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Chemical-looping combustion in a 10 kW prototype using a CuO/Al₂O₃ oxygen carrier: Effect of operating conditions on methane combustion.

Juan Adánez*, Pilar Gayán, Javier Celaya, Luis F. de Diego, Francisco García-Labiano,
Alberto Abad.

Department of Energy and Environment, Instituto de Carboquímica (C.S.I.C.)

Miguel Luesma Castán 4, 50018 Zaragoza, Spain

Phone number: +34 976 733 977

Fax number: +34 976 733 318

E-mail: jadanez@icb.csic.es

Abstract

Chemical Looping Combustion (CLC) is nowadays an attractive option to decrease the greenhouse gas emissions affecting global warming, because it is a combustion process with inherent CO₂ separation and, therefore, without energy losses. The CLC concept is based on the transfer of oxygen from the combustion air to fuel by means of an oxygen carrier in the form of a metal oxide. The system consists of two separate but interconnected reactors, normally fluidized bed type. In the fuel reactor the oxygen carrier particles react with fuel and generate a gas stream mainly composed by CO₂ and H₂O. The reduced metal oxide is later

transported to the air reactor where oxygen from the air is transferred to the particles, obtaining in this way the original metal oxide ready to be returned to the fuel reactor for a new cycle.

In this work, a 10 kW pilot plant composed of two interconnected bubbling fluidized bed reactors has been design and built to demonstrate the CLC technology. The prototype was run during 200 h, of which 120 h burning methane, and the effect of the operating conditions (oxygen carrier to fuel ratio, fuel gas velocity, oxygen carrier particle size and fuel reactor temperature) on fuel conversion was analyzed working with a CuO-Al₂O₃ oxygen carrier prepared by dry-impregnation. Also, the behavior with respect to attrition, agglomeration, and reactivity of the oxygen carrier was analyzed. It was found that the most important parameter affecting the CH₄ conversion was the oxygen carrier to fuel ratio. Complete methane conversion, without CO or H₂ emissions, was reached with this oxygen carrier working at 800°C and oxygen carrier to fuel ratios higher than 1.4.

Keywords: chemical-looping combustion, oxygen carrier, copper oxide, CO₂ capture.

1. Introduction

Carbon dioxide coming from fossil fuel combustion is the most important greenhouse gas contributing to global warming. One of the options to overcome greenhouse effect is the development of CO₂ capture and separation technologies from flue gases. Chemical looping combustion (CLC) technology has been indicated among the best options for reducing the cost of CO₂ capture using fuel gas.^{1,2} The CLC system is made of two interconnected reactors (Figure 1), designated as air and fuel reactors. In the fuel reactor, the fuel gas (C_nH_{2m}) is oxidized to CO₂ and H₂O 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 total amount of heat evolved over the two reactors in the CLC process is the same as in conventional combustion. The flue gas leaving the air reactor contains N₂ and unreacted O₂. The exit gas from the fuel reactor contains only CO₂ and H₂O. After water condensation, almost pure CO₂ can be obtained with little energy lost for component separation.

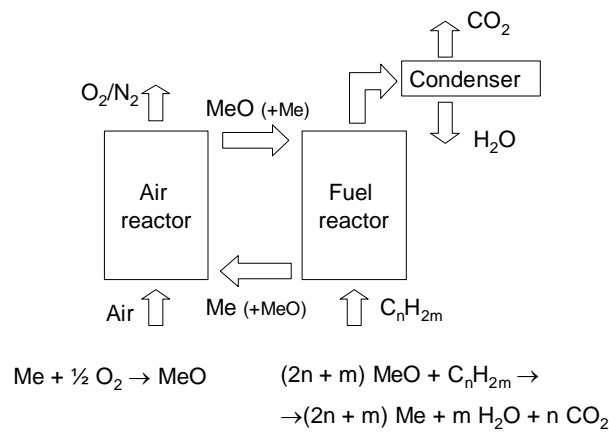


Figure 1. CLC concept

The key issue in the system performance is the oxygen carrier material. The oxygen carrier has to accomplish the following characteristics to perform well: (1) high red-ox reactivity through cycles to reduce the solids inventory, (2) resistance to attrition to minimize losses of elutriated solid, (3) complete fuel conversion to CO₂ and H₂O, (4) negligible carbon deposition what would release CO₂ in the air reactor, and (5) good properties for fluidization (no presence of agglomeration). In addition, other characteristics such as high oxygen transport capacity to reduce circulation of solids between reactors, environmentally friendly, abundant and of easy preparation to reduce costs, are interesting. Iron, nickel, and copper have been selected as the most promising metals to be used in a CLC process³⁻⁵.

A great number of reports concerning CLC can be found in scientific literature, but they are mainly focused on carrier development, reactivity characterization, carbon deposition and side reactions, and behavior in discontinuous batch fluidized beds. However, continuous testing in a CLC prototype is needed to demonstrate the principle of this technology and it is essential to verify the usefulness of the particles developed. There are in the literature several works related with design of CLC plants. Lyngfelt et al.⁶ presented the first design of an atmospheric CLC plant including a high-velocity riser for the air reactor and a low-velocity fluidized bed for the fuel reactor. A conceptual design of a 10 kW CLC working at atmospheric pressure was done by Kronberger et al.⁷. Wolf et al.⁸ analyzed the feasibility of CLC in two interconnected pressurized fluidized bed reactors for a capacity of 800 MW input of natural gas. The CLC process has been successfully demonstrated by Lyngfelt et al.⁹, and Lyngfelt and Thunman¹⁰, in a 10 kW prototype during 100 h of continuous operation burning natural gas and using nickel-based oxygen carrier particles. Ryu et. al.¹¹ working with NiO/bentonite particles as bed material and CH₄ as fuel demonstrated the inherent CO₂ separation, high CO₂ selectivity, high CH₄ conversion and no side reactions (carbon deposition and/or hydrogen generation) in a 50 kW chemical-looping combustor during a total operating time of more than 3.5 hours.

The following steps in the process development will include the design optimization, continuous operation during long time at pilot plant scale, detailed engineering and cost analysis at higher scales. Moreover, the chemical and mechanical stability of the oxygen carrier particles must be proved during long time.

In this work a 10 kW pilot plant composed of two interconnected bubbling fluidized bed reactors has been design and built in order to demonstrate the CLC technology. In this prototype, the behavior of a previously selected CuO-Al₂O₃ oxygen carrier and the effect on

the methane conversion of different operating variables, as oxygen carrier to fuel ratio, gas velocity, particle size, and temperature, were analyzed.

2. Experimental

2.1 Oxygen carrier preparation

Commercial γ -alumina (Puralox NWA-155, Sasol Germany GmbH) particles of 0.1-0.3 and 0.2-0.5 mm with a density of 1.3 g/cm³ and a porosity of 55.4 % were used as support to prepare, by dry impregnation, a Cu-based oxygen carrier with a CuO content of 14 wt %. This oxygen carrier was selected based on results of a previous work¹² where different CuO/Al₂O₃ oxygen carriers were tested in a batch fluidized bed facility during 100 reduction-oxidation cycles to analyze the attrition and agglomeration of the carrier particles.

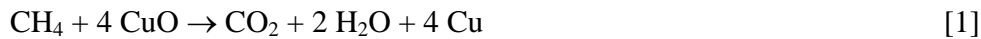
The oxygen carrier was prepared by addition of a volume of copper nitrate solution (5.0 M) corresponding to the total pore volume of the support particles (0.42 cm³/g). The aqueous solution was slowly added to the alumina particles, with thorough stirring at room temperature. Later, the oxygen carrier particles were calcined, in air atmosphere for 30 min at 550°C in a muffle furnace, to decompose the impregnated copper nitrate into insoluble copper oxide. Finally, the oxygen carrier was calcined in air atmosphere for one hour at 850°C.

2.2 Experimental facility

2.2.1. Description

Figure 2 shows the schematic diagram of the 10kW chemical-looping combustor. The CLC plant design allows an easy variation and accurate control of the solid circulation flowrate between both reactors. In this way, it is possible to modify the solid flowrate into the fuel reactor maintaining constant the fuel flow. The plant is basically composed by two interconnected fluidized bed reactors, a riser for solids transport to the fuel reactor, a solid valve for an accurate control of the solids fed to the fuel reactor and two loop seals. The fuel

reactor (1) is a bubbling fluidized bed (0.108 m I.D.) with a bed height of 0.5 m and an extended freeboard of 1.5 m height. In this reactor the oxidation of fuel is carried out by the oxygen carrier by reaction 1 giving CO₂ and H₂O.



This reactor has an oven (6) for heating during start-up and to control the temperature at the different operating conditions. Since the prototype has a furnace for the fuel reactor, the energy balance of the system does not need to be met.

Partially reduced oxygen carrier particles overflow to the air reactor (2) through a U-shaped fluidized loop seal (3b) of 0.108 m I.D. and 0.3 m bed height. This loop seal (3b) was fluidized with N₂ to prevent gas mixing between fuel and air. It is necessary to indicate that in an industrial CLC plant the loop seal would be fluidized with low-pressure steam. Oxygen carrier particles were oxidized in a bubbling fluidized bed (2) (0.16 m I.D.) with a bed height of 0.5 m and with an extended freeboard of 1.0 m height. This reactor was designed for a complete oxidation of the oxygen carrier particles by reaction 2. The air reactor cross-section was higher than the fuel reactor cross-section because a higher volumetric flow is needed in the air reactor due to the reaction stoichiometry and the dilution of oxygen in the air. N₂ and unreacted oxygen left air reactor passing through a cyclone and a filter (9) before the stack. A riser (4) of 3 cm I.D. was used to transport the oxidized oxygen carrier from the air reactor to the fuel reactor by pneumatic transport using air. An air fluidized loop seal (3a) was placed between the air reactor and the riser to avoid solids backflow. The oxygen carrier transported in the riser was recovered by a cyclone and collected in a solids reservoir (7). The solid of this

reservoir avoided the mixing of fuel and the air flowing by the riser. The oxidized oxygen carrier was fed into the fuel reactor by means of a solid valve (5). This valve allowed the control of the solids flowrate fed into the fuel reactor. A diverting solid valve (8) allowed the measurement of the solids circulation flowrate. Fine oxygen carrier particles produced by attrition/fragmentation were recovered in the cyclones and in the filters (9) placed downstream of the fuel and air reactors and riser. Mass flow controllers are employed to feed the reacting and transport gases. Thermocouples and pressure drop transducers were installed to control the operating conditions. The exhaust gases leaving the fuel and air reactors were measured by on-line gas analyzers. CH₄, CO, and CO₂ were measured at the fuel reactor outlet by two IR gas analyzers (FTIR and NDIR) and H₂ by thermal conductivity. CO, CO₂ were measured at the outlet of air reactor by a NDIR analyzer and O₂ by a paramagnetic analyzer. All operating conditions and gas compositions were collected in a computer through a data logger.

After construction of the prototype, initial tests of solids circulation were carried out at ambient temperature with air to learn about the control of the plant. In addition, to test the gas leakage between the reactors, a known flow of CO₂ tracer was introduced together with the fluidization gas in the fuel reactor, air reactor and loop seals and its concentration was measured at the outlet of the fuel and air reactors. This allowed us to find the minimum and optimum values of gas flow to be used in the loop seals for different solids circulation rates and to know the gas distribution between the two branches in the loop seals at different operating conditions (gas velocity and solids circulation rate). The gas introduced in the loop seals produced a dilution in the gas streams obtained at the outlet of the fuel and air reactors, and it was considered to correct the gas concentration measured in the analyzers and for mass balance calculations. No mixing of gases of the fuel and air reactors and a similar gas

distribution between the two branches of the loop seals was observed in the majority of the operating conditions.

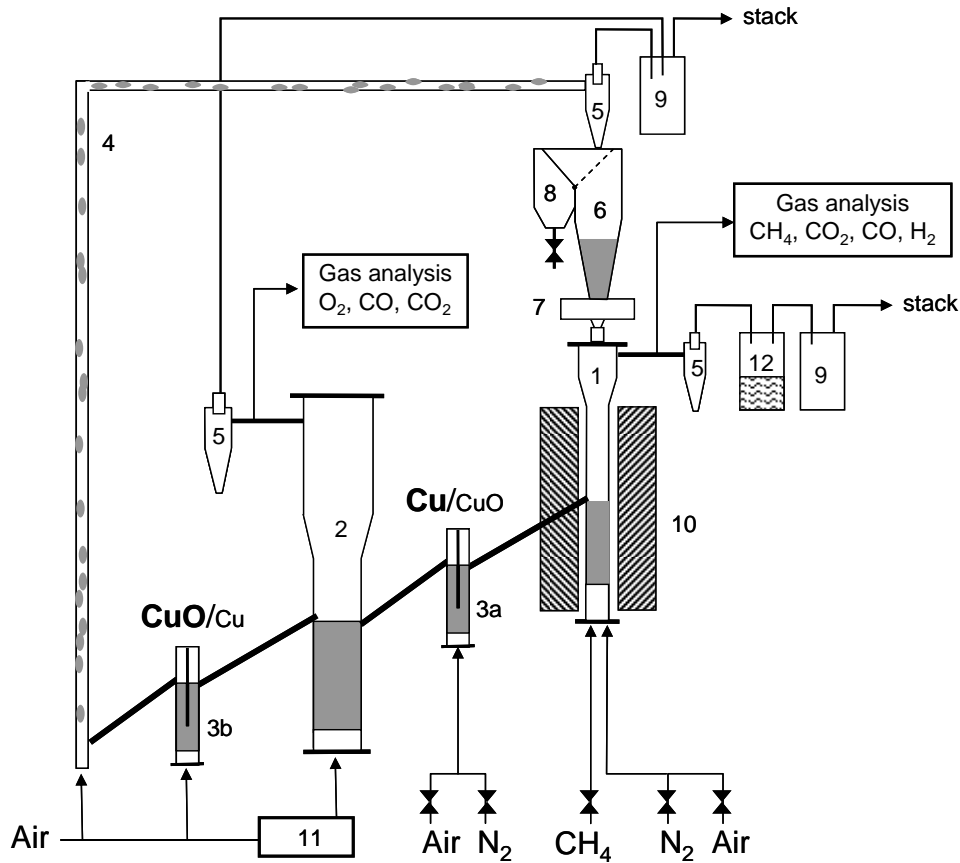


Figure 2. Schematic diagram of the CLC facility. (1) fuel reactor; (2) air reactor; (3) loop seals; (4) riser; (5) cyclone; (6) solid reservoir; (7) solids valve; (8) diverting solid valve; (9) filters; (10) oven; (11) air preheater; (12) water condenser.

2.2.2. Start-up and stop in operation

To begin the redox reactions of the CLC process, it is necessary to pre-heat the oxygen carrier particles to a temperature higher than 500°C. This value, previously found in TGA tests, represented the minimum oxidation temperature at which the reaction rate of Cu with O₂ is acceptable for operation. For the start-up, the fuel and air reactors were fluidized with air. The solids were heated by means of the furnace located around the fuel reactor and by preheated

air introduced to the air reactor. The circulation of solids started when the solids reached 800°C in the fuel reactor, in order to get the system homogenization and the heating of the other parts of the plant. When the solids in the air reactor reached 500 °C, the fuel reactor and loop seal (3b) were purged with N₂ until any O₂ was detected at the outlet stream of fuel reactor. Then, the fuel reactor feed was switched to 25 vol% CH₄ and 75 vol% N₂. The combustion efficiency at those low temperatures is bad but the heat release in the reduction and oxidation reactions was useful to heat the system. It is necessary to indicate that reduction and oxidation reactions are exothermic working with Cu-based carriers. The CH₄ percentage in the fuel feed was gradually increased to 100 vol% as the reactor temperatures reached the desired conditions. The gas flows in the fluidized beds were varied with the temperature increases to fix the gas velocities at the desired values, and to avoid the entrainment of the solids. The whole process of start-up took around 3 hours.

The shut-down of the plant begins switching CH₄ to N₂ to purge the fuel reactor and to avoid explosive mixtures. After that, only air was fed in the whole plant to fluidize all the elements and to circulate the oxygen carrier particles. About one hour later, the temperature in the reactors is low enough to switch off all the flows.

3. Results and discussion

Combustion tests at different operating conditions, working with a Cu-based oxygen carrier and using methane as fuel, were carried out in the facility. The initial oxygen carrier inventory in the system was 22 kg. The circulation rate of solid material in the prototype was fixed with the solid valve. Oxygen carrier circulation flowrates were varied between 60 and 250 kg/h. The temperature in the fuel reactor was varied between 700 and 800°C, and the inlet fuel gas velocity between 7 and 14 cm/s. It is necessary to indicate that gas velocity increases up to

three times in the fuel reactor due to the stoichiometry of the reaction. The air flow in the air reactor was modified to keep the oxygen excess similar in all tests (15-20%). Two different oxygen carrier particle sizes (0.1-0.3 and 0.2-0.5 mm) were tested.

The prototype operated during 200 h in hot conditions, of which 120 h were employed burning methane. Tests under steady state conditions were run for 60 minutes.

Temperatures in the reactors were quite constant and, normally, the temperature in the air reactor was 10-30 °C higher than the temperature in the fuel reactor, due to the higher heat generated in the oxidation reaction of the carrier.

3.1 Agglomeration, attrition, and reactivity.

Cu-based oxygen carriers had been rejected as potential candidates for CLC as a consequence of their agglomeration in fluidized bed reactors^{13, 14}. However, de Diego et al.¹² developed Cu-based oxygen carriers that never presented agglomeration problems in a batch fluidized bed facility during 100 reduction-oxidation cycles. The oxygen carrier used in this work was selected based on these previous results¹², and it was found that the behavior of the oxygen carrier with respect to agglomeration problems was very satisfactory. The different tests carried out in the 10 kW CLC prototype during 200 h in hot conditions never presented defluidization problems due to agglomeration processes.

Attrition or fragmentation of particles leading to the production of fine particles is a critical parameter for the lifetime of the oxygen carrier particles. It is therefore essential to analyze the production of fine particles during the CLC process.

Particles elutriated from the fluidized bed reactors during operation were recovered in the cyclones and filters and weighted to determine the attrition rate. To measure properly the attrition rates, the fresh oxygen carrier particles were firstly in circulation at ambient temperature for 4 hours to eliminate the fines adhered to the particles during the production

process. During hot operation, the loss of fine particles was high at the beginning of the experimental run and rapidly decreases. After 40 h of operation a low value of the attrition rate, $\sim 0.04 \text{ wt\%h}^{-1}$, was reached and it was maintained also constant until the 100 h of operation time. Taking this value as representative of the attrition rate, ~ 3.4 full loads a year of the oxygen carrier would be necessary in a CLC plant. Lower oxygen carrier makeups are expected in an industrial CLC in which oxygen carrier particles recovered by the cyclones are returned to the bed.

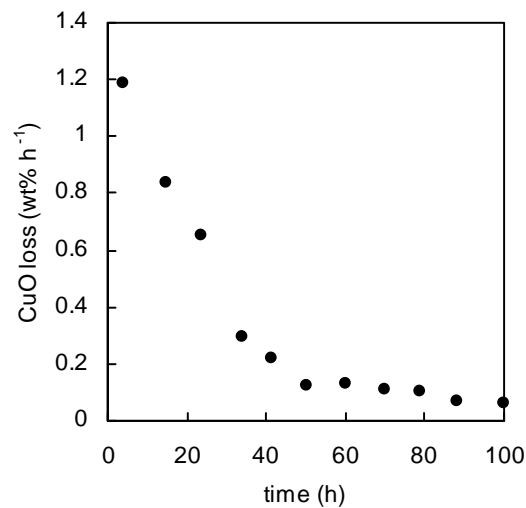


Figure 3. CuO loss rate (wt\% h^{-1}) versus time for the oxygen carrier particles. $d_p=0.2\text{-}0.5 \text{ mm}$.

The CuO content in the particles recovered in the cyclones and filters and in samples taken in the system during operation was determined in a thermogravimetric analyzer (TGA) at 800°C working with H_2 . The CuO content in the particles recovered in the cyclones and filters was significantly higher than in the fresh oxygen carrier particles. On the other hand, the CuO content of the samples taken in the system decreased with increasing the operation time. After 100 h of operation the CuO content of the oxygen carrier was 10 wt%. Figure 3 shows the CuO loss rate versus time for the 0.2-0.5 mm oxygen carrier particles. At the beginning, the CuO

loss is high, but this rate rapidly decreases to $0.2 \text{ wt}\% \text{h}^{-1}$ after 40 h, and to $\sim 0.04 \%$ of the initial CuO weigh per hour after 100 h. The mechanism of CuO loss from the oxygen carrier particles is not yet known and further studies would be needed to know it.

In every cycle the oxygen carrier undergoes important chemical and structural changes at high temperature and, consequently, substantial changes in the reactivity of the oxygen carrier with the number of cycles could be expected. Reactivity of the oxygen carriers before and after used in the CLC combustor was measured in a TGA. Figure 4 shows the transported oxygen to sample mass ratio (φ , defined in Eq. 3) versus time obtained in the TGA at 800°C , using 15 vol% CH_4 / 20 vol% H_2O / 65 vol% N_2 in the oxygen carrier samples taken at different operation times.

$$\varphi = \frac{(\text{oxidized sample mass}) - (\text{reduced sample mass})}{(\text{oxidized sample mass})} \quad [3]$$

As it can be seen in the Figure 4, a decrease in the final value of φ was obtained with increasing the operation time in the CLC plant. This decrease was due to the decrease in the CuO content in the oxygen carrier particles, as pointed out before. However, the maximum φ values were reached after ~ 0.2 min for all the samples, independently of the residence time of the carrier in the CLC plant. Therefore, the reduction reactivity of the oxygen carrier particles was not affected by the operation time in the combustor. The same conclusions were found with respect to the oxidation rates of the different samples and very similar results were observed with both oxygen carrier particle sizes. These results corroborate previous ones found in a batch fluidized bed reactor¹².

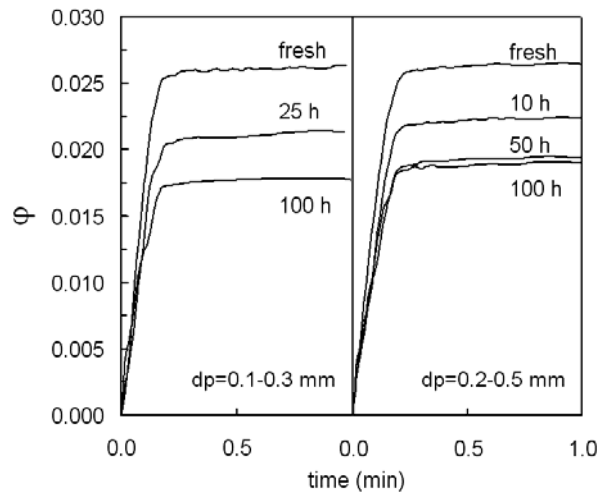


Figure 4. Transported oxygen to sample mass ratio (ϕ) versus time in the reduction reaction of the carrier at different operation times.

3.2 Effect of the operating conditions on methane conversion

Cu-based oxygen carriers have no thermodynamic limitations to reach complete CH_4 combustion. Therefore, the main parameter to evaluate the performance of the system is CH_4 conversion. In the prototype, the effect on the CH_4 combustion of different operating variables, such as oxygen to fuel ratio, fuel gas velocity, oxygen carrier particle size and fuel reactor temperature, has been analyzed. An analysis of the gas streams, CH_4 conversion, carbon shortcuts and incomplete combustion products was carried out. Unburned CH_4 , CO or H_2 at the exit of the fuel reactor is a loss of energy and a possible trouble to CO_2 handling.

3.2.1 Effect of oxygen carrier to fuel ratio

For some carriers, as Fe- or Ni-based, high solid circulation rates are necessary to maintain the temperature in the fuel reactor since the CH_4 reduction with these metals is endothermic. However, for Cu-based oxygen carriers reduction and oxidation reactions are exothermic. Therefore, the circulation solid flowrate is determined to obtain complete CH_4 combustion.

The oxygen carrier to fuel ratio (ϕ) is defined by equation 4, where $\phi=1.0$ corresponds to the stoichiometric CuO amount needed for full conversion of CH_4 to CO_2 and H_2O :

$$\phi = \frac{F_{\text{CuO}}}{4 \times (F_{\text{CH}_4})} \quad [4]$$

Figure 5 shows the effect of oxygen carrier to fuel ratio on fuel conversion working at 800°C and 10 cm/s of inlet gas velocity in the fuel reactor. The use of the stoichiometric oxygen carrier to fuel ratio ($\phi=1.0$) produced low CH_4 conversion, $\sim 90\%$, and an excess of oxygen carrier was necessary to increase the fuel conversion in the fuel reactor. Complete CH_4 conversion was reached at $\phi \sim 1.4$.

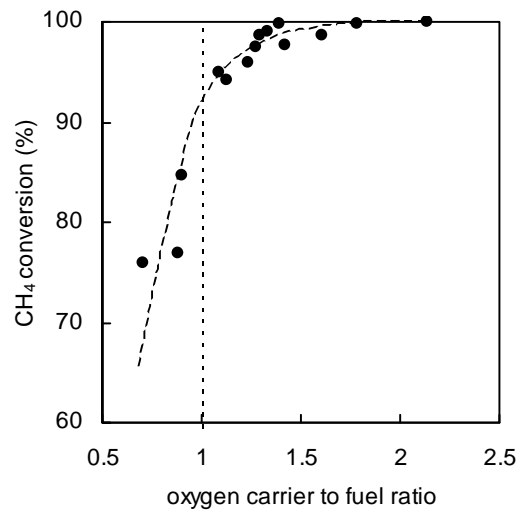


Figure 5. Effect of the oxygen carrier to fuel ratio on the CH_4 conversion. $d_p = 0.2\text{-}0.5 \text{ mm}$, $T = 800^\circ\text{C}$, $u = 10 \text{ cm/s}$.

Figure 6 shows the dry concentrations of unburned CH_4 , CO and H_2 at the outlet of the fuel reactor. These concentrations were recalculated taking into account the N_2 dilution coming

from the loop seal (3b). It can be observed a decrease of the CH_4 concentration with increasing the oxygen carrier to fuel ratio. For values of $\phi < 1$, CO and H_2 in the fuel reactor and CO_2 in the air reactor (not showed) were produced, which indicated that there was CH_4 decomposition and partial oxidation. For values of $\phi > 1$, not CO and H_2 in the fuel reactor neither CO_2 in the air reactor were produced, and only some unreacted CH_4 together with the CO_2 was measured. Finally, for values of $\phi > 1.4$ the CH_4 concentration was zero and only CO_2 (dry basis) was measured.

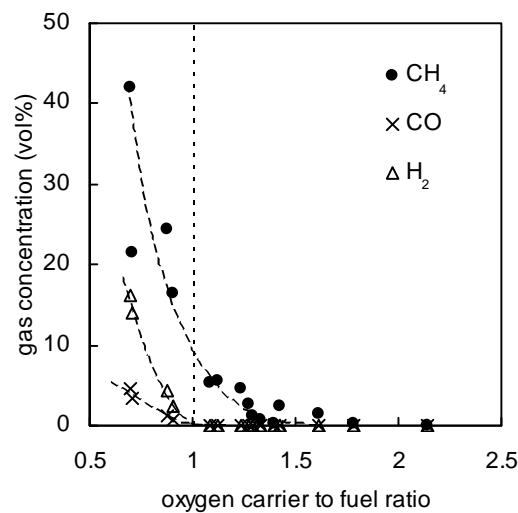


Figure 6. Effect of the oxygen carrier to fuel ratio on CH_4 , CO and H_2 gas concentration (dry basis) at the exit of fuel reactor. $d_p=0.2-0.5$ mm, $T = 800^\circ\text{C}$, $u = 10$ cm/s.

3.2.2 Effect of fuel gas velocity

The fuel gas throughput of the reactor is directly related with the gas velocity (u) at the inlet of the reactor for a fixed reactor area. Figure 7 shows the effect of the oxygen carrier to fuel ratio on the CH_4 conversion at 7, 10 and 14 cm/s of gas velocity at the inlet of the fuel reactor. Higher gas velocities in the bubbling bed produced a decrease in the fuel conversion, and higher oxygen carrier to fuel ratios (ϕ) were necessary to increase the CH_4 conversion. In this

way, $\phi \sim 1.4$ was enough to reach complete CH_4 conversion at gas velocities of 7 and 10 cm/s. However, complete CH_4 conversion was not reached at 14 cm/s with a $\phi = 1.7$. At this gas velocity, oxygen carrier to fuel ratios higher than 1.7 (oxygen carrier circulation rate > 250 kg/h) could not be tested.

The decrease of CH_4 conversion with increasing the inlet gas velocity is expected because a larger amount of fuel has to react with the same amount of oxygen carrier particles in the fuel reactor. Moreover, there is also a less efficient contact between the particles and the gas at higher velocities when a larger fraction of the gas is in the bubble phase.

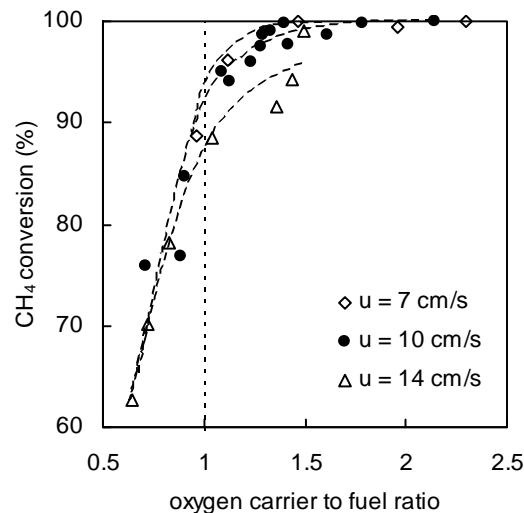


Figure 7. Effect of the oxygen carrier to fuel ratio on CH_4 conversion with different inlet fuel gas velocities. $d_p = 0.2\text{-}0.5$ mm, $T = 800$ °C.

3.2.3 Effect of particle size

Oxygen carrier particles of 0.1-0.3 mm and 0.2-0.5 mm were tested in the CLC prototype to analyze the effect of the particle size of the oxygen carrier. Figure 8 shows a comparison of the CH_4 conversion using both particles sizes, as a function of the oxygen carrier to fuel ratio, at 10 cm/s of inlet gas velocity and 800°C. It can be seen an increase in the CH_4 conversion

when the particle size of the carrier increased. This different behaviour cannot be attributed to different reactivity of the carrier particles because it was found in previous kinetic studies, and it is showed in Figure 4, that the reduction and oxidation reactivities were similar for both particle sizes.

The difference in CH₄ conversion could be due to the different contact efficiency between the particles and CH₄. An increase in the particle size produces an increase in the minimum fluidization velocity, and thus an increase of gas flow in the dense phase.

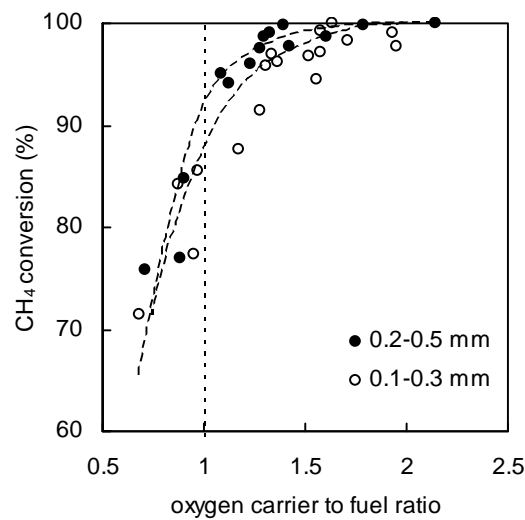


Figure 8. Effect of the oxygen carrier to fuel ratio on CH₄ conversion using two different particle sizes. T = 800°C, u = 10cm/s.

3.2.4 Effect of fuel reactor temperature

The effect of fuel reactor temperature was studied in the CLC plant in the range from 700 to 800°C. In all conditions, the inlet molar flow of CH₄ (mol/h) was maintained constant. Figures 9 and 10 show the effect of the oxygen carrier to fuel ratio on the CH₄ conversion at 700, 750 and 800°C, for 0.1-0.3 mm and 0.2-0.5 mm particle sizes. For the same oxygen carrier to fuel ratio (ϕ), an increase in the fuel reactor temperature produced an increase on the CH₄

conversion. The highest increases were found for changing the temperature from 700 to 750°C for both particle sizes. This increase is related to the reaction rate through an increase in the kinetic constant of the reduction rate.

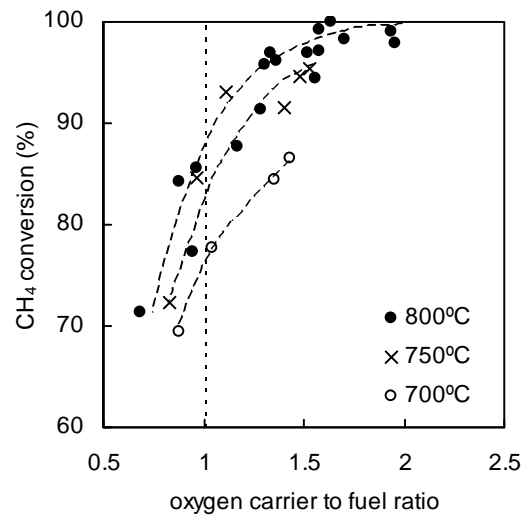


Figure 9. Effect of oxygen carrier to fuel ratio on CH₄ conversion at different fuel reactor temperatures. dp = 0.1-0.3 mm, u = 10 cm/s.

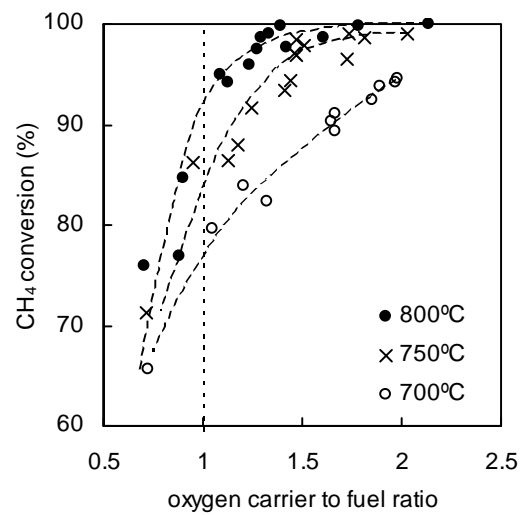


Figure 10. Effect of oxygen carrier to fuel ratio on CH₄ conversion at different fuel reactor temperatures. dp = 0.2-0.5 mm, u = 10 cm/s.

Obviously, to reach complete CH₄ conversion lower ϕ values would be necessary working at higher fuel reactor temperatures. It must be pointed out that for Cu-based oxygen carriers the recirculation rate is not limited by the heat balance, because both the reduction and the oxidation reactions are exothermic. In this case, the recirculation rate will be a compromise between the transport capacity of the riser, and the conversion reached in the air reactor.

4. Conclusions

A 10 kW CLC prototype based on two interconnected bubbling fluidized bed reactors was design and built to analyze the behaviour of a CuO-Al₂O₃ oxygen carrier and the effect of operating conditions (oxygen carrier to fuel ratio, fuel gas velocity, particle size and temperature of fuel reactor) on fuel conversion.

The prototype was satisfactory run during about 200 h, of which 120 h burning methane, working with two particle size distributions of a CuO-Al₂O₃ oxygen carrier prepared by dry impregnation. During operation, no carbon deposition, agglomeration or any other kind of operational problems were found. The attrition rate was high at the beginning of the experimental run and rapidly decreases. After 40 h of operation a low and constant value of attrition rate was reached, which indicated that the CuO/Al₂O₃ particles had a high durability. Finally, it was found that the oxygen carrier reactivity was not affected by the operation time in the combustor. These results show that Cu-based oxygen carriers are suitable to use in CLC processes.

The most important parameters affecting the CH₄ conversion were the oxygen carrier to fuel ratio and the fuel reactor temperature. CO and H₂ concentrations were zero at oxygen carrier to fuel ratios higher than the unity, and complete methane conversion to CO₂ and H₂O was reached at 800°C and oxygen carrier to fuel ratios higher than 1.4.

5. Acknowledgments

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