical applications with longer membranes, the part of the membranes where interaction takes place will become greater and thus the overall hydrogen recovery will suffer from this.

Figure 16: (a) Hydrogen recovery relative to the VM1 case for cases VM3 mid, VM4, VM5 pentagram and VM5 quincunx, and their respective inter-membrane distances; Time-averaged hydrogen mole fractions, averaged over the indicated slices (dashed lines) for the following cases: (b) VM4 ; (c) VM5-Q; (d) VM5-P.

The final design of fluidized beds with vertically immersed membranes should be based on high recoveries, which will require significantly more membranes than we have simulated in the present work. Even with the current parallelized TFM, simulations of fluidized beds with large numbers of vertically immersed membranes would result in unrealistically long simulation times, so a design optimization should preferably be done with a phenomenological model. In such a phenomenological model, the concentration layers around the membranes can be described with a boundary layer theory [39], and the positioning of membranes can be based on the maximum allowable overlap between concentration polarization zones. The final design of fluidized beds with vertically immersed membranes will thus depend on the required total hydrogen recovery; when the overlap is increased, more membranes are required to achieve this recovery, whereas reducing the overlap could result in large amounts of hydrogen bypassing the membranes. A similar type of methodology has previously been used for windmill farm pattern optimization [40,41] and could also be adopted for fluidized beds with vertically immersed membranes. Finally, it should be noted that in general membranes are expensive and a big investment, especially when going towards industrial scale production of hydrogen, so a 5-10% gain in recovery by placing the membranes smartly could be an important step towards optimizing this system.

3.2.2. Solids distribution and bubble properties

The hydrodynamic properties of the fluidized bed helps explaining the observed mass transfer phenomena discussed in the previous section. Therefore, this section discusses the effect of vertically immersed membranes on the solids distribution in the bed and the bubble sizes and size distributions for the simulated cases. The time-averaged solids hold-up profiles that have been averaged over a number of vertical slices are presented in Figure 17 for the three, four and five membranes cases. The vertical slices have been sampled at the positions indicated by the dashed lines in the small sketches placed in the contour plots. Some general observations for most of the cases in Figure 17 are that the highest solids hold-ups are observed near the walls, which is a result of the solids down-flow, interaction of the solids with the bed wall and upward flowing gas which slows down the solids movement. The figures also show a lower solids hold-up at the membranes than near the walls, which means bubbles pass by frequently around the membranes, although less often than in the interstitial space between the membranes. Furthermore, on top of the membranes densified zones are present, whereas at the bottom of the membranes gas pockets are observed. The densified zones are formed on top of the membrane because it is difficult for the gas to reach this area, but they have no direct effect on the mass transfer of hydrogen to the membrane because the rounded-off tops and bottoms of the membranes do not extract hydrogen and were added to the simulation to make the transition between the membrane and mesh smooth. Gas pockets below the membranes have been observed to become normal rising bubbles after they move out from the bottom of the membrane, and these rising bubbles do affect the local hydrogen concentration.

To study the effect of the membrane pitch on the bed hydrodynamics, the three membrane cases with small (VM3 close) and large inter-membrane distances (VM3 far) are compared.

Figure 17a-b shows that the reduced performance of the closely placed membranes can be explained by the formation of densified zones in between the membranes. Less bubbles move through the small volume between the closely packed membranes, and the resulting densified zone reduces hydrogen replenishing. These densified zones are fully absent in the case where the three membranes are further apart, showing that these hydrodynamic effects can be detrimental to the membrane performance. Figure 17c-d present the solids hold-ups for the VM4 and VM5-P cases, which both have no membrane in the center of their bed. These figures shows low solids hold-up in the center of the bed and for the VM5-P case also around radial position -0.02 m, which means that most of the bubbles move through the middle of the bed, and in between the membranes where there is little solids down flow and sufficient space for bubble movement.

Figure 17: Time-averaged solids hold-ups, averaged over the indicated slices (dashed lines) for the following cases: (a) VM3 close; (b) VM3 far; (c) VM4; (d) VM5-P; (e) VM5-Q (sliced diagonally); (f) VM5-Q (sliced cross-wise).

Next to the solids distribution, the effect of vertically immersed membranes on bubble properties has been quantified. The Digital Image Analysis (DIA) method used in the work of Medrano et al. [34] was adopted to perform bubble analyses for TFM simulations of 3D cylindrical fluidized bed membrane reactors. Bubbles were defined as regions with a solids hold-up of 20% and lower. This data, along with the simulated solids distribution can explain the bubble movement through the bed and the progression of bubble sizes and numbers around various numbers of vertically immersed membranes.

Figure 18 presents the equivalent bubble diameters and bubble size distributions for cases with 1, 3, 4 and 5 membranes. The graphs with the number of bubbles are slightly erratic, which is related to the relatively small number of data points, and thus the total number of bubbles that were analyzed, compared to experimental cases because of simulation time restrictions. Figure 18 shows that an increase in the number of membranes increases the number of small bubbles, and decreases the equivalent bubble size, of importance to reduce bubble-to-emulsion phase mass transfer limitations. The bubble size distribution and the data in Table 8 show that increasing the number of membranes increases the total number of bubbles, especially the number of small bubbles, which means the average equivalent bubble diameter decreases. Reduction in bubble size in fluidized beds with vertically immersed objects has also been reported by Ozawa et al. [42], however, they did not study how the effect propagates with increasing number of vertical objects. The reduction in bubble size can be attributed to bubbles passing by right next to the membrane, see for example the images in Table 7. Some of the bubbles move against the membrane and cover part of its boundary and partially move through the membrane, hereby having less volume than the bubble would have if the membrane were not present. Furthermore, the number of gas pockets below the membranes, caused by the pulsating movement of the solids, also increases with increasing number of membranes. The reduction in bubble size is rather gradual with increasing number of membranes, so this effect is expected to be more significant for large-scale reactors with more membranes.

For the case with five membranes (VM5-Q), the bubble diameter is very similar to the case with four membranes. In this relatively small experimental size reactor, the number of bubbles present, and thus the number of bubbles that can be cut by the membranes, is limited, thereby leveling off the bubble size effect when the fluidized bed is filled with more membranes. However, the bubble size distributions show that in the five membrane case has a more bimodal shape compared to the four membrane case. To illustrate why the five membrane case has a bimodal bubble size distribution, the equivalent bubble diameters at various radial positions from the center to the bed walls are displayed in Figure 19. The error bars shown in Figure 19 are the standard deviations for each radial data point. In the center ($r = 0$ m), the diameter and standard deviation are both largest, which shows that the largest bubbles still move through the middle of the reactor, where the central membrane of the VM5-Q case is located. In between the central and corner membranes ($r = 0.005$ m – $r = 0.02$ m), and near the bed walls ($r = 0.04$ m) smaller bubbles are present, whereas around the corner membranes, larger bubbles are passing by again. This explains the bimodal bubble size distribution for the five membrane case in Figure 18. To sum up, the number of vertically immersed membranes present in fluidized beds does affect the bubble properties, to the point where even bimodal bubble size distributions can occur. In future work the effects of closely packed vertically immersed membranes in fluidized beds will be studied to investigate how systems with high hydrogen recoveries will behave compared to the simulated systems in the present work.

Table 8: Total number of bubbles counted in the vertical membrane simulations.

Number of membranes [-]	Number of bubbles [-]
1	626
3	739
4	871
5	798

Figure 18: Bubble diameter at different axial positions and bubbles size distribution for cases with 1, 3 and 4 membranes.

Figure 19: Equivalent bubble diameter versus radial position for the VM5Q case, where 0 is the center of the cylindrical fluidized bed. The bars on the data points indicate the standard deviation of the bubble size.

4. Conclusions

A Two-Fluid Model based on the Kinetic Theory of Granular Flow was used to simulate hydrogen extraction via vertically immersed high-flux palladium-based hydrogen perm-selective membranes, which were installed in laboratory-scale cylindrical fluidized beds. The main mass transfer phenomena in these systems were quantified and the simulation data provided design recommendations for these systems.

Single membrane simulations show that the hydrogen concentration gradient is quite sharp close to the membrane, and concentration polarization prevailed within about 1.5 to 2 cm from the membrane surface. The single membrane simulations show that for cases with multiple membranes an approximate inter-membrane distance of 2 cm is advised to avoid reduced efficiencies due to membranes competing for hydrogen with one another.

A comparison between 2D and 3D simulations shows that in Cartesian 2D simulations concentration polarization effects are qualitatively well predicted, but their extent is overestimated. From the 2D simulations, only an estimate for the actual concentration polarization can be obtained, and improving its predictive capabilities requires accounting for not only geometric effects but also for changes in the bed hydrodynamics.

At the membrane surface, a slight increase in the solids hold-up is found when using 500 μm particles, whereas using 250 μm particles shows a clear increase in the average emulsion phase density near the membrane surface. The densified emulsion phase reduces the hydrogen concentration near the membrane and thus reduces the local hydrogen flux. When installing membranes with double and half the standard permeance, the solids hold-up is affected moderately, so using 500 μm particles for fluidized beds with high-flux membranes is recommended to reduce the formation of densified zones near the membrane as much as possible.

Interaction between the concentration polarization zones of multiple membranes has been observed in the simulations. The brief instantaneous interactions between these zones can barely be seen in the averaged hydrogen concentration contours, but the hydrogen recoveries show that all multiple membrane cases perform worse per membrane than in the single membrane case. This is the result of closely packed membranes competing for hydrogen. Next to the increased competition for hydrogen, there is also less gas volume present in between closely packed membranes compared to membranes with less close packing. When reducing the fluidized bed diameter to approximately the inter-membrane distance, the hydrogen recovery also decreases.

In conclusion, to achieve a high total hydrogen recovery for systems with closely packed membranes can require the installment of additional membranes compared to an ideal case without interaction. The economic advantages of high recoveries with closely packed membranes with reduced reactor diameter should be weighed against the cost of additional membranes due to their reduced efficiency. Future work should focus on the optimization of membrane placement in these types of systems with a phenomenological model that contains a description of the concentration polarization around the membranes in the form of a boundary layer.

The integration of vertically immersed membranes also affects the bubble properties. Most of the bubbles move through the middle of the reactor, as well as in between the membranes. Densified zones are found on top and gas pockets are found below the membranes, but they do not affect the membrane performance since the top and bottom side of the vertical membranes do not extract hydrogen. Increasing the number of membranes increases the total number of bubbles, as well as the fraction of small bubbles, whereas the average equivalent bubble diameter decreases, which is beneficial for the bubble-to-emulsion phase mass transfer rates. The reduction in bubble size can be attributed to bubbles passing by just next to the membrane; the bubbles move against the membrane and cover part of its boundary and partially move through the membrane, hereby having less volume than the bubble would have if the membrane were not present. More gas pockets below the membranes are observed when the number of membranes is increased, which also affects the number of small bubbles observed. Finally, bimodal bubble size distributions are found when the membranes are configured in a quincunx pattern, which shows that bubble properties can become more complex when using specific membrane configurations.

Appendix – Effect of permeance on concentration polarization

Membrane development has significantly improved membrane performance by reducing the palladium layer thickness, hereby increasing the permeance. In Figure A.1 the solids hold-up and hydrogen flux for the VM1 500 μm particles case for three different permeances have been displayed. The hydrogen mole fraction profiles in Figure A.2 clearly show that the main difference between the membranes is the local hydrogen concentration near the membrane surface. The permeances differ with a factor two, the middle permeance representing supported ultra thin-film palladium-silver membranes that are currently used in our laboratories. The figure shows that concentration polarization is a phenomenon that has become more important due to membrane improvements over the last decade and will become more important as membranes are even further improved. However, even though the hydrogen flux at the bottom of the membrane changes almost proportionally with the permeance (approximately a factor 2), the flux after the first 2 cm has already stabilized around a lower value. An improvement of the permeance by a factor 4 will only lead to an increase in the flux by a factor 1.5 related to the decrease in hydrogen partial pressure at the membrane surface. The two membranes with the highest permeances have almost no difference in flux anymore after 1 cm of membrane. The system is therefore not limited by the membrane flux, but almost fully by the mass transfer limitations from the bed to the membrane.

The effect of higher permeance on the solids hold-up is also barely noticeable. The solids hold-up data is very similar for all the permeances that, probably due to limitations in the number of steps used for the time-averaging, the highest extraction does not have exactly the highest solids hold-up near the membrane. Insufficient hydrogen is present to further increase the flux, however, the particle size does significantly affect the system performance. Therefore, relatively large particles of about 500 μm diameter are recommended to be used for fluidized bed membrane reactors.

Figure A.1: (left) Azimuthally, axially and time-averaged solids hold-up versus radial distance along the membrane, and (right) azimuthally and time-averaged hydrogen flux profiles along the axial positions of the membrane, for the VM1 fine case with low, standard and high permeance.

Figure A.2: Azimuthally, axially and time-averaged hydrogen mole fraction versus distance from the membrane surface for three different membrane permeances.

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