**Development of $(\text{Mn}_{0.77}\text{Fe}_{0.23})_2\text{O}_3$ Particles as an Oxygen Carrier for Coal
Combustion with CO_2 capture via *in-situ* Gasification Chemical Looping
Combustion (iG-CLC) aided by Oxygen Uncoupling (CLOU)**

R. Pérez-Vega, A. Abad*, P. Gayán, L.F. de Diego, F. García-Labiano, J. Adánez

Department of Energy and Environment, Instituto de Carboquímica (ICB-CSIC),

Miguel Luesma Castán, 4, Zaragoza, 50018, Spain

*Corresponding author:

Phone: + 34 976733977. Fax: +34 976733318. E-mail: abad@icb.csic.es (Alberto Abad)

Abstract

Chemical Looping Combustion (CLC) involves the use of a solid oxygen carrier to transport the oxygen from the air to a fuel. Attention has recently been focused on oxygen carriers based on Mn-Fe mixed oxides because they are cheap materials that are able to release oxygen at high temperature, the so-called oxygen uncoupling step. The aim of this work was to assess the use of $(\text{Mn}_{0.77}\text{Fe}_{0.23})_2\text{O}_3$ material as an oxygen carrier with the ability to transport oxygen both by reduction with gaseous fuels and by oxygen uncoupling, i.e. typical mechanisms in CLC and in Chemical Looping with Oxygen Uncoupling (CLOU), respectively. The particles prepared by mechanical mixing were screened to obtain particles of sufficient reactivity and mechanical strength for use in a fluidized bed

reactor. The preparation methodology and calcining temperature were varied. The reactivity of one selected material was evaluated by performing redox cycles both in a TGA and a batch fluidized-bed reactor. Thus, its behaviour was assessed during both decomposition-regeneration of bixbyite phase $[(\text{Mn}_{0.77}\text{Fe}_{0.23})_2\text{O}_3]$ in CLOU and the reduction-oxidation of spinel phase $[(\text{Mn}_{0.77}\text{Fe}_{0.23})_3\text{O}_4]$ with gaseous fuels, i.e. H_2 , CO and CH_4 . Its oxygen uncoupling and re-oxidation capability was highly influenced by the reaction temperature and oxygen concentration. On the other hand, CLC redox cycles with gaseous fuels showed high reactivity with H_2 and CO and high oxygen transport capacity by reduction to mangano-wüstite phase $[(\text{Mn}_{0.77}\text{Fe}_{0.23})\text{O}]$. Good fluid-dynamic behaviour was observed for the oxygen carrier particles along the redox cycles without agglomeration problems, regardless of the operating conditions used in the batch fluidized-bed reactor. Thus, the selected material was considered a promising candidate for use in both in CLC with syngas and CLC with coal.

Keywords: CO_2 capture; Chemical Looping Combustion (CLC); Chemical Looping with Oxygen Uncoupling (CLOU); Oxygen Carriers; Manganese Oxides; Iron Oxides.

1. Introduction

Chemical Looping Combustion (CLC) is a promising technology that is able to capture CO_2 at low cost and with a low energy penalty in the power generation process [1]. CLC is based on the transfer of oxygen from the air to the fuel by means of a solid oxygen carrier. In the most common configuration, the oxygen carrier is continuously circulated between two interconnected fluidized-bed reactors, known as the fuel and air reactors [2].

The development of Chemical Looping technology for solid fuel combustion has made an important advance over the last decade by means of two processes: *in-situ* Gasification (*iG-CLC*) and Oxygen Uncoupling (CLOU) [1,2]. The *iG-CLC* concept works by supplying steam and/or recycled CO₂ to the fuel reactor as gasifying agents. *In-situ* gasification of solid fuel (e.g. coal) takes place inside the fuel reactor, as does the subsequent oxidation of the gasification products by gas-solid reactions with the oxygen carrier. Unburnt products, such as H₂, CO and CH₄, are usually found in existing *iG-CLC* facilities. The CLOU concept uses a metal oxide with the ability to release gaseous oxygen in the fuel reactor [3,4]. The solid fuel is subsequently burnt with the gaseous oxygen, avoiding the slow gasification step. Solid fuel conversion by CLOU is thus improved, compared to *iG-CLC* [5,6].

Low cost materials based on iron or manganese ores have mostly been used as oxygen carriers in *iG-CLC* [1,2], while synthetic materials based on copper and manganese are being developed for CLOU [7,8]. Cu-based materials were primarily developed because of their high reactivity. The development of Mn-based materials as oxygen carriers in CLOU has recently become the focus of attention because they are cheaper than those made with copper. In recent years, there has been great interest in the use of mixed oxides of manganese and iron as oxygen carriers due to their potential use in CLOU mode. The thermodynamics of the Mn-Fe-O system have been studied for decades and are being revised periodically with new experimental findings [9]. Phase equilibrium diagrams for the Mn-Fe-O system are replicated in Figure 1 using FactSageTM software, and show stable phases as a function of temperature and the oxygen partial pressure. The temperature and oxygen partial pressure values required for transformation between bixbyite phase, i.e.

$(\text{Mn}_x\text{Fe}_{1-x})_2\text{O}_3$, and spinel phase, i.e. $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$, are suitable for use in the CLOU process; see reaction R3.

This property has been exploited for the design of a relevant number of oxygen carrier materials [10]. Thus, oxidation conditions must allow oxidation to bixbyite [11-14]. According to Larring et al., the optimum operating temperature should be evaluated depending on the Mn:Fe ratio and the existing O_2 partial pressure [11]. For example, considering oxidation in air, the transition temperature between spinel and bixbyite varies from 970 °C for Mn-rich materials to 1030 °C for Fe-rich materials; see Figure 1(a). But transition temperatures are 70 °C lower if the oxygen partial pressure is 0.05 atm. Nevertheless, the oxygen uncoupling ability is facilitated by using Mn-rich materials owing to the narrow gap between bixbyite and spinel phases; see Figure 1(a) [13-15]. Also, conversion to bixbyite will be determined by reaction kinetics, which usually increases with temperature [16]. However, it should be taken into consideration that the increase in temperature increases the oxygen concentration necessary to reach bixbyite phase [11].

With regard to the oxygen transfer from bixbyite, both the oxygen uncoupling mechanism and reactivity with fuel gases must be considered. $(\text{Mn}_x\text{Fe}_{1-x})_2\text{O}_3$ materials showed oxygen uncoupling at 850 °C for the stoichiometric parameter $x > 0.5$, whereas the optimum temperature was 900-950 °C for materials with $x \leq 0.4$ [13]. By way of example, Figure 1(b) shows the phase diagram as a function of oxygen partial pressure and temperature for the Mn/(Mn+Fe) atomic ratio of 0.8. Under fuel reactor conditions, the transition from bixbyite to spinel can be driven by the oxygen uncoupling mechanism.

In addition to its oxygen uncoupling capability, bixbyite can be reduced by fuel gases such as H_2 , CO and CH_4 , and spinel can then be reduced to mangano-wüstite ($Mn_xFe_{1-x}O$), as shown in Figure 1(b); see reactions R2 and R3 for reduction with H_2 . MnO and Fe_3O_4 have also been reported as final products after reduction with 5 vol.% CH_4 or coal [17,18]. Further reduction to metallic Fe is also possible [19,20], but this would be not desirable because thermodynamic restrictions prevent complete combustion to CO_2 and H_2O .

Most of the synthesized Mn-Fe oxygen carriers were tested with gaseous fuels and showed good behaviour during syngas combustion, reaching fuel conversions close to 100 %. Furthermore, some Mn-Fe materials allowed high CH_4 conversion when the material was checked under a suitable reaction temperature [13,16]. In general, reactivity with fuel gases increased with Mn content [11,12,16,21]. Thus, $(Mn_xFe_{1-x})_2O_3$ materials with $x > 0.5$ showed high reactivity against CH_4 at 850 °C [13].

It is worth noting that the theoretical oxygen transport capacity available for the oxygen uncoupling reaction (bixbyite to spinel) is $R_{OC}^{ou} = 3.3$ wt.%, while the reduction of bixbyite to mangano-wüstite offers a theoretical oxygen transport capacity of $R_{OC}^t = 10.1$ wt.%. Reduction to mangano-wüstite can be exploited in the use of Mn-Fe materials for solid fuel combustion in the *i*G-CLC mode. However, few Mn-Fe materials have been tested in a CLC unit. Pérez-Vega et al. [22] tested a Mn-Fe material in a coal-fired CLC unit. Both CO_2 capture and combustion efficiency were improved compared to results obtained with ilmenite. Thus, by transferring a fraction of the oxygen via the oxygen uncoupling mechanism, combustion efficiency could be improved, compared to common Fe- or Mn-

based materials without oxygen uncoupling characteristics. In another work, Rydén et al. [23] obtained high CH₄ conversion in a 300 W CLC unit using particles prepared by spray drying with a Mn:Fe = 1:2 molar ratio. However, mechanical strength was low and a relevant fraction of particles became dust after 4 h of operation.

From previous works, we can infer that the oxygen uncoupling capability of combined Mn-Fe oxides can be exploited under the proper conditions. However, their regeneration capability has not been studied in detail. Moreover, the subsequent reduction of spinel with fuel gases requires further analysis, because a significant amount of oxygen in the combustion of coal could be transferred by solid-gas reactions [22]. It is therefore of interest to analyse both of the oxygen transfer processes involved to allow the conversion of coal by combining *in-situ* gasification and oxygen uncoupling.

The aim of this work was to develop a Mn-Fe mixed oxide material as an oxygen carrier with oxygen transport capability both for oxygen uncoupling and reduction by a fuel, which could be used in CLC with coal assisted by oxygen uncoupling (CLaOU). The composition (Mn_{0.77}Fe_{0.23})₂O₃ was fixed because materials with more Mn are generally more reactive, and because the gap between bixbyite and spinel phases is minimized with this composition; see Figure 1(a). A screening of the preparation methodology of (Mn_{0.77}Fe_{0.23})₂O₃ particles by mechanical mixing was performed with the target of producing highly reactive particles with enough strength for a fluidized bed operation. Oxygen transport capacity, reaction rate and mechanical strength were evaluated for the purpose of selecting an optimal Mn-Fe-based oxygen carrier. The reactivity behaviour against different gaseous fuels and the fluid-dynamic properties of the selected material were analysed in a fluidized bed reactor.

2. Experimental

2.1. Preparation of materials

Ten different materials were prepared by mechanical mixing of precursor powders to screen for the Mn-Fe based oxygen carriers. Table 1 shows a summary of the oxygen carriers manufactured together with their main physical properties. Most of the particles were prepared using Mn_3O_4 (Strem Chemical Inc.) and Fe_2O_3 (Panreac Prs.) powders. In one case, MnO_2 (Sigma-Aldrich) powder was used as the Mn source instead of Mn_3O_4 . The atomic Mn:Fe ratio was set to 77:23, except for Mn60Fe[L4] for which the ratio was 60:40 in order to evaluate the effect of the Mn:Fe ratio on particle properties. Moreover, some materials were produced with addition of graphite (Sigma-Aldrich) or kaolin (SYCA S.L.) with the purpose of increasing the porosity or mechanical strength of the particles, respectively.

Raw materials at the desired fractions were mixed in a ball mill. The milling process was modified in order to obtain three batches of solids with different particle size distribution. Thus, mean particle sizes of 5 μm and 2.6 μm were obtained with milling times of 20 and 90 min, respectively. To obtain a lower mean particle size (1.9 μm), a method adapted from the ferrites manufacturing process was used [24]. The solids mixture was calcined for 4 hours at 1050 $^{\circ}\text{C}$, and the calcined solid was subsequently milled for 300 minutes. Particles identified as [L], [M] or [S] in Table 1 means that the particle size of the powder used as a precursor of the oxygen carrier was 5 μm , 2.6 μm or 1.9 μm , respectively.

After the mixing step, cylindrical pellets (10 mm diameter, 15 mm height) were produced by pressure at 16 MPa, which were calcined for different times (2-18 h) at 950 °C. In some cases, an additional calcination step was performed at 1100 °C for 2 h. Eventually, pellets were crushed and sieved to obtain the desired particle diameter (+100-300 µm).

2.2. Characterization of the particles

Mechanical strength was determined using a Shimpo FGN-5X crushing strength apparatus. It took an average value of 20 measurements of the force needed to fracture a particle. Skeletal density was measured with a Micromeritics AccuPyc II 1340 helium pycnometer. Particle porosity was measured by Hg intrusion in a Quantachrome PoreMaster 33. Identification of the crystalline chemical species was carried out by X-ray diffraction (XRD) diffractogram collected by a Bruker D8 Advance X-ray powder diffractometer equipped with an X-ray source with a Cu anode working at 40 kV and 40 mA and an energy-dispersive one-dimensional detector.

2.3. Thermogravimetric analyser

The oxygen transport capacity (R_{OC}) and reaction rates of the materials were determined in a thermogravimetric analyser (TGA), CI Electronics type. A detailed description of the apparatus has already been reported elsewhere [25]. In all experiments, about 50 mg of sample were introduced into a platinum basket hanging inside a quartz reactor. The sample was initially heated in air up to the desired reacting temperature.

To analyse the oxygen uncoupling properties due to reaction from bixbyite to spinel phases, decomposition-regeneration cycles were performed alternating highly-pure N₂ (< 2 ppm O₂) and air at temperatures in the 800-920 °C interval. During the stage in N₂, reduction to spinel was guaranteed; see Figure 1(b). In addition, oxygen concentration values between 5

and 21 vol.% were used during the oxidation period to evaluate the ability to regenerate bixbyite.

Reduction of bixbyite with gaseous fuels (H_2 , CO and CH_4) was evaluated by performing redox cycles that alternated reducing and oxidizing conditions at 950 °C in order to compare the reactivity of MnFe materials with that of other materials used as oxygen carriers in *i*G-CLC (e.g. ilmenite, iron ore, etc.). H_2O or CO_2 was used in the reacting mixture to prevent the formation of FeO or Fe, which would be undesirable if complete fuel conversion is to be achieved.

2.4. Batch fluidized-bed reactor

A batch fluidized-bed reactor was used to assess the oxygen carrier's performance in terms of reactivity and agglomeration at similar conditions to those existing in a CLC unit. A mass of 350 g oxygen carrier was used. Information regarding the experimental setup can be found elsewhere [26], including the feeding system for reacting gases, the reactor system, and the gas analysers to determine the concentration of gases at the reactor outlet. The concentration vs time curves obtained during the experiments were corrected by means of a deconvolution method in order to correct dispersion and delay effects, thus obtaining the actual concentration at the batch fluidized-bed exit.

The oxygen uncoupling capability of material was evaluated by alternating air and N_2 (300 L_N/h) at 800, 850 and 900 °C. In addition, some redox cycles were carried out at 900 °C using diluted air (5 and 10 vol.% O_2) during the oxidation period to evaluate the regenerability of the material.

Reduction by 50 vol.% H_2 , 50 vol.% CO or 25 vol.% CH_4 was analysed at 900 and 950 °C. The total gas flow was 600 L_N/h for H_2 and CO, while 300 L_N/h was used with CH_4 . In this

way, the same oxygen requirement was required for the fuel combustion regardless of the gas used. Oxidation was performed by using 5 or 10 vol.% O₂.

2.5. Data evaluation

The normalized mass-loss variation (ω) represents the fraction of the actual mass of the oxygen carrier compared to the mass of oxidized particles. It was calculated as:

$$\omega = \frac{m}{m_o} \quad (1)$$

where m is the instantaneous mass of the sample and m_o the initial mass.

The oxygen transport capacity for the redox system i (R_{OC}^i) is defined as the mass fraction of particles being used in the oxygen transference. A normalized R_{OC}^i parameter was calculated as:

$$R_{OC}^i = \frac{m_o^i - m_r^i}{m_{bix}} \quad (2)$$

where m_o^i and m_r^i are the mass of the sample after oxidation and reduction, respectively, while m_{bix} is the mass of the sample, assuming that it was fully oxidized to bixbyite. Note that $m_o^i < m_{bix}$ if the sample is partially oxidized. R_{OC}^{ou} is defined for bixbyite reduction to spinel; see reaction R2. However, for reduction with a fuel gas, e.g. H₂, R_{OC}^g is defined for reduction of spinel phase to mangano-wüstite; see reactions R3. The accumulated or total mass loss from bixbyite to mangano-wüstite is defined by $R_{OC}^t = R_{OC}^{ou} + R_{OC}^g$.

The reduction (X_r^i) and oxidation (X_o^i) conversions corresponding to either oxygen uncoupling ($i=ou$), reduction by gas fuel ($i=g$), or total reduction from bixbyite to mangano-wüstite ($i=t$) were calculated from the mass variations in TGA as:

$$X_r^i = \frac{m_o^i - m}{R_{OC}^i \cdot m_{bix}} \quad (3)$$

$$X_o^i = \frac{m - m_r^i}{R_{OC}^i \cdot m_{bix}} \quad (4)$$

The reactivity of the materials was evaluated by calculating the normalized *Rate index* [27] which is normalized to a reference partial pressure of the fuel gas, P_{ref} , considering the reaction rate obtained at the partial pressure in TGA, P_{TGA} :

$$Rate\ index\ (\% / \min) = 60 \cdot 100 \cdot R_{OC}^i \frac{P_{ref}}{P_{TGA}} \left(\frac{dX_j^i}{dt} \right)_{TGA} \quad (5)$$

P_{ref} was set to 0.15 atm for the reduction, and to 0.10 atm for the oxidation.

In the fluidized bed reactor, the oxygen transfer rate as function of time, $r_O(t)$, during fuel combustion and oxidation periods was calculated as:

$$\text{Reduction: } r_O(t) = (\gamma_{CO} + 2\gamma_{CO_2} + \gamma_{H_2O})_{out} \cdot F_{out} - (\gamma_{CO} + 2\gamma_{CO_2} + \gamma_{H_2O})_{in} \cdot F_{in} \quad (6)$$

$$\text{Oxidation: } r_O(t) = -[2(\gamma_{O_2})_{out} \cdot F_{out} - 2(\gamma_{O_2})_{in} \cdot F_{in}] \quad (7)$$

where γ_g is the molar fraction of gas g , and F_{in} and F_{out} are the molar gas flow at the reactor inlet and outlet, respectively. The oxygen carrier conversion X_o^g was then calculated for the reduction and oxidation steps as:

$$\text{Reduction: } X_o^g(t_r) = 1 - \frac{M_O}{m_{OC} \cdot R_{OC}^g} \int_0^t r_O(t) \cdot dt \quad (8)$$

$$\text{Oxidation: } X_o^g(t_o) = X_o^g(t_{r,max}) + \frac{M_O}{m_{OC} \cdot R_{OC}^g} \int_0^t r_O(t) \cdot dt \quad (9)$$

where m_{OC} is the mass of the fully oxidized oxygen carrier and M_O the oxygen atomic mass.

3. Results

3.1. Screening of Mn-Fe based oxygen carriers

Table 1 shows the main physical characteristics of the prepared materials. Interestingly, bixbyite was formed after a calcination step. The screening of Mn-Fe based oxygen carriers was carried out by means of comparing the crushing strength, oxygen transport capacity and *Rate index* values, both for reduction and oxygen uncoupling. The crushing strength value, although quite simple and insufficient to evaluate the stress suffered by particles in a CLC unit, had been identified as a useful parameter in the initial screening stages [28]. Oxygen transport capacity and the *Rate index* values were obtained through experiments performed in a TGA apparatus consisting of four consecutive redox cycles. Stable reactivity is usually observed in the third redox cycle; thus, the results obtained during the third redox cycle were used in this work.

Oxygen uncoupling capability was evaluated from decomposition-regeneration of the bixbyite phase by alternating highly-pure N₂ and air at 870 °C. The inert period lasted 30 min. Bixbyite decomposition was initially fast, but it slowed down before the reaction was completed. Thus, the mass loss in N₂ was lower than the theoretical values of $R_{OC}^{ou}=3.4$ wt.% for reaction R1; see Table 2. Full decomposition of bixbyite phase was not achieved, with conversion values to spinel recorded in the 62-94 % interval.

Reactivity with a reducing gas was evaluated by performing redox cycles at 950 °C, alternating 5 vol.% H₂ + 40 vol.% H₂O (N₂ to balance) for the reducing period and air in the oxidized step. For example, Figure 2 shows the evolution of the normalized mass-loss with time during redox cycles with H₂ using Mn₇₇Fe[L4] particles. During the purge step, previous to the first reduction, a mass loss of 2.8 wt.% was recorded, corresponding to the

oxygen uncoupling capability of these materials; see reaction R1 and Figure 1. The reduction of the spinel to mangano-wüstite with H₂ subsequently took place by means of reactions R2 and R3. The accumulated mass loss from the initial bixbyite was 9.6 wt.%. Considering that the theoretical mass loss value is 10.1 wt.%, a X_r' value of 95 % was calculated for Mn₇₇Fe[L4] material.

During the subsequent period in air, oxidation was observed of mangano-wüstite phase to spinel phase, but regeneration to bixbyite phase was not possible. Therefore, the re-oxidation of Mn₇₇Fe[L4] was ruled by:

It is worth noting that the oxidation rate greatly increased after the first redox cycle, while no major differences could be observed in the reduction stage. The mass variation during these cycles was found to be 6.6 wt.%, very close to the theoretical value of 6.7 wt.%. This fact agrees with the phase diagram for Mn-Fe mixed oxides, where spinel phase is thermodynamically stable at 950 °C in air; see Figures 1.

The same redox cycles were repeated for all oxygen carrier materials synthesized in this work; see Table 1. A similar behaviour to that shown in Figure 2 was observed in all cases. Similar results were also obtained by Lambert et al. [16] during the reduction with CH₄ at 900 °C in TGA. They concluded that materials with a Mn:Fe atomic ratio higher than 1:1 did not provide gas phase oxygen for CLOU, but that reduction from spinel to mangano-wüstite could be exploited for the *i*G-CLC process.

For screening purposes, the oxygen transport capacity, *Rate index* and crushing strength values observed for the different materials are shown in Table 2. First, the effect of the raw material particle size was observed by comparing results obtained with Mn₇₇Fe[L4],

Mn77Fe[M4] and Mn77Fe[S4]. Interestingly, Mn77Fe[S4] particles showed the lowest mechanical strength and porosity values, which very distinct from those shown by Mn77Fe[L4] and Mn77Fe[M4]. This suggests that the different preparation methods used to obtain the finer powder could critically affect these properties.

With regard to oxygen transport capacity for oxygen uncoupling, the R_{OC}^{ou} value decreased when finer particles were used in the raw materials. The lower R_{OC}^{ou} value compared to the theoretical value for Mn77Fe[S4] may be related to its low porosity; see Table 1. The low rate index for CLOU calculated for these kinds of particles must be highlighted. Thus, low reactivity could limit the available oxygen by kinetic restrictions.

With regard to oxygen transport capacity during reduction with H_2 , see R_{OC}^g values, similar values were found for the three materials. The reduction rate in H_2 was similar for both Mn77Fe[L4] and Mn77Fe[M4]. But this value was significantly decreased for Mn77Fe[S4] manufactured with the lowest particle size of the precursor material. Finally, reactivity for oxygen uncoupling in N_2 and oxidation in air (both for CLOU and CLC) also decreased as the particle size of the raw materials decreased.

The decrease in particle size of the raw materials might be thought to be able to facilitate the migration of Mn and Fe atoms to form the mixed oxide. However, it was demonstrated that bixbyite was always formed. In addition, the Mn77Fe[S4] material was prepared with a mixture of Mn and Fe oxides that had been calcined at 1050 °C for 4 h. Thus, the Mn77Fe[S4] particles were prepared starting from the combined Mn-Fe oxide instead of individual mixed oxides. In this case, reactivity, oxygen transport capacity, porosity and mechanical strength were considerably reduced when compared to the other materials.

From the above considerations, decreasing the particle size of raw materials, in addition to the use of a Mn-Fe mixed oxide as raw material, was not recommended since weaker and/or less reactive particles were obtained. Therefore, materials prepared using Mn and Fe oxides as raw materials with a mean particle size of 5 μm were used in subsequent studies.

In order to evaluate the effect of calcining conditions on the particles characteristics, an additional, more severe calcining step was performed at 1100 $^{\circ}\text{C}$ for 2 h. The oxygen uncoupling capacity was slightly lower with respect to Mn77Fe[L4], but the decomposition rate of the bixbyite was severely decreased. Furthermore, an increase in porosity was observed which could be related to the slight decrease in mechanical strength.

Mixing active metal oxides with an inert material acting as support is a conventional option for improving the physical and chemical properties of oxygen carriers [1]. In this work, the use of kaolin ($\text{Al}_2\text{Si}_2\text{O}_5\cdot(\text{OH})_4$) as binder material was examined. Kaolin phase undergoes structural transformations upon calcination and it is well known for its mechanical properties and resistance to thermal shock. For example, the strength of Cu- and Fe-based oxygen carriers was improved by adding kaolin [29,30]. Both the mechanical strength and reactivity with H_2 of the Mn-Fe material with 20 wt.% kaolin (Mn77FeK[L4]) was higher than for the reference material (Mn77Fe[L4]); however, its oxygen transport capacity both with H_2 and N_2 was accordingly decreased.

Raw manganese oxide can be found in several oxidation states. The effect of the oxidation state of manganese powder was evaluated by preparing particles with the same Mn:Fe ratio, but using MnO_2 as raw material instead of Mn_3O_4 . In this case, a slight decrease in the oxygen uncoupling capacity, R_{OC}^{ou} , was observed for the Mn77Fe[L4Mn^(IV)] material, which may have been due to incomplete oxidation to bixbyite phase; see Table 1. Its reactivity,

both for oxygen uncoupling and reduction with H_2 , was also somewhat lower. Nevertheless, the mechanical strength of these particles had the lowest value of all the materials prepared.

The Mn:Fe ratio also influences mechanical strength. Thus, the material with the lowest Mn content (Mn60Fe[L4]) possessed the highest mechanical strength and reactivity with H_2 . Although oxygen transport capacity for oxygen uncoupling, R_{OC}^{ou} , was maintained, oxygen uncoupling reactivity was significantly reduced. This behaviour agrees with results obtained in previous works [13,14].

From these initial tests, material Mn77Fe[L4] was chosen as benchmarking particles for the following screening based on its high crushing strength and reactivity. Thus, the Mn77FeC[L4] material showed higher porosity and reaction rate with H_2 than the benchmarking material. This was due to the porosity generated when the graphite added to the solids mixture in the preparation stage was burnt during calcination. However, weaker particles were obtained. A similar behaviour was observed even when the calcining time was increased up to 12 and 18 h at 950 °C for Mn77FeC[L12] and Mn77FeC[L18], respectively. Thus, only a marginal improvement was achieved by increasing the calcining time.

From the comprehensive analysis on the mechanical strength, oxygen transport capacity and reactivity, three oxygen carriers could be considered for further studies, namely Mn77Fe[L4], Mn77FeK[L4] and Mn60Fe[L4]. In this work, a detailed study on the reactivity of reduction by fuel gases and oxygen uncoupling, as well as oxidation of reduced particles, was carried out with Mn77Fe[L4]. The Mn77Fe[L4] material was selected because of its easier preparation method, its need for a relatively low calcination

temperature and its relatively high oxygen transport capacity, and owing to the reactivity it demonstrated for oxygen uncoupling. It should be recalled that the aim of this work was the development and assessment of a Mn-Fe based oxygen carrier with oxygen capacity for coal combustion both via *in-situ* gasification and oxygen uncoupling pathways. Further study on reactivity and performance in a fluidized-bed reactor is presented below.

3.2. Comprehensive evaluation of the Mn_{0.77}Fe_{0.23}[L4] material

3.2.1 Analysis of oxygen uncoupling capability

As shown by the phase diagrams in Figure 1(b), (Mn_{0.77}Fe_{0.23})₃O₄ spinel could be formed when the oxygen partial pressure was low enough, or when the temperature was high enough. But its oxygen uncoupling capability was lost for consecutive redox cycles when oxidation was carried out at 950 °C in air because bixbyite phase could not be formed at such conditions; see Section 3.1. Consequently, analysis of the operating conditions for the oxidation stage was required in order to take advantage of the gaseous oxygen release from bixbyite.

The oxygen uncoupling capability of the Mn_{0.77}Fe_{0.23}[L4] particles was analysed as a function of the oxidizing conditions, i.e. reacting temperature and oxygen partial pressure. Redox cycles were performed in a TGA by alternating highly-pure N₂ for the oxygen uncoupling stage and air or diluted air (5 vol.% O₂) for the oxidation stage. The oxidation temperature was varied in the 800-920 °C interval, but temperature in N₂ was 900 °C in all cases in order to ensure full reduction to spinel (Mn_{0.77}Fe_{0.23})₃O₄.

For oxygen uncoupling, the reaction rate was unchanged with the redox cycles. Figure 3(a) shows the conversion vs time curves after 3 cycles for the oxidation period in air at different temperatures. Conversion was calculated for oxidation of spinel to bixbyite, i.e.

X_o^{ou} . Oxidation barely took place at 920 °C, and when oxidized at 900 °C, the reaction showed an induction period lasting around 20 s. A lower temperature in the oxidizing period led to a higher reaction rate up to 850 °C. When the oxidation took place at 820 and 800 °C, a lower reaction rate was observed. This behaviour can be explained as the result of a trade-off between kinetic control and thermodynamic limitation. Thus, when the temperature was increased from 800 °C, the oxidation rate increased because of the increase in the kinetic rate constant. However, when the temperature was higher than 850 °C, the reaction rate decreased because the oxygen concentration was close to the thermodynamic equilibrium. This behaviour was also observed for the oxygen uncoupling rate with Cu-based oxygen carriers, although in this case the reaction rate decreased for temperatures higher than 900-950 °C [31]. Therefore, the adequate oxidizing temperature for regeneration seemed to be in the 820-870 °C interval. Furthermore, it was found that when bixbyite was regenerated, the reduction rate in N₂ was unaffected by the oxidizing conditions. During consecutive redox cycles, a stable oxygen transport capacity of around $R_{OC}^{ou} = 3$ wt.% was obtained for the oxygen uncoupling reaction, which was slightly lower than the theoretical value of 3.4 wt.%.

The regeneration capability of spinel to oxidize to bixbyite in diluted air (5 vol.% O₂) was also analysed; see Figure 3(b). Under such conditions, re-oxidation from spinel to bixbyite did not take place at 885 °C, and it was slow to occur at 850 °C, characterized by a long induction period lasting in the range between 150 and 200 s. The decrease in temperature led to an improvement in the re-oxidation rate. Therefore, the adequate oxidizing temperature using 5 vol.% O₂ was 800-820 °C. It is worth noting that an induction period was observed in all cases, but it was reduced with the temperature decrease. Also, oxidation

was relatively fast up to $X_o^{ou}=0.4$ approx., after which the oxidation rate was significantly decreased. These results agree with the induction period observed by Lambert et al. [16] during oxidation of spinel to bixbyite for $(Mn_xFe_{1-x})_2O_3$ materials with $x \geq 0.5$.

The effect of the temperature on the oxygen uncoupling rate was also analysed in the 850-920 °C range; see Figure 3(c). In these tests, oxidation was carried out at 850 °C in air to ensure quick and complete regeneration to bixbyite. The higher the temperature, the faster the conversion rate observed during the oxygen uncoupling step. Therefore, a high temperature in the fuel reactor would be desirable.

The oxygen uncoupling capability of this material was subsequently tested in the batch fluidized-bed reactor. Several cycles alternating N_2 and air or diluted air were conducted at different temperatures. Figure 4(a) shows the behaviour of the particles subjected to N_2 -Air cycles at temperatures between 800 and 900 °C. During the decompositions, the rise in the temperature led to improved oxygen uncoupling behaviour. The material showed reproducibility when 3 cycles were conducted, regardless of temperature. In addition, agglomeration was not observed in any case, regardless of the reacting temperature or degree of reduction.

The evolution in the oxygen carrier conversion, X_o^{ou} , during both the oxygen uncoupling and the re-oxidation steps is also shown. The variation in the oxygen uncoupling conversion, X_o^{ou} , was 7 % at 800 °C; however, the conversion variation increased to 20 % when the temperature was varied to 850 °C, and it was increased by 4 when the temperature was raised from 800 to 900 °C. Note that in the fluidized-bed reactor, the solid to gas ratio was higher than in the TGA, and conditions in the reactor approached those of equilibrium. Thus, the reaction rate could be increased by temperature, as was observed in TGA tests.

But this increase was limited by oxygen concentration at the thermodynamic equilibrium. It is worthy of note that the concentration of oxygen in exiting gases increased with temperature, which mainly affected the increase in the oxygen carrier conversion.

With regard to oxidation in air, complete regeneration of the particles was observed at 800 °C, which may have been due to the low conversion achieved during the oxygen uncoupling stage. However, full re-oxidation was not observed at higher temperatures. The fraction of oxygen recovered with the increase in temperature was 90 % at 850 °C and 75 % at 900 °C. This result is in agreement with what was observed in the thermogravimetric tests, i.e. the oxidation rate in air decreased when temperature was increased to above 850 °C; see Figure 3. Thus, regeneration was incomplete at 900 °C, even considering that the reaction period was longer for this temperature.

In addition, several cycles alternating N₂ and diluted air (5 or 10 vol.% O₂) were performed at 870 °C in order to evaluate the regeneration capability of Mn₇₇Fe[L4] at lower oxygen concentration values; see Figure 4(b). The first two redox cycles were performed in the fluidized-bed facility using 5 vol.% O₂ in the oxidizing step. A constant oxygen concentration of 1.3 vol.% was recorded during decomposition in N₂. The first period in N₂ lasted 15 min, and a variation was achieved in the oxygen uncoupling conversion of $\Delta X_o^{ou} = 16.4 \%$. Following this, partial oxidation was reached after half hour in 5 vol.% O₂. The material was further reduced during the second cycle in N₂, showing a trend similar to the reduction observed in the first cycle. The oxidizing time was then increased for the second cycle, but again complete re-oxidation was not achieved. Finally, oxidation was performed by using 10 vol.% O₂ in order to observe the influence of oxygen partial pressure on solids conversion. As a result, the particles were full regenerated to bixbyite. Therefore, the

increase in the O₂ partial pressure allowed a faster regeneration to bixbyite phase to be achieved.

3.2.2. Reactivity with gaseous fuels: H₂, CO and CH₄

Reduction by fuel gases could be relevant in the fuel conversion pathway [22], with special interest given to the reduction of spinel to mangano-wüstite, see Reaction R3, which is not driven by the oxygen uncoupling mechanism. Redox cycles were carried out at 950 °C with Mn77Fe[L4] particles both in the TGA and in the batch fluidized bed. In these tests, the spinel was reduced by H₂, CO or CH₄, while oxidation of mangano-wüstite was performed in air.

Initially, the oxygen carrier particles were subjected to 100 redox cycles in the TGA to check the stability of the material regarding oxygen transport capacity and reactivity. Reducing and oxidizing periods lasted 300 and 90 s, respectively. This time was long enough to achieve sequentially complete reduction and oxidation between the spinel and mangano-wüstite phases. Figure 5(a) shows the evolution in the conversion by reaction with fuel gas, X_r^g , obtained in the TGA with Mn77Fe[L4] particles. The reactivity of the particles with H₂ showed an increase throughout the cycles, but oxygen transport capacity remained constant with the cycles to $R_{OC}^g = 6.5$ wt.%. The reactivity increase observed during the last 25 cycles was of lower relevance. In addition, Figure 5(b) shows that oxidation reactivity was maintained with the redox cycles.

The subsequent analysis on reactivity was conducted with cycled particles for the spinel/mangano-wüstite redox pair. Reduction with different gaseous fuels (H₂, CO and CH₄) and oxidation with 10 vol.% O₂ was carried out in the TGA at 950 °C, and the normalized Rate index of Mn77Fe[L4] was calculated; see Figure 6. The reactivity of

Mn77Fe[L4] with H₂ was the highest, followed by that with CO and with CH₄, respectively. The oxidation rate was similar whatever the fuel used in the reduction period. In order to ascertain the potential of this oxygen carrier in CLC, a comparison with other similar materials was performed. For this purpose, the Figure 6 also shows a comparison of Rate index values and oxygen transport capacities between these particles and other low-cost Fe-based materials that had been tested previously, i.e. ilmenite, Fe-ESF, Fe-ore, and a highly reactive Fe-based synthetic oxygen carrier [32]. The oxygen transport capacity of the Mn77Fe[L4], here R_{OC}^g , was the highest among these oxygen carriers. With regard to reactivity with H₂, Mn77Fe[L4] performed significantly better compared to both ilmenite and Fe-ESF. Furthermore, these particles showed similar reactivity to that of the Fe-ore particles. With CO, this Mn-Fe-based oxygen carrier showed similar reactivity to that observed for both Fe-ore and Fe-ESF and it was still better than that of the ilmenite. However, the reactivity of Mn77Fe[L4] with CH₄ was the lowest of all materials tested. With respect to the oxidizing step, these particles were very reactive, showing a rate index value with O₂ close to that obtained with the ilmenite, which showed the highest reactivity. The conversion of H₂, CO and CH₄ was also evaluated through tests carried out in the batch fluidized-bed reactor at 950 °C. Figure 7 shows the evolution of gaseous compounds and variation in solids conversion, ΔX_o^g , over time. Mn77Fe[L4] had high reactivity in presence of H₂, reaching full conversion of H₂ during the first two minutes of reduction; then a small amount of H₂ was detected when $\Delta X_o^g > 40$ %. With CO combustion, the material was able to achieve a gas conversion of 96 %, while CH₄ conversion ranged from 50 to 60 % during the first 3 minutes. Thus, CH₄ showed the lowest reactivity of all gases used, which was already observed in TGA tests.

The maximum degree of reduction for the particles was achieved in the reduction with H_2 , where the variation in the conversion was $\Delta X_o^g = 60\%$. The oxygen carrier particles reached full regeneration after the oxidizing step in all cases. After the reduction step with CH_4 , both CO_2 and CO were observed at the beginning of the oxidizing period because carbon was formed by the thermal decomposition of methane. No O_2 was detected during the purge period after each oxidation, suggesting that bixbyite phase was not formed, and that the oxidation took place with spinel phase.

XRD analysis of samples extracted from the fluidized bed after both reduction and oxidation periods was performed in order to assess the phase changes indicated by performance of the material in the redox cycles. Thus, bixbyite phase was found to be a major component in regenerated samples at temperatures below $870^\circ C$. However, only spinel phase was found in samples oxidized after reduction with fuel gases at $950^\circ C$. XRD analysis was also performed on a sample extracted from the fluidized bed reactor after a reduction period with H_2 . In this case, only mangano-wüstite phase was found. The assignment of crystalline phases was performed through the use of the DIFFRAC.EVA software, based on Joint Committee on Powder Diffraction Standards. Thus, bixbyite phase included $MnFeO_3$ and Mn_2O_3 structures, while Mn_2FeO_4 , $MnFe_2O_4$, Mn_3O_4 and Fe_3O_4 were present in the spinel phase. Finally, crystalline $Mn_xFe_{1-x}O$ and MnO were included in the mangano-wüstite phase.

In general, the results obtained in the fluidized bed agreed with the results obtained in the TGA. Moreover, good fluid-dynamic behaviour of the particles throughout the redox cycles was observed. Proper fluidization was maintained during all conditions used in these tests,

without agglomeration or de-fluidization problems regardless of the operating conditions used, i.e. temperature, fuel gas or degree of reduction.

4. Discussion

From results showed in this work, some practical implications can be drawn from the use of the Mn₇₇Fe[L4] material for fuel combustion via CLC or CLOU.

Prepared Mn-Fe materials could transfer oxygen via oxygen uncoupling and gas-solid reaction with a fuel gas; but their oxygen transport capacity for oxygen uncoupling, R_{OC}^{ou} , was much lower than the total oxygen transport capacity, R_{OC}^t ; see Table 2. It is expected that both mechanisms will be involved in the oxygen transfer process from the oxygen carrier to the fuel [22]. In fact, the overall process for converting a fuel could be described as conventional Chemical Looping assisted by Oxygen Uncoupling (CLaOU). Therefore, both oxygen uncoupling and reduction reactions with fuel gases, which also exist in CLC with coal, must be analysed in order to provide a complete evaluation of these materials.

With regard to reduction with fuel gases, which is a characteristic process in CLC, reduction to mangano-wüstite phase, Mn_{0.77}Fe_{0.23}O, could be exploited. The reactivity of the Mn₇₇Fe[L4] material was similar to that shown by other proposed materials such as ilmenite or iron ore. Fast oxidation to spinel, (Mn_{0.77}Fe_{0.23})₃O₄, is expected in the air reactor, with an oxygen transport capacity of $R_{OC}^s = 6.5$ wt.%. Considering the promising results obtained with Fe-ore or Fe-ESF oxygen carriers burning syngas [33] or coal [34,35], the Mn₇₇Fe[L4] material can be proposed for use in CLC with these fuels. In addition, the high oxygen transport capacity of Mn₇₇Fe[L4] is of relevance, which means that a lower

solids circulation flow would be required, which benefits the CO₂ capture that is achievable in CLC of coal [36].

In addition, the oxygen uncoupling capability of this material could be exploited when bixbyite phase, (Mn_{0.77}Fe_{0.23})₂O₃, was formed. In this case, an improved performance of coal combustion can be expected compared to the CO₂ capture and combustion efficiency achieved with non-CLOU materials [5,6]. For this to occur, the spinel should be able to become oxidized to bixbyite at any oxygen concentration existing inside the air reactor to take advantage of the oxygen uncoupling property of the Mn₇₇Fe[L4] material. The oxygen concentration is high (~21 vol.%) near the air inlet and quick oxidation to bixbyite will be expected at temperatures in the 800-900 °C interval. However, the oxygen concentration decreases as the oxygen reacts with the oxygen carrier. Thus, considering an air excess similar to that used in conventional combustion, the oxygen concentration will decrease to around 4-6 vol.% at the air reactor exit. Under these conditions, the oxidation rate will decrease, but it may be of relevance if the temperature is in the 800-850 °C interval. Thus, an average temperature in the air reactor of around 850 °C would guarantee proper oxidation to bixbyite phase.

With regard to the oxygen uncoupling mechanism, it was determined that a high temperature in the fuel reactor would be desirable. Consequently, the reaction rate of oxygen generation by oxygen uncoupling at 920 °C was calculated to be $1.9 \cdot 10^{-4}$ kg/s per kg of oxygen carrier. This value is half of the reaction rate obtained for Cu-based materials [31], and in the same order of magnitude as that found for Mn-based perovskites at 920 °C [37].

In conclusion, in the CLOU process with Mn-Fe materials, both the oxygen generation from bixbyite decomposition to spinel phase and bixbyite regeneration must take place in the fuel reactor and air reactor, respectively. For the Mn₇₇Fe[L4] material, the maximum temperature inside the air reactor should be 850 °C, while the temperature inside the fuel reactor must be as high as possible. Therefore, a thermal gradient between the fuel and air reactor has to be set in order to take advantage of the oxygen uncoupling capacity of this material. The temperatures in the reactors are closely linked by an overall enthalpy balance to the CLC unit. The lower temperature in the air reactor would be achieved by extracting heat from this reactor. The use of a higher temperature in the fuel reactor could be viable as long as the overall process taking place in the fuel reactor is exothermic when bixbyite is reduced to spinel [10]. Preliminary calculations showed that the thermal gradient would rise to 70 °C, which means that suitable temperatures would be 920 °C in the fuel reactor and 850 °C in the air reactor. However, the overall process in the fuel reactor becomes less exothermic when bixbyite is reduced to mangano-wüstite. This fact would limit the maximum temperature in the fuel reactor. In order to have a higher temperature in the fuel reactor, the temperature in the air reactor must be increased. Thus, the air excess should be increased to facilitate bixbyite regeneration. This option implies increased power consumption for air impulsion; but it could turn out to be an interesting option if the oxygen uncoupling capability of the Mn₇₇Fe[L4] material is preserved. In this way, the expected combustion efficiency would be higher compared to operation without the oxygen uncoupling capability, i.e. in the iG-CLC mode for solid fuels.

5. Conclusions

A screening of $(\text{Mn}_{0.77}\text{Fe}_{0.33})_2\text{O}_3$ particulate material obtained by mechanical mixing followed by pelletizing under pressure was developed for the purpose of producing strong and high reactive particles for use in CLC and CLOU. Bixbyite phase was formed in all cases, showing oxygen transfer via both gas-solid reaction with fuel gases and oxygen uncoupling. $\text{Mn}_{0.77}\text{Fe}_{0.33}[\text{L4}]$, which was prepared from Mn_3O_4 and Fe_2O_3 powders (5 μm) and calcined at 950 °C for 4 h, showed enough reactivity and mechanical strength to be used as an oxygen carrier for both CLC and CLOU. The use of finer powders, Mn-Fe combined oxide or MnO_2 as raw materials, the increase of calcining temperature from 950 to 1100 °C, the addition of graphite to the Mn_3O_4 - Fe_2O_3 mixture, and the modification of the composition to $(\text{Mn}_{0.6}\text{Fe}_{0.4})_2\text{O}_3$ was unable to improve either the reactivity or the mechanical strength of the benchmarking material. Mechanical strength and reactivity were improved by adding kaolin powder to the Mn_3O_4 - Fe_2O_3 mixture, but the oxygen transport capacity was correspondingly decreased as kaolin acts as a diluting material.

The $\text{Mn}_{0.77}\text{Fe}_{0.33}[\text{L4}]$ material was further analysed by tests in a TGA and a fluidized-bed reactor. This material was able to generate oxygen gas phase by the reduction of $(\text{Mn}_{0.77}\text{Fe}_{0.33})_2\text{O}_3$ bixbyite to $(\text{Mn}_{0.77}\text{Fe}_{0.33})_3\text{O}_4$ spinel. The oxygen uncoupling reaction rate increased with temperature, and became fast enough to be exploited in a CLC unit at 900 °C. But oxidation conditions must be carefully controlled in order to take advantage of the oxygen uncoupling mechanism. Thus, a temperature lower than 900 °C in air and 850 °C in 5 vol.% O_2 is advisable to allow bixbyite formation. Therefore, a thermal gradient between the fuel and air reactor of around 70 °C would need to be used in CLOU, with the higher temperature inside the fuel reactor. In addition, complete reduction to mangano-wüstite, $(\text{Mn}_{0.77}\text{Fe}_{0.33})\text{O}$, was achieved by reaction with a gaseous fuel, i.e. H_2 , CO or CH_4 . This

material could be considered a candidate for use as an oxygen carrier in CLC with syngas or coal. Moreover, good fluid-dynamic behaviour of the particles was observed throughout the redox cycles in a fluidized bed without agglomeration problems, regardless of the operating conditions used.

Acknowledgements

This work was partially supported by the Spanish Ministry for Economy and Competitiveness via the ENE2013-45454-R project, by the European Regional Development Fund (ERDF), and by the Spanish National Research Council (CSIC) via the 2014-80E101 project. R. Pérez-Vega is grateful to MICINN for the FPI Fellowship.

Nomenclature

F_i	total molar flow gas at inlet ($i = in$) or outlet ($i = out$) in the batch fluidized-bed reactor (mol/s)
M_o	atomic mass of oxygen ($16 \cdot 10^{-3}$ kg/mol)
m	instantaneous mass of the oxygen carrier (kg)
m_i	mass of oxidized ($i = o$) or reduced ($i = r$) sample of the oxygen carrier (kg).
m_{OC}	mass of the oxygen carrier within the batch fluidized-bed reactor (kg)
$m_{OC,FR}$	solids inventory in the fuel reactor (kg)
P_{ref}	reference partial pressure of reacting gas (atm)
P_{TGA}	partial pressure of the gaseous fuel used in TGA (atm)
R_{OC}^{ou}	oxygen transport capacity by the oxygen uncoupling reaction between bixbyite and spinel (kg oxygen per kg of oxygen carrier)
R_{OC}^g	oxygen transport capacity by the solid-fuel gas reaction between spinel and mangano-wüstite (kg oxygen per kg of oxygen carrier)
R'_{OC}	total oxygen transport capacity of the oxygen carrier between bixbyite and mangano-wüstite (kg oxygen per kg of oxygen carrier)
$r_O(t)$	atomic oxygen transfer rate as function of time from the oxygen carrier to the fuel (mol O/s ⁻¹)
t	time (s)
X_j^{ou}	solids conversion by the oxygen uncoupling reaction between bixbyite and spinel (-)
X_j^g	solids conversion by the solid-fuel gas reaction between spinel and mangano-wüstite (-)
X_j^t	total solids conversion of the oxygen carrier between bixbyite and mangano-wüstite (-)

Greek symbols

γ_i	molar fraction of the gas i ($i = CO, CO_2, H_2O$ or O_2) (-)
ω	normalized mass-loss variation (-)

Acronyms

CCS CO₂ Capture and Storage

CLaOU Chemical Looping assisted by Oxygen Uncoupling

CLC	Chemical Looping Combustion
CLOU	Chemical Looping with Oxygen Uncoupling
FTIR	Fourier Transform Infrared
I.D.	Internal Diameter
<i>iG-CLC</i>	<i>in-situ</i> Gasification Chemical Looping Combustion
NDIR	Non-Dispersive Infrared
TGA	Thermogravimetric Analyser
XRD	X-Ray Diffraction

References

- [1] J. Adanez, A. Abad, F. García-Labiano, P. Gayán, L.F. de Diego, Progress in Chemical-Looping Combustion and Reforming technologies, Prog. Energy. Comb. Sci. 38 (2012) 215-82.
- [2] A. Lyngfelt, Chemical-looping combustion of solid fuels - Status of development, App. Energy 113 (2014) 1869-73.
- [3] T. Mattisson, A. Lyngfelt, H. Leion, Chemical-looping with oxygen uncoupling for combustion of solid fuels, Int. J. Greenhouse Gas Control 3 (2009) 11-9.
- [4] A. Abad, I. Adánez-Rubio, P. Gayán, F. García-Labiano, L.F. de Diego, J. Adánez, Demonstration of chemical-looping with oxygen uncoupling (CLOU) process in a 1.5 kW_{th} continuously operating unit using a Cu-based oxygen-carrier, Int. J. Greenhouse Gas Control 6 (2012) 189-200.
- [5] T. Mendiara, I. Adánez-Rubio, P. Gayán, A. Abad, L. F. de Diego, F. García-Labiano, J. Adánez, Process Comparison for Biomass Combustion: In Situ Gasification-Chemical Looping Combustion (iG-CLC) versus Chemical Looping with Oxygen Uncoupling (CLOU), Energy Technol. 4 (2016) 1130-6.
- [6] J. Adánez, P. Gayán, I. Adánez-Rubio, A. Cuadrat, T. Mendiara, A. Abad, F. García-Labiano, L. F. de Diego, Energy Procedia 37 (2013) 540-9.
- [7] T. Mattisson, Materials for Chemical-Looping with Oxygen Uncoupling, ISRN Chemical Engineering, Volume 2013, Article ID 526375, 19 pages.
- [8] Q. Imtiaz, D. Hosseini, C.R. Müller, Review of Oxygen Carriers for Chemical Looping with Oxygen Uncoupling (CLOU): Thermodynamics, Material Development, and Synthesis, Energy Technol. 1 (2013) 633-47.

- [9] P. Perrot, Ternary Alloy Systems: Phase Diagrams, Crystallographic and Thermodynamics Data. Iron Systems, Part 4; Springer, **2008**, DOI: 10.1007/978-3-540-78644-3_18.
- [10] M. Rydén, H. Leion, T. Mattisson, A. Lyngfelt, Combined oxides as oxygen-carrier material for chemical-looping with oxygen uncoupling, *Appl. Energy* 113 (2014) 1924-32.
- [11] Y. Larring, C. Braley, M. Pishahang, K.A. Andreassen, R. Bredesen, Evaluation of a Mixed Fe–Mn Oxide System for Chemical Looping Combustion, *Energy Fuels* 29 (2015) 3438-45.
- [12] A. Shafiearhood, A. Stewart, F. Li, Iron-containing mixed-oxide composites as oxygen carriers for Chemical Looping with Oxygen Uncoupling (CLOU), *Fuel* 139 (2015) 1-10.
- [13] G. Azimi, H. Leion, M. Rydén, T. Mattisson, A. Lyngfelt, Investigation of Different Mn-Fe Oxides as Oxygen Carrier for Chemical-Looping with Oxygen Uncoupling (CLOU), *Energy Fuels* 27 (2013) 367-77.
- [14] A. Shulman, E. Cleverstam, T. Mattisson, A. Lyngfelt, Manganese/Iron, Manganese/Nickel, and Manganese/Silicon Oxides Used in Chemical-Looping With Oxygen Uncoupling (CLOU) for Combustion of Methane, *Energy Fuels* 23 (2009) 5269-75.
- [15] G. Azimi, M. Rydén, H. Leion, T. Mattisson, A. Lyngfelt, $(\text{Mn}_z\text{Fe}_{1-z})_y\text{O}_x$ Combined Oxides as Oxygen Carrier for Chemical-Looping with Oxygen Uncoupling, *AIChE J.* 59 (2013) 582-88.

- [16] A. Lambert, C. Delquié, I. Cléménçon, E. Comte, V. Lefebvre, J. Rousseau, B. Durand, Synthesis and characterization of bimetallic Fe/Mn oxides for chemical looping combustion, *Energy Procedia* 1 (2009) 375-81.
- [17] B. Wang, C. Gao, W. Wang, H. Zhao, C. Zheng, Sulfur evolution in chemical looping combustion of coal with MnFe_2O_4 oxygen carrier, *J. Env. Sci.* 26 (2014) 1062-70.
- [18] P. Mungse, G. Saravanan, S. Rayalu, N. Labhsetwar, Mixed Oxides of Iron and Manganese as Potential Low- Cost Oxygen Carriers for Chemical Looping Combustion, *Energy Technol.* 3 (2015) 856-65.
- [19] E. Ksepko, R.V. Siriwardane, H. Tian, T. Simonyi, M. Sciazko, Effect of H_2S on Chemical Looping Combustion of Coal-Derived Synthesis Gas over Fe-Mn Oxides Supported on Sepiolite, ZrO_2 , and Al_2O_3 , *Energy Fuels* 26 (2012) 2461-72.
- [20] S. Bhavsar, B. Tackett, G. Veser, Evaluation of iron- and manganese-based mono- and mixed-metallic oxygen carriers for chemical looping combustion, *Fuel* 136 (2014) 268-79.
- [21] M. Abián, A. Abad, M.T. Izquierdo, P. Gayán, L.F. de Diego, F. García-Labiano, J. Adánez. Titanium substituted manganese-ferrite as an oxygen carrier with permanent magnetic properties for chemical looping combustion of solid fuels, *Fuel* 195 (2017) 38-48.
- [22] R. Pérez-Vega, A. Abad, J. Adánez, L.F. de Diego, F. García-Labiano, P. Gayán, Development of a Mn-Fe-Ti based Oxygen Carrier in Chemical Looping Combustion with coal, *Proceedings of the 7th International Conference on Clean Coal Technologies*, Krakow, Poland, 2015.

- [23] M. Rydén, A. Lyngfelt, T. Mattisson, Combined manganese/iron oxides as oxygen carrier for chemical looping combustion with oxygen uncoupling (CLOU) in a circulating fluidized bed reactor system, *Energy Procedia* 4 (2011) 341-8.
- [24] M.I. Rosales, A.M. Plata, M.E. Nicho, A. Brito, M.A. Ponce, V.M. Castaño, Effect of sintering conditions on microstructure and magnetic properties of Mn-Zn ferrites, *J. Mater. Sci.* 30 (1995) 4446-50.
- [25] L.F. de Diego, A. Abad, A. Cabello, P. Gayán, F. García-Labiano, J. Adánez, Reduction and Oxidation Kinetics of a $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ Oxygen Carrier for Chemical-Looping Combustion, *Ind. Eng. Chem. Res.* 53 (2014) 87-103.
- [26] L.F. de Diego, P. Gayán, F. García-Labiano, J. Celaya, A. Abad, J. Adánez, Impregnated $\text{CuO}/\text{Al}_2\text{O}_3$ Oxygen Carriers for Chemical-Looping Combustion: Avoiding Fluidized Bed Agglomeration, *Energy Fuels* 19 (2005) 1850-6.
- [27] M. Johansson, T. Mattisson, A. Lyngfelt, Comparison of oxygen carriers for Chemical-Looping Combustion, *Therm. Sci.* 10 (2006) 93-107.
- [28] A. Cabello, P. Gayán, F. García-Labiano, L.F. de Diego, A. Abad, J. Adánez, On the attrition evaluation of oxygen carriers in Chemical Looping Combustion, *Fuel Proc. Technol.* 148 (2016) 188-197.
- [29] J. Adánez, P. Gayán, A. Abad, F. García-Labiano, L.F. de Diego, Suitability of Cu-based Materials for the Scale-up of Chemical Looping Combustion, in: *Carbon Dioxide Capture for Storage in Deep Geological Formations, Volume 4, Chapter 17*. Ed. K.F. Gerdes, 2015 CPL Press and BPCNAI.

- [30] P. Cho, T. Mattisson, A. Lyngfelt, Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion, *Fuel* 83 (2004) 1215-25.
- [31] I. Adánez-Rubio, P. Gayán, A. Abad, F. García-Labiano, L.F. de Diego, J. Adánez, Kinetic analysis of a Cu-based oxygen carrier: Relevance of temperature and oxygen partial pressure on reduction and oxidation reactions rates in Chemical Looping with Oxygen Uncoupling (CLOU), *Chem. Eng. J.* 256 (2014) 69-84.
- [32] T. Mendiara, R. Pérez, A. Abad, L.F. de Diego, F. García-Labiano, P. Gayán, J. Adánez, Low-Cost Fe-Based Oxygen Carrier Materials for the *i*G-CLC Process with Coal. 1, *Ind. Eng. Chem. Res.* 51 (2012) 16216-29.
- [33] M.A. Pans, A. Abad, L.F. de Diego, F. García-Labiano, P. Gayán, J. Adánez, Performance of a low-cost iron ore as an oxygen carrier for Chemical Looping Combustion of gaseous fuels, *Chem. Eng. Res. Des.* 93 (2015) 736-46.
- [34] T. Mendiara, L.F. de Diego, F. García-Labiano, P. Gayán, A. Abad, J. Adánez, On the use of a highly reactive iron ore in Chemical Looping Combustion of different coals, *Fuel* 126 (2014) 239-49.
- [35] T. Mendiara, L.F. de Diego, F. García-Labiano, P. Gayán, A. Abad, J. Adánez, Behaviour of a bauxite waste material as oxygen carrier in a 500 W_{th} CLC unit with coal, *Int. J. Greenhouse Gas Control* 17 (2013) 170-82.
- [36] J. Adánez, A. Abad, T. Mendiara, P. Gayán, L.F. de Diego, F. García-Labiano, Review and assessment of experimental results from Chemical Looping Combustion units burning solid fuels, *Progress in Energy and Combustion Science*, submitted for publication.

- [37] A. Abad, F. García-Labiano, P. Gayán, L.F. de Diego, J. Adánez, Redox kinetics of $\text{CaMg}_{0.1}\text{Ti}_{0.125}\text{Mn}_{0.775}\text{O}_{2.9-8}$ for Chemical Looping Combustion (CLC) and Chemical Looping with Oxygen Uncoupling (CLOU), Chem. Eng. J. 269 (2015) 67-81.

List of Figure captions

Figure 1. Mn-Fe-O phase diagram as a function of (a) Mn/(Mn+Fe) ratio and temperature with an O_2 partial pressure of 0.05 atm (—) or 0.21 atm (----); and (b): O_2 partial pressure and temperature for the molar ratio Mn/(Mn+Fe) = 0.8. Solid phases calculated with FactSageTM software using FToxid database: βSp : β Spinel; Bix: Bixbyite; Fe(s) and Fe(s2): Iron metal; Hem: Hematite; MW: Mangano-wustite; TSp: Tetragonal Spinel.

Figure 2. Normalized mass-loss variation (ω) of Mn77Fe[L4] at 950 °C for the consecutive reactions R1 and R2+R3: reduction in 5 vol.% H_2 + 40 vol.% H_2O and oxidation in air.

Figure 3. Oxygen carrier conversion for oxygen uncoupling (reaction R1) versus time of Mn77Fe[L4] after 3 redox cycles in TGA: (a) oxidation of spinel in air; (b) oxidation of spinel in 5 vol.% O_2 ; (c) decomposition of bixbyite in highly-pure N_2 .

Figure 4. Oxygen concentration and variation in solids conversion by oxygen uncoupling (reaction R1) during the decomposition-oxidation cycles of Mn77Fe[L4] in the fluidized-bed reactor: (a) N_2 -Air at different temperatures ; (b) N_2 -dilued air at 870 °C.

Figure 5. Evolution of the conversion vs time curves during reduction (reaction R3), X_r^g , and oxidation, X_o^g , reactions for Mn77Fe[L4] particles during 100 redox cycles at 950 °C in TGA: (a): Reduction in 5 vol.% H_2 + 40 vol.% H_2O ; (b): Oxidation in air.

Figure 6. Normalized *Rate index* of Mn77Fe[L4] particles with different gases and oxygen transport capacity, R_{OC}^g , considering spinel/mangano-wustite as the redox system (see reaction R3 as an example for H_2). Data for other previously tested oxygen carriers have been also included for comparison purposes [32].

Figure 7. Gas distribution and variation in the conversion of Mn77Fe[L4] oxygen carrier, ΔX_o^g , for the spinel/mangano-wustite redox system (see reaction R3 as an example for H_2) during the reduction at 950 °C in the fluidized bed with: (a) 50 vol.% H_2 ,+ 20 vol.% H_2O ; (b) 50 vol.% CO + 20 vol.% CO_2 ; (c) 25 vol.% CH_4 , + 10 vol.% H_2O . Subsequent oxidation in air is also included. R: reduction; P: purge; O: oxidation.

Figure 1. Mn-Fe-O phase diagram as a function of (a) Mn/(Mn+Fe) ratio and temperature with an O_2 partial pressure of 0.05 atm (—) or 0.21 atm (-----); and (b): O_2 partial pressure and temperature for the molar ratio Mn/(Mn+Fe) = 0.8. Solid phases calculated with FactSageTM software using FToxid database: β Sp: β Spinel; Bix: Bixbyite; Fe(s) and Fe(s2): Iron metal; Hem: Hematite; MW: Mangano-wustite; TSp: Tetragonal Spinel.

Figure 2. Normalized mass-loss variation (ω) of Mn₇₇Fe[L4] at 950 °C for the consecutive reactions R1 and R2+R3: reduction in 5 vol.% H₂+ 40 vol.% H₂O and oxidation in air.

Figure 3. Oxygen carrier conversion for oxygen uncoupling (reaction R1) versus time of Mn77Fe[L4] after 3 redox cycles in TGA: (a) oxidation of spinel in air; (b) oxidation of spinel in 5 vol.% O_2 ; (c) decomposition of bixbyite in highly-pure N_2 .

Figure 4. Oxygen concentration and variation in solids conversion by oxygen uncoupling (reaction R1) during the decomposition-oxidation cycles of Mn₇₇Fe[L4] in the fluidized-bed reactor: (a) N₂-Air at different temperatures ; (b) N₂-diluted air at 870 °C.

Figure 5. Evolution of the conversion vs time curves during reduction (reaction R3), X_r^g , and oxidation, X_o^g , reactions for Mn77Fe[L4] particles during 100 redox cycles at 950 °C in TGA: (a): Reduction in 5 vol.% H_2 + 40 vol.% H_2O ; (b): Oxidation in air.

Figure 6. Normalized *Rate index* of Mn77Fe[L4] particles with different gases and oxygen transport capacity, R_{OC}^g , considering spinel/mangano-wustite as the redox system (see reaction R3 as an example for H₂). Data for other previously tested oxygen carriers have been also included for comparison purposes [32].

Figure 7. Gas distribution and variation in the conversion of Mn77Fe[L4] oxygen carrier, ΔX_o^g , for the spinel/mangano-wustite redox system (see reaction R3 as an example for H₂) during the reduction at 950 °C in the fluidized bed with: (a) 50 vol.% H₂,+ 20 vol.% H₂O; (b) 50 vol.% CO + 20 vol.% CO₂; (c) 25 vol.% CH₄, + 10 vol.% H₂O. Subsequent oxidation in air is also included. R: reduction; P: purge; O: oxidation.

List of Table captions

Table 1. Summary of the Mn-Fe based oxygen carriers prepared for the screening process.

Table 2. Crushing strength, oxygen transport capacity and *Rate index* values for the materials tested in this work.

1 **Table 1.** Summary of the Mn-Fe based oxygen carriers prepared for the screening process.

OC ⁽¹⁾	Mn ₃ O ₄ (wt.%)	Fe ₂ O ₃ (wt.%)	MnO ₂ (wt.%)	Graphite (wt.%)	Kaolin (wt.%)	Sintering conditions		Skeletal density (kg/m ³)	Porosity (%)	XRD main phases ⁽²⁾
						Time (h)	Temperature (°C)			
Mn77Fe[L4]	76	24	-	-	-	4	950	5000	32.9	MnFeO ₃
Mn77Fe[M4]	76	24	-	-	-	4	950	4992	31.2	MnFeO ₃
Mn77Fe[S4]	76	24	-	-	-	4	950	4893	17.3	MnFeO ₃
Mn77Fe[L4+2]	76	24	-	-	-	4+2	950+1100	5031	54.1	MnFeO ₃
Mn77FeK[L4]	60	20	-	-	20	4	950	4379	29.6	MnFeO ₃ , Al ₂ O ₃ , SiO ₂
Mn77Fe[L4 ^{Mn(IV)}]	-	21	79	-	-	4	950	4843	44.9	MnFeO ₃ , Mn ₂ FeO ₄
Mn60Fe[L4]	58	42	-	-	-	4	950	4982	31.9	MnFeO ₃
Mn77FeC[L4]	76	24	-	5	-	4	950	5004	41.9	MnFeO ₃
Mn77FeC[L12]	76	24	-	5	-	12	950	5006	40.0	MnFeO ₃
Mn77FeC[L18]	76	24	-	5	-	18	950	4943	38.6	MnFeO ₃

⁽¹⁾ Nomenclature includes the Mn fraction, the particle size in raw materials and calcining time. For example, in Mn77Fe[L4]: 77 is x in the stoichiometry (Mn_xFe_{1-x})₂O₃; L means a particle size of raw materials of 5 μm (M=2.6 μm and S=1.9 μm); 4 is the calcining time at 950 °C (an additional calcining step for 2 hours at 1100 °C is described as 4+2). In other materials, K and C mean that kaolin or graphite was in the formula, respectively.

⁽²⁾ MnFeO₃ and Mn₂FeO₄ represent bixbyite and spinel phases, respectively

Table 2. Crushing strength, oxygen transport capacity and *Rate index* values for the materials tested in this work.

	Crushing strength (N)	Oxygen transport capacity (%)			Rate index (%/min)			
		R_{OC}^{ou}	R_{OC}^g	R_{OC}^t	CLOU ⁽¹⁾		CLC ⁽²⁾	
					N ₂	O ₂	H ₂	O ₂
Mn77Fe[L4]	2.7	3.0	6.6	9.6	0.30	1.1	12.2	8.4
Mn77Fe[M4]	2.2	3.1	6.6	9.7	0.28	0.4	12.4	8.0
Mn77Fe[S4]	0.9	2.1	6.4	8.5	0.17	0.1	3.5	7.1
Mn77Fe[L4+2]	2.4	2.6	6.6	9.2	0.14	0.3	16.3	8.1
Mn77FeK[L4]	3.0	2.3	4.9	7.2	0.46	1.5	15.8	8.3
Mn77Fe[L4 ^{Mn(IV)}]	0.8	2.1	6.4	8.5	0.20	0.1	12.4	8.5
Mn60Fe[L4]	3.1	3.0	6.2	9.2	0.15	0.6	16.1	7.8
Mn77FeC[L4]	1.2	3.2	6.6	9.8	0.24	1.1	16.7	8.5
Mn77FeC[L12]	1.3	3.0	6.4	9.4	0.35	1.3	17.6	9.2
Mn77FeC[L18]	1.5	2.9	6.6	9.5	0.31	1.2	16.3	8.4

⁽¹⁾ Cycles N₂-air at 870 °C
⁽²⁾ Cycles H₂-air at 950 °C

3

4