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Highlighting of the impact of periodic operations on the performance of methanol steam reforming process for pure hydrogen generation

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Abstract - In this paper, we focus to highlighting the positive role of periodic operation which can be played for performance improvement of a hydrogen separator reactor integrating a palladium membrane. For this subject, a mathematical approach describing the pure hydrogen production and its pumping during methanol steam reforming process is developed to simulate the effect of the reactor inlet feed and of sweeping gas on reactor performance. The main findings show that the reactor responses exhibit a periodic phenomenon. So, in order to achieve a yield improvement higher than that obtained under the steady state conditions, it is necessary to intensify the process by using a periodic operation. Therefore, when the reactor is simultaneously forced by running the feed composition in the reaction side and by the sweeping gas in the permeate side using a symmetric square function, the magnitude of improvement of methanol conversion and pure hydrogen recovery are higher than that achieved at steady state operation. This is due to the dual effect synergistic, which is could be brought by the potential periodic mode of the inputs coupling.

Résumé - Dans cet article, nous focalisons sur la mise en évidence de l'effet positif du fonctionnement périodique qui peut être impliqué pour l'amélioration des performances d'un réacteur-séparateur d'hydrogène qui fait intégrer une membrane à base de palladium. Pour cet objectif, une approche mathématique décrivant la production d'hydrogène pur et son processus de pompage pendant le vaporeformage du méthanol est développée pour simuler l'effet de la composition d'alimentation du réacteur et des gaz de balayage sur les performances du réacteur. Les principaux résultats obtenus montrent que les réponses du réacteur obtenues présentent un phénomène périodique. Ainsi, afin d'obtenir une amélioration du rendement supérieure à celle obtenue dans les conditions stationnaires, il est impératif d'intensifier le processus par l'utilisation d'une opération périodique. Par conséquent, lorsque le réacteur est forcé par l'exécution simultanée de la composition d'alimentation du côté réaction et du gaz de balayage du côté perméat selon une fonction carrée symétrique, le niveau d'amélioration de la conversion du méthanol et de l'hydrogène récupéré est supérieur à celle obtenue à l'état stationnaire. Ceci est dû à l'effet dualiste synergique, ce qui pourrait être apporté par le potentiel du couplage des paramètres manipulés en mode périodique.

Keywords: Pure hydrogen - Membrane reactor - Hydrogen generation - Methanol steam reforming.

1. INTRODUCTION

Environmental policy constraints impose some limits for energy conversion by its use in different sector such as the automotive one. Thus, the reduction of consuming of oil-derived products and to find other clean-energy option represents a special

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challenge. This is encouraged also by the limited reserves of oil, so a number of alternative fuels among which hydrogen are being considered. The sources of hydrogen are vast and its production processes are as diverse [1, 2].

It can be produced from almost any carbon source ranging from natural gas and oil products to coal and biomass products by various technologies such as steam reforming [1], [3-5]. Hence hydrogen represents a key for creating flexibility for the chemical industry. Hydrogen is a versatile energy carrier that can be used to power nearly every end-use energy need.

Actually, hydrogen energy could find significant applications in the transportation sector [3] and distributed power generation. Because of its high efficiency and environmentally friendly sources of electrical energy, the fuel cell is often seen as one of the main drivers for hydrogen as a fuel of the future [6]. So the fuel cells are a viable alternative for clean energy generation. They are fueled by pure hydrogen, and require a very high purity of hydrogen to avoid the catalyst deactivation. This is achieved if solid carbon is produced during the reactions for it will deactivate the catalyst of the fuel cells and hence, degrading its performance [7].

Except for the case of Direct Methanol Fuel Cells (DMFC), the ideal fuel for Polymer Electrolyte Membrane Fuel Cells (PEMFC) is pure hydrogen, with less than 50 ppm carbon monoxide, as imposed by the poisoning limit of the platinum fuel cell catalyst [8, 9], which imposes the need to produce ultrapure hydrogen. Absolutely the membrane reactor can guarantee this objective, but it must produce significant amounts. For this reason the process intensification is essential. In general, improved performance can be obtained by several ways [10], such as acting on the reactor dimensions [11], reactor configuration and design and/or on the operating parameters.

In this work another alternative is used and established with a new mathematical concept which is the artificial unsteady state, created by a periodic operation [12]. The present work is pointing to study the impact of coupling of two operating parameters (steam and sweeping gas) on the endothermic methanol steam reforming reaction performed in a periodically membrane reactor and to highlighting their major role on the reactor performance, especially on yield of pure hydrogen. For this purpose, the square wave is chosen because it is the most effective [13] and it guarantees the largest possible variation from the mean value [14].

Furthermore, the variations of the molar flow rate of steam in the reaction side and of the molar flow rate of sweeping gas in the permeate side simultaneously are insured by switching of their amplitudes using a symmetric square wave function.

2. REACTOR DESCRIPTION AND MATHEMATICAL MODEL

In this section, we outline the simulation of methanol steam reforming for synthesis of pure hydrogen in a packed bed membrane reactor performed under created unsteady state conditions. Figure 1 shows the scheme of the membrane reactor under study. The process reaction scheme of methanol steam reforming, the rate equations as well as the kinetic and thermodynamic parameters used for calculations of reactions rates are presented in appendix [15-18] (**Table A1** and **Table A2**).

Reactor dimensions, operating conditions and catalyst properties are also presented in **Table A3**. For the simulation purpose, a mathematical model was developed to investigate methanol steam reforming process behavior under periodic operation conditions in a fixed bed membrane reactor to produce pure hydrogen.

The following assumptions are incorporated for the mathematical model development:

a- It is known that the isothermal operation mode represents an idealized situation when the endothermic and exothermic reactions are locally exact balanced. Hence, the heat transfer is one of the main obstacles to overcome in the production of hydrogen, especially by methanol steam reforming [19]. Because the periodic operations provoke a highly turbulent flow and suppress the gradient of concentration and temperature. Then, the whole system may be considered isothermal and isobaric. In addition and to ensure that each change in process performance is due to the periodic operations, the thermal effect was isolated of the periodic operations and it is not taken into account in this study. So, the isothermal conditions are assumed.

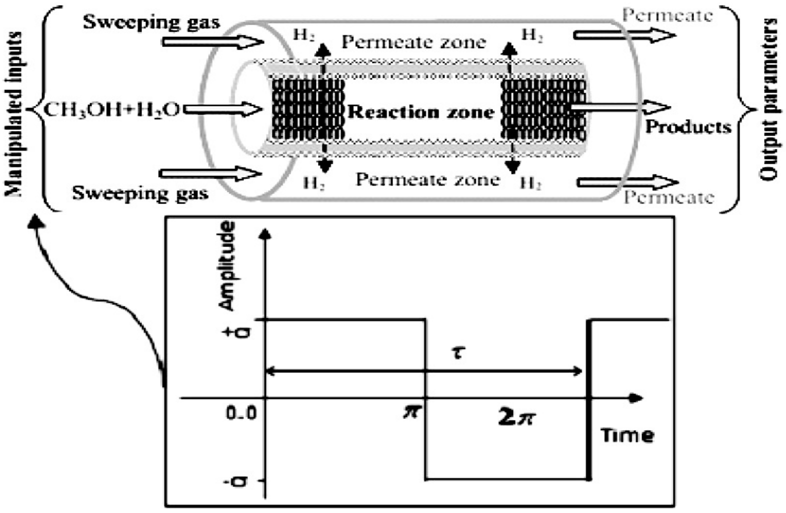


Fig. 1: Scheme of the membrane reactor and modulated inputs by a square wave

b- Plug-flow is assumed for the reaction and permeation sides in steady state conditions,

c- Ideal gas law is applicable,

d- The internal mass transfer resistance is accounted,

e- The catalyst deactivation by coke formation is negligible,

f- The factors affecting the dynamic or periodic operation are complex. In this work, the periodic operation is only imposed *via* a symetric square function for the steam to methanol and sweeping gas to methanol ratios. Thus, the reaction and permeate sides of the reactor are operated under created steady state mode,

g- Under the periodic operations, it is assumed that the composition and sweeping gas ratio imposed exhibit a steady state constant part and a time dependent part,

h- It is known that an improvement is attained if the time-average performance of the periodic operation is larger than that of the corresponding steady-state process [20], *i.e.*, under forcing conditions, we suppose that the period of change of the modulation function is significantly larger than the characteristic process time, so the reactor operates under quasi steady state conditions [21-22],

i- Palladium and palladium composite membranes are used only when ultra-pure hydrogen is needed. Therefore, we assume that the membrane is only permeable to hydrogen and has an infinite selectivity to hydrogen,

j- In practice, the periodic operation is achieved by means of a programmable electronic timers connected to the flow controllers which are used to generate square waves [23, 24]. Furthermore the volumetric flow rates off reactants can be switched periodically between two values to generate a chain of step-changes representing a square-wave variation of reactant concentrations in the feed [25].

For this purpose, the following square wave function $f(t)$ in which its cycle is described by a period $\tau = 2\pi$, an amplitude σ for each modulated input and an angular frequency ω is used. It is noteworthy that the angular frequency gives the frequency in which phase changes in term of usual or ordinary frequency.

$$f = 1/\tau \tag{1}$$

Then, $$\omega = 2\pi/\tau \tag{2}$$

The used square wave (function) is defined as follows:

$$f(t) = \begin{cases} +1 & \text{for} \quad 0 \le t \le t/2 \\ -1 & \text{for} \quad \tau/2 < t < \tau \end{cases} \tag{3}$$

Based on the above assumptions, the mathematical model construction is achieved by means of the following equations:

2.1 Gouverning equations in reaction side

2.1.1 Basic equations (molar flow rates and partial pressures)

The various expressions of the molar flow rates for each species ($i =$ CH_3OH, H_2O, CO_2 and CO) in steady-state conditions are expressed as function of methanol conversion (X_{CH_3OH}), carbon dioxide yield (X_{CO_2}) and of hydrogen recovery (Y_{H_2}). The partial pressures expressions are also evaluated

$$\tilde{F}_{CH_3OH} = F^0_{CH_3OH}(1 - X_{CH_3OH}) \tag{4}$$

$$\tilde{F}_{H_2O} = F^0_{H_2O} - F^0_{CH_3OH} X_{CO_2} \tag{5}$$

$$\tilde{F}_{CO_2} = F^0_{CO_2} + F^0_{CH_3OH} X_{CO_2} \tag{6}$$

$$\tilde{F}_{CO_2} = F^0_{CO_2} - F^0_{CH_3OH} X_{CO_2} + F^0_{CH_3OH} X_{CH_3OH} \tag{7}$$

$$\tilde{F}_{H_2} = F^0_{H_2} + F^0_{CH_3OH} X_{CO_2} + 2\, F^0_{CH_3OH} X_{CH_3OH} - F^P_{H_2} \tag{8}$$

$$\tilde{F}^P_{H_2} = Y_{H_2} F^0_{CH_3OH} \tag{9}$$

$$\tilde{F}_T = F^0_{CH_3OH} \left(1 + (S/F) + 2 X_{CH_3OH} - Y_{H_2}\right) \tag{10}$$

Our approach is based on varying a key input according to a square periodic function. So, under the periodic operations, the steam to methanol ratio can be written at constant methanol inlet feed of as follows:

$$\left(\frac{S}{F}\right)(t) = \frac{F_{H_2O}(t)}{\tilde{F}_{CH_3OH}} \tag{11}$$

By using the defined above periodic function $f(t)$ the imposed steam molar flow rate is equal to the sum of the steady state level and of a time dependent component level.

$$F_{H_2O}(t) = \tilde{F}_{H_2O} + \tilde{F}_{H_2O}\,\sigma_1\, f(t) \tag{12}$$

$$\text{with, } \int_0^{\tau_1} \tilde{F}_{H_2O}\,\sigma_1\, f(t)\,dt = 0 \tag{13}$$

$$F_{H_2O}(0) = \tilde{F}_{H_2O} \tag{14}$$

$$\text{Then, } \left(\frac{S}{F}\right)(t) = \left(\frac{S}{F}\right)(1 + \sigma_1 f(t)) \tag{15}$$

The precedent expression giving the total molar flow rate ({Eq. (10)}) can be rewritten as follows:

$$F_T(t) = F^0_{CH_3OH}\left(1 + \left(\frac{S}{F}\right)(1 + \sigma_1 f(t)) + 2\,X_{CH_3OH} - Y_{H_2}\right) \tag{16}$$

The partial pressures of individual species i that were used in rate expressions calculations were evaluated as follows:

$$P_i = P_r \frac{F_i(t)}{F_T(t)} \tag{17}$$

$$\text{So, } P_{CH_3OH} = P_r \frac{1 - X_{CH_3OH}}{\alpha} \tag{18}$$

$$P_{CO_2} = P_r \frac{X_{CO_2}}{\alpha} \tag{19}$$

$$P_{CO} = P_r \frac{X_{CH_3OH} - X_{CO}}{\alpha} \tag{20}$$

$$P_{H_2O} = P_r \frac{\left(\left(\frac{S}{F}\right) - X_{CO_2}\right)(1 + \sigma_1 f(t))}{\alpha} \tag{21}$$

$$P_{H_2} = P_r \frac{2\,X_{CH_3OH} + X_{CO_2} - Y_{H_2}}{\alpha} \tag{22}$$

$$\alpha = \left(1 + \left(\frac{S}{F}\right)(1 + \sigma_1 f(t)) + 2X_{CH_3OH} - Y_{H_2}\right) \tag{23}$$

2.1.2 Mass balances

a- In gaseous phase

■ The axial differential mass balance in the gaseous phase in terms of molar flow rates is given for each chemical species ($i =$ CH_3OH, H_2O, CO_2, CO and for $j = 1-3$) by the expressions:

$$\frac{dF_i}{dz} = \rho A \sum_j \eta_j \upsilon_{ij} r_j \tag{24}$$

■ Except for hydrogen

$$\frac{dF_{H_2^r}}{dz} = \rho A \sum_j \eta_j \upsilon_{H_2 j} r_j - \frac{dF_{H_2^p}}{dz} \tag{25}$$

■ Boundary conditions

$$\text{At } z = 0: \quad F_i^r = F_i^0 \tag{26}$$

b- In solid phase

■ For $i =$ CH_3OH, H_2O, CO_2, CO and for $j = 1-3$, the internal mass transfer resistances are accounted using the following expression:

$$D_{e,i} \frac{d^2_{P_{s,i}}}{d\xi^2} = \rho_s R T r_P^2 \sum_j \left(\upsilon_{ij} r_{s,j}\right) j \tag{27}$$

■ Boundary conditions

$$\text{At } \xi = 0, \quad \frac{d^2_{P_{s,CH_3OH}}}{d\xi^2} = \frac{d^2_{P_{s,CO_2}}}{d\xi^2} = \frac{d^2_{P_{s,H_2O}}}{d\xi^2} = 0 \tag{28}$$

$$\text{At } \xi = 1, \; P_{s,CH_3OH} = P_{CH_3OH} \,;\; P_{s,CO_2} = P_{CO_2} \,;\; P_{s,H_2O} = P_{H_2O} \tag{29}$$

■ The effectiveness factors and the effective diffusivity were evaluated using the following definitions, respectively:

$$\eta_j = \frac{\int_0^V r_j (P_{s,i}) \, \rho_s \left(\frac{dV}{V}\right)}{r_j (P_i^r) \, \rho_s} \tag{30}$$

$$D_{e,i} = \frac{4\varepsilon_s}{3\tau_s} \frac{r_p}{2} \sqrt{\frac{8RT}{\pi M_i}} \tag{31}$$

2.2 Gouverning equations in permeate side

■ For sweeping gas

$$\frac{dF_I^p}{dz} = 0 \tag{32}$$

■ For hydrogen

Permeation of hydrogen through a dense palladium membrane occurs *via* a solution diffusion mechanism, where the gas molecules dissolve in the membrane surface at the high (partial) pressure side and desorbs at the side with the low partial pressure. A power law equation is used to describe the overall permeation rate of hydrogen through the membrane [7, 26]. The rate of hydrogen permeation can therefore be expressed through the habitual sievert law as a function of the difference in the square root of hydrogen partial pressures on both sides of the membrane.

$$\frac{dF_{H_2,p}}{dz} = 2\pi r_m \left(\frac{Q}{\delta}\right)\left(P_{H_2,r}^{0.5} - P_{H_2,p}^{0.5}\right) \tag{33}$$

■ Boundary conditions

$$\text{At } z = 0: \quad F_I^p = F_I^0 \quad \text{and} \quad F_{H_{2,p}} = 0 \tag{34}$$

Introducing the following dimensionless parameter which is describing the hydrogen recovery as follows:

$$Y_{H_2} = \frac{F_{H_{2,p}}}{F_{CH_3OH}^0} \tag{35}$$

The equation (33) can be written as,

$$\frac{dY_{H_2}}{dz} = \frac{2\pi r_m l}{F_{CH_3OH}^0}\left(\frac{Q}{\delta}\right)\left(P_{H_{2,r}}^{0.5} - P_{H_{2,p}}^{0.5}\right) \tag{36}$$

In equation (36), the hydrogen partial pressure in reaction side was evaluated by equation (22), and the hydrogen partial pressure is evaluated by the following equation as function of total pressure in permeate side, hydrogen recovery and sweeping gas to methanol ratio (I).

$$P_{H_{2,p}} = \frac{Y_{H_2} P_P}{Y_{H_2} + I} \tag{37}$$

$$\text{and, } Q = Q_0 \exp(-\Delta E_p / RT) \tag{38}$$

In the permeation side and under the periodic operation, the feed of sweeping gas changes according to the following expression:

$$F_I(t) = \tilde{F}_I + \tilde{F}_I \sigma_2 f(t) \tag{39}$$

The equation (39) must satisfy the conditions that:

$$\int_0^{\tau_2} \tilde{F}_I \sigma_2 f(t)\,dt = 0 \tag{40}$$

$$F_I(0) = \tilde{F}_I \tag{41}$$

It should be noted that σ_2 is the running amplitude of the sweeping gas and τ_2 is the period of change of the modulation function. Under forcing conditions using the function $f(t)$, the ratio (I) which is defined as the ratio of the sweeping gas flow rate to that of methanol at the inlet can be written as:

$$I = \frac{F_I(t)}{F_{CH_3OH}^0} = \frac{\tilde{F}_I + \tilde{F}_I \sigma_2 f(t)}{F_{CH_3OH}^0}$$

3. NUMERICAL SOLUTIONS

3.1 Procedure

The reactant feed rate and the sweeping gas are periodically varied in the form of a symmetric square wave function as presented in figure 1.

In order to quantify the performance of the membrane reactor during the methanol steam reforming reaction, and taking into account the non steady-state conditions of feed gas composition, the model for the membrane reactor operated under periodic operation consists of a set of differential equations. To simplify the physical interpretation, some variables are converted to a dimensionless ones and are introduced in the concerning equations before their resolution by an appropriate method.

The numerical resolution technique [27] is based on the use of Runge-Kutta fourth-order method to solve the mass first order differential equations, with the initial conditions. The effectiveness factors for the considered reactions, unknown at this stage, are calculated once the partial pressures in the catalyst particle surface are obtained for all components by resolving the set of differential equations given for the solid phase.

To do this, in a first step, the ordinary differential equations which satisfy their boundary conditions are converted into a set of algebraic equation through the use of an orthogonal collocation discretization method [27]. The reformulated problem is solved in a second step by the Levenberg-Marquardt algorithm [28] and all the mathematical calculations were performed using the Matlab software.

The analysis of the effect of the steam to methanol ratio (S/F) and sweeping gas to methanol ratio (I) under forcing conditions was examined and presented by the developed mathematical model.

These inputs are modulated periodically around their steady state values $(S/F=1$ and sweeping gas to methanol ratio $I=3)$ which are corresponding to steam molar flow rate of 1.95×10^{-3} mol/s and sweeping gas molar flow rate of 5.85×10^{-3} mol/s. It is important to note that the best process performance could be obtained with the best strategy in which the square functions used for modulation of S/F and I change both in phase [29].

To find the optimal amplitudes leading to a high conversion and a high amount of hydrogen recovery, the interval of amplitudes is checked step by step for all the manipulated inputs. The molar flow rates of cyclic feed for steam and sweeping gas could be computed using equations (12) and to (38), respectively and are recapitulated in **Table A4**.

It should be noted that the high and low levels of the steam and sweeping gas molar flow rates, which could be achieved along of the used interval of amplitudes are: for steam: high levels change from 1.95×10^{-3} mol/s to 2.535×10^{-3} mol/s and low levels change from 1.95×10^{-3} mol/s to 1.365×10^{-3} mol/s, for sweeping gas, high levels change from 5.85×10^{-3} mol/s to 7.605×10^{-3} mol/s and low levels change from 5.85×10^{-3} mol/s to 4.095×10^{-3} mol/s. It should be noted that the high levels are reached in the first half cycle ([$0 \text{ to } \pi$]) and the low levels are reached in the second half cycle ([π to 2π]).

The reactor performance was evaluated through the measurements of methanol conversion and hydrogen recovery computed under forcing conditions and compared to the steady state levels (the steady state condition is represented by the horizontal line).

3.2 Simulation results and analysis

It is noteworthy that the best performance could be obtained when the process was performed with the condition of the steam to methanol and sweeping gas ratios running in phase according to a symmetric square function [29]. Under our investigated conditions, it can be mentioned that the higher magnitudes that can be achieved in terms of methanol conversion and of hydrogen recovery are possible when the steam to methanol and the sweeping gas ratios are running in phase at the optimal amplitudes of

0.14 and 0.16, respectively. We emphasize that because there was any enhancement in process performance at high amplitudes, the value of 0.3 was adopted as a limit as presented in figure 2.

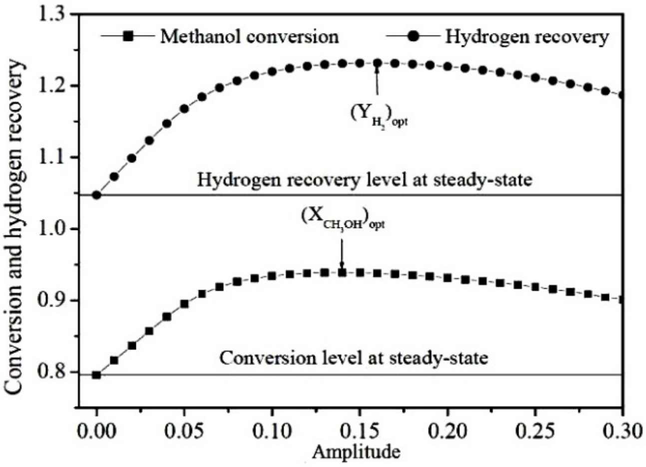


Fig. 2: Conversion and hydrogen recovery from methanol *vs* amplitude

In these optimal amplitudes, the molar flow rates of steam and of sweeping-gas are alternated respectively between the following high to low levels: 2.223×10^{-3} mol/s to 1.677×10^{-3} mol/s and 6.786×10^{-3} mol/s to 4.914×10^{-3} mol/s. It is clear that the overall values computed for the two half cycles equal to that of the steady-state condition. In this case, the real process is not quite periodic with possible favourable transient phenomena but rather a sequence of various steady states conditions with the average time being the parameter which constitutes the created unsteady state operation.

The current study is restricted to analysis the process performances in these optimal amplitudes. The simulation results as presented in figure 3, shows that the conversion and the hydrogen recovery levels obtained under forcing conditions are over the steady state level. Hence, it appears that the reactor performance could be boosted under forced conditions.

The obtained results show that the modulation of studied inputs around their steady state values causes a periodic variation in the output parameters, namely in terms of conversion of methanol and of hydrogen recovery. According to the obtained results the methanol conversion and the corresponding hydrogen recovery responses exhibit a periodic behaviour and it can distinguish two main zones; the first one is located above the steady state level which will be called enhancement zone.

The second one is a no enhancement zone which is below the steady state level. The global behaviour is constituted by a lapse sequence of an expansion and of a compression. This can be explained by the fact that when the two functions used for forcing the steam and sweeping gas at constant methanol inlet feed are running both in phase, the S/F and I ratios change also both in phase.

Then, the conversion of methanol and the hydrogen produced increases, leading to an increase in the hydrogen recovery. The improvement in conversion results from the higher reaction rate due to hydrogen removal from the reaction zone and the positive effect of S/F modulation, which is favourable for the reforming reaction. It is obvious that the S/F ratio favours the hydrogen production *via* the steam reforming reaction and, the sweeping gas favours its pumping through the palladium membrane texture and its evacuation out of the permeate.

It is clear that the dual effect and the symbiosis that exists between modulation of S/F and I which are running both in phase, can boost significantly the reactor performance above the steady state level. *i.e*. the modulation of steam to methanol ratio enhance the conversion, at the same time the modulation of sweeping gas enhance the hydrogen recovery by shifting the equilibrium in the direction of hydrogen production.

In this case, the reverse water gas shift cannot occur and consequently the conversion is still improved again. In addition, the pumping of hydrogen may be eliminate the radial distribution of the hydrogen concentration inside the support pores and keep the permeation side under a low pressure, resulting in a relatively high driving force of hydrogen permeation through the palladium membrane. In addition, the highly turbulent flows provoked by the periodic operation may suppress the gradient of concentration and of temperature, which is may be accomplished by the rising edges of the square functions used for modulation of the steam and sweeping gas.

This leads to a reduction of hydrogen partial pressure in the permeate side, increasing the driving force for permeation and resulting in the higher rates of hydrogen removal from the reaction zone. This phenomenon may be explained also by the following: Here, it is important to note that an ideal square wave has instantaneous transitions between the high and low levels. In practice, this is never achieved because of physical limitations of the system that generates the waveform. It is known that the damping is an effect that reduces the amplitude. When the system is over-damped, the waveform may never actually reach the theoretical high and low levels and the system returns to equilibrium without oscillating.

On the other hand, if the system is under-damped, it will oscillate about the high and low levels before settling down and the amplitude gradually decreasing to zero, which is corresponding to the steady-state conditions. The square wave has many definitions, which are equivalent except at the discontinuities. It can be defined as simply the sign function of a sinusoid as presented in figure 3**b** in which is used to explain the reactor output responses in terms of conversion and hydrogen recovery.

The global behaviour of conversions or of hydrogen recovery could be done with an in-depth analysis by means of two principal stages called enhancement and no enhancement zones. Each zone corresponds approximately to a half cycle. The transition between the two stages is done very quickly, which explains the absence of the transition zone and the amplitudes change rapidly from high to low levels. The enhancement zone is constituted of an expansion in which the inputs change from low to high levels, and a compression in which the inputs change from high to low levels.

The non-enhancement zone possess the same behavior as the enhancement one, but being with a compression with changes of polarity from positive to negative values of the two functions used for steam and sweeping gas.

The overall conversion and hydrogen recovery obtained under periodic operation are equal to the sum of area of the enhancement and non-enhancement zones, which are located above and below the steady state levels, respectively. So, for the complete cycle, it was a capital supplement in conversion and in hydrogen recovery regarding the steady-state levels.

However, the pumping of hydrogen was dependent on the effect of the periodic operations as well as on the effect of the difference in partial pressure of hydrogen between the reaction and the permeation sides. This shows the capital role that can be played by the modulation mode for the improvement of pure hydrogen recovery in comparison to the case when S/F and I are kept constant (steady-state). In fact, it is obvious that the reactor performance is strongly enhanced when the reactor is operated under this condition.

Therefore, we can say that tuning the inlet composition feed and the sweeping gas with square wave function can boost the reactor performance over the steady state level. High conversion and pure hydrogen can be achieved using the defined square function for modulation of considered inputs under the investigated conditions.

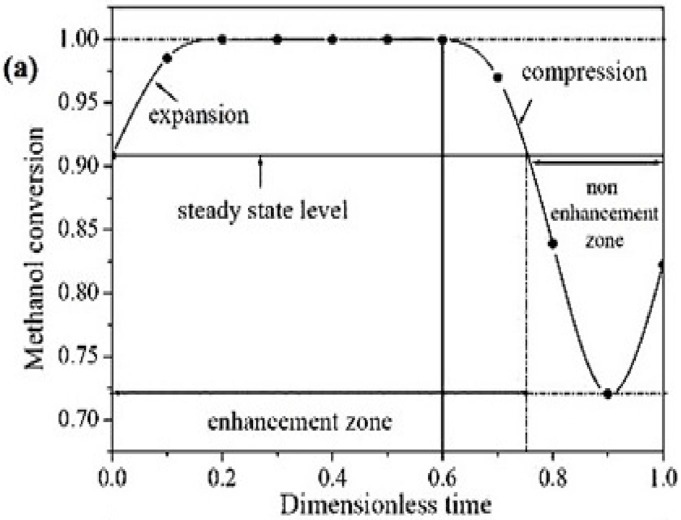
4. CONCLUSIONS

In this case study, an attempt has been made to develop a mathematical model founded on the concept of periodic operation of a packed bed membrane reactor used for methanol steam reforming. Based on the simulation findings, the following conclusions can be drawn. The results emphasize the possible operating conditions leading to a high methanol conversion and for a substantial amount of hydrogen of high purity.

It was found that the application of periodic gas phase modulation is an effective and emergent operating strategy to boost the reactor performance. The use of a hydrogen perm-selective membrane reactor performed under created unsteady state conditions shifts the thermodynamic equilibrium constraints and enhances hydrogen production.

Furthermore, it was found that there was a synergistic effect which could be brought by tuning of the variation of the molar flow rates of steam and sweeping gas using a symmetric square wave running both in phase at optimal amplitudes, and can reasonably generate a higher performance than that achieved at the steady state operation mode, especially in terms of pure hydrogen recovery.

Hence, the results of this study are very useful for choosing the appropriate controlling parameters for operating a draft membrane reactor periodically. Finally, some experiments on the artificial unsteady-state behaviour of such device are required and must be done.



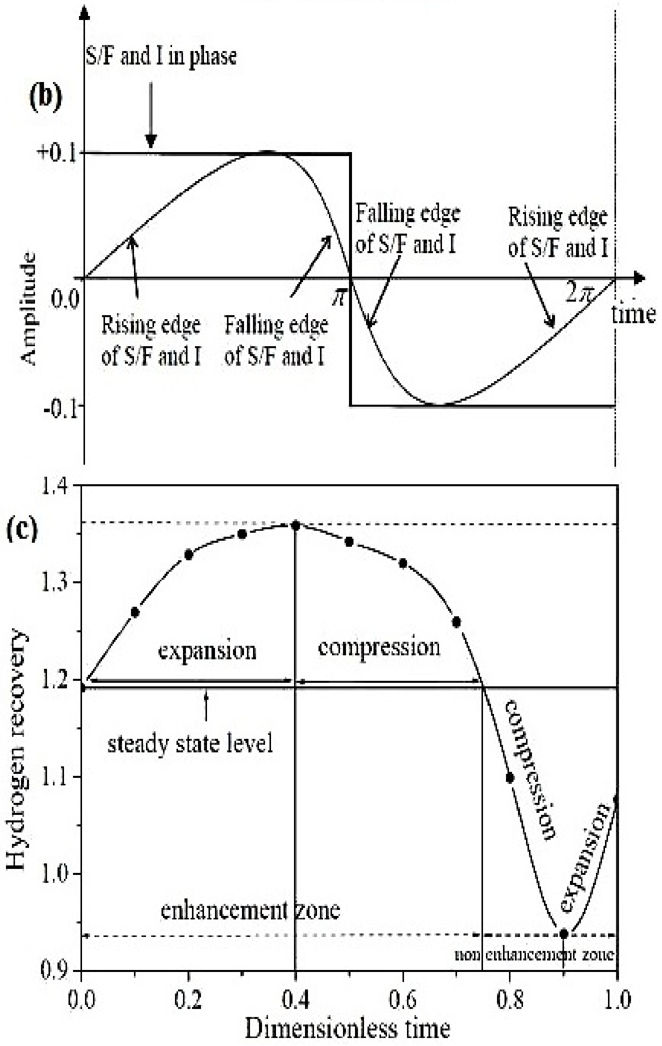


Fig. 3: Methanol conversion **(a)** and hydrogen recovery **(c)** levels achieved under periodic condition using a symmetric square wave **(b)**

NOMENCLATURE

A , Reactor section, m^2
ΔH , Heat of reaction, J/mol
ΔE_p , Hydrogen permeation activation energy, J/mol
I , Sweeping gas ratio
M , Molar mass, kg/mol
r , Reaction rate, mol/kg s
r_p , Radius of the solid particle, m
t , Time, s

D_e , Effective diffusivity, m^2/s
F , Molar flow, mol/s
R , Universal gas constant, 8.314 J/mol K
f , Frequency, Hz
P , Pressure, Pa
r_m , Membrane radius; m
T , Temperature, K
X , Methanol conversion

Y_{H_2} , Hydrogen recovery	V , volume of the catalyst particle, m^3
z , Reactor length, m	
0 , Reactor inlet	D , Decomposition reaction
i , Reaction , i	j , Reaction j
M , Methanol	p , Permeation side
r , Reaction side	T , Total
R , Reforming reaction	S , Catalyst particle surface
w , Water or water gas shift reaction	ε_s , Porosity of catalyst particle
δ , Membrane thickness, m	η , Effectiveness factor
ρ , Catalyst density, kg/m^3	σ , amplitude
τ , Period of the square wave	τ_s , Tortuosity factor
υ , Stoichioetric coefficient	ω , Angular frequency
ξ , Radial coordinate of the catalyst particle, m	Q , permeation coefficient of hydrogen, mol m/m^2 s Pa^{-5}

APPENDICES

Table A1: Reaction network and kinetic of methanol steam reforming process

$$CH_3OH + H_2O \Leftrightarrow 3H_2 + CO_2 \text{, } \Delta H(298K) = +49 \text{ kJ mol}^{-1} \tag{A1}$$

$$CO + H_2O \Leftrightarrow H_2 + CO_2 \text{, } \Delta H(298K) = -41 \text{ kJ mol}^{-1} \tag{A2}$$

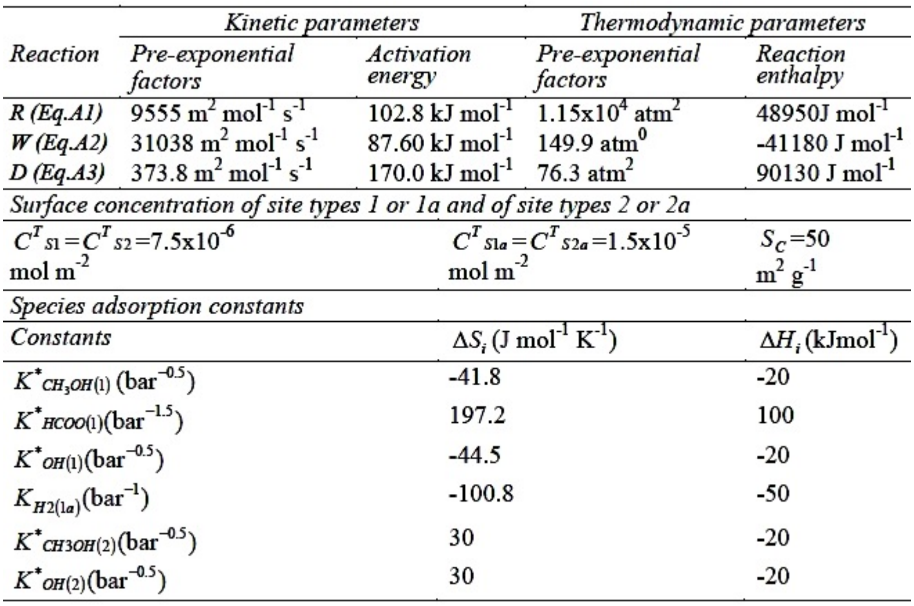
$$CH_3OH \Leftrightarrow 2H_2 + CO \text{, } \Delta H(298K) = +90 \text{ kJ mol}^{-1} \tag{A3}$$

$$r_R = \frac{k_R\, K^*_{CH_3O(1)}\, (P_M / P^{0.5}_{H_2})(1\text{-}P^3_{H_2}\, P_{CO_2} / K_R\, P_M\, P_W)\; C^T_{S1}\, C^T_{Sa1}\, S_C}{(1 + K^*_{CH_3O(1)}\, (P_M / P^{0.5}_{H_2}) + K^*_{HCOO(1)} P_{CO_2} P^{0.5}_{H_2} + K^*_{OH(1)} (P_W / P^{0.5}_{H_2}))(1 + K^{0.5}_{H_{2(1a)}}\, P^{0.5}_{H_2})} \tag{A4}$$

$$r_W = \frac{k_W\, K^*_{OH(1)}\, (P_{CO} P_M / P^{0.5}_{H_2})(1\text{-}P_{H_2}\, P_{CO_2} / K_W\, P_{CO}\, P_W)\; (C^T_{S1})^2\; S_C}{(1 + K^*_{CH_3O(1)}\, (P_M / P^{0.5}_{H_2}) + K^*_{HCOO(1)} P_{CO_2} P^{0.5}_{H_2} + K^*_{OH(1)} (P_W / P^{0.5}_{H_2}))^2} \tag{A5}$$

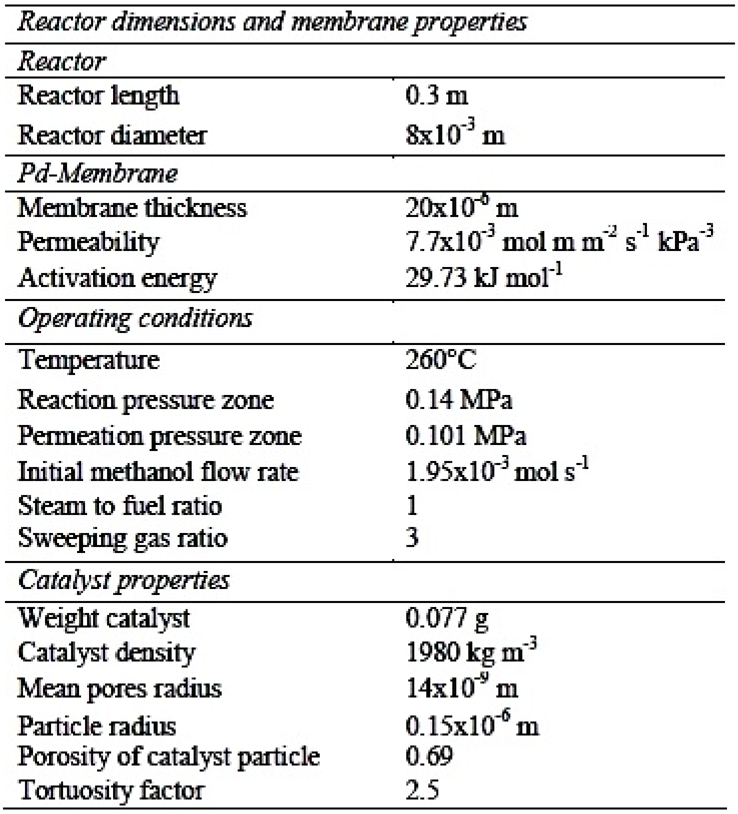
$$r_D = \frac{k_D\, K^*_{CH_3O(2)}\, (P_M / P^{0.5}_{H_2})(1\text{-}P^2_{H_2}\, P_{CO} / K_D\, P_M)\; C^T_{S2}\, C^T_{Sa2}\, S_C}{(1 + K^*_{CH_3O(2)}\, (P_M / P^{0.5}_{H_2}) + K^*_{OH(2)} (P_W / P^{0.5}_{H_2}))(1 + K^{0.5}_{H_{2(2a)}}\, P^{0.5}_{H_2})} \tag{A6}$$

Table A2: Kinetic and thermodynamic parameters for methanol steam reforming on $Cu/ZnO/Al_2O_3$ catalyst



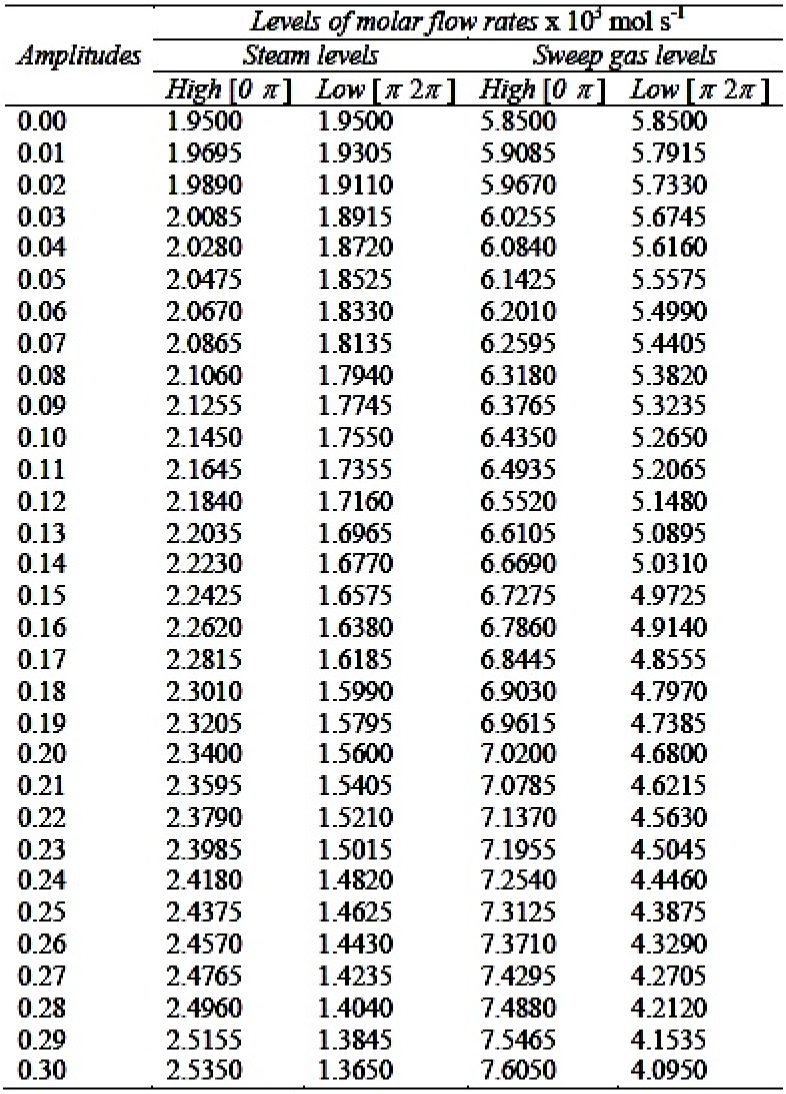
Reaction	*Kinetic parameters*		*Thermodynamic parameters*	
	Pre-exponential factors	*Activation energy*	*Pre-exponential factors*	*Reaction enthalpy*
R (Eq.A1)	9555 $m^2 mol^{-1} s^{-1}$	102.8 kJ mol^{-1}	1.15x10^4 atm^2	48950J mol^{-1}
W (Eq.A2)	31038 $m^2 mol^{-1} s^{-1}$	87.60 kJ mol^{-1}	149.9 atm^0	-41180 J mol^{-1}
D (Eq.A3)	373.8 $m^2 mol^{-1} s^{-1}$	170.0 kJ mol^{-1}	76.3 atm^2	90130 J mol^{-1}
Surface concentration of site types 1 or 1a and of site types 2 or 2a				
$C^T{}_{S1}=C^T{}_{S2}=7.5\times10^{-6}$ mol m^{-2}			$C^T{}_{S1a}=C^T{}_{S2a}=1.5\times10^{-5}$ mol m^{-2}	$S_C=50$ $m^2 g^{-1}$
Species adsorption constants				
Constants			ΔS_i (J mol^{-1} K^{-1})	ΔH_i (kJmol^{-1})
$K^*_{CH_3OH(1)}$ ($bar^{-0.5}$)			-41.8	-20
$K^*_{HCOO(1)}$($bar^{-1.5}$)			197.2	100
$K^*_{OH(1)}$($bar^{-0.5}$)			-44.5	-20
$K_{H2(1a)}$(bar^{-1})			-100.8	-50
$K^*_{CH3OH(2)}$($bar^{-0.5}$)			30	-20
$K^*_{OH(2)}$($bar^{-0.5}$)			30	-20

Table A3: Reactor dimensions, operating conditions and catalyst properties



Reactor dimensions and membrane properties	
Reactor	
Reactor length	0.3 m
Reactor diameter	8x10^{-3} m
Pd-Membrane	
Membrane thickness	20x10^{-6} m
Permeability	7.7x10^{-3} mol m m^{-2} s^{-1} kPa^{-3}
Activation energy	29.73 kJ mol^{-1}
Operating conditions	
Temperature	260°C
Reaction pressure zone	0.14 MPa
Permeation pressure zone	0.101 MPa
Initial methanol flow rate	1.95x10^{-3} mol s^{-1}
Steam to fuel ratio	1
Sweeping gas ratio	3
Catalyst properties	
Weight catalyst	0.077 g
Catalyst density	1980 kg m^{-3}
Mean pores radius	14x10^{-9} m
Particle radius	0.15x10^{-6} m
Porosity of catalyst particle	0.69
Tortuosity factor	2.5

Table A4: Molar flow rates levels of steam and sweep gas reached under periodic operations



Amplitudes	*Levels of molar flow rates* x 10^3 mol s^{-1}			
	Steam levels		*Sweep gas levels*	
	High [*0 π*]	*Low* [*π 2π*]	*High* [*0 π*]	*Low* [*π 2π*]
0.00	1.9500	1.9500	5.8500	5.8500
0.01	1.9695	1.9305	5.9085	5.7915
0.02	1.9890	1.9110	5.9670	5.7330
0.03	2.0085	1.8915	6.0255	5.6745
0.04	2.0280	1.8720	6.0840	5.6160
0.05	2.0475	1.8525	6.1425	5.5575
0.06	2.0670	1.8330	6.2010	5.4990
0.07	2.0865	1.8135	6.2595	5.4405
0.08	2.1060	1.7940	6.3180	5.3820
0.09	2.1255	1.7745	6.3765	5.3235
0.10	2.1450	1.7550	6.4350	5.2650
0.11	2.1645	1.7355	6.4935	5.2065
0.12	2.1840	1.7160	6.5520	5.1480
0.13	2.2035	1.6965	6.6105	5.0895
0.14	2.2230	1.6770	6.6690	5.0310
0.15	2.2425	1.6575	6.7275	4.9725
0.16	2.2620	1.6380	6.7860	4.9140
0.17	2.2815	1.6185	6.8445	4.8555
0.18	2.3010	1.5990	6.9030	4.7970
0.19	2.3205	1.5795	6.9615	4.7385
0.20	2.3400	1.5600	7.0200	4.6800
0.21	2.3595	1.5405	7.0785	4.6215
0.22	2.3790	1.5210	7.1370	4.5630
0.23	2.3985	1.5015	7.1955	4.5045
0.24	2.4180	1.4820	7.2540	4.4460
0.25	2.4375	1.4625	7.3125	4.3875
0.26	2.4570	1.4430	7.3710	4.3290
0.27	2.4765	1.4235	7.4295	4.2705
0.28	2.4960	1.4040	7.4880	4.2120
0.29	2.5155	1.3845	7.5465	4.1535
0.30	2.5350	1.3650	7.6050	4.0950

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