ANOVA ANALYSIS OF AN INTEGRATED MEMBRANE REACTOR FOR HYDROGEN PRODUCTION BY METHANE STEAM REFORMING

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ABSTRACT

In this research, a sensitivity analysis according the factorial design is developed for an integrated membrane reactor producing hydrogen by methane steam reaction. A similar work is not present in literature. The reactor is modelled using the Numaguci kinetic: it is more suitable to describe the system respect to the common used Xu and Froment kinetic. The reactor does not use conventional catalysts, but a Ni(10)/CeLaZr catalyst supported on SSiC ceramic foam. In ANOVA analysis, chosen factors are: inlet temperature, methane flow rate in the feed, hydrogen permeability, the thickness of membrane. The analysed responses are: hydrogen yield, carbon dioxide conversion (in term of production) and methane conversion. Results show that only inlet temperature, methane flow rate, their interaction and the thickens of membrane are significant. To improve the hydrogen production, it is better to increase inlet temperature and methane flow rate.

1. INTRODUCTION
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Hydrogen is the most promising energy vector, thanks to its high capacity of storing energy from primary sources [1]. In particular, it is the most desirable energy carriers due to its cleanness and zero emissions property: it can contribute to energy supply in environmental way, with the condition to have a system economically feasible. In addition, a high energy density of hydrogen contributes to increase the annual energy demand.

Hydrogen can be used for different purpose, as for the production of ammonia, methanol, in Fischer Tropsch synthesis, in petroleum hydrogenation [2]. Furthermore, hydrogen is consumed in fuel cells to generate electricity with high energy efficiency.

In these processes, hydrogen has several advantages over fossil fuels, ensuring a clean and more efficient combustion and producing electricity with high efficiency and environmentally friendly.

Currently, hydrogen is mainly produced from natural gas by three different chemical processes: steam reforming, partial oxidation, and autothermal reforming [3, 4]. However, the steam reforming of natural gas is still the less expensive and the most widespread industrial process. Globally, a large fraction of about 50 million tons of hydrogen produced annually is obtained via reforming of natural gas [2]. It is an endothermic process in which methane reacts with steam in presence of catalyst in the temperature and pressure range of 1073-1273 K and 5-35 bar respectively [5]. In addition to hydrocarbons, also renewable energies as biomass and water, can be used to produce hydrogen using input from renewable energy (sunlight, wind, wave, hydropower).

A high purity of hydrogen can be obtained in membrane reactors, that are getting the attention in the last years. The use of membranes allows to work at very low temperatures and pressures and to have higher conversions. In fact, steam reforming reaction for hydrogen production is limited by thermodynamic equilibrium, so high temperature and pressure are required to have high conversion and hydrogen yield. Instead, the use of membrane allows to work at temperature less than 823 K.

The steam reforming reaction is industrially operated over nickel-alumina based catalysts. Catalysts based on nickel have a high activity, low cost but quickly lose their activity due to coke formation [6]. To overcome this problem, precious metals (Ru, Rh, Pt, Pd, etc.), alkaline earth metals (Mg, Ca, Ba, Sr, etc.) and rare earth metals (La, Ce, Pr, etc.) have been tested as additives to enhance coke resistance [7]. In membrane reactor, catalyst such as Ru instead of Ni, ensures higher performances [8, 9].

Recently, metallic and ceramic foam catalysts (a porous metal inside which many pores are formed) with a high thermal conductivity, an uniform thermal dispersion and a high mechanical strength have been studied widely for the reaction of steam reforming producing hydrogen. These types of catalysts allow to have a higher temperature distribution and lower pressure drops. In fact, the high specific surface area can improve heat and mass transfer, while the porous structure can minimize pressure drops [10, 11].

Different works are reported in literature about the membrane reactor for methane steam reforming with the aim to produce hydrogen [12, 13]. In these works, different reactor configurations are shown. An external or embedded membrane configuration is analysed by De Falco et al. [14]. Borgognoni et al. [15] propose a separate membrane module, in a so called “open architecture”. In other configurations, the solar heat is exploited indirectly through molten salts heat transfer fluid [16, 17] improving the thermal efficiency of the process. It is an environmentally system that can produce hydrogen reducing carbon dioxide emissions and saving other combusted fraction of methane [18, 19].

Mathematical modeling of membrane reactors is an active area of research in developing: it is an effective tool for the design, evaluation and optimization of any reactors and reaction processes.

In this research, an ANOVA analysis for an integrated membrane reactor producing hydrogen by reforming of natural gas is developed. Compared to other systems the palladium membrane is inside and integrated to the reactor, improving its performance. Molten salts ensure the heat for the reaction. It is the first integrated membrane reactor at pilot plant that use a ceramic foam catalyst (Ni(10)/CeLaZr catalyst supported on SSiC ceramic foam) for steam reforming, in Europe. Better performances are then obtained. This integrated membrane reactor is modelled in Matlab using the Numaguci kinetic by Leonzio [2]. The aim of ANOVA analysis is to optimize and find factors influencing the system. Inlet temperature, methane flow rate, hydrogen permeability and the thickness of membrane are the chosen factors. The analyzed responses are methane and carbon dioxide conversion and hydrogen yield. Future researches should verify the obtained results in the pilot plant. Also, a response surface methodology can be applied to find more accurate optimal solutions.

1.1. Materials and method

1.1.1 Modelling of integrated membrane reactor

The analysed integrated membrane reactor for methane steam reforming is shown in Fig. 1: a membrane tube, where sweeping gas flows to drag the permeate hydrogen, is inside the shell, a steel tube. Steam is used as sweeping gas, while membrane is in palladium. This system ensures a recovery of high-grade hydrogen with high conversion of methane at relative low temperature. Table 1 shows the dimensions of the reactor. In the feed, the S/C ratio is equal to 1:3 and Ni(10)/CeLaZr catalyst supported on SSiC ceramic foam is used for the reaction. Temperature and pressure are respectively equal to 823 K and 10 atm. The isothermal conditions are obtained using externally molten salts, a binary mixture of $NaNO_3$/KNO_3 (60/40 %w/w), that is able to exploit the solar energy.

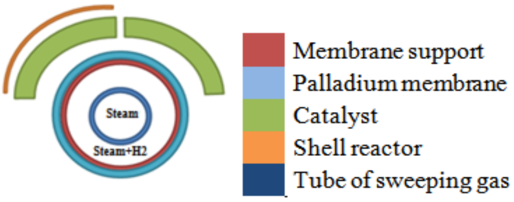

Fig. 1. Section of the integrated membrane reactor [2]

The flow rate of molten salts is equal to 800 kg/h and the membrane area is 0.57 m^2, with a length of 748 mm. The number of tubes is 10 with a length of 900 mm, 1 tube passage. The catalyst volume is 9.6 L and the heat of reaction is equal to 1870 kcal/h. The overall heat transfer coefficient is about 90 $kcal/hm^2{}^\circ C$. The flow rate of feed, permeate and retentate are respectively equal to: 4.59 kg/h. 1.81 kg/h, 4.36 kg/h.

Table 1 Dimensions of the integrated membrane reactor [2]

	Internal diameter (mm)	External diameter (mm)
Membrane support	10	14
Palladium membrane	n.a.	n.a.
Catalyst	16	40
Shell reactor	42.7	48.3
Tube of sweeping gas	6	9

Inside the reactor, the methane steam reforming reactions involves the following reactions, the reforming reaction (see Eq. 1) and the water gas shift reaction (see Eq. 2):

$$CH_4 + H_2O \leftrightarrow CO + 3 \cdot H_2 \qquad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (2)$$

The enthalpy of reaction are respectively equal to 206 kJ/mol and -41 kJ/mol [20]. Generally, the thermodynamic system allows to reach acceptable conversion only for reaction temperature exceeding 973-1023 K, but in this case, the use of membrane allows to have a high conversion at lower temperature [21]. The reactions are modelled according to Numaguci kinetic and not to common used Xu and Fromant kinetic. A better description of the reactor is obtained [2]. According to Numaguci kinetic, the surface reaction is the rate-determining step for methane steam reforming reaction. Considering a hybrid rate equation of Langmuir-Hinshelwood and the power law type the following reaction rates as function of partial pressure are obtained [22]:

$$r_{rf} = k_R{}^o \cdot \exp\left(-\frac{E_R}{R \cdot T}\right) \cdot \frac{\left(P_{CH4} - P_{CH4(eq)}\right)}{\left(P_{CH4}^{\alpha_R} \cdot P_{H2O}^{\delta_R}\right)} \qquad (3)$$

$$r_{sf} = k_S{}^o \cdot \exp\left(-\frac{E_S}{R \cdot T}\right) \cdot \frac{\left(P_{CO} - P_{CO(eq)}\right)}{\left(P_{CH4}^{\alpha_s} \cdot P_{H2O}^{\delta_s}\right)} \qquad (4)$$

where r_{rf} is for steam reforming reaction, r_{sf} is for shift reaction, $P_{CH4(eq)}$ and $P_{CO(eq)}$ are pressure at equilibrium conditions and R is the constant of universal gas, T is temperature in K. Table 5 shows the values of parameters for the above reaction rates [22]:

Table 5 Values of fitted parameters for Numaguci kinetics

Fitted parameters	
$k^o{}_R$	$92 \cdot 10^8$
E_R (kJ/mol)	106.87
α_R	0
δ_R	0,596
$k^o{}_S$	$8{,}688 \cdot 10^5$
Es (kJ/mol)	54.531
α_S	0
δ_S	0

1.1.2 Modelling of ANOVA analysis

The estimation of main and interaction effects is developed by ANOVA analysis (analysis of variance); it is determined if effects and interactions among the investigated factors are significant respect to experimental error (σ_ε). Main factors are evaluated by Yates's algorithm through Excel 2016 software. Statistical significance is checked by F-value (Fischer variation ratio) and p-value (significant probability value). Model terms are selected or rejected based on probability value within 95% of confidence interval (or 5% significance level). In this research, σ_ε is evaluated by means of the mean square (MS) of interactions that are not significant. A 2^4 full factorial design with 16 simulations test is performed for this research [23]. A mathematical model could be obtained with significant factors and the quality of the model was assessed by coefficient of determination R^2. R^2 represents a pure correlation between measured and predicted values, and it is indicative of response variation explained by model. One of the most important advantages of this method is the limited number of experiments necessary to identify the best solution. The analysed factors are: inlet temperature, methane flow rate, hydrogen permeability, thickness of membrane. The chosen response to understand the behaviour of the reactor are: hydrogen yield, methane conversion and carbon dioxide conversion (in term of production).

1.1.2 Material balances of the integrated membrane reactor

The material balances along the length of reactor are developed for components in order to know their flow rate. For methane and carbon dioxide (see Eq. 5-6):

$$\frac{dF_{CH4}}{dz} = \rho \cdot \Omega \cdot \left(-r_{rf} \cdot \eta_{rf}\right) \tag{5}$$

$$\frac{dF_{CO2}}{dz} = \rho \cdot \Omega \cdot \left(+r_{sf} \cdot \eta_{sf}\right) \tag{6}$$

where Ω is reactor section, ρ is catalyst density, η_{rf}, η_{sf}, are the effectiveness factors of steam reforming reaction and shift reaction respectively, z is the length of the reactor, F_{CH4} and F_{CO2} are the flow rate of methane and carbon dioxide respectively. The hydrogen flow through the membrane is expressed by the following relationship (see Eq. 7):

$$\frac{dF_{H2,perm}}{dz} = J_{H2} \cdot 2 \cdot \pi \cdot (r_{\circ} + \delta) \tag{7}$$

with r_o is the inner radius of membrane, δ is the thickness of membrane, z is reactor length, $P_{H2,perm}$ is hydrogen flow rate through membrane, J_{H2} is hydrogen permeation through palladium membrane according the Sieverts' law (the rate of hydrogen permeation can therefore be expressed as a function of the difference in the square root of hydrogen partial pressures on both sides of the membrane) (see eq. 8) [24]:

$$J_{H2} = \frac{Q_{pd}}{\delta} \cdot \left(P_{H2,r}^{0.5} - P_{H2,p}^{0.5}\right) \tag{8}$$

where δ is the thickness of membrabe, Q_{pd} is the permeation of hydrogen, $P_{H2,r}$ and $P_{H2,p}$ are hydrogen pressure in permeate and reaction side. From the above material balances, the methane conversion (consumption), the carbon dioxide conversion (production) and the hydrogen yield, can be obtained respectively according the following relations (see Eq. 9-11):

$$X_{CH4} = \frac{F_{CH4}^{o} - F_{CH4}}{F_{CH4}} \cdot 100 \tag{9}$$

$$X_{CO2} = \frac{F_{CO2}}{F_{CH4}^{o}} \cdot 100 \tag{10}$$

$$Y_{H2} = \frac{F_{H2,perm}}{F_{CH4}^{o}} \tag{11}$$

where $F_{CH4}°$ is the methane flow rate in the feed of reactor, X_{CH4} is methane conversion, X_{CO2} is carbon dioxide conversion, Y_{H2} is the hydrogen yield, F_{CH4} is methane flow rate.

2. RESULTS

An ANOVA analysis is carried out for the integrated membrane reactor. Inlet temperature, methane flow rate in the feed, hydrogen permeability through the membrane and the thickness of membrane are the chosen factors. The analyzed responses are methane and carbon dioxide conversion and hydrogen yield. Table 2 shows the chosen factors and the values of their levels.

Table 2. Factors and values of levels chosen in ANOVA analysis

Code	**Factors**	**Levels**	
		(-)	**(+)**
A	Inlet temperature (K)	550	815
B	Methane flow rate (kmol/h)	0.1	1

C	Hydrogen permeability (m^{3}umatm$^{0.5}$/m^2)	1000	3600
D	Thickness of membrane (m)	0.003	0.02

Fig. 2 shows the results of ANOVA analysis with significant factors.

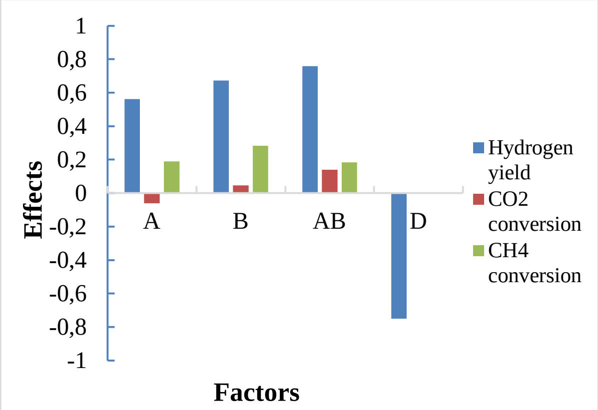

Fig. 1. Results of ANOVA analysis (Factor A: Temperature (K), Factor B: Methane flow rate (kmol/h), Factor C: Hydrogen permeability (m^{3}umatm$^{0.5}$/m^2), Factor D: Thickness of membrane (m)·[10^{-4}])

Table 3, 4, 5 summarize the statistical results of ANOVA analysis for hydrogen yield, carbon dioxide conversion and methane conversion respectively obtained in all tests. Factors with a probability higher than 5% are significant.

Table 3 Result of ANOVA analysis for hydrogen yield (Factor A: Temperature (K), Factor B: Methane flow rate in the feed (kmol/h), Factor C: Hydrogen permeability (m^{3}umatm$^{0.5}$/m^2), Factor D: Thickness of membrane (m)·[10^{-4}])

Factors	Effects	Probability
A	5.63E-01	2.34E-17
B	6.73E-01	1.14E-17
AB	7.59E-01	7.05E-18
C	-2.50E-05	3.74E-01
AC	0.00E+00	1.00E+00
BC	2.50E-05	3.74E-01
ABC	0.00E+00	1.00E+00
D	-7.50E-05	3.99E-02
AD	5.00E-05	1.16E-01
BD	-2.50E-05	3.74E-01
ABD	5.00E-05	1.16E-01
CD	2.50E-05	3.74E-01
ACD	0.00E+00	1.00E+00
BCD	-2.50E-05	3.74E-01
ABCD	0.00E+00	1.00E+00

Table 4 Result of ANOVA analysis for carbon dioxide conversion (Factor A: Temperature (K), Factor B: Methane flow rate in the feed (kmol/h), Factor C: Hydrogen permeability (m^{3}umatm$^{0.5}$/m^2), Factor D: Thickness of membrane (m)·[10^{-4}])

Factors	Effects (%)	Probability
A	-6.05E-02	1.75E-13
B	4.64E-02	5.07E-13
AB	1.39E-01	6.26E-15
C	-2.50E-05	3.74E-01
AC	2.50E-05	3.74E-01
BC	2.50E-05	3.74E-01
ABC	-2.50E-05	3.74E-01
D	-2.50E-05	3.74E-01
AD	2.50E-05	3.74E-01
BD	2.50E-05	3.74E-01
ABD	-2.50E-05	3.74E-01
CD	2.50E-05	3.74E-01
ACD	-2.50E-05	3.74E-01
BCD	-2.50E-05	3.74E-01
ABCD	2.50E-05	3.74E-01

Table 5 Result of ANOVA analysis for methane conversion (Factor A: Temperature (K), Factor B: Methane flow rate in the feed (kmol/h), Factor C: Hydrogen permeability (m^{3}umatm$^{0.5}$/m^2), Factor D: Thickness of membrane (m)·[10^{-4}])

Factors	Effects (%)	Probability
A	1.89E-01	3.02E-09
B	2.83E-01	6.08E-10
AB	1.84E-01	3.43E-09
C	-7.50E-04	4.50E-01
AC	1.35E-03	2.07E-01
BC	7.50E-04	4.50E-01
ABC	-1.35E-03	2.07E-01
D	-9.25E-04	3.61E-01
AD	1.63E-03	1.44E-01

BD	9.25E-04	3.61E-01
ABD	-1.63E-03	1.44E-01
CD	-3.50E-04	7.16E-01
ACD	-2.50E-04	7.94E-01
BCD	3.50E-04	7.16E-01
ABCD	2.50E-04	7.94E-01

Results show that for hydrogen yield, inlet temperature and methane flow rate in the feed has a positive effect.

This is because of the endothermic nature of reaction. Increasing the temperature provides more heat for the process, and leads the reactions to move forward, which results to more hydrogen production [21, 25]. The positive effect of methane flow rate on hydrogen production is confirmed by Nobandegani et al. [21]. In this way the hydrogen production increases by decreasing the $(S/C)_{in}$ ratio. Also, the interaction of these factor A and B is positive. Interaction AB on hydrogen yield has the highest effect. The thickness of membrane has a negative effect, according the relation for hydrogen flux through membrane.

For methane conversion, inlet temperature and interaction between factor A and B have a positive effect. In fact, with a higher hydrogen production there is also a higher methane conversion. Meanwhile, the methane flow rate has a negative effect, because for a fixed conversion a more unreacted methane is present increasing its flow rate.

For carbon dioxide conversion, in term of production, only factor A has a negative effect (the single reaction is exothermic so is not favourite at higher temperature) while factor B and interaction AB have a positive effect. Increasing the inlet methane flow rate, a higher carbon dioxide is produced. This effect is enhanced in interaction with factor A. In fact, with higher methane flow rate, the reaction is shift towards to products, so a higher carbon monoxide is available to produce carbon dioxide.

With significant factors and interactions, a mathematical model for hydrogen yield, carbon dioxide and methane conversion are developed as following relations (see Eq. 12-14):

$$y_{YH2} = 2.75 + 0.28 \cdot X_1 + 0.33 \cdot X_2 + 0.38 \cdot X_1 \cdot X_2 - 0.000038 \cdot X_4 \quad (R^2 = 0.99) \qquad (12)$$

$$y_{XCO2} = 0.28 - 0.03 \cdot X_1 + 0.02 \cdot X_2 + 0.07 \cdot X_1 \cdot X_2 \quad (R^2 = 0.98) \qquad (13)$$

$$y_{XCH4} = 0.85 + 0.09 \cdot X_1 + 0.14 \cdot X_2 + 0.09 \cdot X_1 \cdot X_2 \quad (R^2 = 0.99) \qquad (14)$$

where X_1 is factor A, X_2 is factor B, $X_1 \cdot X_2$ is interaction AB, y_{YH2} is hydrogen yield, y_{XCO2} is carbon dioxide conversion, y_{XCH4} is methane conversion. For the three equations, values of R^2 near to unit ensure a good agreement between the experimental and predicted data. The mentioned models can be considered as a reliable model for methane steam reforming simulation and optimization in an integrated membrane reactor.

Fig. 3 shows the surface plot of hydrogen yield as function of inlet temperature and methane flow rate. It is evident the presence of interaction with a positive effect: the positive effect of factor A is enhanced in interaction with factor B. The thickness of membrane is set to 0.02 m.

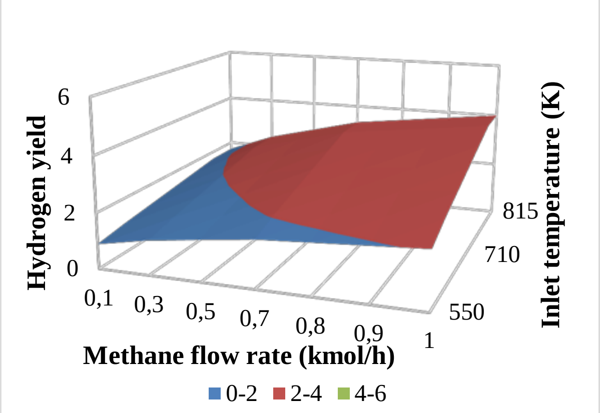

Fig. 2. Surface plot of hydrogen yield as function of inlet temperature and methane flow rate for the thickness of membrane equal to 0.02 m.

Fig. 4 shows the surface plot of carbon dioxide conversion as function of inlet temperature and methane flow rate. In this case, an interaction between the two factors is also present, too, as the plot shows.

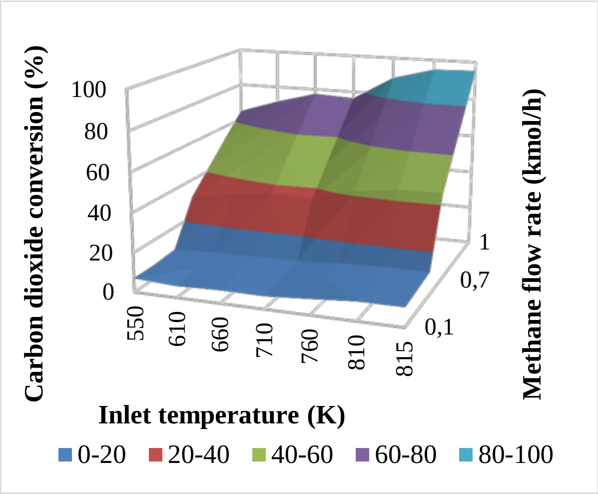

Fig. 3. Surface plot of carbon dioxide conversion as function of inlet temperature and methane flow rate.

Fig. 5 shows the surface plot of methane conversion as function of inlet temperature and methane flow rate.

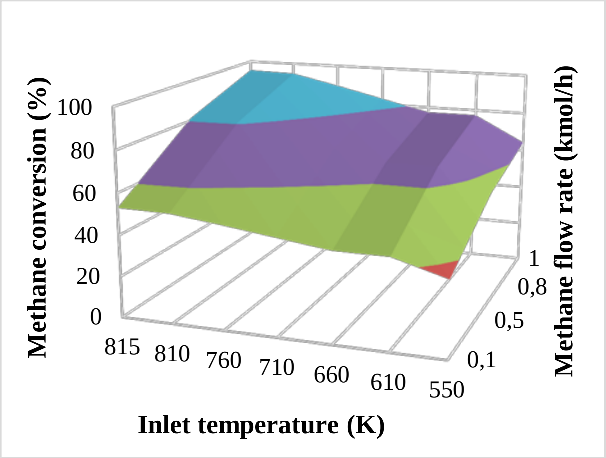

Fig. 4 Surface plot of methane conversion as function of inlet temperature and methane flow rate.

The same considerations are for this plot. Results in the plots show that the optimal operating conditions are obtained with higher temperature and methane flow rate, respectively equal to 815 K and 1 kmol/h.

The better condition of the process with inlet temperature and methane flow rate at higher level is shown by the test of two levels for interaction AB. Considering all analysed responses, as shown in Fig. 6, with factor A at higher level a higher efficiency of the system is also ensured with factor B also at higher level. In addition, in this condition, the process has a higher stability because a lower variability is obtained changing the level of factor B when factor A is at higher level.

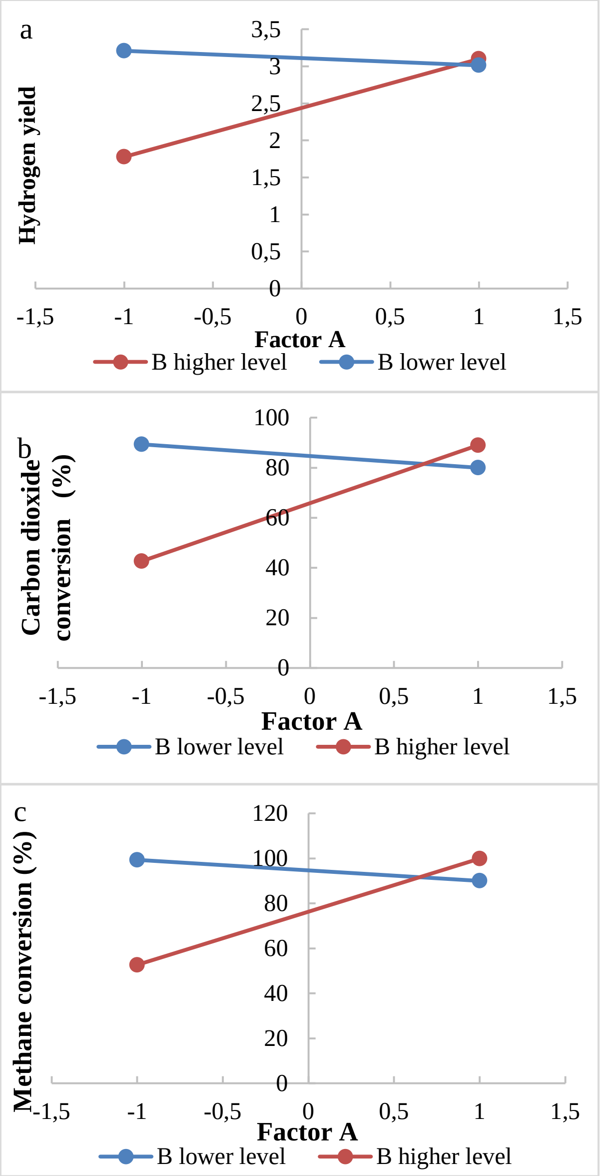

Fig. 5 Test of two levels for interaction AB for different responses: a) hydrogen yield, b) carbon dioxide conversion, c) methane conversion

Even if factor D is a significant factor with a negative effect on hydrogen yield, the effect is so little that it can be overlooked, as shown in Fig. 7, where the hydrogen yield as function of membrane thickness is reported. For high hydrogen flow rate the effect is not so significative.

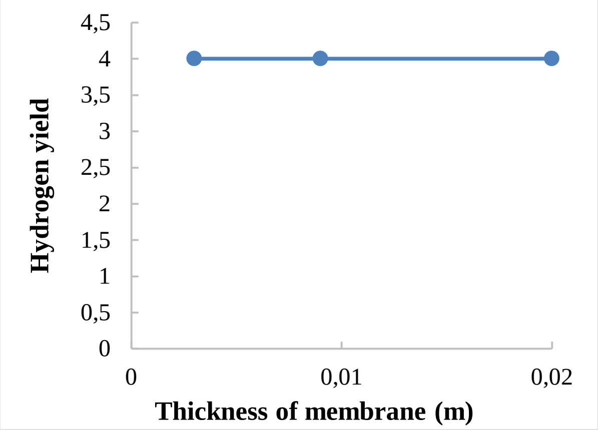

Fig. 6 Hydrogen yield as function of the thickness of membrane

The optimal operating conditions of the process can be obtained with inlet temperature equal to 815 K, methane flow rate equal to 1 kmol/h, hydrogen permeability equal to 3600 $m^3umatm^{0.5}/m^2$, chosen to have better performance of membrane and a thickness equal to 0.003 m in order to reduce the costs.

3. CONCLUSIONS

An ANOVA analysis for an innovative integrated membrane reactor producing hydrogen by methane steam reforming is carried out. Inlet temperature, methane flow rate in the feed, hydrogen permeability through membrane and the thickness of membrane are the chosen factors. The analyzed responses are methane and carbon dioxide conversion and hydrogen yield. Factors that can improve the hydrogen production are found. The thickness of membrane has a very small effect on hydrogen yield, and it can be neglected in the presented model.

The optimal operating conditions of the process can be obtained with inlet temperature equal to 815 K, methane flow rate in the feed equal to 1 kmol/h, hydrogen permeability equal to 3600 $m^3umatm0.5/m^2$ and a thickness equal to 0.003 m.

Future researches should be regarding the development of response surface methodology in order to have an accurate surface plot and modelling of hydrogen yield for the optimization.

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