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Discrete particle simulations of micro membrane-assisted fluidized beds with H₂ extraction

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ABSTRACT

Recent research has shown the potential of membrane-assisted fluidized bed (MAFB) reactors for various applications, and for ultra-pure hydrogen production in particular. For micro MAFBs with gas extraction, the formation of densified zones close to the membrane walls has been recognized to potentially increase the mass transfer resistance from the bed to the membranes. In order to investigate this phenomenon in detail, a classic Euler-Lagrange type model, Discrete Particle Model (DPM) extended with gas-phase component conservation equations has been used to simulate the case with H₂ extraction via perm-selective membranes mounted in the confining walls. The simulated membrane walls were set up such that they closely mimic high-flux, thin film, supported palladium-based membranes. It has been found that the formation of densified zones in micro MAFBs has a very small influence on the H₂ mass transfer from the bed to the membranes. The advantages of micro MAFBs have been highlighted through a fundamental comparison with a micro packed bed membrane reactor.

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Introduction

Membrane-assisted fluidized bed reactors (MAFBRs) have been investigated as a more promising reactor type over packed bed membrane reactors (PBMRs) for ultra-pure H₂ production using methane steam reforming [2,16,23,24,35–38]. Especially, experiments from Patil et al. [38] and Gallucci et al. [23] have demonstrated the possibility of operating MAFBRs at autothermal and virtually isothermal conditions through a combination of steam reforming and partial oxidation (autothermal reforming). In the meanwhile, studies from Refs. [16,17,24,35,37,38] have identified two main limitations in the performance of MAFBRs: i) the hydrogen

permeation rate through the perm-selective membranes and ii) the mass transfer rate from the bubble phase to the emulsion phase [17,24,35,37,38]. In order to overcome these two limitations and improve the reactor performance, the novel reactor concept of a micro-structured membrane-assisted fluidized bed reactor (MMAFBR) has been proposed [44,47], composing of compartments of micro fluidized beds confined by two vertical membrane walls. Considering the potential of fuel cell vehicles [42], it has been expected as promising concept for developing a next generation reactor for downscaled and decentralised production of ultra-pure H₂, for example for PEM fuel cell (typically 1–50 kW) applications.

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Nomenclature

c	number of species, -
d	particle diameter, m
DZ	height of grid cells, m
$\mathcal{D}$	diffusion coefficient, m^2/s
e	coefficient of restitution, -
f	volume fraction, -
$F_{\text{contact},a}$	contact force of particle a , N
g	gravitational acceleration, m/s^2
I	moment of inertia, kg m^2
j	molecular mass flux, $\text{kg}/\text{m}^3/\text{s}$
k	spring stiffness, N/m
k_m	permeability, $\text{mol}/\text{m}/\text{s}/\text{Pa}^{0.5}$
m_a	particle mass, kg
M	molar mass, kg/mol
N_p	particle number, -
P	pressure, Pa
R	gas constant, $\text{J}/\text{mol K}$
S_p	particle drag source term, N/m^3
t	time, s
T	temperature, K
u_g, v_a	gas and solid velocity, m/s
V	volume, m^3
x	mole fraction, -
y	mass fraction, -
Greek symbols	
β	inter-phase momentum exchange coefficient, $\text{kg}/\text{m}^3 \text{ s}$
ε	volume fraction, -
η	damping coefficient, $\text{N s}/\text{m}$
μ	gas phase shear viscosity, Pa s
μ_f	friction coefficient, -
ρ	density, kg/m^3
τ	stress tensor, Pa
ϕ	mass flux, $\text{kg}/\text{m}^2 \text{ s}$
Subscripts	
a, p	particle
g	gas
i, A, B	component
n	normal direction
NZ	cell index for the z direction
t	tangential direction
Abbreviations	
CFD	computational fluid dynamics
DPM	discrete particle model
MAFB	membrane-assisted fluidized bed
MAFBR	membrane-assisted fluidized bed reactor
MMAFBR	micro-structured membrane-assisted fluidized bed reactor
PBMR	packed bed membrane reactor
TFM	two-fluid model

From a hydrodynamic point of view, the effect of gas permeation (both gas addition and extraction) on the hydrodynamic characteristics of MAFBs using porous membranes has been studied both experimentally and numerically (see

e.g. Refs. [9,18,44]). In general, both gas addition and extraction via membranes can greatly change the solids circulation patterns, bed expansion, bubble behavior and the solids holdup distribution in MAFBs. In case of gas extraction, the formation of densified zones close to membrane walls in micro MAFBs has been reported by Refs. [18,44]. However, up to now the studies on the effects of gas permeation via membranes in MAFBRs have been carried out on the basis of porous non-selective membranes and the effect of gas permeation via perm-selective membranes has not yet been investigated. For MAFBRs for H_2 production, the selective H_2 extraction may cause concentration polarization effects which are different from the results obtained from micro MAFBs using non-selective porous membranes. The study on the solids and bubble behavior under different design and operating conditions should therefore be revisited for this case where H_2 is selectively.

Even though the densified zones have been speculated to increase the mass transfer resistance from the bed to the membrane walls, no numerical and experimental works have yet investigated the mass transfer processes in MAFBs with selective gas extraction. In order to find out whether and to what extent the densified zones may affect the mass transfer from the bed to the membrane walls, fundamental investigations on the mass transfer in micro MAFBs with H_2 extraction have been carried out in this study, by utilizing the permeability of state-of-the-art, high-flux, supported palladium-based membranes [25]. Moreover, good understanding of the mass transfer characteristics of micro MAFBs with H_2 extraction via the perm-selective membranes, at different design and operating conditions, is very important for the final rational design of MMAFBRs for H_2 production. In this work, we are using a numerical simulation tool, specifically an Euler-Lagrange Discrete Particle Model (DPM), extended with the gas component conservation equations, to study these processes. Comparing to using simple 1D models, the amount of H_2 that is not captured and required downstream separation or recycling can be easily predicted with DPM simulations. In addition to this, the inlet gas that could have bypassed the membranes by channelling through the bed center can only be studied by using a high-detailed CFD model. Note that this model has been successfully applied in investigating bubble-to-emulsion phase mass transfer, and has been recognized as a powerful CFD tool.

The effect of the superficial gas velocity, operating temperature and pressure on the performance of MAFBRs has been investigated both experimentally and numerically using phenomenological models (a.o [2,11,12,23,35,38]). These works indicate that operation at higher temperatures within the boundaries imposed for membrane stability (i.e. $T < 700^\circ\text{C}$) and higher pressures gives the best reactor performance. Even so, fundamental research on MAFBRs from a hydrodynamic point of view is rather limited. Deshmukh et al. [15] experimentally studied the effect of fluidization conditions on the membrane permeation rate in a MAFB employing inserted vertical ceramic (porous) membranes tubes. They found that the gas permeation increased with an increase in the free-board pressure while the superficial gas velocity and the particle size had no effect on the amount of gas permeated through the membranes. Jašo et al. [21] investigated the

interplay of hydrodynamics, mass transfer and reactions due to the changes of bed geometry and feed policy through utilizing (porous) membranes based on (Eulerian–Eulerian) two-fluid (TFM) simulations with the Fluent software package. Their work focused on the comparison of different designs of fluidized bed reactors (including MAFBRs) for the oxidative coupling of methane. Even though their analysis of the hydrodynamics and its influence on the mass transfer is limited to the qualitative level, it is clear that understanding of the hydrodynamics is very important for optimizing the reactor design and improving the reactor performance. Up to now, detailed quantitative knowledge on how the fluidization characteristics influence the mass transfer and hence membrane reactor performance is still lacking.

This study pioneers the numerical simulation of micro MAFBs employing perm-selective membranes from a fundamental point of view based on detailed DPM modelling. The effect of fluidization conditions, viz. the particle size and operating pressure at constant superficial gas velocity or at constant gas throughput, on the mass transfer rates and hence H_2 permeation rate and H_2 recovery in isothermal micro MAFBs with wall-mounted H_2 perm-selective membranes will be investigated. In addition, a comparison between a micro fluidized bed, a packed-bed and an empty bed with H_2 perm-selective membranes installed in the walls will be carried out in terms of the extent of concentration polarization and H_2 recovery. It has been demonstrated that differences in performance start to become visible even in these very small reactors. This shows that when selecting larger confinements the concentration polarization effects do become quite prominent, and underlines the need for micro-structuring of fluidized bed membrane reactors to avoid concentration polarization.

In the next section, the DPM and mass transfer techniques will be introduced, followed by a discussion of simulations that were performed. We will then discuss the effect of several parameters on the fluidization behavior of the system, the differences in performances of different reactor configurations and wrap up with conclusions from these simulations.

Numerical method

The soft-sphere discrete particle model

The soft-sphere discrete particle model (DPM) employed in this study is based on the pioneering work by Tsuji et al. [41] and has originally been developed by Hoomans et al. [27] and Ye et al. [49]. It is a popular Euler-Lagrange type of model with a discrete description of the particulate phase and a continuous description of the gas phase, and has been widely used in studies on gas–solid fluidized beds. A set of volume-averaged Navier–Stokes equations is solved on the Eulerian grid cells for the gas phase hydrodynamics, assuming ideal gas behavior. For the particle phase, Newton's second law of motion is applied to each individual particle to trace its position and velocities. Because the size of the Eulerian grid cells is larger than the particle diameter, the details of the interactions between the gas phase and

the particles is unresolved and constitutive correlations are required to compute the momentum exchange between the two phases.

A summary of the main equations of the model used in this study is provided in Table 1. In this soft-sphere DPM, the contact force resulting from particle–particle and/or particle–wall interactions is calculated using the linear spring and dashpot model proposed by Ref. [6] and for the gas–particle interaction the classic drag force correlation from Refs. [19] and [45] are utilized. In this model, the particle spring stiffness constant is a key input parameter. It is usually chosen to have a value which is much smaller than the true one derived from material properties in order to increase the allowed time step, and thus reduce the required CPU time [41]. Here, we choose those values such that the maximum overlap between interacting particles and particle–wall at any time step is less than one percent of the particle diameter. For a more detailed explanation of this model, we refer to recent reviews by Refs. [13] and [51].

The transport of chemical components is described in a way similar to the continuity equation of the gas phase, using the mass fraction y_i . For binary gas systems with components A and B, Fick's law can be used for the molecular mass flux j_i , with $-\rho \mathcal{D}_{AB} \nabla y_A$, which is employed in the gas component conservation equation used for this study (Table 1).

Verification of the extended DPM and grid independence

The program of the inherited DPM has been extensively used for detailed understanding of hydrodynamic characteristics in gas–solid fluidized beds (for example, [31,46,48,49]). The program of the component conservation calculation is newly developed and its implementation has been carefully verified by carrying out simulations for simplified systems and comparing the results with theoretical solutions. First, a simulation has been carried out on a process of gas penetrating into a semi-infinite domain in order to validate the implementation of the diffusion terms in the equation (as indicated in Fig. 1). Then, the simulation of a single phase axially dispersed plug flow reactor has been performed for which the conversion can be solved analytically. The comparison between simulation results and the theoretical solutions is presented in Table 2. After that the implementation of the Dankwerts boundary condition has been validated considering a 1D convection–diffusion equation, for which the analytical solution for a semi-infinite domain, initially without this component, is obtained from Ref. [34] (in Fig. 2). For all the cases, the numerical results have been found in a good agreement with the analytical solutions. Moreover, simulations for testing the grid independence have been carried out.

Simulation configuration

Initialization

According to the stoichiometric coefficients in the methane steam reforming reaction equation, the maximum mass fraction of H_2 in the products mixture is 15.4%. In this study focusing on the hydrodynamics and mass transfer, an inlet gas consisting of 15% H_2 and 85% N_2 are used as fluidization

Table 1 – Main governing equations of the soft-sphere DPM extended with gas component conservation equations.

Gas phase continuity equation:

$$\frac{\partial(\epsilon_g \rho_g)}{\partial t} + (\nabla \cdot \epsilon_g \rho_g \mathbf{u}_g) = 0$$

Gas phase momentum equation:

$$\frac{\partial(\epsilon_g \rho_g \mathbf{u}_g)}{\partial t} + \nabla \cdot (\epsilon_g \rho_g \mathbf{u}_g \mathbf{u}_g) = -\epsilon_g \nabla P_g - \mathbf{S}_p - \nabla \cdot (\epsilon_g \tau_g) + \epsilon_g \rho_g \mathbf{g}$$

Gas phase equation of state:

$$\rho_g = \frac{M_g}{RT} P_g \quad \text{with } M_g = \left(\frac{y_i}{M_i} \right)^{-1}$$

Gas phase stress tensor:

$$\tau_g = \mu_g (\nabla \mathbf{u}_g + \nabla \mathbf{u}_g^T) - \left(\lambda_g - \frac{2}{3} \mu_g \right) (\nabla \cdot \mathbf{u}_g) \mathbf{I}$$

Gas-solid momentum exchange rate:

$$\beta = \begin{cases} \frac{3}{4} C_D \frac{\rho_g \epsilon_g (1 - \epsilon_g)}{d_p} \|\mathbf{u}_g - \mathbf{v}_a\| \epsilon_g^{-2.65} & \epsilon_g \geq 0.8 \\ 150 \frac{(1 - \epsilon_g)^2 \mu_g}{\epsilon_g d_p^2} + 1.75 \frac{\rho_g (1 - \epsilon_g)}{d_p} \|\mathbf{u}_g - \mathbf{v}_a\| & \epsilon_g < 0.8 \end{cases}$$

the porosity in DPM simulation:

$$\epsilon_{g, \text{cell}} = 1 - \frac{1}{V_{\text{cell}}} \sum_{\mathbf{v}_a \in \text{cell}} f_{\text{cell}}^a V_p^a$$

Equations of motion for every particle:

$$m_a \frac{d\mathbf{v}_a}{dt} = m_a \frac{d^2 \mathbf{r}_a}{dt^2} = -V_a \nabla P_g + \frac{V_a \beta}{\epsilon_p} (\mathbf{u}_g - \mathbf{v}_a) + m_a \mathbf{g} + \mathbf{F}_{\text{contact},a}$$

$$I_a \frac{d\omega_a}{dt} = \mathbf{T}_a$$

Gas component conservation equations:

$$\frac{\partial}{\partial t} (\epsilon_g \rho_g y_i) + \nabla \cdot (\epsilon_g \rho_g y_i \mathbf{u}_g) = \nabla \cdot (\epsilon_g \rho_g \mathcal{D}_i \nabla y_i)$$

closure equation for component $i = 0$:

$$y_0 = 1 - \sum_{i=1}^c y_i$$

viscosity of a gas mixture:

$$\mu_g = \sum_i \frac{x_i \mu_i}{\sum_j x_j \phi_{ij}} \quad \phi_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{M_i}{M_j} \right)^{1/4} \right]^2}{\left[8 \left(1 + \frac{M_i}{M_j} \right) \right]^{1/2}}$$

agent in the simulated micro MAFBs. Initially, particles are regularly placed layer by layer at the bottom of the bed with a small random fluctuating translational and rotational velocity to make sure that the system is in an asymmetric fluidized

state from the start. The gas in the simulation domain is initialized with pure N₂ and particles are prefluidized for 1 s before the H₂ is extracted. Fig. 3 shows the sizes of the simulated micro MAFBs using particles with 75 and 125 μm , where the position of the membranes are highlighted.

Boundary conditions

For solving the total gas continuity equation, a boundary condition of constant mass flux is applied at the bottom inlet. To solve the N₂ conservation equation, a Danckwert's boundary condition is applied at the bottom inlet (Equation (1)), where the inlet mass fluxes of both H₂ and N₂ are constant during the calculation. Defining $a = -\epsilon_g \rho_g \mathcal{D}_A$; $b = \epsilon_g \rho_g u_{z,g}$ and $c = \phi_{A,g,\text{in}}$, Equation (1) can be discretized as Equation (2) and it is implemented in the program for the bottom inlet.

$$-\epsilon_g \rho_g \mathcal{D}_A \frac{\partial y_{A,g}}{\partial z} \Big|_{z=0} + \epsilon_g \rho_g u_{z,g} y_{A,g} \Big|_{z=0} = \phi_{A,g,\text{in}} \quad (1)$$

$$\left(\frac{b}{2} + \frac{a}{DZ} \right) y_{A,g,NZ=1} + \left(\frac{b}{2} - \frac{a}{DZ} \right) y_{A,g,NZ=0} = c \quad (2)$$

Non-slip and impermeable boundary conditions are applied to the bed walls, since only the N₂ conservation equation is solved simultaneously with the total gas-phase continuity and Navier–Stokes equations for the binary gas system considered in this study. The H₂ permeation via the membranes is taken into account by adding sink terms in the cells next to the two vertical membranes installed in the left and right bed walls. For the continuity equation of the gas phase, the sink term expressed with Equation (3) is implemented. For the momentum conservation equation of the gas phase, $(\phi_{A,g}^{\text{membrane}})^2 / \rho_g$ is implemented as the sink term.

$$\phi_{A,g}^{\text{membrane}} = k_m \left(\frac{RT_g}{M_A} \rho_g y_{A,g,\text{ret}} \right)^{0.5} M_A = k_m \left(M_A RT_g \rho_g \right)^{0.5} y_{A,g,\text{ret}}^{0.5} \quad (3)$$

The H₂ extraction is modelled as a function of H₂ partial pressure in the permeate and retentate sides according to

Fig. 1 – The comparison between the simulation results and the analytical solution for gas penetration into a semi-infinite body: a) gas penetration in a semi-infinite body. 0.0 is the initial concentration, 1.0 is the applied concentration at $t = 0.0$ s;

b) the error function $\text{erf}\left(\frac{z}{\sqrt{4\mathcal{D}t}}\right)$ as a function of z at 2.5 s.

Table 2 – Errors of the simulation results comparing to the theoretical solutions on single phase first order irreversible reactions.

k_r	Pe	Theoretical solution	Simulation results	Absolute error	Relative error
0.01	7.2	0.992039	0.992039	4.94973×10^{-7}	4.98944×10^{-7}
0.1	7.2	0.92381	0.923810	3.85345×10^{-7}	4.17126×10^{-7}
1	7.2	0.479464	0.479458	6.26424×10^{-6}	1.30653×10^{-5}
10	7.2	0.006920	0.006913	7.00242×10^{-6}	0.001013
100	7.2	4.95305×10^{-10}	4.75295×10^{-10}	2.00096×10^{-11}	0.042099

Fig. 2 – Simulation results at different grid resolutions compared to the exact solution (1D convection–diffusion equation).

Sieverts' law, where the H_2 partial pressure in the permeate side is assumed to be negligibly small (Equation (3)). Following the latest developments of the best H_2 selective membranes, the most advanced supported palladium-silver membranes with a permeability of $k_m = 1.2 \times 10^{-3} \text{ mol/m}^2\text{/s/Pa}^{0.5}$ are simulated in this study [20].

Physical property and operating conditions

From experimental studies on fluidized bed membrane reactors using methane steam reforming, it is known that palladium membranes for H_2 extraction are operated at temperatures in the range of 550–900 K. In this study, a temperature of 673 K is used. The gas diffusion coefficient for a H_2 and N_2 binary gas mixture at 673 K of $3.2 \times 10^{-4} \text{ m}^2/\text{s}$ is used [33]. The viscosity of the local gas mixture is calculated with [39] equation based on the local gas composition. At 673 K, the viscosity of pure H_2 is $1.56 \times 10^{-5} \text{ kg/m/s}$ and the viscosity of pure N_2 is $3.20 \times 10^{-5} \text{ kg/m/s}$ [8].

Geldart-A type particles with diameters of 75 and 125 μm are selected for this study, which will be the typical particle type for use in the micro MAFB concept. The parameters for the particle collisions in the DPM model have been kept the same as in previous studies on the hydrodynamics carried out for room temperature [44,47], shown in Table 3. It is known that the hydrodynamic characteristics in fluidized beds change greatly with the operating pressure and the superficial gas velocity [14,30]. Simulations with various operating pressure but constant inlet superficial gas velocity or gas throughput have been designed to investigate the

Fig. 3 – Schematic diagrams of the micro MAFBs, the geometry is indicated with the case using particles of 75 μm .

effect of operating conditions. Note that even though the gas throughputs in the simulations using different particles are different the gas flux is kept constant at $1.38 \times 10^{-2} \text{ kg/m}^2/\text{s}$. The main simulation parameters used in the simulations in this work have been summarized in Table 3.

Results and discussion

Effect of H_2 extraction

The effect of H_2 extraction via perm-selective membranes on the solids holdup distribution in micro MAFBs has been shown in Fig. 4. The formation of densified zones along the membranes is observed at the left and right sides of the bed, along the membranes, for the simulation using particles with $d_p = 75 \mu\text{m}$. The other simulation with larger particles ($d_p = 125 \mu\text{m}$) but otherwise the same settings, shows that the formation of densified zones is largely decreased and is only distinguishable at the top end of the membranes (indicated by the dark red color). The fact that the formation of densified zones in micro MAFBs due to H_2 extraction can be efficiently diminished by using relatively larger particles is in a good agreement with the simulations with non-selective gas extraction.

The extent of densified zones has been defined as the ratio of the volume of the densified zones, with a solids holdup

Table 3 – Summary of the values for the main simulation parameters in the DPM model used in this study.

Particle diameter d_p , μm	75	125
Particle number N_p	42,000	42,000
Particle density ρ_p , kg/m^3	1500	1500
Normal restitution coefficients e_n	0.95	0.95
Tangential restitution coefficients e_t	0.95	0.95
Friction coefficient μ_f	0.1	0.1
Normal spring stiffness k_n , N/m	7	28
Tangential spring stiffness k_t , N/m	2	8
CFD time step, s	1.0×10^{-5}	1.0×10^{-5}
Particle dynamics time step, s	1.0×10^{-6}	1.0×10^{-6}
Domain height, m	1.2×10^{-2}	2.333×10^{-2}
Domain width, m	3.0×10^{-3}	5.0×10^{-2}
Domain depth, m	1.4×10^{-3}	2.0×10^{-2}
Number of grid cells	$60 \times 15 \times 7$	$60 \times 15 \times 7$
Temperature T, K	673	673
Pressure P, bar	1,1.5,2,5,10,15,20	1,1.5,2,5,10,15,20
Inlet superficial gas velocity, m/s	0.06,0.08	0.06,0.08
u/u_{mf}	17.1, 22.9	6.8, 9.1
Gas throughput, kg/s	5.78×10^{-8}	1.60×10^{-7}

above 75% of the solids holdup of a randomly packed bed, to the total volume of the fluidized bed. It is used to quantify the formation of densified zones in the simulated fluidized beds. Following this, the extent of densified zones and gas extraction ratio (the ratio between the amount of H_2 extracted and the total gas inflow from the bottom) have been analyzed for the cases with two different particle sizes and are presented in Table 4. In the simulation using particles with a diameter of $75 \mu\text{m}$, the densified zones close to the membranes occupy about 16% of the total volume of the fluidized beds. Increasing

Table 4 – Extent of densified zones, gas extraction ratio and the H_2 recovery in micro MAFBs with H_2 extracted via membranes.

Particle diameter $[\mu\text{m}]$	Extent of densified zones	Gas extraction ratio [%]	H_2 recovery [%]
75	0.16	13.2	88.2
125	0.02	13.4	89.4

the particle diameter to $125 \mu\text{m}$, the simulations show that the extent of densified zones decreased to only 2% of the total volume of the fluidized bed. With a gas extraction ratio of about 13% and inlet superficial gas velocity around 0.06 m/s , the extent of densified zones in these two simulations is comparable to simulations under similar conditions using simply porous non-selective membranes. Even though the extent of densified zones is larger when using smaller particles, the H_2 recoveries at steady state are quite similar (Table 4). This indicates that the formation of densified zones does not hamper the H_2 extraction from the bed.

Effect of pressure at constant inlet superficial gas velocity

Fig. 5 shows the effect of operating pressure (the total gas pressure at the outlet) on the extent of densified zones in micro MAFBs with perm-selective membranes for H_2 extraction, while the inlet superficial gas velocity and gas composition were kept constant at 0.04 m/s . It shows that the extent of densified zones in micro MAFBs generally decreases with the increase of operating pressure.

Fig. 6 shows how the operating pressure influences the H_2 extraction flux and H_2 recovery in micro MAFBs when the inlet superficial gas velocity was kept constant. For these simulations, the operating pressure was changed from 1 bar to 20 bar, increasing also the H_2 partial pressure linearly with the increase of the operating pressure. Following Sieverts' law that

Fig. 4 – Time-averaged solids holdup distribution in the simulations using particles of (a) $75 \mu\text{m}$ and (b) $125 \mu\text{m}$, where the dark red indicates the densified zones.

Fig. 5 – Effect of pressure on the extent of densified zones in the micro MAFBs using constant inlet superficial gas velocity of 0.04 m/s . Results from the simulations using an inlet superficial gas velocity of 0.06 m/s and operating pressure of 1 bar are also presented as separate points.

Fig. 6 – The effect of operating pressure on the H_2 extraction flux and H_2 recovery in micro MAFBs using constant inlet superficial gas velocity of 0.04 m/s. Results from the simulations using an inlet superficial gas velocity of 0.06 m/s and operating pressure of 1 bar are also presented as separate points.

was implemented for the H_2 permeation, the H_2 extraction flux increases with the increase of H_2 partial pressure or the increase of the operating pressure to the power of 0.5. Despite the increased extraction flux, the H_2 recovery decreases with the increase of operating pressure, also indicated in Fig. 6.

Effect of pressure at constant gas throughput

Fig. 7 shows the effect of operating pressure on the formation of densified zones in micro MAFBs using perm-selective membranes for H_2 extraction, when the gas throughput was kept constant. The extent of densified zones increases with the increase of operating pressure for the simulations using particles of 75 μm in diameter. The increase of pressure results in the increase of H_2 extraction, which also increases the gas extraction ratio relative to the constant gas inflow from the

Fig. 7 – Effect of pressure on the formation of densified zones in the micro MAFBs with constant gas throughput for two different particle sizes.

bottom. As learned from our previous studies [44], the increase of gas extraction ratio can increase the extent of densified zones in micro MAFBs. However, this trend was not observed in the simulations using particles of 125 μm in diameter, which again shows that using larger particles can reduce the formation of densified zones.

As shown in Fig. 7, the increase of operating pressure can also result in a decrease in the extent of densified zones. This can be explained by considering the effects of increased operating pressure on both the gas extraction ratio and the fluidization characteristics. An increase in the operating pressure results in an increase of the gas extraction ratio, which has a potential to increase the extent of densified zones. However, it also improves homogeneous fluidization, which can potentially decrease the extent of densified zones. From the previous study, it was learned that for the micro MAFBs using particles of 125 μm in diameter the extent of densified zones was not sensitive to the gas extraction ratio when using a relatively small (<20%) gas extraction ratio, where the extent of densified zones in the micro MAFBs using 75 μm particles showed a clear sensitivity. So, the decrease in the extent of densified zones in Fig. 7 for the simulations using particles of 125 μm in diameter is the result of increased homogeneity in the fluidized bed due to the increased operating pressure.

Fig. 8 indicates how the operating pressure influences the H_2 extraction flux and H_2 recovery in micro MAFBs when the gas throughput was kept constant. It shows that both the H_2 extraction flux and H_2 recovery increase with the increase of the operating pressure when the gas throughput was kept constant, as expected, since the H_2 extraction flux increases with the increase of operating pressure according to Sieverts' law.

As discussed before in Section Effect of H_2 extraction, the formation of densified zones caused by H_2 extraction did not result in an obvious decrease in the H_2 recovery. In order to find out whether the formation of densified zones increases the mass transfer resistance and hence the H_2 concentration gradient from the bed center to membrane walls, the

Fig. 8 – The effect of operating pressure on the H_2 extraction flux and H_2 recovery in micro MAFBs with constant gas throughput for two different particle sizes.

Fig. 9 – Lateral profiles of H_2 mass fraction in micro MAFBs under different operating pressures, (a) particle diameter of 75 μm ; (b) particle diameter of 125 μm , at 1/4, 1/2 and 3/4 bed height.

lateral H_2 concentration profiles are plotted in Fig. 9. The figure shows that in general the H_2 concentration gradient from the bed center to the membrane walls decreases with the increase of operating pressure. This means that increasing the operating pressure can increase the mass transfer rate from the bed to the membrane walls. A comparison between the left graph and right graph, corresponding to simulations having relatively high and low extent of densified zones, indicates that the formation of densified zones did not increase the H_2 concentration gradient from the bed center to the membrane walls (concentration polarization). Hence, the formation of densified zones in these simulations has a negligible effect on the mass transfer to the membranes, entirely related to the micro-structuring of the bed.

Mass transfer in micro MAFBs

In order to understand the mass transfer in the fluidized beds with H_2 extraction, especially why the densified zones do not induce mass transfer limitations near the membrane walls, further analysis on the simulations of micro MAFBs with H_2 extraction have been carried out. Here, the analysis of the simulations having pronounced densified zones, using particles with diameter of 75 μm and constant gas throughput, is presented and discussed in detail.

Fig. 10 presents a number of snapshots of these simulations under operating pressures of 1, 1.5 and 2 bar. From these snapshots, it is clear that the averaged bubble size decreases with increasing operating pressure. It is well-known that decreasing bubble size can efficiently improve the bubble-to-emulsion phase mass transfer in fluidized beds [28], which consequently improves the mass transfer to the membrane walls. This is why the H_2 concentration gradient from the bed center to the membrane walls (or the concentration polarization) decreases with increasing operating pressure, as shown in Fig. 9.

In Fig. 10, it is noticed that while operating at 1 bar the regions near the membranes with high solids holdup are quite

dynamic due to the motion of the bubbles, which often tear up the solids accumulated near the membrane walls. With the increase in operating pressure, the dynamics created by the motion of big bubbles decreases and densified zones near the membrane walls tends to form in a stable fashion. However, as indicated in Fig. 8 the formation of densified zones along the membranes with increasing operating pressure did not adversely affect the H_2 extraction flux and recovery, especially when comparing to the simulations with negligible densified zones (using particles of 125 μm in diameter). In other words, the densified zones did not increase the mass transfer resistance near the membranes and did not aggravate the concentration polarization (Fig. 9). In the end, a reduced concentration polarization was observed with increasing operating pressure due to the improved bubble-to-emulsion mass transfer.

In order to understand why the formation of densified zones has a negligible influence on the H_2 mass transfer from the bed to the membranes, the time-averaged porosity distribution in the regions having densified zones near the membrane walls is analyzed based on the volume-averaged values in the direction of H_2 extraction. This is plotted in Fig. 11 together with the graph of the time-averaged solids holdup distribution showing the formation of densified zones. As indicated in Fig. 11(b), even though the porosity in the densified zones decreases at higher operating pressures, its absolute value remains above 0.55, a value larger than the averaged porosity of 0.42 in a randomly packed bed. This indicates that the densified zones still provide a more favorable condition for H_2 dispersion compared to packed beds. Moreover, in this dynamic process, particles in the densified zones are constantly refreshed due to the solids circulation and bubble motion, as discussed by Ref. [44]. Generally speaking, the motion of the particles is helpful for the local dispersion of H_2 . Therefore, the formation or the increase of the densified zones caused by H_2 extraction did not result in an increase in mass transfer limitations from the bed to the membrane walls (or concentration polarization) over the bed width in micro MAFBs.

Fig. 10 – Snapshots of the micro MAFBs using particles of $75\ \mu\text{m}$ and constant gas throughput but under different operating pressures ranging from 1 to 2 bar. The bubbles have been identified with the porosity property and colored according to the H_2 concentration, and the concentration field is indicated with the H_2 concentration contour plot of the center slice of the beds. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Comparison between different types of reactors

Gallucci et al. [24] have compared membrane-assisted fluidized bed reactors (MAFBRs) to packed bed membrane reactors

(PBMRs) for ultra-pure H_2 production via methane steam reforming theoretically using phenomenological models. Their calculations demonstrated that MAFBRs provides a better reactor concept compared to PBMRs for H_2 production,

Fig. 11 – (a) Time-averaged solids holdup distribution in the micro MAFBs and (b) porosity distribution in the regions near membranes (with a depth of one grid cell) based on the simulations using particles of 75 μm and constant gas throughput but under different operating pressures.

considering the required membrane area and the possibility to circumvent mass transfer limitations. They also reported the occurrence of concentration polarization in PBMRs even with a membrane tube diameter as small as 1 cm. In order to explore the intrinsic advantages of fluidized beds in mass transfer compared to PBMRs, the processes in MAFBRs and PBMRs have been simulated and compared for the (micro-scale) case considered in this study using the DPM. Note that DPM simulations of a packed bed reactor is easily performed by first allowing the particles to collapse onto each other, after which the equations of motion is switched off for the particles.

In this section, the results from simulations of an empty bed, packed bed and fluidized bed assisted with wall-mounted perm-selective membranes have been compared to explore the separation performance of these different reactor types. The simulation geometry, superficial inlet gas velocity of 0.06 m/s and the operating pressure of 1 bar were kept constant in different types of reactor and particles of 75 μm in diameter were used for both the packed and fluidized beds.

The H_2 concentration profiles in the beds along the vertical direction and over the bed width have been analyzed and plotted in Fig. 12. This figure indicates that the largest

Fig. 12 – H₂ mass fraction as a function of the axial and lateral position in the simulated micro membrane-assisted fluidized bed reactor (MAFBR), packed bed membrane reactor (PBMR) and empty bed.

concentration polarization is in the packed bed, followed by the fluidized bed and the smallest in the empty bed without particles. From this figure, it is also verified that the packed bed, suffering most from the mass transfer limitations, has the largest concentration gradients in both lateral and axial directions. Due to the good mass transfer conditions provided by the fluidization, the lateral and axial concentration gradients in the fluidized bed is much lower compared to the packed bed, although it still suffers from mass transfer limitations when compared to the empty bed. This comparison clearly verified the advantages of fluidized beds in the design of a micro MAFB for ultra-pure H₂ production. Although the concentration gradients are smallest for the empty bed for the considered case of H₂ separation, larger mass transfer limitations are expected when heterogeneously catalyzed steam reforming of methane is considered, assuming that the catalyst (and insufficient quantities) can be impregnated in the porous support of the membranes. In this case the reaction does not take place throughout the column, but only near the walls.

The comparison of these three reactor types in terms of H₂ extraction flux and H₂ recovery is presented in Fig. 13. Following Sieverts' law, the highest H₂ extraction flux has been observed in the packed bed along the first half of the membrane length from the bottom, due to the highest pressure in the bed compared to the fluidized bed and the empty bed (Fig. 13(a)). Along the top half of the membranes, the lowest H₂ extraction flux is observed in Fig. 13(a) for the packed bed. It is probably because the less amount of H₂ remains in the top part of the beds. Fig. 13(b) shows that at the micro scale level these three reactor types perform quite similarly in terms of H₂ recovery for the considered case.

Conclusions

This work has pioneered the CFD modelling of MAFBs with selective gas permeation. The permeability of the most advanced perm-selective membrane (1.2×10^{-3} mol/m²/s/Pa^{0.5}) for H₂ extraction has been used in this work and the required operating

Fig. 13 – (a) H₂ extraction flux as a function of the position in the membrane length and (b) H₂ recovery as a function of the position of bed length in the simulated micro membrane-assisted fluidized bed (MAFBR), packed bed membrane reactor (PBMR) and empty bed.

temperature (400 °C) has been taken into account. The effect of operating conditions on the H₂ extraction and the performance of fluidized beds as a separator unit in terms of H₂ recovery has been successfully investigated using the DPM that was extended with gas component conservation equations.

The newly extended DPM model with gas component conservation equations has been firstly applied to study the effect of H₂ extraction on the hydrodynamics and mass transfer in micro MAFBs operating under various conditions. It has been demonstrated that the densified zones near the membrane walls can be formed by H₂ extraction via permselective membranes in micro MAFBs. It is possible to diminish the formation of densified zones by optimizing the operating conditions, such as the particle size, operating pressure and superficial gas velocity.

It has been found that, when the superficial gas velocity from the bottom inlet is kept constant, both the extent of densified zones and the H₂ recovery decreases with an increase in the operating pressure. However, when the gas throughput is kept constant, the extent of densified zones and the H₂ recovery increased with increasing operating pressure. Nevertheless, in all micro MAFBs the H₂ extraction flux via the membranes in micro MAFBs increased with the increase of operating pressure following Sieverts' law.

Additionally, it is found that the densified zones have a negligible influence on the mass transfer from the bed to the membrane walls for micro MAFBs. It has been further discussed based on the analysis of the bubble size and porosity distribution in the regions having densified zones for the simulated micro MAFBs using particles of 75 µm in diameter. One of the reasons that the formation of densified zones did not increase the mass transfer resistance is the dynamic behavior of the densified zones and the still relatively high porosity in the densified zones.

Finally, a comparison between micro PBMRs and micro MAFBRs has been carried out from a mass transfer point of view. Even though a similar H₂ recovery has been found in the simulated micro PBMR and MAFB, it has been verified that even on the micro-scale level concentration polarization effects or mass transfer limitations are larger in the PBMR than in the MAFBRs. Thus, it is learned that when selecting larger confinements the concentration polarization effects do become quite prominent. This underlines the need for micro-structuring of fluidized bed membrane reactors to avoid concentration polarization.

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