Pure Hydrogen Production from Steam Reforming of Bio-Sources

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Abstract: Two synthetic mixtures simulating biogas (CH_4 /CO_2 = 66.2/33.8) and bioethanol (H_2O/EtOH = 13/1) have been used for producing hydrogen by steam reforming reaction in a commercial dense self-supported Pd-Ag membrane reactor. The experimental campaign was subdivided into two parts. Firstly, we studied biogas steam reforming reaction, evaluating the reaction pressure influence (between 200 and 350 kPa) at 450°C, H_2O/CH_4feed molar ratio = 4/1, GHSV =2370h^{-1}, sweep gas flow rate (N_2) = 28.55 mL/min and countercurrent configuration. As best result, we reached 60% CH_4 conversion and 40% hydrogen recovery at 350kPa.

Successively, we carried out bioethanol steam reforming reaction studying the influence of reaction temperature between 350 and 400°C at 300 kPa of reaction pressure, GHSV=700 h^{-1} in the presence of sweep gas (N_2 = 28.55 mL/min) and countercurrent configuration, obtaining - at 400 °C - maximum ethanol conversion, hydrogen yield and recovery equal to 70%, 50% and 65%, respectively. In addition, we compared the membrane reactor performance with a traditional reactor exercised at the same conditions, only varying the reaction pressure between 200 and 300 kPa. The aim of this work is constituted by the pure hydrogen production from bio-sources exploitation in membrane reactors at bench scale, starting with the utilization of commercial membranes available in the market and in the perspective of scaling up the process for potential industrial development.

Keywords: Biogas, Bioethanol, Membrane reactor, Pd-Ag membrane, Steam reforming, Hydrogen production.

1. INTRODUCTION

Nowadays, most of the world energy demand is satisfied by exploiting sources derived of fossil fuels, but their utilization led to the increase in concentration of greenhouse gases in the atmosphere, harmful to the environment. The scientific community studied for years a new energy carrier, environmental friendly, individuating hydrogen as a possible candidate. The peculiarity of hydrogen is that it can be produced from various raw materials and by different industrial processes. Currently, the world hydrogen production at industrial scale come from such processes as: methane and oil steam reforming reaction (48% and 30%, respectively), coal gasification (18%) and water electrolysis (4%) [1]. Meanwhile, several processes can be adopted for the utilization of renewable sources such as solar, wind energy and biomass [2, 3]. Hydrogen production from biomass can be realized, for example, by thermo-chemical methods (gasification and pyrolysis) and biological fermentation (schematically reported in Figure **1**). Biomass can be obtained from wood and wood wastes (64%), followed by municipal solid waste (24%), agricultural waste (5%) and landfill gases (5%) [4]. In this field, biogas and bioethanol represent a valid alternative to the derived of fossil fuels for producing hydrogen by steam reforming reaction.

Typically, a real biogas mixture is constituted of methane (55-70%) and carbon dioxide (30-45%), with traces of other compounds such as ammonia (100-800 ppm) and hydrogen sulfide (500-400 ppm) [5, 6]. However, there are industrial methods to upgrade biogas to biome thane, such as adsorbition, membrane technology and cryogenic systems [7].

In the specialized literature, hydrogen production via reforming reactions of biogas involves the reactions of dry reforming, steam reforming and water gas shift (eqs. 1, 2 and 3) [8,9]:

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta H_r = 260.6\, kJ/mol \qquad (1)$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H_r = 226.8\, kJ/mol \qquad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_r = 33.86\, kJ/mol \qquad (3)$$

These reactions take place in the presence of catalysts with transition metals such as Ni, or noble metals as Pt, Ir, Pd, Rh and Ru [10]. Today, biogas

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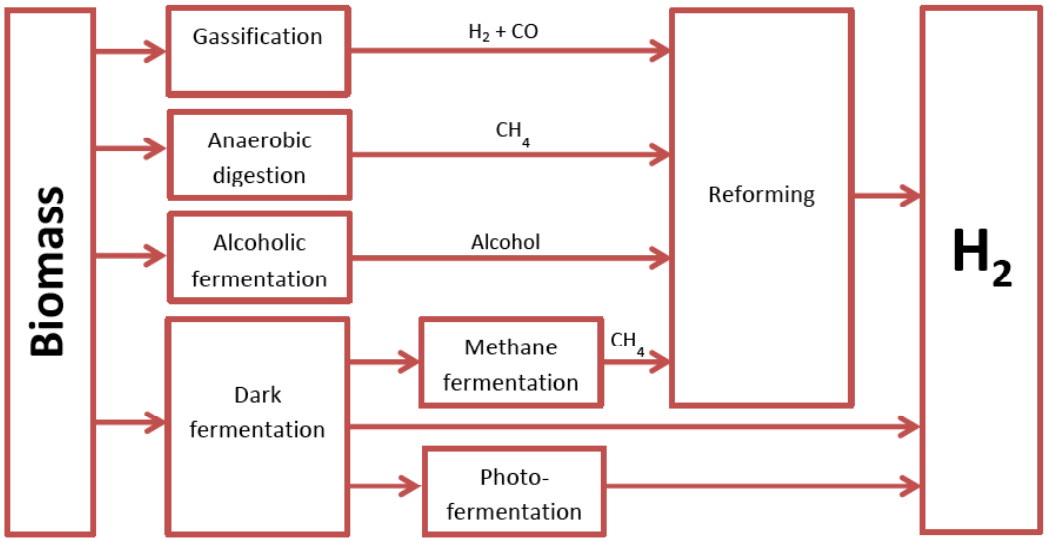

Figure 1: H_2 production from biomass.

steam reforming doesn't exist at industrial level, but Braga *et al*. [11] realized an economic and ecological analysis in this field, concluding that this way for producing hydrogen could have a cost of 0.27 $/kWh and ecological efficiency ≈95%.

Regarding bioethanol production, different kinds of biomass are available: 1st generation of biofuels is produced from edible crops through sugar fermentation or vegetable oil harvesting; the 2nd generation from non-edible crops through lignocellulosic processing; the 3rd generation from algae photo-fermentation, where CO_2 can be utilized as a direct feedstock [12].

The reactions involved in the steam reforming of ethanol were studied extensively in the specialized literature [13-18] and some of them are summarized in Table **1**. To the best of our knowledge, the noble catalysts useful for catalyzing this reaction with high selectivity towards hydrogen (more than 80%) are: Rh, Ru, Pd and Ir, while non-noble metal catalysts are: Ni, Co and Cu. The materials acting as a support include CeO_2, ZnO, MgO, Al_2O_3, zeolites-Y, TiO_2, SiO_2, $La_2O_2CO_3$, CeO_2ZrO_2 and hydrotalcites [19].

In the last decades, there has been a growing interest towards membrane reactor (MR) technology utilization to produce hydrogen from reforming reactions [20-22]. According to IUPAC definition, a MR is an equipment combining the typical characteristics of hydrogen separation of the inorganic membranes with the properties of the chemical reaction in a single process unit [23].

Some applications of MR technology to steam reforming of renewable sources are reported in literature. For example, Iulianelli *et al*. studied the reaction of biogas steam reforming in a MR (housing a composite Pd/Al_2O_3 membrane, having a Pd-layer of 7-8μm) at 380 °C, 200 kPa, $H_2O:CH_4$ =3:1, GHSV = 9000 h^{-1}, loaded with Ni (25 wt %)/Al_2O_3 catalyst. They reached a permeate purity of the recovered hydrogen around 96%, although the conversion (15%) and hydrogen recovery (>20%) were relatively low [6]. Vásquez Castillo *et al*. used a dense Pd-Ag membrane (thickness ≈200 μm) reactor in presence of 0.5wt% Rh/Al_2O_3 catalyst. The biogas steam reforming reaction was conducted at a temperature from 350 to 450 °C and from 0.1 to 0.4 MPa of reaction pressure, obtaining a maximum hydrogen yield of 80% at 450 °C and 0.4 MPa [24].

Regarding, bioethanol steam reforming, Iulianelli *et al*. [25,26] studied this reaction in a MR using a dense self-supported Pd-Ag membrane having thickness of 50 μm, with a H_2O/C_2H_5OH feed molar ratio = 18.7/1 and in the presence Co-Al_2O_3 catalyst, varying the reaction pressure, sweep gas flow rate, WHSV and feed flow configuration. The best results were obtained at 400°C, 300 kPa and WHSV=0.2 h^{-1}, reaching total conversion of simulated bioethanol, about 95% and 60% of hydrogen recovery and yield, respectively. Seelam *et al*. used a synthetic mixture of bioethanol similar to that coming from residues of cheese, with the presence of acetic acid and glycerol (EtOH: H_2O: Acetic Acid: Glycerol = 1: 13:0.18:0.04). The steam reforming reaction was conducted in a MR, housing a composite Pd-based membrane (having Pd-layer of 20

Table 1: Reaction Pathways

Reaction	Equation	Remarks
Sufficient steam supply	$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$	Ideal pathway, the highest hydrogen production
Insufficient steam supply	$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$	Undesirable products, lower hydrogen production
	$C_2H_5OH + 2H_2 \rightarrow 2CH_4 + H_2O$	
Dehydrogenation	$C_2H_5OH \rightarrow 2C_2H_4O + H_2$	Reaction pathways for hydrogen production in practice
Acetaldehyde decomposition	$C_2H_4O \rightarrow CH_4 + CO$	
Acetaldehyde steam reforming	$C_2H_4O + H_2O \rightarrow 3H_2 + 2CO$	
Dehydration	$C_2H_5OH \rightarrow 2C_2H_4 + H_2O$	Undesired pathway, main source of coke formation
Coke formation	$C_2H_4 \rightarrow polymeric\ deposits\ (coke)$	
Decomposition	$C_2H_5OH \rightarrow CO + CH_4 + H_2$	Coke formation, low hydrogen production
	$2C_2H_5OH \rightarrow C_3H_6O + CO + 3H_2$	
	$C_2H_5OH \rightarrow 0.5\ CO_2 + 1.5\ CH_4$	
Reaction of decomposition products		
Methanation	$CO + 3H_2 \rightarrow CH_4 + H_2O$	
	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	
Methane decomposition	$CH_4 \rightarrow 2H_2 + C$	
Boudouard reaction	$2CO \rightarrow 2CO_2 + C$	
Water gas shift reaction (WGSR)	$CO + H_2 \rightarrow CO_2 + H_2O$	Reduce coke formation, enhance hydrogen production

μm supported onto porous stainless steel) at 400°C, by varying the reaction pressure between 800 and 1200kPa and using two catalysts, Ni/ZrO_2 and Co/Al_2O_3. The best performance was achieved at the maximum reaction pressure in presence of Co-based catalyst: bioethanol conversion of 94%, hydrogen recovery about 40%, with a hydrogen purity of 95%[27].In this work, we performed the model biogas and bioethanol steam reforming reaction to produce pure hydrogen by using commercial membranes (hydrogen full perm-selectivity) housed in a bench-scale MR, with the aim of proposing this approach at larger scale.

2. MATERIALS AND METHOD

The bench-scale MR consists of a tubular stainless steel module containing a commercial tubular dense self-supported Pd-Ag membrane (Johnson & Mattey Co.) with a wall thickness of 150 μm, o.d. 10 mm and 145 mm as length (Figure **2**); inside the membrane, 2.8 g of Ni(7.8wt%)-CeO_2 catalyst, prepared by Solution Combustion Synthesis (SCS) from an aqueous solution containing urea as fuel and nitrates as Ni and Ceria precursors, were loaded (detailed description on the preparation procedure and catalyst features were reported by Italiano *et al*. in a previous paper [10]). The experimental plant is schematically represented in Figure **3**. In particular, the feed gases flowed into the MR are controlled by means of Brooks mass flow controllers (MF-100, MF-101 and MF-102), while the liquids are fed by a Dionex P680 HPLC pump (P-100) and vaporized by a heater (E-100). The mixture of reactants is, thus, fed to the MR, which is exercised in the temperature range between 350 and 450 °C, while the reaction pressure was varied from 100 to 300 kPaby means of a backpressure controller (BP-100), placed at the outlet of the retentate stream. The latter, representing one of the two outputs of the MR, before being analyzed, is made anhydrous, by condensing the vapor fraction in an ice trap (V-100). Successively, both

retentate and permeate streams are analyzed by an HP 6890 Series GC system gas chromatograph, containing two columns, Porapack R 50/80 - 8 ft x 1/8 inch and Carboxen TM 1000-15 ft x 1/8 inch, connected in series, followed by a molecular sieve. The start-up of the plant consists of the MR heating up with a temperature increase of 1°C/min, flowing a N_2 stream (~17 mL/min) at atmospheric pressure. Successively, at the set reaction temperature, the catalyst is activated by feeding a binary mixture N_2/H_2=7.55/1 for24 h (volume flow rate ~ 35mL/min). Prior to the reaction tests, the membrane permeative characteristics were analyzed in permeation tests with pure gases of interest (H_2 and N_2). At the end of each reaction tests cycle, the catalyst was regenerated for 2 hour by means of the same procedure followed for the catalyst activation.

Figure 2: Dense self-supported Pd-Ag membrane.

The MR was evaluated using different indexes (eqs. 4, 5 and 6) in order to assess the degree of reaction progress and membrane performance:

Conversion [%]

$$J_{H_2} = \frac{Pe^o}{\delta}\exp\left(-\frac{E_a}{RT}\right)\left(P_{H_2ret}^{0.5} - P_{H_2per}^{0.5}\right) \quad (4)$$

Yield [%]

$$Y_{H2} = \frac{H_{2ret} + H_{2per}}{3CH_{4in}} \cdot 100; \quad Y_{H2} = \frac{H_{2ret} + H_{2per}}{6EtOH_{in}} \cdot 100; \quad (5)$$

Hydrogen recovery [%]

$$R_{H2} = \frac{H_{2per}}{H_{2ret} + H_{2per}} \cdot 100 \quad (6)$$

where, X_{CH4} is the methane conversion, CH_{4in} and CH_{4out} in and out methane molar flow rates, X_{EtOH} ethanol conversion, $EtOH_{in}$ and $EtOH_{out}$ in and out ethanol molar flow rates, Y_{H2} hydrogen yield, R_{H2} hydrogen recovery, H_{2ret} and H_{2per} hydrogen molar flow rates in the permeate and retentate, respectively.

3. RESULTS AND DISCUSSION

3.1. Pure Gas Permeation Tests

Permeation tests were conducted with pure hydrogen and nitrogen on the dense membranes in thetemperature range between 350 and 450°C, setting a constant pressure in the permeate side at 100 kPa and between 150 and 300 kPain the retentate side. In the whole experimental campaign, no N_2 permeation through the membrane was observed, confirming the full hydrogen perm-selectivity of the membrane. As a

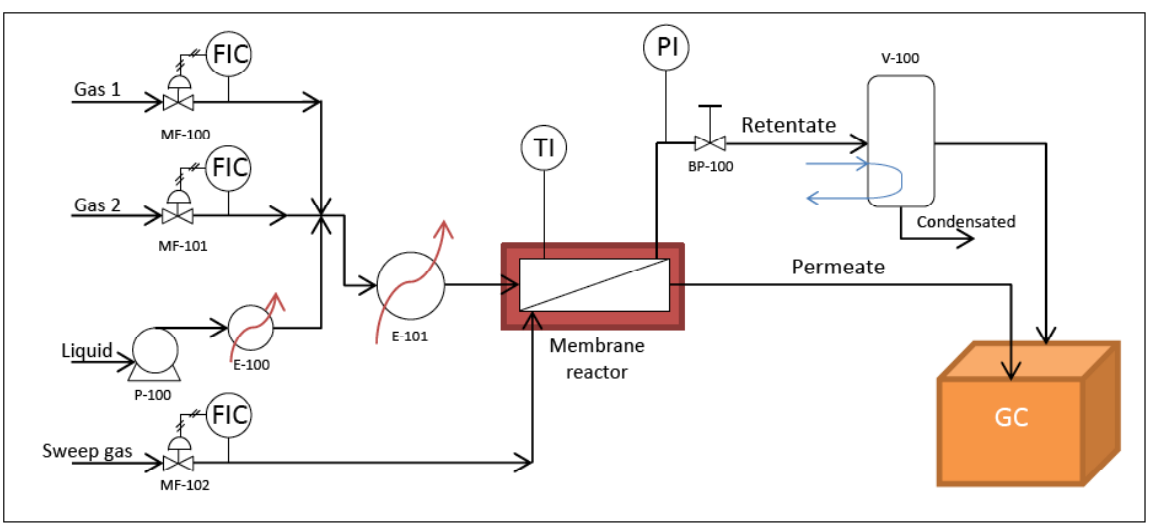

Figure 3: Scheme of the experimental plant.

consequence, the hydrogen permeation through the membrane was described by Fick-Sieverts law (eq. 7):

$$J_{H_2} = \frac{Pe}{\delta}\left(P_{H_2ret}^{0.5} - P_{H_2perm}^{0.5}\right) \quad (7)$$

In the latter expression, the hydrogen permeating flux (J_{H_2}) is proportional to the permeability of hydrogen through the membrane (Pe) and to the difference of the hydrogen partial pressure square roots between retentate and permeate sides $\left(P_{H_2ret}^{0.5} - P_{H_2per}^{0.5}\right)$, while it is inversely proportional to the membrane thickness (δ).

The Figure **4** shows the hydrogen permeating flux as a function of the driving force, while the slope of the linear regression of the experimental points represents the value of Pe/δ at a specific temperature. The permeation of hydrogen through the membrane takes place as a solution/diffusion mechanism and the linear regression well matched the experimental points with the R^2 around 1 for all the temperatures considered in the experiments. Obviously, the higher the temperature the higher the hydrogen permeating flux because of the dependency of Pe on the temperature.

The Pe is an intrinsic property of the membrane and depends on the temperature, according to the Arrhenius law (eq. 8):

$$Pe = Pe^o \exp\left(-\frac{E_a}{RT}\right) \quad (8)$$

where Pe^0, Ea, T and R are the pre-exponential factor, the activation energy, temperature and universal gas constant, respectively. By combining the eqs. (7) and (8), it is possible to obtain the Richardson's law (eq. 9):

$$J_{H_2} = \frac{Pe^o}{\delta}\exp\left(-\frac{E_a}{RT}\right)\left(P_{H_2ret}^{0.5} - P_{H_2perm}^{0.5}\right) \quad (9)$$

where, Pe^0 and Eaparameters were calculated graphically(see Figure **5**), obtaining Pe° = 6.82 10^{-6}mol/m·s·kPa$^{0.5}$(calculated by the exponential of the intercept value of Figure **5**) and Ea = 13.412 J/kmol (calculated by the slope value of Figure **5**).

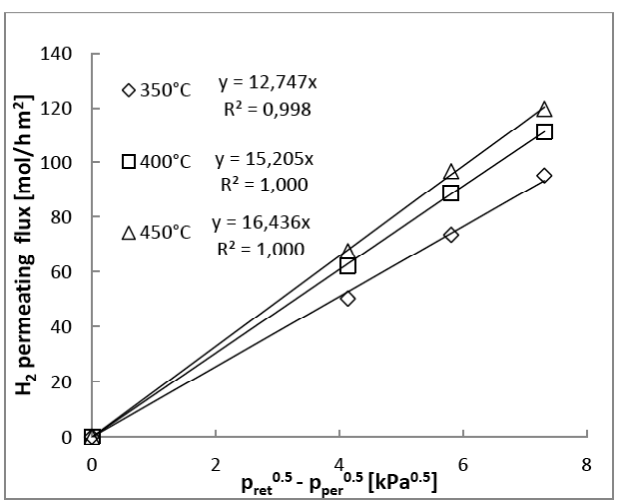

Figure 4: Hydrogen permeating flux vs driving force for the dense Pg-Ag membrane.

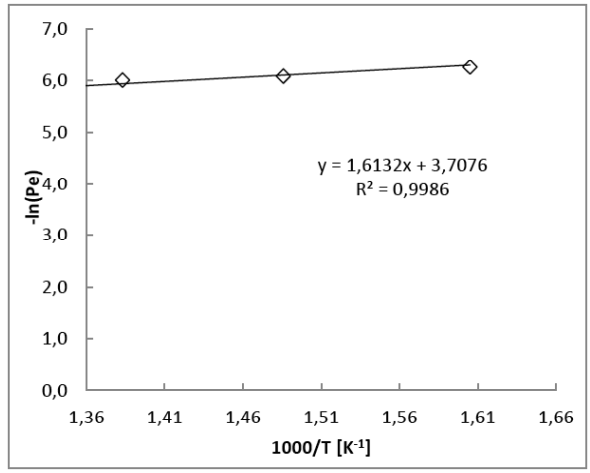

Figure 5: Arrhenius law.

3.2. Reaction Test

3.2.1. Biogas Steam Reforming

Biogas steam reforming reaction was conducted at 450°C, H_2O/CH_4feed molar ratio = 4/1, GHSV =2370 h^{-1}, 100 kPa as permeate pressure, from 200 to 350 kPa as reaction pressure, sweep gas (N_2) = 28.55 mL/min and countercurrent configuration with respect to feed.

During the reaction tests, the Pd-Ag membrane removed as much as possible the produced hydrogen from the reaction zone towards the permeation side and, according to Le Chatelier's principle (shift effect), this increased the products formation. A higher reaction pressure led to a growing hydrogen recovery (Figure **6**) due to a greater hydrogen permeation driving force. In this case, an increase of the reaction pressure of 150 kPa (from 200 to 350kPa) improved the hydrogen recovery of about 150%, even though a slight increase in CH_4conversion was observed at higher pressures (Figure **6**). By analyzing the compositions of the retentate stream (see Figure **7**), the percentage of hydrogen decreased as the reaction pressure increased because of an enhanced hydrogen recovery in the permeate stream. The hydrogen yield showed a costant trend with a value of about 40% (Figure **8**).

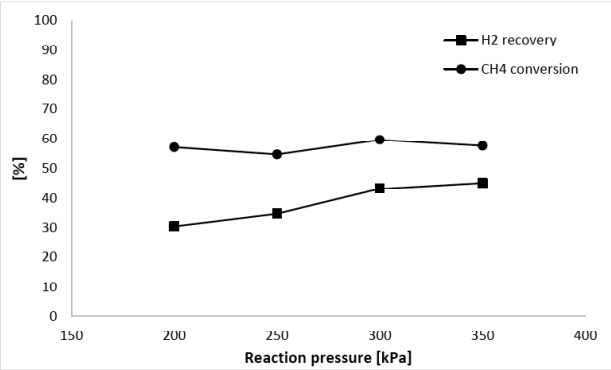

Figure 6: Effect of reaction pressure on CH_4 conversion and H_2 recovery during biogas steam reforming at 450°C, H_2O/CH_4 feed molar ratio = 4/1, GHSV =2370h^{-1}, sweep gas (N_2) = 28.55 mL/min, countercurrent configuration.

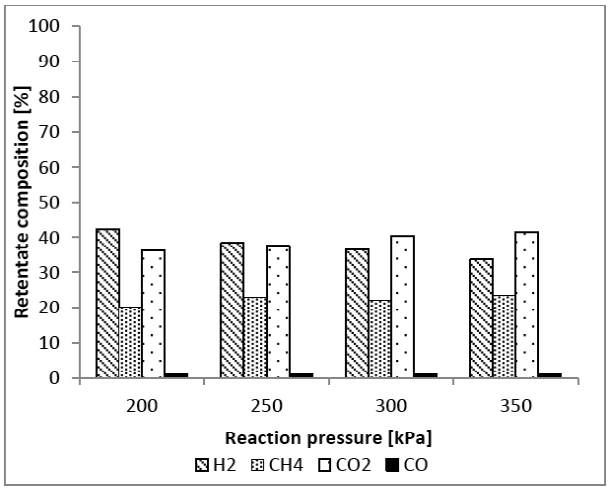

Figure 7: Effect of reaction pressure on retentate composition during biogas steam reforming at 450 °C, H_2O/CH_4 feed molar ratio = 4/1, GHSV =2370h^{-1}, sweep gas (N_2) = 28.55 mL/min, countercurrent configuration.

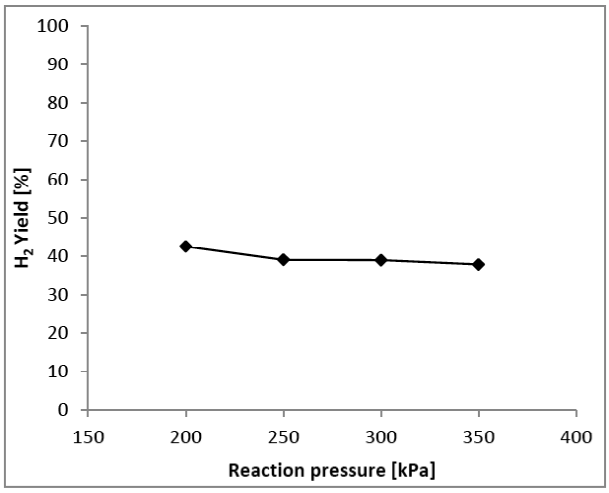

Figure 8: Effect of reaction pressure on H_2 yield during biogas steam reforming at 450°C, H_2O/CH_4 feed molar ratio = 4/1, GHSV =2370h^{-1}, sweep gas (N_2) = 28.55 mL/min, countercurrent configuration.

3.2.2. Bioethanol Steam Reforming

The bioethanol steam reforming reaction was studied starting from the evaluation of the temperature influence, performing the MR at 300 kPa and 100 kPa as reaction and permeate pressures, respectively, GHSV=800 h^{-1}, sweep gas (N_2) flow rate = 28.55 mL/minand countercurrent configuration.

Ethanol conversion increased at higher temperature due to both the higher reaction rate and hydrogen permeability (Figure **9**), resulting in an enhanced hydrogen yield (about 2 times greater with an increase of 50°C). As stated previously, higher temperatures favor an enhancement of the hydrogen permeation through the membrane, positively affecting the hydrogen recovery.

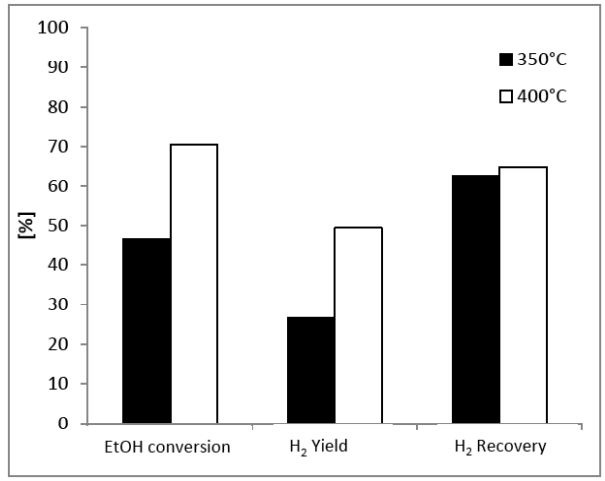

Figure 9: Effect of temperature reaction on performance indexes during bioethanol steam reforming at300 kPa, GHSV=800 h^{-1}, in the presence of sweep gas (N_2 = 28.55 mL/min) and countercurrent configuration.

Then, setting the MR at 400°C, we analyzed the reaction pressure effect on the MR performance, which was compared to those of a traditional reactor (TR) exercised at the same MR experimental conditions. The reaction pressure has a key role, as it influences positively the hydrogen permeation through the membrane, although it affects negatively the reaction, being thermodynamically un-favored at higher pressures. Indeed, the steam reforming of ethanol proceeds with an increase of the moles number and the disadvantage caused by a pressure increase was present in both the reactors (MR and TR), although the MR showed better conversion because of the benefit on the hydrogen permeation driving force (shift effect), Figures **10** and **11**. This was reflected particularly in the hydrogen recovery results (Figure **12**), which showed an opposite trend with respect to the conversion, owing to a higher hydrogen permeation driving force. In

Figure **13**, the permeated hydrogen flow rate is shown. The best result was 0.32 L/h of pure hydrogen reached at 400 °C and 300kPa.

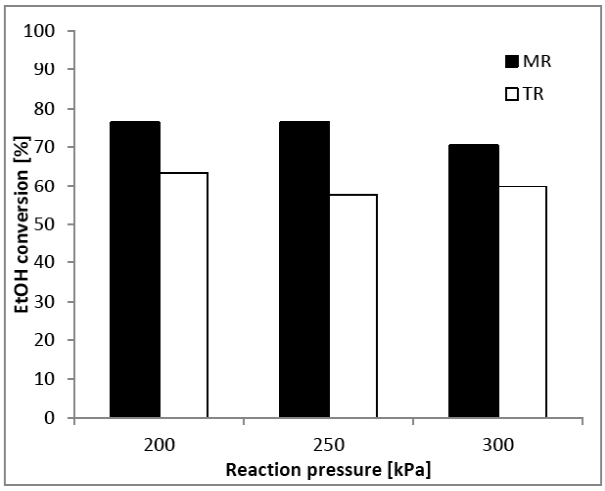

Figure 10: Effect of reaction pressure on the MR and TR performance during bioethanol steam reforming at 400°C, GHSV=800 h^{-1}; for the MR, sweep gas (N_2) flow rate = 28.55 mL/min and countercurrent configuration.

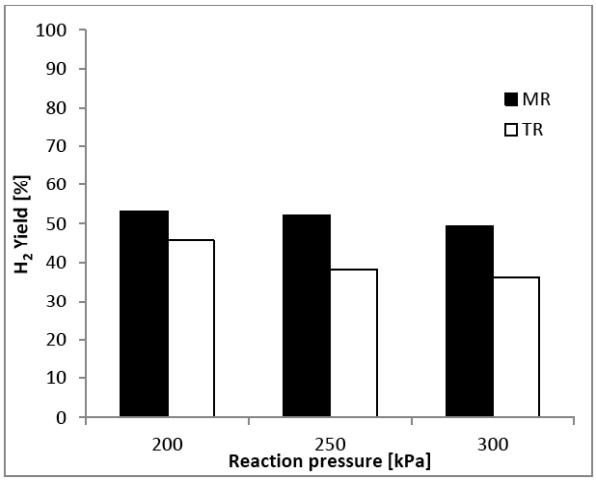

Figure 11: Effect of reaction pressure on the MR and TR performance during bioethanol steam reforming at 400 °C, GHSV = 800 h^{-1}; for the MR, sweep gas (N_2) flow rate = 28.55 mL/min and countercurrent configuration.

CONCLUSION

In this work, we performed the steam reforming reaction of synthetic biogas and bioethanol mixtures using a dense self-supported Pd-Ag membrane allocated in a MR. The best results concerning biogas steam reforming were reached at 350 kPa and 450 °C whit about 40% of pure hydrogen recovered in the permeate and 60% methane conversion, using a H_2O/CH_4 feed molar ratio = 4/1, GHSV=2370 h^{-1}, in presence of sweep gas (N_2=28.55 mL/min) and countercurrent configuration. Regarding the bioethanol

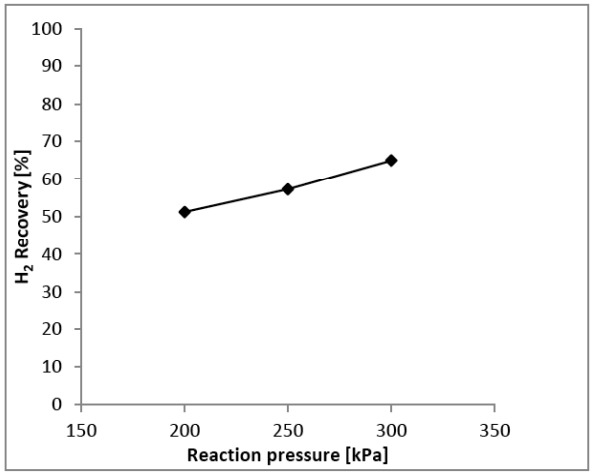

Figure 12: Effect of reaction pressure on H_2 recovery during bioethanol steam reforming exercised at 400°C, GHSV=800 h^{-1}; for the MR, sweep gas (N_2) flow rate = 28.55 mL/min and countercurrent configuration.

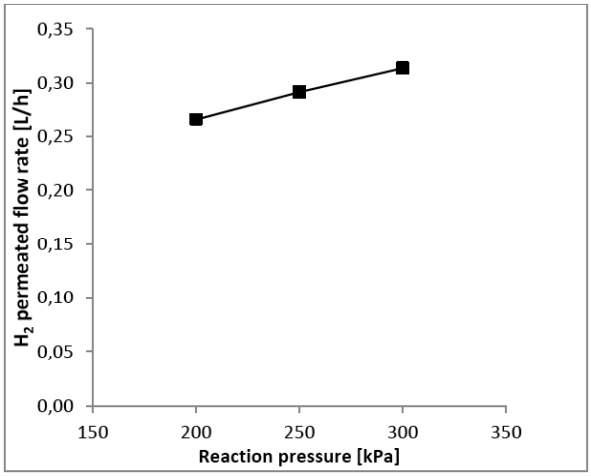

Figure 13: Effect of reaction pressure on H_2 permeated flow rate during bioethanol steam reforming exercised at 400 °C, GHSV = 800 h^{-1}; for the MR, sweep gas (N_2) flow rate = 28.55 mL/min and countercurrent configuration.

steam reforming, we obtained 70% ethanol conversion and about 65% hydrogen recovery at 400 °C, 300 kPa, H_2O/EtOH= 13/1, GHSV =800 h^{-1}, sweep gas (N_2)= 28.55 mL/min and counter-current configuration. Furthermore, we compared MR and TR at the same operating conditions, obtaining in the whole experimental campaign superior performance in the MR with respect to the TR, with the further advantage of producing pure hydrogen.

Therefore, the pure hydrogen produced in the MR during the experimental tests from synthetic renewable sources could constitute an eco-friendly and ideal energy vector. In this study, available commercial membranes in the market were used and we demonstrated the feasibility of the process at lab scale.

The challenge for us in the near future will be the scaling up of this system, meanwhile analyzing the effect of such contaminants present in real renewable sources (real biogas and bioethanol mixtures utilization) on the MR performance, also evaluating the hydrogen production cost.

NOMENCLATURE

CH_{4in} methane molar flow rate in, mol·min^{-1}

CH_{4out} methane molar flow rate out, mol·min^{-1}

Ea activation energy, J·kmol^{-1}

$EtOH_{in}$ ethanol molar flow rate in, mol·min^{-1}

$EtOH_{out}$ ethanol molar flow rate out, mol·min^{-1}

GHSV gas hourly space velocity, h^{-1}

H_{2per} hydrogen molar flow rate in permeate, mol·min^{-1}

H_{2ret} hydrogen molar flow rate in retentate , mol·min^{-1}

J_{H_2} hydrogen permeating flux, mol·m^{-2}·h^{-1}

MR membrane reactor

Pe permeability of hydrogen through the membrane, mol·m^{-1}·s^{-1}·kPa$^{-0.5}$

Pe^0 pre-exponential factor, mol/m·s·kPa$^{0.5}$

p_{H_2per} hydrogen partial pressure in permeate side, kPa

p_{H_2ret} hydrogen partial pressure in retentate side, kPa

R universal gas constant, kmol·J^{-1}· K^{-1}

R_{H_2} hydrogen recovery, %

T temperature, °C/K

TR traditional reactor

WHSV weight hourly space velocity, h^{-1}

X_{CH_4} methane conversion, %

X_{EtOH} ethanol conversion, %

Y_{H_2} hydrogen yield, %

GREEK LETTER

ΔH_r heat of reaction, kJ·mol^{-1}

δ membrane thickness, m

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