Mass transfer phenomena in fluidized beds with horizontally immersed membranes

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Mass transfer phenomena in fluidized beds with horizontally immersed membranes: A numerical investigation

R.J.W. Voncken, I. Roghair*, M. van Sint Annaland

Chemical Process Intensification, Department of Chemical Engineering & Chemistry, Eindhoven University of Technology, P.O. Box 513, 5612 AZ Eindhoven, the Netherlands

**Highlights**
- Design guidelines for horizontal membrane tube banks in fluidized beds are given.
- The flux around a horizontal membrane is lowest on top and highest at the bottom.
- Membranes near bed walls perform worse due to densified zones and gas back-mixing.
- Removing membranes near the walls improves the average performance per membrane.
- A too large distance between the membranes and wall results in gas bypassing.

**Graphical Abstract**

**Abstract**

Mass transfer phenomena in gas-solid fluidized beds with horizontally immersed membrane tube banks in different configurations were investigated using a Two-Fluid Model, considering the case of a binary hydrogen/nitrogen gas mixture fed to a 2D fluidized bed where hydrogen was extracted via hydrogen perm-selective membranes. The simulations showed that the hydrogen flux is strongly non-uniform over the radius of the membranes. The hydrogen flux is lowest on top of the membranes and highest at the bottom of the membranes, which is caused by the formation of densified zones on top of the membranes and the fact that the membranes shield their own top side from hydrogen replenishment. Also, in systems with membrane tube banks, the performance of individual membranes differs significantly. The membranes located near the bed walls perform considerably worse, because of downwards solids flow near the walls, resulting in more densified zones and gas back-mixing. The average hydrogen recovery per membrane is highest for the cases with a staggered tube bank configuration and without membranes positioned close to the bed walls. In-line tube bank configurations suffer from gas channeling, reducing the hydrogen recovery per membrane. The membrane tube banks also significantly improve the bed hydrodynamics by enhanced bubble-breakage, decreasing the bubble size to approximately the membrane pitch.

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**1. Introduction**

The continuing growth in energy demand and the impact of fossil fuel usage on the environment increases the need for alternative energy carriers. Hydrogen is one of the most promising energy carriers that can lead towards reduced greenhouse gas emissions and lowering the exploitation of non-renewable resources. Hydrogen is industrially mostly produced by steam reforming of natural gas. Steam Methane Reforming (SMR) can be performed in (multi-tubular) packed bed reactors, in which methane reacts with steam to form carbon monoxide and hydrogen at temperatures around...
The integration of membranes in packed bed reactors has already been proposed in the literature (Tsotsis et al., 1992). In packed bed membrane reactor systems, catalyzed reactions and separation of product and waste are performed in the same unit. However, a major drawback of packed bed membrane reactors is the low mixing efficiency, causing temperature and concentration gradients in the reactor. When using state-of-the-art membranes, the system is not membrane flux limited, but to a large extent limited by the mass transfer rate of hydrogen from the bulk of the particle bed towards the membrane surface, which is often referred to as concentration polarization (Caravella et al., 2009). To circumvent these drawbacks, fluidized bed membrane reactors have been proposed to extract hydrogen from the reaction mixture (Adris et al., 1994; Gallucci et al., 2008; Hommel et al., 2012; Mleczko and Wurzel, 1997).

Compared to packed bed membrane reactors, fluidized bed membrane reactors have better mixing properties, resulting in reduced mass transfer limitations towards the membranes. The hydrodynamics and mass transfer phenomena of the fluidized suspension can be strongly affected by the membrane configuration. The effect of immersed objects on the performance of a fluidized bed has been researched previously (Bouillard et al., 1989; Kim et al., 2003; Yurong et al., 2004). How membranes affect fluidized bed hydrodynamics has been demonstrated by a.o. De Jong et al. (2011), Dang et al. (2014), Tan et al. (2014), Wassie et al. (2015) and Medrano et al. (2015).

Membranes are often inserted vertically (lengthwise) in reactors. Helmi et al. (2018) have demonstrated that when using state-of-the-art high flux palladium-based membranes, despite
the use of a fluidized bed, mass transfer limitations from the bed to the membrane become limiting. By inserting the membranes horizontally (i.e. perpendicular to the flow direction), the membranes can cut large gas bubbles into smaller ones, hereby improving the mixing efficiency of the bed. Previous studies on horizontally immersed tubes in fluidized beds have already proven that tubes have a significant effect on the bed hydrodynamics (Asegehegn et al., 2011; de Jong et al., 2013; Medrano et al., 2015; Rong et al., 1999; Sarkar et al., 2013; Solnordal et al., 2015; Wang et al., 2015; Yang et al., 2014). Especially tube banks can affect the bubble properties of the system (Asegehegn et al., 2011; de Jong et al., 2013; Medrano et al., 2015). One of the best methods to investigate the mass transfer phenomena in fluidized bed membrane reactors in detail is with Computational Fluid Dynamics (CFD) models. Until now, only a few CFD studies have been performed on mass transfer phenomena in fluidized bed membrane reactors (Jašo et al., 2011; Tan et al., 2017, 2016). However, these works either focus on oxygen perm-selective membranes, or they focus on flat vertical hydrogen perm-selective membranes, whereas the present work will focus on horizontally immersed hydrogen perm-selective membranes.

This work is a numerical study on the mass transfer phenomena in fluidized bed reactors with horizontally immersed membranes. A Two-Fluid Model (TFM) is used to perform the simulations and to obtain detailed information on the mass transfer phenomena occurring near the membranes. The OpenFOAM® v.2.3.0 twoPhaseEulerFoam solver was used as hydrodynamic model, and was extended with species balance equation and realistic membrane models to simulate selective extraction of hydrogen from the system. The extended TFM has been verified and validated. The goal of this work is to identify, describe and explain the most important mass transfer phenomena occurring in fluidized beds with horizontally immersed membranes. Explaining the mass transfer phenomena also requires relating the observed mass transfer phenomena to the hydrodynamics of these systems. Medrano et al. (2015) already found that gas pockets (solids free, non-rising gas bubbles) occur underneath and densified particle zones occur on top of horizontally placed membranes. The gas pockets and densified zones may affect mass transfer towards the membranes and could therefore have a noticeable effect on the system performance, which is studied in detail in this work.

The high cost of palladium-based membranes urges that the membranes are placed only at optimal positions. In an explorative study it was already found that membranes near the bed walls operate at a lower averaged hydrogen flux (Voncken et al., 2015). This work expands on that topic and studies fluidized beds with various membrane tube bank configurations with and without membranes near the bed walls. Fluidized beds with inactive tubes instead of membranes near the walls were also simulated, because simply removing membranes near the bed walls could also reduce the bubble breakage effect of the tube banks, and could induce gas bypassing along the walls.

This paper first discusses the model, its verification and validation, together with a grid convergence study for fluidized beds with horizontally submerged membranes. Special attention will be given to the implementation of the species balance, the implementation of the membrane source terms and the membrane boundary conditions. Subsequently, the simulation settings and tube bank configurations are presented, and the mass transfer phenomena around the membranes are studied in detail, after which the results are linked to the observed changes in the bed hydrodynamics.

2. Two-fluid model

2.1. Model description

A Two-Fluid Model (TFM) considers the gas and solids phases as interpenetrating continua. The governing and constitutive equations are presented in Table 1. The gas phase obeys the ideal gas law and the rheology of the solids phase (solids phase pressure and stress tensor) is modeled with the Kinetic Theory of Granular Flow (KTGF) as a function of the granular temperature, which is a measure of the kinetic energy of the fluctuating velocity of the particles, for which an additional transport equation is solved. Selective extraction of a gas component via a membrane is accounted for with a source term $S_m$ in the gas phase continuity equation and the component mass balances, whereas the associated extraction of momentum is taken into account via the velocity boundary conditions at the membrane surfaces. Details on the membrane source term will be discussed below the mass transfer and membranes sections of this work. The drag between the solids and the gas phase, which accounts for the inter-phase momentum transfer, is evaluated with the often used Gidaspow drag model (Gidaspow, 1994), which combines the drag model by Ergun (1952) and Wen and Yu (1966). Ergun’s model is valid for high solids hold-ups (20% and higher) while Wen & Yu’s model is valid at lower solids hold-ups (below 20%). The drag coefficient $C_d$ is determined based on the particle Reynolds number.

2.1.1. Kinetic theory of granular flow

The KTGF and frictional stress closure equations for the rheological properties of the solids phase are summarized in Table 2 (Nieuwland et al., 1996). Several closure equations were not present in the OpenFOAM code, so they were added to the model. Further details on the TFM and KTGF can be found in the literature (Gidaspow, 1994; Kuipers et al., 1993; Lun et al., 1984; Rusche, 2002; van der Hoef et al., 2006; van Wachem, 2000). For detailed information on the OpenFOAM TFM the interested reader is referred to Liu and Hinrichsen (2014) and Passalacqua and Fox (2011).

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summary of all governing and constitutive equations used in the TFM.</td>
</tr>
<tr>
<td><strong>Continuity equation of the gas phase</strong></td>
</tr>
</tbody>
</table>
| \(
\frac{\partial \rho_g}{\partial t} + \nabla \cdot (\rho_g \mathbf{u}_g) = -\nabla \cdot \mathbf{q}_g
\) |
| **Continuity equation of the solids phase** |
| \(
\frac{\partial \rho_s}{\partial t} + \nabla \cdot (\rho_s \mathbf{u}_s) = 0
\) |
| **Momentum equation gas phase** |
| \(
\frac{\partial \rho_g \mathbf{u}_g}{\partial t} + \nabla \cdot (\rho_g \mathbf{u}_g \mathbf{u}_g) = -\nabla \cdot \mathbf{q}_g - \beta (\mathbf{u}_g - \mathbf{u}_s) + \rho_g \mathbf{g}
\) |
| **Momentum equation solids phase** |
| \(
\frac{\partial \rho_s \mathbf{u}_s}{\partial t} + \nabla \cdot (\rho_s \mathbf{u}_s \mathbf{u}_s) = -\nabla \cdot \mathbf{q}_s - \beta (\mathbf{u}_s - \mathbf{u}_g) + \rho_s \mathbf{g}
\) |
| **Granular temperature equation (non-equilibrium)** |
| \(
\frac{\partial \mathbf{g}}{\partial t} + \mathbf{u}_g \cdot \nabla \mathbf{g} = \mathbf{q}_g \cdot \mathbf{u}_g + \mathbf{q}_s \cdot \mathbf{u}_s - \gamma_i T_i
\) |
| **Viscous stress tensor gas phase** |
| \(
\mathbf{T}_g = -\zeta \rho_g \left( \mathbf{u}_g - \mathbf{u}_g^e \right) \mathbf{u}_g + \frac{1}{2} \rho_g \mathbf{u}_g \mathbf{u}_g^e
\) |
| **Viscous stress tensor solids phase** |
| \(
\mathbf{T}_s = -\zeta \rho_s \left( \mathbf{u}_s - \mathbf{u}_s^e \right) \mathbf{u}_s + \frac{1}{2} \rho_s \mathbf{u}_s \mathbf{u}_s^e
\) |
| **Inter-phase drag coefficient** |
| \(\beta = \frac{150 \rho_g \sqrt{T_g}}{\rho_s \mathbf{u}_g} + 1.75 \frac{\rho_s \sqrt{T_s}}{\rho_g \mathbf{u}_s}
\) for \(\mathbf{u}_s > 0.20\) |
| \(\beta = \frac{1}{2} C_d \frac{\rho_s \mathbf{u}_s}{\rho_g \mathbf{u}_g} \mathbf{u}_g \mathbf{u}_s^e + 0.15 \frac{\rho_s \sqrt{T_s}}{\rho_g \mathbf{u}_s}
\) for \(\mathbf{u}_s < 0.20\) |
| \(C_d = \frac{0.5}{Re_g} (1 + 0.15 Re_g^{0.86})
\) for \(Re_g < 1000\) |
| \(C_d = 0.44\) for \(Re_g > 1000\) |
| \(Re_g = \frac{2 \rho_s \mathbf{u}_s^3}{\eta_s}
\) |
was modified to ensure that momentum leaves the system. Therefore, the boundary condition at the surface of the membranes will also result in momentum extraction from the system. There-fore, the boundary condition at the surface of the membranes will also result in momentum extraction from the system.

To model mass transfer phenomena due to selective extraction of hydrogen via membranes, first a hydrogen mass balance with Fickian dispersion was added to the model. The mass balance is a transient convection-diffusion equation as shown in Eq. (1). The dispersion coefficient was kept constant throughout the fluidized bed systems studied in this work. The effect of the membranes on the system was taken into account explicitly via the source term, $S_m$, which is applied to the computational cells adjacent to a membrane boundary (indicated with the red cells in Fig. 1). The source term in Eq. (1) is the membrane flux calculated with a Sieverts' type law, multiplied by the boundary cell’s area $A_v$, divided by the cell volume $V_v$, see Eq. (2) (Coroneo et al., 2009). The implementation of the membrane source term was validated with experimental data obtained by Helmi et al. (2018).

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

$$S_m = \frac{A_v Q_{m WH}}{V_v} \left[ (\mathbf{X}_{s WH})^* - \mathbf{X}_{s WH}^* \right]$$

The extraction of mass via a membrane (via the source term), will also result in momentum extraction from the system. Therefore, the boundary condition at the surface of the membranes was modified to ensure that momentum leaves the system. The extraction of mass via a membrane (via the source term), will also result in momentum extraction from the system. Therefore, the boundary condition at the surface of the membranes was modified to ensure that momentum leaves the system.

![Fig. 1. Schematic representation of how the membrane source term has been implemented.](Image)

### 2.1.2. Mass transfer and membranes

To model mass transfer phenomena due to selective extraction of hydrogen via membranes, first a hydrogen mass balance with Fickian dispersion was added to the model. The mass balance is a transient convection-diffusion equation as shown in Eq. (1). The dispersion coefficient was kept constant throughout the fluidized bed systems studied in this work. The effect of the membranes on the system was taken into account explicitly via the source term, $S_m$, which is applied to the computational cells adjacent to a membrane boundary (indicated with the red cells in Fig. 1). The source term in Eq. (1) is the membrane flux calculated with a Sieverts’ type law, multiplied by the boundary cell’s area $A_v$, divided by the cell volume $V_v$, see Eq. (2) (Coroneo et al., 2009). The implementation of the membrane source term was validated with experimental data obtained by Helmi et al. (2018).

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The extraction of mass via a membrane (via the source term), will also result in momentum extraction from the system. Therefore, the boundary condition at the surface of the membranes was modified to ensure that momentum leaves the system. The extraction of mass via a membrane (via the source term), will also result in momentum extraction from the system. Therefore, the boundary condition at the surface of the membranes was modified to ensure that momentum leaves the system.
The accuracy of the TFM for densely packed systems is important because densified zones are expected to occur frequently in fluidized bed membrane reactors. Therefore, the TFM’s pressure drop over a packed bed in a pseudo-2D column was compared to the Ergun equation and experimental data (Fig. 2). The TFM results match well with experimental data and with the Ergun equation. The minimum fluidization velocities found by experiments and TFM, 0.218 m/s and 0.212 m/s respectively, also match very well. The small difference between the experimental and TFM/Ergun equation slopes is caused by the small difference between the TFM and experimental porosity at minimum fluidization conditions.

3. Geometries and model settings

3.1. Grid sensitivity

A detailed grid sensitivity study was performed on fluidized bed membrane reactors with a single membrane positioned in the center of the bed. The tested grids are displayed in Fig. 3 and are labeled coarse (28 cells along the circumference of the membrane), middle (64 cells) and fine (128 cells). The mesh is not uniform because it has been refined locally, to ensure capturing the details of the hydrodynamics and mass transfer phenomena around the membranes. At further distances from the membrane, where the refinement stops, the 2D grid was square with 2 mm sides. The fluxes through the membranes were time-averaged over 25 s and compared to each other to determine when grid independent results can be reached. The results are presented in Fig. 4. The coarse grid is clearly not yet grid independent, whereas the middle and fine grid are relatively close to each other. The large number of grid cells used for the fine grid would require the simulations to be run at unfeasibly small time-steps, which would result in very long simulation times, especially when extending this to systems with membrane tube banks. The middle grid was deemed sufficiently

Fig. 2. Pressure drop versus gas velocity for experiments, TFM simulations and Ergun equation based on TFM porosity.

Fig. 3. Grids around membranes for a coarse grid with 28 cells (left), middle grid with 64 cells (middle) and fine grid with 128 cells (right) directly adjacent to the membrane boundary.

Fig. 4. Flux over maximum achievable flux versus angle around the membrane in degrees, for coarse, middle and fine grid. The picture on the right shows where the angles are located.
accurate to describe the current system’s hydrodynamics and mass transfer phenomena, and it was therefore used for all further cases studied in this work. An important observation is that the flux around the membrane is non-uniform; it is lowest on top of the membrane and highest below the membranes. It is more difficult for gas to reach the top of the membrane because the top of the membrane is shielded by the membrane itself, so gas dispersion could play an important role in limiting the flux on top of the membrane. These results will be discussed in more detail in the results section.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>WM FS</th>
<th>WM HS</th>
<th>WM FI</th>
<th>WM HI</th>
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<tbody>
<tr>
<td>Wall Membranes (WM)</td>
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<tr>
<td>(a) Full Staggered (FS)</td>
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<td>(b) Half Staggered (HS)</td>
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<td>(c) Full In-line (FI)</td>
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<td>(d) Half In-line (HI)</td>
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<td>No Wall Membranes (NWM)</td>
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<td>(e) Full Staggered (NWM FS)</td>
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<tr>
<td>(f) Half Staggered (NWM HS)</td>
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<td>(g) Full In-line (NWM FI)</td>
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<td>(h) Half In-line (NWM HI)</td>
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<td>Wall Tubes (T)</td>
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<tr>
<td>(i) Full Staggered (T FS)</td>
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<td>(j) Half Staggered (T HS)</td>
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<td>(k) Full In-line (T FI)</td>
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<td>(l) Half In-line (T HI)</td>
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</table>

Fig. 5. Membrane tube bank configurations: Wall Membranes (a) Full Staggered (WM FS); (b) Half Staggered (WM HS); (c) Full In-line (WM FI); (d) Half In-line (WM HI). No Wall Membranes (e) Full Staggered (NWM FS); (f) Half Staggered (NWM HS); (g) Full In-line (NWM FI); (h) Half In-line (NWM HI). Wall Tubes portrayed as black circles (i) Full Staggered (T FS); (j) Half Staggered (T HS); (k) Full In-line (T FI); (l) Half In-line (T HI). All measures are given in mm.
3.2. Geometries and settings

The grid sensitivity study has shown that local grid refinement around the membranes is required to capture the details of the mass transfer phenomena. For cases with membrane tube banks simulation times could therefore become quite high. To keep simulation times realistic when simulating fluidized beds with membrane tube banks, 2D simulations were performed. Asegehegn et al. (2012) already reported that the bubble behavior is quite similar for 2D and 3D flat fluidized beds with immersed tube banks, so 2D simulations will suffice as learning model for this study.

To demonstrate which mass transfer phenomena are important in fluidized beds with horizontally immersed membranes, single membrane simulations have been set up. First, a case with one membrane in the middle of the bed (placed at 150 mm from the left wall and at a vertical position of 225 mm) and one membrane next to the wall (placed at 25 mm from the left wall at the same height of 225 mm) were compared. To show how gas dispersion may limit the mass transfer towards the membrane surface, the simulations with a single membrane in the middle of the bed were performed for three different constant dispersion coefficients, viz. 5.0 \times 10^{-5}, 1.0 \times 10^{-4} and 5.0 \times 10^{-4} m^2/s. The membrane permeation flux data have been taken from previous work (Helmi et al., 2018) 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 membrane is numerically described with Sieverts’ law, as presented in Eq. (2), corresponding to bulk diffusion being the rate limiting step.

The dimensions of the more industrially oriented tube bank configurations simulated with the TFM are presented in Fig. 5 and Table 3. Configurations (a)–(d) are the base cases called Wall Membranes (WM), because membranes are present close to the bed walls. Configurations (e)–(h) are called No Wall Membranes (NWM), because membranes closest to the walls have been replaced with inactive tubes (the open black circles). The Tubes cases have the same membrane area as the No Wall Membranes cases, but the same membrane/tube locations as the Wall Membranes cases. The hydrodynamic effects that objects near the bed walls have on the system performance can hereby be quantified. The membrane tube banks have either been placed in a staggered or in an in-line configuration. The Full Staggered (FS) cases are configured in the same way as the Half Staggered (HS) cases, except they have double the number of membranes, similarly for the Full In-line (FI) and Half In-line (HI) configurations. The simulation settings are summarized in Table 4.

In the next section, first the results of the single membrane cases will be discussed. The most important mass transfer phenomena around horizontally immersed membranes in fluidized beds will be quantified and a comparison between membranes placed in the center of the bed and near the wall will be made. These results will quantify the hydrogen flux distribution around the membrane, and will show any differences in membrane performance related to membrane placement. Changing the dispersion coefficient to a higher and lower value will show whether the flux distribution around the membrane can be improved by improving dispersion. Observations for the single membrane cases will then be extended to the cases with membrane tube banks. The performance of various membrane tube bank configurations will be compared and the fluxes at different locations in the bed will be investigated to investigate the main possibilities to improve the membrane placement, and hereby the system’s performance. Finally, the hydrodynamic phenomena occurring in the tube bank systems will be quantified. From these results, design guidelines for fluidized beds with horizontally immersed membranes can be derived, which will help in the further exploitation of fluidized bed membrane reactor systems.

### Table 3

<table>
<thead>
<tr>
<th>Geometry and membrane data of all the tube bank configurations.</th>
</tr>
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<tbody>
<tr>
<td><strong>Wall Membranes</strong></td>
</tr>
<tr>
<td>Number of membranes [-]</td>
</tr>
<tr>
<td>Total membrane area [m²]</td>
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<tr>
<td>Min./max. starting width of tubes [mm]</td>
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<tr>
<td>Starting height of tubes [mm]</td>
</tr>
<tr>
<td>Axial &amp; lateral membrane pitch [mm]</td>
</tr>
<tr>
<td><strong>No Wall Membranes</strong></td>
</tr>
<tr>
<td>Number of membranes [-]</td>
</tr>
<tr>
<td>Total membrane area [m²]</td>
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<tr>
<td>Min./max. starting width of tubes [mm]</td>
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<td>Starting height of tubes [mm]</td>
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<tr>
<td>Axial &amp; lateral membrane pitch [mm]</td>
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<tr>
<td><strong>Tubes</strong></td>
</tr>
<tr>
<td>Number of membranes [-]</td>
</tr>
<tr>
<td>Number of inactive tubes [-]</td>
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<tr>
<td>Total membrane area [m²]</td>
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<tr>
<td>Min./max. starting width of tubes [mm]</td>
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<td>Starting height of tubes [mm]</td>
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### Table 4

<table>
<thead>
<tr>
<th>Summary of TFM simulation settings for all horizontal membrane cases.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity</td>
</tr>
<tr>
<td>Width (x)</td>
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<tr>
<td>Depth (z)</td>
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<tr>
<td>Number of membranes</td>
</tr>
<tr>
<td>Axial &amp; lateral membrane pitch</td>
</tr>
<tr>
<td>Tube diameter</td>
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<tr>
<td>Tube length</td>
</tr>
<tr>
<td>Tube density</td>
</tr>
<tr>
<td>Tube permeability</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
</tbody>
</table>
4. Results and discussion

4.1. Mass transfer phenomena around horizontally immersed membranes

First, the cases with a single membrane are discussed to identify the mass transfer phenomena in the system, after which results for the membrane tube banks cases will be described. The single membrane cases show that the placement of the membranes is critical for their performance. Both the membrane in the middle and the one near the wall suffer from a reduced hydrogen flux at the top of the membrane, where the membrane in the middle still outperforms the membrane near the wall by a factor 2, as shown by the angular H\textsubscript{2} flux profiles in Fig. 6. The flux is reduced at the top because the top of the membrane is shielded from the upward gas flow (preventing hydrogen replenishment) and because densified zones prevail on top of the membrane.

Low gas dispersion may be part of the cause for the reduced hydrogen concentrations on top of the membranes. In Fig. 7, the importance of gas dispersion is shown by comparing cases with different dispersion coefficient (assumed constant throughout the entire bed). As expected, higher dispersion coefficients result in higher permeation fluxes. However, for all cases the flux on top of the membrane is still only about half the flux at the bottom, and thus the non-uniform flux distribution around the membrane has not changed. This suggests that a higher mixing efficiency is required to exchange and refresh the densified zone at the top of the membranes more regularly. A higher dispersion coefficient thus helps increasing the overall performance of the membranes. One of the easiest methods to increase dispersion is to increase the particle size, but one has to keep in mind that increasing the particle size could increase internal mass transfer limitations for catalytic reactions such as SMR and WGS. Another possible strategy to reduce the mass transfer limitations to the top of the membranes could perhaps be a non-uniform (pulsating) inlet gas flow. However, this is not explored further in this work.

4.2. Mass transfer limitations for tube banks

The performance of the membranes at various positions in the tube banks has been analyzed. It is found that the main mass transfer limitations in fluidized beds with horizontally immersed membrane tube banks are at the membranes located near the bed walls (see Fig. 8). The time-averaged hydrogen mole fractions are lowest on top of the membranes near the walls. For the full in-line configuration (Fig. 5c) the time-averaged hydrogen flux of the membranes at the walls is not even half the flux of the membranes in the middle, which is similar to the single membrane cases. The flux of the membranes in the center of the bed does show a similar profile over the membrane circumference as the flux of the membranes near the walls, i.e. the mass transfer is mostly limited on top of the membranes, whereas the best performance is found at the bottom of the membranes.

The flux profiles can be related to hydrodynamic effects that have already been observed by Medrano et al. (2015). In their work, densified zones and gas pockets were found to be potential mass transfer limitations. In the next section, the effect of densified zones and gas pockets on hydrogen mass transfer towards horizontal membranes will be discussed in more detail. Furthermore, the gas flow profiles will be looked at to investigate how the hydrogen is distributed along the membranes.

4.3. Densified zones, gas pockets and gas flow profiles

Gas pockets and densified zones are observed in our TFM simulations, similar to the experimental observations by Medrano et al. (2015). Gas pockets are formed because the downward movement of solids shields the lower side of the membrane, causing areas with very little solids content to form underneath the membranes. Gas pockets most often appear at membranes near the walls, can be found underneath all horizontally immersed membranes.

No significant effect of the gas pockets on the mass transfer rate towards the membranes was found. Fig. 9 shows two snapshots, one taken just before the gas pocket appears, and one while the gas pocket was at its largest size. Similar to regular bubbles in
fluidized beds, the gas mixture follows the path of least resistance and therefore flows through areas with the lowest particle content, such as gas pockets. The streamlines show that the gas flowing around the membrane has a significant effect on where reduced hydrogen concentrations are observed. The gas cannot easily flow to the top of the membranes, which enables solids to be accumulated there (densified zones), making it more difficult to quickly replenish hydrogen.

Densified zones can be present on top of the membranes anywhere in the reactor, but they mostly prevail at the membranes that are located near the bed walls, because the solids flow downwards onto the top of the membranes there. This is because the time-averaged solids circulation pattern in the simulations shows an upwards motion in the center of the bed, while the solids flow down along the walls. This is a generically seen flow pattern, also for fluidized beds without internals (Dang et al., 2014; Laverman et al., 2008; Tan et al., 2014). The time-averaged hydrogen mole fractions in Fig. 10 show that the densified zones have a detrimental effect on the mass transfer rate towards the membrane. On top of the membrane, the hydrogen mole fractions (thus also the fluxes) are significantly lower compared to elsewhere around the membrane. The effect is most pronounced for membranes near the walls, but also for membranes in the middle of the reactor a lower hydrogen flux was observed on top of the membrane compared with the flux at the bottom. This is intrinsic to the way the membranes are placed compared to the flow direction. The gas cannot always reach the top of the membrane easily, because the membrane itself shields the top-side of the membrane. In Fig. 8 this is also visible, because the time-averaged hydrogen flux is also lower on top of the membranes in the middle.

Fig. 11 shows that an important cause for the formation of densified zones is that gas cannot easily reach the wall membranes. There is gas back mixing, especially in the top of the bed where the highest solids velocities are found, which means the solids are pushing some of the fresh hydrogen away from the membranes. The gas has insufficient momentum near the walls to move the downward flowing solids away from the membranes near the walls.

4.4. Effect of tube bank configurations on hydrogen flux and recovery

4.4.1. Hydrogen flux

The main mass transfer limitations towards the membranes have already been identified near the bed walls. This section will
quantify how the mass transfer limitations affect the flux of various membrane tube bank configurations. The left graphs of Figs. 12 and 13 present the time-averaged hydrogen flux profiles averaged over the membranes’ horizontal location for all the full in-line and half in-line configurations. For the full and half in-line configurations, the membranes near the walls perform approximately three to five times worse than the membranes in the middle of the reactor. Adding inert tubes near the walls does not have a significant effect on the system performance. The polar plots in Figs. 12 and 13 show that when active membranes are placed at the walls, the flux averaged over all membranes in the bed is reduced. The in-line configurations with half tube banks show similar behavior to the full tube bank configurations. The flux is slightly higher for the membranes in the middle of the half tube bank configurations, because in the full tube bank configurations a lot of the hydrogen has already been extracted before it reaches the highest positioned membranes, which results in lower fluxes for the membranes in the top, and thus it lowers the average membrane performance.

In general, the flux is more equally distributed over the width in the full staggered configuration than in the full in-line configuration (see Fig. 14). Some of the membranes closest to the walls that have not been removed in the full staggered configuration still have reduced flux compared to the center ones. However, the difference between the lowest and the highest flux is only a factor two, which means that the staggered tube bank configuration performs better than the in-line one. In general, the results show that membranes that are approximately within 8 cm distance of the walls (about 20% of the total bed width) suffer from reduced fluxes. Because the gas cannot channel through the staggered membrane tube banks, the membranes near the walls perform better in a staggered configuration than in an in-line one. The next sub-section on hydrogen recoveries will show how the gas channeling affects the membrane performance.

4.4.2. Hydrogen recovery

The performance of the membrane tube bank configurations with and without membranes near the walls is compared. The overall hydrogen recoveries have been calculated for all cases by dividing the amount of hydrogen extracted via the membranes by the total amount of hydrogen fed (Fig. 15 left). Especially when moving towards large-scale production of hydrogen via SMR and WGS, the overall recovery should be high to ensure...
high reaction rates and sufficient hydrogen extraction. Because the configurations have a different number of membranes (and thus a different membrane area), the overall recoveries do not tell the full story on the reactor performance. The average recoveries per membrane for each configuration have therefore been calculated (Fig. 15 right).
The wall membrane cases have higher overall recoveries than the cases without wall membranes because they have more membranes, which results in more hydrogen being exacted, and there is less hydrogen by-pass. The cases with inactive tubes near the walls do not perform better or worse than the cases without membranes near the walls. The performance per membrane shows that for the full and half staggered cases there is a clear increase in performance when wall membranes are removed. The in-line cases do not show this trend, which suggests that the channeling and bypassing of hydrogen is quite significant for these cases, and that moving membranes too far away from the walls reduces the average membrane performance. Systems with horizontally immersed membranes should thus be designed in a way that membranes are in a staggered configuration, and that membranes are not too close to the walls (to prevent low fluxes by these membranes) but also not too far away from the reactor walls (to prevent hydrogen slip). The staggered configuration also showed lower flux changes over the reactor width. It should be noted that the recoveries in these simulation systems are fairly low because the gas pressure is relatively close to ambient pressure, which causes the permeation flux to be low and therefore more membranes are required to achieve higher recoveries.

4.5. Bubble properties

To quantify the effect of the tube bank configurations on the bubbles, the bubble size distributions and equivalent bubble diameters of the full and half tube bank configurations are presented in Figs. 16 and 17. The bubble properties have been obtained with the Digital Image Analysis (DIA) code from Medrano et al. (2015).
which was adapted for OpenFOAM simulation data. In the present work, bubbles are defined as areas with a solids hold-up of 20% or less. The bubble size distributions show that having immersed tubes that start at the bottom of the bed and move all the way to the top of the bed significantly increases the number of small bubbles. The bubble size in full banks also increases slower with axial position than for the half bed. The bubble size increase levels off at around 4.5–5 cm, which is approximately the distance between two membranes (the ‘pitch’). The bubble cutting effect of horizontally immersed membranes can thus clearly provide a hydrodynamic advantage for fluidized bed membrane reactors by increasing the bubble-to-emulsion phase mass transfer.

The bubble size distributions and equivalent bubble diameters for all the full in-line cases and all the full staggered cases are presented in Figs. 18 and 19. The effect of the removal of wall membranes on the bubble size is negligible for both the full in-line and full staggered cases. Similar to the hydrogen flux, the addition of inert tubes near the walls does not cause a significant performance change, therefore making the inert tubes redundant for this specific purpose. The explanation that bubbles are almost unaffected by the removal of wall membranes is similar to why the membranes at the walls perform worse than those in the middle of the reactor. Gas bubbles move mostly towards the center, and solids move down near the walls. Especially in a 30 cm wide fluidized bed, the small bubbles in the bottom of the bed move towards the center because of bubble coalescence, so that most of these bubbles do not even flow past the membranes at the walls.

To conclude, wall membranes reduce the overall membrane performance and they do not offer a hydrodynamic advantage to the system, so they can better be left out of the reactor for these purposes.

5. Conclusions

In this work we have used a TFM to simulate fluidized beds with horizontally immersed membranes. The membrane performance was studied for single membrane and tube bank cases for hydrogen separation from a binary H₂/N₂ mixture. The simulations clearly show that the hydrogen permeation flux is not uniform along the circumference of the membranes. The lowest flux was found on top of the membranes and the highest flux was found at the bottom of the membranes, because the top of the membranes is shielded from upwards flowing gas.

In systems with tube banks of horizontally immersed membranes, the membranes placed close to the bed walls have a significantly lower flux than membranes placed in the center of the bed. The down flow of solids causes gas back-mixing near the fluidized bed walls, and densified zones occur here, which block fresh hydrogen from reaching the membranes. Contrary to densified zones, gas pockets have no negative effect on the mass transfer of hydrogen towards the membranes. Nevertheless, gas pockets could reduce the performance of catalytic systems. Gas pockets contain almost no solids, so in catalytic systems reduced reaction rates are expected in the gas pockets, which could reduce hydrogen production close to the membranes.

The average system performance increases when the membranes near the walls are removed. When membranes are placed too far from the bed wall, hydrogen recoveries drop because there is too much gas bypassing. For this reason, the staggered placement of membranes is preferred and the in-line placement of membranes should be avoided. The placement of membranes is critical for the system performance, so future studies should look at the effect of the axial and lateral membrane pitch on the system performance.
The addition of inactive tubes near the bed walls did not improve the system performance, because most of the gas and bubbles move through the middle of the reactor. In principle these inactive tubes can be left out of the reactor, but they may be of use when additional heat needs to be supplied or withdrawn from the system, or they can be used to selectively add oxygen to the system to combust some of the hydrogen to enable auto-thermal operation.

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References


