Achievements of European projects on membrane reactor for hydrogen production

Gioele Di Marcoberardino [a, *], Marco Binotti [a], Giampaolo Manzolini [a], José Luis Viviente [b], Alba Arratibel [b, c], Leonardo Roses [d], Fausto Gallucci [c]

[a] Politecnico di Milano, Dipartimento di Energia, Via Lambruschini 4, 20156, Milano, Italy
[b] TECNALIA Research & Innovation, Mikeletegi Pasealekua 2, 20009, San Sebastian-Donostia, Spain
[c] Chemical Process Intensification, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5612 AZ, Eindhoven, The Netherlands
[d] HyGear B.V., Westervoortsedijk 73, P.O. Box 5280, 6802 EG, Arnhem, The Netherlands

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ABSTRACT

Membrane reactors for hydrogen production can increase both the hydrogen production efficiency at small scale and the electric efficiency in micro-cogeneration systems when coupled with Polymeric Electrolyte Membrane fuel cells. This paper discusses the achievements of three European projects (FERRET, FluidCELL, BIONICO) which investigate the application of the membrane reactor concept to hydrogen production and micro-cogeneration systems using both natural gas and biofuels (biogas and bio-ethanol) as feedstock. The membranes, used to selectively separate hydrogen from the other reaction products (CH_4, CO_2, H_2O, etc.), are of asymmetric type with a thin layer of Pd alloy (<5 μm), and supported on a ceramic porous material to increase their mechanical stability. In FERRET, the flexibility of the membrane reactor under diverse natural gas quality is validated. The reactor is integrated in a micro-CHP system and achieves a net electric efficiency of about 42% (8% points higher than the reference case). In FluidCELL, the use of bio-ethanol as feedstock for micro-cogeneration Polymeric Electrolyte Membrane based system is investigated in off-grid applications and a net electric efficiency around 40% is obtained (6% higher than the reference case). Finally, BIONICO investigates the hydrogen production from biogas. While BIONICO has just started, FERRET and FluidCELL are in their third year and the two prototypes are close to be tested confirming the potentiality of membrane reactor technology at small scale.

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1. Introduction

The constant increase of electricity and heat demand has led to an intensification of fossil fuels utilization that today, despite the impressive development of renewables, still account for more than 80% of the overall primary energy consumptions worldwide (International Energy Agency, 2015). Carbon dioxide emissions associated with the utilization of fossil fuels are considered one of the main responsible for CO_2 concentration rise in the atmosphere and of the consequent greenhouse effect. Several options for anthropogenic CO_2 emissions reduction are being investigated: Van Vuuren et al. (2007) although accepting the absence of a silver bullet, indicate carbon capture and storage (CCS) as the most

attractive technology. The same vision is also share by Wennersten et al. (2015) that underline how effective communication is crucial to favour public acceptance of this technology. Yong et al. (2016) explore clean electricity production systems either based on renewables or implementing CCS, Karschin and Geldermann (2015) propose and optimize local bioenergy production and distribution systems as function of biomass availability, number of heat customers and heat loss in the system. Dovì et al. (2009) focus on systems based on renewables and on the production of biofuels and hydrogen. As suggested by Dovì et al. (2009) and supported by Maack and Skulason (2006), hydrogen can replace fossil fuels in power generation and transportation in the long term. Hydrogen production should be based on electrolysis exploiting renewable electricity (wind, PV) or on biofuels as biogas. When moving to the short period, one of the most interesting options to reduce CO_2 emissions in the residential sector is the combined heat and power generation on micro scale (micro-CHP) that increases fuel

exploitation compared to conventional separated heat and electricity production. Alanne and Saari (2004) outlined the potentiality of micro-CHP systems comparing in terms of performance and costs four different technologies (reciprocating engines, Stirling-engines, Fuel Cells, Micro Turbines), while Campanari et al. (2009a,b) evaluated that micro-CHP systems based on fuel cells applied to single-user residential applications could achieve 25% primary energy saving. The advantages in terms of efficiency and CO$_2$ savings are even larger when the electricity is produced by polymer electrolyte membrane (PEM) fuel cells based systems: PEM offer an efficient source of electricity with high primary energy saving potential at micro-cogeneration scale (Campanari et al., 2009a). However, they require non-contaminated (ultra-pure) hydrogen as fuel (CO tolerance below 10 ppm).

Both in short and long term perspectives, the development of efficient and cost effective hydrogen fuel processors is therefore crucial (Taanman et al., 2008). Membrane reactors (MR) for hydrogen production are foreseen as a promising technology for process intensification. Gallucci et al. (2013) reviewed the most suitable membrane materials for hydrogen separation together with commercially available concepts and Paglieri and Way (2002) focused on Palladium membranes for hydrogen separation. The main advantage of membrane reactors is the capability of producing and separating hydrogen in a single reactor with thermodynamic and economic benefits. Recent studies demonstrate that membrane reactors overcome the performance of conventional fuel processors (Di Marcoberardino et al., 2016c; Foresti and Manzolini, 2016). Campanari et al. (2009a,b) calculated a 25% electric efficiency increase when replacing conventional fuel processors based on steam reforming, water gas shift and preferential oxidizer with a membrane reactor. The same advantage was confirmed by Di Marcoberardino et al. (2016,b,c), while the adoption of membrane reactor when using bio-ethanol as feedstock has an efficiency increase of about 15% than conventional configurations (Foresti and Manzolini, 2016).

Between the fixed bed and fluidized bed configurations, the latter can significantly reduce heat and mass transfer issues related to reforming reaction and H$_2$ permeation. Fluidization impact on catalyst and membrane and has been explored (Roses et al., 2011).

Three EU projects FERRET (Gallucci et al., 2014), FluidCELL (Viviente et al., 2014), BIONICO (Binotti et al., 2015) are investigating the application of the membrane reactor concept to hydrogen production and micro-CHP systems using different fuels. BIONICO project focuses on hydrogen production from biogas produced by landfill or anaerobic digestors. FERRET and FluidCELL deal with the integration of the fluidized membrane reactor to PEM based micro-CHP systems: in FERRET, the flexibility of the membrane reactor with respect to the diverse NG quality is validated, while in FluidCELL the performance of an off-grid micro-CHP system using bio-ethanol as fuel is evaluated.

This work outlines the advantages of membrane reactor in each of the considered applications through the main achievements within the three projects. The paper is organized as follows: a dedicated section will describe the membrane reactor concept and its characteristics and then, three separate sections will summarize each project goals and results.

2. Membrane reactor concept

Conventional fuel processors for hydrogen production or combined with PEM micro-cogeneration systems are usually based on the concept shown in Fig. 1. Hydrogen production and purification from hydrocarbons requires several steps carried forward in different reactors: (a) a reformer operating at high temperatures[1] either autothermal (ATR) or conventional steam reforming (SR), followed by (b) two water gas shift reactors (WGSR), one at high and one at low temperatures to enhance carbon monoxide conversion to hydrogen, and (c) a final purification step that depends on the hydrogen application. In case of H$_2$ utilization in PEM based micro-CHP systems, a PReferential OXidizer (PROX) is required to oxidize CO and obtain a final composition at the outlet with 40÷60 %$_{mol}$ of H$_2$ diluted with CO$_2$, steam and N$_2$. The net electric and thermal efficiencies of commercial systems based on the above-mentioned technology are in the range of 32% and 60% respectively [15]. In case of hydrogen production, the purification is carried out in a Pressure Swing Adsorption system (PSA) splitting a pure hydrogen stream from the other gases. The reference hydrogen production efficiency is of around 60% for a system size of 100 kg$_{H2}$/day (Di Marcoberardino et al., 2016b).

In this work, the adoption of hydrogen selective membrane in an autothermal reforming reactor is considered (see Fig. 2). The fluidized bed configuration is preferred thanks to the more uniform temperature achieved. Additionally, bed-to-wall mass transfer limitations, often very detrimental for packed bed membrane reactors, are largely reduced. The fluidized membrane reactor advantages with respect to a conventional fuel processor are the following:

- the entire production and purification process is carried out in one reactor, the membrane reactor;
- hydrogen separation with membranes drives the reaction conversion towards product side; so the same fuel conversion of conventional batch processes can be achieved at lower operating temperatures;
- the extent of hydrocarbon conversion can be defined in the design phase by means of adequate selection of stream pressures and membrane area.

In the micro-CHP cases, the membrane separates pure hydrogen which can directly feed the fuel cell. Feeding pure hydrogen compared to the diluted one increases the electric conversion efficiency: Minutillo et al. (2008) measured a decrease in the output voltages (about 8−10%) when reformate was used instead of pure hydrogen. Through a detailed PEM modelling (Minutillo and Perna, 2008), it was shown that the presence of carbon dioxide does not only dilute hydrogen, but leads also to carbon monoxide formation of by reverse WGS reaction.

The higher CH$_4$ conversion and H$_2$ separation factor (SF) of membrane reactors with respect to conventional configurations (w/o membranes) are outlined in Fig. 3. Experimental tests are carried out feeding a mixture of pure methane, steam and air for ATR at 550 °C and S/C equal to 3 varying the operating pressure between 2 and 4 bar. The SF and the O/C ratio are defined as follows:

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

$$SF = \frac{F_{H_2,perm}}{F_{H_2,ret} + F_{H_2,perm}} \tag{2}$$

Fig. 3 shows as the adoption of the membrane reactor (w/Mem. case) increases the methane conversion (therefore the hydrogen production) more than 15% with respect to the conventional fuel

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[1] The reforming temperature depends on fuel type. NG and biogas requires temperatures above 800 °C while, in the ethanol case, temperature are set around 600 °C.
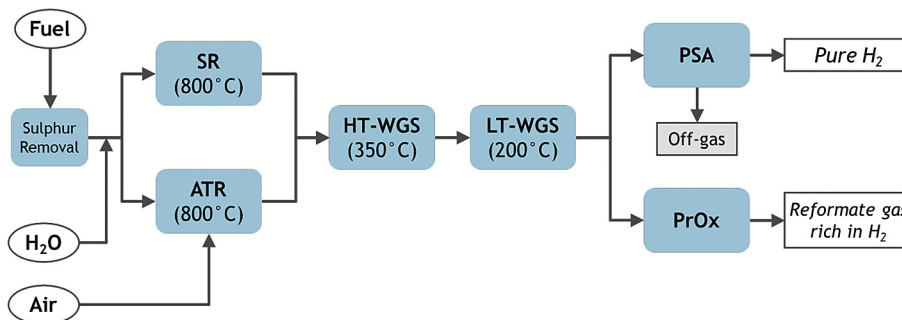
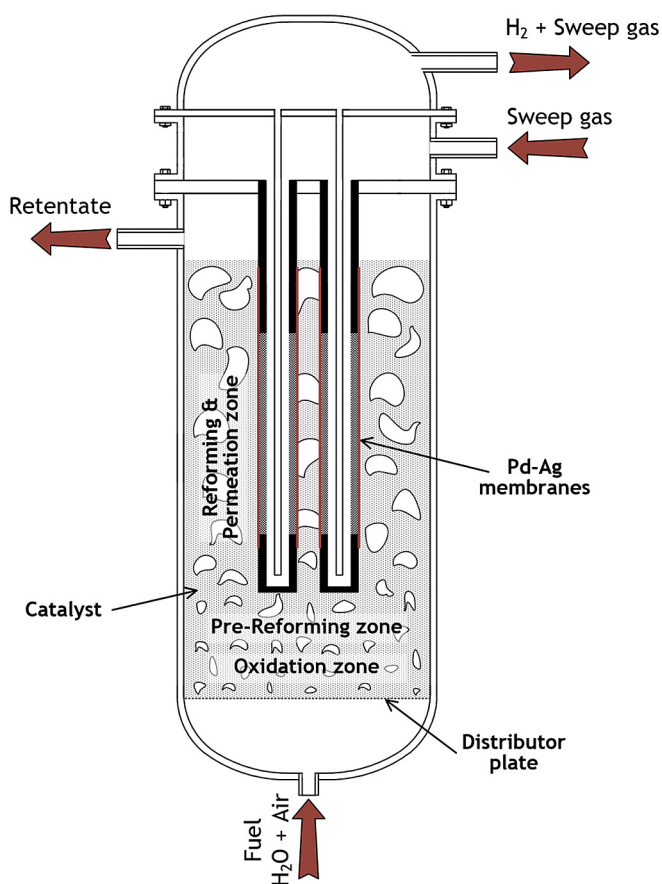**Fig. 1.** Conventional fuel processors for hydrogen production.

Fig. 2. Schematic of a membrane reactor.

processor (w/o Mem. case).

On the other hand, to enhance the hydrogen permeation, two different reactor configurations can be designed: with vacuum or with sweep gas at the permeate side, both aiming at decreasing hydrogen partial pressure in order to increase the hydrogen flux and consequently reduce the membrane required area. Further information about the two configurations using NG as feedstock can be found in (Di Marcoberardino et al., 2016c), while the bio-ethanol case is discussed in (Foresti and Manzolini, 2016).

The main characteristics required by the membranes are (i) mechanical and thermal stability, (ii) high hydrogen fluxes and (iii) high perm-selectivity (defined as the ratio between the permeance of hydrogen and the permeance of other species). The technology identified by Tecnalia which addresses all these three requirements is based on asymmetric supported membranes made by Pd alloy.

The support is either made of ZrO_2 with 100 nm pore size as in FERRET project or alumina supported as in FluidCELL with a 1–4 μm thick Pd-Ag layer: the lower the thickness the higher the flux, but with penalties from selectivity point of view. The adoption of thin Pd-Ag layers requires supports with low roughness having small pores (<200 nm) with uniform pore size distributions, therefore dedicated efforts in the projects are devoted to the support manufacturing process. The developed membranes present H_2/N_2 perm-selectivities larger than 7000 and nitrogen permeance $<8 \times 10^{-11}$ mol m^{-2} s^{-1} Pa^{-1} at 300 °C. The performance of the membranes adopted in FluidCELL and FERRET are aligned with the ones of other manufacturers as reported in two review works (Fernandez et al., 2015a, 2015b).

In FERRET, 30 membranes of 25 cm length were manufactured while in FluidCELL the number of membranes is 37 and they are 50 cm long. The two membrane types are shown in Fig. 4. In BIO-NICO, the presence of H_2S in the biogas feedstock requires the adoption of different Pd alloy currently under investigation. A preliminary calculation assessed that around 100 membranes 50 cm long should be manufactured to guarantee a hydrogen production of 100 kg/day.

3. FERRET: Flexible micro-CHP system

The FERRET project, started in April 2014, aims at developing a micro-CHP system flexible towards the variability of NG compositions in the European Union. The NG compositions variation affects the design of the system, its performance and/or its lifetime. Four different compositions, representative of the different European biogases (see Table 1), were selected for assessing the system flexibility. 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. In addition, the considered compositions vary in terms of inert concentration: inert gases reduce the H_2 fraction and thus the permeation driving force across the membrane. The definitions of H_2 potential, Pt_{H2}, and Wobbe index, WI, are as follows.

$$Pt_{H_2} = \frac{mol\ H_{2,NG}}{mol\ NG} \tag{3}$$

$$WI = \frac{HHV}{\sqrt{\rho_{NG}/\rho_{air}}} \tag{4}$$

The considered layout of the micro-CHP system is shown in Fig. 5. It shows two streams of water pumped by P-1 and P-2 for feed and sweep, respectively. Liquid feed water is mixed with compressed air, then evaporated through HX-0 and HX-1 and finally superheated in HX-2. At the reactor inlet, compressed NG
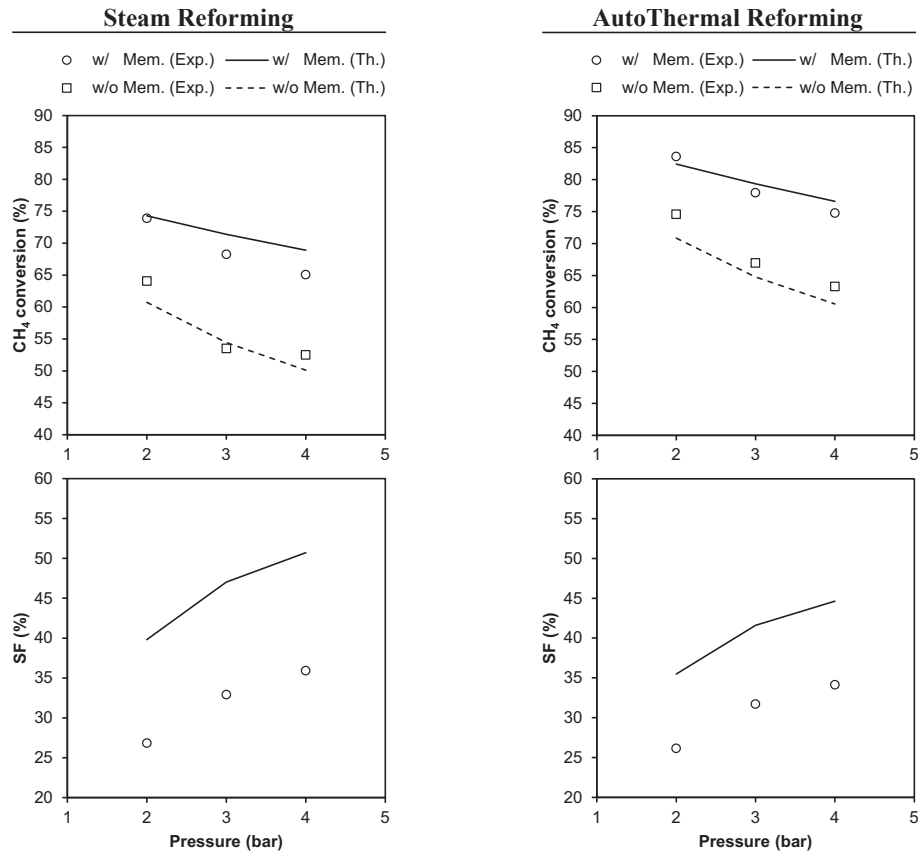
Fig. 3. Methane conversion (top) and Separation Factor (bottom) for SR and ATR with (w/) and without (w/o) membranes at different pressures. Experiments carried out at 550 °C, S/C = 3 and, for ATR, O/C = 0.25.
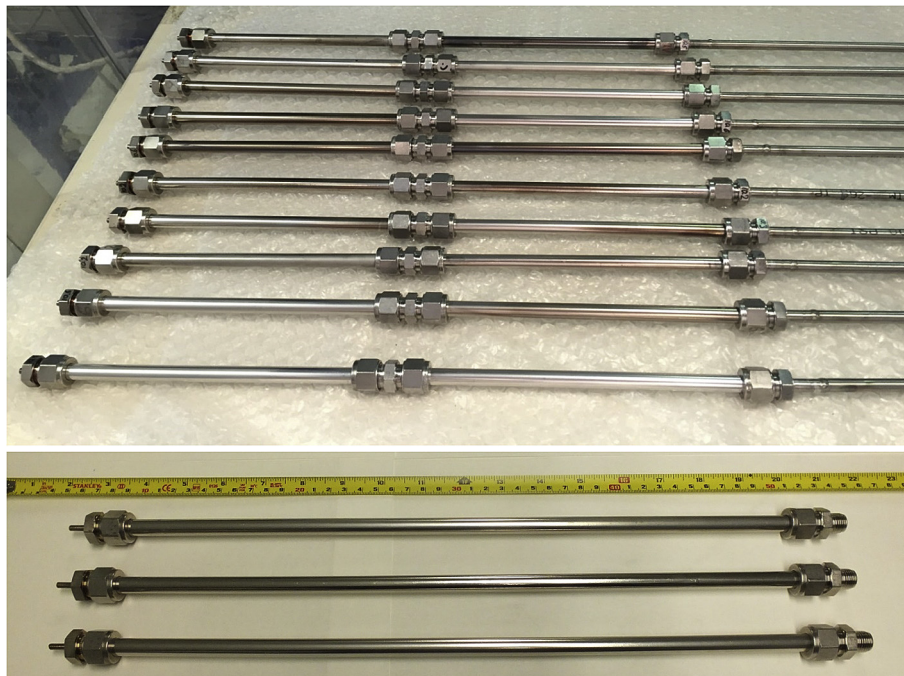
Fig. 4. FERRET (top) and FluidCELL (bottom) membranes to be inserted in the prototype reactor.

and a preheated mix of air and steam are fed from the bottom section. Sweep gas is evaporated through HX-3 and HX-4 and fed separately to the reactor as shown in Fig. 5. At the outlet, the retentate and hydrogen exit from the top section of the reactor.

Table 1
Natural Gas compositions.

Species	units	NG type			
		NL	UK	IT	ES
CH_4	%mol	81.230	92.070	99.581	81.570
C_2H_6	%mol	2.850	3.405	0.056	13.380
C_3H_8	%mol	0.370	0.761	0.021	3.670
$n\text{-}C_4H_{10}$	%mol	0.080	0.177	0.002	0.400
$i\text{-}C_4H_{10}$	%mol	0.060	0.140	0.006	0.290
$n\text{-}C_5H_{12}$	%mol	0.020	0.048	0	0
$i\text{-}C_5H_{12}$	%mol	0.020	0.061	0.002	0
C_{6+}	%mol	0.080	0.090	0.007	0
CO_2	%mol	0.890	0.865	0.029	0
N_2	%mol	14.400	2.375	0.296	0.690
LHV	MJ/kg	38.0	46.7	49.7	48.6
Pt_{H2}	mol_{H2}/mol_{NG}	3.52	4.07	3.99	4.66
WI	MJ/Nm^3	43.6	52.0	53.1	56.6

**Table 2**
ATR-MR system performance using different NG (Di Marcoberardino and Manzolini, 2017).

Results	units	UK	NL
S/C and Temperature reactor	-/°C	2.5/600	2.5/600
Pressure reaction/permeate side	bar	8/1.3	8/1.3
NG feed	Nm^3/h	1.19	1.38
NG power input [LHV base]	kW	12.06	12.13
NG power input [HHV base]	kW	13.35	13.44
Net AC power output	kW	5.00	5.00
Fuel Cell AC power output	kW	6.09	6.12
Balance of plant	kW	1.09	1.12
Thermal recovery	kW	6.78	6.81
Net electric efficiency [LHV base]	$\%_{LHV}$	41.48	41.21
Net electric efficiency [HHV base]	$\%_{HHV}$	37.45	37.19
Net thermal efficiency	$\%_{LHV}$	56.23	56.12
Total efficiency [LHV base]	$\%_{LHV}$	97.71	97.33
Total efficiency [HHV base]	$\%_{HHV}$	88.22	87.83
Total membrane area	m^2	0.264	0.283
H_2 production/permeation	Nm^3/h	3.42	3.44
HRF	%	92.0	92.1

After cooling, the remaining fuel in the retentate is combusted in the burner to generate steam in HX-1 and HX-3 closing the cycle. A closed loop for heat recovery which includes HX-7, the fuel cell (HX-9) and HX-6 is designed. Process water is recycled via condensation in three separators downstream permeate, retentate and exhaust gases cooling.

The system performance was assessed using both UK and NL natural gas compositions outlining their impact on the net electric efficiency (see Table 2). In general, the net electric efficiency is 10% points higher than commercially available micro-CHP systems based on PEM fuel cell of the same size. Focusing on NG composition impact, the results indicate 1% higher electric efficiency for UK case, as consequence of the different NG compressor consumption (lower volumetric flow thanks to the higher WI), and a 7%

membrane area reduction due to lower inert gases concentration. Starting from these two system designs, the performances at different NG compositions are evaluated. The NL case, that has the high inert gases concentration, was selected as reference for the system design and the overall performance for different NG composition was assessed (Fig. 6). The rationale behind the selection of the worst case (NL composition) as reference is to have a slight increase of the net electric efficiency with other NG compositions, and, in addition, an easier reactor control (Di Marcoberardino and Manzolini, 2017). Limited efficiency variation are obtained, hence demonstrating the flexibility of the membrane
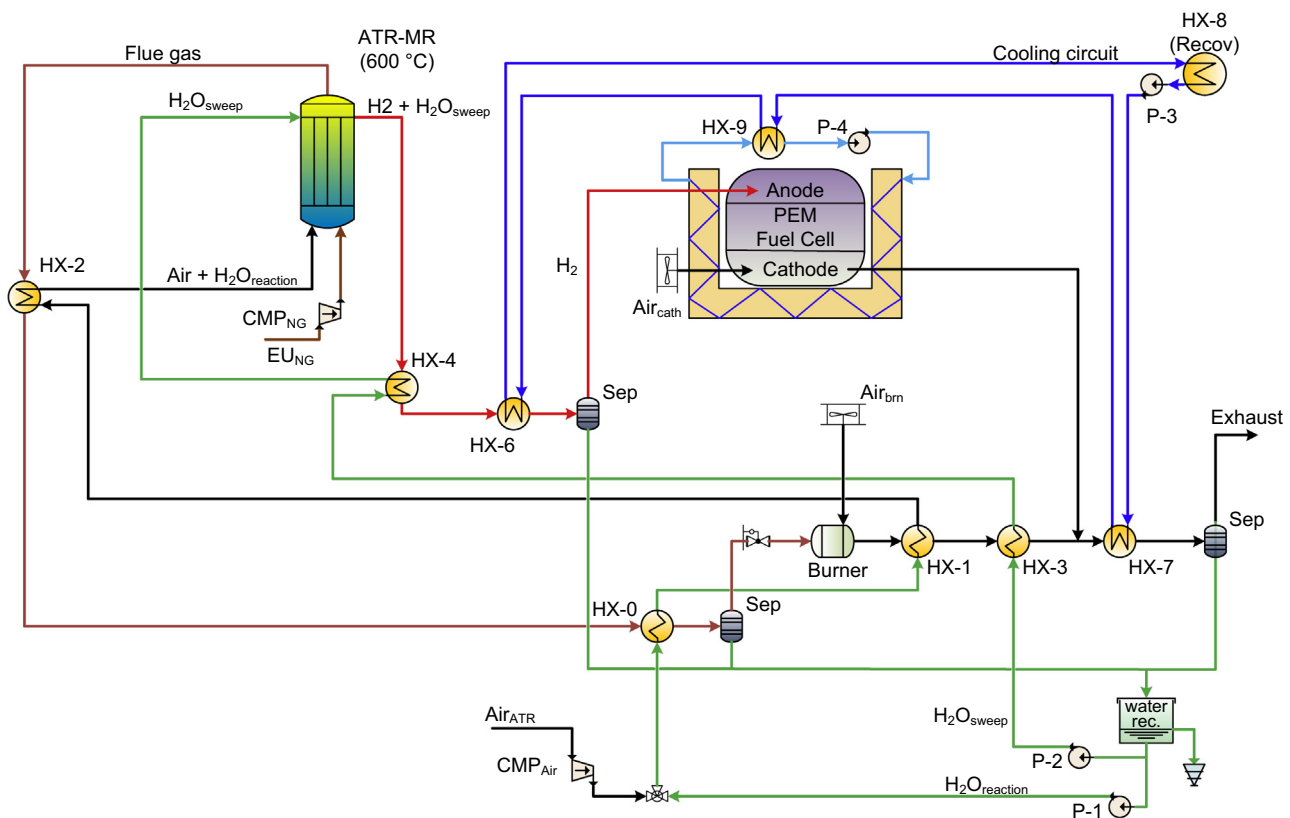
Fig. 5. FERRET Layout of micro-CHP system using sweep gas (Di Marcoberardino and Manzolini, 2017).
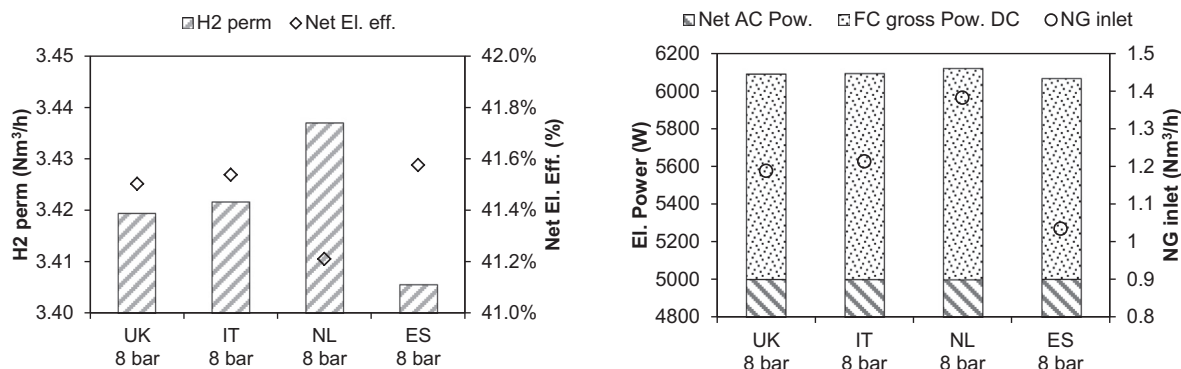
Fig. 6. NL base case with sweep: micro-CHP flexibility under different NG qualities (Di Marcoberardino et al., 2016a).

reformer.

Once defined the reference NG composition, the system lay-out and operating parameters, the design was finalized and the construction of the ATR membrane reformer prototype was started. The flexible fuel processor was designed to work with different fuels with WI ranging from 43.6 to 56.6 MJ/Nm^3 and with hydrogen potential from 3.52 to 4.66 mol$_{H2}$/mol$_{NG}$. A picture of the membrane reactor is shown in Fig. 7.

4. FluidCELL: Advanced bio-ethanol micro-CHP

FluidCELL project, started in April 2014, aims at developing a high efficient m-CHP system based on PEM fuel cell and integrating a low temperature fluidized membrane reactor. The system is fuelled with bio-ethanol and intended for off-grid applications. A

Fig. 7. FERRET ATR membrane reactor.

pre-commercial system developed by Helbio, based on conventional fuel processor, is rated 5 kW$_{el}$ with an electric efficiency of 22.5% (Rossetti et al., 2012): detailed simulations of the system showed an increase of the electric efficiency up to 31% when improving heat integration (Rossetti et al., 2015).

The layout developed in FluidCELL is depicted in Fig. 8. The W/EtOH mixture feed is pumped through a series of heat exchangers: it evaporates cooling the exhausts (HX1) and is then superheated by the retentate flow (HX2). No additional fuel for reactants heating is considered, thus the retentate combustion energy must cover the whole feed heat duty. Air is compressed and directly fed to the reactor. The permeate gas is cooled evaporating the sweep water (HX3), to prevent hydrogen contamination in case of leakages. Then, the sweep stream is heated up to the reactor temperature by the exhaust gases (HX4). Finally, the retentate flow is cooled down to 120 °C, throttled and combusted.

Main results of the simulations for the FluidCELL layout, together with the reference case based on conventional fuel processor (SR) are summarized in Table 3. The adoption of membrane reactor increases the net electric efficiency by 7% points with respect to the reference case calculated using the same assumptions. On the contrary, the thermal efficiency is lower for the FluidCELL case because the higher electric efficiency reduces the heat that can be recovered.

Compared to the FERRET project which uses NG case, the membrane area of FluidCELL case is larger even with a higher feed pressure. This is due to the lower reactor temperature (500 °C vs 600 °C) which reduces the hydrogen partial pressure from 1.7 bar to 1.1 bar together with the membrane permeance, being the former the most relevant aspect. Once defined the system operating conditions and membrane area requirements, the membrane reactor manufacturing started and it is now complete. A sketch of the fuel processor is shown in Fig. 9.

5. BIONICO: Biogas MR for decentralized H$_2$ production

The BIONICO project, started in September 2015, will develop, build and demonstrate a novel reactor concept integrating H$_2$ production and separation in a single vessel in a biogas production plant. The BIONICO pilot plant will be built in an ENC landfill plant in Portugal and is expected to start-up in July 2018. The hydrogen production capacity will be of 100 kg/day. The adoption of biogas as fuel input makes the hydrogen produced green and is justified by the remarkable growth of biogas production expected in the next decades. Roughly 10,000 biogas plants in agriculture, industry and waste water treatment are in operation in Europe, but the European potential for biogas is still enormous as the production of biogas could be multiplied by a factor of four to five (European Biogas
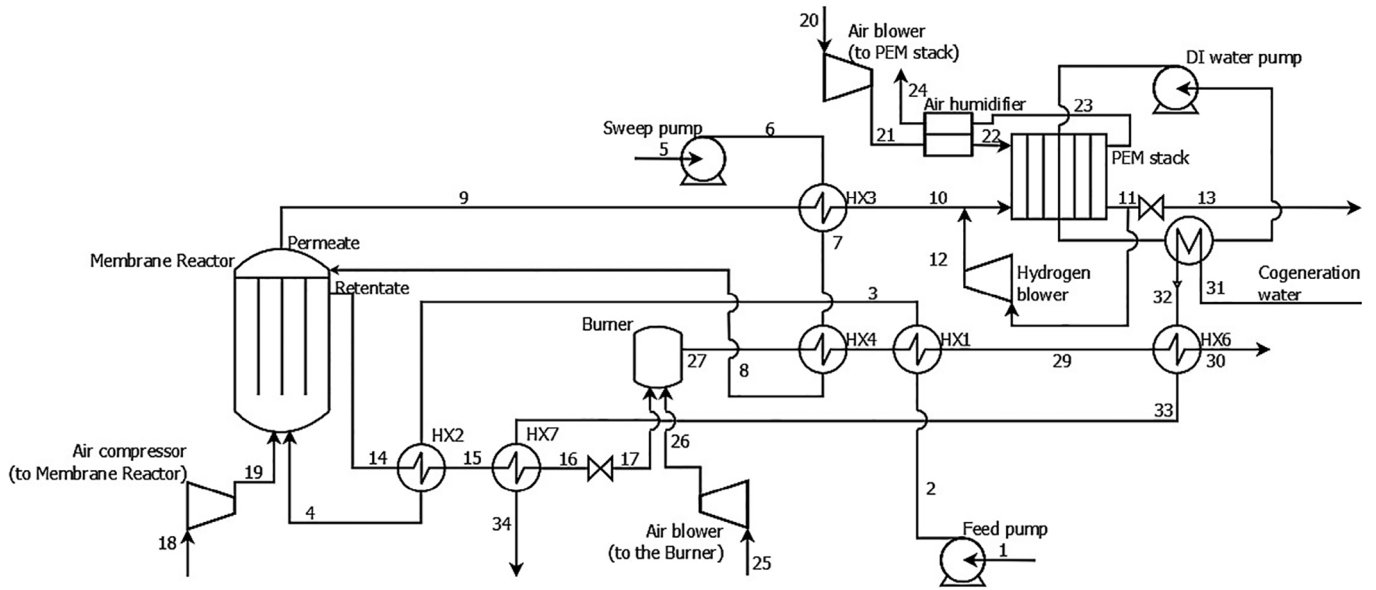
Fig. 8. FluidCELL Layout with sweep gas (Foresti and Manzolini, 2016).

Table 3
Simulation results on performance of the ATR-MR system (Foresti and Manzolini, 2016).

Results	units	Reference case	FluidCELL Case Sweep gas		
W/EtOH, Temperature reactor	–	6/600 °C	3.6/500 °C	4.2/500 °C	3.6/500 °C
Pressure reaction/permeate side	bar	2	12/1.3	12/1.3	16/1.3
EtOH power input [LHV base]	kW	12.29	12.73	12.44	12.44
EtOH power input [HHV base]	kW	13.62	14.10	13.78	13.78
Net AC power output	kW	5.00	5.00	5.00	5.00
Gross DC power output	kW	5.44	5.65	5.65	5.68
Balance of plant	kW	0.44	0.65	0.65	0.068
Thermal recovery	kW	9.08	6.54	6.89	6.61
Net electric efficiency [LHV base]	$\%_{LHV}$	33.1	40.6	39.3	40.2
Net electric efficiency [HHV base]	$\%_{HHV}$	29.9	36.6	35.5	36.3
Net thermal efficiency [LHV base]	$\%_{LHV}$	63.0	53.1	54.2	53.3
Net thermal efficiency [HHV base]	$\%_{HHV}$	57.1	47.9	48.9	48.1
Total membrane area	m^2	–	0.37	0.30	0.22
H_2 production/permeation	Nm^3/h	4.12	3.18	3.18	3.20
HRF	%	–	65.9	63.8	65.7

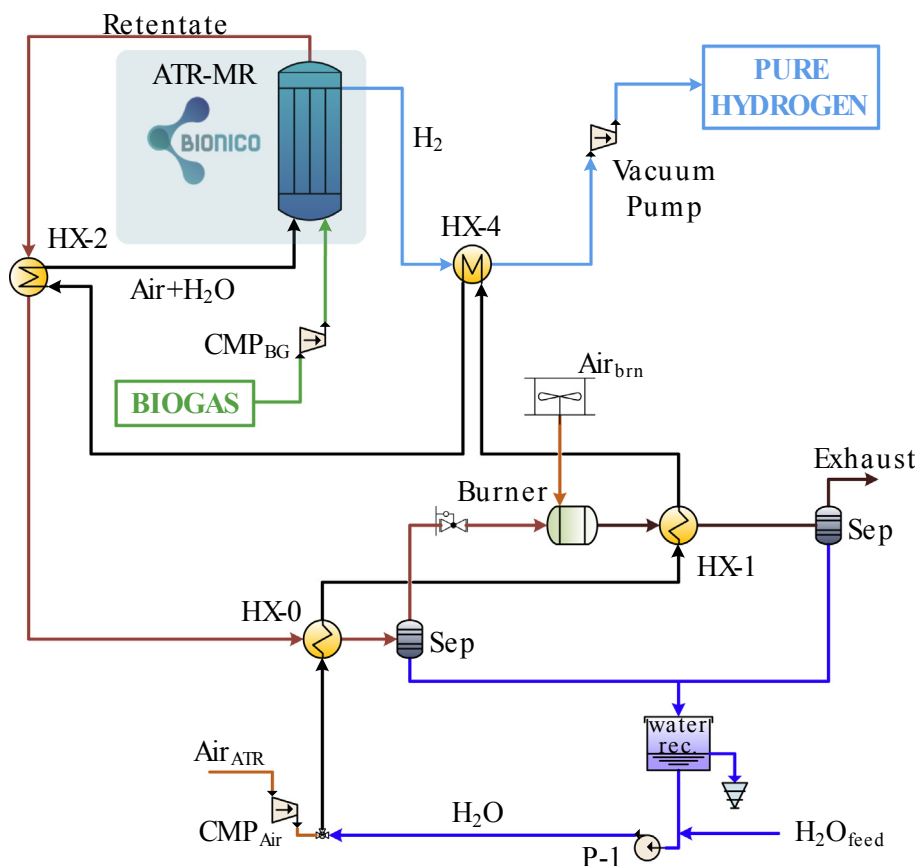**Fig. 9.** FluidCELL ATR membrane reactor.

Fig. 10. BIONICO system layout.

Association, 2015). Typical applications of biogas are the power generation through internal reciprocating engines or upgrading to biomethane by CO_2 separation. When moving to hydrogen production from biogas, the conversion process is more complex since biogas can have variable gas compositions depending on primary matter sources. In addition, traditional reforming based conversion technologies are energy and capital intensive since, as already seen, several process steps are involved. The adoption of a membrane fluidized reactor can increase the hydrogen production efficiency up to 70%, reducing at the same time the system complexity (see Fig. 10). As term of comparison, conventional processes for hydrogen production from biogas have an efficiency around 64%. The hydrogen purity target is set at 99.99% equal to the one required by automotive applications which is one of the hydrogen production target. The 100 kg/day production capacity is also aligned with the features of automotive refuelling stations. The presence of sulphur in the biogas requires the development of dedicated membranes capable of dealing with sulphur content up to few ppm. Tecnalia is focusing on thin film Pd-Ag-Au membranes on top of ceramic supports.

6. Conclusions

This paper summarized the activities and achievements carried out in three European projects: FERRET, FluidCELL and BIONICO. The three projects have developed a fluidized membrane reactor to enhance the hydrogen production and micro-CHP system efficiencies. The simulations and laboratory experiments confirmed the potentiality of the technology for the considered applications: the hydrogen production can be improved from 60% to more than

70% and the micro-CHP system net electric efficiency fed with natural gas and ethanol can be as high as 42% and 40% respectively, which is around 10% higher than competitive systems based on the same concept. In addition, the hydrogen production in one single reactor reduces the system complexity with further advantages of this technology over the competitive ones.

Nomenclature

p	Pressure, bar
T	Temperature, °C

Acronyms

AC	Alternate Current
ATR	Autothermal reformer
ART-MR	Autothermal membrane reformer
CHP	Combined heat and power

DC	Direct Current
ES	Spain
EtOH	Ethanol
EU	European Union
FC	Fuel Cell
FCH JU	Fuel Cell and Hydrogen Joint Undertaking
HHV	High Heating value [MJ/kg]
HRF	Hydrogen recovery factor
HX	Heat exchanger
IT	Italy
LHV	Low heating value [MJ/kg]
Mem	Membrane
MR	Membrane reactor
NG	Natural Gas
NL	The Netherlands
O/C	Oxygen to carbon molar ratio
P	Pump
PEM	Polymer electrolyte membrane type
PSA	Pressure Swing Adsorption
PROX	Preferential oxidizer
S/C	Steam to carbon molar ratio
SF	Separation Factor
SR	Steam reformer
UK	United Kingdom
W/EtOH	Water to ethanol molar ratio
WGSR	Water gas shift reactor

Greek letters

ρ_i Density of species or mixtures, kg/m^3

Subscripts
perm   Permeate
ret   Retentate

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