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# Synthesis gas generation by chemical-looping reforming using a Ni-based oxygen carrier

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## Abstract

This work presents the experimental results obtained during auto-thermal chemical looping reforming (CLR) in a 900 W<sub>th</sub> circulating fluidized bed reactor using methane as fuel. An oxygen carrier based on NiO and supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was used during more than 50 hours of operation and the effect of different operating variables, like fuel reactor temperature, H<sub>2</sub>O/CH<sub>4</sub> molar ratio and solid circulation rate, on CH<sub>4</sub> conversion and gas product distribution was analyzed. It was found that in all operating conditions CH<sub>4</sub> conversion was very high (>98%) and the most important variable affecting to the gas product distribution was the solid circulation rate, that is, NiO/CH<sub>4</sub> molar ratio. During operation the oxygen carrier particles maintained their physical and chemical properties. These results suggest that this oxygen carrier could have a high durability, being a suitable oxygen carrier for a CLR system.

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Keywords: Chemical looping; Oxygen carrier; Nickel Oxide; Fluidized bed

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## 1. Introduction

It is widely accepted today that carbon dioxide coming from fossil fuel combustion is the most important greenhouse gas contributing to global warming. One of the options to overcome anthropogenic greenhouse effect is the development of CO<sub>2</sub> capture and storage technologies from flue gases of power plants.

Catalytic reforming of CH<sub>4</sub>, natural gas or light hydrocarbons is a commercial process to produce synthesis gas, which is the main source for the production of ammonia, methanol, hydrogen, and many other important products. At the present, steam reforming of natural gas, where the reforming takes place in reactor tubes packed with catalyst, is the most important method for synthesis gas production, although, this method produces also large

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amounts of  $\text{CO}_2$  as by-product. In the CACHET project the integration of  $\text{CO}_2$  capture technologies with  $\text{H}_2$  production systems for power generation and fuel applications are being studied [1]. The overall goal of the CACHET project is to develop innovative technologies which will substantially reduce the cost of  $\text{CO}_2$  capture whilst simultaneously producing  $\text{H}_2$  from natural gas fuel. Some of the technologies investigated are based in Chemical-Looping Combustion (CLC) process.

CLC is a novel combustion technology with inherent separation of the greenhouse gas  $\text{CO}_2$  that involves the use of an oxygen carrier, which transfers oxygen from air to the fuel avoiding the direct contact between them. CLC system is made of two interconnected reactors, designated as air and fuel reactors. In the fuel reactor, the fuel gas ( $\text{C}_n\text{H}_{2m}$ ) is oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by 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  $\text{N}_2$  and unreacted  $\text{O}_2$ . The exit gas from the fuel reactor contains only  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . After water condensation, almost pure  $\text{CO}_2$  can be obtained with little energy lost for component separation.

Chemical-Looping auto-thermal Reforming (CLR), as described in Figure 1, was proposed by Mattisson et al. [2]. This new process uses the metal oxide to transfer oxygen to the fuel, being the main difference with CLC that the desired product is syngas ( $\text{H}_2 + \text{CO}$ ). In the CLR process the air to fuel ratio is kept low to prevent the complete oxidation of the fuel to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The major advantage of this process is that the heat needed for converting  $\text{CH}_4$  to  $\text{H}_2$  and  $\text{CO}$  is supplied without costly oxygen production and without mixing of air with carbon containing fuel gases. An important aspect to be considered in a CLR system is the heat balance. The oxidation reaction of the metal oxide is very exothermic, however, the reduction reactions are endothermic. So, the heat for the endothermic reduction reactions is 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.

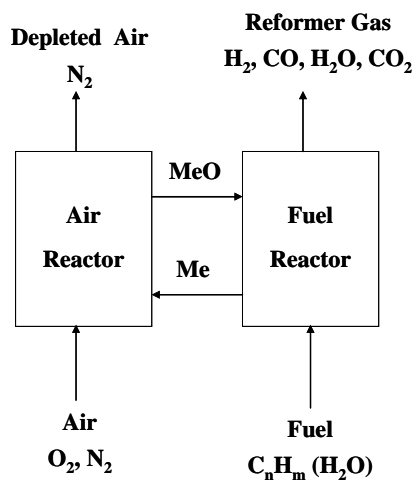


Figure 1: Chemical-Looping Reforming.

An oxygen carrier for CLR should have enough reactivity through cycles to reduce solids inventory, high resistance to attrition, complete fuel conversion to  $\text{CO}$  and  $\text{H}_2$ , negligible carbon deposition, and good fluidization properties. Iron, nickel, copper and manganese are promising active metals to be used in a CLR process, but Ni appears the most interesting due to its strong catalytic properties. Metallic Ni is used in most commercial steam reforming catalyst.

There are some works studying different oxygen carriers for CLR. Zafar et al. [4-5] observed in a laboratory fluidized bed reactor and in a thermogravimetric analyzer (TGA) that working at  $950\text{ }^\circ\text{C}$ , oxygen carriers based on

Ni, Fe, and Mn and supported on  $\text{SiO}_2$  underwent considerable reactivity deactivation with the redox cycles. On the contrary oxygen carriers supported on  $\text{MgAl}_2\text{O}_4$  showed high reactivities during reduction and oxidation. Several oxygen carriers for CLR have been also tested by Ryden et al. in a fixed bed reactor [6] and in a continuous laboratory reactor consisting of two interconnected fluidized beds [7-8]. Almost complete conversion of natural gas and high selectivity towards  $\text{H}_2$  and  $\text{CO}$  was achieved with oxygen carriers made of NiO and supported on  $\text{MgAl}_2\text{O}_4$  or  $\text{Al}_2\text{O}_3$ . Formation of solid carbon was reduced or eliminated by adding steam to natural gas. These authors confirmed that the concept chemical-looping reforming is feasible and should be further investigated. Johansson et al [9] compared two different oxygen-carriers, NiO/ $\text{NiAl}_2\text{O}_3$  and NiO/ $\text{MgAl}_2\text{O}_4$ , using both continuous and pulse experiments in a batch laboratory fluidized bed. They found that NiO/ $\text{MgAl}_2\text{O}_4$  offers higher methane conversion, higher selectivity to reforming and lesser tendency for carbon formation.

In a previous work, our group [10] studied in a TGA and in a batch fluidized bed reactor several Ni-based oxygen carriers prepared by impregnation on alumina. The tests carried out showed that Ni-based oxygen carriers prepared by incipient wetness impregnation on  $\gamma\text{-Al}_2\text{O}_3$ ,  $\theta\text{-Al}_2\text{O}_3$ , and  $\alpha\text{-Al}_2\text{O}_3$  are suitable for auto-thermal reforming of methane during long periods of time without carbon formation. In this work, a Ni-based oxygen carrier prepared by impregnation on  $\gamma\text{-Al}_2\text{O}_3$  has been used in a 900  $\text{W}_{\text{th}}$  CLR continuous pilot plant to set the suitability of this material for CLR. The effect of operating conditions, such as oxygen carrier-to-fuel ratio, fuel reactor temperature and the  $\text{H}_2\text{O}/\text{CH}_4$  molar ratio, on the process efficiency has been analyzed.

## 2. Experimental Section

### 2.1. Materials

The behaviour of an oxygen carrier with NiO (21 wt%) as active phase and  $\gamma\text{-Al}_2\text{O}_3$  as support was analyzed in this work. NiO21- $\gamma\text{Al}_2\text{O}_3$  was prepared by incipient wetness impregnation over Commercial  $\gamma\text{-Al}_2\text{O}_3$  (Puralox NWA-155, Sasol Germany GmbH). The details of the preparation of the oxygen carrier have been described elsewhere [10-11]. The oxygen carrier was physically and chemically characterized by several techniques. Table 1 shows the main properties of the oxygen carrier.

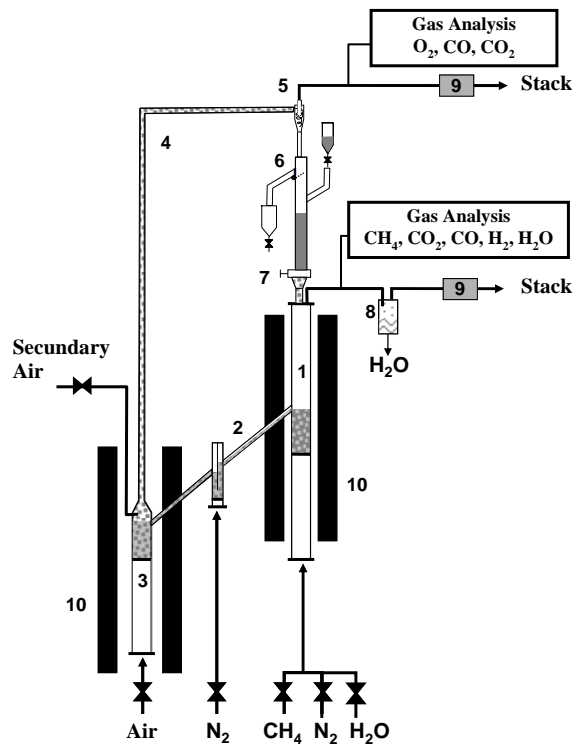
**Table 1.** Physical properties and solid composition of the oxygen carriers

Oxygen carrier	Density ( $\text{g}/\text{cm}^3$ )	Crushing strength (N)	BET ( $\text{m}^2/\text{g}$ )	Porosity (%)	XRD
NiO21- $\gamma\text{Al}_2\text{O}_3$	1.7	2.6	83.4	50.7	$\gamma\text{-Al}_2\text{O}_3$ , $\text{NiAl}_2\text{O}_4$
NiO21- $\gamma\text{Al}_2\text{O}_3$ After 50 h operation	1.9	2.4	29	48.4	$\gamma\text{-Al}_2\text{O}_3$ , $\text{NiAl}_2\text{O}_4$ , NiO

The oxygen carrier was also analyzed in a scanning electron microscope (SEM) ISI DS-130 coupled to an ultra thin window PGT Prism detector for energy-dispersive X-ray (EDX) analysis. The oxidation and reduction reactivities of the oxygen carrier were determined in a TGA, CI Electronics type, described elsewhere [11].

### 2.2. Experimental Facility

Figure 2 shows the schematic diagram of the 900  $\text{W}_{\text{th}}$  continuous atmospheric CLR pilot plant used for the tests. The pilot plant was basically composed of two interconnected fluidized-bed reactors, a riser for solids transport from the air reactor (AR) to the fuel reactor (FR), a solid valve to control the flow rate of solids fed to the fuel reactor, a loop seal and a cyclone. This design allowed the variation and control of the solid circulation flow rate between both reactors.



**Figure 2:** Schematic diagram of the Chemical-Looping Reforming facility.

The FR (1) consisted of a bubbling fluidized bed (0.052 m i.d.) with a bed height of 0.1 m. In this reactor the NiO of the oxygen carrier is reduced by the fuel to Ni. Reduced oxygen carrier particles overflowed into the AR (3) through a U-shaped fluidized bed loop seal (2), to avoid gas mixing between fuel and air. The oxidation of the carrier took place at the AR, which consisted of a bubbling fluidized bed (0.05 m i.d.) with a bed height of 0.1 m, followed by a riser (4) of 0.02 m i.d. and 1 m height. The regeneration of the oxygen carrier happened in the dense bed part of the AR allowing residence times high enough for the complete oxidation of the reduced carrier. Secondary air could be introduced at the top of the bubbling bed to help particle entrainment. N<sub>2</sub> and unreacted O<sub>2</sub> left the AR passing through a high-efficiency cyclone (5) and a filter (9) before the stack. The oxidized solid particles recovered by the cyclone were sent to a solids reservoir setting the oxygen carrier ready to start a new cycle. In addition, these particles avoid the leakage of gas between the FR and the riser. The regenerated oxygen carrier particles returned to the FR by gravity from the solids reservoir through a solids valve (7) which controlled the flow rates of solids entering the FR. A diverting solids valve (6) located below the cyclone allowed the measurement of the solids flow rates at any time. Fine particles produced by fragmentation/attrition in the plant were recovered in the filters that were placed downstream of the FR and AR.

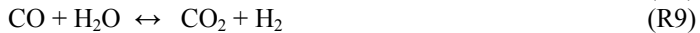
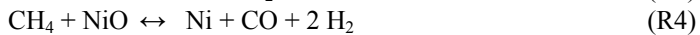
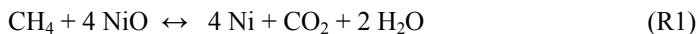
The prototype had several tools of measurement and system control. Thermocouples and pressure drop transducers located at different points of the plant showed the current operating conditions in the plant at any time. Specific mass flow controllers gave accurate flow rates of feeding gases and H<sub>2</sub>O. The gas outlet streams of the FR and AR were drawn to respective on-line gas analyzers to get continuous data of the gas composition. CH<sub>4</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O were measured at the fuel reactor outlet by two infrared gas analyzers, via Fourier transform infrared (FTIR, Temet CX4000) and nondispersive infrared (NDIR, Maihak S710/OXOR-P) analyses. H<sub>2</sub> was measured using a thermal conductivity analyzer (Maihak S710/THERMOR). At the outlet of air reactor, CO and CO<sub>2</sub> were

measured by an NDIR analyzer (Siemens/Ultramat 22P), and O<sub>2</sub> by a paramagnetic analyzer (Siemens/Oxymat 5E). All data were collected by means of a data logger connected to a computer.

### 3. Results and discussion.

Reforming tests under different operation conditions were conducted in the facility with the oxygen carrier using CH<sub>4</sub> as fuel. The total solids inventory in the system was about 1.5 kg of oxygen carrier. The temperature in the FR was varied over a range of 800-900 °C. The temperature in the AR was always kept constant at about 950±15 °C. The gas fed to the FR was composed of 50 vol.% of CH<sub>4</sub> and 50 vol.% of H<sub>2</sub>O + N<sub>2</sub>. The H<sub>2</sub>O/CH<sub>4</sub> molar ratio was varied in the feeding gas from 0 to 0.5, so the composition of the feeding gas was 50 vol.% CH<sub>4</sub>, 0-25 vol.% H<sub>2</sub>O, and balanced N<sub>2</sub>. The inlet flow of methane was 87.2 NI/h, it means that the inlet gas velocity in the fuel reactor was 10 cm/s at 900 °C. The inlet air flow in the AR was 720 NI/h as primary air and 150 NI/h as secondary air. The effect of oxygen carrier to fuel ratio on the methane conversion and gas product distribution was analyzed by controlling the solid circulation flow rates by means of the solids valve, and took values from 2 to 11 kg/h. The steady-state for the different operating conditions was maintained at least for an hour in each test. A total of more than 50 hours of operation, from which more than 40 h corresponded to the reaction period, were carried out.

The main reactions happening with different contribution in the fuel reactor during the oxygen carrier reduction period are:



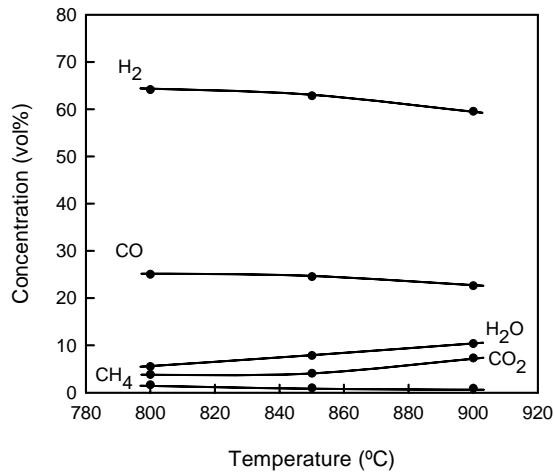
And in the air reactor during the oxygen carrier oxidation:



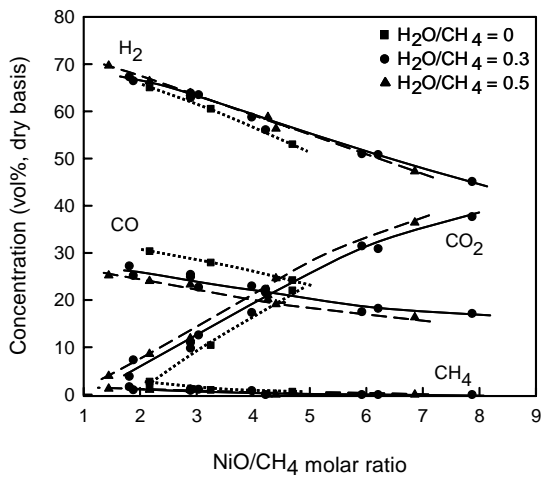
The gases product concentrations of the fuel and air reactors were measured by on line analyzers. These gases concentrations were used to calculate the conversion of the oxygen carrier during the reduction and oxidation periods and to make carbon, hydrogen and oxygen mass balances over the whole reactor system. For better comparison, the results showed in this work are presented in N<sub>2</sub> free basis and/or dry N<sub>2</sub> free basis.

#### 3.1. Effect of Fuel Reactor Temperature

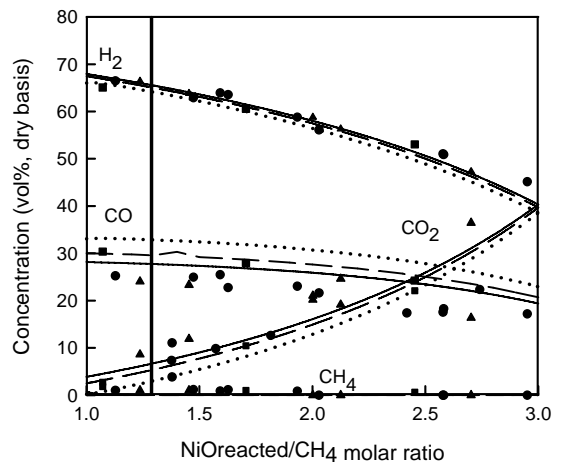
Figure 3 shows the effect of fuel reactor temperature, in the range of 800-900°C, on the gas product concentrations. The CH<sub>4</sub> conversion was very high (>98%) in all range of temperature tested. For the same oxygen carrier-to-fuel ratio, an increase in the fuel reactor temperature produced a small increase in the CH<sub>4</sub> conversion, a slight increase in the CO<sub>2</sub> and H<sub>2</sub>O concentrations and a slight decrease in the H<sub>2</sub> and CO concentrations. The increase in the CH<sub>4</sub> conversion with increasing the FR temperature could be due to the increase of R1, R4, and R5 reaction rates, and the increase in the CO<sub>2</sub> and H<sub>2</sub>O concentrations and decrease in the H<sub>2</sub> and CO concentrations due to the increase of R1, R2, and R3 reaction rates. It must take into account that an increase in the FR temperature increased the oxygen carrier conversion and as a consequence more oxygen was available for oxidation.



**Figure 3:** Effect of fuel reactor temperature on the gas product concentrations.  $H_2O/CH_4 = 0.3$ ;  $NiO/CH_4 = 1.8$ .



**Figure 4:** Effect of oxygen carrier-to-fuel ratio on the gas product concentrations with different  $H_2O/CH_4$  molar ratios.  $T = 900^\circ C$ .



**Figure 5:** Effect of  $NiO_{reacted}/CH_4$  molar ratio on the gas product composition. Lines: thermodynamic equilibrium data. (■, .....):  $H_2O/CH_4 = 0$ , (●, -----):  $H_2O/CH_4 = 0.3$ , (▲, —):  $H_2O/CH_4 = 0.5$ .

### 3.2. Effect of $H_2O/CH_4$ molar ratio

The  $H_2O/CH_4$  molar ratio was varied from 0 to 0.5 (0 – 25%  $H_2O$ ) in the fuel gas fed to FR. Figure 4 shows the effect of  $H_2O/CH_4$  molar ratio on the gas product concentration at the exit of the FR with different oxygen carrier-to-fuel ratios. A slight increase of  $H_2$  and  $CO_2$  concentrations and a slight decrease of  $CO$  concentration were found increasing the  $H_2O/CH_4$  molar ratio, because  $H_2O$  enhances the methane reforming reaction (reaction R5) and specially the water gas shift reaction (reaction R9).

In these tests, working without feeding H<sub>2</sub>O (H<sub>2</sub>O/CH<sub>4</sub> = 0) and with low solid circulation rates (e.i. low NiO/CH<sub>4</sub> molar ratios), CO and/or CO<sub>2</sub> were detected at the outlet of the AR due to the reactions R11 and R12. This indicated carbon formation due to reaction R6 at these operating conditions.

### 3.3. Effect of Oxygen Carrier-to-Fuel Ratio

An important operating parameter for CLR process is the oxygen carrier-to-fuel molar ratio which, for a given fuel flow rate fed to the FR, depends on the solid circulation flow rate between both reactors. Figure 4 shows the effect of oxygen carrier-to-fuel ratio on the gas product concentration measured at the outlet of the FR working with different H<sub>2</sub>O/CH<sub>4</sub> molar ratios at a temperature of 900°C. The methane conversion was very high in all operating conditions and it was found an increase in the CO<sub>2</sub> and H<sub>2</sub>O concentrations and a decrease in the H<sub>2</sub>, CO and CH<sub>4</sub> concentrations increasing the oxygen carrier-to-fuel ratio. An increase in the oxygen carrier circulation flow rate increased the contribution of the oxidation reactions (reactions R1-R3) to the overall global process.

Taking into account the conversion reached by the oxygen carrier, Figure 5 show the gas product composition measured at the outlet of the FR, working at 900 °C with different H<sub>2</sub>O/CH<sub>4</sub> molar ratios, as a function of the reacted NiO to CH<sub>4</sub> molar ratio. It was found that these gas product compositions were close to thermodynamic equilibrium and the best gas composition in order to maximize the syngas production was obtained at low reacted NiO to CH<sub>4</sub> molar ratios (NiO<sub>reacted</sub>/CH<sub>4</sub>≈1).

As mentioned above, an important aspect to be considered in a CLR system is the heat balance. The oxidation reaction of the metal oxide is very exothermic, however, the reduction reactions are endothermic. So, the heat necessary for the endothermic reduction reactions is given by the hot solids coming from the air reactor. The heat generated in the air reactor must be high enough to fulfil the heat balance in the whole system. A NiO<sub>reacted</sub>/CH<sub>4</sub> molar ratio of ≈1.25 was calculated to the fulfilment of the heat balance. In these operating conditions a dry gas product composition of ≈65vol.% H<sub>2</sub>, ≈25vol.% CO, ≈9 vol.% CO<sub>2</sub>, and ≈1-1.5 vol.% CH<sub>4</sub> can be obtained in the auto-thermal CLR process.

### 3.4. Behaviour of the oxygen-carrier particles

A total of more than 50 hours of operation with the oxygen carrier, from which more than 40 hours corresponded to the reaction period, were carried out. The oxygen carrier particles never showed agglomeration or defluidization problems and the loss of fine solids due to attrition was negligible. Table 1 shows the main properties of the oxygen carrier both fresh and after ≈50 hours of operation. It was found a small increase in the density of the used particles. A slightly decreased of the mechanical strength of the particles was observed. The carrier porosity slightly decreased with the respective mean pore size shifting towards pores of higher size. The BET specific surface area decreased, these features suggest that some accumulative thermal sintering was occurring in the oxygen carrier particles along the time during operation in the prototype but, fortunately, they did not deactivate the oxygen carrier reactivity. The reactivities measured in the TGA for the fresh and used oxygen carrier particles showed that the reduction reactivity of the used particles increased and the oxidation reactivity did not change.

The powder XRD patterns of the used NiO21-γAl<sub>2</sub>O<sub>3</sub> revealed the presence of a new crystalline phase, NiO, and they also revealed that after 50 hours of operation γ-Al<sub>2</sub>O<sub>3</sub> did not evolved to α-Al<sub>2</sub>O<sub>3</sub>. The general appearance of the used particles analyzed by SEM-EDX was similar to the fresh particles. No changes in the surface texture and the solid structure of the used particles were detected compared to fresh particles.

## 4. Conclusions

A Ni-based oxygen carrier, NiO21-γAl<sub>2</sub>O<sub>3</sub>, prepared by incipient wetness impregnation, has been tested in a 900 W<sub>th</sub> CLR pilot plant to analyze its behaviour with regarding to the reforming of CH<sub>4</sub>. During operation the effect of

different operating variables, like fuel reactor temperature,  $\text{H}_2\text{O}/\text{CH}_4$  molar ratio and solid circulation rate, on  $\text{CH}_4$  conversion and gas product distribution was analyzed.

It was observed that in all operating conditions the  $\text{CH}_4$  conversion was very high (>98%). The most important operating variable affecting the gas product distribution was the oxygen carrier circulation rate, that is, the  $\text{NiO}/\text{CH}_4$  molar ratio. An increase in the  $\text{NiO}/\text{CH}_4$  molar ratio produced an increase in the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  concentrations and a decrease in the  $\text{H}_2$ ,  $\text{CO}$  and  $\text{CH}_4$  concentrations. The best gas product composition was obtained for  $\text{NiO}_{\text{reacted}}/\text{CH}_4$  molar ratios near 1. However, a  $\text{NiO}_{\text{reacted}}/\text{CH}_4$  molar ratio of  $\approx 1.25$  was calculated to the fulfillment of the heat balance. In these operating conditions a dry gas product composition of  $\approx 65\text{vol.}\% \text{H}_2$ ,  $\approx 25\text{vol.}\% \text{CO}$ ,  $\approx 9 \text{vol.}\% \text{CO}_2$ , and  $\approx 1\text{--}1.5 \text{vol.}\% \text{CH}_4$  can be obtained in the auto-thermal CLR process.

Important changes in the surface texture and the solid structure of the oxygen carrier particles were not detected after 50 hours of operation. In addition, the oxygen carrier did not show agglomeration or defluidization problems and the loss of fine solids due to attrition was negligible. These results suggest that this oxygen carrier could have a high durability, being suitable oxygen carrier for a CLR system.

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