

A two-fluid model study of hydrogen production via water gas shift in fluidized bed membrane reactors

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A TWO-FLUID MODEL STUDY OF HYDROGEN PRODUCTION VIA WATER GAS SHIFT IN FLUIDIZED BED MEMBRANE REACTORS

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ABSTRACT

Fluidized bed membrane reactors have been proposed as a promising reactor concept for the production of ultra-pure hydrogen via Water Gas Shift (WGS). High-flux thin-film dense palladium-based membranes are used to selectively extract hydrogen from the reaction medium, which shifts the thermodynamic equilibrium towards the products' side, increasing the conversion. A Two-Fluid Model (TFM) has been used to investigate the effect of hydrogen extraction via perm-selective membranes on the WGS reaction rates in the fluidized bed. A thorough TFM verification study was performed, which showed that the model is able to accurately predict the concentration profiles for various types of n^{th} order and equilibrium chemical reactions. Also, the implementation of the WGS reaction rate in the TFM was checked. The results have shown a clear positive effect of the hydrogen permeation on the WGS reaction rates, both for vertically and horizontally immersed membranes. In systems with horizontally immersed membranes, gas pockets that contain a very small amount of catalyst develop underneath the membrane tube, resulting in reduced local reaction rates. Densified zones on top of the membrane tube show increased local reaction rates. Mass transfer limitations from the emulsion phase to the membrane surface is the most pronounced effect that reduces the overall reactor performance. The developed model allows further investigating different configurations and operation modes to further optimize the reactor's performance.

Keywords: Two-Fluid Model, Water Gas Shift, hydrogen, fluidized bed, membrane.

NOMENCLATURE

Latin Symbols

A	area	[m ²]
A_{WGS}	pre-factor WGS reaction rate	[mol/(bar kg _{cat} s)]
B_{WGS}	Relative equilibrium ratio eq.	[-]
C_d	drag coefficient	[-]
C_1	constant for Gibbs calc.	[J/(mol K ³)]
C_2	constant for Gibbs calc.	[J/(mol K ²)]
C_3	constant for Gibbs calc.	[J/(mol K)]
C_4	constant for Gibbs calc.	[J/mol]
D	diffusion coefficient	[m ² /s]
E_{act}	Activation energy	[J/mol]
e	restitution coefficient	[-]

G	Gibbs free energy	[J/mol]
H	enthalpy	[J/mol]
g	gravitational acceleration	[m/s ²]
k_{WGS}	WGS reaction rate constant	[mol/(bar kg _{cat} s)]
$K_{eq,WGS}$	WGS equilibrium constant	[-]
M	molar weight	[kg/mol]
n	power in Sieverts' law	[-]
p	pressure	[Pa]
P	partial pressure	[Pa]
Q	membrane permeance	[mol/(m ² s Pa ⁿ)]
R	universal gas constant	[J/(mol.K)]
R_{WGS}	chemical reaction rate	[mol/(kg _{cat} s)]
Re	Reynolds number	[-]
S	membrane mass source term	[kg/(m ³ .s)]
t	time	[s]
T	temperature	[K]
u	velocity	[m/s]
V	volume	[m ³]
X	molar fraction	[-]
Y	mass fraction	[-]

Greek Symbols

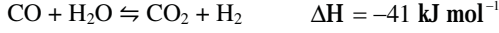
α	hold-up fraction	[-]
β	interphase drag coefficient	[kg/(m ³ s)]
γ	dissipation of fluct. energy	[kg/(m s ³)]
θ	granular temperature	[m ² /s ²]
κ	conductivity of fluct. energy	[kg/(m s)]
μ	shear/dynamic viscosity	[Pa.s]
ρ	density	[kg/m ³]
τ	shear stress tensor	[N/m ²]
ω_{cat}	catalyst mass fraction	[-]

Sub/superscripts

c	cell
g	gas
i	phase
m	membrane
mf	minimum fluidization
p	particle
ret	retentate
s	solid
sim	simulation
tot	total
w	wall

INTRODUCTION

Hydrogen is industrially mostly produced via Steam Methane Reforming (SMR) carried out in multi-tubular packed bed reactors. First, methane reacts with steam to form carbon monoxide and hydrogen at temperatures around 1000 °C. Consecutively, the formed carbon monoxide reacts with steam to form carbon dioxide and hydrogen via the Water Gas Shift (WGS) reaction, given by



WGS is thermodynamically favoured at low temperatures and kinetically favoured at higher temperatures. Traditionally, WGS reactors consist of two stages; in the first reactor most of the CO is converted at 300-450 °C and in the second reactor the remaining CO is converted at 200-300 °C. However, to produce hydrogen efficiently, low hydrogen concentrations are required to achieve high CO conversions. Costly and energy intensive separation units, such as pressure swing adsorption units, are required to separate the hydrogen from the outlet gas mixture. The process will have an additional cost and energy penalty, if the unwanted byproduct CO₂ should be separated from the gas mixture and stored underground (Medrano et al. (2014)).

Both packed bed membrane reactors (Tiemersma et al. (2006)) and fluidized bed membrane reactors (Fernandez et al. (2015)) have been proposed as alternative reactor systems for hydrogen production via WGS. This work will focus on the development of fluidized bed membrane reactors (FBMRs) for hydrogen production via WGS. In FBMRs, the reaction and separation steps have been integrated in one single unit; ultra-pure hydrogen is obtained from the reactor by extracting it from the gas mixture with modern high-flux hydrogen perm-selective supported palladium-based membranes. The hydrogen extraction drives the reaction equilibrium towards the products' side, which will increase the reaction rate and reactant conversion. The WGS reaction is highly suitable for hydrogen production in an FBMR, because hydrogen can be produced at 400 °C, high enough to avoid problems associated with membrane embrittlement and low enough to circumvent problems related to the membrane chemical/mechanical stability and membrane sealing.

Fluidized bed membrane reactors have already been investigated by a.o. Adris et al. (1994), Gallucci (2008) and Mleczko et al. (1996), and many others. Most of the previous fluidized bed membrane reactor studies were either focused on experimental demonstration or using phenomenological models. More recently, various CFD studies on fluidized bed membrane reactors have been performed, which have mostly investigated the bed hydrodynamics (De Jong et al. (2012), Tan et al. (2014) and Medrano et al. (2015)). Only a few studies have investigated FBMRs with CFD models focused on mass transfer phenomena and chemical reactions (e.g. Hommel et al. (2012), Voncken et al. (2015) and Helmi et al. (2017)).

The present work uses CFD simulations to visualize and quantify the mass transfer phenomena and reaction rates throughout FBMR systems in which hydrogen is produced via WGS. The OpenFOAM v.2.3.0 solver **twoPhaseEulerFoam**, a Two-Fluid Model (TFM), was used to model hydrodynamics, mass transfer and chemical reactions occurring in various fluidized bed membrane reactor configurations. The chemical species balances, selective membrane extraction and chemical reactions are our own implementations that were coupled to the TFM hydrodynamics. A thorough verification was carried out for all these aspects. To ensure the reaction terms have been implemented properly, numerous simple chemical reactions in a batch reactor have been simulated and compared to analytical and numerical solutions. The more complex kinetics of the WGS reaction have also been implemented in the TFM and compared to a batch reactor model.

The objective of this research is to understand and quantify the effect of selective hydrogen permeation on the performance of fluidized bed reactors for hydrogen production via WGS. The Numaguchi and Kikuchi (1988) reaction kinetics for WGS were implemented in the TFM. Both horizontally and vertically immersed membrane configurations were studied. These results were compared to the performance of a fluidized bed reactor without membranes.

First, the model equations and the verification of their implementation will be discussed. Special attention will be given to the species balance and the reaction kinetics. Next, the used simulation settings and geometries will be presented. In the results section, the effect of the extraction via the membranes on the reaction rates and reactor performance will be discussed.

MODEL DESCRIPTION

The TFM considers the gas and solids phases as interpenetrating continua. The most important governing and constitutive equations are presented in equations 1 through 4, showing the continuity and Navier-Stokes equations of both the gas and solids phases. The source term \mathbf{S} is added to the gas continuity equation to account for the extraction of gas via the membranes, which will be detailed later. The gas phase is considered as an ideal, Newtonian fluid. The solids phase rheology (solids pressure \mathbf{p}_s and stress tensor $\boldsymbol{\tau}_s$ is described with closures from the Kinetic Theory of Granular Flow, for which the granular temperature equation (4) is solved.

$$\frac{\partial(\alpha_i \rho_i)}{\partial t} + \nabla \cdot (\alpha_i \rho_i \mathbf{u}_i) = \mathbf{S}_m, \quad i = s, g \quad (1)$$

$$\begin{aligned} & \frac{\partial(\alpha_g \rho_g \mathbf{u}_g)}{\partial t} + \nabla \cdot (\alpha_g \rho_g \mathbf{u}_g \mathbf{u}_g) \\ & = -\nabla \cdot (\alpha_g \boldsymbol{\tau}_g) - \alpha_g \nabla \mathbf{p} - \beta (\mathbf{u}_g - \mathbf{u}_s) + \alpha_g \rho_g \mathbf{g} \end{aligned} \quad (2)$$

$$\begin{aligned} & \frac{\partial(\alpha_s \rho_s \mathbf{u}_s)}{\partial t} + \nabla \cdot (\alpha_s \rho_s \mathbf{u}_s \mathbf{u}_s) = -\nabla \cdot (\alpha_s \boldsymbol{\tau}_s) \\ & - \alpha_s \nabla \mathbf{p} - \nabla \mathbf{p}_s + \beta (\mathbf{u}_g - \mathbf{u}_s) + \alpha_s \rho_s \mathbf{g} \end{aligned} \quad (3)$$

$$\frac{3}{2} \left(\frac{\partial (\alpha_s \rho_s \theta)}{\partial t} + \nabla \times (\alpha_s \rho_s u_s \theta) \right) = -\gamma_s - 3\beta\theta \quad (4)$$

$$-(\mathbf{p}_s \mathbf{I} + \alpha_s \boldsymbol{\tau}_s) : \nabla u_s + \nabla \times (\alpha_s \kappa_s \nabla \theta)$$

The fluid-particle drag is modelled according to Gidaspow (1994), which combines the drag models by Ergun et al. (1949) and Wen et al. (1966), where Ergun's model is valid for high solids hold-ups (above 20%) and Wen's model is applied at lower solids hold-ups (below 20%). The drag coefficient C_d is determined based on the Reynolds particle number. The drag models are described in equations 5 until 9.

$$\beta = 150 \frac{\alpha_s^2 \mu_g}{\alpha_g d_p^2} + 1.75 \frac{\alpha_s \rho_g |u_g - u_s|}{d_p} \quad (\alpha_s \geq 0.20) \quad (5)$$

$$\beta = \frac{3}{4} C_d \frac{\alpha_g \alpha_s \rho_g}{d_p} |u_g - u_s| \alpha_g^{-2.65} \quad (\alpha_s < 0.20) \quad (6)$$

$$C_d = \frac{24}{Re_p} (1 + 0.15 Re_p^{0.687}) \quad \text{for } Re_p \leq 1000 \quad (7)$$

$$C_d = 0.44 \quad \text{for } Re_p > 1000 \quad (8)$$

$$Re_p = \alpha_g \frac{\rho_g d_p |u_g - u_s|}{\mu_g} \quad (9)$$

Kinetic Theory of Granular Flow

To simulate the rheological properties of the solids phase's continuum approximation, various KTGF closure equations are required. The closure equations used in this work are summarized in Table 1.

Table 1: KTGF closures used for TFM simulations.

Quantity	Closure
Solids shear viscosity	Nieuwland et al. (1996)
Solids bulk viscosity	Lun et al. (1984)
Solids pressure	Lun et al. (1984)
Frictional stress	Srivastava & Sundaresan (2003)
Conductivity of fluct. energy	Nieuwland et al. (1996)
Radial distribution function	Ma & Ahmadi (1984)
Dissipation of gran. energy	Nieuwland et al. (1996)

Further details on the TFM-KTGF can be found a.o. in Lun et al. (1984), Kuipers et al. (1992), Gidaspow (1994), Van Wachem (2000), Rusche (2003) and Van Der Hoef et al. (2006). Details on the OpenFOAM TFM can be found in Passalacqua et al. (2011) and Liu et al. (2014).

Mass transfer, membranes and reactions

Mass transfer phenomena and extraction of hydrogen via membranes were modeled with an approach similar to that described by Coroneo et al. (2009), see equation 10. Extraction of hydrogen via the membranes was modeled via source term, S_m , to the species equation of hydrogen. This membrane source term is applied to the

computational cells adjacent to a membrane. The membrane source term is calculated with Sieverts' law, which is commonly used to describe the hydrogen flux through dense palladium membranes (see equation 11). The parameters in Sieverts' law are obtained from experiments. The extraction of mass via a membrane will also result in momentum extraction from the system. Therefore, a boundary condition was added for the membranes to ensure momentum leaves the system via the membranes, see equation 12.

$$\frac{\partial \alpha_g \rho_g Y_i}{\partial t} + \nabla \times (\alpha_g \rho_g u_g Y_i) \quad (10)$$

$$= \nabla \times (\alpha_g \rho_g D_i \nabla Y_i) + S_m + R_i$$

$$S_m = \frac{A_c}{V_c} Q_m M_{H_2} \times \left[(X_{H_2}^{ret} p_{tot})^n - (X_{H_2}^{perm} p_{tot})^n \right] \quad (11)$$

$$u_m = \frac{S_m RT}{p M_{H_2}} \frac{V_c}{A_c} \quad (12)$$

The Numaguchi and Kikuchi (1988) kinetics for the WGS reaction were implemented in the TFM model. The reaction rate equation and their corresponding parameters (reaction rate constants, pre-factors, equilibrium constants) are presented in Table 2 and Table 3.

Table 2: Chemical reaction rates for WGS.

$$R_{WGS} = k_{WGS} \frac{P_{CO} P_{H_2O} - \frac{P_{CO_2} P_{H_2}}{K_{eq,WGS}}}{P_{H_2O}}$$

$$k_{WGS} = A_{WGS} \exp\left(-\frac{E_{act}}{RT}\right)$$

$$K_{eq,WGS} = \exp\left(\frac{-\Delta G_{WGS}}{RT}\right)$$

$$\Delta G_{WGS} = C_1 T^3 + C_2 T^2 + C_3 T + C_4$$

Table 3: Parameters for reaction rate expressions.

Parameter	Value
A_{WGS}	$2.45 \times 10^2 \text{ mol}/(\text{bar kg}_{cat} \text{ s})$
E_{act}	$54.5 \times 10^3 \text{ J}/(\text{mol K})$
C_1	$1.760 \times 10^{-6} \text{ J}/(\text{mol K}^3)$
C_2	$-1.065 \times 10^{-2} \text{ J}/(\text{mol K}^2)$
C_3	$48.04 \text{ J}/(\text{mol K})$
C_4	$2.075 \times 10^2 \text{ J}/\text{mol}$

Extraction of hydrogen via the membrane should move the reaction away from equilibrium, towards the product side. The relative equilibrium ratio will be used to quantify the deviation from equilibrium (see equation 13). The addition of membranes to a fluidized bed is expected to significantly lower the local equilibrium ratio compared to a fluidized bed without membranes.

$$B_{\text{WGS}} = \frac{\left(\frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}} \right)}{K_{\text{eq,WGS}}} \quad (13)$$

Boundary conditions

All simulations have been performed with a 2D computational domain. For the gas mixture, a no-slip boundary condition was applied to the left and right walls, a constant gas velocity was imposed at the inlet, an imposed pressure condition was set at the outlet and the boundary condition of equation 12 was applied at the surface of the membranes. For the solids velocity and granular temperature, a Johnson & Jackson partial slip boundary condition with a specular coefficient of 0.50 was applied on the walls and the membranes (see Johnson et al. (1987)).

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 time-step was selected each iteration based on a maximum Courant number of 0.1. A combination the second order Gauss linear and Van Leer scheme was used for the spatial discretization. The model's absolute tolerances for all quantities were within $1 \cdot 10^{-11}$ each iteration.

VERIFICATION, GEOMETRIES AND SETTINGS

Reaction verification

The hydrodynamics and mass transfer parts of the model have been carefully verified and validated in our earlier works, see Medrano et al. (2015), Voncken et al. (2015) and Helmi et al. (2017). Gas flow profiles, packed bed pressure drop, convection-diffusion and diffusion only systems have all been verified with their respective analytical solutions. The fluidized bed's bubble properties and the membrane's hydrogen flux have been validated with experimental data. To verify whether the WGS reaction terms were implemented correctly, different types of basic reactions were compared to their analytical solutions. Furthermore, the WGS reaction has been simulated with the TFM and compared to a simple MATLAB numerical batch reactor model.

A first and second order reaction have been performed in a gas only batch reactor. The TFM mass fraction profiles in Figure 1 match very well with the analytical solution. The mass fraction profiles for an equilibrium reaction with two species reacting to a product was also predicted correctly by the TFM (Figure 2).

The implementation of the WGS reaction rate equation was then checked by simulating a simple gas batch reactor system with the TFM, and comparing it with a gas batch reactor system in MATLAB. For this gas only verification study the catalyst efficiency for the WGS reaction was removed from the reaction rate equation. Figure 3 shows that the TFM results for WGS compares well with the gas batch reactor results obtained from the MATLAB code. These results verify that the TFM can be used to simulate various types of chemical reactions

and can predict the resulting concentration profiles accurately. To ensure equilibrium concentrations are correctly predicted by the TFM, the WGS verification simulation will be run for a longer period of time in future studies.

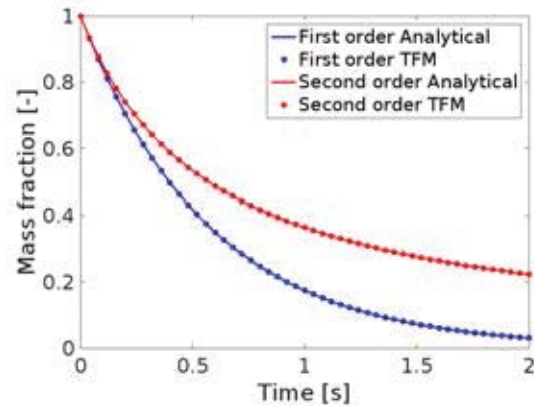


Figure 1: Analytical solution and TFM simulation result for a first and second order reaction.

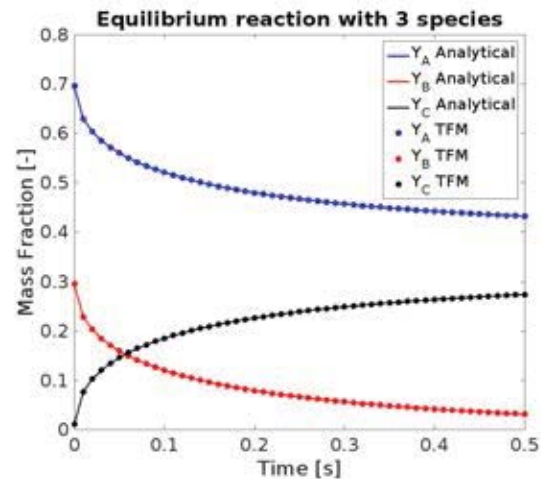


Figure 2: Analytical solution and TFM simulation result for a three species equilibrium reaction $A + B \rightleftharpoons C$.

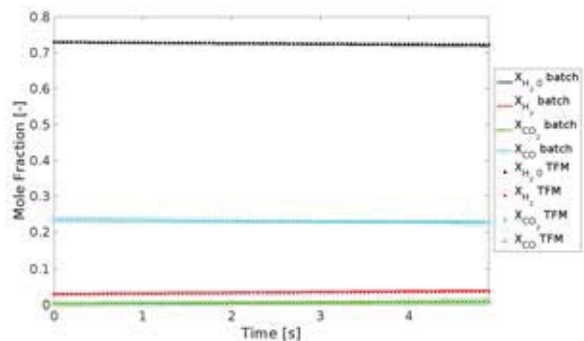


Figure 3: TFM simulation and batch reactor model comparison for the WGS reaction.

Geometries and model settings

To quantify the effect of hydrogen extraction via a membrane on the reaction rate, systems with and without membranes were simulated. Both vertically and horizontally positioned membranes were looked into.

Fully 2D simulations have been performed. The geometries of all simulations are presented in Table 4 and Figure 4. The horizontal membrane's diameter was set to 3.5 mm. Only one horizontal membrane has been simulated to show the effects that can occur in the system, in general, tube banks are best to be used to avoid hydrogen bypassing. The bed depths are only important for the calculation of the membrane area and do not hold any physical meaning in these 2D cases. The simulation settings can be found in Table 5. The vertical membrane was always placed at the left boundary. The horizontal membrane was placed at half of the reactor width.

Table 4: Geometries of all TFM WGS simulations.

Case	Width	Height	Depth
Vertical/no membrane	0.0356 m	0.0712 m	0.016 m
N_{cells} vert./no memb.	40	80	-
Horizontal membrane	0.0356 m	0.0712 m	0.032 m
N_{cells} horizontal memb.	40	80	-

Table 5: Summary of simulation settings for the WGS cases.

Quantity	Value	Unit
d_p	250	μm
ρ_p	1700	kg/m^3
e_{pp}, e_{pw}	0.97	-
u/u_{mf}	3	-
D	$1.0 \cdot 10^{-4}$	m^2/s
Q_{pd}	$4.3 \cdot 10^{-3}$	$\text{mol}/(\text{m}^2\text{sPa}^n)$
n	0.50	-
T	678	K
X_{H_2}	0.1	-
X_{CH_4}	0.1	-
$X_{\text{H}_2\text{O}}$	0.35	-
X_{CO}	0.35	-
X_{CO_2}	0.1	-
ω_{cat}	0.10	-
p_{outlet}	3	bar
p_{perm}	$0.01 \cdot 10^5$	Pa
t_{sim}	10	s
Δt	$5 \cdot 10^{-6}$	s

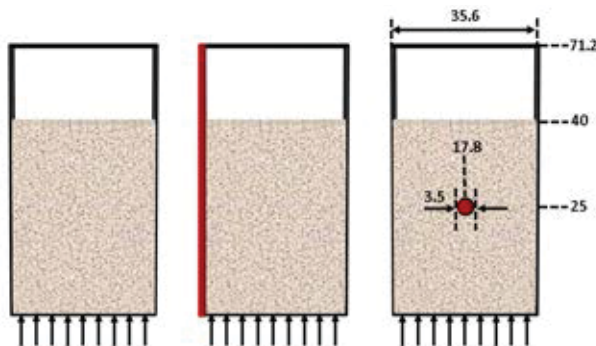


Figure 4: A fluidized bed: (left) without membranes; (middle) with a membrane at the left boundary; (right) with a horizontally immersed membrane. Dimensions are in mm.

RESULTS

Water Gas Shift

This section presents the results obtained by simulating fluidized beds with and without membranes in which the WGS reaction takes place. The reaction rate and equilibrium ratio will be used to assess the effect of the membrane on the system. The different types of membranes are not directly comparable, because they have different amount of hydrogen bypass and because the horizontal membrane affects the hydrodynamics. However, the effects that occur in these reactors can be described.

Reaction rate and equilibrium

The instantaneous and time-averaged reaction rates, and the time-averaged relative equilibrium ratio for a regular fluidized bed, fluidized bed with a vertical membrane and fluidized bed with a horizontal membrane are displayed in Figure 5. From the plot showing spatial distribution of the instantaneous reaction rates the position of the gas bubbles can be easily discerned as areas with reduced reaction rates related to the lower catalyst concentration inside the bubbles. The time-averaged reaction rates near the vertical membrane (the red line in the second row of Figure 5) are a factor 2 to 2.5 higher than the ones in a regular fluidized bed without membranes. The reaction is also further from its equilibrium state near the membrane than elsewhere in the reactor, which shows that the membrane flux is so high that kinetic and mass transfer limitations start to play a role.

Temporary gas pockets with low catalyst content occur underneath horizontally immersed membranes (Medrano et al. (2015)). Similar to bubbles, lower reaction rates are expected inside gas pockets compared to elsewhere in the reactor. This reduction in reaction rate is slightly visible in the time-averaged reaction rate plots for the horizontal membrane case. When the membrane tube is placed lower in the bed and closer to the wall the effect of gas pockets on a catalytic reaction rates is more pronounced (not shown). Contrary to the gas pockets, densified zones on top of the horizontal membrane increase the reaction rate locally with about a factor 4 to 5 compared to regular fluidized beds. However, despite the increased driving force, the hydrogen flux is still lowest on top of the horizontal membrane. Further investigation is required to quantify the mass transfer limitations in these densified zones and the effect of the position of the membranes in the bed.

Hydrogen concentrations and membrane geometry

Figure 6 shows the hydrogen mole fraction profiles for a fluidized bed with a vertically and a horizontally immersed membrane. In both systems the membranes suffer from mass transfer limitations from the emulsion phase towards the membrane surface. Insufficient hydrogen is supplied to the membrane, so its flux is significantly lower than its maximum theoretical flux, which is referred to as concentration polarization. Caravella et al. (2009) and Helmi et al. (2017) have shown that concentration polarization are to be expected for systems with high flux membranes to extract one

chemical component from a gas mixture. Extraction of hydrogen increases the reaction rate and thus the hydrogen production. Clearly, the mass transfer rates of reactants and hydrogen towards the membrane is insufficient to maintain high hydrogen concentrations near the membrane, which are required to keep the driving force for permeation and the fluxes high. The differences in hydrogen mole fraction profiles clearly shows how differently vertically and horizontally

immersed membranes behave. The vertically immersed membrane is able to extract a large amount of hydrogen, hereby causing severe concentration polarization via a vertical concentration boundary layer. The underside of the horizontally immersed membranes is hardly limited by concentration polarization due to the direction of the gas flow, whereas the top has a high degree of concentration polarization, partially due to densified (defluidized) zones (see Voncken et al. (2015)).

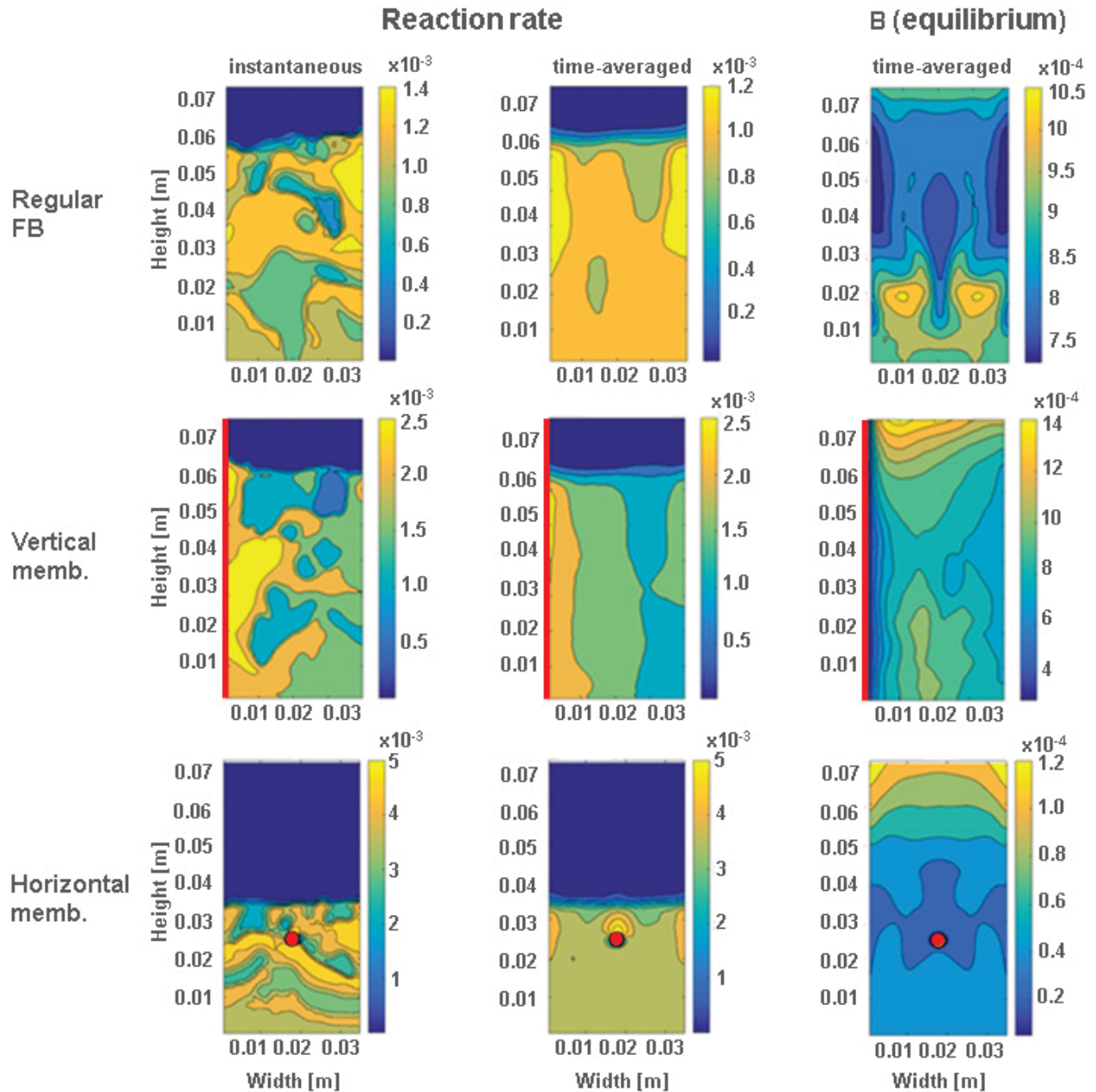


Figure 5: Instantaneous and time-averaged WGS reaction rates and time-averaged relative equilibrium ratio. Membranes are portrayed in red.

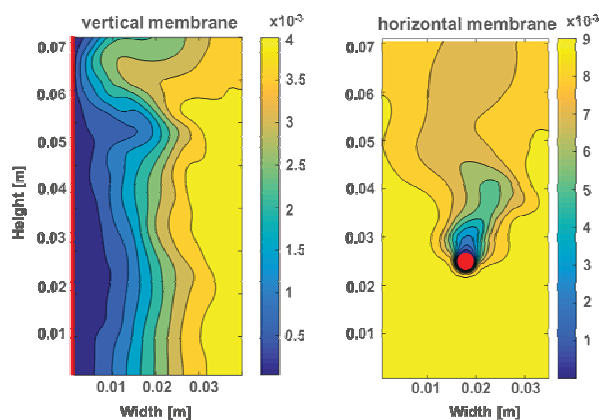


Figure 6: Hydrogen mole fraction profiles for fluidized bed reactors with a horizontally and vertically immersed membrane. The membranes are portrayed in red.

CONCLUSION

A TFM with mass transfer, membranes and reactions was verified with various simple reactions such as n^{th} order, multi-species equilibrium reactions and Water Gas Shift. The verified TFM was then used to simulate WGS in fluidized beds without and with membranes. The membranes increase the reaction rate by a factor 2 to 5, depending on the geometry and orientation of the membrane. The extraction of hydrogen shifts the equilibrium of the reaction, especially in the vicinity of the membrane. For systems with vertically immersed membranes vertical mass transfer boundary layers develop, whereas for systems with horizontally immersed membranes, gas pockets with reduced reaction rates and densified zones with increased reaction rates prevail. Future studies will focus on the quantification of the concentration polarization effects and extend the investigations to Steam Methane Reforming.

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