



Hydrogen Production by a Fe-based Oxygen Carrier and Methane-Steam Redox Process: Thermodynamic Analysis

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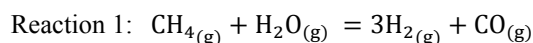
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Abstract— The redox performance of iron oxide magnetite (Fe_3O_4) as an oxygen carrier was investigated for hydrogen (H_2) and/or syngas (H_2+CO) production through a methane-steam redox process using a thermodynamic analysis and process simulation to find most favorable reactions conditions (MFRC). The reaction system was divided in two reactors. In the first reduction step the following reactions were targeted: $\frac{1}{4} \text{CH}_4(\text{g}) + \text{Fe}_3\text{O}_4 = 3\text{FeO} + \frac{1}{4} \text{CO}_2(\text{g}) + \frac{1}{2} \text{H}_2\text{O}(\text{g})$ and $\text{CH}_4(\text{g}) + \text{Fe}_3\text{O}_4 = 3\text{FeO} + 2\text{H}_2(\text{g}) + \text{CO}(\text{g})$, which both represent complete and partial oxidation of methane by an oxygen carrier (Fe_3O_4). While several other reactions were allowed to proceed such as the carbon formation by methane decomposition as well as further iron reduction to Fe. The $\text{CH}_4/\text{Fe}_3\text{O}_4$ molar ratio was varied from 0.25-1 in a temperature range from 300-900 °C. In the second oxidation reactor the solid products from the first reactor were combined with steam to regenerate the oxygen carrier by: $3\text{FeO} + \text{H}_2\text{O}(\text{g}) = \text{Fe}_3\text{O}_4 + \text{H}_2(\text{g})$ using a fixed feed of 5.5 mols of H_2O in a temperature range of 300-900 °C. Thermodynamic analysis by the Gibbs free energy minimization technique and process simulation were performed in Aspen Plus. Criteria used to find MFRC were: carbon-free formation conditions, reduction and oxidation carrier phases as FeO and Fe_3O_4 , respectively, avoiding the formation of metallic Fe (carbon formation promoter) and the minimum possible operating temperatures for energy saving reasons. Results indicate that in the reduction reactor the MFRC consist in $T = 650\text{-}700^\circ\text{C}$ and $\text{CH}_4/\text{Fe}_3\text{O}_4 = 0.75\text{-}1$, While for the regenerator were: $T = 520\text{-}600^\circ\text{C}$. Details of the mass and heat balances are also presented.

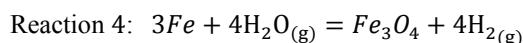
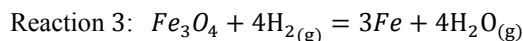
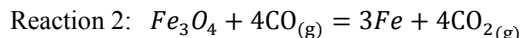
Keywords— Methane-Steam Redox Process; Oxygen carrier, Thermodynamic Analysis.

I. INTRODUCTION

Hydrogen, apart from being an important industrial chemical worldwide, can be considered as the choice of carrier for the emerging renewable energy generation technologies. However, today hydrogen production relies on the use of fossil fuels, being steam methane reforming (SMR) the preferred route for the industrial production of hydrogen, since it accounts for more than a half of the world hydrogen production. SMR is a highly endothermic catalytic reaction ($\Delta H_{298}^\circ = 206 \text{ kJ/mol}$), which takes place in a temperature range of 700-850°C according to:

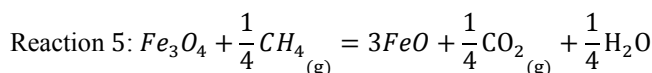


The economic feasibility of SMR units are restricted by scale, since small-scale plants make hydrogen production uneconomical. Therefore, large centralized industrial plants have been found to be the most cost-effective [1]. World consumption of hydrogen is projected to increase 3.5 percent annually through 2018 to more than 300 billion cubic meters and is expected to grow to about 5-6% in the next five years [2]. Therefore, an alternate approach that may include the use of near and remote natural gas reserves, especially those coming from the recent shale gas sites being explored worldwide, is needed for more cost-effective small scale H_2 production. Consequently, there is a renewed interest in the old and mature steam-iron process [3]. This process, in principle, is one of the few processes that do not require the step of gas separation to produce a high purity hydrogen stream at small scale. This process involves a series of the redox reactions, where the reduction of iron oxide with syngas (a mixture of CO and H_2) is followed by the oxidation of the reduced metallic iron with steam according to the following reactions:



This process make use of a metal oxide (Fe_3O_4) as an oxygen carrier to perform the redox reactions (2-4) and at the same time serves as a heat transfer medium between the two reactors (reduction and oxidation) in a cycle reaction loop in order to make a continuous process and to increase energy efficiency. Gaseous carbon oxides rich stream is achieved after steam condensation from the reduction reactor (reactions 2 and 3) and a high purity hydrogen stream can be obtained after steam condensation from the oxidation reactor (reaction 4). Due to the significant characteristics of this process, this has been used as a reference for the production of H_2 in the chemical looping combustion [4] and H_2 storage [5].

For the specific case of the reduction of iron oxide with a gas fuel such as methane and the redox iron pair being $\text{Fe}_3\text{O}_4/\text{FeO}$ the following reaction applies:



Even though several other metal oxides have been proposed under the chemical looping concept for hydrogen production, the $\text{Fe}_3\text{O}_4/\text{Fe}$ redox system is one of the most studied systems due to the fact that employs inexpensive materials and because it produces a high yield of H_2 per mass of iron (48 g H_2/kg Fe, from equation 4). One of the main challenges of a looping operation of the steam-iron process lies in the temperature swings and different gaseous atmospheres that the material needs to be exposed in order to perform a cycle operation in the process. This operation mode, performed at high temperatures, often produce sintering in the material with the consequent loss of activity and this being reflected in a significant decrease of lifetime, thus reducing the overall efficiency of the process.

In order to overcome this problematic, several studies have concentrated in improving reactor kinetics and the stability of the materials by modifying iron oxide with the addition of metals like Al, Mo and Ce as reported by Otsuka et al [6]. Takenaka et al [7] employed a mixture of Ni–Cr– FeO_x reacted with methane followed by reaction with steam to produce pure hydrogen, where Cr species in Ni–Cr– FeO_x were stabilized as octahedral Cr^{3+}O_6 in the ferrites $\text{Cr}_x\text{Fe}_{3-x}\text{O}_4$ during the redox reactions. It was concluded that Cr helped to inhibit sintering of iron species. While Urasaki et al [8] added palladium and zirconia to the iron-based oxygen carrier to accelerate both the reduction and oxidation rates and also found that zirconia enhanced structural and thermal stability in iron oxides. Zafar et al [9] used SiO_2 and MgAl_2O_4 as supports to reduce the sintering of iron oxide, while Galvita and Sundmacher [10] proposed the use of Cr_2O_3 – Fe_3O_4 – CeO_2 – ZrO_2 to provide stability to the oxygen carrier up to 100 redox cycles. However, some carbon monoxide in the hydrogen product stream was observed during the re-oxidation phase, whereas Liotta et al [11] examined the redox behavior and structural stabilization of ceria-zirconia solid solutions supported on alumina towards the CO oxidation catalysis. The unique oxygen storage capacity of the CeO_2 – ZrO_2 combined with iron oxides produced an oxygen carrier that combines this important feature with the thermal stability and activity as confirmed by several research studies [12-14].

Moreover, several researchers [15-19] have proposed a novel two-step SMR process for hydrogen production based on the chemical looping concept and a scheme of this is presented in in Figure 1.

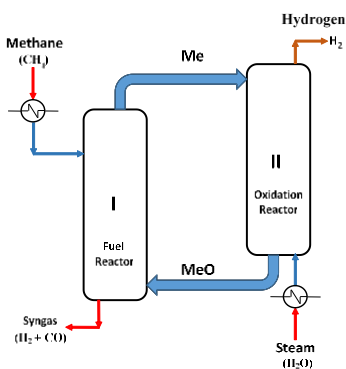
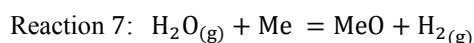
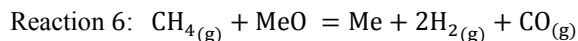


Figure 1. Conceptual scheme of the SMR chemical looping

In the fuel reactor (I) the oxygen carrier, typically a metal oxide (MeO), is reacted with methane to produce syngas and the reduced metal (Me) according to:



Finally, the regenerated oxygen carrier is sent back to the fuel reactor to complete one full loop or reaction cycle. The combination of reactions (6) and (7) leads to reaction (1), which is the SMR reaction. The reaction process indicated in Figure 1 is usually called as chemical looping steam methane reforming (CL-SMR). This process separate the feed of methane and steam in two step reactors thus, producing a syngas stream in the first and a H_2 gas product in the second that needs no further purification.

One critical issue of this proposed reaction scheme deals with the relatively low reactivity of the oxygen carrier towards the reoxidation of the reduced metal (reaction 6). Several metal oxides have been reported as oxygen carriers for the CL-SMR such as Fe_3O_4 , WO_3 , SnO_2 , Ni–Fe, (Zn, Mn)–Fe, Cu–Fe and Ce-based oxides [15]. Among all these oxygen carriers such as Fe-oxides have proven to be suitable for the CL-SMR. Nevertheless, thermodynamic constrains for the hydrogen evolution make this oxygen carrier to behave in a complex way, since in some cases the complete reduced Fe phase is required for a high H_2 production yield, while the complete oxidation with steam beyond Fe_3O_4 is thermodynamically limited [20]. However, this oxygen carrier can be considered ideal for CL-SMR applications and this is based on its reduced propensity to carbon formation and resistance to form agglomerates. These last features are critical for an oxygen carrier to retain its activity over continuous redox cycles. Furthermore, iron oxide oxygen carriers are not susceptible to form sulfide or sulfate compounds under sulfur-containing atmospheres [21], while large natural reserves and low cost make them suitable for implementation at large scales [22-24]. Some drawbacks of these Fe-based oxygen carriers include weak redox characteristics, relatively low oxygen storage capacity (OSC), and limited reactivity towards gaseous fuels like methane [25].

Additionally, Fe presents multiple oxidation states such as Fe_2O_3 , Fe_3O_4 , FeO and Fe and as indicated above it presents thermodynamic limitations, since only the transformation from Fe_2O_3 to Fe_3O_4 is feasible for the total oxidation of methane, whereas partial oxidation of methane (POX) is favored in the transition reduction from FeO to Fe according to Monzam et al [26].

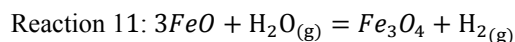
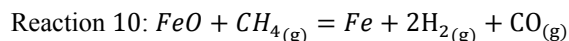
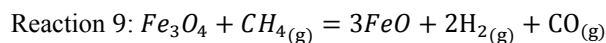
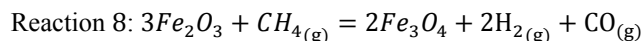
Thermodynamic Considerations

Several thermodynamic analyses have studied different approaches to the CL-SMR process. Fraser et al. [26] performed a thermodynamic analysis of the reformer sponge iron cycle (RESC) process that consisted in the hydrogen production including a hydrocarbon reformer and a sponge iron reactor (SIR). The reformer output gas (H_2 and CO) reduces the pellets from magnetite (Fe_3O_4) and wuestite (FeO) into iron metal (Fe) through reactions (2) and (3) and the reduced Fe is reoxidized with steam by reaction (4). They found that the process offers hydrocarbon to hydrogen conversion efficiencies in the order of



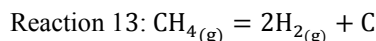
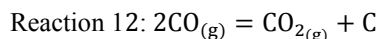
75% vs LHV for methane and at a temperature range of 750 °C and above. Steinfeld and Kuhn [27] presented a high temperature thermochemistry analysis of the Fe_3O_4 reduction with methane for the production of syngas. They studied the reaction system at temperatures above 1000 °C aimed for the use of concentrated solar radiation as the energy source. They found that a mixture of 66.7% H_2 and 33.3% CO can be achieved with complete reduction to metallic Fe. Kang et al [28] performed a Thermodynamic analysis of the three-reactor chemical-looping process (TRCL), which consisted in a fuel reactor, a steam reactor, and an air reactor. In the fuel reactor, natural gas (mainly CH_4) is oxidized to CO_2 and H_2O by the lattice oxygen of the oxygen carrier (Fe_2O_3 , WO_3 , and CeO_2). In the steam reactor, the steam is reduced to hydrogen through oxidation of the reduced oxygen carrier, while in the air reactor; the oxygen carrier is fully oxidized by air. Results indicate that an expected hydrogen production of 2.64 mol H_2 per mol CH_4 under thermo-neutral conditions can be achieved and this was affected mainly by the steam-conversion rate. Bohn et al [29] studied the hydrogen production with simultaneous capture of CO_2 using the redox reactions of iron oxides in packed beds. They examined the thermodynamics of exposing Fe_2O_3 to a syngas to produce a high purity CO_2 stream ready for sequestration, while the oxidation of FeO to Fe_3O_4 with steam produced a high purity hydrogen stream. They found that reduction to Fe, rather than FeO , in step 1 gave low levels of H_2 and after 10 cycles of reduction and oxidation led to the deposition of carbon at lower temperatures. Furthermore, Svoboda et al [30] studied the thermodynamic and chemical equilibrium of the reduction of Fe_3O_4 by CH_4 and oxidation of iron by steam. The study was concentrated on finding convenient conditions for reduction of Fe_3O_4 to iron at temperatures from 400- 800 K, but also on the possible formation of undesired soot, Fe_3C and iron carbonate. Reduction of magnetite with methane did not produce iron carbides or carbonates, whereas conditions favored the formation of Fe and CO_2 , and H_2O as gas products.

From all previous thermodynamic studies related to the use of iron oxides as oxygen carrier for the complete oxidation of methane (reactions 2 and 3) or the partial oxidation of methane, which is a special case of the so called chemical looping steam methane reforming (CL-SMR) that involve the partial oxidation of methane through:



This last reactions present the advantage to produce a syngas mixture in the iron reduction reactor (reactions 8-10), while the regeneration of the reduced Fe with steam is able to produce a high purity H_2 stream. However, this regeneration will only produce Fe_3O_4 as reaction (11) is thermodynamically limited. Therefore, in a cyclic operation the redox reaction between the two reactors of Figure 1 will only be reactions (9) and (11). However, carbon deposition during the operation is another

important aspect to be considered in this process through the Boudouard and methane pyrolysis reactions:



Galvita and Sundmacher [31] studied the CL-SMR reaction system and concluded that at a reduction of approximately 60% of the Fe_2O_3 carbon formation was avoided. Further reduction towards Fe produced carbon deposits on the oxygen carrier. Therefore, the restrictions in order to avoid carbon formation and the steam oxidation of the reduced iron lead to select the $\text{Fe}_3\text{O}_4/\text{FeO}$ as the ideal redox pair for the CL-SMR process.

Up to date, no thermodynamic analysis have been performed to explore optimal reactions conditions. From one end: complete oxidation of methane by Fe_3O_4 (steam iron process, SIP, which produce only CO_2 and FeO in the reduction reactor) to the other end: partial oxidation of methane (POX-MeO or CL-SMR, where syngas and FeO is produced) and subsequent hydrogen production from reoxidation of FeO . This proposed process operation aims to restrict the oxidation states between the two reactors of Figure 1 to the $\text{Fe}_3\text{O}_4/\text{FeO}$ redox pair, while avoiding carbon formation to insuring a high purity hydrogen stream from the steam oxidation reactor.

Therefore, the aim of the present investigation is to perform a thermodynamic and process simulation studies to find optimal operating conditions (avoiding carbon formation) close to equilibrium for a high H_2 and/or syngas production. In addition, these under the SIP/CL-SMR reaction system using methane as a feed (for the fuel reactor) and steam (for the oxidation reactor), while employing the $\text{Fe}_3\text{O}_4/\text{FeO}$ redox pair between the reduction and oxidation reactors. This analysis will include the evaluation of the thermodynamic equilibrium composition of the reaction system, the behavior of the $\text{Fe}_3\text{O}_4/\text{CH}_4$ and $\text{H}_2\text{O}/\text{FeO}$ feed molar ratios as a function of temperature and products composition for the reduction and oxidation reactors, respectively. Furthermore, it is expected that the feed molar ratio of Fe_3O_4 to CH_4 will determine the operation mode of the process from complete oxidation (SIP) to a partial oxidation of methane (CL-SMR). Consequently, a process simulation will examine oxygen carrier recirculation from the oxidation to the reduction reactors and its influence on the process operating conditions.

II. METHODS

Thermodynamics Method

Thermodynamic calculations in the present study were performed by the Gibbs free energy minimization technique. In a reaction system where many simultaneous reactions take place, equilibrium calculations can be performed through the Gibbs energy minimization approach (also called the nonstoichiometric method). Details of this technique can be found elsewhere [32]. All calculations were performed using the ASPEN Plus® RGIBBS reactor model and the Redlich-Kwong equation of state for correction of non-ideal conditions. In a RGIBBS reactor the equilibrium composition of all possible combination of reactions that are able to take place within the

thermodynamic system. The RGIBBS program of this reactor finds the most stable phase combination and establish the phase compositions where the Gibbs free energy of the reaction system reaches its minimum at a fixed mass balance, constant pressure, and temperature. For the oxidation of methane and regeneration of the iron oxide species the gaseous species included were: CH_4 , CO , CO_2 , H_2 , and H_2O , while solid species were: C , Fe , FeO , Fe_2O_3 , F_3C , and FeCO_3 .

For the fuel reactor the temperature was varied in the range of 300-900 °C at 1 atm. While, the $\text{CH}_4/\text{Fe}_3\text{O}_4$ feed molar ratio was varied from 0.25 (stoichiometric value according to reaction (5)) to 1 (stoichiometric value according to reaction (9)). Whereas, for the oxidation reactor the temperature was also varied in the range of 300-900 °C at 1 atm. The solid product of the fuel reactor was fed to the steam oxidation reactor. In this reactor, the FeO is to be reacted with steam according to reaction (11). In this reactor the $\text{FeO}/\text{H}_2\text{O}$ feed molar ratio was varied from 3 (stoichiometric value according to reaction (11)) to 0.546. This represents a gradual increase from 1 kmol/h of H_2O per 3 kmol/h of FeO up 6 kmol/h of H_2O per 3 kmol/h of FeO . This feed steam variation was intended to find the minimum amount of steam needed in order to regenerate FeO to Fe_3O_4 at a reasonable oxidation temperature, where kinetics are favorable (500-600 °C) [39]. It is important to notice that all the present simulation calculations are based on theoretical thermodynamic considerations and these are to be taken as a guide to further experimental evaluation of the reaction systems, since no heat and mass diffusional limitations as well as kinetics effects were taken into account for the conformation of the present thermodynamic analysis.

Process Simulation Method

Process simulation calculations was performed using the Aspen-Plus© Engineering Process Simulator. This is a program for simulation of chemical processes in which the analysis of chemical processes as well as heat integration can be made. This simulator was employed for the analysis of the process scheme of Fig. 2. The module of Aspen-Plus that was used to evaluate the reaction systems were: the RGibbs (Gibbs Reactor), wherein RGibbs method is based on the Gibbs free energy minimization technique for multiphase reactions and material balance, cyclone units were used to separate solid and gas streams.

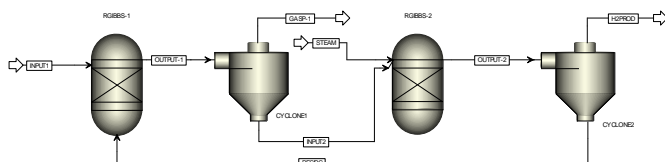


Figure 2. Process simulation flowsheet.

III. RESULTS AND DISCUSSION

A. Thermodynamic Analysis

The Fuel Reactor

This section presents results from the equilibrium amounts of H_2 , CO , CO_2 , CH_4 and C , Fe , FeO , Fe_2O_3 and Fe_3O_4 from the

fuel reactor in a temperature range of 300-900 °C and $\text{CH}_4/\text{Fe}_3\text{O}_4$ feed molar ratios from 0.25 to 1. At the studied conditions the conversion of methane was gradually increased from about 4% at 300 °C, 90% at 500 °C and up to 99.9% at 600°C. This is associated to the intrinsic equilibrium reactivity of a solid Fe_3O_4 with respect to a gaseous fuel such as CH_4 and availability of the metal oxide lattice oxygen into the gas phase. Fig. 3 shows the equilibrium production of H_2 (3a) and CO (3b) from the fuel reactor (dry basis) in kmol/h as a function of temperature and $\text{CH}_4/\text{Fe}_3\text{O}_4$ feed molar ratio.

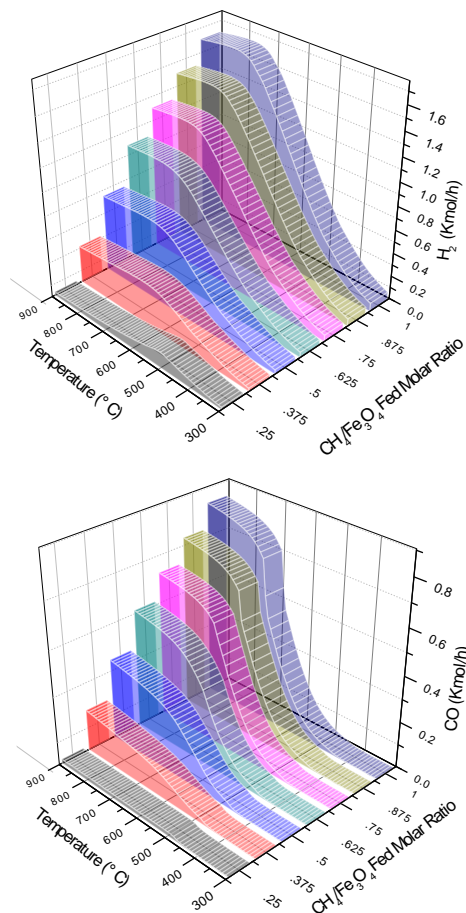


Figure 3. Equilibrium content of H_2 (a) and CO (b) for the fuel reactor

At low temperatures (300-500 °C) and where $\text{CH}_4/\text{Fe}_3\text{O}_4$ ratio is small (below 0.5), there is not enough temperature and/or oxygen available for the reaction between Fe_3O_4 and methane to produce syngas ($\text{CO} + \text{H}_2$) and therefore, this metal oxide is poorly reactive towards reaction (9). However, the small reactivity in this region is attributed to the complete oxidation of methane by Fe_3O_4 (reaction 5) where at the SIP conditions ($\text{CH}_4/\text{Fe}_3\text{O}_4 = 0.25$ and higher but not greater than 0.5) the production of CO_2 and H_2O dominate. Greater temperatures than 500 °C and $\text{CH}_4/\text{Fe}_3\text{O}_4$ ratios than 0.5 will lead to the promotion of the partial oxidation of methane by Fe_3O_4 to form syngas through reaction (9) according to results presented in Figures 3(a) and 3(b).

Figures 4(a) and 4(b) present results of unreacted CH_4 and formed CO_2 contents in the gas product from the fuel reactor.

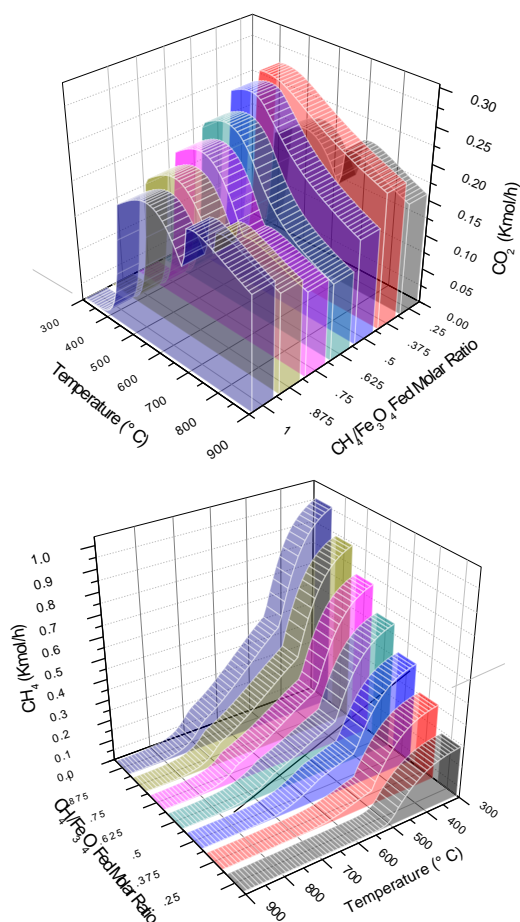


Figure 4. Equilibrium content of CO_2 (a) and CH_4 (b) for the fuel reactor

In this Figure it is evident that low temperatures ($T < 500$ °C) and small $\text{CH}_4/\text{Fe}_3\text{O}_4$ ratios, CO_2 formation is favored, which is the region where complete oxidation of methane is promoted and the CO_2 content is reduced as the available oxygen content is increased as the $\text{CH}_4/\text{Fe}_3\text{O}_4$ ratio is also grown. Also in Figure 4(b) it is evident that methane reactivity is high at low oxygen lattice content (Fe_3O_4) and this is reflected in small methane content in the product gas at temperatures greater than around 500 °C and small $\text{CH}_4/\text{Fe}_3\text{O}_4$ ratios (smaller than 0.5). Here in this plot the gradual increase in methane conversion is clear that increases as temperature rises and the $\text{CH}_4/\text{Fe}_3\text{O}_4$ ratio decrease, which is translated in the promotion of the partial oxidation of methane reaction with Fe_3O_4 (oxygen starving conditions, reaction 9)

Moreover, Figure 5 describe de behaviors of the FeO and C solid content at the effluent stream from the fuel reactor of Figure 1.

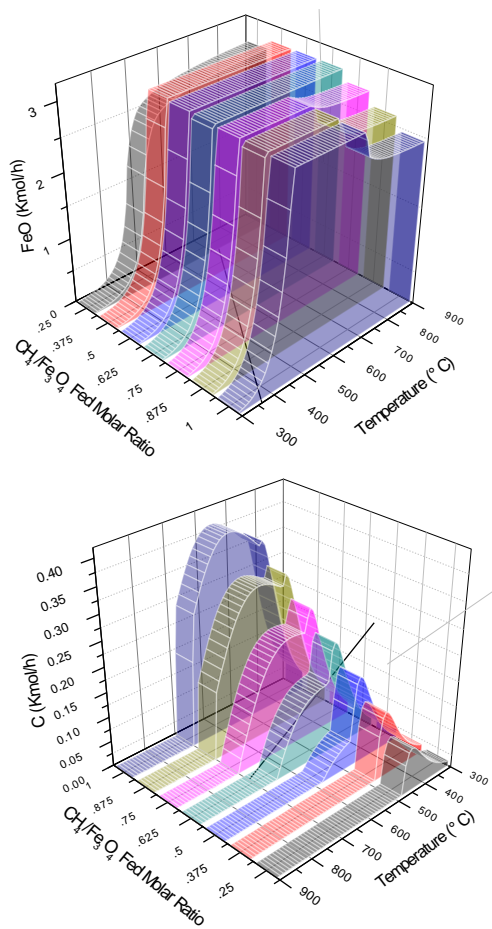


Figure 5. Equilibrium content of FeO (a) and C (b) for the fuel reactor

In this plot the maximum conversion from Fe_3O_4 to FeO at a feed of 1 kmol/h of Fe_3O_4 is according to reaction (5) of 3 kmol/h and that means that the iron oxide is in the oxidation state where in the next reactor can be combined with the appropriate amount of steam to produce a pure hydrogen stream. Therefore, optimal reaction conditions will be those which complete conversion of Fe_3O_4 to FeO is achieved and those are where the amount of FeO in Figure 5 (a) is 3 kmol/h. From this figure, it is clear that those conditions are achieved at temperatures between 500 to 700 °C at all $\text{CH}_4/\text{Fe}_3\text{O}_4$ ratios. At those conditions, methane is able to reduce iron oxide to magnetite either through complete or partial oxidation of methane. However, not only at those conditions magnetite is also thermodynamically stable, greater temperatures from 700 up to 900 °C in a $\text{CH}_4/\text{Fe}_3\text{O}_4$ range from 0.375 to 0.625 will also insure the production of magnetite and these last conditions coincide with partial oxidation of methane through equation (9).

Also important in the present investigation is to find operating conditions where no carbon formation is feasible, since any carbon contamination over the oxygen carrier will be gasified in the oxidation reactor, thus producing carbon dioxide gases that will ultimately combine with the expected hydrogen production and consequently become a gaseous byproduct. Figure 5(b) show that the carbon free operating windows of the

fuel reactor are as follows: from $\text{CH}_4/\text{Fe}_3\text{O}_4 = 0.25-0.375$ no carbon is present in a temperature range of 480-900 °C, $\text{CH}_4/\text{Fe}_3\text{O}_4 = 0.5$ from 580-900 °C, $\text{CH}_4/\text{Fe}_3\text{O}_4 = 0.625$ from 660-900 °C and $\text{CH}_4/\text{Fe}_3\text{O}_4 = 0.75-1$ from 700-900 °C. These free carbon regions that can be seen in Figure 5(b) is where either the Boudouard and/or the methane decomposition reactions (12 and 13) are not thermodynamically favorable. These results agree well with experimental results reported by Tang et al [40].

A more careful analysis of the generated data allows to conclude that according to the previous thermodynamic analysis optimum conditions in order to produce a maximum hydrogen production and carbon free operation is at $T = 650-700^\circ\text{C}$ and $\text{CH}_4/\text{Fe}_3\text{O}_4 = 0.75-1$. It is important to indicate that no metallic iron (Fe) was present at the studied fuel reactor conditions.

The Oxidation Reactor

This section presents results from the equilibrium amounts of H_2 and Fe_3O_4 from the oxidation reactor in a temperature range of 500-600 °C and H_2O feed molar flowrate range from 1-6 kmol/h. At the studied conditions, it is expected to find the minimum amount of steam per three kmols of FeO at a reasonable temperature from 500-600 °C, where the reaction kinetics are reported to be favorable [39]. Figure 6 (a) and (b) presents results from the oxidation reactor at conditions above described.

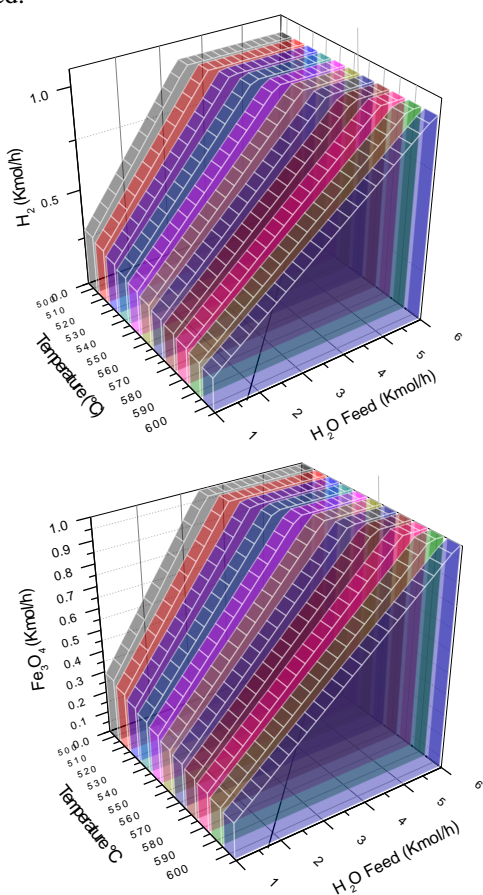


Figure 5. Equilibrium content of H_2 (a) and H_2O (b) for the oxidation reactor.

In plot 5 (a) the maximum hydrogen production can be seen as a function of temperature and the feed molar flow to the reactor. From this figure, it is evident that there is a defined region where the maximum hydrogen production is achieved which happens to be of 1 kmol/h. These conditions increase as the amount of steam and temperature both increase. For example, at 500 °C a minimum range of 3.4 to 6 kmol/h of steam is needed in order to produce the maximum amount of hydrogen according to reaction (11), while at 550 °C a range of steam of 4.6-6 kmol/h are needed to obtain the maximum possible H_2 production. Finally, at 600 °C 6 kmol/h of steam or greater are needed for this purpose. However, research points out that H_2 evolution via water the splitting reaction (11) requires Fe phase to be as fully reduced as possible, while it is difficult for Fe phase to be completely oxidized beyond Fe_3O_4 by using steam [40]. Moreover, other research indicate that the reduction from Fe_3O_4 to Fe promotes carbon deposition [31].

Furthermore, Figure 5(b) presents the Fe_3O_4 content at different steam feed to the oxidation reactor. Here in this plot it can be seen that the only conditions where complete conversion of FeO to Fe_3O_4 is achieved at regions where the amount of steam and temperature both increase. These results mimic the same conditions where the maximum hydrogen production is achieved from Figure 5(a). Therefore, this regenerated 1 kmol/h is expected to be recirculated back to the fuel reactor.

Process Simulation

Fig. 1 presented a diagram of the process scheme employed during the simulation of the SIP/CL-SMR reaction system with either the production of pure CO_2 or a syngas stream from the fuel reactor, while in the oxidation reactor the H_2 evolution and iron oxide regeneration is achieved. While, Table 1 summarizes results from the process simulation of selected streams from Figure 1.

Table 1. Summary of process simulation results of the SIP process

Stream Name	INPUT1	RECIRC	OUTPUT-1	GASP-1	INPUT2	STEAM	OUTPUT-2	H2PROD
Mole Flow, Kmol/h								
CH4	0.25	0	4.1329E-07	4.13E-07	0	0	0	0
CO	0	0	0.0174931	0.017493	0	0	0	0
CO2	0	0	0.2325064	0.232506	0	0	0	0
H2	0	0	0.0505711	0.050571	0	0	0.9319341	0.9319341
H2O	0	0	0.449428	0.449428	0	6	5.068066	5.068066
FE3O4	0	1	0.0680659	0	0.068066	0	1	0
FE0	0	0	2.795802	0	2.795802	0	0	0
FE	0	0	0	0	0	0	0	0
Mole Flow, Kmol/h	0.25	1	3.6138672	0.749999	2.863868	6	7	6
Mass Flow, Kg/h	4.01069	231.5386	235.54928	18.92108	216.6282	108.0917	324.71989	93.18129
Volume Flow, m ³ /h	20.38051	0.044524	61.1744308	61.1246	0.049831	429.693	429.823224	429.7787
Temperature, °C	720	600	720	720	720	600	600	600

In this Table, the extreme case where complete production of CO_2 is targeted (SIP) and therefore the $\text{CH}_4/\text{Fe}_3\text{O}_4$ feed molar ratio is equal to 0.25. Here in this table stream INPUT-1 denotes the fresh CH_4 feed of 0.25 kmol/h, while the RECIRC stream contains the 1 kmol/h of Fe_3O_4 . Stream OUTPUT-1 contains the products from the fuel reactor at a temperature of 700 °C where no carbon formation is possible and the complete oxidation of methane by magnetite is favored. In this stream, a methane conversion of 99.99% is reflected with the production of 0.23 kmol/h of CO_2 compared to the theoretical 0.25 kmol/h according to reaction (5) makes these operating conditions very



convenient, while the other carbon specie produced is CO with 0.017 kmol/h accompanied with the production of water. Furthermore, in this stream only 2.79 kmol/h of FeO is produced, while only a small amount of unreacted Fe₃O₄ is present (0.068 kmol/h). Gases and solids are separated in streams GASP-1 and INPUT-2, where this last is fed to the oxidation reactor together with stream STEAM, which consist of 6 kmol/h at a reactor temperature of 600 °C. Stream OUTPUT-2 contains the products from the oxidation reactor where 0.93 kmol/h of H₂ combined with 1 kmol/h of Fe₃O₄ and 5 kmols/h of excess steam are produced. This stream is separated in H2PROD and RECIRC streams, where this last one is stent back to the fuel reactor. The yield of this process based on the hydrogen product is of 3.72 mols of H₂ produced per mols of methane being fed.

Moreover, Table 2 presents results from the simulation of the other process (CL-SMR), which represents the other mode of operation of the process described in Figure 1. In this simulation a CH₄/Fe₃O₄ feed molar ratio is equal to 1 was employed in the fuel reactor.

Table 2. Summary of process simulation results of the CL-SMR process

Stream Name	INPUT1	RECIRC	OUTPUT-1	GASP-1	INPUT2	STEAM	OUTPUT-2	H2PROD
Mole Flow, Kmol/h								
CH4	1	0	0.100206	0.100206	0	0	0	0
CO	0	0	0.7035638	0.7035638	0	0	0	0
CO2	0	0	0.1962302	0.1962302	0	0	0	0
H2	0	0	1.536961	1.536961	0	0	1.358652	1.358652
H2O	0	0	0.2626274	0.2626274	0	8.2	6.841348	6.841348
Fe3O4	0	1	0	0	0	0	1	0
FeO	0	0	2.641348	0	2.641348	0	0	0
FE	0	0	0.3586516	0	0.3586516	0	0	0
Mole Flow, Kmol/h	1	1	5.799588	2.799588	3	8.2	9.2	8.2
Mass Flow, Kg/h	16.0	231.5	247.6	37.8	209.8	147.7	357.5	126.0
Volume Flow, m ³ /h	81.5	0.0	223.7	223.6	0.0	587.2	587.4	587.4
Temperature, °C	720	0	700	700	700	600	600	600

In this table stream INPUT-1 contains the fresh CH₄ feed of 1 kmol/h, while the RECIRC stream contains also 1 kmol/h of Fe₃O₄. Stream OUTPUT-1 comprises the products from the fuel reactor at a temperature of 700 °C where no carbon formation is possible and the complete oxidation of methane by magnetite is favored. In this stream a methane conversion of 90% is reflected with the production of 1.53 kmol/h of H₂ compared to the theoretical 2 kmol/h according to reaction (9), while the production of CO was 0.7 kmol/h compared to the theoretical value of 1 kmol/h of the same reaction. With respect to the reaction of the Fe₃O₄ with methane, it is significant that two reduced iron species were produced with a combination of 2.64 and 0.36 kmol/h of FeO and Fe₃O₄, respectively. Here, it is possible that the syngas formed (H₂ + CO) is able to further reduce the FeO to a small extent.

Gases and solids are separated in streams GASP-1 (syngas) and INPUT-2 (solid product), where this last is fed to the oxidation reactor together with stream STEAM, which consist of 8.2 kmol/h at a reactor temperature of 600 °C. This excess of steam being fed at the oxidation reactor in further needed to re-oxide FeO and Fe reduced species back to Fe₃O₄. Stream OUTPUT-2 contains the products from the oxidation reactor where 1.36 kmol/h of H₂ combined with 1 kmol/h of Fe₃O₄ and 6.8 kmols/h of excess steam are found. This stream is separated

in H2PROD and RECIRC streams, where this last one is stent back to the fuel reactor. The yield of this process based on the hydrogen product is of 1.35 mols of H₂ produced per mols of methane being fed. While based on the syngas produced is 2.24 mols of syngas (CO+H₂) per mol of methane fed at a H₂/CO product ratio of 2.19, which is very convenient, since this streams can be used in the Fischer-Tropsch process for the production of liquid fuels (GTL).

IV. CONCLUSIONS

In the present research, the redox performance of iron oxide magnetite (Fe₃O₄) as an oxygen carrier was investigated for hydrogen (H₂) and/or syngas (H₂+CO) production through a methane-steam redox process using a thermodynamic analysis and process simulation to find most favorable reactions conditions. The studied reaction system was divided in two reactors. In the fuel reactor the complete or the partial oxidation of methane with Fe₃O₄ were studied. Results indicate that in the reduction reactor the most favorable reactions conditions consisted in T = 650-700°C and CH₄/Fe₃O₄ = 0.75-1, While for the regenerator were: T = 520-600 °C. Finally, these results can be taken as a basis for future experimental and theoretical studies in search for a suitable catalyst and conditions to evaluate the present proposed technology.

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