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Definition of validated membrane reactor model for 5 kW power output CHP system for different natural gas compositions

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ABSTRACT

Over the last years, many studies focused on the development of membrane reactors for micro-cogeneration systems based on PEM fuel cells, thanks to its unique feature of separating pure hydrogen. This work deals with (i) the design of a fluidized bed membrane reactor flexible towards different natural gas (NG) qualities and (ii) its integration in PEM based systems of 5 kW power output. Four typical NG compositions from reference European countries have been identified in this study featuring an average condition and three extreme cases. Two different membrane reactor models were developed: a 1D phenomenological model and a quasi-lumped model inside the overall system implemented in Aspen Plus. Results show the importance of taking into account the natural gas composition in the design phase: only assuming the NG with the highest inert content as base case, the target electric efficiency of 39% can be reached for any other case.

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Introduction

In the last decades, the growing electricity and heat demand led to an intensification of the fossil fuel exploitation which contributes above 30% to the overall primary energy consumption [1]. The main issue is about the CO₂ concentration rise in the atmosphere which is considered one of the cause of greenhouse effect. Therefore, the greenhouse gas emissions mitigation is one of the challenge of this decades supported by many governments through incentives for energy efficiency and use of renewables [2]. Micro-combined heat and power (micro-CHP) generation is one of the cheapest and interesting

options to increase energy efficiency in the residential sector: the simultaneous production and utilization of heat and power [3,4] increases the primary energy exploitation (i.e. reducing CO₂ emissions) compared to separated heat and electricity production.

Stationary low temperature polymer electrolyte membrane (PEM) fuel cells based systems offer a clean and efficient source of electricity with the highest primary energy saving potential at micro-cogeneration scale. PEM are characterized by (i) low operating temperatures, (ii) high power density, and (iii) the use of low-cost materials. In addition, conversion efficiency of PEM increases at partial load. However, they require non-contaminated (ultra-pure) hydrogen as fuel (CO

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tolerance below 10 ppm). Hence, the development of an efficient fuel processor for hydrogen production is mandatory. Natural gas (NG) is selected as reference fuel for hydrogen production since it is the most widespread distributed fuel in industrialized countries and it can give the highest hydrogen yield per carbon dioxide unit emitted.

Among the commercial micro-CHP systems with natural gas, the reciprocating internal combustion engines and the Stirling engine has an electric efficiency around 25–30% [5] and 10% respectively [6], while for the fuel cell based systems the efficiency grows up to 32–35% for the conventional PEMFC based [7,8] and to 35–40% for the high temperature solid oxide fuel cell (SOFC) [7].

Recent studies have demonstrated that membrane reactors, which combine hydrogen production and separation in one vessel, have better performance than conventional fuel processors operated in the same regime [8,9]. Moreover, membrane reactors based on fluidized beds (FBMR), as shown in Fig. 1, overcome some issues occurring in conventional fixed bed configurations [10–12]: these include (i) no internal mass and heat transfer limitations (as smaller particles, 100–500 μm , can be used due to the negligible pressure drop), (ii) virtually isothermal operation and (iii) reduced bed-to-wall mass transfer limitations. The main disadvantage is that the inlet gas flow rate must be kept above a minimum required to keep the catalyst bed under suspension along the reactor (the minimum fluidization velocity should be reached). It is important to outline that the considered system can work up to 40% of the nominal load, therefore the minimum fluidization velocity must be assumed at minimum load.

In comparison with packed beds, the fluidization regime tends to show lower diffusion limitations within the emulsion phase itself, but the presence of bubbles may introduce bubble-to-emulsion mass transfer limitations and gas back mixing. As a matter of fact, several projects have been investigating this technology in order to overcome all the barriers that limit their industrial exploitation [11].

In the European project Ferret, the development and demonstration of a flexible natural gas membrane reformer

for micro-CHP applications is carried out [13]. The goal of Ferret is the design and construction of a membrane reformer capable of dealing with different natural gas compositions with limited efficiency penalties: a prototype of the micro-CHP system based on an ATR membrane reactor and PEM fuel cell will be accomplished.

The differences in the NG compositions have a significant impact on the performance of the micro-CHP system and the fuel processor life time. Moreover, the design and construction of a unique system for entire Europe can reduce production costs that are currently the main barrier to the diffusion of this technology.

This work deals with (i) the design of a FBMR flexible towards different NG qualities and (ii) its integration in PEM based systems of 5 kW power output. In the literature, there is quite a number of papers dealing with membrane reactors and their integration into micro-CHP systems [10,14,15], but none of these consider the impact of the natural gas composition on the electric and thermal efficiency, which is the main objective of this paper.

Definition of system layout and natural gas quality

Layout concept and assumptions

A conventional fuel processor for hydrogen production is usually based on (i) a reformer which can be either autothermal (ATR) or not (SR) operating at temperatures above 850 °C, followed by (ii) two water gas shift reactors (WGSR), at different temperatures to enhance the carbon monoxide conversion to hydrogen, and (iii) a final PReferential OXidizer (PROX), which burns the unconverted CO. Since NG in the pipelines contains sulphur compounds, a sulphur removal unit based on active carbon¹ is required upstream of the reactors chain: sulphur may poison both the reforming and FC catalysts and the membranes. The tolerance of catalyst and membranes towards sulphur is below 1 ppm [16,17].

In this work, hydrogen selective membranes are integrated in the autothermal reforming reactor. This configuration allows carrying out the entire production and purification process in one reactor and the product extraction through the membrane drives the hydrocarbon conversion towards the products' side (thus enhancing the yield). In the design phase, the extent of hydrocarbon conversion can be defined by means of an adequate selection of stream pressures and membrane area. Respect to the conventional fuel processor, the same conversion can be achieved at lower operating temperatures, with potential advantages for the materials selection and costs. The heat required by the endothermic reforming reaction is balanced by the oxidation of feed fuel fraction with air. The optimum in terms of electric efficiency is achieved when the unconverted methane energy balances the water/gas heating, so that no additional NG is required. Additionally, the

Fig. 1 – Fluidized bed membrane reactor scheme.

¹ No on-site active carbons regeneration is considered. Active carbons are assumed to be replaced when saturated, hence not affecting the energy performance but they are accounted as consumable cost.

Fig. 2 – Layout of the micro-CHP PEMFC based system using a vacuum pump.

conversion efficiency of the fuel cell increases when feed with pure hydrogen compared to diluted feeds [18,19].

The investigated layout adopts a vacuum pump in order to reduce the hydrogen partial pressure on the permeate side, hence decreasing the required membrane area. Thanks to the choice of the vacuum pump, instead of a sweep gas (i.e. water), the CHP layout turns out to be simpler in terms of manifolds and thermal management. The number of components required for the system is reduced: heat exchangers to heat up the steam and the sweep feed pump are avoided, which is also favourable for start-up control because it avoids the need for evaporating the sweep water. Also the reactor design and manufacturing is easier because no internal ducts for sweep distribution are necessary. The main drawback lies in the lower electrical efficiency due to the higher power consumption [15].

The micro-CHP system layout is defined to optimize the net electric efficiency while keeping under control the membrane surface area which is the main parameter affecting the economics (membranes costs is currently in the range of 3000 €/m²). The system layout, shown in Fig. 2, is implemented in Aspen Plus® and it is designed for a net power output of 5 kW_{el}. The feed water is pumped by P-1 and is mixed with compressed air, then evaporated through HX-0, HX-1, HX-4 and finally superheated in HX-2. Compressed natural gas (point 1) and the preheated mix of air and steam (point 2) feed the ATR membrane reactor from the bottom section. The permeate stream is cooled down in HX-4 and HX-6 before being compressed by the vacuum-pump. The compression is carried out at the lowest temperature achievable by the cooling system to minimize the compression work. Finally, the hydrogen is saturated and sent to the fuel cell. The retentate (point 3) and hydrogen (point 6) leave the reactor from the top section. After cooling down, the remaining

combustible species are combusted in the burner to generate steam in HX-1 and HX-7 closing the thermal balance. A closed loop for heat recovery which includes HX-7, the fuel cell (HX-9) and HX-6 is designed. The process water is recycled from the condensation in all the three separators downstream the cooling of the permeate, retentate and exhaust gases.

The design parameters and the main assumptions for the reference case have been summarized in Table 1. Values in brackets represent the feasible operating range investigated in the sensitivity analysis. The values adopted for the system components are taken from benchmark technologies, typical O&M specifications, requirements for domestic heating and materials. A detailed summary of the parameters can be found in Ref. [15]. The S/C ratio shown in Table 1 for the ATR-MR is calculated as in Equation (1) after the O₂ is consumed in the total oxidation. The resulting S/C ratio that would be obtained if calculated at the inlet of the reactor (prior to oxidation) is also shown in the results in Table 3.

$$S/C = \frac{F_{H_2O}}{\sum_{i=1}^4 i \cdot F_{C_i H_{2i+2}}} \quad (1)$$

The O/C ratio is defined as follows:

$$O/C = \frac{2 \cdot F_{O_2}}{\sum_{i=1}^4 i \cdot F_{C_i H_{2i+2}}} \quad (2)$$

Another important parameter is the Hydrogen Recovery Factor (HRF), which is defined as the ratio between the flow rate of the permeated hydrogen and the maximum flow rate of hydrogen that could be produced. It can be determined from the outlet streams of the reactor (points 6 & 3, permeate and retentate in Fig. 2) as follows²:

² This calculation assumes that the possible species in the retentate are CH₄, CO, CO₂, H₂, N₂ and H₂O.

Table 1 – Reference case model assumptions and design parameters.

Parameter	Units	Value ^a
Feed & operating conditions		
Natural gas composition: CH ₄ , C ₂ H ₆ , C ₃ H ₈ , n-C ₄ H ₁₀ , i-C ₄ H ₁₀ , n-C ₅ H ₁₂ , i-C ₅ H ₁₂ , C ₆ H ₁₄ , N ₂ , CO ₂	%molar	see Table 2
Uniform reforming temperature	°C	600 (575–600)
Pressure reaction side	bar	8 (6–12)
Pressure permeate side	bar	0.3
S/C	–	3.0
λ _{cath} (air to cathode)	–	2
λ _{ATR-MR} (air to ATR-MR) ^b	–	≈0.23
Heat recovery supply/return temperature	°C	45/30
Fuel Cell		
Single cell voltage with feed of saturated H ₂	V	0.752
Fuel utilization (dead-end configuration)	–	0.99
Auxiliaries, controls and power conditioning		
Controller consumption	W	100
Pumps hydraulic efficiency	%	70
Pumps motor mechanical efficiency	%	90
Compressors/fans isentropic efficiency	%	70
Compressors/fans motor mechanical efficiency	%	85
DC _{stack} /AC _{230V@50Hz} conversion efficiency	%	95

^a Where a range of interest is shown between brackets, the most likely value is indicated separately.

^b Air flow rate to the ATR-MR is adjusted in order to control the temperature at the exit of the reactor.

$$HRF = \frac{F_{H_2, perm}}{4 \cdot F_{CH_4, ret} + F_{CO, ret} + F_{H_2, ret} + F_{H_2, perm}} \quad (3)$$

The fuel cell (FC) is assumed to be setup for dead-end anode operation. Ideally, such setup would allow a complete utilization of the hydrogen fed (100% fuel utilization factor), however, since in real operations periodic purging of the anodic chamber need to be carried out in order to dissipate accumulated inert gases, fuel utilization is considered equal to 99%. This is a conservative assumption (optimized purge cycles can reduce the hydrogen vent below 0.5% [20]) in view of membrane selectivity uncertainties. The single cell voltage of the fuel cell is related to its conversion efficiency “ η_{LHV} ” (in terms of LHV of hydrogen) as in Equation (4) below.

$$V = \frac{\eta_{LHV} \cdot LHV_{H_2}}{2 \cdot F} \quad (4)$$

Natural gas qualities

The micro-CHP system aims to be flexible towards the variability of natural gas compositions most present in the EU. The variation in NG compositions has an impact on the design of the system, its performance and/or its life time. Starting from 6 reference European countries (Italy (IT), France (FR), Spain (ES), Netherlands (NL), United Kingdom (UK) and Germany (DE)), four different cases were selected and their properties are shown in Table 2. The sulphur content is not

reported because the table shows the feed composition after the desulphuriser. They are selected as representative of the entire European situation. The UK composition features an average NG, the Italian case is almost pure methane, while the NL and the ES cases have the minimum and maximum Wobbe index respectively. Moreover, the considered compositions vary in terms of inert concentration, where inerts reduces the H₂ fraction and consequently the permeation driving force across the membrane.

The definitions of H₂ potential, x in C_xH_y and Wobbe index are expressed below.

$$H_2 \text{ potential} = \frac{\text{maximum mol } H_2 \text{ produced}}{\text{mol NG}} \quad (5)$$

$$x = \sum y_i \cdot n_i \quad (6)$$

$$\text{Wobbe index} = \frac{HHV}{\sqrt{\rho_{NG}/\rho_{air}}} \quad (7)$$

where x gives the C_x equivalent hydrocarbon, y_i is the molar fraction of species i and n_i the index in C_nH_{2n+2}.

Fluidized bed membrane reactor model

Reactor configuration

Fig. 1 showed a schematic view of the reactor. The reaction takes place over a bed of fine catalyst (average particle size of 200 μm) fluidized in a regime that could be either the bubbling or turbulent fluidization regime. In the fluidized bed reactor, the emulsion phase mixing induced by the rising bubbles, enhances the heat transfer inside the reactor, leading to a virtually uniform temperature and also lowering bed-to-wall mass transfer limitations [21]. The stream at the inlet of the reactor is a mixture of NG, steam and air where the overall composition is defined by the exact amount of NG to produce the H₂ feeding the FC as well as the S/C and O/C ratios. The reactions of reforming (R.1–R.2) and oxidation (R.4) of the hydrocarbons and the water gas shift (R.3) are described in Table 3. The heat required by the endothermic reforming reactions is balanced by the partial oxidation of feed fuel with

Table 2 – Natural gas compositions.

Species	Units	NG type			
		NL	UK	IT	ES
CH ₄	%mol	81.230	92.070	99.581	81.570
C ₂ H ₆	%mol	2.850	3.405	0.056	13.380
C ₃ H ₈	%mol	0.370	0.761	0.021	3.670
n-C ₄ H ₁₀	%mol	0.080	0.177	0.002	0.400
i-C ₄ H ₁₀	%mol	0.060	0.140	0.006	0.290
n-C ₅ H ₁₂	%mol	0.020	0.048	0.000	0.000
i-C ₅ H ₁₂	%mol	0.020	0.061	0.002	0.000
C ₆₊	%mol	0.080	0.090	0.007	0.000
CO ₂	%mol	0.890	0.865	0.029	0.000
N ₂	%mol	14.400	2.375	0.296	0.690
LHV	MJ/kg	38.0	46.7	49.7	48.6
H ₂ potential	mol H ₂ /mol NG	3.52	4.07	3.99	4.66
x in C _x H _y	–	0.89	1.04	1.00	1.22
Wobbe index	MJ/Nm ³	43.6	52.0	53.1	56.6

air (R.4). The intake of air is below stoichiometry and its regulation allows controlling the FBMR operating temperature. A section of the reactor is filled only with catalyst where partial oxidation and reforming reactions take place to prevent hot spots on the membranes and to increase the hydrogen content at the membrane surface.

The expression used for hydrogen permeation is described in Equation (8) where “ P_{H_2} ” is the pure hydrogen permeance value ($\text{mol/s m}^2 \text{Pa}^n$), the term inside brackets represents the driving force for the permeation, and “ n ” is the exponential factor. In this work, the parameters of an asymmetric membrane, developed by Tecnalia, with a Pd–Ag layer of $4.5 \mu\text{m}$ on a ceramic support, are used for the simulations. The permeance is assumed equal to $P_{H_2} = 2.17 \cdot 10^{-3} \text{mol/s m}^2 \text{Pa}^{0.5}$ at 400°C with a corresponding $n = 0.5$ while the activation energy is about 10 kJ/mol [22]. It should be noted here that the use of thin membranes (but with lower fluxes) in fluidized beds at high temperatures (600°C) has already been reported in the literature [23,24]. However, the thin membranes used in this paper shows much high fluxes, are stable at temperatures around 550°C but need still further improvement to be used at higher temperatures [25]. The driver towards working at 600°C is a compromise between efficiencies and membrane area required (thus capital costs). The reactor has an initial section without membranes where the hydrogen production takes place (also referred to as pre-reforming), then in the membrane section, the extraction of hydrogen drives the equilibrium reaction towards the products.

$$F_{H_2,perm} = \int_0^{A_{mem}} P_{H_2} \cdot (p_{H_2,ret}^n - p_{H_2,perm}^n) dA \quad (8)$$

Two different FBMR models approach are adopted and presented. One model is implemented in the Aspen Plus® simulation of the entire micro-CHP system. This quasi-lumped model has a simple construction and does not take into account information about the reactor geometry and the interaction between emulsion and bubble phases as well as mass transfer limitations. As a matter of fact, it allows an estimation of the membrane surface area where concentration polarization is neglected, while the temperature is considered uniform along the reactor bed (both radially and axially). In Aspen Plus®, the modelling approach is a compromise between computational speed and the amount of system variables, such as streams, components and controls.

Therefore, a phenomenological 1D two-phase model is used to compare and validate the fuel processor implemented in the CHP system model. It is able to investigate the extent of bubble-to-emulsion phase mass transfer and/or reaction

kinetics limitations starting from a defined reactor geometry and operating conditions. The phenomenological 1D two-phase model has been extensively validated through dedicated experiments [23,24].

In the next sections details about the two FBMR models are explained.

Quasi-lumped MR model in Aspen Plus®

The first model of the ATR-MR is implemented in Aspen Plus® as shown in Fig. 3: in this model, the membrane reformer is discretized in a series of reactors and separators. Each reactor is set to equilibrium conversion of reactions by Gibbs free energy minimization. Pure hydrogen is extracted in the separators (infinite perm-selectivity is assumed) according to the permeation expression in Equation (8). The Peng-Robinson cubic equation of state [26] is used for all thermodynamic properties except for liquid molar volume evaluation and for steam properties where the Rackett model [27] and NBS/NRC steam tables [28] are adopted respectively. At the inlet of the reactor, due to the presence of oxygen and the faster kinetics of reactions R.4 with respect to reforming reactions, the higher hydrocarbons (C_2 – C_6) and some of the methane are oxidized [29].

The phenomenological MR model

The phenomenological 1D two-phase FBMR model described in Refs. [30,31] consists of a series of stirred tank reactors (CSTRs). The model simplifies the emulsion phase to be perfectly mixed [32]. The steady state overall (bubble and emulsion phases) component mass conservation equations and the total volume balance (to calculate the excess velocity) have been formulated, taking chemical transformations in the emulsion phase and a net gas production due to the chemical reactions and gas removal via membranes into account. The total mass balance is expressed in Equation (9), while the bubble and emulsion mass balance are respectively expressed in Equations (10) and (11). The bubble phase gas is assumed to be in plug flow, where the bubble size and the bubble rise velocity are assumed to be constant along the bed height and equal to the average values. The reactions take place only in the emulsion phase, assuming that the bubble phase is free of catalytic particles. The number of CSTRs for the emulsion and bubble phase was taken as 10 and 30 respectively following [24]. As assumed in the quasi-lumped model, the temperature is assumed uniform throughout the catalyst bed.

$$(u_{\theta-1}\rho_{b,\theta-1}\epsilon_{b,\theta-1} - u_{\theta}\rho_{b,\theta}\epsilon_{b,\theta} + u_{\theta-1}\rho_{e,\theta-1}\epsilon_{e,\theta-1} - u_{\theta}\rho_{e,\theta}\epsilon_{e,\theta})A_T - (M_{H_2}A_{mem,\theta}(J_{H_2,b,\theta}\epsilon_{b,\theta} + J_{H_2,e,\theta}\epsilon_{e,\theta})) = 0 \quad (9)$$

$$(u_{\theta-1}\rho_{b,\theta-1}\epsilon_{b,\theta-1} - u_{\theta}\rho_{b,\theta}\epsilon_{b,\theta})A_T - \sum_{i=1}^{N_S} K_{be,i,\theta} V_{b,\theta} \rho_{b,\theta} (x_{b,i,\theta} - x_{e,i,\theta}) - M_{H_2}A_{mem,\theta}J_{H_2,b,\theta}\epsilon_{b,\theta} = 0 \quad (10)$$

$$(u_{\theta-1}\rho_{e,\theta-1}\epsilon_{e,\theta-1} - u_{\theta}\rho_{e,\theta}\epsilon_{e,\theta})A_T + \sum_{i=1}^{N_S} K_{be,i,\theta} V_{b,\theta} \rho_{b,\theta} (x_{b,i,\theta} - x_{e,i,\theta}) + \sum_{i=1}^{N_R} v_{j,i}r_j V_{e,\theta} \rho_{e,\theta}\epsilon_{e,\theta} - M_{H_2}A_{mem,\theta}J_{H_2,e,\theta}\epsilon_{e,\theta} = 0 \quad (11)$$

Table 3 – Reactions prevailing in the membrane reactor.

Reactions	$\Delta H_{298 K}^0$ [kJ/mol]	
$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	206	(R.1)
$\text{C}_n\text{H}_{2n+2} + n \text{H}_2\text{O} \rightleftharpoons n \text{CO} + (2n+1) \text{H}_2$	$346 \div 954$	(R.2)
$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	–41	(R.3)
$\text{C}_n\text{H}_{2n+2} + (3n+1)/2 \text{O}_2 \rightleftharpoons n \text{CO}_2 + (n+1) \text{H}_2\text{O}$	$-802 \div -3885$	(R.4)

Fig. 3 – Fluidized bed membrane reactor scheme in Aspen Plus®.

A schematic representation of the two-phase model is depicted in Fig. 4. The empirical correlations for the model parameters have been taken from the literature [33–36] and are summarized in Annex [Hydrodynamic parameters used in the phenomenological model](#). Since these correlations were originally obtained for beds without membranes, this work discusses two cases: (i) the worst, where the fluidised bed reactor with membranes doesn't influence the bubble diameter and rise velocity, (ii) the break-up, where the insertion of membranes enhances bubble break-up, resulting in improved bubble-to-emulsion phase mass transfer. However, this aspect is still under investigation: it is clear that a more detailed description of this effect is required to avoid under- or overestimation of the mass transfer rates and thus the performance of the reactor [9].

The kinetic rate expressions for combustion and reforming of the hydrocarbons and for the water gas shift are taken from Refs. [29,37–39]. Moreover, the thermodynamic properties of the hydrocarbons heavier than methane (C_2 – C_6) are introduced in the model.

Results and discussion

Micro-CHP system performance

The micro-CHP system must perform well with all the EU NG compositions (in this work represented by the four selected NG). Accordingly, the design and the selection of the operating conditions for all these NG compositions should be carried out to identify the most suitable one. To limit the number of cases to be investigated, two different designs for two different NG's have been carried out: one for the UK NG which represents the average composition and one for the NL case which features the highest hydrogen dilution, hence the lowest permeation driving force. The main results of these cases have been summarized in Table 4.

Power balances show that the operating conditions (pressure and temperature) have the same impact on the two considered NG qualities. Increasing the feed pressure negatively affects the methane and air compression works,

Fig. 4 – Scheme of 1D two-phase (emulsion and bubble) FBMR model.

while the membrane surface area decreases thanks to the higher driving force. The vacuum pump shares about 16% of the total auxiliary consumptions and also the power losses in DC/AC conversion are significant. As expected for the ATR concept, the power consumption for air compression is more than twice that of NG. The fuel composition mostly affects the NG flow rate and the membrane area: the NL case has higher fuel flowrate due to the lower Wobbe index increasing the NG compression work and consequently reducing the net electric efficiency. The higher fuel flowrate and inert content in the NL case leads to larger membrane surface area.

Starting from these results, 600 °C, S/C 3.0 and 8 bar were selected as design conditions, because they represent a good compromise between electric efficiency, required membrane surface area and system complexity. Even if the operating temperature is quite high for membrane application, experimental tests have been carried out showing a good long term stability [23]. At higher pressures, the electric efficiency decreases together with the membrane area. Although the risks of leakages and the amount of palladium are reduced, the additional auxiliary consumptions and the equipment costs due to the higher pressure are significant.

An extended analysis on the operating conditions and their effect on relevant parameters as electric efficiency and membrane area for the Dutch NG is summarized in Fig. 5.

Once defined the two design of the CHP system, the flexibility under different NG qualities was verified keeping the electric power output (5 kW_{el}) constant for all the cases. The control parameters are the operating reactor pressure and the relative air flow rate λ_{ATR} . In both cases, the NL case has the lowest electric efficiency due to the largest amount of N₂ in the NG, as shown in Figs. 6 and 7, which implies a higher power input and auxiliary losses. On the other hand, it has the

Fig. 5 – Electrical efficiency and membrane area at different operating conditions and S/C ratios for NL natural gas composition.

highest thermal recovery since less energy is converted into electricity allowing it to be recovered as heat. The other three NG qualities have quite similar performance: the ES case, with the largest amount of hydrocarbons heavier than methane, has the best electric performance. Considering the control strategy, the layout case designed for the NL composition allows to avoid exceeding the operating pressure of 8 bar and also to achieve higher net electric efficiency. These considerations are underlined by Fig. 8. Selecting the NL composition as reference allows a slight increase in the net electric efficiency when other NG compositions are considered, together with an easier control of the reactor since the pressure need only to be reduced. As a result of this analysis, the adoption of the NL composition for designing the system seems to be the most appropriate approach as well as the most conservative. Therefore, the following analysis on the membrane reactor design will be carried out for the NL case.

Table 4 – Simulation results on the performance of the micro-CHP system with ATR-MR.

Results	Units	NL case					UK case	
S/C	–	3	3	3	3	3	3	3
Temperature reactor	°C	600	600	600	575	600	600	575
Pressure reaction side	bar	7	8	12	8	8	12	8
S/C ratio at inlet of ATR-MR	–	1.80	1.80	1.80	1.81	1.80	1.80	1.81
O/C ratio at inlet of ATR-MR	–	0.93	0.93	0.92	0.92	0.92	0.92	0.92
NG feed	Nm ³ /h	1.45	1.44	1.48	1.45	1.24	1.28	1.26
NG power input [LHV base]	kW	12.73	12.68	13.00	12.70	12.60	12.91	12.63
NG power input [HHV base]	kW	14.11	14.06	14.40	14.07	13.96	14.30	13.93
Net AC power output	kW	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Fuel Cell AC power output	kW	6.38	6.42	6.57	6.42	6.39	6.54	6.40
NG compressor	kW	0.16	0.17	0.22	0.17	0.15	0.20	0.15
Air compressor	kW	0.34	0.36	0.44	0.35	0.35	0.43	0.35
Cathode air blower	kW	0.19	0.19	0.19	0.19	0.19	0.19	0.19
Vacuum pump	kW	0.26	0.26	0.26	0.26	0.26	0.26	0.26
Balance of plant	kW	0.44	0.44	0.45	0.44	0.44	0.45	0.44
Thermal recovery	kW	7.24	7.16	7.36	7.16	7.09	7.29	7.1
Net electric efficiency [LHV base]	% _{LHV}	39.28	39.44	38.48	39.39	39.71	38.73	39.66
Net electric efficiency [HHV base]	% _{HHV}	35.45	35.59	34.73	35.55	35.85	34.97	35.81
Net thermal efficiency	% _{LHV}	56.84	56.43	56.62	56.43	56.24	56.48	56.32
Total efficiency [LHV base]	% _{LHV}	96.12	95.87	95.10	95.82	95.95	95.21	95.98
Total efficiency [HHV base]	% _{HHV}	86.74	86.52	85.82	86.47	86.62	85.95	86.64
Total membrane area	m ²	0.178	0.141	0.081	0.145	0.125	0.067	0.128
Hydrogen permeation	Nm ³ /h	3.59	3.61	3.69	3.61	3.59	3.67	3.59
Hydrogen Recovery Factor	%	91.7	92.7	92.2	92.1	92.6	92.1	92.1

Fig. 6 – NL base case system design: H_2 permeation flow rate and net electric efficiency (left), power balance and required NG feed flow rate (right) for different NG qualities.

Fig. 7 – UK base case system design: H_2 permeation flow rate and net electric efficiency (left), power balance and required NG feed flow rate (right) for different NG qualities.

Fig. 8 – Flexibility of the micro-CHP system designed for UK or NL natural gas (labels represent the operating reactor pressure).

The detailed results for the NL base case have been summarized in Table 5. The net electric efficiency for the NL case has the lowest value (39.44%), while the ES has the highest value (40.00%) which is greater than the UK one by 0.16 points. The electric efficiency for the NL case has an upper shift of 0.2% points with respect to the case designed on UK NG. The feed pressure in the reactor can be reduced down to 7.55 bar (with IT NG) to keep the net power output equal to 5 kW. Due to the differences in the Wobbe index, the NG

volumetric flow rates at the inlet of the system vary of about 20% between the four different NG cases.

Membrane reactor comparison and validation

In the previous section, the required membrane area together with the system performance were assessed with the quasi-lumped model. In this section, the two membrane modelling approaches are compared assuming the same operating

Table 5 – Micro-CHP system performance for different NG qualities.

CHP system results	Units	UK	ITA	NL	ES
S/C	—	3.0	3.0	3.0	3.0
Pressure reaction side	bar	7.7	7.55	8	7.7
NG power input [LHV base]	kW	12.56	12.55	12.68	12.51
Net AC power output	kW	5.0	5.0	5.0	5.0
Fuel Cell AC power output	kW	6.38	6.38	6.42	6.35
Thermal recovery	kW	7.06	7.07	7.16	6.98
Net electric efficiency	% _{LHV}	39.84	39.87	39.44	40.00
Net thermal efficiency	% _{LHV}	56.21	56.36	56.43	55.75
Total efficiency	% _{LHV}	96.05	96.24	95.87	95.75
λ_{ATR} (air to fuel molar)	—	0.229	0.233	0.234	0.23
Total membrane area	m ²	0.114	0.114	0.114	0.114
Hydrogen permeation	Nm ³ /h	3.58	3.58	3.61	3.56
Hydrogen Recovery Factor	%	92.7	92.7	92.7	92.7
NG compressor	kW	0.15	0.15	0.17	0.13
Air compressor	kW	0.35	0.34	0.36	0.34
Cathode air blower	kW	0.19	0.19	0.19	0.19

Table 6 – Model comparison: summary of involved parameters.

Input data from Aspen model	Output data from 1D two-phase model	Objectives
Feed flow (S/C, O/C)	u/u_{mf}	H ₂ permeated flow
Operating Conditions	T	Retentate flow
Pressure	P	
permeate side	Membranes	
Membrane	Reactor	
Area	Geometry	
	Average Bubble Diameter	
	Number Length	
	Diameter	
	Length	
		NG conversion

conditions, the same flow input and membrane area. The comparison is carried out only for the NL natural gas for brevity, however, the considerations can be extended to any NG composition. Regarding the phenomenological model, u/u_{mf} and D_t , that are respectively the ratio between the inlet velocity (u) and the minimum fluidization velocity (u_{mf}) and the free space reactor diameter (D_t), can be varied while keeping the reactor inlet flow rate constant. Table 6 gives an overview of the parameters involved in the quasi-lumped model validation.

A first comparison was made assuming ideal conditions neglecting kinetics limitations (reactions at equilibrium conversion) as well as mass transfer limitations. In these conditions, as expected, the two models give identical performance in terms of H₂ extraction and NG conversion and the choice of different values for u/u_{mf} and D_t do not affect the results. Therefore, the two models works properly.

Afterwards, simulations were performed introducing first kinetics limitations (KL), then emulsion-to-bubble mass transfer limitations (MTL) and finally combining both effects (KL + MTL). The reactor design implemented in the 1D two-phase model considers the presence of 12 membranes with an outer diameter of 0.1 m and a length of 0.38 m. Membranes are arranged to keep a distance of 0.025 m from each other, see Fig. 9.

The worst case scenario (1), which uses closure equations ignoring the presence of, and the gas permeation through, the membranes on the fluidised bed hydrodynamics, allows bubbles growth up to a bubble diameter equal to D_t ($D_{eq} = D_t$ in

Equation (19)), as shown in Fig. 11. All simulations resulted in an average bubble diameter at the MR outlet bigger than the free space between the membranes. As expected, the bubble size increases for high flow rates (which corresponds to a high u/u_{mf}) lowering the mass transfer rates between bubble and emulsion phases. Fig. 10 points out that the kinetic rate limitations do not have a significant impact on the reactor performance, indicating that the oxidation and reforming reaction rates are very fast compared to the mass transfer rates. Results of the phenomenological model show an H₂ permeation flow rate of 3.1 Nm³/h at u/u_{mf} of 2.5, which corresponds to 86% of the amount obtained with the quasi-lumped model. The maximum H₂ extraction value cannot be achieved because the inlet feed velocity is not high enough to sustain the fluidization regime along the entire membrane reactor (Fig. 11). The gap between the two models (14%) can be reduced down to 8% increasing the membrane area 2 times (CH₄ conversion reaches 94.5%), or down to 6% when increasing the membrane area to 5 times the original area (CH₄ conversion at 95%).

Regarding the bubble break-up case (scenario 2), setting a limit to the growth of the bubble size in the maximum bubble diameter relation [33] is reasonable if the reactor contains internals (membranes). In this work, the limit (D_{eq}) is set as the maximum distance between membranes (0.025 m) as described in the following equation:

$$d_{b,max} = \min\left(D_{eq}, 0.65 \frac{\pi}{4} D_t^2 (u_0 - u_{mf})\right) \quad (12)$$

where:

$D_{eq} = D_t$ for the worst case

$D_{eq} = 0.025 \text{ m}$ (membranes distance) for the break-up case

For this case, the results from the two MR models are comparable (Fig. 12 and Fig. 13), especially at the low feed velocity where the difference of both the permeated flow rate and methane conversion are under 3% without additional membrane area.

On the other hand, the FBMR has to be designed to work in the fluidization regime even at partial load: this implies the adoption of a relatively high u/u_{mf} value, i.e. close to 5. Under this condition, the required membrane area increases by 30% compared to the original one (the relative errors of the quasi-lumped model for the hydrogen flow rate on the permeate side and the CH₄ conversion are 5% and 3%, respectively). Regarding the other NG compositions, the trend is quite

Fig. 9 – Example of membrane reactor cross-section designed for $u/u_{mf} = 3$.

Fig. 10 – MR model results for the worst case: H₂ permeation and CH₄ conversion at ideal conditions and when accounting for kinetic and mass transfer limitations.

Fig. 11 – MR model results for the worst case: average of bubble diameter and u/u_{mf} @ MR outlet at ideal conditions and when accounting for kinetic and mass transfer limitations.

Fig. 12 – Comparison of worst (1) and bubble break-up (2) cases: H_2 permeation rate and CH_4 conversion for ideal conditions and when accounting for kinetic and mass transfer limitations.

Fig. 13 – Comparison of worst (1) and bubble break-up (2) cases: average of bubble diameter and u/u_{mf} @ MR outlet when accounting for both kinetic and mass transfer limitations.

similar, i.e. at the same feed velocity, membrane area for the UK NG has to be increased by 20% achieving a CH_4 conversion of 97% and a relative error in the permeated flow rate under 5%.

Finally, Fig. 14 shows a comparison of the reactant composition along the membrane reactor computed by the two models, where the 1D model works at u/u_{mf} equal to 3 assuming the bubble break-up scenario. The solid lines indicate the results obtained with the quasi-lumped model, while the dotted lines are related to the phenomenological model results (the variations in the phenomenological model curves are related to the number of CSTRs used in the model). No

Fig. 14 – Example of the reactant composition along the membrane reactor: solid line shows the quasi-lumped model results whereas the dotted line shows the 1D two-phase model results ($u/u_{mf} = 3$; bubble break-up scenario).

significant differences can be outlined supporting the quasi-lumped approach for the system calculations.

Conclusions

This work investigated the impact of different NG compositions on the design and performance of a micro-CHP system based on membrane reactor. The assessment was carried out setting net power output of 5 kW. The system lay-out and the operating conditions (pressure, temperature) of the fluidized bed membrane reactor were defined in order to achieve a high electric efficiency, while keeping a moderate membrane surface area. Performance of the micro-CHP system designed for different natural gas compositions were compared, showing that the adoption of the most diluted natural gas (NL case) is suggested in order to guarantee an electric efficiency higher than 39% for any other NG composition keeping the maximum pressure at 8 bar. A 1D two-phase phenomenological FBMR model was used to compare and validate the quasi-lumped membrane reactor model developed in Aspen Plus. The 1D model has highlighted the importance of some reactor design parameters such as u/u_{mf} and bubble size (average and maximum diameter) on the permeated hydrogen flow rate and the NG conversion. Considering the bubble break-up due to the presence of the membranes, the quasi-lumped model underestimates the required membrane area by 20–30% for all the NG qualities. Starting from the 1D two-phase results, the reactor designed for NL NG case has a diameter of 0.1–0.12 m and a length of 0.4 m with a membrane area of 0.18 m².

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ANNEXES

Nomenclature

Ar	Archimedes number
A_{mem}	membrane area, m^2
A_T	area of bed cross section, m^2
C_{xH_y}	equivalent hydrocarbon
d_b	bubble diameter, m
$d_{b,0}$	initial bubble diameter, m
$d_{b,max}$	maximum bubble diameter, m
$d_{b,avg}$	average bubble diameter, m
d_p	particle diameter, m
D_{eq}	equivalent diameter for Equation (12), m
D_g	gas diffusivity, m^2/s
D_t	free space bed diameter, m
F	Faraday constant, 96485.34 C/mol
F_i	molar flow of species i, mol/s
g	gravitational acceleration, 9.81 m/s^2
$\Delta H_{298 K}^0$	heat of reaction in standard conditions, kJ/mol
H_f	fluidized bed height, m
H_{mf}	minimum fluidized bed height, m
$J_{H_2, \theta}$	hydrogen flux through membrane in cell θ , mol/m^2s
K_{bc}	volumetric interchange coefficient between bubble and cloud phase, s^{-1}
K_{be}	volumetric interchange coefficient between bubble and emulsion phase, s^{-1}
K_{ce}	volumetric interchange coefficient between cloud and emulsion phase, s^{-1}
$K_{be,i,\theta}$	bubble-to-emulsion phase mass transfer coefficient for component
L	total membrane length
M_{H_2}	hydrogen molar mass, kg/kmol
n	exponential factor for membrane
n_i	index of hydrocarbon i
N_S	number of species
N_R	number of reactions
p	pressure, bar
p_i	partial pressure of species i, Pa
P_{H_2}	hydrogen membrane permeance
r_j	reaction rate for reaction j, $mol\ kg_{cat}^{-1}\ s^{-1}$
T	temperature, $^{\circ}C$
u	feed gas velocity, m/s
u_0	gas velocity at inlet, m/s
u^s	superficial gas velocity, m/s
u_b	bubble velocity, m/s
u_{br}	rising of single bubble velocity, m/s
$u_{b,avg}$	average of bubble velocity, m/s
u_{mf}	minimum fluidization velocity, m/s
V	fuel cell voltage, V
V_e	bubble phase volume, m^3
V_e	emulsion phase volume, m^3
x_i	species mass fraction i
y_i	Species molar fraction i
z	axial coordinate of membrane

Acronyms

1D	one dimensional model
ATR	autothermal reformer

ART-MR	autothermal membrane reformer
BPR	back pressure regulator
CSTR	continuously stirred tank reactor
CHP	combined heat and power
EU	European
FBMR	fluidized bed membrane reactor
FC	fuel Cell
HRF	hydrogen recovery factor
HX	heat exchanger
NG	natural gas
P	pump
PEM	polymer electrolyte membrane type
PROX	preferential oxidizer
S/C	steam to carbon molar ratio
SR	steam reformer
SR-MR	steam membrane reformer
WGSR	water gas shift reformer
O/C	oxygen to carbon molar ratio
MEA	membrane electrode assembly
LHV	low heating value
HHV	high Heating value
MR	membrane reactor
LT	low temperature
NL	Netherlands
UK	United Kingdom
ES	Spain
IT	Italy
FR	France
DE	Germany
KL	kinetic limitation
MTL	mass transfer limitation
KL + MTL	kinetic & mass transfer limitation

Greek letters

δ_b	bubble phase fraction
δ_e	emulsion phase fraction
ϵ_b	bubble phase porosity
ϵ_e	emulsion phase porosity
ϵ_{mf}	bed voidage at minimum fluidization velocity
η_{LHV}	conversion efficiency of fuel cell in terms of LHV of hydrogen
λ_{cath}	air to flow to fuel cell cathode ratio
λ_{ATR-MR}	air to flow to ATR-MR inlet ratio
μ_g	gas viscosity, Pa s
$\nu_{j,i}$	Stoichiometric coefficient for reaction j and species i
ρ_i	density of species or mixtures, kg/m^3
ρ_p	density of particles, kg/m^3

Subscripts

b	bubble phase
e	emulsion phase
$perm$	permeate
ret	retentate
$stack$	fuel Cell Stack
pp	heat exchanger pinch point
θ	number of CSTRs for emulsion or bubble phase

Hydrodynamic parameters used in the phenomenological model

Table A – Phenomenological parameters.

Parameters	Expressions	Eq.	Ref.
Archimedes number	$Ar = d_p^3 \rho_g (\rho_p - \rho_g) g / \mu_g^2$	(13)	[33]
Minimum fluidization velocity	$u_{mf} = (\mu_g / d_p \rho_g) (\sqrt{(27.2)^2 + 0.0408 Ar} - 27.2)$	(14)	[34]
Bed voidage at minimum fluidization velocity	$\varepsilon_{mf} = 0.586 Ar^{-0.029} \left(\frac{\rho_g}{\rho_p} \right)^{0.021}$	(15)	[34]
Velocity of rise of swarm of bubbles	$u_b = u_o - u_{mf} + u_{br}$	(16)	[33]
Rising velocity of single bubble	$u_{br} = 0.711 (g d_{b,avg})^{1/2}$	(17)	[33]
Emulsion velocity	$u_e = \frac{u_o - \delta u_b}{1 - \delta}$	(18)	[33]
Average bubble diameter	$d_{b,avg} = d_{b,max} - (d_{b,max} - d_{bo}) \exp\left(-\frac{0.3H}{D_t}\right)$	(19)	[35]
Maximum bubble diameter	$d_{b,max} = \min\left(D_{eq}, 0.65 \frac{4}{3} D_t^2 (u_o - u_{mf})\right)$ where $D_{eq} = D_t$ for the worst case $D_{eq} = 0.025$ m (membranes distance) for the break-up case	(12)	[35]
Initial bubble diameter	$d_{bo} = 0.376 (u_o - u_{mf})^2$	(20)	[36]
Bubble phase fraction	$\delta_{bn} = \frac{u_b^s}{u_b} \pi$	(21)	[36]
Emulsion phase fraction	$\delta_{en} = 1 - \delta_{bn}$	(22)	[36]
Maximum superficial bubble gas velocity	$u_{b,max}^s = u_o - u_{mf}$	(23)	[36]
Initial superficial bubble gas velocity	$u_{b,o}^s = u_{br,o} \delta_{bo}$ where $\delta_{bo} = (1 - H_{mf}/H_f)$	(24)	[36]
Height of bed at minimum fluidization velocity	$H_{mf} = H_s \frac{1 - \varepsilon_s}{1 - \varepsilon_{mf}}$	(25)	[35]
Height of bed expansion	$H_f = H_{mf} \frac{C_1}{C_1 - C_2}$ where, $C_1 = 1 - \frac{u_{b,o}}{u_{b,avg}} \exp\left(-\frac{0.275}{D_t}\right)$ $C_2 = \frac{u_b^s}{u_{b,avg}} \left[1 - \exp\left(-\frac{0.275}{D_t}\right)\right]$	(26) (27) (28)	[36]
Average bubble rise velocity	$u_{b,avg} = u_o - u_{mf} + 0.711 (g d_{b,avg})^{1/2}$	(29)	[36]
Gas exchange coefficient	$K_{bc} = 4.5 \left(\frac{u_{mf}}{d_p}\right) + 5.85 \left(\frac{D_g^{1/2} g^{1/4}}{d_b^{5/4}}\right)$ $K_{ce} = 6.77 \left(\frac{D_g \varepsilon_{mf} u_b}{d_b^3}\right)^{1/2}$ $\frac{1}{K_{pe}} = \frac{1}{K_{bc}} + \frac{1}{K_{ce}}$	(30) (31) (32)	[36]

REFERENCES

- [1] International Energy Agency. Key world energy statistics. OECD/IEA; 2013. <http://www.iea.org/publications/freepublications/publication/KeyWorld2013.pdf>.
- [2] European Commission, Europe 2020 – EU-wide headline targets for economic growth, (n.d.). http://ec.europa.eu/europe2020/europe-2020-in-a-nutshell/targets/index_en.htm.
- [3] Alanne K, Saari A. Sustainable small-scale CHP technologies for buildings: the basis for multi-perspective decision-making. *Renew Sustain Energy Rev* 2004;8:401–31. <http://dx.doi.org/10.1016/j.rser.2003.12.005>.
- [4] Campanari S, Macchi E, Manzolini G. Membrane reformer PEM cogeneration systems for residential applications-Part B: techno-economic analysis and system layout. *Asia-Pacific J Chem Eng* 2009;4:311–21. <http://dx.doi.org/10.1002/apj.247>.
- [5] SenerTec Dachs mini-CHP. 2015. <http://www.senertec.co.uk/products/dachs-mini-chp.htm>.
- [6] Valenti G, Silva P, Fergnani N, Campanari S, Ravidà A, Di Marcoberardino G, et al. Experimental and numerical study of a micro-cogeneration Stirling unit under diverse conditions of the working fluid. *Appl Energy* 2015;160:920–9. <http://dx.doi.org/10.1016/j.apenergy.2015.05.112>.
- [7] Ene.Field. Fuel cells x combined heat and power. 2014. <http://enefield.eu/category/field-trials/technology/>.
- [8] Roses L, Bonalumi D, Campanari S, Iora P, Manzolini G. Simulation comparison of PEMFC micro-cogeneration units with conventional and innovative fuel processing. In: ASME 2010 8th Int. Fuel Cell Sci. Eng. Technol. Conf, vol. 1. ASME; 2010. p. 431–8. <http://dx.doi.org/10.1115/FuelCell2010-33020>.
- [9] Gallucci F, Fernandez E, Corengia P, van Sint Annaland M. Recent advances on membranes and membrane reactors for hydrogen production. *Chem Eng Sci* 2013;92:40–66. <http://dx.doi.org/10.1016/j.ces.2013.01.008>.
- [10] Roses L, Gallucci F, Manzolini G, Campanari S, van Sint Annaland M. Comparison between fixed bed and fluidized bed membrane reactor configurations for PEM based micro-

- cogeneration systems. *Chem Eng J* 2011;171:1415–27. <http://dx.doi.org/10.1016/j.cej.2011.05.061>.
- [11] Gallucci F, Van Sint Annaland M, Kuipers JAM. Theoretical comparison of packed bed and fluidized bed membrane reactors for methane reforming. *Int J Hydrogen Energy* 2010;35:7142–50. <http://dx.doi.org/10.1016/j.ijhydene.2010.02.050>.
 - [12] Di Marcoberardino G, Sosio F, Manzolini G, Campanari S. Fixed bed membrane reactor for hydrogen production from steam methane reforming: experimental and modeling approach. *Int J Hydrogen Energy* 2015;40:7559–67. <http://dx.doi.org/10.1016/j.ijhydene.2014.11.045>.
 - [13] Ferret EU Consortium, FERRET. A flexible natural gas membrane reformer for m-CHP applications. 2014. <http://www.ferret-h2.eu>.
 - [14] Lattner JR. Comparison of conventional and membrane reactor fuel processors for hydrocarbon-based PEM fuel cell systems. *Int J Hydrogen Energy* 2004;29:393–417. <http://dx.doi.org/10.1016/j.ijhydene.2003.10.013>.
 - [15] Di Marcoberardino G, Roses L, Manzolini G. Technical assessment of a micro-cogeneration system based on polymer electrolyte membrane fuel cell and fluidized bed autothermal reformer. *Appl Energy* 2016;162:231–44. <http://dx.doi.org/10.1016/j.apenergy.2015.10.068>.
 - [16] Mardilovich IP, Castro-Dominguez B, Kazantzis NK, Wu T, Ma YH. A comprehensive performance assessment study of pilot-scale Pd and Pd/alloy membranes under extended coal-derived syngas atmosphere testing. *Int J Hydrogen Energy* 2015;40:6107–17. <http://dx.doi.org/10.1016/j.ijhydene.2015.03.001>.
 - [17] Ayturk ME, Kazantzis NK, Ma YH. Modeling and performance assessment of Pd- and Pd/Au-based catalytic membrane reactors for hydrogen production. *Energy Environ Sci* 2009;2:430. <http://dx.doi.org/10.1039/b821109b>.
 - [18] Jannelli E, Minutillo M, Galloni E. Performance of a polymer electrolyte membrane fuel cell system fueled with hydrogen generated by a fuel processor. *J Fuel Cell Sci Technol* 2007;4:435. <http://dx.doi.org/10.1115/1.2756568>.
 - [19] Minutillo M, Perna A. Behaviour modelling of a PEMFC operating on diluted hydrogen feed. *Int J Energy Res* 2008;32:1297–308. <http://dx.doi.org/10.1002/er.1424>.
 - [20] Nikiforow K, Karimäki H, Keränen TM, Ihonen J. Optimization study of purge cycle in proton exchange membrane fuel cell system. *J Power Sources* 2013;238:336–44. <http://dx.doi.org/10.1016/j.jpowsour.2012.11.153>.
 - [21] Grace J, Adris AEM, Boyd T, Lim CJ. Hydrogen from an internally circulating fluidized bed membrane reactor. *Int J Chem React Eng* 2005;3:1–12. <http://www.scopus.com/inward/record.url?eid=2-s2.0-31044455453&partnerID=tZOTx3y1>.
 - [22] Fernandez E, Helmi A, Coenen K, Melendez J, Viviente JL, Pacheco Tanaka DA, et al. Development of thin Pd–Ag supported membranes for fluidized bed membrane reactors including WGS related gases. *Int J Hydrogen Energy* 2015;40:3506–19. <http://dx.doi.org/10.1016/j.ijhydene.2014.08.074>.
 - [23] Roses L, Gallucci F, Manzolini G, van Sint Annaland M. Experimental study of steam methane reforming in a Pd-based fluidized bed membrane reactor. *Chem Eng J* 2013;222:307–20. <http://dx.doi.org/10.1016/j.cej.2013.02.069>.
 - [24] Gallucci F, Van Sint Annaland M, Kuipers JAM. Autothermal reforming of methane with integrated CO₂ capture in a novel fluidized bed membrane reactor. Part 1: experimental demonstration. *Top Catal* 2008;51:133–45. <http://dx.doi.org/10.1007/s11244-008-9126-8>.
 - [25] Fernandez E, Coenen K, Helmi A, Melendez J, Zuñiga J, Pacheco Tanaka DA, et al. Preparation and characterization of thin-film Pd–Ag supported membranes for high-temperature applications. *Int J Hydrogen Energy* 2015;40:13463–78. <http://dx.doi.org/10.1016/j.ijhydene.2015.08.050>.
 - [26] Peng DY, Robinson DB. New two-constant equation of state. *Ind Eng Chem Fundam* 1976;15:59–64.
 - [27] Rackett HG. Equation of state for saturated liquids. *J Chem Eng Data* 1970;15:514–7. <http://www.scopus.com/inward/record.url?eid=2-s2.0-33947293984&partnerID=tZOTx3y1>.
 - [28] Haar L, Gallagher J, Kell GS. NBS/NRC steam tables: thermodynamic and transport properties and computer programs for vapor and liquid states of water in S.I. Units. Washington: Hemisphere Publishing Corporation; 1984.
 - [29] Ma L, Trimm DL, Jiang C. The design and testing of an autothermal reactor for the conversion of light hydrocarbons to hydrogen I. The kinetics of the catalytic oxidation of light hydrocarbons. *Appl Catal A Gen* 1996;138:275–83.
 - [30] Deshmukh SARK, Laverman JA, Cents AHG, van Sint Annaland M, Kuipers JAM. Development of a membrane-assisted fluidized bed reactor. 1. Gas phase back-mixing and bubble-to-emulsion phase mass transfer using tracer injection and ultrasound experiments. *Ind Eng Chem Res* 2005;44:5955–65. <http://dx.doi.org/10.1021/ie049102e>.
 - [31] Kato K, Wen CY. Bubble assemblage model for fluidized bed catalytic reactors. *Chem Eng Sci* 1969;24:1351–69. <http://www.scopus.com/inward/record.url?eid=2-s2.0-0014552424&partnerID=tZOTx3y1>.
 - [32] Patil CS, van Sint Annaland M, Kuipers JAM. Design of a novel autothermal membrane-assisted fluidized-bed reactor for the production of ultrapure hydrogen from methane. *Ind Eng Chem Res* 2005;44:9502–12. <http://dx.doi.org/10.1021/ie050244y>.
 - [33] Kunii D, Levenspiel O. Fluidization engineering. Elsevier; 1991. <http://dx.doi.org/10.1016/B978-0-08-050664-7.50012-3>.
 - [34] Shiau C-Y, Lin C-J. Equation for the superficial bubble-phase gas velocity in fluidized beds. *AIChE J* 1991;37:953–4. <http://dx.doi.org/10.1002/aic.690370619>.
 - [35] Mori S, Wen CY. Estimation of bubble diameter in gaseous fluidized beds. *AIChE J* 1975;21:109–15. <http://dx.doi.org/10.1002/aic.690210114>.
 - [36] Gallucci F, Van Sint Annaland M, Kuipers JAM. Autothermal reforming of methane with integrated CO₂ capture in a novel fluidized bed membrane reactor. Part 2 comparison of reactor configurations. *Top Catal* 2008;51:146–57. <http://dx.doi.org/10.1007/s11244-008-9127-7>.
 - [37] Rostrup-Nielsen J. Activity of nickel catalysts for steam reforming of hydrocarbons. *J Catal* 1973;31:173–99. [http://dx.doi.org/10.1016/0021-9517\(73\)90326-6](http://dx.doi.org/10.1016/0021-9517(73)90326-6).
 - [38] Huang X, Reimert R. Kinetics of steam reforming of ethane on Ni/YSZ (yttria-stabilised zirconia) catalyst. *Fuel* 2013;106:380–7. <http://dx.doi.org/10.1016/j.fuel.2012.09.081>.
 - [39] Rakib MA, Grace JR, Lim CJ, Elnashaie SSEH. Modeling of a fluidized bed membrane reactor for hydrogen production by steam reforming of hydrocarbons. *Ind Eng Chem Res* 2011;50:3110–29. <http://dx.doi.org/10.1021/ie100954a>.