



# Thermodynamic Evaluation and process simulation of the production of Hydrogen-Syngas Using Mixed Fe-based oxides with Methane

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# ABSTRACT

Hydrogen-syngas production is one of the actual and continuous problem in the petrochemical and refining industry, whereas a process that exhibits an optimal industrial efficiency and usage is needed. The use of mixed metal oxides (FeMO<sub>4</sub>, FeMoO<sub>4</sub>, Fe2ZnO<sub>4</sub>, Fe<sub>2</sub>MnO<sub>4</sub>) as oxygen carriers is proposed to minimize the disadvantages of the current partial oxidation of methane. The objective of the present work is to identify oxides that help the production of syn-gas and are able to regenerate through favorable conditions. This is accomplished by simulating an arrangement of two reactors. The main reduction reaction is carried out in the first reactor:  $CH_4 + Fe_2MO_4 = H_2 + CO + Fe + M$ . While in the second reactor the following reaction is carried out: Fe + M + H<sub>2</sub>O = Fe<sub>2</sub>MO<sub>4</sub> + H<sub>2</sub>. Results indicate that It is possible for the oxide to be completely regenerated, while optimal reaction parameters were obtained for each reactor observing that the material were completely regenerated while not affecting the hydrogen. FeMoO<sub>4</sub> produced syn-gas at 750 ° C. However, it was possible not regenerate at favorable conditions. Otherwise, Fe<sub>2</sub>ZnO<sub>4</sub> produced syn-gas at 730 ° C and regeneration was feasible at 440 °C. Finally, Fe<sub>2</sub>MnO<sub>4</sub> produced syn-gas at 640 °C with regeneration at 600 °C, being the one with the best operating conditions among the studied materials. Simulation results of the different oxides are presented using Aspen-Plus<sup>©</sup>.

Keywords: Fe2MnO4; syn-gas; Hydrogen; reduction





### 1. Introduction

Currently about 80% of the energy demand is supplied by fossil fuels (natural gas and oil), 14% of different renewable energies and 6% by nuclear energy. These proportions need to be changed so that there is less dependence on fossil fuels as the global energy demand increases. It is necessary that the renewable energy and the nuclear energy increase considerably and consequently the energy of fossil fuels will eventually decrease. Hydrogen itself is not a source of energy, but if it is an energy vector, it can serve as a transition for the industry between the use of energy provided by hydrocarbons and energy from renewable sources [1].

Hydrogen is a fundamental raw material for the petrochemical and refining industries, it can be produced by various sources of energy from fossil fuels to renewable energy sources via electricity. The most economical route to produce hydrogen is from hydrocarbons, such as natural gas and methanol, through the methane reformation process (SMR) [1,6].

 $CH_4 + H_2O \rightarrow CO + 3H_2$ 

(1)

Currently, there are large capacity hydrogen generating plants, due to the great demand of the refining industry, due to the new regulations that restrict fuels with a very low content of sulfur and aromatics, since the hydrodesulphurization process requires a large amount of hydrogen [6]

The main disadvantage for this process is the hydrogen yield that occurs. With SMR it is possible to achieve energy efficiencies of 13.1-14.6 GJ / 1000 Nm<sup>3</sup> giving a yield of 2.4-2.7 mol  $H_2$  for each mole of CH<sub>4</sub> [3].

An even more notable disadvantage is the significant amount of  $CO_2$  that is released during the process. Other processes have been investigated, such as the reforming of methane with  $CO_2$  with the use of metal catalysts [2-5]. The process consists in the reaction of reforming a greenhouse gas as would  $CH_4 + CO_2$  to syn-gas ( $CO + H_2$ ). The problem that occurs with these catalysts is the sintering that they suffer from the operating conditions and their deactivation by the formation of carbon (in the case of nickel-based catalysts) [4].

The current focus on hydrogen production is to find a way to obtain hydrogen from a renewable source of energy, for example; the electrolysis of water, the gasification of biomass or even nuclear energy. Currently the production of hydrogen by the above methods is not viable. The solution will continue to be to obtain hydrogen from natural gas, since a greater quantity is obtained despite its high  $CO_2$  emissions. Therefore, it becomes necessary to find new ways to obtain hydrogen from hydrocarbons that reduce production costs,  $CO_2$  emissions and increase their performance. [3]

It has been reported that the process of partial oxidation of methane (reaction 2, POX) has a better performance for the production of syn-gas and also has other advantages such as





being an exothermic reaction requiring less energy than the SMR and in addition to needing the use of small reactors because the residence time is short due to rapid kinetics (compared to the SMR). The reaction has been studied using catalysts of different compositions and natures. However, this presents some disadvantages as for example; the operating temperature is very high (900-1000  $^{\circ}$  C) and the need for an oxygen plant, which increases the initial investment of the process, making it more expensive.

 $2CH_4 + O_2 = 4H_2 + 2CO$ 

(2)

Recently, an improvement to the POX process has been reported, which consists in the partial oxidation through a chemical loop process (Chemical Looping Partial Oxidation, CLPO) which is a technology for the production of syn-gas, from natural gas and light hydrocarbons [7], this process was proposed by Ryden and Lyngfelt [9] and continued by Mattisson and Lyngfelt [8]. The most important advantage of this process is that from the produced syn-gas, the production of pure H2 is also feasible in a second stage of the process. Because heat transfer occurs directly between the gas and the oxygen carrier, it is convenient to reduce the size of the reactor, these factors make the CLPO a cheaper technology than the conventional one [7,9].

Use of metal oxides as carriers of oxygen is a strategy that avoids the expense of an oxygen plant to carry out the reaction 2. Since in the fuel reactor a reduction reaction is carried out to the metal oxide (MeO) providing the necessary oxygen (reaction 3) so that the partial oxidation of the methane is carried out and thus obtain syn-gas, in addition to the reduced metal as a reaction product. In the next step, the reduced metal is fed to the second reactor where it will be oxidized with water vapor (reaction 4). In Figure 1 you can see a basic outline of the CLPO process. It can also be seen that the final product of the first reactor is syn-gas and of the second, pure hydrogen is obtained.

 $CH_4 + MeO = 2H_2 + CO + Me$ (3)

 $H_2O + Me = MeO + H_2$ 

(4)







Fig. 1 CLPO process scheme

The MeO is used again in the fuel reactor, thus completing the cycle. This process has also been termed as POX-MeO. The performance of this process is determined by the performance of the oxygen carrier. Therefore, an ideal oxygen carrier must remain reactive after extensive redox cycles, in addition to its capacity as an oxygen carrier and its structural stability must be high [13].

The metal oxides that have been used have been studied for their performance as carriers of oxygen. In 2014 there were more than 700 oxygen carriers that had been synthesized and studied to improve this process [14]. The carriers are composed of two parts; the primary oxide and the inert support. In the study of primary oxides, the oxides of Fe, Ni, Cu, Mn, Co, Ti, etc. have been proposed as candidates. [7] Several processes have used the concept of CLPO as an example can be found; Ni-and Co-based carriers for pure hydrogen production developed by Svoboda et. to the. [18] the fluidized bed reactor using NiO on  $\alpha$ -Al2O3 as oxygen carrier proposed by Diego et al. to the. [19] the three-reactor scheme (TRCL) projected by Kang et. to the. [20]. Examining recent CLPO studies, you can find the syngas chemical looping process by Fan et. to the. [21] using OCs based on Fe, Ni, and Ce. The results show a purity obtained from syn-gas of> 90% with Ni- and Fe-based OCs but to these conditions the deposition of carbon and the formation of carbon are shown. carbides (Fe<sub>3</sub>C). Other proposed metals have avoided the deposition of carbon but have limited the conversion of methane, reducing the production of syngas.

There are many limitations with the single metals oxides, like thermodynamics and reaction kinetics, in order to solve these limitations, the binary metal oxides were proposed to enhance the kinetics and thermodynamics of the process, as well as the selectivity of the OCs for syngas production. Several examples can be found like the mixed metal ferrites studied by Aston et. al [22] with the 99% yield towards  $H_2$  and the re-oxidation of the OC was confirmed. Results were compared with a single Fe-oxide and the mixed metal spinnels and showed a higher extent of reduction under the same reaction conditions, which





produced more H<sub>2</sub> than the Fe-based material (Fe<sub>2</sub>O<sub>3</sub>). The Fe-Mn oxides were studied by Lambert et. al. [16] for the chemical looping combustion process, showing a fast reduction of (Mn,Fe)<sub>2</sub>O<sub>3</sub> to (MnO + Fe<sup>o</sup>) proving that the Fe-based binary oxides are an excellent proposal for the POX-MeO process for their re-oxidation feasibility and low-cost material. Due to these important features it was decided to study Fe-based binary oxides (FeMO<sub>4</sub>, M = Mn, Mo, Zn) that will provide high methane conversions towards syngas production, while providing chemical reactivity and high temperature stability of the OC's. Furthermore, the proposed Fe-based OCs (FeMO<sub>4</sub>) are expected to follow the next reactions scheme:

$4CH_4 + FeMO_4 \rightarrow 8H_{2(g)} + 4CO_{(g)} + Fe + M$	(5)
$CH_{4(g)} + FeMO_4 \rightarrow 2H_2O_{(g)} + CO_{2(g)} + Fe + M$	(6)
$CH_{4(g)} \rightarrow C + 2H_{2(g)}$	(7a)
$2CO_{(g)} \rightarrow C + CO_{2(g)}$	(7b)
$4H_2O_{(g)} + Fe + M \rightarrow FeMO_4 + 4H_{2(g)}$	(8)
$C + H_2O_{(g)} \rightarrow H_{2(g)} + CO_{(g)}$	(9a)
$C + 2H_2O_{(q)} \rightarrow 2H_{2(q)} + CO_{2(q)}$	(9b)

The POX-MeO-1 (reaction 5) produces syngas ( $H_2 + CO$ ) along with the reduced metallic species (Fe + M), while POX-MeO-2 (reaction 6) shows the complete oxidation of methane to produce ( $CO_2 + H_2O$ ). Under these conditions other reactions may arise such as the methane decomposition and the Boudard reactions (reactions 7a and 7b, respectively), these reactions produce coal which is an undesirable product. The re-oxidation of the reduced metallic species is described by reaction 8 to produce the original FeMO<sub>4</sub> and H<sub>2</sub>. Coal gasification may simultaneously occur in the re-oxidation stage (reactions 9a and 9b) leading to hydrogen production and carbon oxide species (CO and CO<sub>2</sub>). Due to the reported reaction behavior of Ni and Co ferrites as OCs in the syngas production and the re-oxidation of its reduced species (Fe and Mn) make this reaction concept very attractive to be evaluated using similar metallic oxides, such as; Fe<sub>2</sub>MnO<sub>4</sub>, FeMoO<sub>4</sub> and Fe<sub>2</sub>ZnO<sub>4</sub> under a CLPO reaction scheme.

The aim of the present work is to evaluate the theoretical feasibility of these metal oxides on a CLPO scheme, through the use of thermodynamic analyses and process simulation for the production of syngas. These will consist in the thermodynamic calculations of every reaction involved in the process to determine feasible operating conditions being; temperature, CH<sub>4</sub>/FeMO<sub>4</sub> molar feed ratio in the fuel reactor and temperature and steam/Fe-M molar ratio in the oxidation reactor. Process simulations using Aspen Plus<sup>®</sup> will focus in determining process material and energy balances as well as optimal operating conditions in both reactors and in the entire process. The simulation results will be used to evaluate the





thermal efficiency  $H_2$  and syngas yields of the process and compare them with current similar CLPO processes previously reported in the literature to estimate the potential of this technology.

# 2. Methodology

# 2.1. Thermodynamic analysis

Each reaction will be studied in terms of the Gibbs free energy as a function of temperature. Calculations of equilibrium concentrations in the CLPO for Fe<sub>x</sub>MO4 oxygen carriers (M = Mn, Mo, Zn) were performed using the RGIBBS reactor model of Aspen Plus ©. Since this reactor makes use of a method based on the technique of minimization of Gibbs free energy and that includes all possible reactions that may have an effect according to the possible compounds and phases in the reaction system. For this method it is necessary to define all the compounds that will be involved in the reaction. Therefore, the following gaseous compounds were defined: CH<sub>4</sub> (g), CO, CO<sub>2</sub>, H<sub>2</sub>, Zn and H<sub>2</sub>O, while for the solid compounds were included: C, Fe<sub>2</sub>MnO<sub>4</sub>, Fe2ZnO<sub>4</sub>, FeMoO<sub>4</sub>, MnO<sub>2</sub>, MnO, Mn, ZnO, Zn, MoO<sub>3</sub>, MoO<sub>2</sub>, MoO, Mo and Fe. The aim of this thermodynamic analysis is to evaluate the feasibility of the binary metal oxides in the reaction scheme, using the flowsheet shown in Fig. 2.



Fig. 2. Flowsheet for the thermodynamic analysis

# 2.2. Process Simulation

The simulation using Aspen Plus<sup>©</sup> concentrated on determining the material and energy balance of the process and finding the optimal operating conditions for each reactor. In the thermodynamic evaluation, the process variables studied were: reactor temperature, which varied from 100-1000 °C to 1 atm, the FeMO<sub>4</sub> molar feed which varied from 1 to 3 kmol/h.





Likewise, in the oxidation reactor the molar flow of  $H_2O$  was studied from 2 to 9 kmol/h in a temperature range of 100-1000 °C.

Simulation conditions used were: a thermodynamic system based on the Redlich-Kwong-Aspen (EOS) state equation to calculate the physical properties of the chemical compounds involved. The molar flow of  $CH_4$  was fixed at 4 kmol/h, in addition to search for the conditions where coal formation is not possible.

Once the process units were established several sensitivity analyses were performed to obtain the optimal operating conditions for the process, while finding the highest yield towards syngas (fuel reactor) and hydrogen (oxidation reactor) and simultaneously avoiding carbon formation in the fuel reactor. The first sensitivity analysis was performed in the fuel reactor aiming to find the molar feed ratio  $CH_4/FeMO_4$  and the operating temperature where the highest yield towards syngas and no carbon formation were obtained. The second sensitivity analysis was performed in the oxidation reactor aiming the complete regeneration of FeMO<sub>4</sub> and the highest yield of pure hydrogen production.

## 2.3. Syngas yield and thermal efficiency

The energy efficiency will be evaluated using equation (10) proposed by Abbott et al. [23], which is based on the first law of thermodynamics and is defined as the ratio between the energy produced ( $H_2 + CO$ ) and the energy required ( $CH_4$ ).

$$\eta = \frac{\dot{m}_i \times LHV_i}{\dot{m}_i \times LHV_i + W_i + q_i} \tag{10}$$

where  $m_i$  and  $LHV_i$  are the mass flow and the lower heating value of the "i" species, respectively, while  $W_i$  and  $q_i$  are the mechanical work and the required heat of the components "i", respectively. This latter refers mainly to the mechanical work and energy requirements of the equipment involved in the process to be evaluated. The mechanical work were not taken into account because it is out of the scope of the present work and the energy requirements are automatically calculated. Fuerthermore, the thermal effienciency was calculated according to the following expression:

$$\eta = \frac{\dot{m}_{H_2} \times LHV_{H_2} + \dot{m}_{CO} \times LHV_{CO}}{\dot{m}_{CH_4} \times LHV_{CH_4} + q_i}$$
(11)

The thermal efficiency can be calculated with the high caloric value (HHV) to obtain an suitable range of thermal efficiency. Table 1 shows the LHV and HHV of the species of interest involved in the process.





Fuel	HHV(MJ/kg)	LHV(MJ/kg)
Hydrogen	142.2	121.2
Carbon	10.1	10.1
monoxide		
Methane	55.5	50.0

Table 1. HHV and LHV of process species

Moreover, the yield to syngas was calculated from simulation results as a the mean yield of  $H_2$  and CO, according to the following expression:

$$Y_{syngas} = \frac{Y_{H_2} + Y_{CO}}{2} * 100$$
(12)

Besides, to reduce energy costs a Pinch Analysis was performed using heat exchangers from Aspen Plus, in order to exploit the temperature gradients between products and reactants involved in the process.

The CLPO process for the OC's scheme is shown in Fig. 3. The aim of the pinch analysis was to optimize the thermal efficiency of the process. To achieve this, heat exghangers were strategically placed where product streams (GAS-1 and GAS-2) were able to exchange heat with feed streams (methane) to be preheated and to generate steam (STEAM and CH4-PRH streams). Also, in Figure 3 details of the entire process streams, recirculations and heat generation by burners to provide energy to reactors, stream splits and separation of gases from solids (cyclone separators) are presented.



Fig. 3. Process Simulation Flowsheet

## 3. Results and Discussion

# 3.1. Thermodynamic analysis





Fig. 4 presents the thermodynamic analysis of the process variables, showing the operation area where the target conditions are achieved (No carbon formation and full OC regeneration).



Fig. 4. Free-carbon operation area in fuel reactor (a) and full OC's oxidation area in oxidation reactor (b).

Results of the thermodynamic analyzes indicate that the widest area belongs to Fe<sub>2</sub>ZnO<sub>4</sub> followed by FeMoO<sub>4</sub> and Fe<sub>2</sub>MnO<sub>4</sub>. In the case of the regeneration area, the largest one belongs to Fe<sub>2</sub>MnO<sub>4</sub>, then to Fe<sub>2</sub>ZnO<sub>4</sub>, while complete oxidation is not possible when using FeMoO<sub>4</sub> as OC for the process. Therefore, FeMoO<sub>4</sub> can be discarded as a possible OC for the process, since it cannot be completely oxidized under the studied conditions. Although, Fe<sub>2</sub>ZnO<sub>4</sub> presents the largest area of operation without carbon generation, its regeneration area is very small, thus limiting the conditions of the oxidation reactor T < 400 °C and H<sub>2</sub>O  $\leq$  9 kmol/h. However, this temperature is too low for a relatively fast desired reaction kinetics, whereas, a high amount of water used increases energy costs. On the other hand, Fe<sub>2</sub>MnO<sub>4</sub> shows a good carbon-free operating area, with conditions of T > 620 °C and Fe<sub>2</sub>MnO<sub>4</sub> > 1.4 kmol/h, which comply with a presumably fast desired reaction kinetics. For the case of the oxidation reactor, there is a good range of temperature and molar flowrate of H<sub>2</sub>O where a complete regeneration can be obtained, making it possible to achieve suitable conditions for the entire process.

As a result of the thermodynamic analysis it can be deduced that the only OC that can satisfy with the previously stated requirements for the CLPO of methane process is  $Fe_2MnO_4$ , hence the process simulation was performed only for  $Fe_2MnO_4$ , which is presented in the following section.

#### 3.2. Process Simulation



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Simulation of the process was performed in two stages. In the first stage, the optimal parameters of each reactor were found by sensitivity analyses and results of the previous thermodynamic analysis. In the second stage, an optimal energy balance was achieved through an energy sensitivity analysis (Pinch Analysis) by adding heat exchangers between the input and output streams, thus obtaining the final simulation scheme presented in Figure 3.

Since, the avoidance of carbon formation in the fuel reactor is one of the main objectives of the simulation, a sensitivity analysis was carried out to study the variations presented as a function of the operating temperature and the molar feed to the POX-MeO reactor (fuel reactor).

Fig.5b shows results of this sensitivity analysis on carbon, where the stoichiometric methane feed (4 kmol/h) was fixed (according to the stoichiometric value in reaction 5). In this figure it can be seen that within the POX-MeO reactor carbon free operation can be achieved at conditions of T > 620°C and molar flowrates of Fe<sub>2</sub>MnO<sub>4</sub> > 1.4 kmol/h. Fig. 5a presents other results of the sensitivity analysis on the production of hydrogen, which show a greater production of hydrogen at T > 600°C, and a trend to generate more hydrogen by feeding less Fe<sub>2</sub>MnO<sub>4</sub>, while the point of greatest hydrogen production (H<sub>2</sub> = 7.89 kmol/h) occurs at conditions of T = 1000 °C and Fe<sub>2</sub>MnO<sub>4</sub> = 1 kmol/h.



Fig. 5. Surface response of  $H_2(a)$  and C (b) formation in POX-MeO reactor

In Fig 6a it can be observed that the formation of CO has a similar behavior to the production of hydrogen, it is desirable that the molar  $H_2$ /CO ratio to be equal or greater than 2, which can be achieved at temperatures higher than 620 °C and molar flowrates greater than 1.4 kmol/h. Results presented in Fig. 6b also show that reaction 6 is promoted at conditions of T = 620 °C and at higher OC molar flowrates, while at higher temperatures the CO<sub>2</sub>





generation decreases. Even though it is not one of the main objectives of the present simulation, low  $CO_2$  production is encouraged.



Fig. 6. Surface response of CO(a) and CO<sub>2</sub> (b) formation in POX-MeO reactor

Fig. 7a shows the production of reduced Fe, where it is promoted at the same conditions where no carbon formation is allowed, thus confirming that the operating conditions for the reaction 5 to be carried out at temperatures higher than 620 °C. Also, in Fig. 7b the production of MnO is shown, which is a product that does not agree with reaction 5, since at the thermodynamic conditions studied here the reduction of the MnO<sub>4</sub> ion was limited to



Fig. 7. Surface response of Fe(a) and MnO (b) formation in POX-MeO reactor





the formation of MnO because Mn generation was not favored. Here in this Figure it is also evident that the behavior of MnO production is very similar to Fe generation.

In order to find optimal operating conditions, a comparision of different syngas production scenarios is presented in Table 2. In this Table the production of H<sub>2</sub>, CO, Fe and MnO at temperatures of 650°C, 700°C, 750°C, 800°C, 850°C and 900°C were obtained at a fixed molar flowrate of 1.63 kmol/h of Fe<sub>2</sub>MnO<sub>4</sub>. Likewise, this molar flowrate is proposed for an operating window, where no carbon formation is possibile.

Temperature (ºC)	H <sub>2</sub> (kmol/hr)	CO (kmol/hr)	Fe (kmol/hr)	MnO (kmol/hr)
650	5.31	1.61	3.2	1.6
700	6.17	2.54	3.2	1.6
750	6.84	3.33	3.2	1.6
800	7.21	3.62	3.2	1.6
850	7.36	3.69	3.2	1.6
900	7.39	3.75	3.2	1.6

	Table	<b>2.</b> H <sub>2</sub> ,	CO, Fe,	MnO	Production in	function	of temperature
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When analyzing the production of hydrogen with respect to temperature it can be noted that from 800°C there is no considerable variation in terms of syngas generation since only a marginal increase is presented. These extreme conditions (T > 800 °C) will ultilmately impact in the associated energy costs of the entire process. Therefore, a temperature within the range of 750°C-800°C is very appropriate for the present study. When evaluating this temperature range the temperature of 775°C was considered suitable due to the fact that the syngas gemerated shows a H<sub>2</sub>/CO molar ratio of 2.03, which is very convenient for further processing of theis gas, for example towards the Fischer Tropsch process. Also, at these conditions Fe<sub>2</sub>MnO<sub>4</sub> is completely reduced to Fe and MnO according to reaction 5.

Fuerthermore, Fig. 8 shows the contour plot of methane conversion as a function of reactor temperature ( $^{\circ}$ C) and Fe<sub>2</sub>MnO<sub>4</sub> molar feed (kmol/h). By analyzing these results under the proposed required conditions, a methane conversion of 95.9% can be obtained. The 99% of methane conversion can be obtained at higher temperatures than 800 °C and higher Fe<sub>2</sub>MnO<sub>4</sub> molar flowrates of 2.0, but this results in a minimal increase in conversion, compared with higher temperatures that would have to be reached at these conditions.

Consequently, the optimal operating conditions for the fuel reactor (POX-MeO) can be considered as T = 775 °C and Fe<sub>2</sub>MnO<sub>4</sub> = 1.6 kmol/h feed. Finally, this is an important result since these are the conditions where there is no carbon deposition is feasible and a complete reduction of Fe<sub>2</sub>MnO<sub>4</sub> also occurs, along with a high conversion of methane (95.9%) and a high production of syngas (CO + H<sub>2</sub> = 10.52 kmol/h) that has a H<sub>2</sub>/CO molar ratio of 2.03, which is very convenient as described above.







Fig. 8. Contour plot of methane conversion as function of temperature and Fe<sub>2</sub>MnO<sub>4</sub>

Moreover, Fig 9a and 9b show the production of pure hydrogen and the regeneration of the OC, respectively, with respect to the molar steam feed and the temperature of the oxidation reactor (REGEN) for the selection of the more favorable operating conditions in the process.

In Fig. 9b it is shown that the oxidation of Fe and MnO is feasible at very low temperatures (i.e. 100 °C) and a maximum H<sub>2</sub> production of 5.19 kmol/h can be obtained. However, in order to favor the kinetics of reaction (8), it is convenient to use temperatures above 500 °C, according to the results reported by Voldsund et. al. [24]. Thus, the optimum operating condition for the oxidation reactor can be established at T = 500 °C and a steam molar flowrate of 6.8 kmol/h resulting in a production of Fe<sub>2</sub>MnO<sub>4</sub> = 1.6 kmol/h and H<sub>2</sub> = 5.19 kmol/h.



Fig. 9. Surface response of H<sub>2</sub>(a) and Fe<sub>2</sub>MnO<sub>4</sub> (b) formation in REGEN reactor

Furthermore, Table 3 presents the material and energy balance of the process simulation where two methane burners (BURNER1 and BURNER2) and two heat exchangers (HEATX1 and HEATEX2) were used according to the process scheme of Figure 3. The heat exchangers were used to preheat the methane and water fed to the process using the product gas streams of each reactor (GAS-1 and GAS-2). Methane is preheated and reaches a separator (S1) where it is divided into two streams, one for the reactor feed of 4 kmol/h (CH4-RXN stream) and the other stream for the burners, which will reach another separator (S2) to feed each burner (streams B1 and B2).

In order to achieve a temperature of approximately 775 °C in the POX-MeO reactor, it is necessary that the BURNER1 generates a heat of 987.73 MJ/h (Q1). Likewise, for the REGEN reactor to reach a temperature of approximately 500 °C, the BURNER2 is required to generate a heat of 192.35 MJ/h (Q2).

Furthermore, methane used as fuel combined with air to reach the required temperature in both reactors, these parameters were established by sensitivity analysis, once obtained for optimum parameters the results of the mass balance was obtained and results are reported in Table 3.

Table 3 shows the products of the POX-MeO reactor, with H<sub>2</sub> production of 7.05 kmol/h, together with 3.47 kmol/h, 0.38 kmol/h and 0.65 kmol/h of CO, CO<sub>2</sub> and H<sub>2</sub>O, respectively. Finally, it is observed that 0.15 kmol/h of unreacted methane in the final syngas product stream. On the other hand, in the solids stream, a complete reduction of Fe<sub>2</sub>MnO<sub>4</sub> is observed where 1.63 kmol/h of MnO and 3.2 kmol/h of Fe were achieved.

Otherwise, results of the REGEN reactor consisted of a complete regeneration of  $Fe_2MnO_4$ , with a flowrate of 1.63 kmol/h, which was recirculated to the POX-MeO reactor. In the case of hydrogen, 4.89 kmol/h was obtained, together with 1.91 kmol/h of  $H_2O$  (GAS-2).





Reported results of a typical steam methane reforming process (SMR) are approximately 75% H<sub>2</sub>, 12% CO, 6% CO<sub>2</sub>, and 7% CH<sub>4</sub>, while results obtained by the POX-MeO process are 60% H<sub>2</sub>, 30 % CO, 6% H<sub>2</sub>O, 3% CO<sub>2</sub> and 1% CH<sub>4</sub>. Although, the POX-MeO achieves a lower mole fraction of H<sub>2</sub> compared with steam reforming. However, POX-MeO generates a greater conversion of methane and syngas with less impurities than SMR. These results can also be compared with a similar CLPO processes, but with Ni-based OCs which obtained a dry gas product composition of 65% H<sub>2</sub>, 25% CO, 9% CO<sub>2</sub> and 1% CH<sub>4</sub> [19]. These results are similar, but it can be noted that the H<sub>2</sub>/CO molar ratio is less than 2, which is not a convenient feature for a syngas.

STREAM	CH4	CH4-PRH	CH4-RXN	MEO	POX-MEO	GAS-1	SYNGAS	ME	WATER	GAS-2	STEAM	REGEN	H2
Temperature (ºC)	25.00	750.00	750.00	501.21	775.63	775.63	191.70	775.63	25.00	501.21	102.43	501.21	287.95
Pressure (atm)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Mole Flows (kmol / hr)	5.40	5.40	4.00	1.63	16.59	11.70	11.70	4.89	6.80	6.80	6.80	8.43	6.80
CH4	5.40	5.40	4.00	0.00	0.15	0.15	0.15						
со			-		3.47	3.47	3.47						
CO2					0.38	0.38	0.38					-	
H2					7.05	7.05	7.05			4.89		4.89	4.89
H2O					0.65	0.65	0.65		6.80	1.91	6.80	1.91	1.91
FE2MNO4				1.63								1.63	
MNO			-		1.63			1.63					
FE			-		3.26			3.26					

#### Table 3. Simulation results for the production of syngas from $CH_4$ and $Fe_2MnO_4$

#### 3.3. Thermal Efficiency

Comparing with other reported studies, the use of a binary oxide as an oxygen carrier greatly helps to reduce temperature operating conditions, since reported operating temperature for the POX-MeO reactor using  $Fe_3O_4$  can reach temperatures equal or greater than 1500°C [21]. Therefore, results reported in the present work represent an important improvement for this process.

The thermal efficiency was calculated as previously indicated in the methodology section using the equation (10), resulting in a theoretical thermal efficiency that varied between 88.7% (using LHV) and 92.8% (using HHV).

In direct comparison with the efficiency of the SMR process (70-85%), the current process of CLPO (POX-MeO using  $Fe_2MnO_4$  as OC), the efficiency of the process is between 3.7-22.8% higher, attributed entirely to the hydrogen generated in the regeneration stage, which makes the  $H_2$ /fuel molar ratio higher than 2.0, hence meaning a higher thermal efficiency.





#### 3.4. Process Yield

According to the results of the mass balance, shown in Table 3. The theoretical yield obtained towards synthesis gas was calculated by the procedure described above. In addition, the molar ratio of  $H_2$ /fuel and  $H_2$ /CO were calculated and compared with other chemical looping processes already reported in literature. This comparison is shown in Table 4.

Tabla	1 Thormal	Efficiency	of the	DOX MoO	with	othor	nrococcoc
rapie	<b>4.</b> mermai	Eniciency	or the	POX-IVIEO	witri	other	processes

Process	Thermal efficiency
SMR [25]	70-85%
ATR [26]	60-75%
POX [19]	60-75%
POX-MeO (Fe <sub>2</sub> MnO <sub>4</sub> )	88.7-92.8%

Furthermore, Table 5 presents a comparison of the obtained results of the POX-MeO process using  $Fe_2MnO_4$  as OC with respect to other processes for syngas production reported in the literature. Here, in this Table it is evident that the present CLPO (POX-MeO) compared to a SMR process [25] produced twice more  $H_2$  for each mole of CH<sub>4</sub> being fed. This is mainly attributed to the  $H_2$  produced in the regeneration of  $Fe_2MnO_4$  with steam. Additionally,  $Fe_2MnO_4$  has proven to be a convenient OC since, compared to the results reported by de Diego [19],  $Fe_2MnO_4$  obtains a 20% yield and a  $H_2$ /fuel molar ratio of 0.5, which is higher than that reported for Ni-based OCs. The  $H_2$ /fuel ratio is close to that reported for the autothermal methane process (ATR) by De Souza [26] with only 0.07 difference, but the POX-MeO process reports a greater methane conversion.

Process	H <sub>2</sub> /Fuel molar ratio	Y <sub>Syngas</sub> (%)	H <sub>2</sub> /CO molar ratio
SMR [25]	1.47	86.7	3.0-5.0
ATR [26]	2.91	61	1.6-2.6
POX [19]	2.5	67	2.6
POX-MeO (Fe <sub>2</sub> MnO <sub>4</sub> )	2.98	87.4	2.03-3.44

Table 5. Comparison of the POX-MeO process with respect other similar CL processes

#### 4. Conclusion

Different types of  $Fe_xMO_4$  (FeMoO<sub>4</sub>, Fe<sub>2</sub>ZnO<sub>4</sub>, Fe<sub>2</sub>MnO<sub>4</sub>) were evaluated by thermodynamic analyses and process simulation for the production of hydrogen-synthesis gas (syngas) using Aspen Plus. According to the thermodynamic analysis, it can be concluded that Fe<sub>2</sub>MnO<sub>4</sub> is the best oxygen carrier among the Fe-based studied materials for the production of H<sub>2</sub> and syngas. Simulation results found optimal reaction conditions to carry out the POX-MeO process. The optimum temperature in the fuel reactor was 775°C, obtaining a methane conversion of 95.9% without carbon formation, while the temperature of the oxidation reactor was established at 501°C for a complete regeneration of the OC, in addition to a stream of pure hydrogen. Furthermore, these results show a syngas stream with a H<sub>2</sub>/CO molar ratio of 2.03 from the POX-MeO reactor and high purity hydrogen stream from the REGEN



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reactor. The thermal efficiency (88.7-92.8%) and yield (87.4%) obtained are higher compared to other conventional syngas production processes. Finally, an experimental evaluation of the present process is recommended, to assess the results obtained and the viability of this process.

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