MODELING OF PARTIAL OXIDATION OF METHANE IN A MEMBRANE REACTOR

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ABSTRACT

Partial oxidation of methane is one of the most important chemical processes for the production of syngas. In recent years, the abundant availability of natural gas and the increasing demand of hydrogen have led to high interest to further develop this process increasing the yield of syngas. In this work the partial oxidation of methane was studied from a modeling point of view in a membrane reactor and in a conventional reactor. A mathematical model of a membrane reactor used for partial oxidation of methane, assuming steady-state conditions, was developed to simulate and compare the maximum yields and operating conditions in the reactor with that in a conventional reactor. Simulation results show that different parameters affect methane conversion and H_2/CO ratio, such as temperature, operating conditions, and membrane parameters such as membrane permeance. In a membrane reactor an increase in the operating pressure corresponds to an increase in methane conversion, since allows for a greater partial pressure gradient between the reaction and permeate zone, thus contributing to shift the equilibrium towards the products. As such, the membrane reactors are a good alternative to produce syngas especially for GTL processes. Operating conditions can be set to control the H_2/CO ratio to a desired value, and high conversions at mild temperatures can be achieved reducing capital and operational costs.

Keywords: membrane reactor, partial oxidation, methane, modeling

NOMENCLATURE

A	tube sectional area [m^2]
C_P	heat capacity [J/g.K]
F_i	flow rate of component *i* [mol/h]
k_i	rate constant of reaction *i*
K_i	equilibrium constant of reaction *i* or adsorption coefficient of component *i*
P_i	partial pressure [atm]
P_T	total pressure in the reaction zone [atm]
R_i	rate of reaction *i* [mol/h.g$_{cat}$]
r_m	radius of the membrane [m]
r_T	radius of the reaction tube [m]
T	temperature [K]
u_S	superficial velocity [m/h]
z	distance from the inlet of the reaction tube [m]

Greek symbols

ρ_b	catalyst density [g/m^3]

Superscripts

AZ	air flow zone
RZ	reaction zone

INTRODUCTION

Partial oxidation of methane has attracted substantial interest over the years for the production of syngas and hydrogen. In recent years, the abundant availability of natural gas and the increasing demand of hydrogen have led to high interest to further develop this process increasing the yield of syngas.

The partial oxidation reaction has been extensively studied for the production of syngas (Ashcroft et al., 1990; Disanayake et al., 1991; Rajaput & Prabhakar, 1992; Hickman & Schmidt, 1993). Partial oxidation of methane involves one non-reversible reaction (methane combustion) and two reversible reactions (steam reforming and carbon dioxide reforming). Methane combustion is a very fast and highly exothermic reaction, which releases a great quantity of energy demanding a good temperature control as not to compromise the reactor and reaction tubes structure. So a membrane reactor offers the possibility of supplying oxygen for the reaction throughout the entire reactor length controlling the combustion reaction in the reactor and spreading the heat release throughout the reactor not only at its beginning.

The development of oxygen permeable membranes has opened up a new possibility to enhance the partial oxidation of methane process. New improvements are been done in membrane materials and structures, which supports the selective compound in porous alumina, porous ceramic substrate, and in nanostructured carbides, and several works suggests the oxygen-permeating dense membranes have potential applications in partial oxidation of methane (Balachandran et al., 1997; Tsai et al., 1997; Kao et al., 1997).

The modeling and simulation of catalytic membrane reactors for methane conversion to syngas has been done by some authors, specially on steam reforming of methane and oxidative coupling of methane (Shu et al., 1994; Wang and Lin, 1995; Kao et al., 1997; Assaf et al., 1998; Chen et al., 2003; Lin et al., 2003; Gallucci et al., 2004). Very few works have dealt with partial oxidation of methane in membrane reactors (Tsai et al., 1997; Jin et al., 2000) and none dealing with the production of syngas for gas-to-liquid (GTL) processes.

This work presents the mathematical modeling of a one-dimensional, isothermal membrane reactor operating at steady-state, comparing and discussing reactor and yield improvements.

MEMBRANE REACTOR

In partial oxidation of methane, the catalytic fixed-bed reactor is fed with a gas mixture of CH_4 and O_2. Commercial catalyst is composed of zirconium and platinum supported in alumina or nickel supported in alumina and the reactor is composed of vertical tubes (between 10 and 900 tubes inside the reactor) with internal diameters from 7 to 16 cm and lengths from 6 to 12 m, inserted in a radiant furnace chamber. The feed temperature is about 800C. The maximum temperature that the reactor can support is limited by the metallurgical limitations of the tubes, since at higher temperatures the metal tubes can creep under stress.

The membrane reactor configuration is quite simple and consists of an external steel tube (shell) with an inner membrane wall tube which contains the catalyst. Air flows in the outer tube and oxygen permeates to the inner tube through the membrane. Methane and optionally O_2 are continuously fed into the catalytic zone. A scheme of the reactor and mathematical model is shown in Fig. 1.

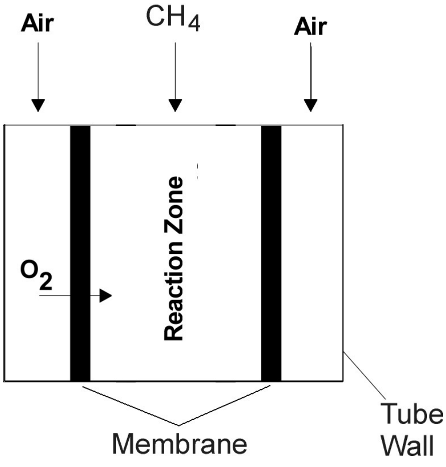


Figure 1. Scheme of the membrane reactor.

MATHEMATICAL MODEL

The basic assumptions made for the membrane reactor were:

Steady-state operation;
Isothermal conditions;
Plug-flow on both reaction and air zones;
No boundary layer on membrane surfaces;
Intrinsic kinetics for methane combustion, carbon dioxide reforming and steam reforming reactions;
Adsorption is the determinant step of the kinetic process (Xu & Froment, 1989);
The catalyst active sites have different adsorption capabilities for CH_4, O_2, H_2O and CO_2;

Since the partial oxidation of methane is a mildly exothermic reaction and diluted feed is used, the assumption of an isothermal reactor is reasonable (Jin et al., 2000).

Partial oxidation of methane involves one non-reversible reaction and two reversible reactions, which were thoroughly studied by Arai, Yamada and Eguchi (1986), Ross & Steel (1973), Richardson and Paripatydar (1990) and Xu and Froment (1989).

$$CH_4 \quad O_2 \quad CO_2 \quad 2H_2O \tag{1}$$

$$CH_4 \quad H_2O \quad CO \quad 3H_2 \tag{2}$$

$$CH_4 \quad CO_2 \quad 2CO \quad 2H_2 \tag{3}$$

The kinetic model for the reaction on a Ni/Al_2O_3 catalyst is based on a Langmuir-Hinshelwood reaction mechanism which rate expressions for reactions (1) to (3) are given by:

$$R_1 \quad \frac{k_1 \quad P_{CH4} \quad P_{O2}^{0.5}}{1 \quad K_{CH4} \quad P_{CH4} \quad K_{O2} \quad P_{O2} \quad ^2} \tag{4}$$

$$R_2 \quad k_2 \quad P_{CH4} \quad P_{H2O} \quad 1 \quad \frac{P_{CO} \quad P_{H2}^3}{K_2 \quad P_{CH4} \quad P_{H2O}} \tag{5}$$

$$R_3 \quad k_3 \quad P_{CH4} \quad P_{CO2} \quad 1 \quad \frac{P_{CO2}^2 \quad P_{H2}^2}{K_3 \quad P_{CH4} \quad P_{CO2}} \tag{6}$$

The changes on the components CH_4, CO, H_2, CO_2 and H_2O along the reactor length are given by:

$$\frac{dF_i}{dz} \quad {}_b \; A \quad \sum_j \quad {}_{ij} \; R_j \tag{7}$$

The changes on the component O_2 along the reactor length are given by:

$$\frac{dF_{O2}}{dz} \quad {}_b \; A \quad 2 \; R_1 \quad 2 \quad r_M \; F_M \tag{8}$$

Oxygen permeation was calculated based on the permeation of a $La_{0.6}Sr_{0.3}Co_{0.2}Fe_{0.8}O_3$ membrane described by Jin et al. (2000) who correlated the permeation to oxygen partial pressure and temperature.

$$\begin{aligned} &F_M \quad 9.77 \; 10^{\;6} \; T \quad 1.37 \; 10^{\;8} \; T^2 \\ &P_{O2}^{RZ} \; 10^{\;5} \quad ^{2.26\,10^{\;3} \;\; 1.62\,10^{\;5}\,T} \\ &P_{O2}^{AZ} \; 10^{\;5} \quad ^{2.26\,10^{\;3} \;\; 1.62\,10^{\;5}\,T} \qquad 0.044 \end{aligned} \tag{9}$$

The kinetic parameters for the reaction are presented in Table 1. The simulated operating conditions are presented in Table 2.

Table 1. Kinetic parameters for partial oxidation of methane.

Parameter	Pre-Exponential Factor	Ea or H [J/mol]
k_1	1.10 [$mol/s.g_{cat}.Pa^{1.5}$]	166000
k_2	4.19 $x10^{-9}$ [$mol/s.g_{cat}.Pa^2$]	29000
k_3	2.42 $x10^{-9}$ [$mol/s.g_{cat}.Pa^2$]	23700
K_{CH4}	6.65 $x10^{-4}$ [Pa^{-1}]	103500
K_{O2}	1.77 $x10^5$ [$Pa^{-0.5}$]	66200

Table 2. Operating conditions and reactor parameters.

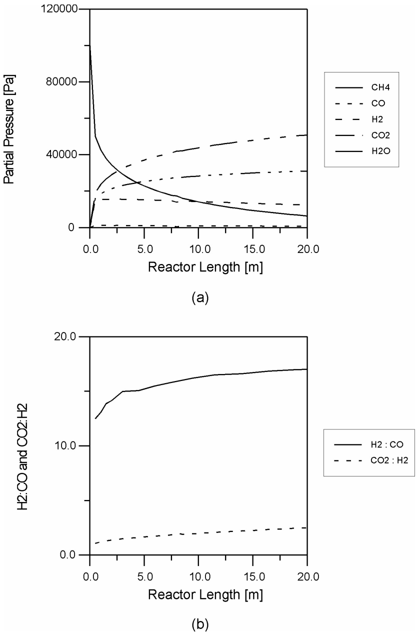
Methane flow rate [mol/h]	5200.0
Total Pressure [atm]	1.0
Catalyst Density [g_{cat}/m^3]	2355.2
Bed Porosity	0.30
Reactor Length [m]	20.0
Tube internal radius [m]	0.1016
Tube external radius [m]	0.1322
Membrane external radius [m]	0.1500
Membrane thickness [m]	0.0150

The differential equations 7 and 8 were solved by numerical integration using a 5th order Runge-Kutta-Gill method.

The kinetic data were obtained by Xu & Froment (1989) and validated for a fixed bed reactor by Tsai et al. (1997), which has studied this reaction over the entire range of temperature and pressure employed in the present study. The oxygen permeation rate through the membrane was studied and validated by Jin et al. (2000) over the range of temperature T = 1000 to 1200 K at pressure of P = 1 atm. The computational program used in the present study was tested with the data presented by Tsai et al. (1997) over a traditional fixed bed reactor and the data presented by Jin et al. (2000) was used to test the membrane reactor program and the responses of the membrane. After validation with literature data, the model was used to simulate industrial like conditions for syngas production.

RESULTS AND DISCUSSION

The major advantage of the membrane reactor is to spread the combustion of methane throughout the reactor length not letting the combustion occur solely at the beginning of the reactor what could damage the reactor due to the amount of heat released by the reaction. Using a membrane, the oxygen is fed continuously through the reactor giving an almost linear consumption of methane (Figs. 2 to 4).



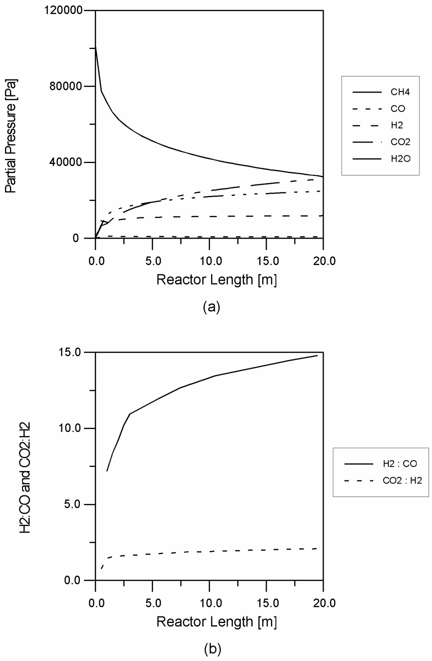
(a)

(b)

Fig. 2. Partial pressure (a), and H_2:CO ratio and CO_2:H_2 ratio (b) for membrane reactor operating at isothermal conditions as function of the reactor length (T = 1173 K, F_{CH4}^0 = 0.50 mol/s).

The production of carbon dioxide is considerable due to the combustion of methane. Steam and carbon dioxide reforming are responsible for the formation of syngas, which occurs only to a certain extent, and the reaction selectivity to carbon monoxide is low.

A maximum production of hydrogen is obtained around a conversion of methane of 40 to 60%, depending on reaction temperature, after which the equilibrium of the reactions (2) and (3) take a major shift towards the reactants reducing the amount of hydrogen and carbon monoxide in the reactor. So, the partial oxidation of methane should not proceed to its completion (total consumption of methane). At a methane conversion of 90% the shift towards the production of CO_2 and H_2O is especially high and the amount of H_2 and CO in the reaction decreases rapidly. The H_2/CO ratio is high and tends to increase as the reaction proceeds up to a methane conversion of 90% when these products tend to be consumed by the equilibrium reactions (Fig. 2b to 4b).



(a)

(b)

Fig. 3. Partial pressure (a), and H_2:CO ratio and CO_2:H_2 ratio (b) for membrane reactor operating at isothermal conditions as function of the reactor length (T = 1123 K, F_{CH4}^0 = 0.50 mol/s).

Influence of Temperature

Temperature plays an important role in partial oxidation of methane both in the conversion of methane and in the H_2:CO ratio. As the temperature increases, the conversion of methane also increases, and for temperatures above 1250 K, the conversion of methane is total even for high gas loads (Fig. 4a). Below 1000 K, the conversion per pass is very low and product recycling is needed.

The effect of temperature on the H_2:CO ratio is complex but it decreases when temperature increases, so higher temperatures favors lower H_2:CO ratios which can be needed for processes such as the Fischer-Tropsch synthesis (Fig. 4b), which requires H_2/CO ratios near 2:1. Any way, pos processing of the syngas is required in order to remove the excess of hydrogen in the syngas if it is to be used in Fischer-Tropsch synthesis.

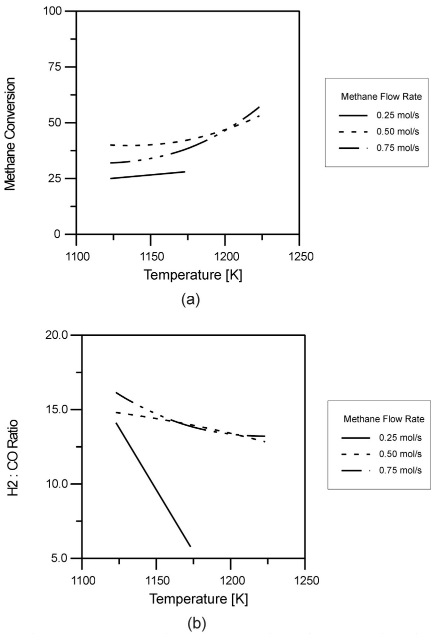


Fig. 4. Methane conversion (a) and H_2/CO ratio (b) for a membrane reactor as function of temperature and gas load.

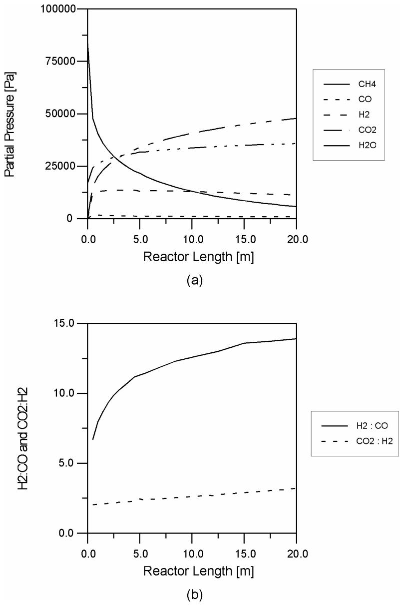


Fig. 5. Partial pressure (a), H_2:CO ratio and CO_2:H_2 ratio (b) for membrane reactor operating at isothermal conditions as function of the reactor length (T = 1223 K, F_{CH4}^{0} = 0.50 mol/s). Initial flow rate of CO_2 = 0.2 CH_4 flow rate.

Influence of CH_4/CO_2 ratio

Carbon dioxide reforming usually proceeds in the presence of an excess of carbon dioxide to enhance reforming. The effect of molar carbon dioxide-to-methane (CO_2/CH_4) ratio was examined by varying this ratio from 0.2 to 0.6. Partial pressure profiles for the reaction for two different CO_2/CH_4 ratios are shown in Figs. 5 and 6, and results for three different temperatures are shown in Fig 7.

Recycling the CO_2 produced by the combustion reaction and not converted to syngas back to the reactor feed can enhance the production of syngas shifting the carbon dioxide reforming towards the production of syngas. Higher amounts of carbon dioxide in the reactor help to lower the H_2/CO ratio and the amount of syngas produced is also higher.

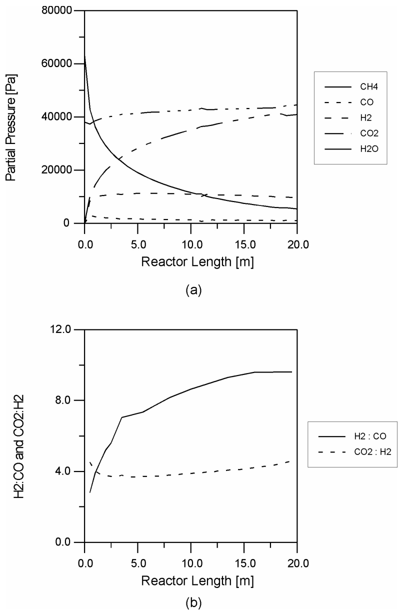


Fig. 6. Partial pressure (a), H_2:CO ratio and CO_2:H_2 ratio (b) for membrane reactor operating at isothermal conditions as function of the reactor length (T = 1223 K, F_{CH4}^{0} = 0.50 mol/s). Initial flow rate of CO_2 = 0.6 CH_4 flow rate.

Influence of CH_4/H_2O ratio

Steam reforming usually proceeds in the presence of an excess of steam to enhance reforming and syngas production. The effect of molar steam-to-methane (H_2O/CH_4) ratio was examined by varying this ratio from 0.2 to 0.6. Partial pressure profiles for the reaction for a H_2O/CH_4 ratio is shown in Figs. 8, and results for three different temperatures are shown in Fig 9. Adding steam to the reactor feed can enhance the production of syngas shifting the steam reforming towards the production of syngas, but at the expense of a higher H_2/CO ratio which can be undesirable for GTL processes.

Influence of membrane permeability

Membrane permeability is directly related to the flow rate of oxygen from the air stream zone to the reaction zone and therefore influences the rate of methane combustion. Total conversion of methane increases as the oxygen flow rate through the membrane increases, due to the greater amount of oxygen available to the reaction (Fig 10). Temperature inside the reaction zone is directly affected by the highly exothermic combustion reaction and temperature control can be attained by controlling the amount of oxygen that can flow to the reaction zone.

Lower oxygen partial pressure inside the air zone can lower the oxygen flow rate to the reaction zone, as well as, the use of membranes that allows the flow of a limited amount of oxygen to the reaction zone. In the latter case the membrane should be chosen during the project of the reactor and can be used as to set a maximum permeability for the system.

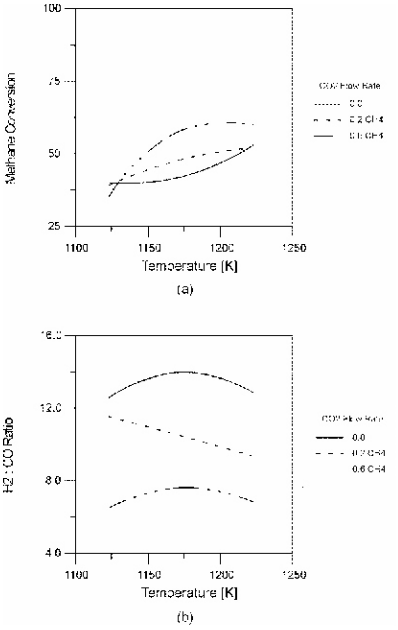


Fig. 7. Methane conversion (a) and H_2/CO ratio (b) for a membrane reactor as function of temperature and carbon dioxide flow rate at the maximum hydrogen production point.

Controlling the H_2/CO Ratio

Controlling the H_2/CO ratio is important, especially to gas-to-liquid processes (GTL) where the optimum ratio varies from 0.7 up to 3.0, and influences hydrocarbon product distribution. In partial oxidation of methane, the H_2/CO ratio is large and lowering this ratio would require operating in high temperatures, which gives the lowest H_2/CO ratio. Even so, the ratio remains very high for use in GTL process and further processing is required to control the H_2/CO ratio. An option is to pass the crude syngas through a membrane absorption unit so hydrogen can permeate through the membrane correcting the H_2/CO ratio to the desired level. The membrane absorption unit can be shaped as a multitube heat exchanger where the syngas passes through the inner or outer side of the membrane tubes. Hydrogen permeates from the syngas towards the hydrogen-poor sweep gas adjusting the H_2/CO ratio to a desired value.

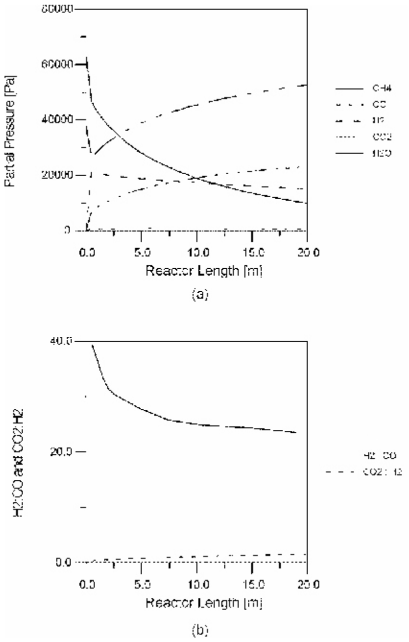


Fig. 8. Partial pressure (a), H_2:CO ratio and CO_2:H_2 ratio (b) for membrane reactor operating at isothermal conditions as function of the reactor length (T = 1173 K, $F_{CH4}{}^{0}$ = 0.50 mol/s). Initial flow rate of H_2O = 0.6 CH_4

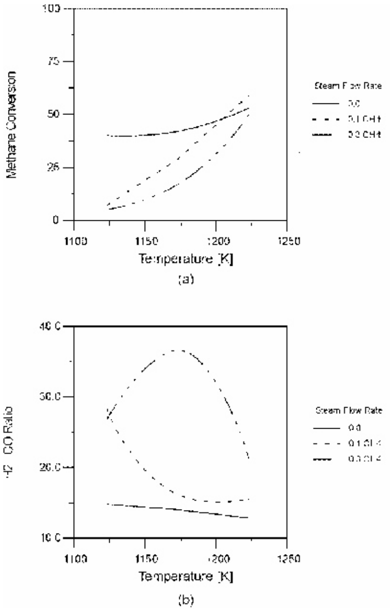


Fig. 9. Methane conversion (a) and H_2/CO ratio (b) for a membrane reactor as function of temperature and steam flow rate at the maximum hydrogen production point.

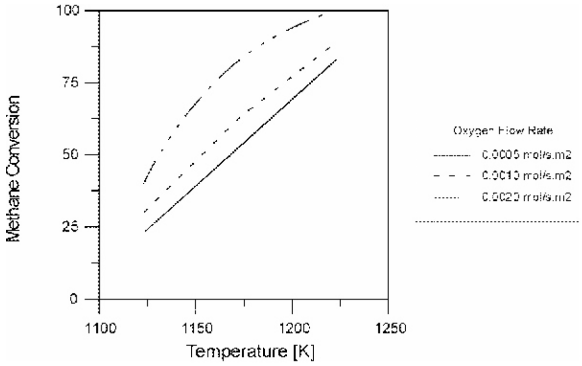


Fig. 10. Methane conversion for a membrane reactor as function of temperature and oxygen flow rate through the membrane (conversion at reactor length = 20 m).

CONCLUSIONS

The partial oxidation of methane was studied from a modeling point of view in a membrane reactor. Simulation results show that different parameters affect methane conversion and H_2/CO ratio, such as temperature, molar flow rate, steam and carbon dioxide recycling. Enhanced conversion of methane to syngas can be attained by recycling carbon dioxide and steam back to the reactor entrance as to shift the equilibrium reactions towards syngas. As such, the membrane reactors are a good alternative to produce syngas for GTL processes or pure hydrogen. Operating conditions can be set to control the H_2/CO ratio to a desired value, removing H_2 through the membrane. New simulations are needed to optimize the reactor and to study the reaction in multiple steps changing the temperature of each step as to produce a greater quantity of syngas and to reduce the amount of gas that has to be recycled.

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