



On concentration polarisation in a fluidized bed membrane reactor for biogas steam reforming: Modelling and experimental validation



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HIGHLIGHTS

- Fluidized bed reactor model accounting for concentration polarization.
- Reduction of concentration polarization in fluidized bed is demonstrated.
- Experimental demonstration and model validation of biogas steam reforming in a FBMR.
- The H₂ productivity is proportionally related to the concentration polarization.

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ABSTRACT

The production of pure hydrogen through the steam reforming of biogas in a fluidized bed membrane reactor has been studied. A phenomenological one-dimensional two-phase fluidized bed reactor model accounting for concentration polarisation with a stagnant film model has been developed and used to investigate the system performance. The validation of the model was performed with steam reforming experiments at temperatures ranging from 435 °C up to 535 °C, pressures between 2 and 5 bar and CO₂/CH₄ ratios up to 0.9. The permeation performance of the ceramic-supported PdAg thin-film membrane was first characterized separately for both pure gas and gas mixtures. Subsequently, the membrane was immersed into a fluidized bed containing Rh supported on alumina particles and the reactor performance, viz. the methane conversion, hydrogen recovery and hydrogen purity, was evaluated under biogas steam reforming conditions. The resulting hydrogen purity under biogas steam reforming conditions was up to 99.8%. The model results were in very good agreement with the experimental results, when assuming a thickness of the stagnant mass transfer boundary layer around the membrane equal to 0.54 cm. It is shown that the effects of concentration polarisation in a fluidized bed membrane reactor can be well described with the implementation of a film layer description in the two-phase model.

1. Introduction

The increasing energy demand over the last decades, in combination with the need to reduce greenhouse gas (GHG) emissions, has given rise to the development of more efficient conversion technologies and alternative energy carriers. Hydrogen is the most promising energy carrier, as it can be produced from renewable energy sources and no CO₂ is emitted at the end user. Most of the hydrogen produced nowadays is made via steam reforming of natural gas, producing significant GHG emissions. The current demand for hydrogen and its potential use in the new energy systems requires the development of a sustainable route for

its production. Biogas is one of the renewable sources that could be used in the production of hydrogen.

Biogas is produced from biomass, which consists of organic matter (that captured carbon from atmospheric CO₂ over a relatively short timescale), mainly through anaerobic digestion of organic substrates (manure, sewage sludge, organic fractions of industry waste and energy crops) [1]. The composition of biogas varies significantly depending on the source of biomass. Typical biogas compositions from an anaerobic digester and landfill production are shown in Table 1.

The methane in the biogas can be converted into a hydrogen rich gas by steam reforming (SR): methane reacts with steam at high

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Nomenclature

Ar	Archimedes number
A_j	Arrhenius pre-exponential factor
A_T	Area of bed cross section [m ²]
$d_{b,0}$	Initial bubble diameter [m]
d_b	Bubble diameter [m]
$d_{b,avg}$	Average bubble diameter [m]
$d_{b,max}$	Maximum bubble diameter [m]
d_p	Particle diameter [m]
D_g	Gas diffusivity [m ² s ⁻¹]
D_T	Bed diameter [m]
$E_{act,j}$	Activation energy for reaction j
f_k	Fraction of phase k
F_i	Molar flow of species i [mol s ⁻¹]
g	Gravitational acceleration [m s ⁻²]
H_{mf}	Height of the bed at minimum fluidization velocity [m]
H_f	Height of the fluidized bed [m]
H_s	Height of the packed bed [m]
K_{ce}	Volumetric interchange coefficient between cloud and emulsion [s ⁻¹]
K_{bc}	Volumetric interchange coefficient between bubble and cloud [s ⁻¹]
$K_{be,i,n}$	Volumetric interchange coefficient between bubble and emulsion phase [s ⁻¹]
K_j^{eq}	Equilibrium constant for reaction j
$M_{w,i}$	Molar weight of component I [kg mol ⁻¹]
N_i	Molar flux component i [mol m ⁻² s ⁻¹]
P_0	Pre-exponential factor for permeability of membrane [mol m ⁻¹ s ⁻¹ Pa ⁻ⁿ]
P_i	Partial pressure of species i [bar]
r_j	Reaction rate of reaction j [mol kg ⁻¹ s ⁻¹]
$R_{memb.}$	Radius of the membrane

$SF(Q)$	Heaviside function of Q
t	Thickness of Membrane selective layer thickness [m]
$u_{k,n}^s$	Superficial velocity of phase j in cell k [m s ⁻¹]
u_{mf}	Minimum fluidization velocity [m s ⁻¹]
u_0	Superficial gas velocity at inlet
u_b	Bubble rise velocity
$u_{b,avg}$	Average bubble rise velocity
$V_{D,i}$	Diffusion volume for component i
$V_{k,n}$	Volume of phase k in cell n [m ³]
$w_{k,i,n}$	Weight fraction of phase k, component i in cell n
$x_{i,bulk}$	Molar fraction of species i in the bulk
$x_{i,memb.}$	Molar fraction of species i adjacent to the membrane

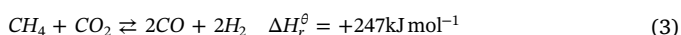
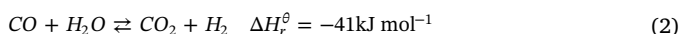
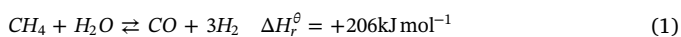
Greek symbols

δ	Thickness of the stagnant film layer [m]
ΔH_r^\ominus	Reaction enthalpy at standard conditions [kJ/mol]
$\varepsilon_{k,n}$	Fraction of phase k in cell n
ε_{mf}	Bed voidage at minimum fluidization velocity
μ_g	Gas viscosity [Pa s]
$\nu_{j,i}$	Stoichiometric coefficient of reaction j component i
$\rho_{k,n}$	Density of phase k in cell n [kg m ⁻³]

Subscripts

b	Bubble phase
e	Emulsion phase
g	Gas phase
i	Species
j	Reaction
n	Number of CSTR in emulsion or bubble phase
s	Solid phase

temperatures over a nickel-based catalyst to produce CO and H₂ via the Steam Methane Reforming reaction (SMR), Eq. (1). To increase the hydrogen yield this process is combined with Water Gas Shift (WGS), Eq. (2). Because of the high CO₂ content, Dry Reforming (DR), Eq. (3), is likely to take place as well.



The reforming of methane is highly endothermic and requires high temperatures (> 900 °C) and is favoured at low pressures. Moreover, to obtain high purity hydrogen from the SR process, downstream separation and purification steps are required. The application of biogas in the SR process has significant challenges: (i) the combination of the nickel catalyst and high operation temperatures makes the system prone to

coking, (ii) the high CO₂ content of biogas induces equilibrium limitations and (iii) the presence of H₂S even if present in trace amounts requires intensive cleaning of the biogas. The development of reforming catalysts with a high resistancy to carbon formation have increased the potential for hydrogen production from biogas [3]. Noble metal catalysts, such as Rh, Ru, Pt and Pd show a high activity and selectivity for hydrogen production [4]. Generally Rh has been found to have the best performance along the different noble metal catalysts. To remove the H₂S, the biogas can be upgraded by cleaning using e.g. pressurized water scrubbing, pressure swing adsorption, amine absorption or membrane absorption [2]. However, these methods significantly increase the energy consumption and costs of hydrogen [2]. The emerging technology of palladium-based membrane reactors shows a high degree of process intensification for the production of hydrogen and has demonstrated significant advantages over the conventional SR process [5]. The hydrogen is selectively extracted from the reaction system, thus combining the SMR, WGS and H₂ separation (and purification) in one single unit. The in-situ extraction of hydrogen can overcome the equilibrium limitations of the biogas reforming thanks to the product recovery. The shift in equilibrium also allows operation at lower temperatures and higher pressures. Finally, pure hydrogen is obtained directly from the membranes without the requirement of downstream separations, hence reducing the process complexity and the associated capital costs. These advantages of membrane reactors can make hydrogen production on smaller scales from a decentralized source such as biogas attractive. Previous works investigated the application of biogas steam reforming in a membrane reactor. Sato et al. [6] identified the membrane reactor as a promising technology for hydrogen production from biogas. Steam reforming of a biogas mixture derived from supercritical water gasification of glucose was performed using a PdAg

Table 1

Anaerobic digestion or landfill biogas composition [2].

Component	AD biogas	Landfill biogas	Unit
CH ₄	53–70	30–65	vol%
CO ₂	30–50	25–47	vol%
N ₂	2–6	< 1–17	vol%
O ₂	0–5	< 1–3	vol%
H ₂	NA	0–3	vol%
C _x H _y	NA	NA	vol%
H ₂ S	0–2000	30–500	ppm
NH ₃	< 100	0–5	ppm
Chlorines	< 0.25	0.3–225	mg Nm ³
Siloxane	< 0.08–0.5		µg/g-dry

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