Optimization of Hydrogen Production by Chemical-Looping Auto-Thermal Reforming Working with Ni-based Oxygen-Carriers

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Abstract

Chemical-Looping auto-thermal Reforming (CLRa) is a new process for hydrogen production from natural gas that uses the same principles as Chemical-Looping Combustion (CLC). The main difference with CLC is that the desired product is syngas ($H_2 + CO$) instead of $CO_2 + H_2O$. For that, in the CLRa process the air to fuel ratio is kept low to prevent the complete oxidation of the fuel. The major advantage of this

technology is that the heat needed for converting CH_4 to syngas is supplied without costly oxygen production and without mixing of air with carbon containing fuel gases.

An important aspect to be considered in the design of a CLRa system is the heat balance. In this work, mass and heat balances were done to determine the auto-thermal operating conditions that maximize H_2 production in a CLRa system working with Ni-based oxygen-carriers. It was assumed that the product gas was in thermodynamic equilibrium at the exit of the air and fuel-reactors and the equilibrium gas compositions were obtained by using the method of minimization of the Gibbs free energy of the system. It was found that to reach auto-thermal conditions the oxygen-to-methane molar ratio should be higher than 1.20, which means that the maximum H_2 yield is about 2.75 mol H_2/mol CH_4. The best option to control the oxygen-to-methane molar ratio is to control the air flow fed to the air-reactor because a lower air excess is needed to reach auto-thermal conditions.

Keywords: Hydrogen production, Chemical looping, Oxygen-carrier, Nickel oxide, Heat balance.

1. Introduction

Carbon dioxide is an important greenhouse gas that strongly affects global warming. The global atmospheric concentration of carbon dioxide has increased from a preindustrial value of about 280 ppm to 390 ppm in 2010 [1] being the combustion of fossil fuels in the transport sector one of the main contributors to it. In 2008, transport was responsible for 22% of world energy-related greenhouse gas emissions with about three quarters coming from road vehicles [2]. There are different strategies to mitigate

the emissions produced in transport such as improvement of the engine's efficiency, electric or hybrid vehicles or the use of alternatives fuels like biofuels and hydrogen.

Hydrogen is presented as a good alternative to be used as fuel in transport due to it does not produce emissions aside from water when is burned; however, hydrogen is an energy carrier that must be produced from a primary source of energy. Nowadays, hydrogen is mainly produced from natural gas via steam methane reforming (SMR) [3]. In this technology the endothermic methane reforming reaction takes place in reformer tubes packed with a Ni catalyst. In order to supply the heat needed for the endothermic reaction, the reformers tubes are located inside a furnace where natural gas or an off-gas is burned and in consequence large amounts of CO_2 emissions are produced. With SMR it is possible to reach energy efficiencies of about 13.1-14.6 GJ/1000 Nm^3, corresponding to a H_2 yield of 2.4-2.7 mol H_2 per mol CH_4 [4]. Auto-thermal reforming (ATR) is a possible alternative to conventional SMR [3]. In this process the exothermic partial oxidation of methane is used as heat source for the reforming reaction CH_4, H_2O and O_2 (or air) are fed together to an adiabatic reactor where both partial oxidation and reforming of methane happen. The main drawback of this process is the use of an air separation unit to produce the oxygen needed for the partial oxidation, which involves high energy consumption and costs, or if air is used instead of O_2 a CO_2 capture step is needed. Different processes of CH_4 reforming with CO_2 capture have shown values for H_2 production ranging from 2.1 to 2.6 mol H_2 per mol CH_4 [5].

New studies have been focused in hydrogen produced from renewable energy sources, for example, from electrolysis of water using wind energy or from biomass via gasification. The drawback of using renewable energy is its high costs, so, it seems that

the production of hydrogen from fossil fuels, mainly from natural gas, will continue being the dominant technology for the next decades, despite the appreciable amount of CO_2 released during those processes. Therefore, the development of new concepts for H_2 production from fossil fuels, with reduced capital costs and CO_2 emissions, is highly desirable.

1.1. Chemical-looping auto-thermal Reforming

Chemical-Looping auto-thermal Reforming (CLRa) is proposed as a new process for hydrogen production from natural gas without the need of an external heat supply, avoiding in this way the CO_2 emissions involved in the heat production. CLRa uses the same principles as Chemical-Looping Combustion (CLC), a novel combustion technology with inherent separation of the greenhouse gas CO_2 that involves the use of an oxygen-carrier, which transfers oxygen from air to the fuel avoiding the direct contact between them [6].

A CLC system is made of two interconnected fluidized bed reactors, designated as air- and fuel-reactors. In the fuel-reactor, the fuel gas (C_nH_{2m}) is oxidized to CO_2 and H_2O by an oxygen-carrier, usually a metal oxide (MeO) that is reduced to a metal (Me) or a reduced form of MeO. The metal or reduced oxide is further transferred into the air-reactor where it is oxidized with air, and the material regenerated is ready to start a new cycle. The flue gas leaving the air-reactor contains N_2 and unreacted O_2. The exit gas from the fuel-reactor contains only CO_2 and H_2O. After water condensation, almost pure CO_2 can be obtained with little energy lost for component separation.

CLRa as described in Figure 1 was proposed by Mattisson and Lyngfelt [7]. This new process also uses the metal oxide to transfer oxygen to the fuel, being the main

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difference with CLC that the desired product is syngas (H_2 + CO). In the CLRa process the oxygen to fuel ratio is kept low to prevent the complete oxidation of the fuel to CO_2 and H_2O. The major advantage of this process is that the heat needed for converting CH_4 to H_2 and CO is supplied without costly oxygen production and without mixing of air with carbon containing fuel gases.

A key issue for the Chemical-Looping Reforming (CLR) technology development is the selection of an oxygen-carrier with suitable properties: enough reactivity through cycles to reduce solids inventory; high resistance to attrition to minimize losses of elutriated solid; high selectivity for fuel conversion to CO and H_2; negligible carbon deposition what would release CO_2 in the air-reactor; and good properties for fluidization (no presence of agglomeration). In addition, the cost of the oxygen-carrier, environmental characteristics, and health aspects are also important. Different metal oxides supported on different inert materials have been proposed as oxygen-carriers for CLRa. Zafar et al. [8, 9] prepared and tested different oxygen-carriers based on oxides of Fe, Mn, Ni and Cu and supported on SiO_2 and $MgAl_2O_4$. The Ni-based oxygen-carriers showed the highest selectivity toward H_2 and CO, while oxygen-carriers based on Fe-, Cu- and Mn- suffered from poor selectivity and produced mostly CO_2, H_2O and unconverted CH_4.

As Ni-based oxygen-carriers seem to be the most suitable for CLRa due to its strong catalytic properties, they have been widely studied. Particles prepared by different methods (freeze granulation, impregnation, and spray drying) and using different supports (Al_2O_3, $MgAl_2O_4$, Mg-ZrO_2), and NiO contents have been tested [10-12]. In fact, CLR has been demonstrated working with Ni-based oxygen-carriers by Rydén et al. [13-15] and by de Diego et al. [16] in small laboratory units, and by Pröll et al. [17]
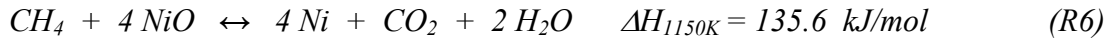
in a 140 kW fuel power in a dual circulating fluidized bed installation. These authors found that the methane conversion was high, the product gas was close to thermodynamic equilibrium, and no carbon formation observed. In addition, Pröll et al. achieved to work in auto-thermal operating conditions in the 140 kW pilot plant and found that the minimum air-to-fuel ratio to work under CLRa conditions was between 0.46 and 0.52 depending on the operating temperature.

If Ni-based oxygen-carriers are used in a CLRa system, the main reactions happening with different contribution in the fuel-reactor are:

$$CH_4 + NiO \leftrightarrow Ni + CO + 2 H_2 \qquad \Delta H_{1150K} = 212.6 \ kJ/mol \qquad (R1)$$

$$CH_4 + H_2O \leftrightarrow CO + 3 H_2 \qquad \Delta H_{1150K} = 226.9 \ kJ/mol \qquad (R2)$$

$$CH_4 + 2 H_2O \leftrightarrow CO_2 + 4 H_2 \qquad \Delta H_{1150K} = 192.7 \ kJ/mol \qquad (R3)$$

$$CH_4 \leftrightarrow C + 2 H_2 \qquad \Delta H_{1150K} = 91.04 \ kJ/mol \qquad (R4)$$

$$C + H_2O \leftrightarrow CO + H_2 \qquad \Delta H_{1150K} = 135.8 \ kJ/mol \qquad (R5)$$

Reactions R2-R4 are catalyzed by metallic Ni appearing through reaction R1. The O/C molar ratio considered in this work is always higher than 1. In these conditions thermodynamic analyses showed that carbon formation by methane decomposition reaction does not occur. So, carbon never appeared in the calculations made for mass and heat balance in this work. This agrees to the fact that carbon formation has not been detected in experimental works.

If an excess of oxygen is transferred to the fuel-reactor, CO_2 and H_2O can appear in some extension as products of combustion:

$CH_4 + 4\,NiO \leftrightarrow 4\,Ni + CO_2 + 2\,H_2O \qquad \Delta H_{1150K} = 135.6\ kJ/mol \qquad (R6)$

$CO + NiO \leftrightarrow CO_2 + Ni \qquad\qquad\qquad \Delta H_{1150K} = -48.5\ kJ/mol \qquad (R7)$

$H_2 + NiO \leftrightarrow H_2O + Ni \qquad\qquad\qquad \Delta H_{1150K} = -14.3\ kJ/mol \qquad (R8)$

and the water gas shift equilibrium modifies the composition of gases as:

$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad\qquad\qquad \Delta H_{1150K} = -34.2\ kJ/mol \qquad (R9)$

In the air-reactor the oxygen-carrier is regenerated by oxidation with air:

$Ni + \frac{1}{2}\,O_2\ (air) \leftrightarrow NiO\ (+\,N_2) \qquad\qquad \Delta H_{1150K} = -234.3\ kJ/mol \qquad (R10)$

In CLRa, hydrogen must be produced without the need of an external heat supply. Thus, an important aspect to be considered in the design of a CLRa system is the heat balance. The oxidation reaction (R10) of the metal oxide is very exothermic, whereas the reduction reactions R1 and R6, and the steam reforming reaction (R2) are very endothermic. So, the heat for the endothermic reactions happening in the fuel-reactor must be given by the circulating solids coming from the air-reactor at higher temperature. The heat generated in the air-reactor must be enough high to fulfil the heat balance in the system without requirement for energy from an external source to the CLRa process.

The aim of this work was to determine the auto-thermal operating conditions that maximize H_2 production in a CLRa system working with Ni-based oxygen-carriers. For that, mass and heat balances in a CLRa system, varying the main operating parameters, like oxygen-to-fuel molar ratio, oxygen-carrier circulation flow-rate and H_2O/CH_4

molar ratio, have been done. Once the auto-thermal operating conditions for the CLRa system were determined, a heat balance to the global process, integrating the CLRa system with pre-heaters and a water gas shift reactor, was done.

2. Procedure

To determine the auto-thermal operating conditions that maximize H_2 production in a CLR system, mass and heat balances were carried out. The study has been made considering the use of Ni-based oxygen-carriers. As the heat balance depends on the NiO content in the oxygen-carrier and its conversion variation, ΔX_s, the most adequate NiO content and ΔX_s of the Ni-based oxygen-carrier to optimize the H_2 production were also determined.

The mass balance in the fuel-reactor of the CLR system, based on the O_{NiO}/CH_4 molar ratio, can be expressed as

$$\frac{F_s x_{NiO,ox}}{M_{NiO}} \Delta X_s = F_{CH_4} \frac{O_{NiO}}{CH_4} \tag{1}$$

where F_s is the oxygen-carrier circulation flow-rate, $x_{NiO,ox}$ is the fraction of NiO present in the oxygen-carrier when it is completely oxidized, M_{NiO} is the molecular weight of NiO, and F_{CH_4} is the molar flow of CH_4 fed to the fuel-reactor. The O_{NiO}/CH_4 molar ratio is the amount of oxygen transferred by chemical reaction with NiO to the fuel gas per mol of CH_4 fed. The variation of the oxygen-carrier conversion between the fuel and air-reactors, ΔX_s, was defined as:

$$\Delta X_s = X_{AR} - X_{FR} \tag{2}$$

$$X_{AR} = \frac{x_{NiO,AR} - x_{NiO,red}}{x_{NiO,ox} - x_{NiO,red}} \quad \text{and} \quad X_{FR} = \frac{x_{NiO,FR} - x_{NiO,red}}{x_{NiO,ox} - x_{NiO,red}} \tag{3}$$

being X_{AR} and X_{FR} the conversions of the oxygen-carrier at the exit of the air and fuel-reactors respectively, and $x_{NiO,i}$ the fraction of NiO in the oxygen-carrier.

The mass balance in the air-reactor, based on ΔX_{O_2}, can be written as:

$$\frac{F_s x_{NiO,ox}}{M_{NiO}} \Delta X_s = F_{O_2,in} \Delta X_{O_2} \tag{4}$$

$$\Delta X_{O_2} = \frac{F_{O_2,in} - F_{O_2,out}}{F_{O_2,in}} \tag{5}$$

where $F_{O_2,in}$ is the molar flow of oxygen fed to the air-reactor, $F_{O_2,out}$ is the molar flow of oxygen leaving the air-reactor and ΔX_{O_2} is the conversion of the oxygen in the air-reactor which is consumed by the oxygen carrier.

The molar flow-rate of each gas (CH_4, CO, CO_2, H_2, H_2O, O_2, and N_2) at the exit of the air- and fuel-reactors was obtained by reactions R1-R10 assuming that the product gas was in thermodynamic equilibrium [13-17]. Thus, the gas composition depended on the oxygen transferred from the air to fuel, i.e. O_{NiO}/CH_4 and the flow of steam, i.e. H_2O/CH_4. The equilibrium gas compositions were obtained with the HSC Chemistry 6.1 software [18], which uses the method of minimization of the Gibbs free energy in the system. The molar flow-rate of NiO and Ni in the air and fuel-reactors were obtained as

a function of ΔX_{O_2} and ΔX_s by eq. (4). Complete oxidation of the oxygen-carrier in the air-reactor was assumed. Therefore $\Delta X_s = 1 - X_{FR}$, $F_{NiO,,inFR} = F_s x_{NiO,ox}$ and $F_{Ni,inFR} = 0$, $F_{Ni,outFR} = X_{FR} F_s x_{NiO,ox}$ and $F_{NiO,outFR} = (1 - X_{FR}) F_s x_{NiO,ox}$.

Mass balance to the global process integrating the CLR system with the water gas shift reactor and varying the oxygen-to-fuel molar (O_{NiO}/CH_4) and the H_2O/CH_4 molar ratios was done. The water gas shift reactor was placed down-stream to the CLR system in order to increase the output of hydrogen via water gas shift equilibrium, see reaction R9.

The heat balance in the CLRa system was done considering that the oxygen-to-fuel molar ratio can be controlled by two ways: (Case 1) limiting the oxygen introduced to the air-reactor by the air flow ($F_{O_2,in}$), i.e. varying the global air-to-fuel ratio, or (Case 2) restricting the oxygen supplied to the fuel-reactor by the oxygen-carrier circulation flow-rate (F_S). In the first case, all the oxygen introduced to the air-reactor is transferred to the fuel-reactor (i.e. $\Delta X_{O_2} = 1$) and the oxygen-carrier circulation flow-rate can be selected to maintain $\Delta X_S \leq 1$, quite the opposite the second case where $\Delta X_{O_2} \leq 1$ but $\Delta X_S = 1$. Thus, in the second case the global air-to-fuel ratio can be higher than the oxygen-to-fuel ratio supplied to the fuel-reactor but the oxygen-carrier circulation flow-rate is fixed for a given O_{NiO}/CH_4 molar ratio. In both cases, the following assumptions were made:

  - Gas fuel fed to the fuel reactor was CH_4 (1 mol/s).
  - Temperature in the fuel-reactor was kept constant at 1150 K.

- Gases are fed to both reactors at 750 K. It was assumed that these gases are heated with the sensible-heat of the gas outlet streams of both reactors.

- There were not heat losses in the reactors.

With these assumptions the heat balance over fuel- and air-reactors was done taking into account the enthalpy of the particles, fuel and air coming to the reactors and the enthalpy of the particles and gases leaving the reactors, which can be expressed as:

$$H_{reac} = H_{prod} - \Delta H \tag{6}$$

$$H_{reac} = \sum r_i h_i \tag{7}$$

$$H_{prod} = \sum p_i h_i \tag{8}$$

where the enthalpy of component i was calculated from

$$h_i = h_{oi} + \int_{298}^{T} C_{pi}(T) dT \tag{9}$$

All thermochemical data were adopted from Barin [19]. All the gases (CH_4, CO, CO_2, H_2, H_2O, O_2, N_2) and solids (Ni, NiO and the inert material used as support for the oxygen-carrier -Al_2O_3-) present in the reactors were considered as reactants and product for the heat balance. In equation (6), when ΔH is equal to 0 the system is auto-thermic. On the contrary, a $\Delta H > 0$ means that the heat generated in the air-reactor is not enough to fulfil the heat balance and an external heat supply would be needed, and a $\Delta H < 0$ means that there is excess of energy in the system.

Once the auto-thermal operating conditions for the CLRa system were determined, a global heat balance integrating the CLRa system with pre-heaters and water gas shift

reactor (see Figure 2) was done. In this global heat balance, the sensible-heat of the gas outlet streams at high temperature is used to pre-heat the gas inlet streams to the reactors and to evaporate and heat the water fed to the water gas shift reactor. Depending on the operation conditions, an excess of heat can be recovered from the global CLR process, here referred as "surplus energy", which could be used for energy production or steam/energy demands in a side process.

3. Results and discussion

3.1. Mass balance to the CLR global process

A mass balance to the global process, integrating the CLRa system with the water gas shift reactor, was done varying the oxygen-to-fuel and the H_2O/CH_4 molar ratios in the fuel-reactor. H_2O can be fed to the fuel-reactor, to the water gas shift reactor or to both places, but it was found that, for the same H_2O/CH_4 molar ratio, it did not affect the H_2 production though it did affect the heat balance as it will be seen forward. The oxygen present in the gases can come from H_2O added (see reactions R2, R3 and R9) or from the oxygen contained in NiO (see reactions R1 and R6-R8). Never mind the oxygen source (H_2O or NiO), the stoichiometric oxygen–to–methane molar ratio must be $O/CH_4 =1$ to form CO and H_2 or $O/CH_4 =2$ in order to reach full conversion of CH_4 to CO_2 and H_2. Here the O/CH_4 molar ratio was defined as $O/CH_4 = (O_{H2O}/CH_4) + (O_{NiO}/CH_4)$, O_{H2O} being oxygen coming from the H_2O and O_{NiO} oxygen coming from the NiO of the oxygen-carrier.

Figure 3 shows the H_2 produced after the water gas shift reactor as a function of the O_{NiO}/CH_4 molar ratio, considering a total H_2O/CH_4 molar ratio of 2. With this value the oxygen supply for the stoichiometric conversion of CH_4 to CO_2 and H_2 is guaranteed in

all cases (see reaction R3). It can be observed that a maximum in the hydrogen

production is obtained when the O_{NiO}/CH_4 molar ratio is zero. In this case, the formation

of hydrogen comes from reactions R2 and R9, corresponding to the case of steam

methane reforming without oxygen supply by the oxygen-carrier. The theoretical

maximum hydrogen yield should be 4 mol H_2/mol CH_4. This value is not reached

because some CO remains unconverted at equilibrium conditions after the water gas

shift reactor. As the oxygen supplied by the oxygen-carrier increases, i.e. O_{NiO}/CH_4

increases, the H_2 production decreases because the hydrogen yield in partial oxidation

(R1) was lower than those in steam methane reforming (R2). When the O_{NiO}/CH_4 molar

ratio reaches the unity, all the oxygen needed to convert methane to CO and H_2 is

supplied by the oxygen-carrier, and the effective role of H_2O is shifting the gas

composition by reaction R9. It must be remembered that thermodynamic equilibrium is

always assumed, and the equilibrium compositions do not depend on the reaction

mechanism followed but only on the initial operating conditions used.

From this analysis, it can be concluded that it will be desirable to use low O_{NiO}/CH_4

molar ratios in order to maximize the hydrogen yield. However, the process must be

auto-thermal. Therefore, the energy required for endothermic reactions and to heat the

gases to the temperature of the CLR system should be supplied by partial oxidation of

the fuel, which is exothermic. This oxidation of the fuel is a combination of the

reactions R1, R6 and R10 and the result are the following global reactions:

$$CH_4 \; + \; \tfrac{1}{2} \, O_2 \;\; \leftrightarrow \;\; CO \; + \; 2 \, H_2 \qquad \Delta H_{1150K} = \text{-21.7 kJ/mol} \qquad\qquad \text{(R11)}$$

$$CH_4 \; + \; 2 \, O_2 \;\; \leftrightarrow \;\; CO_2 \; + \; 2 \, H_2O \qquad \Delta H_{1150K} = \text{-801.8 kJ/mol} \qquad\qquad \text{(R12)}$$

In any system for methane reforming working at auto-thermal conditions, e.g. ATR or CLRa, the weak heat supplied by the partial oxidation of CH_4 (R11) is not enough to heat the reacting gases to the reaction temperature and an additional energy must be supplied by burning some fraction of the CH_4 by the reaction R12. For example, for a reaction temperature of 1150 K when the gas inlet streams are preheated to 750 K, it is needed to have an oxygen-to-fuel molar ratio of 1.18 to reach auto-thermal operating conditions (O_{NiO}/CH_4=1.2 for a CLRa system). At these conditions the H_2 produced is near to 2.8 mol/mol CH_4 (see Figure 3).

3.2. Heat balance to the CLRa system

As mentioned before, the heat balance of the CLRa system was done considering that the O_{NiO}/CH_4 molar ratio can be controlled by two ways: Case 1) limiting the oxygen supplied by the air flow fed to the air-reactor, or Case 2) restricting the oxygen supplied to the fuel-reactor by the oxygen-carrier circulation flow-rate. In the case 1, all oxygen in air is transferred to the fuel-reactor (i.e. ΔX_{O_2} =1) and the global air-to-fuel ratio is equal to the O_{NiO}/CH_4 molar ratio in the fuel-reactor. Therefore, an additional advantage is that an almost pure N_2 gas stream at the exit of the air-reactor is obtained [17].

A general assessment about the heat balance in a CLR system is carried out for the Case 1. In a CLR system the heat needed for the endothermic reactions happening in the fuel-reactor is supplied by the circulating solids coming from the air-reactor at higher temperature. For the same oxygen-to-fuel molar ratio, the oxygen-carrier circulation flow-rate depends on the NiO content and its conversion variation between the two reactors, ΔX_s. Therefore, the temperature difference between the fuel- and air-reactors will depend on the same variables. Figure 4 shows the effect of the NiO content and its

ΔX_s on the air-reactor temperature working in auto-thermal operation conditions for a fixed temperature in fuel-reactor of 1150 K. To reach auto-thermal conditions, a O_{NiO}/CH_4 molar ratio is needed for every temperature difference between the air- and fuel-reactors, i.e. for each air-reactor temperature curve in Figure 4. As it can observed, the temperature in the air-reactor increases when the NiO content in the oxygen-carrier increases for a constant ΔX_s or when the ΔX_s increases for a constant NiO content. The same temperature difference between the two reactors can be achieved working with an oxygen-carrier with high NiO content and low ΔX_s or working with an oxygen-carrier with low NiO content and high ΔX_s. In order to reduce the production costs of the oxygen-carrier, this second option is more desirable.

Figure 5 shows the effect of the temperature difference between the air-reactor and fuel-reactor on the H_2 production. Auto-thermal operating conditions are reached by fitting the air-to- fuel ratio in every case, i.e. the O_{NiO}/CH_4 molar ratio as it will be discussed below. An increase in the temperature in the air-reactor (i.e. an increase in the temperature difference between both reactors) produces a decrease in the H_2 produced because more energy is required to rise the gas temperature in the air-reactor, which is supplied by increasing the methane oxidation. As a consequence, a higher O_{NiO}/CH_4 molar ratio is needed to reach auto-thermal operating conditions and more CO_2 and H_2O are produced at expenses of CO and H_2. So, in order to maximize the H_2 production the temperature difference between the air and fuel reactors must be as low as possible. A low temperature difference involves working at high oxygen-carrier circulation flow-rates, therefore, the temperature difference will be limited by the oxygen-carrier circulation flow-rate which will depend on the characteristics of the oxygen-carrier

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(reactivity, particle size, etc), the operation conditions and the configuration of the riser of the CLRa installation.

de Diego et al. [16] worked in a continuous fluidized bed CLR bench scale prototype with two Ni-based oxygen-carriers prepared by impregnation with a similar NiO content but supported on different inert material. Similar gas product compositions were obtained with both oxygen-carriers although working with different oxygen-carrier circulation flow-rates and therefore the ΔX_s reached by each oxygen-carrier was also different. The Ni-based oxygen-carrier with a 21wt.% of NiO content supported on γ-Al_2O_3 reached a ΔX_s of about 0.5 and the oxygen-carrier with 18 wt.% of NiO content supported on α-Al_2O_3 reached ΔX_s higher than 0.8. To evaluate the feasibility of these oxygen-carriers for the CLR process, Figure 6 shows the effect of the oxygen-carrier circulation flow-rate on the temperature difference between the air- and fuel-reactors and the oxygen-carrier conversion for auto-thermal operating conditions working at a fuel-reactor temperature of 1150 K and using an oxygen-carrier with a NiO content of 20 wt.%, i.e. similar to the 18 wt.% and 21 wt.% of the cited materials. It can be observed that a desired temperature difference between both reactors can be achieved working with Ni-based oxygen-carriers with a NiO content of 20%, as for the lower reactive oxygen-carrier ($\Delta X_S = 0.5$), as for the most reactive oxygen-carrier ($\Delta X_S = 0.8$). So, the following heat balances were done considering a Ni-based oxygen-carrier with a 20 wt.% of NiO content.

To optimize the H_2 production, an analysis to determine the auto-thermal conditions as a function of the O_{NiO}/CH_4 molar ratio was done. Figure 7 shows the overall heat balance of the CLRa system defined by ΔH as a function of the O_{NiO}/CH_4 molar ratio working

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with different oxygen-carrier circulation flow-rates. In this figure, a $\Delta H > 0$ means that the heat generated in the air-reactor is not enough to fulfil the heat balance and it is needed an external heat supply; $\Delta H = 0$ means that heat balance is enough to fulfil the heat balance and the system is auto-thermic; and when $\Delta H < 0$ there is excess of energy in the system which should be removed to keep constant the fuel-reactor temperature. As can be seen, in all cases the CLRa system is endothermic, i.e. $\Delta H > 0$, at the stoichiometric O_{NiO}/CH_4 ratio of unity. As the oxygen transferred is increased, the energy requirements decrease until the auto-thermal condition is reached ($\Delta H = 0$). Further increases in the O_{NiO}/CH_4 molar ratio involve an excess of energy in the CLRa system ($\Delta H < 0$). Here, the oxygen-carrier circulation flow-rate must be enough high to be able to transfer the oxygen defined by the O_{NiO}/CH_4 ratio. Thus, for the lowest circulation flow-rate simulated (0.5 kg/s per mol of CH_4) the maximum theoretical O_{NiO}/CH_4 molar ratio is about 1.35 when the variation of oxygen-carrier conversion is 1 ($\Delta X_S = 1$). An increase in the air-to-fuel ratio involves the exit of un-reacted oxygen from the air-reactor, i.e. it can not be maintained the condition $\Delta X_{O_2} = 1$ and it is not further increased the O_{NiO}/CH_4 molar ratio.

The effect of the oxygen-carrier circulation flow-rate on the heat balance is clearly showed in Figure 7. An increase in the oxygen-carrier circulation flow-rate produced a decrease in the O_{NiO}/CH_4 molar ratio needed to reach auto-thermal operating conditions because the temperature difference between the reactors decreases as the oxygen-carrier circulation flow-rate increases, see Figure 6. So, to maximize the H_2 production in auto-thermal operating conditions it would be necessary to work at a low temperature difference between the two reactors and a high oxygen-carrier circulation flow-rate which means low ΔX_s or low NiO content. For example, if a temperature difference

between the two reactors of about 150 K is desired, an oxygen-carrier circulation flow-rate about 1.4 kg/s per mol CH_4 is needed. In these conditions, the variation of the oxygen-carrier (20 wt.% NiO) conversion is 0.32 and the O_{NiO}/CH_4 molar ratio is 1.21. The corresponding H_2 yield is about 2.75, see Figure 3.

The results obtained for mass and heat balances in Case 1 were compared to those calculated for Case 2. In the case 2, the oxygen transferred in a CLRa system is considered to be limited by the oxygen-carrier circulation flow-rate. To simulate this case, it was assumed that the variation of the oxygen-carrier conversion between the air- and fuel-reactors (ΔX_s) is 1, that is, the oxygen-carrier is completely reduced in the fuel-reactor and completely oxidized in the air-reactor. Thus, the oxygen transferred to the fuel-reactor depends only on the oxygen-carrier circulation flow-rate. Figure 8 shows the overall heat balance of the CLRa system as a function of the O_{NiO}/CH_4 molar ratio working with different air excess in the air-reactor. The air excess was defined as

$$\text{Air excess} = \left(\frac{\text{oxygen in air}}{\text{stoichiometric oxygen}} - 1 \right) \times 100 \qquad (10)$$

being the stoichiometric oxygen referred to the conversion of CH_4 to CO and H_2, (see reaction R1). The maximum oxygen-to-methane molar ratio transferred by the oxygen-carrier to the fuel-reactor depends on the excess of air. When the excess of air is 0%, the stoichiometric oxygen to convert CH_4 to CO and H_2 is supplied by air. In this case, the oxygen-to-methane molar ratio transferred by the oxygen-carrier can not be higher than the unity, whereas when the air excess is 50%, the maximum oxygen-to-methane ratio that can be reached is 1.5.

As can be seen in Figure 8, the energy requirement for the CLRa system decreases as the oxygen transferred to the fuel-reactor increases, i.e. as the O_{NiO}/CH_4 ratio increases. In addition, the energy requirement increases with the excess of air because a higher flow of air must be heated up to the air-reactor temperature. It can be observed that the auto-thermal operating conditions working with excess of air lower than 30% can not be reached. At an air excess higher than 30%, an increase of the air excess produced a slight increase in the O_{NiO}/CH_4 molar ratio needed to reach auto-thermal conditions. It was found that to reach auto-thermal operating conditions in a CLRa system working with an oxygen-carrier with 20 wt % of NiO, the O_{NiO}/CH_4 molar ratio must be higher than 1.3 which corresponds with an oxygen-carrier circulation flow-rate of 0.5 kg/s per mol CH_4.

Figure 9 shows the temperature difference between the air-reactor and the fuel-reactor as a function of O_{NiO}/CH_4 molar ratio working at auto-thermal operating conditions for the Case 1 and Case 2. For the Case 1, when the oxygen-carrier circulation flow-rate increases, the O_{NiO}/CH_4 molar ratio to reach auto-thermal operating conditions decreases, the temperature difference between both reactors decreases until values near of zero and the H_2 production increases. However, for the Case 2, the temperature difference between the two reactors decreases working with higher air excesses, which produces an increase in the O_{NiO}/CH_4 molar ratio needed to work in auto-thermal conditions and as a consequence, the H_2 production decreases. For the case 1, working at a O_{NiO}/CH_4 molar ratio of 1.21 in auto-thermal conditions, 2.75 mol H_2/mol CH_4 are produced, being the temperature difference between the two reactors 150 K, while for the Case 2, working at the minimum O_{NiO}/CH_4 molar ratio to reach auto-thermal conditions (O_{NiO}/CH_4 =1.3) the temperature difference between both reactors is 400 K

and the H_2 production is 2.62 mol /mol CH_4. To decrease the temperature difference between both reactors, for the Case 2, without increasing the O_{NiO}/CH_4 molar ratio, the use of an oxygen-carrier with a lower NiO content is needed. As it can be observed in the Figure 4, an oxygen-carrier with an 8 wt % of NiO (assuming a $\Delta X_s = 1$) would be enough to have a temperature difference of 150 K. Obviously, a higher NiO content would be needed if the ΔX_S is lower than 1.

In conclusion, the control of the O_{NiO}/CH_4 molar ratio by the air flow fed to the air-reactor (Case 1) is preferred to the control by the oxygen-carrier circulation flow-rate (Case 2) because a lower excess of air is needed in the first case and the H_2 production is higher.

The effect of the H_2O/CH_4 molar ratio fed to the fuel-reactor on the heat balance of the CLRa system was also analyzed working at a constant oxygen-carrier circulation flow-rate (Figure 10(a)) and working with a constant air excess (Figure 10(b)). In both cases an increase in the H_2O/CH_4 molar ratio fed to the fuel-reactor produces a slight increase in the O_{NiO}/CH_4 molar ratio needed to reach auto-thermal operating conditions and in consequence the H_2 production decreases. H_2O is not needed to convert the methane in the fuel-reactor because the O_{NiO}/CH_4 molar ratio is always higher than 1. Although carbon formation is not thermodynamically favored at these conditions, some feed of H_2O to the fuel-reactor could be needed to avoid carbon formation in a real system [16]. So, the H_2O/CH_4 molar ratio fed to the fuel-reactor should be the minimum necessary to avoid carbon formation.

3.3. Application of heat balances to experimental data

Pröll et al. [17] worked in a 140 kW$_{th}$ dual circulating fluidized bed installation in auto-thermal operating conditions controlling the O_{NiO}/CH_4 molar ratio by limiting the oxygen supplied by the air flow fed to the air-reactor. A 50:50 mixture of two Ni-based oxygen-carriers supported on $MgAl_2O_4$ and $NiAl_2O_4$ and natural gas as fuel were used. The experimental work was carried out at temperatures between 1023 and 1173 K in the fuel-reactor and air/fuel ratios from 0.45 to up to 1.1. The air/fuel ratio was defined as:

$$Air/fuel\ ratio\ =\ (O_2\ fed\ to\ the\ AR\ )/(2\ CH_4\ fed\ to\ the\ FR) \tag{11}$$

With this definition, an air/fuel ratio of 1 means that the oxygen fed in the air-reactor is the stoichiometric oxygen needed to fully convert the fuel gas to CO_2 and H_2O.

It was found that the natural gas conversion was very high with the residual amount of methane unconverted decreasing with increasing fuel-reactor temperature. The fuel-reactor exhaust gas was in thermodynamic equilibrium, and no carbon species were detected in the air-reactor exhaust gas. This is remarkable because no steam was added to the natural gas feed except for the part of the lower loop seal fluidization that might have been directed back into the fuel-reactor. The minimum air-to-fuel ratios to work under auto-thermal operating conditions were between 0.46 and 0.52 (O_{NiO}/CH_4 = 1.84-2.08). In these conditions the hydrogen production is in the range of 1.90 and 2.15 mol H_2/mol CH_4.

The O_{NiO}/CH_4 molar ratios needed to work under auto-thermal operating conditions were higher that the found in this work. This can be due to neither air nor fuel were

preheated before entering the reactors and due to the heat losses in the pilot plant. So, the heat balance was done assuming that the gases fed to both reactors were not preheated and it was found that for a fuel-reactor temperature of 1173 K the O_{NiO}/CH_4 molar ratio to work in auto-thermal conditions increased from 1.22 to 1.56, which is smaller than the air-to-fuel ratios found by Pröll et al. Therefore, the increase from 1.56 to 2.08 in the air-to-fuel ratio to work in auto-thermal conditions must be due to heat losses in the pilot plant. Solving the heat balance for the experimental values obtained in the 140 kW$_{th}$ power plant, it was estimated that the heat losses in this installation were in the range of 15-20%. Obviously, in a bigger industrial plant the heat losses would be lower, so, the O_{NiO}/CH_4 molar ratio to work in auto-thermal operating conditions in an industrial plant would be between the values found in this work and the values found by Pröll et al.

3.4. Integration H$_2$ and energy production by CLRa process

Once the auto-thermal operating conditions for the CLRa system were determined, a heat balance to the global process, integrating the CLRa system with pre-heaters and the water gas shift reactor (see Figure 2) was done. In this global heat balance, the sensible-heat of the gas outlet streams at high temperature is used to pre-heat the gas inlet streams and to evaporate and heat the water fed to the water gas shift reactor. It was assumed that the temperature in the fuel-reactor was kept at 1150 K, the water gas shift reactor worked at 523 K and the gas outlet streams were cooled to 373 K and it was not taken into account the energy coming from water condensation.

It was found that, assuming that there are not heat losses in the system, the heat balance of the global process is fulfilled for all the auto-thermal operating conditions

determined. An excess of heat can be recovered from the system, which could be used for pre-heat the gases fed to the reactors to a higher temperature than 750 K or it could be used for energy production or steam/energy demands in a side process. The heat extracted from the gas outlet streams would be enough to pre-heat the gas inlet streams up to 973 K. Figure 11 shows the effect of the gas inlet streams temperature on the H_2 production and the energy excess in the system (surplus energy). An increase in temperature of the gas inlet streams produces an increase in H_2 production because a lower O_{NiO}/CH_4 molar ratio to work in auto-thermal operating conditions is needed, but it also produces a decrease in the excess of energy that can be recovered from the system.

4. Conclusions

To determine the auto-thermal operating conditions that maximize H_2 production in a CLRa system mass and heat balances varying the main operating parameters affecting to the process, like oxygen-to-fuel ratio, oxygen-carrier circulation rate and H_2O/CH_4 molar ratio, were done. The study was made considering the use of Ni-based oxygen-carriers. It was observed that when oxygen supplied to the fuel-reactor of a CLR system was at stoichiometric conditions to convert CH_4 to CO and H_2, the process was energy demanding. An excess of oxygen was needed to reach auto-thermal conditions, which reduces the H_2 yield in relation to stoichiometric conditions. The excess of oxygen in a CLRa system depended on the oxygen-carrier circulation flow-rate, the excess of air, and the H_2O/CH_4 molar ratio fed to the fuel-reactor. The control of the oxygen excess by the air flow fed to the air-reactor was preferred to the control of the oxygen transferred to the fuel-reactor by the oxygen-carrier circulation flow-rate because a lower excess of air was needed in the first case.

Controlling the oxygen excess by the air flow fed to the air-reactor, an increase in the oxygen-carrier circulation flow-rate decreases the temperature difference between the fuel and air-reactors to reach auto-thermal operating conditions, decreasing the O_{NiO}/CH_4 molar ratio needed, and so, increasing the H_2 production. An appropriate temperature difference between both reactors can be achieved working with a Ni-based oxygen carrier with a NiO content of 20 wt% or even lower if the reactivity of the carrier is high. It was also found that an increase in the H_2O/CH_4 molar ratio fed to the fuel-reactor produces a slight increase in the O_{NiO}/CH_4 molar ratio needed to reach auto-thermal conditions, and as a consequence the H_2 production decreases.

Working at optimum operation conditions, integrating the CLRa system with pre-heaters and a water gas shift reactor, and assuming that there were not heat losses in the system, auto-thermal conditions could be reached with an O_{NiO}/CH_4 molar ratio of about 1.18. In these conditions, 2.75 mol H_2/mol CH_4 could be produced after the water gas shift reactor and an excess of heat is recovered from the system, which could be used for energy production or steam/energy demands in a side process. This H_2 production is similar to the maximum H_2 yield that could be obtained in an ATR process (2.8 mol H_2/mol CH_4) working at similar operating conditions, but the CLRa technology has advantages, from the point of view of mitigation of CO_2 emissions, because it does not need a CO_2 capture step or an air separation unit.

Acknowledgments

Nomenclature

C_{pi} = heat capacity of the compound i (kJ mol^{-1} K^{-1})

F_{CH_4} = molar flow of CH$_4$ fed to the fuel-reactor (mol s^{-1})

$F_{Ni,inFR}$ = molar flow of Ni coming to the fuel-reactor

$F_{NiO,inFR}$ = molar flow of NiO coming to the fuel-reactor

$F_{Ni,outFR}$ = molar flow of Ni leaving the fuel-reactor

$F_{NiO,outFR}$ = molar flow of NiO leaving the fuel-reactor

$F_{O_2,in}$ = molar flow of oxygen fed to the air-reactor (mol s^{-1})

$F_{O_2,out}$ = molar flow of oxygen leaving the air-reactor (mol s^{-1})

F_s = oxygen-carrier circulation flow-rate (kg s^{-1} mol$_{CH4}$$^{-1}$)

h_i = enthalpy of component i (kJ mol^{-1})

h_{oi} = enthalpy of component i at 298 K (kJ mol^{-1})

H_{prod} = enthalpy of the reactants (solids and gases) (kJ s^{-1})

H_{reac} = enthalpy of the products (solids and gases) (kJ s^{-1})

M_{NiO} = molecular weight of NiO (kg mol^{-1})

O_{H2O} = oxygen coming from the H$_2$O (mol)

O_{NiO} = oxygen coming from the NiO of the oxygen-carrier (mol)

p_i = molar flow-rate of reactant i (mol s^{-1})

r_i = molar flow-rate of product i (mol s^{-1})

T = temperature (K)

$x_{NiO,AR}$ = fraction of NiO present in the oxygen-carrier at the exit of the air-reactor

$x_{NiO,FR}$ = fraction of NiO present in the oxygen-carrier at the exit of the fuel-reactor

$x_{NiO.ox}$ = fraction of NiO present in the oxygen-carrier completely oxidized

$x_{NiO,red}$ = fraction of NiO present in the oxygen-carrier completely reduced

ΔH = variation of enthalpy

ΔX_{O_2} = oxygen consumed by the oxygen carrier in the air-reactor

ΔX_s = variation of the oxygen-carrier conversion

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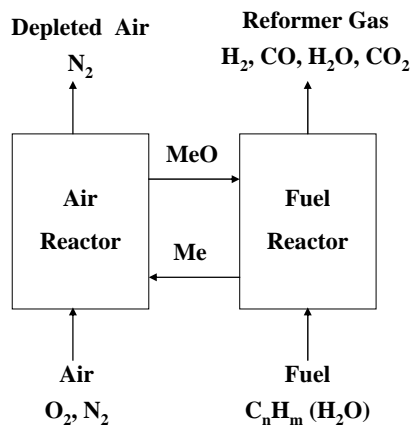
Captions for figures

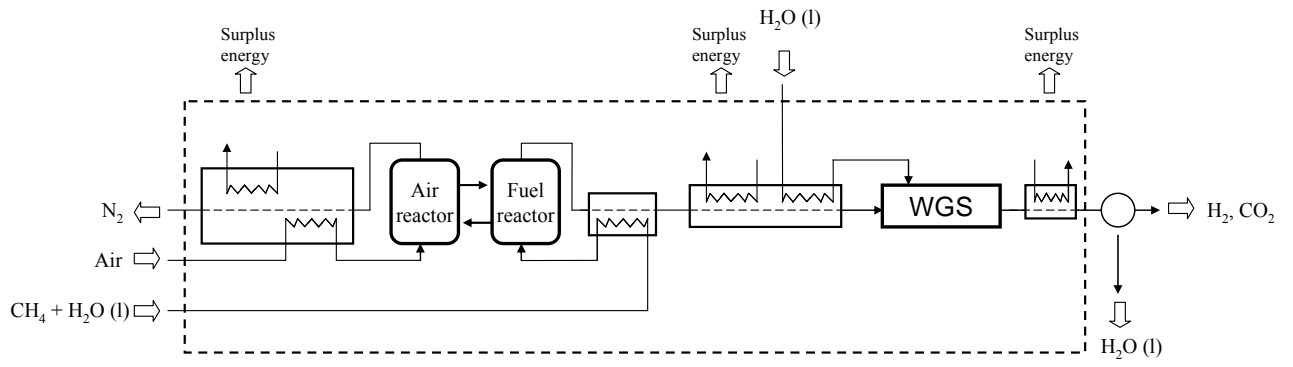**Figure 1.** Chemical-Looping Auto-thermal Reforming Scheme.

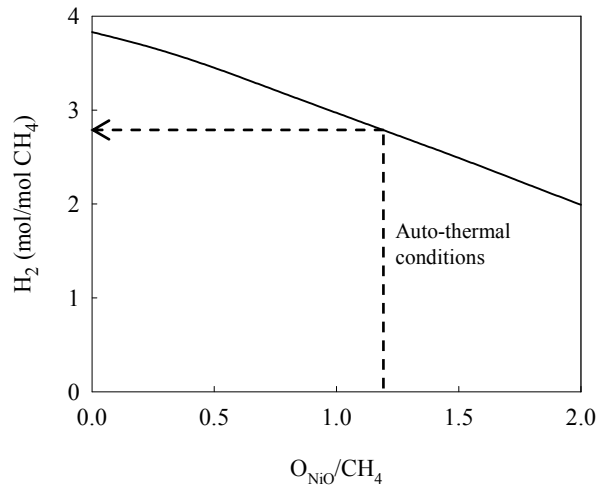**Figure 2**. Diagram of an integrated CLRa system.

Figure 3. Effect of the O_{NiO}/CH_4 molar ratio on the production of H_2. Equilibrium composition at 523 K and H_2O/CH_4 molar ratio of 2.
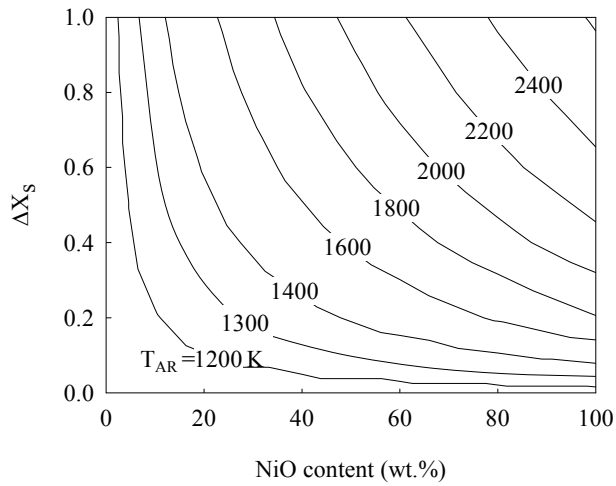
Figure 4. Effect of the NiO content in the oxygen-carrier and its ΔX_s on the temperature in the air-reactor working at auto-thermal operating conditions. T_{FR}= 1150 K. (Simulated for Case 1)
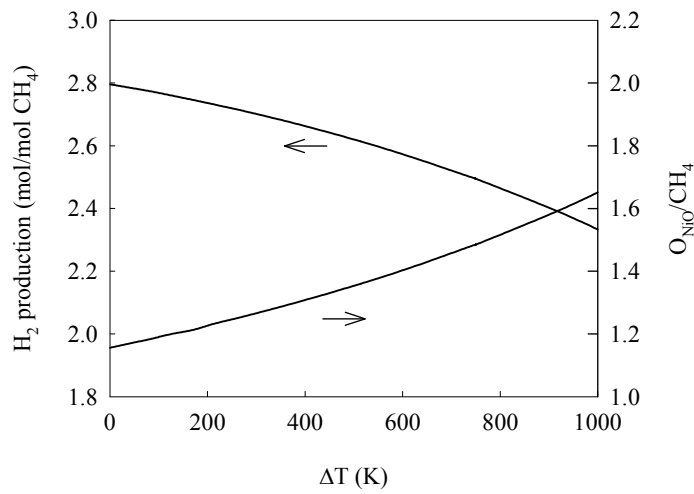
Figure 5. Effect of the temperature difference between the air- and fuel-reactors on the H_2 production and the O_{NiO}/CH_4 molar ratio working at auto-thermal operating conditions. (Simulated for Case 1).
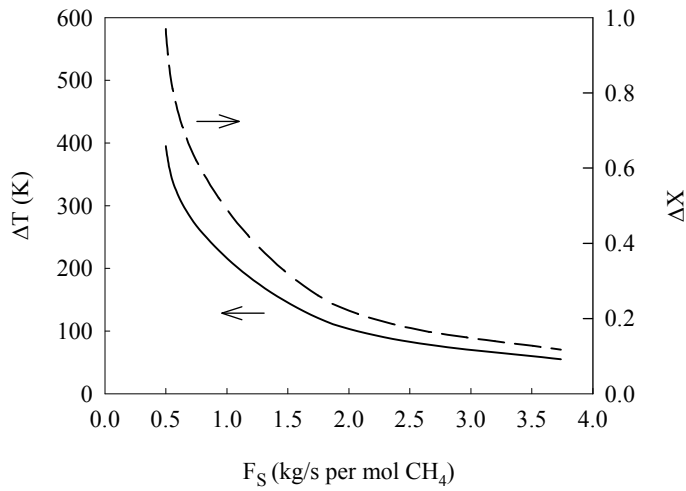
Figure 6. Effect of the oxygen-carrier circulation flow-rate on the temperature difference between the air- and fuel-reactors and the oxygen-carrier conversion for auto-thermal operating conditions. $H_2O/CH_4 = 0$ in fuel-reactor. T_{FR}=1150 K, NiO content = 20 wt.%. (Simulated for Case 1)

Figure 7. Effect of the O_{NiO}/CH_4 molar ratio on the overall CLRa heat balance for several oxygen-carrier circulation flow-rates. T_{FR} = 1150 K, NiO content = 20 wt.%, $H_2O/CH_4 = 0$ in FR. (Simulated for Case 1).

Figure 8. Effect of the O_{NiO}/CH_4 molar ratio on the overall CLRa heat balance for several excess of air fed to the CLRa system. T_{FR} = 1150 K, NiO content = 20 wt.%, $H_2O/CH_4 = 0$ in FR. (Simulated for Case 2)

Figure 9. Temperature difference between the air- and fuel-reactors for auto-thermal operating conditions for Case 1 and Case 2. T_{FR} = 1150 K, NiO content = 20 wt.%, $H_2O/CH_4 = 0$ in FR.

Figure 10. Effect of the H_2O/CH_4 molar ratio fed to the fuel-reactor on the overall heat balance of the CLRa system limited by (a) Case 1 (F_s = 0.9 kg/s per mol CH_4) and (b) Case 2 (air excess = 40 %). NiO content = 20 wt.%. Total H_2O/CH_4 = 2

Figure 11. Effect of the temperature of gas inlet streams on the H_2 production and the "Surplus Energy". T_{FR} = 1150 K, NiO content = 20 wt.%, H_2O/CH_4 = 0 in FR.

Figure 1. Chemical-Looping Auto-thermal Reforming Scheme.

Figure 2. Diagram of an integrated CLRa system.

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and H_2O/CH_4 molar ratio of 2.

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Figure 5. Effect of the temperature difference between the air- and fuel-reactors on the H_2 production and the O_{NiO}/CH_4 molar ratio working at auto-thermal operating conditions. (Simulated for Case 1).

Figure 6. Effect of the oxygen-carrier circulation flow-rate on the temperature difference between the air- and fuel-reactors and the oxygen-carrier conversion for auto-thermal operating conditions. H_2O/CH_4 = 0 in fuel-reactor. T_{FR}=1150 K, NiO content = 20 wt.%. (Simulated for Case 1)

Figure 7. Effect of the O_{NiO}/CH_4 molar ratio on the overall CLRa heat balance for several oxygen-carrier circulation flow-rates. T_{FR} = 1150 K, NiO content = 20 wt.%, H_2O/CH_4 = 0 in FR. (Simulated for Case 1).

Figure 8. Effect of the O_{NiO}/CH_4 molar ratio on the overall CLRa heat balance for several excess of air fed to the CLRa system. T_{FR} = 1150 K, NiO content = 20 wt.%, H_2O/CH_4 = 0 in FR. (Simulated for Case 2)
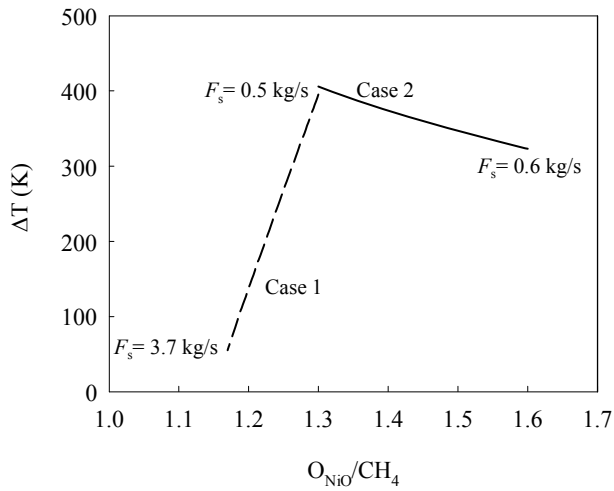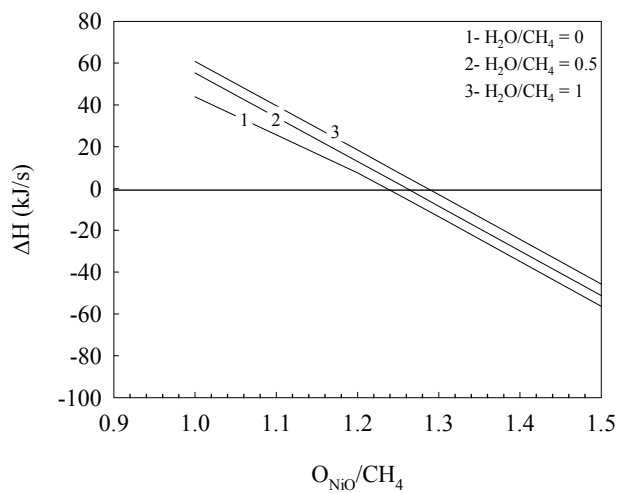

Figure 9. Temperature difference between the air- and fuel-reactors for auto-thermal operating conditions for Case 1 and Case 2. T_{FR} = 1150 K, NiO content = 20 wt.%, H_2O/CH_4 = 0 in FR.
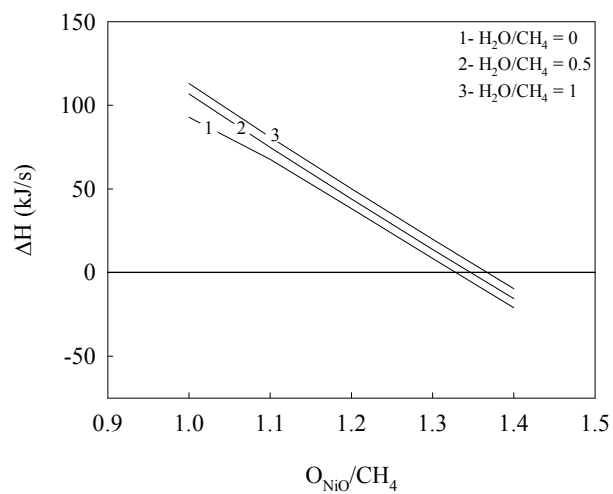
a)

b)

Figure 10. Effect of the H_2O/CH_4 molar ratio fed to the fuel-reactor on the overall heat balance of the CLRa system limited by (a) Case 1 ($F_s = 0.9$ kg/s per mol CH_4) and (b) Case 2 (air excess = 40 %). NiO content = 20 wt.%. Total $H_2O/CH_4 = 2$
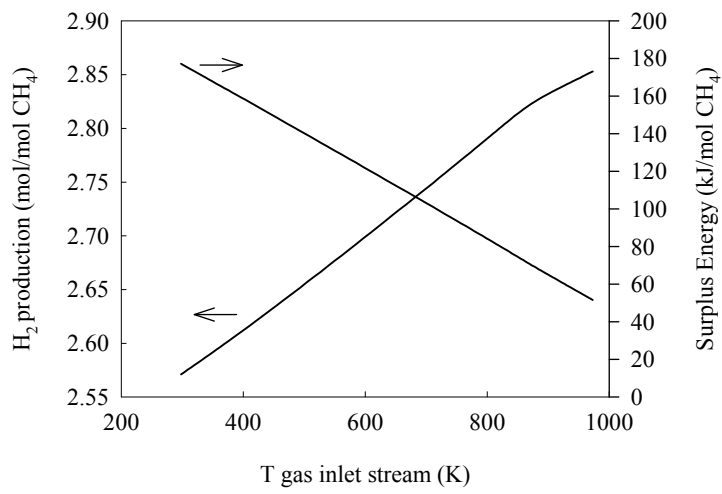
Figure 11. Effect of the temperature of gas inlet streams on the H_2 production and the "Surplus Energy". T_{FR} = 1150 K, NiO content = 20 wt.%, H_2O/CH_4 = 0 in FR.