Chemical Looping Combustion of liquid fossil fuels in a 1 kW_{th} unit using a Fe-based oxygen carrier

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ABSTRACT

The integrated use of low-value hydrocarbons from the refining of crude oil under Chemical Looping Combustion (CLC) conditions can satisfy the demands of heat and steam of the refining process itself while at the same time reducing CO₂ emissions up to 50% in oil refineries. This work evaluated the use of three different fossil liquid fuels, i.e., diesel, mineral lubricant oil and synthetic lubricant oil in a 1 kW_{th} CLC continuous unit working with a Fe-based oxygen carrier prepared by impregnation method. The effect of key parameters of the CLC process behavior was studied with the same batch of oxygen carrier particles for a total of 150 operation hours. With regard to the results obtained, every fuel tested was able to achieve 90% combustion efficiency being synthetic lubricant oil the most reactive fuel studied. Hydrocarbon reactivity seems to depend on the nature of the chemical bonds, being higher for alkenes (synthetic lubricant oil) than for alkanes (diesel and mineral lubricant oil). CH₄ was revealed as a relatively stable intermediate combustion product for these liquid fuels. Therefore,

oxygen carrier's reactivity towards this gas becomes crucial for the overall conversion. The characterization carried out to the oxygen carrier after operation revealed no evidence of changes derived from the sulphur or impurities present in the fuel. Therefore, the Fe-based material herein used seems to be suitable for conversion of fossil liquid fuels.

Keywords: CO₂ capture; liquid fossil fuels, chemical looping combustion; oxygen carrier.

1. Introduction

The international commitment to limit global temperature increase to as far below 1.5 degrees Celsius above pre-industrial levels will require considerable and steady reductions in global emissions. The most economical way of reaching this reduction requires a significant investment in a portfolio of technologies, in which the use of fossil fuels and biomass with Carbon Capture and Storage (CCS) are believed to play an important role [1]. Cost saving is key focus of CCS technology improvement, hence important steps have been promoted in recent years to develop new cost effective CCS technologies. Chemical Looping Combustion (CLC) may be a prime example since it is recognized as one of the most economical technology for CO₂ capture [2, 3]. CLC is a combustion method based on the transfer of oxygen from air to fuel by means of a solid oxygen carrier. The oxygen carrier circulates between two interconnected fluidized beds where it is continuously reduced in the fuel reactor (FR) and oxidized in the air reactor (AR). Doing so, direct contact between air and fuel is avoided and as a result a flue gas stream containing only CO₂ and H₂O is produced.

At the initial stages of the investigation most of the work in CLC was focused on the implementation of gaseous and solid fuels [4] due to their simple handling and currently more than 7000 hours of operational experience have been reached [5]. But CLC offers flexibility and more possibilities as it can also be applied to liquid fuels.

Oil refineries produce a broad range of outputs from naphtha to low-value products such as lubricants, heavy fuel oil or asphalt. Those heavy hydrocarbons could be great candidates to be used as fuels in CLC to satisfy the demands of heat and steam of the refining process itself. In this way, CO₂ emissions at refineries could be reduced since furnaces, boilers and other utilities to produce electricity and steam are key sources of CO₂, which amount to 50% of a refinery's emissions even at highly efficient installations [6]. On a global scale, refineries rise to the third position in stationary CO₂ sources, proceeded only by the power and cement sectors. Currently, 638 oil refinery plants are in operation, which emit $798 \cdot 10^6$ metric ton CO₂ per year. In this context, the implementation of a CCS technology, such as the CLC, would lead to a significant reduction in CO₂ emissions since refineries are responsible for 4% of the global CO₂ emissions [7].

Due to the ever-increasing interest stirred by the use of fossil liquid fuels under CLC conditions, several works have been published in recent years, dealing with the use of liquid fuels such as bitumen, dodecane, kerosene and fuel oil [8, 9]. Among these publications the work in continuous CLC units undertaken by Moldenhauer et al. [10-14] stands out. First, they studied the behavior of a nickel based oxygen carrier working with sulphur free kerosene as fuel in a continuous 300 W_{th} CLC unit [10]. Then, two oxygen carriers based on manganese and copper were tested under CLC and CLOU (Chemical Looping Oxygen Uncoupling) conditions in the same reactor working also with sulphur free kerosene. It was the first time that the CLOU process was successfully

demonstrated with liquid fuels [11]. Further, the mineral ilmenite was tested in the continuous 300 W_{th} CLC unit working with sulphur-free kerosene and kerosene containing 0.57 mass% of sulphur [12]. In this work, it was observed that the reactivity of the oxygen carrier even improved thanks to the presence of sulphur in the fuel. Later, they built a 10 kW_{th} CLC unit, in which they used fuel oil as fuel. The proof of concept was shown with a calcium manganite-based oxygen carrier and then long term experiments were done with ilmenite [13]. Finally, they performed combustion tests with highly viscous vacuum residue, a fuel oil, and blends of those in the 10 kW_{th} CLC unit with ilmenite and a calcium manganite-based oxygen carrier. Successful injection of different heavy liquid fuel blends and stable operation was achieved [14].

The choice of a suitable oxygen carrier is a priority issue for the proper functioning of the CLC process. In recent years, significant efforts have been made to develop oxygen carriers with new and improved properties. As a result, currently more than a thousand materials have been tested in CLC units ranging from 300 W to 1 MW [5]. The choice of iron based oxygen carriers for chemical looping processes offers numerous advantages over other metal oxides, such as their low cost and a low environmental impact. In previous works, these oxygen carriers exhibited high reactivity under atmospheric [15-17] and pressurized conditions [18]. They showed high reactivity towards CO and H₂ and there was no thermodynamic barrier that would inhibit full conversion of CH₄, CO and H₂ when the oxygen carrier was reduced from hematite (Fe₂O₃) to magnetite (Fe₃O₄). In addition, if alumina is used as a support, FeAl₂O₄ can be found as crystalline phase. The system FeAl₂O₄ / Fe₂O₃.Al₂O₃ has an oxygen transport capacity that is three times higher than that of the system Fe₂O₃ / Fe₃O₄, while still being capable of fully converting CH₄, CO and H₂ into CO₂ and H₂O [19-22]. Also,

iron based oxygen carriers did not encourage carbon deposition [23] and exhibited a low tendency to be deactivated in the presence of sulphurous compounds [22, 24, 25].

This work analyzes the employability of three different fossil liquid fuels, i.e., diesel, mineral lubricant oil and synthetic lubricant oil, in a continuous CLC process. It can be seen as an intermediate step to the employment of heavy liquid fuels. An iron based material developed by ICB-CSIC previously used for the combustion of methane, sour gas and acid gas in a continuous CLC unit was selected as oxygen carrier. Moreover, the influence of sulphur and impurities present in lubricant oils on the possible deactivation of the oxygen carrier was studied via a comprehensive characterization of the solid material.

2. Experimental

2.1 Fuels

Diesel, mineral lubricant oil and synthetic lubricant oil type 15W40 were selected as liquid fuels to be tested under CLC conditions. Diesel and mineral lubricant oils are a mixture of naturally occurring hydrocarbons, which lack a uniform molecular structure, and their characteristics vary greatly with quality, source of crude oil and oil refining process. In contrast, synthetic lubricant oils are practically pure substances made from ethylene with a uniform molecular structure.

Table 1 shows the main properties of the fuels. Ultimate analysis was determined in a Thermoflash 1112 apparatus and standard methods were used for determining both the higher heating value (ISO 1928) and the ash content (ASTM D482). The metallic content in the ashes was determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) in a Spectroblue apparatus (Ametec) after preparing the samples according to a standard method (ASTM D3682-92).

Diesel contains neither metals nor sulphur. Conversely, lubricant oils contain sulphur and ashes coming from the additives used during its manufacture. Additives are chemicals such as detergents, dispersants or corrosion inhibitors, which provide improved properties to oil but also add traces of heavy metals or impurities to it. The CLC process can be affected by the presence of these compounds in two ways. From an environmental perspective, metals or impurities could be emitted at the outlet of the air reactor, which can lead to problems with the fulfillment of the gaseous emissions legislation, or they could be emitted at the outlet of the fuel reactor, which would affect the CO₂ quality. Regarding operational problems, metals or impurities can react with the oxygen carrier causing its poisoning and therefore a reduction in its reactivity. It can be seen in Table 1 that Mg, Zn and P were the main impurities in mineral oil, while synthetic oil contained mostly Ca and Zn [26].

The distillation curves for each fuel were obtained using the standard determination of distillation characteristics at atmospheric pressure for petroleum products (ISO 3405:2011), see Fig. 1. The shapes of the distillation curves supported the fact that the composition of the synthetic oil is much more homogenous than the ones for diesel and mineral lubricant oil. These last fuels followed a continuous growing tendency with temperature, since they are composed of a wide variety of hydrocarbons with different volatilities. In contrast, synthetic lubricant oil showed a two-step curve. First an increasing trend where only 30% of the sample was recovered. Above 375 °C the tendency became vertical, which suggest the presence of hydrocarbons with uniform structure leading to similar boiling points.

To facilitate calculations, average empirical formulas for each fuel were assumed. Diesel and lubricant oils are a complex mixture of low and high molecular weight aliphatic and aromatic hydrocarbons, i.e., C₇-C₂₀ for diesel and C₁₁-C₂₅ for lubricant

oils. According to the ultimate analysis, the carbon content and the H:C molar ratio (1.9:1) are similar for the different fuels. Therefore, hydrocarbons corresponding approximately with the 50% of the distillation fraction and that fit the H:C ratio given by the ultimate analysis were considered, being $C_{15}H_{28}$ for diesel, $C_{19}H_{38}$ for mineral oil, and $C_{23}H_{46}$ for synthetic oil.

2.2 Oxygen carrier

In the present work an oxygen carrier based on Fe was used [21]. The oxygen carrier was prepared impregnating the support (γ - Al_2O_3) heated at 353 K in a planetary mixer with a saturated iron nitrate solution [$Fe(NO_3)_3 \cdot 9H_2O$] at 333–353 K (3.8 M). The material resulting from the impregnation was calcined at 823 K in air atmosphere for 30 min to decompose the impregnated metal nitrate into the metal oxide. After the second impregnation, the oxygen carrier was sintered in a furnace at 1223 K for 1 h. Its designation is Fe20- γ Al, i.e., 20 wt% Fe_2O_3 on a support of γ - Al_2O_3 . Previous works showed good results with this oxygen carrier operating in continuous units with gaseous fuels [22, 24, 25] and ethanol [27].

The oxygen carrier was physically and chemically characterized before and after its use in the continuous unit, and the main properties are shown in Table 2. The Fe_2O_3 content was determined by ICP-AES analysis. Crushing strength was obtained by standard method in a Shimpo FGN-5X apparatus. Apparent density was determined by Helium pycnometry in a Micrometrics AccuPyc II 1340. The porosity was measured by Hg intrusion in a Quantachrome PoreMaster 33. Specific surface area was calculated following the Brunauer-Emmett-Teller (BET) method in a Micrometrics ASAP-2020. Crystalline phases were identified by powder X-ray diffraction in a Bruker AXS D8ADVANCE equipped with a X-ray source with a Cu anode working at 40 kV and 40

mA and an energy-dispersive one-dimensional detector. In addition, used samples were also characterized by scanning electron microscopy (SEM) in an ISI DS-130 coupled to an ultra-thin window PGT Prism detector for energy dispersive X-ray (EDX) analysis to investigate the microstructure of the particles, and possible heavy metal deposition and changes in the active phase.

The oxygen transport capacity of the material, R_{OC} , was calculated by Eq. 1.

$$R_{OC} = x_{MeO} R_O \quad (1)$$

where x_{MeO} is the mass fraction of metal oxide in the oxygen carrier. The oxygen transport capability of the redox reaction, $Fe_2O_3 \cdot Al_2O_3 / FeAl_2O_4$, was considered to be $R_O = 10\%$.

2.3 CLC facility

Fig. 2 shows an outline of the 1 kW_{th} experimental facility used for the combustion tests. The CLC facility consists of two interconnected fluidized bed reactors, referred to as air (AR) and fuel (FR) reactors, a riser to convey solids from AR to FR, a loop seal to prevent gas mixing, a cyclone and a valve to manage the solid circulation flow fed to the FR. The liquid fuel was supplied by a peristaltic pump, and fully evaporated before being fed to the FR. The evaporator furnace was kept at a fixed temperature of 450 °C, to be sure that all the fuel was fed in gaseous form. In order to assess complete fuel feeding, the evaporator temperature was raised up to 800 °C and flushed with air after daily operation to check possible carbon formation. CO₂ was never detected at the outlet of the FR, which demonstrated that liquid fuel was properly fed.

The FR (1) was a bubbling fluidized bed with conical shape (0.026 m i.d. at the bottom and 0.085 m i.d. in the upper part) with a bed height of 0.15 m. The FR was conic to prevent solids elutriation as a consequence of the gas expansion taking place during

liquid fuel combustion. Reduced particles flow to the AR (3) through a U-shaped fluidized-bed loop seal (2) to be again oxidized. The AR was also a bubbling fluidized bed (0.052 m. i.d.) with a bed height of 0.15 m.

Gas composition outlet streams from the AR and FR were continuously measured by online gas analyzers. CO₂, CO and CH₄ from the FR were measured by a non-dispersive infrared analyzer (Maihak S710), while the concentration of H₂ was determined in a thermal conductivity analyzer (Maihak S710/THERMOR). A gas chromatograph (Clarus 580 Arnel 4016 PPc and Haye Sep columns) was located at the outlet of the FR to quantify unburned hydrocarbons up to C₁₀. CO₂ and O₂ at the outlet of the AR were measured by a non-dispersive infrared analyzer (Siemens Ultramat 22P) and a paramagnetic analyzer (Siemens/Oxymat 5E), respectively.

2.4. Data analysis

To assess the performance of the combustion process it is important to know the reactions that can take place, both in FR and AR during the reduction and oxidation periods for each fuel. Global reactions schemes to describe hydrocarbon combustion are complex and the knowledge is very scarce [28]. Moreover, under CLC conditions the reactions taking place can differ considerably from traditional combustion.

Fuentes et al. [29] investigated the composition of the gases evolved from the thermal decomposition of different lubricant oils in a batch laboratory scale tubular reactor. They found that the volatile compounds were mainly composed of CH₄, CO, C₂H₄ and C₃H₆. Accordingly, it was considered that the reaction mechanism occurred via fuel decomposition and later combustion of these gaseous products. Carbon deposition is highly unwanted, since deposited carbon might leak into the AR, where it will be burnt with oxygen, which in turn decreases the CO₂ capture efficiency.

Presented below are the reactions that can take place in FR and AR with the fuels and

the oxygen carrier considered. The fuel C_nH_m , in gaseous phase, can react directly with the oxygen carrier and may be fully converted to CO_2 and H_2O according to reaction R.1. If the contact between the gaseous and solid phases is not good enough, there may exist reducing zones in the FR, where partial oxidation of the fuel takes place according to reaction R.2. There is also a possibility of thermal decomposition of the liquid fuel (reaction R.3). In this case, gaseous products generated would react with the oxygen carrier (reaction R.4) and carbon would be gasified with steam and CO_2 produced during combustion (reactions R.5 and R.6). Additionally, Water Gas Shift equilibrium must be always considered (reaction R.7).

The regeneration of the oxygen carrier takes place in the air reactor according to reaction R.8. If carbon formation occurs, it will be burnt with air (reaction R.9) which decreases CO_2 capture efficiency.

Fuel reactor

Air reactor:

To assess the performance of the CLC process with liquid fuels, the combustion efficiency (η_c) and the oxygen carrier to fuel molar ratio (ϕ) were selected as key parameters. η_c was defined as the ratio between the oxygen consumed by the gases measured at the outlet of the FR and the oxygen required to fully convert the fuel to CO_2 and H_2O , according to Equation 2. Partially oxidized hydrocarbons, i.e., $\text{C}_x\text{H}_y\text{O}_z$, at the FR outlet stream were assumed negligible for calculations. As η_c reaches the value 1, complete combustion of the fuel is achieved in FR.

$$\eta_c = \frac{(2x_{\text{CO}_2} + x_{\text{CO}} + x_{\text{H}_2\text{O}})F_{\text{out}}}{(2n + m/2)x_{\text{C}_n\text{H}_m}F_{\text{in}}} \quad (2)$$

F_{in} and F_{out} are the inlet and outlet molar gas flow rates, and x_i is the molar fraction of gas i . As the gas streams are determined after water condensation, F_{out} was calculated through an N_2 balance. For that, N_2 flow fed into the FR as fluidizing agent plus the flow derived from the loop-seal branch to the FR were considered equal to the N_2 stream obtained at the outlet of the FR.

The oxygen carrier to fuel molar ratio, ϕ , was calculated as the ratio between the oxygen available in the oxygen carrier in its oxidized form and the oxygen required to fulfill complete fuel combustion, as described in Equation 3,

$$\phi = \frac{F_{\text{Fe}_2\text{O}_3}}{b \cdot F_{\text{fuel}}} \quad (3)$$

$F_{\text{Fe}_2\text{O}_3}$ is the iron oxide molar flow rate, F_{fuel} is the molar flow rate of the fuel, and b is the stoichiometric coefficient for each fuel (see reaction R.1). In this work, the redox pair $\text{Fe}_2\text{O}_3/\text{FeAl}_2\text{O}_4$ was considered, which is the typically assumed for this type of

oxygen carriers prepared by impregnation. When ϕ is equal to 1, the oxygen transported by the oxygen carrier equals the oxygen required to achieve complete fuel conversion to CO_2 and H_2O .

3. Results and discussion

During the experimental campaign carried out in the 1 kW_{th} unit a total of 150 hours of successful operation at hot conditions were accomplished with one batch of particles of Fe₂O₃- γ -Al₂O₃. It has to be mentioned that this batch of particles had already been tested in the same unit with ethanol as fuel during 36 hours of operation [27].

The operating conditions applied during the tests are summarized in Table 3. Several temperatures, fuel inputs and solid flow rates were established in order to study the CLC process in a wide range of operating conditions. The total solids inventory was kept constant at a value of 1.8 kg, out of which 0.8 kg were in the FR. For each fuel, the effect of oxygen carrier to fuel ratio and fuel reactor temperature on gas product distribution and combustion efficiency were analyzed. In addition, long tests were carried out with synthetic oil, up to 98 hours of combustion operation, to analyze the possible interaction between the oxygen carrier and the impurities existing in the synthetic oil.

Carbon formation in FR was assessed through CO_2 concentrations measured at the outlet of the AR. Since CO_2 was never detected and considering the lower detection limit of the analyzer (0.1 vol.%), CO_2 capture efficiencies above 98% were reached in all CLC tests. In addition, mass balances of carbon, hydrogen and oxygen were carried out for each test based on the gas concentrations measured by the online gas analyzers and the gas chromatograph. In most tests, the balance was nearly closed, with deviations lower than 5%.

Fig. 3 shows the gas product distributions obtained from the FR outlet stream as a function of the oxygen carrier to fuel molar ratio, ϕ , at 900 °C for the three liquid fuels. CO, H₂ and CH₄ were the major unburnt gaseous compounds detected. The amount of hydrocarbons C₂-C₁₀ quantified by gas chromatography was always below 0.2 vol.%. Hence, almost complete conversion of the fuel was achieved. For values of ϕ above 3, fuel was almost completely converted into CO₂ and H₂O with a minor presence of CH₄ and CO. As the value of ϕ decreased, the amount of unburned products increased due to a lower amount of oxygen available for combustion. The concentration of the unburned products was highest for the lowest value of ϕ investigated, i.e., 1.

Among unburned products, CO was in most cases found in the highest amount due to thermal or catalytic decomposition of the fuel (reaction R.3), partial combustion of hydrocarbons with the oxygen carrier (reaction R.4) or that produced by means of the Water Gas Shift reaction (reaction R.7). The concentration of CH₄ for $\phi < 3$ remained constant at values ≈ 5 vol.% within the conditions studied. For $\phi > 3$, CH₄ concentration held constant for synthetic oil but decreased at values close to zero working with diesel and mineral oil. This finding supports the idea that CH₄ could be a stable intermediate product during fuel conversion from hydrocarbons to CO₂, which agrees with the observation made by Moldenhauer et al. [12]. Also, it was proven in preceding works working with this oxygen carrier, Fe₂O₃- γ -Al₂O₃, that CH₄ reforming and partial oxidation reactions were slower than the ones for CO and H₂ [21].

From the experimental data, combustion efficiency was calculated according to Equation 2. Fig. 4 shows the combustion efficiency as a function of ϕ for the three different liquid fossil fuels tested. In addition, data corresponding to ethanol combustion were also included for comparison purposes [27].

According to Fig. 4, ethanol, diesel and mineral lubricant oil followed the same trend and combustion efficiencies over 95% were achieved for values of ϕ about 4. The behavior of synthetic oil stands out as it was able to achieve combustion efficiencies over 90% at fairly low ϕ values, i.e., $\phi < 1.6$, whereas at higher ϕ values, only slight improvements were achieved due to the relatively constant fraction of CH_4 as the main unburned compound.

Considering that the main challenge to obtain full combustion is the conversion of CH_4 , the increase of the fuel reactor temperature above 900 °C would be a recommendable solution for the use of these types of liquid fuels with Fe-based oxygen carriers [22].

In an effort to gain a deeper understanding of the results obtained, the molecular structure of the fuels tested was taken into consideration. Diesel and mineral oil are composed of about 60-75% saturated hydrocarbons (primarily paraffins including n, iso, and cycloparaffins) and 25-40% aromatic hydrocarbons (naphthalenes and alkylbenzenes). On the other hand, synthetic lubricant oils consist mostly of polyalphaolefins, which are linear hydrocarbons with one double bond in one end of the molecule. Polyalphaolefins belong to the group of alkenes [30].

In terms of reactivity, that depends on the nature of the chemical bonds existing in the fuel. Alkanes are the less reactive because their molecules are constituted solely by single chemical bonds, which are particularly strong. Alkenes are much more reactive than alkanes due to the presence of a double chemical bond in its structure, which allows additional reactions to occur [31]. Thus, the behavior observed with the synthetic oil could be attributed to its molecular structure. Considering the results shown in Fig. 4, it is seen how the order of reactivities of the different hydrocarbons

described above is indeed fulfilled. Combustion efficiencies for values of $\phi < 3$ were higher for alkenes, i.e., synthetic lubricant oil, than for alkanes, i.e., diesel and mineral lubricant oil.

In order to explain the behavior observed for values of ϕ larger than 3, it must be taken into consideration the reactivity of the intermediate oxidation products, generated through thermal and catalytic decomposition, with the oxygen carrier. This reactivity is likely to have a great influence in the overall efficiency of the combustion process. For values of ϕ above 3, more CH_4 remained unreacted when processing synthetic oil, which leads to lower combustion efficiency values in comparison with other fuels such as ethanol, diesel and mineral oil.

Other relevant aspects regarding fuel conversion in presence of Fe-based oxygen carriers would be the intermediate compounds produced during fuel decomposition. It is well known that iron oxides, or even elemental Fe, catalyze heavy oil cracking [32]. In our tests, metallic Fe was never produced in the oxygen carrier because to reach high reduction degrees to FeO, and beyond to Fe, would be necessary to operate under very low solid circulation rates ($\phi < 1$), much lower than the used in this work. In addition, from a thermodynamic point of view, the presence of H_2O prevents the possibility to obtain so high reduction degree. In any case, no differences on catalytic decomposition of the liquid fuels used in this work can be inferred from the CLC tests carried out in this work.

3.1 Long term tests

To analyze the possible interaction between the oxygen carrier and the impurities present in the fuel, long term tests were carried out (50 h) at 900 °C. Synthetic lubricant oil was used as fuel because it has the largest content of impurities, i.e., ash and sulphur.

Fig. 3 shows the gas product distribution attained with the synthetic lubricant oil as a function of ϕ and with the operation hours with fuel feeding visible. Some operating conditions were repeated after several hours of operation to detect possible variations, out of the normal experimental deviations. However, no time-induced variations from the general trend of the combustion efficiency were observed. Hence, the performance of the oxygen carrier was not visibly affected by the presence of ash or sulphur in the synthetic lubricant oil. It must be considered that the H_2S concentration reached in the FR for a typical test would be ≈ 600 vppm, reaching 800 vppm in those tests at the maximum fuel inlet. In any case, a stable and reliable operation was achieved throughout the whole experimental work.

Earlier works have dealt with the effect of sulphur on the oxygen carrier in CLC conditions. Cabello et al. [22], who used the same batch of the oxygen carrier Fe2O₃- γ -Al₂O₃, found that the presence of 2000 vppm of H_2S in CH_4 had no effect on the combustion efficiency. This confirms the finding of the present study, in which oxygen carrier reactivity remained constant throughout the experimental work. Moldenhauer et al. [12], who used mineral ilmenite as oxygen carrier, conversely observed a clear increase in oxygen carrier reactivity as they fed sulphurous kerosene (0.57 mass% of sulphur). In that work, SO_2 emissions were only detected at the outlet of the fuel reactor.

3.2 Oxygen carrier characterization

A comprehensive characterization of the used material after the whole experimental campaign was carried out with the aim to analyze the influence of ash and sulphur present in the fuel on the reactivity and the microstructure of the oxygen carrier particles.

As showed in Table 2, the main physical and chemical properties of the oxygen carrier were maintained during operation except for the BET specific surface area. This behavior is usual in any oxygen carrier, where a high decrease in the specific surface area takes place during the first operating hours at high temperature. However, the variation of this property hardly affects the reaction rates of the CLC process.

In addition, reactivity tests were carried out in a thermogravimetric analyser. Fresh oxygen carrier and such that was used during the whole experimental campaign with ethanol (36 hours) and fossil fuels (150 hours), were subjected to successive redox cycles at 950 °C, atmospheric pressure, 15 vol.% CH₄ as reducing gas and pure air as oxidizing gas. Fig. 5 shows oxygen carrier conversion over time for both samples. These tests showed that the oxygen carrier reactivity was not visibly affected neither by the high number of operation hours, nor by ash or sulphur present in the fuels. These results were in accordance with the experimental data obtained in the continuous unit since no sign of activation or deactivation was observed. In addition, thermodynamic calculations previously done [24, 25] showed that it is not possible any interaction between sulphur and the compounds existing in the Fe-based oxygen carrier under combustion conditions. Iron sulfides are only thermodynamically possible at sub-stoichiometric conditions.

The microstructure of the particles and possible changes in the composition of the material were studied by scanning electronic microscopy (SEM) and X-ray analysis (EDX). Fig. 6 shows images of fresh and after used particles. Fresh particles exhibited the irregular shape characteristic of the alumina used as support. By contrast, used particles were rounded due to attrition in the circulating fluidized-bed.

To determine iron distribution and possible deposition of fuel impurities inside the particles, they were embedded in resin epoxy, cut and polished. Cross sections images

of a fresh and a used particle are shown. EDX profiles revealed that Fe distribution was homogeneous along the cross section in fresh particles with some iron deposited in the external part as a consequence of the manufacture method. In contrast, used particles presented several white spots distributed through the particle, which corresponded to zones with high iron content in EDX analyses. This means that some migration of the iron took place during long term operation. However, no consequences on the reactivity of the oxygen carrier were inferred, as it was above concluded from the TGA reactivity tests. In addition, negligible amounts of the fuel ash components or sulphur were detected by EDX inside the particles. It is worth mentioning that no agglomerated particles were observed in any of the SEM images taken, which is consistent with the good fluidization behavior exhibited by the material during operation.

4. Summary and Conclusions

Chemical looping combustion tests have been successfully carried out in a 1 kW_{th} CLC unit during 150 hours using a Fe-based oxygen carrier with three different liquid fossil fuels, i.e., diesel, mineral lubricant oil and synthetic lubricant oil.

Conversion of the different fuels tested and CO₂ capture efficiency are compared based on the gas product distribution obtained at the outlet of the fuel and air reactors, respectively. In addition, possible interaction of fuel ash components and sulphur with the oxygen carrier material was studied in a long-term test series. The oxygen carrier's reactivity as well as a set of physical properties was determined before and after the experiments.

The main conclusions obtained from this work were the following:

- The hydrocarbon structure, i.e. the type of chemical bond, of the fuel determines its reactivity. Alkenes are more reactive than alkanes.

- CH₄ is a relatively stable intermediate combustion product for liquid fuels and the oxygen carrier's reactivity towards CH₄ is crucial for the overall conversion.
- The Fe-based oxygen carrier material herein used is suitable for conversion of liquid fuels similar to the ones tested here. No evidence was found that this should be different for heavier fuels with more impurities, including sulphur.

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Captions of Tables.

Table 1. Properties of the selected fuels.

Table 2. Chemical and physical properties of the oxygen carrier.

Table 3. Operating conditions for the experiments conducted.

Captions of the Figures.

Fig. 1. Distillation curves of the selected fuels.

Fig. 2. Schematic diagram of the 1 kW_{th} unit.

Fig. 3. Effect of oxygen carrier to fuel ratio on gas product distribution including long term tests with synthetic oil. T_{FR}= 900 °C.

Fig. 4. Effect of oxygen carrier to fuel ratio on combustion efficiency. T_{FR}=900 °C.

Fig. 5. TGA reactivity test of fresh and used particles. Reducing gas composition: 15 vol.% CH₄ in N₂ . The oxidizing gas was air. T = 950 °C.

Fig. 6. SEM-EDX characterization of the fresh and used oxygen carrier particles. a) entire particles, b) cross section of the particles, and c) EDX line profiles along the cross sections.

Table 1. Properties of the selected fuels.

	Diesel	Mineral lubricant oil	Synthetic lubricant oil
Ultimate analysis, wt. %			
C	86.53	84.92	85.1
H	13.70	13.67	13.6
N	0	0.25	0.5
S	0	0.95	0.7
Higher heating value, kJ/kg	45019	45823	44693
Ash content, wt. %	<0.01	0.45	1.05
Ash composition, wt. %			
Mg		18.37	0.02
Ca		2.49	31.33
Zn		14.93	22.09
Ba		0.15	0.13
Pb		0.03	0.57
P		13.78	6.78
S	<15 ppm	3.84	5.56
Distillation curves			
5% distilled, °C	150	225	230
95% distilled, °C	350	395	395

Table 2. Chemical and physical properties of the oxygen carrier.

		Fresh	After operation*
Particle size	μm	100 - 300	100 - 300
Fe_2O_3 content	wt. %	20.0	20.0
Oxygen transport capacity, R_{OC}	wt. %	2.0	2.0
Crushing strength	N	1.5	1.1
Apparent density	kg/m^3	3950	4036
Porosity	%	50.5	49.8
BET Specific surface area	m^2/g	39.1	5.1
Phases detected by XRD		$\text{Fe}_2\text{O}_3, \alpha\text{-Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3, \alpha\text{-Al}_2\text{O}_3$

* 36 h operation with ethanol and 150 h with fossil fuels.

Table 3. Operating conditions for the experiments conducted.

		Diesel	Mineral lubricant oil	Synthetic lubricant oil
Fuel reactor temperature	°C	800-900	900	800-900
Air reactor temperature	°C	900	900	900
Fuel input	W_{th}	254-776	447-521	365-528
Fuel flow	g/h	20-62	36-42	29-43
Solid flow rate (circulation)	kg/h	5-20	8-29	6-23
Oxygen carrier to fuel ratio, ϕ	-	1.0-4.1	1.3-4.6	1.2-4.5
Fuel operation time	h	36	16	98

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