



GHGT-9

Effect of Gas Impurities on the Behavior of Ni-based Oxygen Carriers on Chemical-Looping Combustion

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Abstract

Chemical Looping Combustion (CLC) is a two-step gas combustion process that produces a pure CO₂ stream, ready for compression and sequestration. A solid oxygen carrier (OC) circulates between two reactors and transports oxygen from the combustion air to the fuel. Since the fuel is not mixed with air, the subsequent CO₂ separation process is not necessary. A key aspect in CLC process using refinery and industrial gases is to know the behavior of the oxygen carriers under real gas mixtures that contain impurities as for example, sulfur and light hydrocarbons. The objective of this work was to analyze the effect of these impurities on the behavior of a Nickel-based oxygen carrier prepared by dry impregnation on α -Al₂O₃. The tests were carried out in a continuous 500 W_{th} CLC plant. Based on these results, important conclusions with respect to design of CLC plants are derived, which can help to the development of this technology in the near future.

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Keywords: Chemical-Looping Combustion; nickel; oxygen carrier; sulfur; hydrocarbons; refinery gas

1. Introduction

Chemical-Looping Combustion (CLC) technology has been suggested among the best alternatives to reduce the economic cost of CO₂ capture using fuel gas [1]. In this process, CO₂ is inherently separated from the other flue gas components (N₂ and unused O₂) and thus no energy is expended for the separation. In CLC, oxygen is transferred from the air to the fuel by means of a solid oxygen carrier (OC) in the form of a metallic oxide, thus avoiding the direct contact between the combustion air and the fuel. The solid circulates between two interconnected reactors, the fuel (FR) and the air reactor (AR). In the FR, the metal oxide reacts with the gaseous fuel to produce CO₂ and H₂O. Pure CO₂, ready to compression and sequestration, will be readily recovered by condensing the steam. The OC is oxidized again in the AR, and it is ready to start a new cycle. The heat involved in the global process is the same as for normal fuel gas combustion. As gaseous fuels in the CLC process can be used natural gas, synthesis gas from

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coal gasification, refinery gas or other industrial gases. These gaseous fuels can contain variable amounts of light hydrocarbons (LHC), i.e. C2-C5, and sulfur compounds, such as H₂S and COS. In addition to methane, the LHC content may be up to 10 vol% in crude natural gas and up to 30 vol% in refinery gas. The natural gas usually contains very small amounts of H₂S (\approx 20 vppm) but up to 800 vppm H₂S can be found in refinery fuel gas, and this value can be increased up to 8000 vppm for raw syngas. The design of an industrial CLC plant can be affected by the presence of LHC and sulfur compounds in different ways. By the one hand, 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. By the other hand, the reaction of sulfur compounds with the OC may form several sulfur compounds that probably are poisonous to OC. This process is especially important when Ni-based oxygen carriers are used. Moreover, the low melting point of some sulfides could produce agglomeration and affect to the solids circulation pattern between the FB reactors [2,3].

The aim of this work was to test the behavior of a Nickel-based oxygen carrier when the fuel, CH₄, contains variable amounts of LHC and H₂S under continuous operation in a 500 W_{th} CLC pilot plant. The influence of temperature, solid circulation rate, LHC and H₂S concentrations on the gas products distribution, combustion efficiency, carbon formation, oxygen carrier deactivation, and material agglomeration was investigated.

2. Experimental

2.1. Oxygen carrier

The oxygen carrier (OC) used in this work –denoted here as Ni19- α Al:HI– was selected in previous works as a promising material to be used in a CLC system [4,5]. The material was prepared by hot incipient wet impregnation (HIWI) of Ni(NO₃)₂ on α -Al₂O₃. A volume of a saturated solution (6 M) of Ni(NO₃)₂·6H₂O (>99.5% Panreac) at 333-353 K, which corresponds to the total pore volume of the support particles, was added to the hot α -Al₂O₃ (353 K) particles of 100-300 μ m. The desired NiO fraction —19 wt%— was achieved by applying two successive impregnations followed by calcinations at 823 K, in air atmosphere for 30 minutes. Finally, the material was calcined for 2 hours at 1223 K. A detailed description of the preparation method can be found elsewhere [5].

2.2. CLC prototype (500 W_{th})

The schematic diagram of the 500 W_{th} Chemical-Looping Combustion prototype used for the experimental tests is shown in Figure 1. The FR (1) and AR (3) consisted in bubbling fluidized beds (0.05 m i.d. and 0.1 m height). Following the AR was a riser (4) of 0.02 m i.d. and 1 m height. In the FR (1) the fuel reacts with the oxygen carrier to give CO₂ and H₂O. The solids were transported from FR to AR through a nitrogen-flowing loop seal (2). The complete oxidation of the oxygen carrier took place in the dense bed part of the AR. The OC was entrained in the riser (4), recovered by a high-efficiency cyclone (5), and sent to a solids reservoir (7), setting the solid ready to start a new cycle. The loop seal (2) and the solids reservoir (7) prevent the gas mixing between AR and FR flows. The solids valve (8) controlled the flow rate of solid entering the FR. A diverting solids valve (6) 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 total solids inventory in the system was \approx 1.3 kg of solid material, which 0.3 kg and 0.5 kg was in the FR and AR, respectively. The inlet flows were 170 L_N/h in the FR, 720 L_N/h air in the bottom AR, 150 L_N/h air in the riser, and 37.5 L_N/h N₂ in the particle loop-seal. The prototype was provided with specific mass flow controllers, thermocouples and pressure drop transducers. Unburnt hydrocarbons, CH₄, CO, H₂, CO₂, H₂S and SO₂ concentrations were analyzed from the FR. O₂, CO₂, CO and SO₂ concentrations were measured at the gas from the AR. A detailed description of the analysis system was shown elsewhere [6].

The behavior of the CLC was evaluated calculating the combustion efficiency, η_c , defined as

$$\eta_c = \frac{(2x_{\text{CO}_2} + x_{\text{CO}} + x_{\text{H}_2\text{O}})_{\text{out}} F_{\text{out}} - (x_{\text{H}_2\text{O}})_{\text{in}} F_{\text{in}}}{(4x_{\text{CH}_4} + 7x_{\text{C}_2\text{H}_6} + 10x_{\text{C}_3\text{H}_8})_{\text{in}} F_{\text{in}}} \quad (1)$$

where F_{in} and F_{out} are the molar flows at the inlet and outlet of the FR, respectively, and x_i is the molar fraction of gas i . The oxygen carrier-to fuel ratio (ϕ) was defined by eq 2, where F_{MeO} is the molar flow rate of the metal oxide and F_{Fuel} is the inlet molar flow 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 CO_2 and H_2O .

$$\phi = \frac{F_{MeO}}{b F_{fuel}} \quad \text{where } b = \frac{4x_{CH_4} + 7x_{C_2H_6} + 10x_{C_3H_8}}{x_{CH_4} + x_{C_2H_6} + x_{C_3H_8}} \quad (2)$$

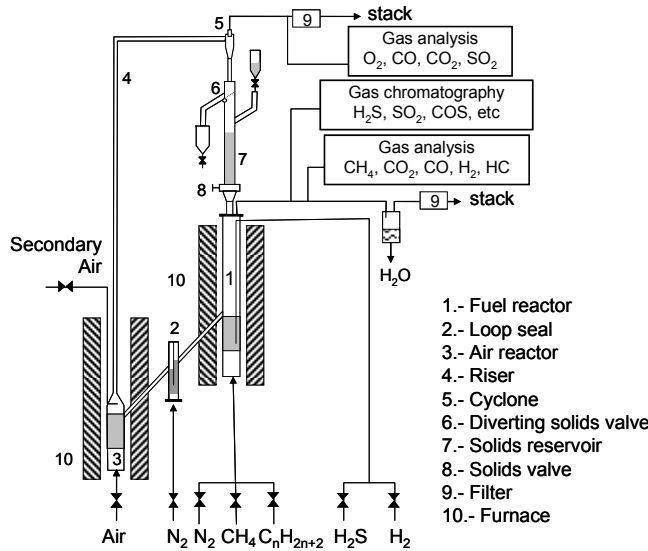


Figure 1. Schematic diagram of the 500 W_{th} CLC prototype.

3. Results

3.1. Methane combustion in the 500 W_{th}

Combustion tests using methane as fuel gas –30 vol% diluted in N_2 – were conducted in the facility with Ni19- α Al:HI under different operation conditions. Two experimental test series, at 1073 and 1153 K, were carried out varying the solid circulation flow rate between 7 and 14 kg/h, corresponding to ϕ values of 1.9 and 3.8 respectively. In all cases, the temperature in the AR was kept constant at 1223 K. Figure 2 shows an example of the temperature profiles and gas product distribution obtained in the FR and the AR when ϕ was fixed at 3.8 and the FR temperature was 1153 K. Stable combustion was reached in less than 10 minutes. After the start-up period, the steady-state was maintained at least for two hours in each test, which gave us a total of 20 hours of operation with the same OC.

Figure 3a shows the effect of the ϕ value on the combustion efficiency at 1073 and 1153 K, and Figure 3b shows the gas composition obtained at the outlet of the FR at 1153 K as a function of ϕ value. Methane was fully converted for all tests, but CO and H_2 concentrations increased as solids circulation rate decreased. Using Ni-based oxygen carriers, thermodynamic limitations prevent the full conversion of methane into CO_2 and H_2O , because the existence of small amounts of CO and H_2 at equilibrium condition. Combustion efficiencies and CO and H_2 concentrations close to equilibrium values were obtained working at high oxygen carrier to fuel ratios ($\phi > 3$), both a 1073 and 1153 K. A maximum value for efficiency of 99 % was obtained for ϕ about 3.8. Decreasing the ϕ value the combustion efficiency decreases because of the lower availability of oxygen in the FR. Higher combustion efficiencies were obtained at higher temperatures as a consequence of the higher oxygen carrier reactivity.

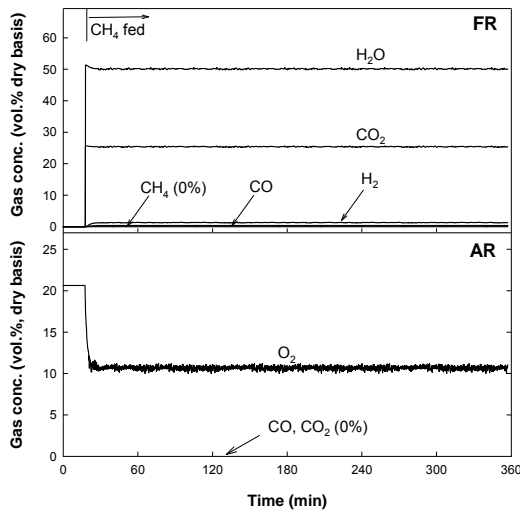


Figure 2. Gas product distribution at the outlet of AR and FR during a typical experiment in the 500 W_{th} CLC prototype. Experiment was maintained for 6 h. 30 vol% CH₄; T_{FR}= 1153 K; T_{AR}= 1223 K; ϕ = 3.8.

A suitable OC should not promote formation of solid carbon in the FR. Carbon formation reduces the CO₂ capture efficiency of the system, and could produce deactivation of the OC and/or give agglomeration problems into the system. Carbon formation was evaluated in the CLC prototype by measuring CO and CO₂ concentration in the outlet from the AR. As there was not gas leakage from the FR to AR, any carbon containing gas present in the AR outlet should come from solid carbon following the oxygen carrier particles. CO or CO₂ was not detected in the AR outlet stream in any test. 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 turned 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, no CO or CO₂ was detected in the flue gases in any case. From these results, it was concluded that carbon formation did not happen at relevant extension in the system, i.e. deposited on the oxygen carrier particles nor anywhere in the FR.

3.2. Effect of the presence of LHC in the fuel gas

Several experiments were carried out to investigate the effect of the presence of LHC, ethane and propane, in the feeding gas. Two gas compositions were tested where part of inlet methane (10%) was substituted by ethane or propane. The gas composition was 20 vol% CH₄ and 5.7 vol% C₂H₆ or 4 vol% C₃H₈ in each case. The gas mixture was chosen in order to have the same oxygen consumption in all cases. It must be considered that ethane and propane need more oxygen for combustion than CH₄. During these experiments, 15 vol% H₂O was introduced to avoid carbon formation in the distributor plate of the FR. Analogous to the methane combustion procedure, experiments were carried out at FR temperatures of 1073 and 1153 K, and the oxygen carrier to fuel ratio, ϕ , was varied between 1.9 and 3.8. Similar to results showed for methane combustion, the steady-state for each was easily maintained at least for two hours in each test, which gave us a total of 40 hours of operation with the same OC.

Full conversion of CH₄ and LHC was obtained in the FR, but some CO and H₂ were also obtained at the outlet. Figure 3b shows that the amount of CO and H₂ increased as the oxygen carrier-to-fuel ratio decreased, but no unburnt hydrocarbons were observed at any circumstance. It is clear that higher CO and H₂ concentrations were observed when ethane or propane was introduced in the fuel gas mixture. 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 1. Figure 3a 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 CH₄ 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 H₂O and CO₂ prevent 100% combustion efficiencies using Ni-based oxygen carriers. The conversion efficiency at equilibrium conditions is roughly constant with the H/C molar ratio, being $\eta_c \approx 99.6\%$ at 1073 K and $\eta_c \approx 99.5\%$ at 1153 K. Combustion efficiencies close to equilibrium values were obtained working at high oxygen carrier to fuel ratios ($\phi > 3$) at the two temperatures tested. Similar to methane combustion, the FR temperature is an important operating parameter when the oxygen carrier to fuel ratio decreases. At 1073 K the combustion efficiency, η_c , showed a sharp decrease for all the gas compositions at low values of ϕ , whereas at 1153 K the decrease in η_c was less important.

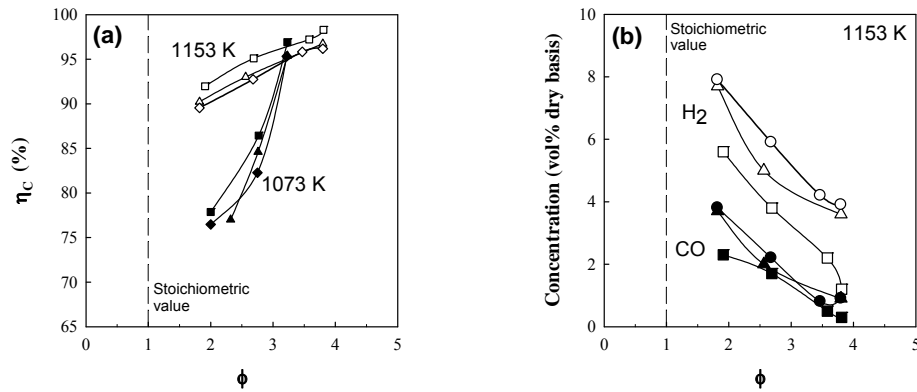


Figure 3. Effect of the oxygen carrier-to-fuel ratio and temperature on (a) the combustion efficiency, and (b) H₂ and CO concentrations measured at the outlet of the FR in the 500 W_{th} CLC prototype. Fuel gas composition: (□, ■) 30 vol% CH₄, (△, ▲) 20 vol% CH₄+ 5.7 vol% C₂H₆, (○, ●) 20 vol% CH₄+ 4 vol% C₃H₈.

Using Ni-based oxygen carriers, carbon deposition on particles could happen in the FR because of the catalytic activity of Ni formed after reduction of the OC. LHC have higher tendency to carbon formation with respect to pure CH₄, mainly due to coke formation from olefins coming from intermediate reactions with LHC. However, no evidences for carbon formation were observed in the CLC system using ethane or propane in the fuel gas mixture. Moreover, neither OC deactivation nor agglomeration was detected during operation in the continuous CLC plant.

3.3. Effect of the presence of sulfur in the fuel gas flow

The behavior of the Nickel-based oxygen carrier when the gas fuel, CH₄, contains variable amounts of H₂S under continuous operation in a 500 W_{th} CLC pilot plant has been evaluated. Thermodynamic studies carried out by Mattisson et al. [2], Jerndal et al. [3] and García-Labiano et al. [7] showed that, at the conditions which may be encountered in the FR, H₂S could react with the oxygen carrier (NiO or Ni) to form sulfides, being Ni₃S₂ the thermodynamically most stable compound. The experiments herein carried out were designed based on thermodynamic calculations, considering conditions which Ni₃S₂ could be formed or not from thermodynamic calculations [3]. Table 1 shows the operating conditions selected to avoid (tests 1b, 2, 3 and 4) or to favor (tests 5, 6 and 7) the formation of Ni₃S₂ during continuous operation in the prototype, depending on the temperature or the H₂S concentration. Every test corresponds to one day of operation, and about five hours of continuous operation with H₂S feeding. During tests 6b and 7b, the H₂S concentration was increased after 4 hours of steady state operating conditions to analyze the performance of the OC with a higher H₂S concentration. The reference conditions without H₂S feeding, see Figure 2, was referred as test 0, and in test 1 the H₂S was fed after two hours of operation at reference conditions.

Figure 4a shows the dry basis concentrations obtained at the outlet of the FR and AR for test 1. The first 2 hours (test 1a) corresponds to the reference operating conditions used in test 0, and after that, 500 vppm of H₂S was fed into the system (test 1b). After H₂S feeding, CO₂ decreased and some unconverted CH₄ appeared ≈ 10 minutes later, while the CO and H₂ concentrations increased slowly up to 1.5 and 3 vol%, respectively. These effects were

attributed to OC deactivation by the presence of sulfides, which prevents the catalytic action of the metallic Ni on the partial oxidation and CH₄ reforming. H₂S and SO₂ were found at very low concentrations (< 10 vppm) in the FR outlet stream. Moreover, SO₂ was detected in the AR and their concentration increased with time, which indicated the transfer of sulfur as nickel sulfide from the FR to the AR through the oxygen carrier. These results indicated that a part of the sulfur fed into the FR was released as SO₂ in the AR and the other was being accumulating in the OC as sulfides or sulfates.

Table 1. Tests carried out in the 500 W_{th} CLC prototype using CH₄ with H₂S as fuel. The solids circulation rate was fixed at 14 kg/h, corresponding to $\phi = 3.8$, CH₄ concentration was 30 vol%, and AR temperature was 1223 K in all cases.

	Test 1b	Test 2	Test 3	Test 4	Test 5	Test 6a	Test 6b	Test 7a	Test 7b
Operating conditions									
T _{FR} (K)	1143	1143	1143	1143	1103	1143	1143	1103	1103
H ₂ S fed (vppm)	500	500	300	100	300	800	1000	300	800
Thermodynamic calculation									
Ni ₃ S ₂ formation	No	No	No	No	Yes	Yes	Yes	Yes	Yes
Sulfur distribution (%)									
OUT gas FR	-	5.3	9.1	15.4	4.9	2.9	3.0	11.3	12.2
OUT gas AR	-	42.8	47.3	23.4	0	69.3	74.4	16.4	12.4

As an example of the experimental data obtained during longer tests with H₂S addition, Figure 4b shows the gas product distribution profiles obtained in FR and AR during test 3. The solids used in test 2 were heated in air and started solids circulation. The CH₄ feeding started after reaching the desired temperatures in the reactors, but no H₂S was added. At the beginning, some CH₄ was detected at the outlet of the FR due to the presence of sulfides or sulfates in the OC formed in the previous test. However, the CH₄ concentration was decreasing and the CO₂ increasing until reach steady state conditions similar to the reference test. Some SO₂ was detected from the AR as a consequence of the solid sulfur compounds decomposition. These facts indicated that the OC was able to recover their reactivity after certain time without H₂S feeding. After H₂S feeding, the deactivation of the OC started again with similar consequences to the above explained in Figure 4a.

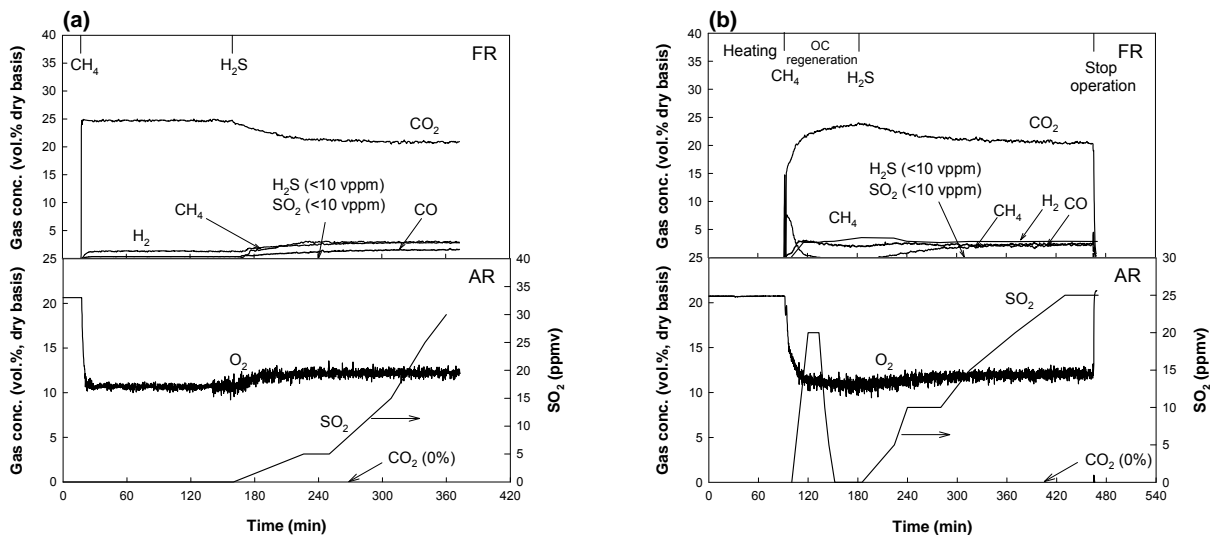


Figure 4. Gas product distribution at the outlet of AR and FR during test 1 (a) and test 3 (b) in the 500 W_{th} CLC prototype.

A similar behavior, although quantitatively different, was observed in all the tests carried out with H₂S feeding. Figure 5 shows the combustion efficiency obtained for all tests after 5 h of operation with H₂S feeding. The loss on combustion efficiency is more important as highest is the H₂S concentration fed and lower is the temperature. In any case, the formation of sulfides in the FR was evident from the experimental data even in those operating conditions selected to avoid sulfides formation. To explain this phenomenon, new thermodynamic calculations were carried out to simulate the gas atmosphere in the lower zone of the FR. At these conditions it is observed that for CO + H₂ concentrations above 0.4%, the formation of Ni₃S₂ was favored. This situation would be valid in the whole reactor if the fuel was not fully converted, being the formation of Ni₃S₂ possible in the CLC system at all the operating conditions showed in Table 1. The main difficulty of sulfides formation takes root in their low melting point that could lead to the OC agglomeration, in addition to the lower reactivity. However, during the whole experimental time –65 h, of with 35 hours were with H₂S addition– the solid circulation rate was almost constant and never were detected agglomeration in the system.

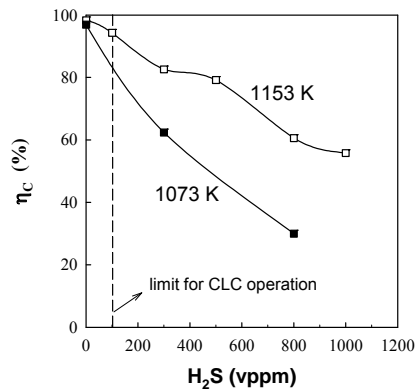


Figure 5. Effect of H₂S concentration in the fuel gas fed in the 500 W_{th} CLC prototype on the combustion efficiency. For experimental conditions, see Table 1.

As commented before, SO₂ was detected at the AR outlet stream and its concentration depended on the H₂S concentration fed into the FR. The sulfides formed in the FR were carried to AR where reacted in the oxidant atmosphere of the AR to give SO₂, which depends on the temperature and O₂ concentration. However, the temperature in the AR was not high enough to fully decompose the sulfur in the oxygen carrier, and sulfur was partially recirculated towards the FR. Therefore, sulfur fed with the fuel to the FR is distributed between the gaseous sulfur species obtained at the outlet gases from FR and AR, and the solid sulfur species formed on the OC, see Table 1. Sulfur mass balances indicated the gradual accumulation of sulfur in the OC particles.

4. Implications of the presence of LHC or sulfur compounds in an industrial CLC plant

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. Although the tolerance limits of hydrocarbons in the CO₂ stream is not as restrictive as other impurities, and values <5 vol% would be admissible, experimental tests in the 500 W_{th} 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.

Regarding sulfur content of fuel gas, the design of industrial CLC plants must consider both operational and environmental aspects. Firstly, no operational problems derived from agglomeration are expected, and if the temperature in the AR and riser is high enough, the sulfur fed into the FR can be released as SO₂ and the OC will be returned to the FR fully reactivated. Regarding the environmental point of view, the SO₂ emissions released from the AR must fulfill the legislation about emissions. Considering that all the sulfur fed is released as SO₂ in the AR

the maximum sulfur content in the fuel gases would be ≈ 120 vppm H_2S . Moreover, a part of the sulfur can be also released in the FR gas stream. The sulfur concentration in the FR downstream will depend on the purity requirements of the liquefied CO_2 for transport and storage, and very different values can be found ranging from <70 ppmv for a modest CO_2 quality to <2 ppmv for a very high CO_2 quality. From the experiments herein carried out, typical concentrations <10 vppm of H_2S and SO_2 were obtained. According to the above considerations and the experimental data obtained in the tests carried out in the 500 W_{th} CLC prototype, several options can be adopted in an industrial CLC plant regarding sulfur in fuel. The more realistic option would be to avoid the sulfur components entering the CLC system. The limit would be ≈ 100 ppm of H_2S considering the low deactivation effect on the OC observed during the tests herein carried out—see Fig 5—and that will fulfill legislation about emissions if all SO_2 is released as SO_2 in the AR. Otherwise, new downstream units to overcome both technical and legal restrictions must be included, both from the AR and the FR streams. In current refinery practice the gaseous fuel sulfur concentration is designed below 20 vppm. Therefore, these gases could be an adequate fuel to be used in a CLC plant.

5. Conclusions

Several tests have been carried out in a CLC prototype (500 W_{th}) under continuous operation with a Ni-based oxygen carrier to analyze the effect of light hydrocarbons and sulfur content of fuel in relation to CH_4 combustion efficiency, oxygen carrier reactivity and agglomeration process. Totally, the prototype was successfully operated at combustion conditions using two batches of oxygen carrier particles: first, 60 h with CH_4 and LHC, and second, 65 h during test for the evaluation of the effect of H_2S addition. No agglomeration problems were detected in any case.

Some lower efficiencies were observed when LHC (ethane and propane) were present in the fuel gas mixture with respect to CH_4 , although neither carbon formation nor unburnt hydrocarbons were detected in any of the experiments. 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 LHC in the fuel gas of a CLC plant

The effect of H_2S presence on the fuel gas was analyzed under different H_2S concentrations in the gas fuel (up to 1000 vppm) and FR temperature. In all cases, the formation of sulfides was inferred with a bypass of sulfur to the air reactor, which appeared as SO_2 , even in operating conditions where the formation of sulfides was not thermodynamically favored. The presence of sulfur in the FR decreased the activity of the oxygen carrier, and therefore, the fuel conversion. However, the oxygen carrier recovers its initial activity when H_2S feeding was stopped. Considering both operational and environmental aspects, it can be concluded that fuels with sulfur contents below 100 vppm H_2S could be adequate to be used in an industrial CLC plant

Acknowledgement

This research was conducted with financial support from the European Commission, under the 6th Framework Program, Contract no. 019800-CLC GAS POWER, by the CCP2 (CO₂ Capture Project), a partnership of BP, Chevron, Conoco-Phillips, Eni Technology, Norsk Hydro, Shell, Suncor, and Petrobras, and by Spanish Ministry of Science and Innovation (MICINN, Project CTQ2007-64400). C. Dueso thanks MICINN for a F.P.I. fellowship.

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