Effect of Fuel Gas Composition in Chemical-Looping Combustion with Ni-Based Oxygen Carriers. Part 2. Fate of Light Hydrocarbons

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ABSTRACT.

Chemical-Looping Combustion (CLC) has been suggested among the best alternatives to reduce the economic cost of CO₂ capture using fuel gas because CO₂ is inherently separated in the process. Natural gas or refinery gas can be used as gaseous fuels, which may contain different amounts of light hydrocarbons (LHC). The purpose of this work was to investigate the effect of the presence of light

hydrocarbons (C_2H_6 and C_3H_8) in the feeding gas of a CLC system using a nickel-based oxygen carrier prepared by impregnation on alumina. The reactivity of the oxygen carrier with light hydrocarbons and the combustion efficiency of the process were analyzed in a batch fluidized bed (FB) and a continuous CLC plant. The experiments in the batch FB showed that light hydrocarbons can be fully converted in a CLC process at temperatures above 1173 K. The influence of the fuel reactor temperature (1073-1153 K), solid circulation flow rate (7-14 kg/h), and gas composition were studied in a continuous CLC plant (500 W_{th}). Neither unburnt hydrocarbons nor carbon formation were detected at any experimental condition. Moreover, no agglomeration problems were detected in any case. High energy efficiencies, close to the thermodynamic limit using Ni-based materials, were reached when the oxygen carrier-to-fuel ratio was higher than 3 and the fuel reactor temperature was 1153 K. According to the results found in this work it was concluded that no special measures should be taken in a CLC process with respect to the presence of LHC in fuel gas, e.g. refinery gas or crude natural gas.

1. Introduction

Fossil fuels represent an abundant and cheap resource for energy production, yet increasing levels of atmospheric carbon dioxide. It is well known that CO_2 , which is the largest by-product of fossil-fuel combustion, is an important greenhouse gas that strongly affects global warming.¹ In this sense, CO_2 capture and sequestration (CCS) is an important option to reduce CO_2 emissions to the atmosphere from power plants.² There are different CCS technologies available or currently under development but most of them have high energy penalty as a consequence of the gas separation step, which result in an increase of the cost of energy production.

Chemical-Looping Combustion (CLC) technology has been suggested among the best alternatives to reduce the economic cost of CO_2 capture using fuel gas. In this process, CO_2 is inherently separated from the other flue gas components (N_2 and unused O_2) through the use of a solid oxygen carrier (OC) and thus no energy is expended for the separation.³ The description of the process is well known considering the increasing development of this technology in the last few years for combustion of

natural gas⁴⁻⁶ or for gas from coal gasification.⁷⁻⁹ Also, refinery and industrial gases have been considered to be used as fuel gas in a CLC system.¹⁰ Recently, interest in combustion of solid fuels, e.g. coal, introducing the fuel directly to the FR, has arisen.¹¹⁻¹³ Gaseous fuels can contain variable amounts of sulfur and light hydrocarbons (LHC), i.e. C₂-C₅. In addition to methane, the LHC content may be up to 10 vol% in crude natural gas¹⁴ and up to 30 vol% in refinery gas.¹⁵ As an example, a typical composition of refinery fuel gas is shown in Table 1.¹⁵ The effect of sulfur has been analyzed in a previous work.¹⁶ However, it is also important to know the behavior of the OC using gas mixtures containing LHC, especially when using refinery and industrial gases or high-LHC content natural gas. To obtain high combustion and CO₂ capture efficiencies, hydrocarbons might be fully converted in a CLC system. Depending on the reactivity of the OC with the hydrocarbons, incomplete fuel conversion could happen, having a significant effect on the combustion efficiency of the CLC process. Although non-converted hydrocarbons could be addressed in different ways, e.g. adding some oxygen at the fuel reactor outlet to oxidize minor amounts of unconverted fuel¹⁷ or separating hydrocarbons from the CO₂ gas stream, it would be desirable to get full conversion of hydrocarbons in the CLC system.

There are a high number of works in the literature regarding the use of LHC in the presence of Nickel catalysts^{14,18-20} although they are not referred to the specific process of CLC. The possible reactions involved in a CLC process using a nickel-based oxygen carrier increase with the presence of LHC with respect to the use of pure CH₄. The main reactions involved in the CLC process are shown in Table 2. Metallic nickel appears as product of the reaction between hydrocarbons and NiO initially present in the OC (see reactions 1 and 2). The set of reactions 3-11 are the same as those processes where metallic nickel is used as catalyst. The relative importance of reactions in gas phase depends on the operating conditions such as temperature, composition, residence time, catalytic activity, etc. Using Ni-based oxygen carriers, carbon deposition on particles could happen in the fuel reactor because of the catalytic activity of metallic Ni formed during reaction of the OC with the fuel gas. Carbon formation (reactions 10 and 1) is favored at low temperatures, whereas reaction 9 becomes increasingly important at higher temperatures.¹⁹ The higher tendency to carbon formation of hydrocarbons with respect to pure CH₄,

mainly due to coke formation from olefins (reactions 7 and 8),¹⁸ could produce deactivation of the OC and/or give agglomeration problems into the system. Depending on the operating conditions, carbon can be gasified with the CO₂ and H₂O by the reverse of reactions 10 and 11 in the fuel reactor or bypass to the air reactor together with OC particles where carbon reacts with the oxygen in air. In the last case, there is a loss of efficiency in the CO₂ capture because CO and/or CO₂ are present together with N₂ and unused O₂ at the air reactor exit. Finally, gas products (CH₄, olefins, CO and H₂) can also react with the metallic oxide NiO (reactions 12-15).

Using Ni-based oxygen carriers, hydrocarbons can be fully converted but thermodynamic limitations prevent the full selectivity of fuel gases towards CO₂ and H₂O, because the existence of small amounts of CO and H₂ at equilibrium.²¹ The equilibrium composition depends on the H/C molar ratio in the fuel gas and is given by equilibrium of reactions 14 and 15 in Table 2. Figure 1 shows the equilibrium concentrations at two temperatures as a function of the H/C molar ratio of the hydrocarbon. It is observed that CO increase and H₂ decrease as higher is the hydrocarbon, i.e. lower H/C molar ratio. Moreover, these equilibrium concentrations increase as the temperature increase. Table 3 shows the maximum combustion efficiencies at equilibrium conditions, defined as the ratio of the amount of oxygen taken up by the gas to the amount of oxygen that would have been taken up if conversion to CO₂ and H₂O was complete. The conversion efficiency, η_c , were roughly constant with the H/C molar ratio, being $\eta_c \approx 99.6\%$ at 1073 K and $\eta_c \approx 99.4\%$ at 1223 K.

The aim of this work was to test by the first time the behavior of a Nickel-based oxygen carrier when the fuel, CH₄, contains variable amounts of LHC: ethane and propane. The experiments were carried out in a batch fluidized bed and in a 500 W_{th} CLC pilot plant under continuous operation. The influence of temperature, solid circulation rate and LHC concentration on the gas products distribution, combustion efficiency, carbon formation and material agglomeration was investigated.

2. Experimental

2.1. Oxygen carrier

The oxygen carrier used in this work was prepared by hot incipient wet impregnation (HIWI) using NiO as active phase and α -Al₂O₃ as support. Previous work was carried out to determine the effect of the support on the Ni-based OC,²² and it was found that α -Al₂O₃ was a suitable material to prepare impregnated oxygen carrier particles. Commercial γ -Al₂O₃ (Puralox NWA-155, Sasol Germany GmbH) particles of 100-300 μ m were sintered in a furnace at 1423 K for two hours to obtain α -Al₂O₃ as support ($\rho = 1900 \text{ kg/m}^3$, $\varepsilon = 48.5\%$). The material was prepared by the addition over the hot α -Al₂O₃ (353 K) of a volume of a saturated solution (6 M) of Ni(NO₃)₂·6H₂O (>99.5% Panreac) at 333-353 K. The amount of solution corresponds to the total pore volume of the support particles. The aqueous solution was slowly added to the support particles with thorough stirring at 353 K in a planetary mixer. The desired active phase loading was achieved by applying two successive impregnations followed by calcinations at 823 K, in air atmosphere for 30 minutes, to decompose the impregnated metal nitrate into insoluble oxide. Finally, the OC was calcined for 2 hours at 1223 K, obtaining a material –denoted here as Ni19- α Al:HI– whose main characteristics are showed in Table 4. The oxygen transport capacity was defined as the mass fraction of oxygen that can be used in the oxygen transfer, calculated as $R_{OC} = (m_{ox} - m_{red})/m_{ox}$, where m_{ox} and m_{red} are the masses of the oxidized and reduced form of the oxygen carrier, respectively.

2.2 Thermogravimetric analysis

Reactivity tests of the Nickel-based oxygen carrier with LHC were carried out in a thermo-gravimetric analyzer (TGA), CI Electronics type, which was described in detail in a previous work.²³ The composition of the gas chosen for the reducing experiments was composed by a variable amount (2-15 vol%) of fuel gas (CH₄, C₂H₆ or C₃H₈), 20 vol% H₂O, and N₂ balance. The gas used for oxidation was 100 vol% air. The experiments were carried out at 973, 1073 and 1223 K.

2.3. Batch fluidized bed reactor

To investigate the effect of LHC on the gas product distribution during CLC with Ni-based oxygen carriers, several reduction-oxidation cycles were carried out in a batch fluidized bed. Figure 2 shows the

experimental setup. It consisted of a system for gas feeding, a fluidized bed reactor, two filters that recovered the solids elutriated from the FB, and the gas analysis system. The gas feeding system had different mass flow controllers connected to an automatic three-way valve. This allowed the feeding of the fuel gas (CH_4 , C_2H_6 , C_3H_8 or mixtures of them) during the reducing period and air for oxidation of the OC. Nitrogen was introduced between the two periods to avoid the contact between the fuel and the oxygen. The FB reactor was 54 mm I.D. and 500 mm height, with a preheating zone just under the distributor. The total solid inventory in the reactor was 400 g. The entire system was inside an electrically heated furnace. The differential pressure drop in the bed was measured by means of two pressure taps connected to the reactor, and were used to detect possible agglomeration problems in the bed. The gas analysis system consisted of several on line gas analyzers. CO , CO_2 , and CH_4 concentrations were measured using non-dispersive infrared (NDIR) analyzers (Maihak S710 / UNOR), a FTIR analyzer (Gasmeter CX4000) measured the H_2O concentration, H_2 concentration was determined using a thermal conductivity detector (Maihak S710 / THERMOR), and O_2 concentration by using using a paramagnetic analyzer (Maihak S710 / OXOR-P). The unburnt hydrocarbons were measured with a total hydrocarbons analyzer (Bernath Atomic BA-9900). All data were collected by means of a data logger connected to a computer. To improve data analysis, the gas flow dispersion through the sampling line and the analyzers was corrected for all the measured gas concentrations versus time profiles in order to obtain the actual concentration of the gases at the bed exit.

From the gas product distribution obtained during reducing period, it was possible to know the rate of oxygen transferred from the OC to the fuel gas, r_{O} , as a function of reduction time using the following equation

$$r_{\text{O}}(t) = (x_{\text{CO}} + 2x_{\text{CO}_2} + x_{\text{H}_2\text{O}})_{\text{out}} F_{\text{out}} \quad (17)$$

The conversion of solids in the FB for reduction reaction can be calculated from the integration of $r_{\text{O}}(t)$ with time

$$X_{OC}(t) = \frac{1}{N_{O,OC}} \int_{t_{r,0}}^t r_O(t) dt \quad (18)$$

being $N_{O,OC}$ the molar amount of active oxygen in the OC, calculated as

$$N_{O,OC} = \frac{m_{ox} R_{OC}}{M_O} \quad (19)$$

The oxygen carrier reactivity was evaluated by derivation of eq 18, i.e. dX_{OC}/dt . Also, for comparison purposes among different experiments, the combustion efficiency, η_c , was obtained at each operating condition (temperature and fuel gas composition), defined according to the following equation

$$\eta_c(t) = \frac{r_O(t)}{(4x_{CH_4} + 7x_{C_2H_6} + 10x_{C_3H_8})_{in} F_{in}} \quad (20)$$

where F_{in} is the molar flow of the inlet gas stream.

Special attention was put on the carbon formation during experimental tests in the batch FB reactor. Carbon formation during reduction time was first detected by CO and CO₂ evolution during inert and oxidation period. The total amount of carbon formed, N_C , was calculated as

$$N_C = \int_{t_{i,0}}^{t_{i,f}} (x_{CO} + x_{CO_2})_{out} F_{out} dt + \int_{t_{o,0}}^{t_{o,f}} (x_{CO} + x_{CO_2})_{out} F_{out} dt \quad (21)$$

Additionally, carbon formation was calculated by carbon balance during reduction period. So, the difference between inlet carbon to the reactor and outlet carbon from the reactor was attributed to carbon formed in the reactor

$$N_C = \int_{t_{r,0}}^{t_{r,f}} (x_{CH_4} + 2x_{C_2H_6} + 3x_{C_3H_8})_{in} F_{in} dt - \int_{t_{r,0}}^{t_{r,f}} (x_{CH_4} + 2x_{C_2H_6} + 3x_{C_3H_8} + x_{CO} + x_{CO_2})_{out} F_{out} dt \quad (22)$$

The accumulated carbon in the FB reactor calculated in this way was in line to the carbon contained in CO and CO₂ in the gases during the oxidation period given by eq 21. Therefore, carbon formation can be calculated accurately by carbon balance during reducing period. This fact was used to calculate the carbon formation rate, r_C , as a function of time during reducing period as

$$r_C(t) = \left(x_{CH_4} + 2x_{C_2H_6} + 3x_{C_3H_8} \right)_{in} F_{in} - \left(x_{CH_4} + 2x_{C_2H_6} + 3x_{C_3H_8} + x_{CO} + x_{CO_2} \right)_{out} F_{out} \quad (23)$$

Finally, the carbon formation rate was expressed as the carbon formation to carbon inlet in the fuel gases ratio

$$r_C^*(t) = \frac{r_C(t)}{\left(x_{CH_4} + 2x_{C_2H_6} + 3x_{C_3H_8} \right)_{in} F_{in}} \quad (24)$$

2.4. CLC prototype (500 W_{th})

Figure 3 shows the schematic diagram of the 500 W_{th} Chemical-Looping Combustor used for the continuous tests. The FR (1) consisted in a bubbling fluidized bed (0.05 m i.d.) with a bed height of 0.1 m. In this reactor the fuel reacts with the oxygen carrier to give CO₂ and H₂O. The solids reduced in the FR were then transported to the AR (3) through a nitrogen-flowing loop seal fluidized bed reactor (2). The AR 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 took place in the dense bed part of the AR allowing residence times high enough for achieving the complete oxidation of the reduced carrier. Secondary air can be introduced at the top of the bubbling bed to help particle entrainment. The fully oxidized carrier was recovered by a high-efficiency cyclone (5), and sent to a solid reservoir (6), setting the solid ready to start a new cycle. The outlet gas from the AR, composed of N₂ and unreacted O₂, was sent to stack. The regenerated oxygen carrier returned to the FR by gravity from the solid reservoir located above a solids valve (7) which controlled the flow rate of solid entering the FR. A diverting solids valve (6) located below the cyclone allowed the measurement of the solid flow rates at any time. The fines produced by fragmentation/attrition in the plant were recovered in filters (9) located in the FR and AR lines.

The prototype was provided with several tools of measurement and system control. Thermocouples and pressure drop transducers located at different points of the plant showed the current operating conditions at any time. Accurate flow rates of feeding gases were obtained by means of specific mass

flow controllers. 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. Unburnt hydrocarbons, CH₄, CO, H₂, and CO₂ concentrations in the gas outlet stream from the FR were obtained after steam condensation. O₂, CO, and CO₂ concentrations were measured at the gas outlet stream from the AR. The gas analysis system was the same to the above showed for the batch FB experiments.

The behavior of the CLC was evaluated calculating the combustion efficiency, η_c , from the gas product distribution obtained in the FR, defined according to the following equation

$$\eta_c = \frac{\left(2x_{\text{CO}_2} + x_{\text{CO}} + x_{\text{H}_2\text{O}}\right)_{\text{out}} F_{\text{out}} - \left(x_{\text{H}_2\text{O}}\right)_{\text{in}} F_{\text{in}}}{\left(4x_{\text{CH}_4} + 7x_{\text{C}_2\text{H}_6} + 10x_{\text{C}_3\text{H}_8}\right)_{\text{in}} F_{\text{in}}} \quad (25)$$

The oxygen carrier-to fuel ratio (ϕ) was defined by eq 26, where F_{MeO} is the molar flow rate of the metal oxide and F_{Fuel} is the inlet molar flow rate of the fuel in the FR. A value of $\phi = 1$ corresponds to the stoichiometric MeO amount needed for a full conversion of the fuel to CO₂ and H₂O:

$$\phi = \frac{F_{\text{MeO}}}{b x F_{\text{fuel}}} \quad (26)$$

where b is the stoichiometric coefficient of the fuel gas mixing, calculated as

$$b = \frac{4x_{\text{CH}_4} + 7x_{\text{C}_2\text{H}_6} + 10x_{\text{C}_3\text{H}_8}}{x_{\text{CH}_4} + x_{\text{C}_2\text{H}_6} + x_{\text{C}_3\text{H}_8}} \quad (27)$$

3. Results

3.1 Thermogravimetric experiments

Experiments at different temperatures and gas concentrations were carried out in a TGA to determine the reactivity of the OC with respect to the LHC. Figure 4 shows, as example, the weight variations obtained with 15 vol% of C₃H₈ at three temperatures for the first reduction time of fresh particles. The curve obtained at 1223 K with 15 vol% CH₄ was also represented for comparison. The OC exhibited a high initial reactivity with the C₃H₈, similar to the observed with CH₄. As was indicated in a previous work,²⁴ this period was related to reduction of highly reactive free NiO. Nevertheless, after a short

period of time, the weight increased due to carbon formation. In this case, reactivity with CH₄ decreased due to the fact that part of the NiO was in the form NiAl₂O₄ spinel, which has lower reactivity than free NiO. Carbon formation was observed for propane and ethane at all temperatures and took place even in the presence of 20 vol% H₂O, which was not found using CH₄ as reducing agent. During the reduction with CH₄, full conversion of the OC was obtained without carbon formation. Therefore, it was found that ethane and propane presented higher tendency to carbon formation on OC particles than methane, and this fact was proved when the OC reactivity decreased as solids conversion increased. This phenomenon was further analyzed in the batch FB reactor and the continuously CLC system. Unfortunately, carbon formation in the TGA prevented the determination of kinetic data of higher HC.

3.2. Batch FB experiments

The batch FB experiments were carried out to investigate the effect on the OC reactivity and bed agglomeration of the presence of LHC, such as ethane or propane, in the combustible gas. These tests let us know the gas product distribution during different reduction and oxidation periods, and therefore determine the operating conditions (temperature and residence time) that avoid the presence of LHC in the flue gas of the FR obtaining combustion efficiencies close to equilibrium conditions (see Table 3). The presence of LHC in the feeding gas could also produce a higher carbon deposition with respect to the use of CH₄. Therefore, carbon formation during experimental tests was carefully analyzed.

The concentration of hydrocarbons used in the fuel gas is shown in Table 5, which was calculated to have the same oxygen consumption in all cases. It must be considered that ethane and propane need more oxygen for combustion than CH₄

H₂O was not introduced to the reactor. All the compositions were tested at four temperatures (1073, 1123, 1173, and 1223 K) and two different reduction times (1 and 3 minutes). Every operating condition was repeated at least three times, which corresponded to about 120 reduction/oxidation cycles with the

same batch of OC. It must be mentioned that no agglomeration problems were detected at any time, even in those tests with high carbon formation. Indeed, a reference condition (25% CH₄ at 1173 K) was repeated every 20 redox cycles to evaluate differences on reactivity with the cycle number. Similar results were obtained in all cases, indicating that the OC reactivity was roughly constant during the experimental tests.

As an example, Figure 5 shows the gas product distribution obtained with 14.3 vol% of C₂H₆ at 1073 and 1223 K and 3 minutes of reducing time. Full combustion of hydrocarbon was obtained initially, being CO₂ and H₂O the unique gas products. During this period H₂ and CO was below the detection level, and likely these gases were close to the concentration given by thermodynamic equilibrium for Ni-based OC. Later, CO and H₂ were formed, and finally, some unburnt hydrocarbons appeared at the experiments carried out at 1073 and 1123 K, but not at higher temperatures. The CO and CO₂ that appeared during inert and oxidation period corresponded to the combustion of the carbon formed during the reducing period. Similar results were found for CH₄, C₃H₈ and gas mixtures given in Table 5. The gas product distribution obtained with other gas compositions followed the same pattern although were quantitatively different.

Figure 5 also shows the solid conversion evolution during the reduction period obtained from eq 18. During the experimental tests the final solid conversion increased from 0.4 at 1073 K to 0.5 at 1223 K because of the higher OC reactivity with temperature. As an example, Figure 6 shows the effect of the solid conversion on the OC reactivity in the FB and the combustion efficiency, η_c , for C₂H₆ calculated using eq 20. During the full combustion period, i.e. combustion efficiency close to 100%, the reactivity of the OC was limited by the fuel flow fed into the FB reactor. In this stage, the actual reactivity of the OC should be higher than those showed in Figure 6. After the first period, the combustion efficiency decreases, i.e. H₂ and CO appeared while H₂O and CO₂ fell due to the OC reactivity decreases at higher solid conversion. Similar behavior was obtained for all tested gases. At this point, X_{fc} was defined as the maximum solids conversion when full combustion was obtained. Figure 7 shows X_{fc} for all gas mixture compositions. X_{fc} varies in the range $X_{fc} = 0.1-0.3$ depending on the temperature, and increases as the

temperature increases from 1073 to 1173 K. However, at 1223 K loss of reactivity and combustion efficiency started at lower solids conversion. The different behavior showed at 1223 K was due to carbon formation, as discussed below.

The loss of reactivity at solids conversion higher than 0.25-0.3 can be related to the relative amount of Ni as free NiO or NiAl_2O_4 spinel.²⁴ The reactivity of free NiO is high enough to fully convert the fuel gas into CO_2 and H_2O at all the temperature range tested (1073-1223 K). However, the reactivity of NiAl_2O_4 is lower, and fuel gas does not have the enough residence time in the FB reactor to get the oxygen needed to be fully converted into CO_2 and H_2O . This fact agrees with that found in TGA analysis. Differences during the last period were found with the temperature, i.e. reduction of NiAl_2O_4 . Whereas only H_2 and CO were found in the reacted gases at 1073 and 1123 K, some H_2O and CO_2 were found at 1173 and 1223 K, indicating that the reactivity of fuel gas with NiAl_2O_4 increases with the temperature, as it can be seen in Figure 6. During the low reactivity period, low levels of unburnt HC were detected (<1 vol%) at 1073 and 1173 K, but disappeared at higher temperatures.

The influence of LHC in carbon formation in the system was another important parameter to be analyzed. Carbon deposition on the OC could produce its deactivation and, as a consequence, a decrease in the combustion efficiency and maybe agglomeration problems inside the bed. Furthermore, loss of the CO_2 capture efficiency will happen if carbon formed is transported together with the OC particles into the AR, and burned there with air. As described above, carbon formation was evaluated from gas product distribution obtained during reduction and oxidation periods (see eqs 21-24). Differences on carbon formation were observed between experiments at 1123 K and the rest of temperatures (1073-1173 K). In the range from 1073 to 1173 K, carbon formation was not observed at the first moment during the reduction period, but was evidenced after the OC reactivity loss. In this case, carbon was formed when CO_2 and H_2O concentration decrease. Likely, the net accumulated carbon was a balance between carbon formation rate (reactions 9-11) and carbon disappearance rate through reaction 16 and reverse of reactions 10 and 11. This balance is gained by carbon formation during the low OC reactivity period. In these conditions, the rate of carbon formation, r_C , is maintained roughly constant during the

reduction time, and r_C was used as parameter to evaluate the effect of LHC on carbon formation. Figure 8 shows the carbon formation rate at low OC reactivity period as a function of the temperature for every gas mixture. It can be observed that the presence of LHC favored carbon formation in comparison with pure CH_4 , and all the gaseous compositions exhibited a minimum at 1173 K, which agrees with the inhibition of carbon formation via reactions 10 and 11 as temperature increases.¹⁹ However, at 1223 K, carbon formation started earlier than at lower temperatures, usually with solid conversions lower than 15%. Likely, the mechanism of carbon formation is dominated by coke formation via reaction 9 at the higher temperature.¹⁹ Carbon formation produced an OC deactivation before than at lower temperatures, when carbon is accumulated on the OC surface, This fact produces a decrease in the combustion efficiency (see Figure 6 and 7). At this point, it is remarkable that agglomeration was never observed during the batch FB experiments, even when carbon accumulation was evident.

To confirm the avoidance of carbon accumulation during the high reactivity period, new experiments were carried out with 1 minute of reduction time. In these cases, carbon accumulation was never detected, except for experiments carried out at 1223 K.

In a previous work,²⁴ it was found that the relative amount of NiO and NiAl_2O_4 in a Ni-based OC prepared by HIWI depended on the reduction degree in the FR, being both, NiO and NiAl_2O_4 , active compounds to transfer oxygen in a continuous CLC system. As higher is the reduction conversion, higher is the amount of free NiO present in the OC, which varies depending the experimental condition in a continuous CLC system, as discussed below. As NiAl_2O_4 must be at least partially reduced in a CLC system, temperatures should be in the range 1123-1173 K to obtain high combustion efficiency and no carbon formation in a CLC system.

3.3. Experimental tests in the 500 W_{th} CLC plant

Based on the experience gained during operation in the batch FB, combustion tests under continuous operation were conducted in the 500 W_{th} CLC facility described above. The total solids inventory in the system was ≈ 1.3 kg of solid material. The inlet gas velocity in the fuel reactor was 0.1 m/s, which represents about 2-3 times the minimum fluidization velocity of the OC. The temperature in the FR was

varied from 1073 to 1153 K, and the temperature in the AR was always kept at 1223 K. The solid circulation flow rate was varied between 7 and 14 kg/h, corresponding to oxygen carrier-to-fuel ratios, ϕ , of 1.9 and 3.8 respectively. Several gas compositions, similar to those used in the batch FB, were chosen for these tests (see Table 6). When the feeding gas was composed by a mixture of methane and LHC, water was introduced to avoid carbon formation in the distributor plate of the FR. The steady-state for the different operating conditions was maintained at least for two hours in each test, which gave us a total of 40 hours of operation with the same OC.

Figure 9 shows an example of the temperature profiles and gas product distribution obtained in the FR and the AR when gas mixture B in Table 6 was used. In this case, the experiment was maintained for six hours. Stable combustion was reached usually in less than 10 minutes. After this startup time, the outlet gas concentration and temperature were maintained uniform during the whole combustion time. Gas concentrations were a bit lower than theoretically expected as a consequence of the dilution produced by N_2 coming from the loop seal, and mass balances were found to be accurate by using the measurements of the analyzers from the AR and FR. Full conversion of CH_4 and LHC was obtained in the FR, but some CO and H_2 were also obtained at the outlet. Figure 10 shows that the amount of CO and H_2 increased as the oxygen carrier-to-fuel ratio decreased, but no unburnt hydrocarbons were observed at any circumstance.

The experimental data obtained after the tests gave us the combustion efficiency, η_c , obtained at each operating condition (temperature, fuel gas composition, and solid circulation rate), calculated according to the eq 25. Figure 11 shows the effect of the oxygen carrier-to-fuel ratio, ϕ , on the combustion efficiency for different hydrocarbons mixtures at two temperatures. At 1153 K, the best efficiencies were obtained for CH_4 as fuel gas, and this slightly decreased when ethane or propane was present. As previously was mentioned, thermodynamic limitations to fully convert the hydrocarbons to H_2O and CO_2 prevent 100% combustion efficiencies using Ni-based oxygen carriers. Combustion efficiencies close to equilibrium values were obtained working at high oxygen carrier to fuel ratios ($\phi > 3$).

The FR temperature is an important operating parameter. It was observed that, at 1073 K, the combustion efficiency decreased for all the gas compositions at low values of ϕ . Surprisingly, the combustion efficiency increased a lot for ϕ values above 3 and similar efficiencies to the obtained at 1153 K were reached. It must be also remarked that unburnt HC nor CH₄ were never detected at the flue gas of the FR. The loss of combustion efficiency was due to the CO and H₂ concentrations present at the outlet stream, as it can be seen in Figure 10.

These results were in line to those obtained from the analysis of the batch FB experiments. The OC showed a high reactivity period until a solids conversion of 25-30%. It must be considered that, assuming full oxidation of the OC in the AR, the solids conversion is related to the oxygen carrier-to-fuel ratio in a CLC system as

$$X_{oc} = \frac{\eta_c}{\phi} \quad (31)$$

Therefore, the oxygen carrier-to-fuel ratio must be in the range 3-4 in order to obtain high combustion efficiency in a CLC system. If $\phi < 3$, the less reactive NiAl₂O₄ compound would be reduced in the FR, and would give lower combustion efficiencies. Moreover, at $\phi < 3$ an increase in the temperature produced higher combustion efficiency because the reactivity of NiAl₂O₄ increased with the temperature, as it was showed above.

The carbon formation process was also analyzed during continuous operation in the plant. The carbon formed on the OC particles in the FR should be transferred to the AR and burned giving CO and/or CO₂. Nevertheless, CO and CO₂ were never detected at the outlet of the AR, indicating no carbon formation in the FR. Thus in the used operating conditions there were no losses in CO₂ capture by carbon transfer to the AR. Additional tests were performed to determine if carbon was accumulated on particles or somewhere in the system, e.g. reactor walls or distributor plate. In these tests, the fuel gas was turn off and FR was fluidized with nitrogen. After two minutes nitrogen was replaced by air as fluidization agent, so any carbon deposition in the system should burn into CO or CO₂. However, CO or CO₂ was never detected in the flue gases. From these results, it was concluded that carbon formation did not

happen at relevant extension in the system, i.e. on oxygen carrier particles or anywhere in the reactor. Moreover, neither OC deactivation nor agglomeration was detected during operation in the continuous CLC plant.

4. Use of light hydrocarbons in an industrial CLC plant.

The CLC technology was first developed for the use of natural gas or syngas from coal gasification. However, refinery and industrial gases containing variable amounts of light hydrocarbons (LHC), i.e. C₂-C₅, could be also suitable fuels for this type of systems.

The concerns about the presence of these LHCs in the fuel gas would be related with the reactivity of the oxygen carrier with respect to these LHCs, and their effect on CO₂ transport and storage steps if they are present in the flue gas. It is known than some hydrocarbons may increase the compression and transmission energy consumption by changes on density and compressibility properties with respect to pure CO₂.²⁵ However, the tolerance limits of hydrocarbons in the CO₂ stream is not as restrictive as other impurities, and values <5 vol% would be admissible.²⁶ Although non-converted hydrocarbons could be easily addressed in different ways, e.g. adding some oxygen at the fuel reactor outlet to oxidize minor amounts of unconverted fuel¹⁶, this would not be necessary since experimental tests in the 500 Wth CLC plant have demonstrated that full conversion of LHC can be easily reached. Moreover, no detrimental effects on the oxygen carrier due to agglomeration or carbon formation were detected. According to these results, it can be concluded that no operational problems are expected in an industrial CLC plant by the presence of light hydrocarbons in the fuel gas.

5. Conclusions

The effect on the combustion efficiency of the presence of light hydrocarbons, ethane and propane, in the feeding gas of a CLC plant has been analyzed using a Ni-based oxygen carrier prepared by incipient wet impregnation. Moreover, oxygen carrier reactivity, agglomeration and carbon formation have been studied in different facilities.

Reactivity tests in TGA and batch fluidized bed were carried out using several gas mixing of methane, ethane and propane. In both facilities, two reaction steps were detected related to the presence of free NiO and NiAl₂O₄ in the oxygen carrier. First, fast reduction of free NiO was observed, and later the slower reduction of NiAl₂O₄ was observed. The experiments carried out in a batch fluidized bed reactor using pure hydrocarbons and mixtures of them, showed that light hydrocarbons can be fully converted in a CLC process.

Carbon deposition on particles in TGA and batch fluidized bed experiments were evidenced during the slow reduction of NiAl₂O₄. This fact made impossible the determination of the kinetic parameters of hydrocarbon combustion with Ni-based oxygen carriers in TGA. In the batch FB, carbon formation decreased with temperature from 1073 to 1173 K. However, at 1223 K, carbon formation raised because of hydrocarbons decomposition. Carbon formation rate was higher when ethane or propane was present in the feeding gas.

Finally, the combustion of hydrocarbons was tested in a 500 W_{th} CLC pilot plant for 40 hours of continuous operation. The influence on the hydrocarbon combustion efficiency of the temperature, the solid circulation flow rate, and gas composition was analyzed. Neither carbon formation nor unburnt hydrocarbons were detected in any of the experiments. Agglomeration of the oxygen carrier was never observed. To reach high energy efficiencies (near to the maximum allowed by the thermodynamic equilibrium with Ni-based materials) an oxygen carrier-to-fuel ratio higher than 3 and a temperature of 1153 K were necessary. According to the results found in this work, it can be concluded that no special measures should be adopted due to the presence of light hydrocarbons in the fuel gas of a CLC plant.

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Nomenclature

b = stoichiometric coefficient of the fuel gas mixing

F = total molar flow, mol s^{-1}

m = instantaneous mass of the oxygen carrier, kg

m_{ox} = mass of the oxygen carrier as fully oxidized, kg

m_{red} = mass of the oxygen carrier as fully reduced, kg

M_{O} = atomic mass of oxygen, kg mol^{-1}

N_{C} = molar amount of carbon formed, mol

$N_{\text{O,OC}}$ = molar amount of active oxygen in the OC, mol

r_{C} = rate of carbon formation, mol s^{-1}

r_{C}^* = normalized rate of carbon formation

r_{O} = rate of transference of oxygen from the oxygen carrier to the fuel gas, mol s^{-1}

R_{OC} = oxygen transport capacity of the oxygen carrier

t = time, s

T = temperature, K

x_i = molar fraction of the gas i

X_{fc} = maximum solids conversion which was obtained full combustion of fuel gas in FB experiments

X_{OC} = reduction conversion of the oxygen carrier

Greek symbols

$\varepsilon_{\square}$ = particle porosity

ϕ = oxygen carrier to fuel ratio

η_c = combustion efficiency

ρ = particle density, kg m^{-3}

Subscripts

0 = initial time

c = combustion

C = carbon

f = final time

fc = full combustion

fuel = fuel gas

i = inert period

in = inlet flow

MeO = metal oxide

o = oxidation period

ox = fully oxidized state

out = outlet flow

r = reduction period

red = fully reduced state

O = oxygen

OC = oxygen carrier

Acronyms

AR = air reactor

CLC = chemical looping combustion

FB = fluidized bed

FR = fuel reactor

HC = hidrocarbons

LHC = light hidrocarbons

OC = oxygen carrier

References

- (1) *Climate Change 2007: Mitigation of Climate Change*; Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change; Cambridge University Press: Cambridge, United Kingdom and New York, NY, USA., 2008; available at <http://www.ipcc.ch>
- (2) *IPCC Special Report on Carbon Dioxide Capture and Storage*; Prepared by Working Group III of the Intergovernmental Panel on Climate Change; Cambridge University Press: Cambridge, United Kingdom and New York, NY, USA, 2005; available at <http://www.ipcc.ch>.
- (3) Kerr, H.R. *Capture and separation technologies gaps and priority research needs*; in: Thomas, D., Benson, S. (Eds.), *Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO₂ Capture Project*; Elsevier Ltd.: Oxford, UK, 2005; vol. 1, chapter 38.
- (4) Ishida, M.; Zheng, D.; Akehata, T. Evaluation of a Chemical-Looping Combustion Power Generation System by Graphic Exergy Analysis. *Energy* **1987**, 12(2), 147.
- (5) Lyngfelt A.; Leckner B.; Mattisson T. A Fluidized-Bed Combustor Process with Inherent CO₂ Separation; Application of Chemical-Looping Combustion. *Chem. Eng. Sci.* **2001**, 56, 3101.
- (6) Abad, A.; Adánez, J.; García-Labiano, F.; de Diego, L.F.; Gayán, P.; Celaya, J. Mapping of the Range of Operational Conditions for Cu-, Fe-, and Ni-based Oxygen Carriers in Chemical-Looping Combustion. *Chem. Eng. Sci.* **2007**, 62, 533.
- (7) Anheden, M.; Svedberg, G. Exergy Analysis of Chemical-Looping Combustion Systems. *Energy Convers. Mgmt.* **1998**, 39(16-18), 1967.

- (8) Abad, A.; García-Labiano, F.; de Diego, L.F.; Gayán, P.; Adánez, J. *Energy Fuels* **2007**, *21*, 1843-1853.
- (9) Mattisson, T.; García-Labiano, F.; Kronberger, B.; Lyngfelt, A.; Adánez, J.; Hofbauer, H. Chemical-Looping Combustión Using Syngas as Fuel. *Int. J. Greenhouse Gas Control* **2007**, *1*, 158.
- (10) Morin, J.-X.; Béal, C. *Chemical Looping Combustion of Refinery Fuel Gas with CO₂ Capture*; in: Thomas, D., Benson, S. (Eds.), Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO₂ Capture Project; Elsevier Ltd.: Oxford, UK, 2005; vol. 1, chapter 37.
- (11) Cao, Y.; Pan, W.P. Investigation of Chemical Looping Combustion by Solid Fuels. 1. Process Análisis. *Energy Fuels* **2006**, *20*, 1836.
- (12) Scott, S.A.; Dennis, J.S.; Hayhurst, A.N.; Brown, T. In Situ Gasification of a Solid Fuel and CO₂ Separation using Chemical Looping. *AIChE J.* **2006**, *52*(9), 3325.
- (13) Leion, H.; Mattisson, T.; Lyngfelt, A. Solid Fuels in Chemical-Looping Combustion. *Int. J. Greenhouse Gas Control* **2008**, *2*, 180.
- (14) Olafsen A.; Daniel C.; Schuurman Y.; Råberg L. B.; Olsbye U.; Mirodatos C. Light Alkanes CO₂ Reforming to Synthesis Gas over Ni Based Catalysts. *Catalysis Today* **2006**, *115*, 179.
- (15) Middleton, P.; Hurst, P.; Walker, G. *GRACE: Pre-Combustion De-Carbonisation Hydrogen Membrane Study*; in: Thomas, D., Benson, S. (Eds.), Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO₂ Capture Project; Elsevier Ltd.: Oxford, UK, 2005; vol. 1, chapter 23.
- (16) García-Labiano, F.; de Diego, L. F.; Gayán, P.; Adánez, J.; Abad, A.; Dueso, C. Effect of Fuel Gas Composition in Chemical-Looping Combustion with Ni-based Oxygen Carriers. Part 1. Fate of Sulfur. *Ind. Eng. Chem. Res.* (Preceeding paper).

- (17) Eide, L. I.; Anheden, M.; Lyngfelt, A.; Abanades, C.; Younes, M.; Clodic, D.; Bill, A. A.; Feron, P.H.M.; Rojey, A.; Giroudière, F. Novel Capture Processes. *Oil&Gas Science and Technology* **2005**, 60(3), 497.
- (18) Rostrup-Nielsen, J. R. Production of Synthesis Gas. *Catalysis Today* **1993**, 18, 305.
- (19) Trimm, D. L. A Catalysts for the Control of Coking During Steam Reforming. *Catalysis Today* **1999**, 49, 3.
- (20) Löffler, D. G.; Taylor, K.; Mason, D. A Light Hydrocarbon Fuel Processor Producing High-Purity Hydrogen. *Journal of Power Sources* **2003**, 117, 84.
- (21) HSC Chemistry 6.1[®] 6.1. 2008. Chemical Reaction and Equilibrium Software with Thermochemical Database and Simulation Module. Outotec Research Oy.
- (22) Gayán, P.; de Diego, L. F.; García-Labiano, F.; Adánez, J.; Abad, A.; Dueso, C. Effect of support on reactivity and selectivity of Ni-based oxygen carriers for chemical-looping combustion. *Fuel* **2008**, 87, 2641.
- (23) Adánez J.; de Diego, L. F.; García-Labiano, F.; Gayán, P.; Abad, A.; Palacios, J.M. Selection of Oxygen Carriers for Chemical-Looping Combustion. *Energy&Fuels* **2004**, 18, 371.
- (24) Adánez J.; Dueso, C.; de Diego, L. F.; García-Labiano, F.; Gayán, P.; Abad, A. Methane Combustion in a 500 W_{th} Chemical-Looping Combustion System Using an Impregnated Ni-based Oxygen Carrier. *Energy&Fuels*, submitted for publication.
- (25) Sass, B.; Monzyk, B.; Ricci, S.; Gupta, A.; Hindin, B.; Gupta, N. *Impact of Sox and NOx in flue gas on CO2 separation, compression, and pipeline transmission*; in: Thomas, D., Benson, S. (Eds.), Carbon Dioxide Capture for Storage in Deep Geologic Formations—Results from the CO₂ Capture Project; Elsevier Ltd.: Oxford, UK, 2005; vol. 2, chapter 17.

(26) Fout, T. Oxy-combustion: Research, development and system analysis. 3rd Meeting of the Oxy-fuel Combustion Network. March 2008. Yokohama, Japan.

Table 1. Typical Grangemouth Complex Fuel gas composition.¹⁵

Component	mol %
Methane	67.8
Ethane	9.5
Ethene	0.02
Propane	7.4
Propene	0.01
iso-Butane	1.1
n-Butane	3.1
iso-Butene	0.05
Methyl-1-Butenes	0.1
iso-Pentane	0.16
n-Pentane	0.04
Hydrogen	7.9
Oxygen	0.03
Nitrogen	0.75
Carbon Monoxide	0
Carbon Dioxide	2.0
Hydrogen Sulphide	0.005

Table 2. High temperature reactions for light hydrocarbons in presence of NiO-Ni.

Main reactions		
combustion	$C_nH_{2n+2} + (3n+1) NiO \rightarrow (3n+1) Ni + n CO_2 + (n+1) H_2O$	(1)
partial oxidation	$C_nH_{2n+2} + n NiO \rightarrow n Ni + n CO + (n+1) H_2$	(2)
Reactions of the gas main components		
steam reforming	$C_nH_{2n+2} + n H_2O \rightarrow n CO + (2n+1) H_2$	(3)
dry reforming	$C_nH_{2n+2} + n CO_2 \rightarrow 2n CO + (n+1) H_2$	(4)
water-gas shift	$CO + H_2O \leftrightarrow CO_2 + H_2$	(5)
methanation	$CO + 3 H_2 \leftrightarrow CH_4 + H_2O$	(6)
dehydrogenation	$C_nH_{2n+2} \leftrightarrow C_nH_{2n} + H_2$	(7)
cracking	$C_nH_{2n+2} \leftrightarrow C_{n-1}H_{2(n-1)} + CH_4$	(8)
coke formation	$C_nH_{2n+2} \leftrightarrow n C + (n+1) H_2$	(9)
coke formation	$CO + H_2 \leftrightarrow C + H_2O$	(10)
Boudouard	$2 CO \leftrightarrow C + CO_2$	(11)
Reaction of gas products with NiO		
	$CH_4 + 4 NiO \rightarrow 4 Ni + CO_2 + 2 H_2O$	(12)
	$C_nH_{2n} + 3n NiO \rightarrow 3n Ni + n CO_2 + n H_2O$	(13)
	$CO + NiO \leftrightarrow Ni + CO_2$	(14)
	$H_2 + NiO \leftrightarrow Ni + H_2O$	(15)
	$C + NiO \leftrightarrow CO + Ni$	(16)

Table 3. Maximum combustion efficiencies at equilibrium conditions for hydrocarbons in presence of Nickel at 1073 and 1223 K.

Hydrocarbon	Combustion efficiency (η_c)	
	1073 K	1223 K
CH ₄	99.60	99.43
C ₂ H ₆	99.62	99.44
C ₃ H ₈	99.63	99.44
C ₄ H ₁₀	99.63	99.45
C ₅ H ₁₂	99.64	99.45

Table 4. Main Characteristics of the Ni19- α Al:HI oxygen carrier.

NiO content (wt%)	19
Particle size (mm)	0.1-0.3
Particle density (kg/m ³)	2500
Mechanical strength (N)	4.3
Porosity (%)	41.7
Specific surface area BET (m ² /g)	6.8
Oxygen transport capacity, R _{OC}	0.04

Table 5. Hydrocarbon concentrations in the tests carried out in the batch fluidized bed facility.

Composition	CH ₄	C ₂ H ₆	C ₃ H ₈
	vol %	vol %	vol%
A	25		
B		14.3	
C			10
D	15	5.7	
E	15		4

Table 6. Composition of the feeding gas in the experiments carried out in the CLC 500 W_{th} pilot plant.

Composition	Equilibrium data at 1153 K					
	CH ₄	C ₂ H ₆	C ₃ H ₈	H ₂ O	CO	H ₂
	vol%	vol%	vol%	vol%	vol%	vol%
A	30				0.151	0.25
B	20	5.7		15	0.154	0.29
C	20		4.0	15	0.160	0.29

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Figure 8. Normalized rate of carbon formation calculated as eq 24, as a function of reduction temperature in the batch FB, using fuel gas compositions showed in Table 5: ($\square$) CH_4 , ($\blacktriangle$) C_2H_6 , ($\bullet$) C_3H_8 , ($\triangle$) $CH_4+C_2H_6$, ($\circ$) $CH_4+C_3H_8$.

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Figure 10. Concentrations of CO (empty symbols) and H₂ (filled symbols) measured at the outlet of the FR in the 500 W_{th} CLC prototype. T_{FR} = 1153 K. Fuel gas composition given in Table 6: (□, ■) CH₄, (△, ▲) CH₄+C₂H₆, (○, ●) CH₄+C₃H₈.

Figure 11. Effect of the oxygen carrier-to-fuel ratio and temperature on the combustion efficiency for the use of hydrocarbons in the 500 W_{th} CLC prototype. Fuel gas composition given in Table 6: (□, ■) CH₄, (△, ▲) CH₄+C₂H₆, (○, ●) CH₄+C₃H₈.

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