Effect of gas composition in Chemical-Looping Combustion with copper based oxygen carriers: Fate of light hydrocarbons


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Abstract

Chemical-Looping Combustion (CLC) is an emerging technology for CO₂ capture because separation of this gas from the other flue gas components is inherent to the process and thus no energy is expended for the separation. Natural or refinery gas can be used as gaseous fuels and they may contain different amounts of light hydrocarbons. This paper presents the combustion results obtained with a Cu-based oxygen carrier using mixtures of CH₄ and light hydrocarbons (LHC) (C₂H₆ and C₃H₈) as fuel. The effect
on combustion efficiency of the fuel reactor temperature, solid circulation flow rate and
gas composition was studied in a continuous CLC plant (500 $W_{th}$). Full combustions were
reached at 1073K and 1153K working at oxygen to fuel ratios, $\phi$, higher than 1.5 and 1.2
respectively. Unburnt hydrocarbons were never detected at any experimental conditions
at the fuel reactor outlet. Carbon formation can be avoided working at 1153 K or at
$\phi$ values higher than 1.5 at 1073K. After 30 hours of continuous operation, the oxygen
carrier exhibited an adequate behaviour regarding attrition and agglomeration. It can be
concluded that no special measures should be taken in a CLC process with Cu-based OC
with respect to the presence of LHC in the fuel gas.

Keywords: CO$_2$ capture, chemical-looping combustion, copper, hydrocarbons.

1. Introduction

It is well-known that CO$_2$ is an important greenhouse gas that strongly affects
global warming (IPCC, 2007). The CO$_2$ capture and storage (CCS) is a process
involving the separation of CO$_2$ emitted by industry and energy-related sources, and the
storage for its isolation from the atmosphere over the long term. There are different
CCS technologies available or under development, but most of them high energy
penalty as a consequence of the gas separation step, which results in an increase of the
cost of energy production.
Chemical Looping Combustion process (CLC) has been suggested among the best alternatives to reduce the economic cost of CO$_2$ capture using fuel gas (Kerr, 2005). In this process, CO$_2$ is inherently separated from other combustion products, N$_2$ and unused O$_2$, through the use of a solid oxygen carrier (OC) and thus no energy is expended for the separation. The description of the CLC process is well-known considering the increasing development of this technology in the last few years for combustion of natural gas (Ishida et al., 1987; Lyngfelt et al., 2001; Adánez et al., 2006) or syngas from coal gasification (Anheden and Svedberg, 1998; García-Labiano et al., 2007a; Mattisson et al., 2007). Also, refinery and industrial gases have been considered to be used as fuel gas in a CLC system (Morin and Béal, 2005). Recently, interest in combustion of solid fuels e.g. coal, introducing the fuel directly to the Fuel Reactor (FR), has arisen (Cao and Pan, 2006; Scott et al., 2006; Leion et al., 2008).

The CLC process has been demonstrated for methane combustion in 10 kW (Lyngfelt and Thunman, 2005; Adánez et al., 2006; de Diego et al., 2007; Linderholm et al., 2008), 50 kW (Ryu et al., 2005) and 120 kW (Mayer et al., 2008) units. However, smaller plants have been designed, 300-500 W$_{th}$, to investigate the behavior of different OCs with natural gas (Abad et al., 2006, 2007a; Johansson et al., 2006; Adánez et al., 2009a).

Gaseous fuel can contain variable amounts of light hydrocarbons (LHC), i.e. C$_2$-C$_5$. In addition to methane, the LHC content may be up to 10 vol% in crude natural gas (Olafsen et al., 2006) and up to 30 vol% in refinery gas (Middleton et al., 2005). To obtain high combustion and CO$_2$ 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 fuel (Eide et al., 2005) or separating hydrocarbons from the CO₂ gas stream, it would be desirable to get full conversion of hydrocarbons in the CLC system.

A key part in the successful development of a CLC system is the OC, which besides having a high reactivity with the gas fuel and air for many cycles of reduction-oxidation, must meet other characteristics such as low attrition, no agglomeration during fluidized bed operation, and no carbon deposition. Moreover, full fuel conversion to CO₂ and H₂O is desirable. Among the different metal oxides proposed in the literature for the CLC process, Cu-based oxygen carriers have shown high reaction rates and oxygen transfer capacity (Adánez et al., 2004), and have no thermodynamic restrictions for complete fuel conversion to CO₂ and H₂O. In addition, the use of Cu-based oxygen carriers does not have the environmental problems associated with the use of Ni-based OC. Another advantage of using copper is the low price in comparison to other metals used such as nickel, cobalt, manganese, etc.

Our research group at the Instituto of Carboquímica (CSIC) has undertaken several studies using oxygen carriers based on copper. In previous works potential Cu-based oxygen carriers were prepared using different supports (Adánez et al., 2004). The effects of oxygen carrier composition and preparation method were also investigated in
a TGA (de Diego et al., 2004) to develop oxygen carriers with high reaction rates and durability. It was found that the optimum preparation method for Cu-based oxygen carriers was the impregnation on a support. Later, the preparation conditions and oxygen carrier characteristics were optimized to avoid the agglomeration of the Cu-based materials during their operation in a fluidized bed (de Diego et al., 2005), which was the main reason adduced in the literature to reject this kind of materials for their use in a CLC process. Based on these findings, an oxygen carrier was finally selected to test its behaviour in a 10 kW<sub>th</sub> CLC prototype using methane as fuel. The results obtained during 200 h of continuous operation were very successful both regarding methane combustion efficiencies and particle behaviour (Adánez et al., 2006; de Diego et al., 2007). Finally, a waste management study from the CLC plant using Cu-based residues was also carried out (García-Labiano et al., 2007b). It was concluded that this solid residue can be classified as a stable non-reactive hazardous waste acceptable for landfilling as a non-hazardous waste.

The possible reactions involved in a CLC process using a Cu-based OC increase with the presence of LHC with respect to the use of pure CH<sub>4</sub>. Although there are some works in the literature regarding the use of LHC in the presence of copper catalysts (Finocchio et al., 1997; Kumar and Murthy, 1982; Faungnawakij et al., 2009), they are not referred to the specific process of CLC. In a previous work, our research group analyzed the effect of LHC in the CLC process using a Ni-based OC (Adánez et al., 2009b). It was found that is possible get full gas conversion without formation neither unburnt hydrocarbons nor carbon.
The main reactions involved in the CLC process with Cu-based OC are shown in Table 1. Metallic copper appears as a product of the reaction between hydrocarbons and CuO, initially present in the OC (see reactions 1 and 2). The set of reactions 3-11 are the same as those processes where metallic copper 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. Carbon formation (reactions 10 and 11) is favored at low temperatures, whereas reaction 9 becomes increasingly important at higher temperatures (Ishida et al., 1998; Jerndal, 2006). The higher tendency to carbon formation of hydrocarbons with respect to pure CH₄ (Rostrup, 1993), mainly due to coke formation from olefins (reactions 7 and 8), could produce deactivation of the OC and/or cause agglomeration problems in the system. Using Cu-based oxygen carriers, no carbon formation on the carrier from thermal decomposition of methane has been detected (Adánez et al., 2006), although this situation can be different when using LHC. 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 of the 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 (olefins, CO and H₂) can also react with the metallic oxide CuO (reactions 12-15).

The aim of this work was to test the behavior of a copper based oxygen carrier when the fuel, CH₄, contains variable amounts of light hydrocarbons: ethane and propane. The experiments were carried out in TGA, in a batch fluidized bed and in a 500 Wth
CLC prototype under continuous operation. The influence of LHC concentration, temperature and solids circulation rate on gas products distribution, combustion efficiency, carbon formation, attrition and material agglomeration was investigated.

2. Experimental

2.1. Oxygen carrier

Previous works were carried out by de Diego et al. (2004, and 2005) to determine the effects of carrier composition, preparation method, metal content, and calcination temperature on the oxygen carriers reactivity, gas product distribution, attrition rate and agglomeration. It was found that copper based oxygen carriers prepared by impregnation are good candidates for the CLC process.

Therefore, the oxygen carrier used in this work was prepared by the incipient wet impregnation method using CuO as active phase and $\gamma$-Al$_2$O$_3$ as support. The material was prepared by the addition of a volume of a saturated copper nitrate solution (5.0 M) corresponding to the total pore volume of the support particles. Commercial $\gamma$-alumina particles (Puralox NWa-155, Sasol Germany GmbH) with a density of 1.3 g/cm$^3$ and a porosity of 55.4 % were used as support. The aqueous solution was slowly added to the support particles of 300-500 µm, with thorough stirring at room temperature. The mix was subsequently calcined for 30 min at 823 K in a muffle oven to decompose the impregnated copper nitrates into insoluble copper oxide and finally was stabilized in air atmosphere for 1 hour at 1123 K, obtaining an oxygen carrier whose main characteristics
are showed in Table 2. The final active CuO content (14%) was determined using thermogravimetric techniques (TGA). It must be considered that, for this type of Cu-based oxygen carriers, both the CuO and the copper aluminates are active species for reaction with the gas fuel (de Diego et al., 2007). The oxygen transport capacity, defined as the mass fraction of oxygen that can be used in the oxygen transfer, was calculated as 

$$R_{o,OC} = \frac{(m_{ox} - m_{red})}{m_{ox}}$$

where $m_{ox}$ and $m_{red}$ are the masses of the oxidized and reduced form of the oxygen carrier, respectively (Adánez et al., 2004).

### 2.2 Thermogravimetric analysis

Reactivity tests of the copper 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 (Adánez et al., 2004). The composition of the gas chosen for the reducing experiments was composed by a variable amount (2-15 vol%) of fuel gas (CH$_4$, C$_2$H$_6$ or C$_3$H$_8$), 30 vol% H$_2$O, and N$_2$ balance. The gas used for oxidation was 100 vol% air. The experiments were carried out at 973, 1073 and 1153 K.

### 2.3. Batch fluidized bed reactor

To investigate the effect of LHC on the gas product distribution during CLC with Cu-based oxygen carriers, several reduction-oxidation cycles were carried out in a batch fluidized bed. Detailed information about the instrument and operating procedure used can be found elsewhere (de Diego et al., 2005). The total solid inventory in the reactor was 0.3 kg.
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, $r_0$, as a function of reduction time using the following equation

$$r_0(t) = \left( x_{CO} + 2x_{CO_2} + x_{H_2O} \right)_{\text{out}} F_{\text{out}}$$

(16)

where $F_{\text{out}}$ is the molar flow of the outlet gas stream ($\text{mol s}^{-1}$), and $x_i$ is the molar fraction of the gas $i$.

The conversion of solids in the fluidized bed for the reduction reaction can be calculated from the integration of $r_0(t)$ with time

$$X_{OC}(t) = \frac{1}{N_{O,OC}} \int_{t_o}^t r_0(t) dt$$

(17)

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

$$N_{O,OC} = \frac{m_{ox} R_{O,OC}}{M_O}$$

(18)

where $M_O$ is the atomic mass of oxygen ($\text{kg mol}^{-1}$) and $m_{ox}$ is the mass of the oxidized form of the oxygen carrier (kg).

### 2.4. CLC prototype (500 Wth)

Figure 1 shows a schematic diagram of the 500 Wth CLC prototype, which was designed and built at Instituto of Carboquímica (CSIC). The atmospheric Chemical-Looping Combustor prototype was composed of two interconnected fluidized-bed reactors separated by a loop seal, a riser for solids transport to the fuel reactor, a cyclone...
and a solid valve to control the solids fed to the fuel reactor. This design allowed the variation and control of the solids circulation rate between both reactors. The FR, (A) consisted of a bubbling fluidized bed (0.05 m i.d.) with a bed height of 0.1 m. In this reactor the fuel combustion was performed by the oxygen carrier, giving CO$_2$ and H$_2$O according to eqs. (1,12-14). Reduced oxygen carrier particles overflowed into the AR (C), through a U-shaped fluidized loop seal (B), to avoid gas mixing between fuel and air. The oxidation of the carrier took place at the AR, which consisted of a bubbling fluidized bed (0.05 m i.d.) with a bed height of 0.1 m. It was followed by a riser (D) of 0.02 m i.d. and 1 m height. The regeneration of the oxygen carrier happened in the dense bed of the AR allowing residence times high enough for the complete oxidation of the reduced carrier. Secondary air could be introduced at the top of the bubbling bed to help particle entrainment. N$_2$ and unreacted O$_2$ left the AR passing through a high-efficiency cyclone (E) and a filter (F) before the stack. The recovered solid particles by the cyclone were sent to a reservoir of solids setting the oxygen carrier ready to start a new cycle and avoiding the mixing of fuel and air out of the riser. The regenerated oxygen carrier particles returned to the FR by gravity from the reservoir of solids located above a solids valve (G) which controlled the solids circulation rate entering the FR. A diverting solids valve (H) located below the cyclone allowed the measurement of the solid flow rates at any time. Fine particles produced by fragmentation/attrition in the plant were recovered in the filters that were located downstream of the FR and AR.

Thermocouples and pressure drop transducers located at different points of the plant showed the current operating conditions in the plant at any time. Specific mass flow controllers gave accurate flow rates of feeding gases. 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, CH$_4$, CO, CO$_2$ and H$_2$, concentrations in the gas outlet stream from the FR were measured after steam condensation. O$_2$, CO, and CO$_2$ concentrations were obtained at the gas outlet stream from the AR. CO, CO$_2$, and CH$_4$ concentrations were measured using non-dispersive infrared (NDIR) analyzers (Maihak S710 / UNOR), a FTIR analyzer (Gasmet CX4000) measured the H$_2$O concentration, H$_2$ concentration was determined using a thermal conductivity detector (Maihak S710 / THERMOR), and O$_2$ concentration by using a paramagnetic analyzer (Siemens Oxymat 5E). The unburnt hydrocarbons were measured with a total hydrocarbons analyzer (Bernath Atomic BA-9900) and are presented as CH$_4$ equivalent. 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.

The behavior of the CLC was evaluated calculating the combustion efficiency, $\eta_c$, which was defined as the ratio of the oxygen consumed by the gas leaving the FR to that consumed by the gas when the fuel is completely burnt to CO$_2$ and H$_2$O multiplied by 100. So, $\eta_c$ gives an idea about how the CLC operation is close or far from the full combustion of the fuel, i.e. $\eta_c = 100\%$.

$$\eta_c = \frac{\left(2x_{CO_2} + x_{CO} + x_{H_2O}\right)_{out} - \left(x_{H_2O}\right)_{in}}{\left(4x_{CH_4} + 7x_{C_2H_6} + 10x_{C_3H_8}\right)_{in}} \times 100$$  \hspace{1cm} (19)

where $F_{in}$ is the molar flow of the inlet gas stream, $F_{out}$ is the molar flow of the outlet gas stream, and $x_i$ is the molar fraction of the gas $i$.
The oxygen carrier-to fuel ratio ($\phi$) was defined by eq. 20, where $F_{CuO}$ is the molar flow rate of the copper 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 CuO amount needed for a full conversion of the fuel to CO$_2$ and H$_2$O:

$$\phi = \frac{F_{CuO}}{bF_{Fuel}}$$ (20)

where $b$ is the stoichiometric coefficient of the fuel gas mixture, calculated as:

$$b = \frac{4x_{CH_4} + 7x_{C_2H_6} + 10x_{C_3H_8}}{x_{CH_4} + x_{C_2H_6} + x_{C_3H_8}}$$ (21)

3. Results and Discussion

3.1. Thermodynamic calculations

Several thermodynamic calculations were carried out to evaluate the possibility of carbon formation regarding the use of LHC as fuel in a CLC process in the presence of a Cu-based oxygen carrier. The HSC Chemistry 6.1 (2008) software finds the most stable phase combination and seeks the phase composition where the Gibbs energy of the system reaches its minimum value at a fixed balance, constant pressure and temperature.

With regard to the combustion efficiency, hydrocarbons can be fully converted to CO$_2$ and H$_2$O when Cu-based oxygen carriers are used. Therefore, thermodynamically
100% of gas conversion can be reached in the FR of the CLC, independently of the operation temperature.

Under certain conditions, solid carbon deposition on the oxygen carrier particles may occur if a carbon-containing fuel is used. Carbon formation in the fuel reactor depends on temperature, pressure and the amount of oxygen added to the reactor with the metal oxide (Jerndal et al., 2006) i.e. the oxygen ratio, which has been defined as the oxygen reacted with the fuel with respect to the stoichiometric amount of oxygen needed to reach complete fuel conversion. This process was analyzed in a previous work using a Ni-based OC (Adánez et al., 2009b). Figure 2 shows the oxygen ratio needed to avoid carbon formation as a function of temperature for different hydrocarbons (C$_1$–C$_5$). It was found that the oxygen ratio needed to avoid carbon formation decreases for all LHC when the temperature increases. Only slight differences can be observed between the curves of the hydrocarbons C$_2$-C$_5$. At temperatures above 1100 K, the oxygen ratio remains almost constant with a value $\approx$0.3. Nevertheless, in the case of CH$_4$, the needed oxygen is quite lower at every temperature, with a final value for the oxygen ratio $\approx$0.25. The region of no carbon formation is due to the presence of the combustion products, CO$_2$ and H$_2$O, which produce the carbon gasification according to the reverse of reactions 10 and 11. This fact shows the higher tendency to carbon formation of higher hydrocarbons with respect to pure CH$_4$. 
3.2. 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 3 shows, as an example, the weight variations obtained at 1073 K with C$_3$H$_8$ at different concentrations for the first reduction period of fresh particles. The curve obtained with 5 vol% CH$_4$ was also represented for comparison. The OC exhibited a high initial reactivity with the C$_3$H$_8$, similar to that observed with CH$_4$. Nevertheless, after a short period of time, the weight increased because of the carbon formation. Carbon formation was observed at high concentrations of propane and ethane at all temperatures and took place even in the presence of 40 vol% H$_2$O. During the reduction with CH$_4$, 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 the OC particles than methane.

Experiments at low LHC concentrations were made to determine the effect of the temperature on the carrier reactivity. Figure 4 shows, as an example, the reactivity of the oxygen carrier with 2 vol% of C$_3$H$_8$ and C$_2$H$_6$ at three temperatures for a typical reduction and oxidation cycle of OC particles. At the highest temperature (1073 and 1153 K) the reaction rate is very fast and particles are completely reduced within 20 s. At the lowest temperature, i.e. at 973 K, the reduction reaction rate is fast until $X \approx 0.7$, and then the reaction rate slows down. At higher temperatures, reaction is predominantly controlled by chemical reaction (García-Labiano et al. 2004).
The oxidation reaction rate was very fast at all temperatures and the samples were oxidized back to their initial condition within 12 s at all temperatures. At the lowest temperatures (973 K) the degree of conversion was somewhat less than 0.9 (see figure 4). This is due to the fact that the final degree of conversion reached in the previous reduction period was low. However, in all cases the oxygen carrier was fully oxidized back to its original form after each oxidation period.

In a CLC plant it is unlikely that the oxygen carrier will be reduced and oxidized to a high degree of conversion (Abad et al. 2007b). Moreover, the temperatures in the fuel and air reactor are expected to be well above 1073 K; thus it can be assumed that the chemical reaction is the only resistance controlling the reaction of propane or ethane with the oxygen carrier at CLC conditions.

The effect of gas composition on the OC reactivity was analyzed using different hydrocarbon concentrations, but keeping the same oxygen consumption in all cases. Figure 5 shows the conversion versus time curves for the reduction and oxidation of the Cu-based oxygen carrier using a gas concentration of 2 vol% C$_3$H$_8$, 2.8 vol% C$_2$H$_6$ and 5 vol % CH$_4$ at 1073 K. It must be remembered that ethane and propane need more oxygen for combustion than CH$_4$.

\[
\begin{align*}
4 \text{CuO} + \text{CH}_4 & \rightarrow 4 \text{Cu} + 2 \text{H}_2\text{O} + \text{CO}_2 \quad (22) \\
7 \text{CuO} + \text{C}_2\text{H}_6 & \rightarrow 7 \text{Cu} + 3 \text{H}_2\text{O} + 2 \text{CO}_2 \quad (23) \\
10 \text{CuO} + \text{C}_3\text{H}_8 & \rightarrow 10 \text{Cu} + 4 \text{H}_2\text{O} + 3 \text{CO}_2 \quad (24)
\end{align*}
\]
The three LHC gases were very reactive, reaching full OC conversion in less than 1 minute both for reduction and oxidation reactions. Moreover, no important differences in reactivity can be seen between methane, ethane and propane.

3.3. Batch FB experiments

The batch FB experiments were carried out to investigate the effect of the presence of LHC, such as ethane or propane, in the fuel gas on the OC reactivity and bed agglomeration. Moreover, these tests allow us to know the gas product distribution during different reduction and oxidation periods and, therefore, to determine the operating conditions (temperature and residence time) that allow obtaining full combustion efficiencies without the presence of LHC in the flue gas of the FR. The concentration of hydrocarbons and their mixtures with methane used as fuel gas are shown in Table 3 and were calculated keeping the same oxygen consumption in all cases.

All the compositions were tested at two different temperatures (1073, 1153 K) and two reduction times (1 and 3 minutes) during several cycles, which corresponded to about 40 reduction/oxidation cycles with the same batch of OC. It must be mentioned that no agglomeration problems were detected at any time and experimental conditions. Indeed, a reference condition (25% CH₄ at 1073 and 1153 K) was repeated every 10 redox cycles to evaluate differences on reactivity. Similar results were obtained in all cases, indicating that the OC reactivity was roughly constant during the experimental tests.
As an example, Figure 6 shows the gas product distributions obtained with A, B and C compositions showed in Table 3 at 1073 and 1153 K and 3 minutes of reducing time. Full combustion of hydrocarbon was obtained initially, being CO\textsubscript{2} and H\textsubscript{2}O the only gas products. Only when most of the OC was reduced the CH\textsubscript{4} concentration increase, the CO\textsubscript{2} and H\textsubscript{2}O concentrations decrease, and the generation of CO and H\textsubscript{2} started. Only for C\textsubscript{3}H\textsubscript{8} at 1073 K, unburnt LHC at the end of reduction period were detected. In some cases, CO was detected during the inert period. This fact can be due to the solid-solid phase reaction between carbon formed during the reducing period and the oxygen present in the oxygen carrier as other authors found for Ni-based OC (Johansson et al. 2008). The CO and CO\textsubscript{2} that appeared during oxidation period corresponded to the final combustion of the carbon with the oxygen of the air.

It can be seen that, an increase in the fuel reactor temperature produced a decrease in the CH\textsubscript{4} and unburnt LHC concentrations. This effect was due to the higher oxygen carrier reactivity as a consequence of the dependence of the kinetic constant with the temperature. Similar results were found for the gas mixtures given in Table 3. The gas product distribution obtained with the mixture of methane with LHC (D and E) followed the same pattern although were quantitatively different. The analysis of the gas product distribution in the batch FB showed that the unburnt LHC concentration and carbon deposition tendency were higher for C\textsubscript{3}H\textsubscript{8} than for C\textsubscript{2}H\textsubscript{6} for the same operating conditions as the thermodynamic analysis predicted.
Figure 6 also shows the solid conversion evolution during the reduction period obtained from eq. 17. The final solid conversion increased as the reactor temperature increased because of the higher OC reactivity. During the full combustion period, i.e. combustion efficiency equal to 100%, the conversion of the OC is lower than 0.8. These OC conversions are easily attained in a CLC plant because for $\Delta X < 0.8$ no more than $\phi > 1.25$ are necessary for full combustion (Abad et al., 2007b).

It is remarkable that agglomeration or particle deactivation was never observed during the batch FB experiments, even when carbon accumulation was evident.

3.4. Experimental tests in the 500 W$_{th}$ CLC prototype

In this section combustion tests under continuous operation were conducted in the 500 W$_{th}$ CLC prototype described above. The total solids inventory in the system was $\approx$1.3 kg of OC. The inlet gas velocity in the fuel reactor was 0.14 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 7.0 and 10.5 kg/h, corresponding to oxygen carrier to fuel ratios, $\phi$, from 1.0 to 1.5 respectively. Several gas compositions, similar to those used in the batch FB, were chosen for these tests (see Table 4). Water was always introduced with the fuel gas 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 30 hours of operation with the same OC particles.
As an example, Figure 7 shows the evolution with time of the gas product distribution from the FR and the AR for experimental test C using C\textsubscript{3}H\textsubscript{8} and CH\textsubscript{4} as fuel. The temperature in the FR and AR were 1153 K and 1223 K respectively and the solids circulation rate was 9.3 kg/h, corresponding to a $\phi$ value of 1.3. Stable combustion was reached usually in less than 5 minutes. After this startup time, the outlet gas concentration and temperature were maintained uniform during the whole combustion time. As it can be seen, the gas outlet concentrations in FR shows full conversion of fuel (H\textsubscript{2} = 0 %, CO = 0 %, unburnt = 0 % and CO\textsubscript{2} $\approx$ 27.5 vol.% in dry basis). Gas concentrations were a bit lower than theoretically expected as a consequence of the dilution produced by N\textsubscript{2} coming from the loop seal, and mass balances were found to be accurate by using the measurements of the gas analyzers from the AR and FR. Full conversion of CH\textsubscript{4} and LHC was obtained in the FR. CO or CO\textsubscript{2} at the outlet the AR were not detected in this test, indicating the absence of carbon formation at relevant extension in the system.

**3.4.1 Effect of oxygen carrier to fuel ratio ($\phi$)**

To study the effect of the oxygen carrier to fuel ratio, $\phi$, on the gas combustion efficiency, several experiments at two temperatures were performed using different solid circulation rates and maintaining all the other experimental conditions constant.

The experimental data obtained after the tests gave the combustion efficiency, $\eta_c$, obtained at each operating condition (temperature, fuel gas composition, and solid
circulation rate), calculated according to the eq. 19. Figure 8 shows the effect of the oxygen carrier to fuel ratio, $\phi$, on the combustion efficiency for different hydrocarbons mixtures at two temperatures. An increase in $\phi$ produces an important increase in the combustion efficiency. Similar tendencies were obtained at both temperatures for the different gas mixtures of hydrocarbons, indicating a poor effect of the gas composition on the combustion efficiency. As it was previously shown, similar reactivities for the three LHC gases were found.

The FR temperature is an important operating parameter. Figure 8 also shows the effect of reactor temperature on the combustion efficiency for different fuel mixtures. An increase in the fuel reactor temperature produced an important increase in the combustion efficiency. This effect was due to the higher reaction rate of the oxygen carrier, as it was shown by the TGA analysis. Obviously, to obtain complete combustion of the fuel, lower $\phi$ values would be necessary working at higher FR temperatures. Full combustion efficiencies were obtained at 1153 K working with mixtures CH$_4$-LHC at $\phi$ values above 1.2. These good results display that working with natural gas or refinery gas in a CLC plant, the oxygen carrier/ fuel ratios required to reach full combustion would be the same as those working with pure methane.

The loss of combustion efficiency could be due to the CO, H$_2$, unburnt LHC, and CH$_4$ concentrations present at the outlet stream of the FR and to the CO$_2$ concentration at the outlet stream of the AR (coming from the FR as C deposited on the OC particles). Figure 9 shows the FR gas outlet compositions at different $\phi$ and fuel gas compositions. It can be seen that the amount of CO and H$_2$ increased as the oxygen carrier to fuel ratio
decreased for all fuel gas compositions, which could be explained by partial oxidation reactions of the fuel as the oxygen available for full combustion decreased (eq. 2). Considering that the H₂/CO ratios in the gas outlet of the FR are higher than 4.5 other simultaneous reactions as steam reforming (eq. 3), coke formation (eq. 9) and/or dehydrogenation (eq. 7) must been take place in the mechanism of LHC combustion.

It must be remarked that unburnt LHC concentrations at the outlet of the FR were never detected for any fuel gas compositions and φ values tested. However, the amount of CH₄ increased as the oxygen carrier to fuel ratio decreased. This behavior could be partially due to the less oxygen available for combustion, and by the role of the cracking reactions of the LHC (eq. 8) in the combustion mechanism of ethane and propane.

Similar gas outlet compositions were measured for mixtures of CH₄ – C₂H₆ or CH₄ – C₃H₈ indicating similar behavior of these LHC in the CLC process. It must be pointed out that high CO, H₂ and CH₄ concentrations are measured working at low temperature (1073 K) and φ ratios (< 1.4). The FR gas outlet composition working at high temperature (1153 k) or high φ (> 1.5) are composed only of CO₂ + H₂O since full combustion efficiencies were measured at this operation conditions in the 500 Wₑ CLC prototype.

3.4.2 Carbon formation

The carbon formation process was also analyzed during continuous operation in the prototype. The carbon formed on the OC particles in the FR could be transferred to the
AR and burnt giving CO and/or CO$_2$. CO was never detected at the outlet of the AR. Nevertheless in some cases (working at low FR temperature), CO$_2$ was detected in the gas outlet of the AR, indicating some carbon formation in the FR. However, neither OC deactivation nor agglomeration was detected during operation.

Figure 10 shows the effect of the oxygen to fuel ratio, $\phi$, on the carbon formation, which is expressed as the ratio of carbon generated (measured as CO+CO$_2$ at the AR outlet) to total C inlet in the fuel gas for the different fuel mixtures. It can be seen that the presence of LHC favored carbon formation in comparison to pure CH$_4$ (Adánez et al., 2006). However this effect is reduced as the temperature or the $\phi$ value increase. The carbon formation is negligible at 1153 K for all gas mixtures tested independently of the $\phi$ value used. It can be concluded that to operate in avoidance of carbon deposition in the CLC plant is necessary to work at $\phi$ values > 1.5 at 1073K or FR temperatures > 1153 K.

Although OC deactivation or agglomeration were never detected during operation with carbon formation, the loss of CO$_2$ capture efficiency due to the carbon formed is an important issue that forces to avoid operation of the CLC plant in these conditions.


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 suitable fuels for this type of systems.
The concerns about the presence of these LHC in the fuel gas is related with the reactivity of the OC with respect to these LHC, and their effect on CO$_2$ 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 because of changes on density and compressibility properties with respect to pure CO$_2$ (Sass et al., 2005). However, the tolerance limits of hydrocarbons in the CO$_2$ stream is not as restrictive as other impurities, and values <5 vol% would be admissible (Fout, 2008).

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 fuel, this would not be necessary since experimental tests in the 500 W$_{th}$ CLC plant using a Cu-based OC have demonstrated that full conversion of CH$_4$ and mixtures CH$_4$ - LHC can be easily reached working at $\phi$ values above 1.5 at 1073 K and 1.2 at 1153 K.

5. Conclusions

The effect on the combustion efficiency of the presence of light hydrocarbons, ethane and propane, in the feeding gas of a 500 W$_{th}$ CLC prototype has been analyzed using a Cu-based oxygen carrier prepared by impregnation. Moreover, oxygen carrier reactivity, agglomeration and carbon formation have been studied in different facilities.
Reactivity tests in TGA showed that OC reactivity of methane, ethane and propane are similar. 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 at 1073K – 1153K without agglomeration or deactivation problems.

The combustion of hydrocarbons was also tested in a 500 Wth CLC prototype for 30 hours of continuous operation with the same OC at 1073K and 1153K. Agglomeration or deactivation of the oxygen carrier was never observed. The influence on the combustion efficiency of the temperature, the solid circulation flow rate, and fuel gas composition was analyzed. Unburnt hydrocarbons were never detected at any experimental conditions. Carbon formation could be avoided working at 1153 K or at $\phi$ values higher than 1.5 at 1073 K. To reach full combustion efficiencies an oxygen carrier to fuel ratio higher than 1.2 at 1153 K or 1.5 at 1073 K were necessary.

According to the results found in this work, it can be concluded that the Cu-based oxygen carrier prepared by impregnation could be used in a CLC plant for combustion of natural gas in the presence of LHC. Moreover, no special measures should be adopted due to the presence of light hydrocarbons in the fuel gas of a CLC plant.

**Acknowledgements**

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REFERENCES


Figure Captions

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Figure 5. Effect of fuel gas composition on OC reactivity with 2 vol% C$_3$H$_8$, 2.8 vol% C$_2$H$_6$ and 5 vol% CH$_4$. All tests used 30% H$_2$O for the reduction. Air (100 vol%) was used for the oxidation reaction. T = 1073K.

Figure 6. Gas product distribution (dry basis) during oxygen carrier reduction and oxidation in batch FB with (a) 25 vol% CH$_4$, (b) 14.3 vol% C$_2$H$_6$ and (c) 10 vol% C$_3$H$_8$ at 1073 and 1153 K. H$_2$O concentration as measured in a FTIR analyzer.

Figure 7. Gas product distribution obtained at the outlet of AR and FR during a typical test in the 500 W$_{th}$ CLC prototype. Gas composition C in Table 4: 20 vol% CH$_4$, 3.8 vol% C$_3$H$_8$, 15 vol% H$_2$O; T$_{FR}$= 1153 K; T$_{AR}$= 1223 K; $\phi$ = 1.3.

Figure 8. Effect of the presence of LHC in the fuel gas on the combustion efficiency in the 500 W$_{th}$ CLC prototype for different oxygen carrier to fuel ratios, $\phi$, and FR temperatures. Fuel gas composition given in Table 4: (□□□□, □□□□) CH$_4$, (△△△△, △△△△) CH$_4$+C$_2$H$_6$, (○○○○, ○○○○) CH$_4$+C$_3$H$_8$.

Figure 9. Effect of the fuel gas composition on the CO, H$_2$, CH$_4$ and unburnt LHC at the FR outlet in the 500 W$_{th}$ CLC prototype at different oxygen carrier to fuel ratios, $\phi$. Inlet fuel gas composition given in Table 4. T$_{FR}$ = 1073 K.

Figure 10. Carbon formation as a function of $\phi$ for different fuel gas compositions in the 500 W$_{th}$ CLC prototype. T$_{FR}$ = 1073 K (empty symbols) and T$_{FR}$ = 1153 K (filled symbols). Fuel gas composition given in Table 4: (□□□□, □□□□) CH$_4$, (△△△△, △△△△) CH$_4$+C$_2$H$_6$, (○○○○, ○○○○) CH$_4$+C$_3$H$_8$. 
Tables

**Table 1.** High temperature reactions for light hydrocarbons in presence of CuO-Cu.

**Table 2.** Main characteristics of the copper based oxygen carrier.

**Table 3.** Hydrocarbon concentrations in the tests carried out in the batch fluidized bed facility. N$_2$ was used for balance.

**Table 4.** Composition of the feeding gas in the experiments carried out in the 500 W$_{th}$ CLC prototype.
Table 1. High temperature reactions for light hydrocarbons in presence of CuO-Cu.

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reaction Equation</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Main reactions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>combustion</td>
<td>( C_nH_{2n+2} + (3n+1) CuO \rightarrow (3n+1) Cu + n CO_2 + (n+1) H_2O )</td>
<td>(1)</td>
</tr>
<tr>
<td>partial oxidation</td>
<td>( C_nH_{2n+2} + n CuO \rightarrow n Cu + n CO + (n+1) H_2 )</td>
<td>(2)</td>
</tr>
<tr>
<td><strong>Reactions of the gas main components</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>steam reforming</td>
<td>( C_nH_{2n+2} + n H_2O \rightarrow n CO + (2n+1) H_2 )</td>
<td>(3)</td>
</tr>
<tr>
<td>dry reforming</td>
<td>( C_nH_{2n+2} + n CO_2 \rightarrow 2n CO + (n+1) H_2 )</td>
<td>(4)</td>
</tr>
<tr>
<td>water-gas shift</td>
<td>( CO + H_2O \leftrightarrow CO_2 + H_2 )</td>
<td>(5)</td>
</tr>
<tr>
<td>methanation</td>
<td>( CO + 3 H_2 \leftrightarrow CH_4 + H_2O )</td>
<td>(6)</td>
</tr>
<tr>
<td>dehydrogenation</td>
<td>( C_nH_{2n+2} \leftrightarrow C_nH_{2n} + H_2 )</td>
<td>(7)</td>
</tr>
<tr>
<td>Cracking</td>
<td>( C_nH_{2n+2} \leftrightarrow C_{n-1}H_{2(n-1)} + CH_4 )</td>
<td>(8)</td>
</tr>
<tr>
<td>coke formation</td>
<td>( C_nH_{2n+2} \leftrightarrow n C + (n+1) H_2 )</td>
<td>(9)</td>
</tr>
<tr>
<td>coke formation</td>
<td>( CO + H_2 \leftrightarrow C + H_2O )</td>
<td>(10)</td>
</tr>
<tr>
<td>Boudouard</td>
<td>( 2 CO \leftrightarrow C + CO_2 )</td>
<td>(11)</td>
</tr>
</tbody>
</table>

Reaction of gas products with CuO
\[ C_nH_{2n} + 3n \text{CuO} \rightarrow 3n \text{Cu} + n \text{CO}_2 + n \text{H}_2\text{O} \] 
\[ \text{(12)} \]

\[ \text{CO} + \text{CuO} \leftrightarrow \text{Cu} + \text{CO}_2 \] 
\[ \text{(13)} \]

\[ \text{H}_2 + \text{CuO} \leftrightarrow \text{Cu} + \text{H}_2\text{O} \] 
\[ \text{(14)} \]

\[ \text{C} + \text{CuO} \leftrightarrow \text{CO} + \text{Cu} \] 
\[ \text{(15)} \]

\[ n \text{ = number of carbon atoms of the hydrocarbon} \]
Table 2. Main characteristics of the copper based oxygen carrier.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO content, $w_o$ (wt%)</td>
<td>14</td>
</tr>
<tr>
<td>Particle size (mm)</td>
<td>0.3-0.5</td>
</tr>
<tr>
<td>Particle density (g/cm$^3$)</td>
<td>1.6</td>
</tr>
<tr>
<td>Mechanical strength (N)</td>
<td>2.4</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>50</td>
</tr>
<tr>
<td>Specific surface area BET (m$^2$/g)</td>
<td>77</td>
</tr>
<tr>
<td>Oxygen transport capacity $R_{o,OC}$ (%)</td>
<td>2.8</td>
</tr>
</tbody>
</table>
**Table 3.** Hydrocarbon concentrations in the tests carried out in the batch fluidized bed facility. N$_2$ was used for balance.

<table>
<thead>
<tr>
<th>Composition</th>
<th>CH$_4$ (vol %)</th>
<th>C$_2$H$_6$ (vol %)</th>
<th>C$_3$H$_8$ (vol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>14.3</td>
<td>14.3</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>15</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>15</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>
Table 4. Composition of the feeding gas in the experiments carried out in the 500 W<sub>th</sub> CLC prototype.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Gas fed (vol%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>A</td>
<td>30</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
</tr>
<tr>
<td>C</td>
<td>20</td>
</tr>
</tbody>
</table>

<sup>a</sup>N<sub>2</sub> was used for balance
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