Thermochemical assessment of Chemical Looping *assisted by* Oxygen Uncoupling with a MnFe-based oxygen carrier

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ABSTRACT

A previously developed manganese-iron mixed oxide doped with TiO₂ shows promising properties for the combustion of solid fuels with intrinsic CO₂ capture by Chemical Looping *assisted by* Oxygen Uncoupling (CLaOU) owing to its oxygen uncoupling capability, i.e. ability to generate gaseous oxygen at high temperature, and to oxidize gaseous fuels such as H₂, CO or CH₄ by reacting with lattice oxygen. In this work, a window of suitable operating conditions was determined to facilitate the use of this material in a CLaOU unit. For this purpose, mass and enthalpy balances were performed for the whole CLaOU unit considering theoretical values of thermochemical parameters, such as the equilibrium constant of relevant reactions in CLaOU and the formation enthalpies of reacting solids. An air reactor temperature of 1148 K and a high air excess ratio are suggested in order to promote the transfer of oxygen via the oxygen uncoupling mechanism, which would be preferable for the combustion of solid fuels. Auto-thermal operation of the CLaOU unit is guaranteed for air excess ratio values $\lambda < 3$. The fuel

reactor temperature is highly influenced by the oxygen carrier-to-fuel ratio (ϕ) and the oxygen carrier regeneration in the air reactor. Assuming a 50-75% regeneration of the oxygen uncoupling capability, and $\phi = 4-6$, the fuel reactor temperature would be between 35 and 50 K above the air reactor temperature. The higher temperature in the fuel reactor could promote the fuel conversion, while oxygen carrier regeneration would be guaranteed by the lower air reactor temperature.

Keywords: CO₂ capture; Chemical Looping Combustion; Oxygen uncoupling; Manganese; Iron; Oxygen carrier.

1. Introduction

The capture of CO₂ from power plants has been pointed out as an important strategy for the mitigation of global warming. Among CO₂ capture technologies, Chemical Looping Combustion (CLC) stands out for its relatively low energy penalty compared to other CO₂ capture techniques [1]. In CLC, a solid oxygen carrier is continuously circulated between two fluidized-bed reactors [2]: the air reactor where the oxygen carrier takes oxygen from air; and the fuel reactor where oxygen in the oxygen carrier is used to burn a fuel. Exhaust gases from the air reactor are mainly composed of N₂ from air, while a separate stream mainly comprising CO₂ and H₂O is obtained from the fuel reactor. Thus, the CO₂ capture is inherent to this process.

Combustion of solid fuel by CLC can be performed via the processes of *in-situ* Gasification Chemical Looping Combustion (*iG-CLC*) or Chemical Looping with Oxygen Uncoupling (CLOU) [3]. In *iG-CLC*, the solid fuel is gasified *in-situ* inside the fuel reactor, and the

gasification products are oxidized to CO_2 and H_2O by taking lattice oxygen from the oxygen carrier in the gas-solid reactions. In CLOU, the oxygen carrier is able to release gaseous oxygen in the fuel reactor, which burns the solid fuel in the same way as that of conventional combustion in air.

In most cases, unburnt products appear together with the CO_2 stream in *iG-CLC* mode [3], which increase with the volatile content of the solid fuel [4]. Thus, an oxygen polishing step is proposed downstream from the fuel reactor, where unburnt products could be fully oxidized with pure O_2 [5]. Interestingly, there is clearly a significant improvement in combustion efficiency with CLOU mode compared to *iG-CLC* owing to the combustion of the fuel with the oxygen released by the oxygen carrier [3,4]. Cu-based oxygen carriers have mainly been studied for the CLOU process owing to the high ability of this metal oxide to release gas-phase oxygen at a fast rate [6]. Thus, complete combustion of coal and biomass has been found with Cu- and CuMn-based materials burning both coal [7] and biomass [8]. However, novel materials consisting of manganese-iron mixed oxide have recently drawn great attention owing to their constituents being more economical than copper [9]. Mn-Fe mixed oxides have suitable thermochemical properties for the oxygen uncoupling process if the redox system formed by bixbyite, $(\text{Mn}_x\text{Fe}_{1-x})_2\text{O}_3$, and spinel, $(\text{Mn}_x\text{Fe}_{1-x})_3\text{O}_4$, is considered [10].

A Mn-Fe mixed oxide material with addition of TiO_2 and stoichiometric formula $(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_3 \cdot (\text{TiO}_2)_{0.15}$ was identified as a promising oxygen carrier with oxygen uncoupling capability [11]. The procedure by which particles are produced can affect the reactivity and mechanical stability of the prepared material [12]. Thus, suitable and fluidizable particles of the $(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_3 \cdot (\text{TiO}_2)_{0.15}$ material, named Mn66FeTi7, were obtained by the spray-drying method followed by thermal treatment at 1473 K [13].

Mn66FeTi7 showed high reactivity and mechanical strength. This oxygen carrier was able to transport a high amount of oxygen ($R'_{OC,exp} = 0.088$), of which about 30% was released by oxygen uncoupling ($R^{ou}_{OC,exp} = 0.026$). In addition, Mn66FeTi7 showed magnetic properties, which would allow the recovery of the oxygen carrier particles otherwise lost in the purge ash stream when a solid fuel is burnt, thus reducing the need to replace the oxygen carrier material [14].

The reactions involved in the oxygen transfer with Mn66FeTi7 are shown Table 1. At the temperature of interest to burn a fuel, above 1073 K, this material is able to release gas-phase oxygen under an inert environment following an oxygen uncoupling mechanism through the decomposition of bixbyite, $(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_3 \cdot (\text{TiO}_2)_{0.15}$, to spinel, $(\text{Mn}_{0.66}\text{Fe}_{0.34})_3\text{O}_4 \cdot (\text{TiO}_2)_{0.225}$; reaction (R1) [13]. Bixbyite regeneration is defined by the reverse of this reaction with oxygen. Moreover, bixbyite can be reduced to spinel by the reaction of lattice oxygen with reducing gases (e.g. H_2 or CO) through reactions (R2)-(R3), as in the common CLC process. These reducing agents come from the *in-situ* solid fuel gasification by H_2O and/or CO_2 . Furthermore, spinel can be reduced to mangano-wüstite, $(\text{Mn}_{0.66}\text{Fe}_{0.34})\text{O} \cdot (\text{TiO}_2)_{0.075}$, by reaction with those same gases through reactions (R4)-(R5) [15]. Whenever this takes place, spinel can be regenerated through the oxidation of mangano-wüstite to spinel through reaction (R6). Considering that oxygen can be transferred by both gas-solid reactions and the oxygen uncoupling mechanism, the entire process has been given the name Chemical Looping *assisted by* Oxygen Uncoupling (CLaOU) [16]. The relevance of oxygen uncoupling in relation to the reaction of fuel with lattice oxygen would depend on the relative reaction rates [17]. It is likely that both mechanisms would be relevant for Mn-Fe mixed oxides; however, combustion performance

would be improved with enhancement of the oxygen uncoupling mechanism, in a similar way to that occurring with CaMn perovskites [18].

Table 1. Chemical reactions involved in the oxygen transfer when using Mn66FeTi7 material as oxygen carrier.

$6(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_3 \cdot (\text{TiO}_2)_{0.15} \rightleftharpoons 4(\text{Mn}_{0.66}\text{Fe}_{0.34})_3\text{O}_4 \cdot (\text{TiO}_2)_{0.225} + \text{O}_2$	(R1)
$3(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_3 \cdot (\text{TiO}_2)_{0.15} + \text{H}_2 \rightarrow 2(\text{Mn}_{0.66}\text{Fe}_{0.34})_3\text{O}_4 \cdot (\text{TiO}_2)_{0.225} + \text{H}_2\text{O}$	(R2)
$3(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_3 \cdot (\text{TiO}_2)_{0.15} + \text{CO} \rightarrow 2(\text{Mn}_{0.66}\text{Fe}_{0.34})_3\text{O}_4 \cdot (\text{TiO}_2)_{0.225} + \text{CO}_2$	(R3)
$(\text{Mn}_{0.66}\text{Fe}_{0.34})_3\text{O}_4 \cdot (\text{TiO}_2)_{0.225} + \text{H}_2 \rightleftharpoons 3(\text{Mn}_{0.66}\text{Fe}_{0.34})\text{O} \cdot (\text{TiO}_2)_{0.075} + \text{H}_2\text{O}$	(R4)
$(\text{Mn}_{0.66}\text{Fe}_{0.34})_3\text{O}_4 \cdot (\text{TiO}_2)_{0.225} + \text{CO} \rightleftharpoons 3(\text{Mn}_{0.66}\text{Fe}_{0.34})\text{O} \cdot (\text{TiO}_2)_{0.075} + \text{CO}_2$	(R5)
$6(\text{Mn}_{0.66}\text{Fe}_{0.34})\text{O} \cdot (\text{TiO}_2)_{0.075} + \text{O}_2 \rightarrow 2(\text{Mn}_{0.66}\text{Fe}_{0.34})_3\text{O}_4 \cdot (\text{TiO}_2)_{0.225}$	(R6)

A suitable design for a CLC unit burning solid fuels must consider optimum operating conditions depending on the oxygen carrier and the characteristics of the fuel [19]. Given the better performance of CLOU compared to *i*G-CLC, coal combustion via the oxygen uncoupling mechanism is encouraged. In order to take advantage of the oxygen uncoupling capability with Mn-Fe mixed oxides, regeneration of the bixbyite phase must be guaranteed; see reaction (R1). This requirement entails critical control over both oxidation temperature and oxygen concentration during the course of the reverse reaction (R1) [20]. For the Mn66FeTi7 material [13], a suitable temperature for bixbyite regeneration was determined to be in the 1123-1173 K interval. In addition, bixbyite regeneration is enhanced by increasing the partial pressure of oxygen at values higher than 0.05 atm O₂. In practice, this condition is achieved by increasing the air excess flow supplied to the air reactor, although this increases the energy losses in the flue gas from the air reactor and the energy cost for blowing. Therefore, operating conditions in the entire CLaOU unit should

be optimized as a function of the air excess supplied to the air reactor. Moreover, conditions in the fuel reactor must guarantee the highest temperature possible. The complete process taking place in the fuel reactor for the combustion of a solid fuel in CLOU mode with Mn-Fe mixed oxides is believed to be exothermic [21]. Therefore, the temperature of fuel reactor could be higher than that of the air reactor for the Mn₆₆FeTi₇ under specific operating conditions, similar to that occurring with Cu-based materials [22]. However, there are no studies dedicated to the thermal integration of a CLaOU unit with a Mn-Fe mixed oxide found in the literature. Mass and enthalpy balances for the whole CLaOU unit would be required to determine suitable and optimum conditions in both the fuel and air reactors [23]. Nevertheless, there is little information on most of the thermochemical parameters for Mn-Fe mixed oxide materials, such as enthalpy of solids and equilibrium constant for reactions (R1)-(R6). In addition, the oxygen partial pressure at equilibrium for reaction (R1) is highly affected by temperature and the degree of bixbyite conversion, due to the coexistence of mixtures of bixbyite and spinel [24], and there is no available data to calculate this under all the possible conditions existing in the air and fuel reactors.

The aim of this work was to determine suitable operating conditions in both fuel and air reactors when the Mn₆₆FeTi₇ material is used as oxygen carrier in the CLaOU process. Mass and enthalpy balances are made for the fuel and air reactors, and the energetic integration between them is performed and evaluated as a function of operating conditions, mainly air excess ratio, solids circulation rate and degree of bixbyite regeneration. For this purpose, thermochemical parameters such as equilibrium constants and enthalpy for oxygen carrier reactions are inferred from theoretical studies. Optimization of the CLaOU unit is conditional on maximizing the fraction of bixbyite being regenerated in the air reactor,

which is the only compound involved in the oxygen transfer via oxygen uncoupling to burn the fuel in the fuel reactor. The methodology showed in this work could be extended to any other Mn-Fe material with a different Mn:Fe ratio.

2. Methodology for the thermochemical evaluation

The thermochemical evaluation of a CLaOU unit was performed for the Mn₆₆FeTi₇ oxygen carrier developed [11] and characterized [13] in previous studies. Several operating conditions were considered, all involving the reaction of the different solid compounds both via the oxygen uncoupling mechanism and via gas-solid reactions with lattice oxygen; see reaction (R1)-(R6). The solids conversion value defines the fraction of reacting compounds in the solids, i.e. bixbyite, spinel or mangano-wüstite, and it determines the mass and enthalpy balances for the CLaOU unit.

2.1. Definition of oxygen carrier conversion

Three concepts for the oxygen carrier conversion of Mn-Fe mixed oxides were defined, depending on the compounds considered for the oxidized and reduced state [13]. The total amount of oxygen provided by the Mn₆₆FeTi₇ material was calculated by means of the mass variation between the fully oxidized and reduced states, i.e. bixbyite and mangano-wüstite, respectively. This allowed the total oxygen transport capacity to be calculated by means of Eq. (1) given the mass of the oxygen carrier fully oxidized to bixbyite, m_{bix} , and fully reduced to mangano-wüstite, m_{mw} .

$$R'_{OC} = \frac{m_{bix} - m_{mw}}{m_{bix}} \quad (1)$$

Total conversion of the oxygen carrier, X_r^t , was defined considering the reduction of the mass of the oxygen carrier, m , with regard to the total oxygen transport capacity, R_{OC}^t .

$$X_r^t = \frac{m_{bix} - m}{R_{OC}^t \cdot m_{bix}} \quad (2)$$

The oxygen carrier transports oxygen from the air reactor to the fuel reactor. As a consequence, there is a difference between the rate of solids conversion in both reactors, ΔX_s^t , calculated by:

$$\Delta X_s^t = X_{r,FR}^t - X_{r,AR}^t \quad (3)$$

This difference in solids conversion depends on the oxygen being transferred from the air reactor to the fuel reactor, i.e. on the oxygen carrier solids circulation rate, $\dot{m}_{OC}$. The effect of the solids circulation rate is commonly assessed by the oxygen carrier-to-fuel ratio, ϕ , and calculated by Eq. (4) [19]. The denominator of this equation is the oxygen required to fully convert the fuel to CO_2 and H_2O , which is calculated by multiplying the oxygen demand for the stoichiometric combustion of 1 kg of solid fuel, Ω_{SF} , and rate at which the solid fuel is fed into the fuel reactor, $\dot{m}_{SF}$.

$$\phi = \frac{R_{OC}^t \cdot \dot{m}_{OC}}{\Omega_{SF} \cdot \dot{m}_{SF}} \quad (4)$$

The variation in the rates of solids conversion depends on both the oxygen carrier-to-fuel ratio and combustion efficiency, η_{comb} , [25], and can be calculated by Eq (5).

$$\Delta X_s^t = \frac{\eta_{comb}}{\phi} \quad (5)$$

The theoretical maximum oxygen transport capacity for the Mn₆₆FeTi₇ material is $R'_{OC} = 0.094$ [13]. The total oxygen transferred involves both oxygen uncoupling and gas-solid reactions with lattice oxygen, representative of the CLOU and CLC processes, respectively. Each mechanism is characterized by the reaction of different compounds. Thus, oxygen uncoupling involves the reduction of bixbyite to spinel through reaction (R1), while the gas reaction with lattice oxygen is characteristic of the reduction of spinel to mangano-wüstite; see reactions (R4)-(R5). To clarify the differences between the total conversion, and conversion for oxygen uncoupling and gas-solid reaction, Fig. 1 shows a scheme where the degree of reduction is related to the oxygen transport capacity for each reaction. The reaction of a gas with lattice oxygen in the bixbyite could also occur, as described in reactions (R2) and (R3). However, with regard to the mass and enthalpy balances in the overall process of the fuel reactor, it is irrelevant to consider either the direct reaction of the fuel with lattice oxygen, reactions (R2) and (R3), or the reaction as the sum of oxygen uncoupling (R1) and the subsequent oxidation of the fuel with the oxygen generated. For this reason, the conversion between bixbyite and spinel was defined for oxygen uncoupling, while the gas reaction with lattice oxygen was unequivocally characteristic of the reduction of spinel to mangano-wüstite because spinel has no oxygen uncoupling capability.

The oxygen transport capacity for these reactions, i.e. for oxygen uncoupling (R^{ou}_{OC}) and conversion for gas reaction with lattice oxygen (R^g_{OC}), is defined by Eqs. (6) and (7), respectively. The mass variation between bixbyite, m_{bix} , and spinel, m_{sp} , is used for R^{ou}_{OC} ; while the mass variation between spinel, m_{sp} , and mangno-wüstite, m_{mw} , is used for R^g_{OC} .

$$R^{ou}_{OC} = \frac{m_{bix} - m_{sp}}{m_{bix}} \quad (6)$$

$$R_{OC}^g = \frac{m_{sp} - m_{mw}}{m_{bix}} \quad (7)$$

The oxygen uncoupling capability ($R_{OC}^{ou} = 0.032$) represents about one third of the total oxygen transport capacity. The degree of conversion of the oxygen uncoupling reaction, X_r^{ou} , is calculated as:

$$X_r^{ou} = \frac{m_{bix} - m}{R_{OC}^{ou} \cdot m_{bix}} \quad (8)$$

Fig. 1. Relation between the oxygen carrier-to-fuel ratio, ϕ , total solids conversion, X_r^t , and the total oxygen transport capacity, R_{OC}^t , considering the conversion and oxygen transport capacity for both oxygen uncoupling (X_r^{ou} and R_{OC}^{ou}) and gas reaction with lattice oxygen (X_r^g and R_{OC}^g).

Thus, $X_r^{ou}=1$ means that all the bixbyite is transformed into spinel. At this condition, the total reduction conversion is $X_r^t = 0.34$, which means that the oxygen carrier-to-fuel ratio parameter must be $\phi > 3$ in order to guarantee the prevalence of the oxygen uncoupling mechanism. Full regeneration of bixbyite in the air reactor is assumed in this case. If this is not the case, higher ϕ values will be required, as assessed below.

If the ϕ value is lower than 3, reduction of spinel to mangano-wüstite must take place, driven by gas reactions with lattice oxygen. The degree of spinel reduction is defined by the conversion X_r^g calculated by:

$$X_r^g = \frac{m_{sp} - m}{R_{OC}^g \cdot m_{bix}} \quad (9)$$

The corresponding conversion for the degree of oxidation, X_o^{ou} or X_o^g , is calculated by:

$$X_o^i = 1 - X_r^i \quad (10)$$

In order to find the working region in Fig. 1, as well as the rate of solids conversion, the following methodology was used: (1) definition of the values of the parameters of oxygen carrier-to-fuel ratio (ϕ), degree of bixbyite regeneration in the air reactor, i.e. X_o^{ou} , and combustion efficiency, η_{comb} ; (2) the total conversion in the air reactor calculated by Eqs. (2), (8) and (10) as:

$$X_{r,AR}^t = (1 - X_o^{ou}) \frac{R_{OC}^{ou}}{R_{OC}^t} \quad (11)$$

(3) the total conversion in the fuel reactor calculated by Eqs. (3) and (5) as:

$$X_{r,FR}^t = X_{r,AR}^t + \frac{\eta_{comb}}{\phi} \quad (12)$$

(4) total conversion in the fuel reactor to define the working area, either CLOU or CLC, as depicted in Fig. 1. The corresponding $X_{r,FR}^{ou}$ or $X_{r,FR}^g$ was calculated.

$$X_{r,FR}^{ou} = X_{r,FR}^t \frac{R_{OC}^t}{R_{OC}^{ou}} \quad \text{if } X_{r,FR}^t < \frac{R_{OC}^{ou}}{R_{OC}^t} = 0.34 \quad (13)$$

$$X_{r,FR}^g = X_{r,FR}^t \frac{R_{OC}^t}{R_{OC}^g} - \frac{R_{OC}^{ou}}{R_{OC}^g} \quad \text{if } X_{r,FR}^t > \frac{R_{OC}^{ou}}{R_{OC}^t} = 0.34 \quad (14)$$

The calculated solids conversion for oxygen uncoupling, or for the gas reaction with lattice oxygen if required, was used to calculate the thermochemical properties of the Mn66FeTi7 material, depending on its degree of oxidation.

2.2. Thermochemical parameters

Equilibrium constants for reactions (R1)-(R6) in Table 1, as well as formation enthalpy of the Mn-Fe-Ti solid oxide mixtures were calculated using FactSageTM software [23] as a function of the temperature and the solids conversion. The parameters of fit used to calculate the thermochemical properties are shown in Table 2. Two different cases are considered: (1) for bixbyite-spinel mixtures, i.e. reactions (R1)-(R3) and CLOU region in Fig. 1, the conversion X_r^{ou} for oxygen uncoupling were considered; and (2) for spinel-mangano-wüstite mixtures, i.e. reactions (R4)-(R6) and CLC region in Fig. 1, the conversion X_r^g for gas-solid reaction was used. Moreover, constants at equilibrium as a function of the temperature for the reduction of the monometallic Mn and Fe oxides with H₂ and CO were calculated from Barin [27]; see Table 3. In this way, the equilibrium constants for Mn66FeTi7 could be compared to Mn-, and Fe-based monometallic oxides. Formation enthalpy for gaseous compounds was also calculated from Barin [27].

Table 2. Equations and coefficients used to calculate the equilibrium constants for reaction (R1) (K_{eq,O_2}^{ou}), reaction (R4) with H_2 (K_{eq,H_2}^g) and reaction (R5) with CO ($K_{eq,CO}^g$). FactSageTM software with FToxid database [26]. Confidence interval: 1123-1273 K.

	p	q	r
$K_{eq,O_2}^{ou} = P_{O_2} = a + b \cdot (X_r^{ou}) + c \cdot (X_r^{ou})^2$			
$a = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$	16.20	$-3.65 \cdot 10^4$	$2.05 \cdot 10^7$
$b = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$	-3.05	$6.76 \cdot 10^3$	$-3.74 \cdot 10^6$
$c = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$	$8.07 \cdot 10^{-3}$	29.23	$-4.27 \cdot 10^4$
$K_{eq,H_2}^g = \frac{P_{H_2O}}{P_{H_2}} = a \cdot \exp(b \cdot X_r^g)$			
$a = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$	$3.08 \cdot 10^5$	$1.21 \cdot 10^8$	$3.94 \cdot 10^{11}$
$b = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$	93.67	$2.24 \cdot 10^5$	$1.20 \cdot 10^8$
$K_{eq,CO}^g = \frac{P_{CO_2}}{P_{CO}} = a \cdot \exp(b \cdot X_r^g)$			
$a = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$	$6.74 \cdot 10^5$	$-2.57 \cdot 10^9$	$2.21 \cdot 10^{12}$
$b = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$	$1.44 \cdot 10^2$	$-3.41 \cdot 10^5$	$1.87 \cdot 10^8$

Table 3. Equations and coefficients used to calculate the equilibrium constants of reactions of manganese and iron oxides with H_2 and CO as a function of the temperature [27].

	a	b	c	$K_{eq,i}^g$ (1173 K)
$K_{eq,H_2}^g = \frac{P_{H_2O}}{P_{H_2}} = \exp\left(a + \frac{b}{T} + \frac{c}{T^2}\right)$				
$3 Mn_2O_3 + H_2 \leftrightarrow 2 Mn_3O_4 + H_2O$ (R7)	2.00	$1.93 \cdot 10^4$	$-6.10 \cdot 10^5$	$6.44 \cdot 10^7$
$Mn_3O_4 + H_2 \leftrightarrow 3 MnO + H_2O$ (R8)	7.32	$3.86 \cdot 10^3$	$-7.75 \cdot 10^5$	$2.31 \cdot 10^4$
$3 Fe_2O_3 + H_2 \leftrightarrow 2 Fe_3O_4 + H_2O$ (R9)	10.6	$9.22 \cdot 10^2$	$-1.55 \cdot 10^5$	$8.03 \cdot 10^4$
$Fe_3O_4 + H_2 \leftrightarrow 3 FeO + H_2O$ (R10)	6.66	$-6.48 \cdot 10^3$	$-1.81 \cdot 10^5$	2.73
$K_{eq,CO}^g = \frac{P_{CO_2}}{P_{CO}} = \exp\left(a + \frac{b}{T} + \frac{c}{T^2}\right)$				
$3 Mn_2O_3 + CO \leftrightarrow 2 Mn_3O_4 + CO_2$ (R11)	-1.37	$2.25 \cdot 10^4$	$-1.61 \cdot 10^5$	$4.97 \cdot 10^7$

$\text{Mn}_3\text{O}_4 + \text{CO} \leftrightarrow 3 \text{MnO} + \text{CO}_2$	(R12)	3.95	$7.13 \cdot 10^3$	$-3.27 \cdot 10^5$	$1.79 \cdot 10^4$
$3 \text{Fe}_2\text{O}_3 + \text{CO} \leftrightarrow 2 \text{Fe}_3\text{O}_4 + \text{CO}_2$	(R13)	7.29	$4.13 \cdot 10^3$	$3.19 \cdot 10^5$	$6.23 \cdot 10^4$
$\text{Fe}_3\text{O}_4 + \text{CO} \leftrightarrow 3 \text{FeO} + \text{CO}_2$	(R14)	3.58	$-3.85 \cdot 10^3$	$6.05 \cdot 10^5$	2.10

2.3. Mass and enthalpy balances

Mass and enthalpy balances were performed for the chemical looping unit, taking into consideration the gaseous and solids streams entering and exiting the air and fuel reactors, as well as heat management in the air reactor; see Fig. 2. Balance calculations were performed for the area inside the contour line. Table 4 summarizes equations used for mass balances on the entering and exiting streams in both the fuel and air reactors.

Fig. 2. CLaOU scheme with Mn66FeTi7 considered in the mass and enthalpy balances including heat supplied to ($Q_{AR} > 0$) or recovered from ($Q_{AR} < 0$) the air reactor.

Table 4. Mass balances based on molar flows of bixbyite, spinel and mangano-wüstite in the stoichiometric forms $(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_3$, $(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_{8/3}$ and $(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_2$. TiO_2 considered an inert phase. Basis: $F_{C,in} = 1 \text{ mol/s}$.

Fuel reactor inlet	Fuel reactor outlet
$F_{\text{MnFe},in} = F_{\text{bix},in} + F_{\text{sp},in} + F_{\text{mw},in} = 2\phi F_{C,in}$	$F_{\text{MnFe},out} = F_{\text{bix},out} + F_{\text{sp},out} + F_{\text{mw},out} = F_{\text{MnFe},in}$
	If $X_{r,FR}^t > \frac{R_{OC}^{ou}}{R_{OC}^t} = 0.34$ If $X_{r,FR}^t < \frac{R_{OC}^{ou}}{R_{OC}^t} = 0.34$
$F_{\text{bix},in} = F_{\text{MnFe},in} \cdot X_{o,AR}^{ou}$	$F_{\text{bix},out} = F_{\text{MnFe},in} \cdot (1 - X_{r,FR}^{ou})$ $F_{\text{bix},out} = 0$
$F_{\text{sp},in} = F_{\text{MnFe},in} \cdot (1 - X_{o,AR}^{ou})$	$F_{\text{sp},out} = F_{\text{MnFe},in} \cdot X_{r,FR}^{ou}$ $F_{\text{sp},out} = F_{\text{MnFe},in} \cdot (1 - X_{r,FR}^g)$
$F_{\text{mw},in} = 0$	$F_{\text{mw},out} = 0$ $F_{\text{mw},out} = F_{\text{MnFe},in} \cdot X_{r,FR}^g$
$F_{\text{TiO}_2,in} = 0.15 \cdot F_{\text{MnFe},in}$	$F_{\text{TiO}_2,out} = F_{\text{TiO}_2,in}$
$F_{\text{H}_2\text{O},in} = (S/C)_{\text{ratio}} F_{C,in}$	$F_{\text{H}_2\text{O},out} = F_{\text{H}_2\text{O},in}$
	$F_{\text{CO}_2,out} = F_{C,in}$
Air reactor inlet	Air reactor outlet
$(F_{\text{MnFe}} + F_{\text{TiO}_2})_{inAR} = (F_{\text{MnFe}} + F_{\text{TiO}_2})_{outFR}$	$(F_{\text{MnFe}} + F_{\text{TiO}_2})_{outAR} = (F_{\text{MnFe}} + F_{\text{TiO}_2})_{inFR}$
$F_{\text{O}_2,in} = \lambda \cdot F_{C,in}$	$F_{\text{O}_2,out} = (\lambda - 1) \cdot F_{\text{O}_2,in}$
$F_{\text{N}_2,in} = \frac{79}{21} \cdot F_{\text{O}_2,in}$	$F_{\text{N}_2,out} = F_{\text{N}_2,in}$

The following assumptions were adopted:

- The solid fuel was assumed to be carbon. The basis for calculation was a carbon feeding rate into the fuel reactor of $F_{C,in} = 1 \text{ mol/s}$ (corresponding to a thermal power input of 393.5 kW_{th}).
- Carbon was fully converted to CO_2 inside the fuel reactor.
- Preheated steam at 673 K was supplied to the fuel reactor as the fluidizing and gasifying agent with a steam/carbon ratio of $(S/C)_{\text{ratio}} = 0.5$.
- The air stream supplied to the air reactor was preheated to 673 K .
- Gas and solids exiting streams from the fuel and air reactors were at the temperature of each reactor.

- The fuel reactor was considered adiabatic ($\Delta H_{FR} = 0$), but heat exchange was considered in the air reactor to fulfil the enthalpy balance ($Q_{AR} = \Delta H_{AR}$).
- The air reactor temperature was set at 1148 K in order to guarantee suitable regeneration rate of bixbyite [13].
- No unoxidized mangano-wüstite was found at the air reactor exit, i.e. $X_{o,AR}^g = 1$ and $X_{o,AR}^{ou} \geq 0$. This assumption was based on the quick oxidation of mangano-wüstite to spinel phase with Mn66FeTi7 [13]. Therefore, the solids stream entering the fuel reactor consisted of mixtures of bixbyite and spinel.
- The solids stream exiting from the fuel reactor contained mixtures of two phases, with no consideration given to tri-component mixtures. The compounds that formed each mixture were calculated as a function of the ϕ parameter. Thus, bixbyite and spinel were considered when ϕ was high enough to avoid further reduction of spinel to mangano-wüstite (i.e. CLOU region in Fig. 1); spinel and mangano-wüstite were considered when ϕ was low enough to require oxygen being transferred in the CLC region in Fig. 1.

The enthalpy balance for one reactor j , with j being either the fuel reactor or the air reactor, considers all gaseous and solids streams at the inlet and outlet of the reactor. The molar flow of inlet and outlet compounds, F_i , and the formation enthalpy of every compound i , $\Delta H_{f,i}$, are considered in the enthalpy balance shown in Eq. (15).

$$\Delta \dot{H}_j = \sum (F_i \cdot \Delta H_{f,i})_{out,j} - \sum (F_i \cdot \Delta H_{f,i})_{in,j} \quad (15)$$

The formation enthalpies of Mn-Fe mixed oxides in the Mn66FeTi7 material were obtained with FactSageTM software [26]. The parameters of fit used to calculate them as a function of the temperature and solids conversion rate are shown in Table 5. The formation enthalpy of

gaseous compounds, as well as for C and TiO₂ as a separate phase, were calculated from thermodynamic data available in the literature [27], and shown in Table 6.

Fuel reactor temperature was calculated from the enthalpy balance, given the assumption that this reactor is adiabatic, i.e. $\Delta\dot{H}_{FR} = 0$. In addition, the heat management in the air reactor was also calculated considering the heat being removed ($Q_{AR} = \Delta\dot{H}_{AR} < 0$) or supplied ($Q_{AR} = \Delta\dot{H}_{AR} > 0$) from or to the air reactor; see Fig. 2.

Table 5. Equations and coefficients used to calculate the formation enthalpies of Mn-Fe mixed oxides as a function of the temperature and solids conversion rate for bixbyite/spinel or spinel/mangano-wüstite. FactSageTM software with FToxid database [26]. Confidence interval: 1123-1273 K.

	p	q	r
$\Delta H_{f,k} = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$			
$k = \text{Bixbyite}$	$-4.54 \cdot 10^5$	$-5.94 \cdot 10^8$	$2.38 \cdot 10^{11}$
$k = \text{Spinel}$	$-4.15 \cdot 10^5$	$-5.89 \cdot 10^8$	$2.37 \cdot 10^{11}$
$k = \text{Mangano-wüstite}$	$-3.30 \cdot 10^5$	$-4.28 \cdot 10^8$	$1.37 \cdot 10^{11}$
$\Delta H_{f,i}^p = a + b \cdot (X_r^i) + c \cdot (X_r^i)^2$			
$p = \text{ou: Bixbyite/Spinel redox system}$			
$a = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$	$-4.54 \cdot 10^5$	$-5.94 \cdot 10^8$	$2.38 \cdot 10^{11}$
$b = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$	$3.89 \cdot 10^4$	$5.15 \cdot 10^6$	$-4.09 \cdot 10^8$
$c = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$	0	0	0
$p = \text{g: Spinel/Mangano-wüstite redox system}$			
$a = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$	$-3.86 \cdot 10^5$	$-6.60 \cdot 10^8$	$2.80 \cdot 10^{11}$
$b = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$	$-2.84 \cdot 10^3$	$2.75 \cdot 10^8$	$-1.86 \cdot 10^{11}$
$c = p + q \cdot \left(\frac{1}{T}\right) + r \cdot \left(\frac{1}{T^2}\right)$	$1.83 \cdot 10^5$	$-3.38 \cdot 10^8$	$2.31 \cdot 10^{11}$

Table 6. Equations and coefficients used to calculate the formation enthalpies of gaseous compounds, as well as C and TiO₂, as a function of the temperature [27].

	$\Delta H_f = \Delta H_f^{T_{ref}} + \int_{T_{ref}}^{T_i} C_p(T) \cdot dT$		$C_p = a + b \cdot T + c \cdot T^2$ (J/mol · K)		
	$\Delta H_f^{T_{ref}}$ (J/mol)	T_{ref} (K)	a	b	c
O ₂	0	298	$2.77 \cdot 10^1$	$2.99 \cdot 10^{-3}$	$-1.37 \cdot 10^{-6}$
N ₂	0	298	$2.73 \cdot 10^1$	$5.13 \cdot 10^{-3}$	$3.97 \cdot 10^{-8}$
CO ₂	-393505	298	$3.38 \cdot 10^1$	$2.32 \cdot 10^{-2}$	$-4.65 \cdot 10^{-3}$
H ₂ O (v)	-241826	298	$3.04 \cdot 10^1$	$9.54 \cdot 10^{-3}$	$1.18 \cdot 10^{-6}$
C	3964	600	$5.75 \cdot 10^1$	$2.37 \cdot 10^{-2}$	$-7.85 \cdot 10^{-6}$
TiO ₂	-910981	800	$6.27 \cdot 10^1$	$1.69 \cdot 10^{-2}$	$-4.77 \cdot 10^{-6}$

3. Results

3.1. Thermochemical properties for the Mn66FeTi7 material

The thermochemical capability of the Mn66FeTi7 material to oxidize a fuel by the CLaOU process was defined by the equilibrium constants for reactions (R1)-(R6). The equilibrium constant of reaction (R1) defined the maximum oxygen concentration available during the oxygen uncoupling mechanism, as well as the minimum oxygen concentration required to regenerate the bixbyite. On the contrary, very low oxygen concentration values at equilibrium were estimated for reaction (R6). The equilibrium for this reaction was not evaluated as this fact implied that spinel could be easily regenerated. Also, very high values were estimated for the equilibrium constants of reactions (R2)-(R3). These equilibrium constants were not evaluated in this work as this fact implied that H₂ and CO could be highly converted to H₂O and CO₂ in any case. But H₂ and CO conversion could be limited by thermochemical equilibrium for reactions (R4)-(R5) in which spinel is being reduced to mangano-wüstite, in a similar way to that in which magnetite (Fe₃O₄) is reduced to wustite (FeO) [28]. Therefore, their equilibrium constants will be discussed here. Reaction enthalpy of reactions (R1)-(R6) will be also evaluated, which will have relevance on the enthalpy

balance of the process. Note that the enthalpy balance was reached by calculating the thermochemical properties as a function of the oxygen carrier conversion.

3.1.1. Oxygen at equilibrium for the oxygen uncoupling mechanism

In the Mn-Fe-Ti-O system, bixbyite is able to release gas-phase oxygen in an inert environment by means of its decomposition to spinel through the oxygen uncoupling reaction; see reaction (R1). The partial pressure of oxygen at equilibrium conditions for the Mn₆₆FeTi₇ material as a function of the reacting temperature was calculated with parameters shown in Table 2, and is shown in Fig. 3(a). Rutile phase (TiO₂) was present together with both bixbyite and spinel phases during the oxygen uncoupling process. Therefore, the introduction of a low amount of TiO₂ on the Mn-Fe mixed oxide did not modify the oxygen concentration at equilibrium conditions compared to a pure Mn-Fe mixed oxide.

Fig. 3. Effect of reacting temperature (a) and solids conversion for oxygen uncoupling X_r^{ou} (b) on the partial pressure of oxygen at equilibrium conditions. FactSageTM software with FToxid database [26]; β Sp: β Spinel; A-ilm: Ilmenite; Bix: Bixbyite; Rut: Rutile.

The oxygen concentration at equilibrium rises with the temperature. In addition, a gap between the area corresponding to the bixbyite and spinel phases is observed, which is related to the variation in oxygen concentration at equilibrium as the decomposition of bixbyite to spinel takes place. The oxygen concentration at equilibrium conditions decreases as the conversion of the oxygen uncoupling reaction, X_r^{ou} , increases; see Fig. 3(b).

The oxygen concentration at equilibrium conditions has relevant implications for the operating conditions of the fuel and air reactors. On the one hand, there is an upper limit in the available oxygen concentration in the fuel reactor. Thus, the partial pressure of oxygen at equilibrium conditions was 0.035 and 0.112 atm at 1173 and 1223 K, respectively, when bixbyite was completely regenerated in the air reactor and low variation in the solids conversion, i.e. $X_r^{ou} \approx 0$ for very high ϕ values. However, the oxygen concentration in the fuel reactor decreased as both X_r^{ou} and ϕ values approached the unity. So, when almost all the bixbyite had reacted to spinel, i.e. $X_r^{ou} \approx 1$, equilibrium oxygen concentration values of 0.026 and 0.086 at 1173 and 1223 K, respectively, were predicted. It is worth noting that these oxygen concentration values are potentially higher compared to those of Cu-based materials [6]. In addition, a higher temperature in the fuel reactor will be beneficial for fuel combustion as a higher oxygen concentration will be possible for thermodynamic reasons, and the oxygen generation rate will most likely be increased [13].

On the other hand, complete regeneration of bixbyite from the spinel can be achieved at temperatures below 1266 K in air ($P_{O_2} = 0.21$ atm), but this temperature must be lower if the partial pressure of oxygen is decreased, e.g. 1185 K with 0.05 atm O_2 . This value corresponds to the outlet concentration of industrial boilers. This finding will be relevant

for the design of the operating conditions of the air reactor, where the oxygen carrier must be regenerated by air. Thus, the air excess ratio, λ , will be a critical parameter for the oxidation of spinel to bixbyite. The optimum temperature both in air and fuel reactors will be determined through mass and enthalpy balances for the whole chemical looping unit.

3.1.2. H_2 and CO at equilibrium for the oxygen carrier reduction

It is well known that reduction of iron oxide to wüstite has a thermochemical limitation, which prevents the complete conversion of H_2 or CO into H_2O or CO_2 [28]. However, possible thermodynamic limitations in the reduction of spinel to mangano-wüstite in Mn-Fe mixed oxides as oxygen carriers have not been previously evaluated. In order to assess the capability of the Mn₆₆FeTi₇ material to convert H_2 and CO by reactions (R4) and (R5), their equilibrium constants were calculated and are discussed here; see Table 2. The evolution of equilibrium constants at several temperatures for the spinel reduction to mangano-wüstite, both with H_2 and CO, is shown in Fig. 4. The equilibrium constant is highly affected by the solids conversion rate, X_r^g . As a consequence, the fraction of H_2 or CO being converted into H_2O or CO_2 at equilibrium conditions decreases monotonically as reaction (R4) or (R5) progresses. For practical purposes, the unconverted fraction of these fuels, f_{H_2} and f_{CO} , at equilibrium conditions is calculated by Eq. (16).

$$f_i = \frac{1}{K_{eq,i} + 1} \quad (16)$$

For example, a value of the equilibrium constant of $K_{eq,i} = 10^2$ means that the unconverted fraction of fuel, either H_2 or CO, is ~1 % ($f_i \approx 0.01$), i.e. the conversion degree to H_2O or CO_2 is ~99 %. If a reacting temperature of 1173 K is assumed, this value of the equilibrium constant is achieved at $X_r^g = 0.69$ for H_2 and $X_r^g = 0.67$ for CO. Higher values of the solids

conversion limit the H₂ or CO conversion to values lower than 99%.

Fig. 4. Effect of the conversion of spinel to mangano-wüstite, X_r^g , on the equilibrium constant of reaction (R4) with H₂ (a) or reaction (R5) with CO (b). Equilibrium constant for physical mixtures of Mn₃O₄ + Fe₃O₄ in the same proportion than Mn₆₆FeTi₇ are also included (dashed line).

However, the Mn-Fe mixed oxide improves the performance of the physical mixture of monometallic Mn and Fe oxides; see Fig. 4. The evaluation of the singles oxides was performed taking into account a mixture with both oxides (i.e., Mn₃O₄ + Fe₃O₄) in the same proportion as that of the Mn₆₆FeTi₇ material. Considering the results obtained at 1173 K from data in Table 3, no thermodynamic limitations exist for the conversion of H₂ or CO to H₂O or CO₂, while Mn₃O₄ is reduced to MnO as the equilibrium constants are high; see reactions (R8) and (R12). When all the Mn₃O₄ is reduced to MnO ($X_r^g = 0.682$), reduction of Fe₃O₄ to FeO following reactions (R10) or (R14) begins with the subsequent sharp decrease in the equilibrium constant values to $K_{eq,H_2}^g = 2.73$ and $K_{eq,CO}^g = 2.10$. Consequently,

the unconverted fraction of H_2 and CO can be as high as 26.8% and 32.3%, respectively. However, the reduction of spinel to mangano-wüstite in $Mn_{66}Fe_{34}$ allows higher solids conversion values to be achieved with equilibrium constants well above to those required for the reduction of Fe_3O_4 to FeO in a mixture of manganese and iron oxides. This allows a larger amount of fuel to be converted by using $Mn_{66}Fe_{34}$ material with respect to case where there is a mixture of monometallic oxides. Even in the case of considering complete reduction to mangano-wüstite ($X_r^g = 1$), $Mn_{66}Fe_{34}$ would be able to oxidize up to 83.6 % H_2 or 79.2 % CO to H_2O or CO_2 , respectively at 1173 K, but a mixture of monometallic oxides would only convert 73.2% H_2 , or 67.7% CO .

3.1.3. Reaction enthalpies involving $Mn_{66}Fe_{34}$

The formation enthalpy of the Mn-Fe mixed oxide as a function of the total solids conversion, X_r^t , calculated from data in Table 5, is shown in Fig. 5 for several temperatures. Note that pure bixbyite, spinel and mangano-wüstite compounds corresponded to X_r^t values of 0, 0.34 and 1, respectively; see Section 2.1.

Formation enthalpies for bixbyite/spinel mixtures (i.e. $X_r^t < 0.34$) showed a linear trend with the total solids conversion, and could be calculated as a weighted average of the formation enthalpies of pure bixbyite and pure spinel. However, formation enthalpy values for mixtures of spinel/mangano-wüstite as a function of the X_r^t did not follow a linear trend with total solids conversion, which suggests a strong influence of the amount of oxygen in these mixtures on the thermochemical properties of the Mn-Fe mixed oxides compared to the properties of the physical mixtures of manganese and iron oxides. Thus, the formation enthalpy was calculated with a second order function with respect to X_r^g .

Note that X_r^g describes the degree of reduction from spinel to mangano-wüstite.

Fig. 5. Effect of the total solids conversion, X_r^t , on the formation enthalpy of Mn-Fe mixed oxides at several temperatures. Bixbyite $(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_3$, spinel $(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_{8/3}$ and mangano-wüstite $(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_2$ correspond to X_r^t values of 0, 0.34 and 1, respectively.

Formation enthalpies can be used to calculate reaction enthalpies. For example, the following reaction enthalpies are calculated at 1173 K:

The regeneration reactions with oxygen are exothermic, no matter which compound is being oxidized, spinel or mangano-wüstite. However, the oxidation of carbon to CO_2 is exothermic if bixbyite is the oxygen source. Note that the oxygen uncoupling reaction

involved in the mechanism of reaction (R15), i.e. reverse of reaction (R17), is an endothermic process. However, the overall process including the combustion of carbon with O_2 is exothermic. On the contrary the process in the fuel reactor is endothermic when spinel is the reacting solid. Nevertheless, the overall process in the whole chemical looping unit is exothermic, and the overall enthalpy variation, i.e. addition of reactions (R15)+(R17) or (R16)+(R18), is the same combustion enthalpy of carbon with oxygen (396 kJ/mol).

These results will have critical relevance for the temperature difference between the air and fuel reactors, but also for the determination of the auto-thermal conditions of the CLaOU unit regarding the air excess ratio. Higher temperature in the fuel reactor could be achieved when bixbyite is reduced to spinel, but lower temperature in the fuel reactor would be reached if spinel is reduced to mangano-wüstite. Thus, the existence of a maximum achievable temperature in the fuel reactor can be anticipated as a function of the degree of solids conversion in both the air and fuel reactors.

3.2. Determination of suitable operating conditions in the CLC unit

3.2.1. Operating conditions in the air reactor

Different regimes can be found when a material with oxygen uncoupling capability is used [29]. In the case of using a Mn-Fe mixed oxide, the solid fuel can be converted via *iG*-CLC, i.e. solid fuel is gasified and gasification products are subsequently oxidized to CO_2 and H_2O by the oxygen carrier in the spinel form, which would be reduced to mangano-wüstite. In such a case, low air excess ratios and high temperatures (about 1200-1300 K) can be used in the air reactor because there are no thermodynamic limitations to the regeneration of the spinel phase. Although high combustion efficiency has been achieved with Mn-Fe mixed oxides [30], difficulties are expected in the *iG*-CLC mode to achieve complete

combustion of the solid fuel [3].

In order to improve the combustion efficiency of the chemical looping process, exploitation of the oxygen uncoupling capability of the Mn-Fe mixed oxide system would be recommended. To do this requires regeneration of bixbyite because this is the only phase with oxygen uncoupling capability. Oxidation conditions greatly influence bixbyite regeneration. For the Mn₆₆FeTi₇ material [13] the optimum oxidation temperature was found to be in the 1123-1173 K interval. In addition, the higher the oxygen concentration, the higher the regeneration rate, with recommended oxygen concentration values above 5 vol%. The oxygen concentration in the air reactor depends on the air excess ratio, λ . Thus, the oxygen concentration at the air reactor outlet can be calculated from Eq. (17), and it increases with λ ; see Fig. 6. Therefore, the regeneration capability of the bixbyite is expected to be improved by increasing the air excess ratio.

$$\lambda = \frac{F_{O_2,in}}{F_{O_2,stoich}} = 1 + \frac{F_{O_2,out}}{F_{O_2,stoich}} = \frac{0.21 \cdot (1 - P_{O_2,outAR})}{0.21 - P_{O_2,outAR}} \quad (17)$$

However, a variation in the air-to-fuel ratio modifies the enthalpy balance in the air reactor and, therefore, the whole system. Fig. 6 shows the results obtained from an enthalpy balance considering a suitable value for the air reactor temperature of 1148 K, and assuming two different temperatures for the solids coming from the fuel reactor: higher (1273 K) or lower (1123 K) than the temperature in the air reactor. The heat generated in the fuel combustion could be extracted from both the circulating solids and exhaust gases [19]; see Fig. 2. Here, it was assumed that the heat extraction from solids was performed by managing the heat balance in the air reactor. The heat extracted from the air reactor, Q_{AR} , has a linear dependence on the air excess ratio, λ . In addition, the temperature considered in

the fuel reactor barely affects the heat withdrawn from the air reactor. At low λ values, a fraction of the thermal power must be extracted ($Q_{AR} < 0$) from the air reactor. But the heat flow from the air reactor decreases as the air excess ratio increases owing to the increase in the thermal heat present in the exiting air flow. When the air excess ratio is increased up to $\lambda \approx 3$, there is no longer any need to remove heat from the air reactor, i.e., $Q_{AR} = 0$. This condition corresponds to the upper limit for λ , where auto-thermal operation of the entire CLC unit is achieved. Thus, at the higher value of $\lambda > 3$, the operation is thermally unfeasible unless the CLC unit is heated by an external source. For $\lambda = 3$, the oxygen concentration at the air reactor outlet would be 15 vol%, which would guarantee the higher rate of bixbyite regeneration [13]. Nevertheless, the optimum value of λ must also take into consideration other economic and energy costs, as well as potential issues affecting the air reactor design related to the high air flow supplied.

Fig. 6. Effect of the air excess ratio, λ , on the heat flow from the air reactor, Q_{AR} , and partial pressure of the oxygen at the air reactor outlet. Fuel reactor temperature considered: 1123 K (—) or 1273 K (—).

3.2.2. Operating conditions in the fuel reactor

By fixing the operating conditions in the air reactor, the fuel reactor temperature becomes linked to the solids circulation rate ($\dot{m}_{OC}$) through the enthalpy balance to the fuel reactor [23]. For example, it is well known that the temperatures in both reactors become closer as the solids circulation rate increases [19]. Usually, the solids circulation rate is evaluated by means of the oxygen carrier-to-fuel ratio, ϕ , by Eq. (4); see Section 2.1. Fig. 7 shows the effect of the ϕ parameter on the thermal gradient between the fuel and air reactors (ΔT_{FR-AR}), as well as the fuel reactor temperature, assuming a temperature in the air reactor of 1148 K. Owing to possible kinetic limitations to the full regeneration of the bixbyite in the air reactor, several degrees of of spinel oxidation to bixbyite, X_o^{ou} , in the air reactor were considered.

Fig. 7. Effect of the oxygen carrier-to-fuel ratio, ϕ , on the thermal gradient between the fuel and air reactors (ΔT_{FR-AR}) and fuel reactor temperature for several values of oxidation conversion of spinel to bixbyite, X_o^{ou} , in the air reactor. $T_{AR} = 1148$ K.

In Fig. 7, a maximum in the fuel reactor temperature with the ϕ value can be observed for each degree of spinel oxidation to bixbyite. For example, considering the bixbyite to be fully regenerated in the air reactor (i.e. $X_o^{ou} = 1$), the reduction to the spinel phase is limited to values $\phi > 3$. In this case, the fuel combustion by oxygen uncoupling mechanism will be relevant; see Fig. 1. In such a case, carbon combustion in the fuel reactor is an exothermic process; see reaction (R15), which implies a temperature increase in the solids coming from the air reactor, i.e. $\Delta T_{FR-AR} > 0$. But ΔT_{FR-AR} decreases as the solids circulation rate increases, i.e. when the ϕ parameter is increased, because a higher amount of solids must be heated with the same generated heat [19].

However, further reduction to mangano-wüstite must happen for $\phi < 3$, which behaves endothermically; see reaction (R16). Thus, the exothermicity of the overall process involved in carbon combustion decreases, and as a consequence the temperature difference between the reactors decreases. The maximum in the fuel reactor temperature is found at $\phi = 2.6$ because the effect of a lower solids circulation rate from $\phi = 3$ to 2.6 is more relevant than the endothermic behaviour linked to the reduction of spinel.

In addition, Fig. 7 shows that the degree of bixbyite regeneration in the air reactor has a relevant effect on the fuel reactor temperature. The oxygen available for transfer by oxygen uncoupling, i.e. the exothermic process, is lower as the amount of bixbyite in the oxygen carrier decreases, i.e. X_o^{ou} in the air reactor decreases. This has two consequences:

(1) A lower amount of carbon is burnt by taking oxygen from the bixbyite, while more oxygen comes from the reduction of spinel. This drives to the overall process to become endothermic with higher solids circulation rates as the amount of bixbyite decreases. As a consequence, the maximum in the fuel reactor temperature is achieved at higher ϕ values as

X_o^{ou} decreases. It should be highlighted that when there is no bixbyite coming from the air reactor, i.e. $X_o^{ou} = 0$, the process is endothermic regardless of the ϕ value. This means that the temperature in the fuel reactor is always lower than that in the air reactor.

(2) Maximum fuel reactor temperature decreases as X_o^{ou} decreases, reducing about 15 K per each 25% of decrease in the degree of spinel oxidation. Thus, the maximum increase in the fuel reactor temperature is $\Delta T_{FR-AR} = 67$ K when $X_o^{ou} = 1$, decreasing to $\Delta T_{FR-AR} = 20$ K when $X_o^{ou} = 0.25$.

4. Discussion

To define the suitable operating conditions for the fuel and air reactors with the Mn₆₆FeTi₇ material, both results previously achieved in an experimental work [13] and the theoretical results from mass and enthalpy balances to a CLaOU unit presented in this work are considered. Some important concepts can be deduced for its use as oxygen carrier.

One material based on Mn-Fe mixed oxide can be used in the *i*G-CLC process regardless of air excess or reactor temperature. This regime is characterized by the reaction of a reducing agent with lattice oxygen in the solid, and it prevails at a low oxygen carrier-to-fuel ratio or when the degree of spinel oxidation to bixbyite is low in the air reactor. In this case, it is mainly the spinel phase that acts as the oxygen carrier, which can be easily regenerated at high temperatures and low oxygen concentration. The spinel/mangano-wüstite redox system in the Mn₆₆FeTi₇ material is able to transfer 6.2 wt% of its mass through reaction of a gaseous fuel with lattice oxygen. This value is higher compared to previously tested low-cost Fe or Mn-based materials, whose oxygen transport capacity is about 2.5 wt% for Fe-ore or the sand fraction of red mud [31], 3 wt% for Mn-ore [32] or about 2-4 wt% for

ilmenite [33]. The major relevance of this fact is that a lower solids circulation rate would be required, increasing the CO₂ capture of the *i*G-CLC process [34]. In order to maximize the performance of the Mn₆₆FeTi₇ material in *i*G-CLC, the temperature in the fuel reactor must be as high as possible. For example, the fuel reactor temperature must be kept above 1250 K in order to maximize coal gasification [34] and CO₂ capture [35]. This fact requires a higher temperature to be set in the air reactor, since the overall process inside the fuel reactor is endothermic; see Fig. 7 for $X_o^{out} = 0$. For example, for $\phi = 3$ the air reactor temperature would be 63 K higher than the fuel reactor temperature.

Significant improvement in combustion efficiency can be achieved when using synthetic Mn-Fe mixed oxides for coal combustion in an *i*G-CLC unit in comparison with other Fe-based oxygen carriers, such as ores or wastes [30]. Nevertheless, it should be highlighted that CO₂ capture and combustion efficiency are improved through the CLOU process compared to the *i*G-CLC process [3.4]. Thus, it is highly recommendable to take advantage of oxygen uncoupling capability of the Mn-Fe mixed oxides with solid fuels, particularly to increase the combustion efficiency of volatile matter in the fuel reactor.

To enhance the CLOU process, air reactor conditions must be carefully selected. The air reactor temperature must be limited to the 1123-1173 K interval in order to promote the oxidation of spinel to bixbyite [13]. Oxidation would still be possible at somewhat higher temperatures, but there would be a decrease in the oxidation rate as the oxygen at the equilibrium condition approaches the existing oxygen concentration. With regard to the effect of the partial pressure of O₂, the spinel is capable of being oxidized to bixbyite at 1148 K with an oxygen pressure higher than $P_{O_2} = 0.015$ atm from thermochemical considerations; see Section 3.1.1. However, a higher oxygen partial pressure is required in

order to provide high enough reaction rates to properly regenerate the bixbyite. For example, the oxidation degree varies from $X_o^{ou} = 6.2\%$ to $X_o^{ou} = 80.7\%$ by increasing the oxygen concentration from 5 vol% to 21 vol% O₂ [13].

With this in mind, it can be assumed that the oxygen concentration at the air reactor outlet determines the degree of bixbyite regeneration. Thus, the bixbyite regeneration, and therefore significance of the oxygen uncoupling, would be improved by increasing the air excess ratio, λ . This would allow combustion efficiency to be improved, which would reduce or even avoid the need for the additional energy and O₂ required by an oxygen polishing stage. However, high air flow would involve an extra energy cost owing to the increase in air impulsion power.

These facts imply that the air excess ratio must be optimized depending on the percentage decrease in the energy penalty as combustion efficiency is improved, but also considering the increase in the energy penalty as a higher air flow is supplied. The key question is: how much must the oxygen demand be reduced in order to offset the rising energy costs caused by higher air flow? A simplified answer can be given when considering the energy cost per a given rise in the air flow; see Eq. (18).

$$\left| \Delta E_{Air\ flow} \right| = \frac{\text{Energy penalty}}{\text{Increase in air excess}} \quad (18)$$

Fig. 8(a) traces the evolution of the energy penalty when varying the air excess ratio for different values of $\left| \Delta E_{Air\ flow} \right|$, showing that the energy penalty increases with the air excess ratio. An air excess value of $\lambda = 1.2$ was taken as a reference, while the evaluation was performed in order to consider auto-thermal conditions, i.e. the maximum allowed air excess ratio was $\lambda = 3$; see Fig. 6.

Fig. 8. (a) Effect of the increase in air excess (%) on energy loss (in percentage points) as a function of the energy penalty $|\Delta E_{Air\ flow}|$, and its relationship with (b) the required decrease in the oxygen demand to offset the energy lost as a function of the energy savings $|\Delta E_{Oxygen\ demand}|$.

The energy savings due to a lower oxygen demand is characterized by the term $|\Delta E_{oxygen\ demand}|$ in Eq. (19), and can be expressed as a function of the decrease in oxygen demand and the variation in the energy savings per a given increase in the air excess ratio; see Eq. (20).

$$|\Delta E_{oxygen\ demand}| = \frac{Energy\ savings}{Oxygen\ demand\ decrease} \quad (19)$$

$$\frac{Energy\ savings}{Increase\ in\ air\ excess} = |\Delta E_{oxygen\ demand}| \times \frac{Oxygen\ demand\ decrease}{Increase\ in\ air\ excess} \quad (20)$$

Fig. 8 is plotted in order to facilitate the calculation of the reduction in oxygen demand required to offset the increase in energy costs for a higher air flow. As an example, values of the energy costs and savings estimated in the literature are used here [3]. Thus, a value

for the energy penalty due to the air increase of $|\Delta E_{Air\ flow}| = 0.01$ has been estimated [36]. If a value of the air excess ratio of $\lambda = 2$ is considered, the energy penalty is 0.6 percentage points caused by the increase in air flow; see Fig. 8(a). This energy penalty must be offset by the energy savings due to a decrease in oxygen demand, which is calculated by using Fig. 8(b). Lyngfelt and Leckner [5] estimated a value for the energy saving per a given value of decreased oxygen demand of $|\Delta E_{Oxygen\ demand}| = 0.05$. Thus, a reduction in the oxygen demand of at least 12 percentage points must be achieved in order to offset the energy penalty caused by the increase in the air excess ratio to $\lambda = 2$.

These considerations must be taken into account in order to determine suitable experimental conditions for a Mn-Fe mixed oxide material in a CLC unit. The air reactor temperature must be limited in order to maximize the fraction of bixbyite being regenerated, which in turn is largely affected by the air excess ratio, λ . The degree of regeneration also affects the enthalpy balance for the system; see Fig. 7. Thus, the maximum temperature in the fuel reactor decreases as the degree of oxidation decreases. Both, the conversion to bixbyite and the fuel reactor temperature will affect the combustion efficiency in the fuel reactor.

Finally, the increase in the air excess ratio must be only justified if a significant decrease in the oxygen demand of the CLC process is achieved. In the *i*G-CLC process, total oxygen demand using low-cost materials as oxygen carriers is expected to be in the 10-20% interval with coal [3], and somewhat higher with biomass [4]. A high decrease in the oxygen demand would allow for the use of higher air excess ratio values. This fact should be determined by testing the Mn₆₆FeTi₇ material in a CLC unit in future works. These results will be very useful for a techno-economic assessment of the CLaOU process with

Mn-Fe mixed oxides, which must account for additional considerations, such as the different fraction of the energy extracted from either solids or exhaust gases in the air reactor.

5. Conclusions

Suitable operating conditions to enhance the oxygen uncoupling capability of a promising Mn-Fe mixed oxide, namely Mn₆₆FeTi₇, were determined by performing a comprehensive thermochemical assessment of the Chemical Looping *assisted by* Oxygen Uncoupling (CLaOU) process.

Where the solids circulation rate is low ($\phi < 2-3$) or bixbyite is not regenerated in the air reactor, spinel can be reduced to mangano-wüstite by reaction of a gaseous fuel with lattice oxygen. However, the conversion of the spinel phase should be limited to $X_r^g < 0.70$ in order to allow high H₂ and CO conversion to H₂O and CO₂. In addition, a high degree of spinel reduction should be avoided to allow a high temperature in the fuel reactor.

On the contrary, the temperature of solids in the fuel reactor may be up to 67 K higher than that of solids in the air reactor by promoting bixbyite regeneration and with a solids circulation rate corresponding to $\phi = 2-3$, given that to the entire process taking place in the fuel reactor is exothermic in this case. At these conditions, the equilibrium concentration of O₂ becomes about 0.1 atm at 1223 K, which is potentially high enough for the combustion of a solid fuel.

The optimum condition in the fuel reactor to maximize the fuel combustion depends on the regeneration conditions in the air reactor. Bixbyite regeneration may be promoted by using air excess ratio values higher than 1.2 and a reactor temperature in the 1123-1173 K

interval. The upper limit for the air excess ratio in this work was $\lambda = 3$ in order to keep the CLaOU unit at auto-thermal conditions. However, the air excess ratio should be defined considering that the improvement in the fuel combustion must offset the energy costs associated with high air flow. Thus, the use of an air excess ratio of $\lambda = 2$ must guarantee a reduction in the oxygen demand of at least 12 percentage points.

The results presented in this work may be useful for the identification of suitable operating conditions with Mn-Fe mixed oxide materials.

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Nomenclature

C_p	specific heat as function of the temperature of one compound ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
f_i	unconverted fraction of one gaseous fuel i ($i = \text{H}_2$ or CO) (-)
$F_{C,in}$	molar flow of carbon fed to the fuel reactor ($\text{mol}\cdot\text{s}^{-1}$)
F_{MnFe}	molar flow of Mn-Fe mixed oxide defined for the stoichiometric formula shown in Table 4 ($\text{mol}\cdot\text{s}^{-1}$)
F_{bix}	molar flow of bixbyite according to the stoichiometric formula $(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_3$ ($\text{mol}\cdot\text{s}^{-1}$)
F_{mw}	molar flow of mangano-wüstite according to the stoichiometric formula $(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_2$ ($\text{mol}\cdot\text{s}^{-1}$)
F_{sp}	molar flow of spinel according to the stoichiometric formula $(\text{Mn}_{0.66}\text{Fe}_{0.34})_2\text{O}_{8/3}$ ($\text{mol}\cdot\text{s}^{-1}$)
F_{TiO_2}	molar flow of TiO_2 ($\text{mol}\cdot\text{s}^{-1}$)
F_{CO_2}	molar flow of CO_2 ($\text{mol}\cdot\text{s}^{-1}$)
$F_{\text{H}_2\text{O}}$	steam molar flow ($\text{mol}\cdot\text{s}^{-1}$)
F_{N_2}	molar flow of N_2 ($\text{mol}\cdot\text{s}^{-1}$)
F_{O_2}	molar flow of O_2 ($\text{mol}\cdot\text{s}^{-1}$)
$F_{\text{O}_2,stoich}$	stoichiometric molar flow of O_2 needed to fully fuel conversion to CO_2 and H_2O ($\text{mol}\cdot\text{s}^{-1}$)
$K_{eq,CO}^g$	equilibrium constant for spinel reduction with CO via gas-solid reaction (-)
K_{eq,H_2}^g	equilibrium constant for spinel reduction with H_2 via gas-solid reaction (-)
K_{eq,O_2}^{ou}	equilibrium constant for bixbyite decomposition by oxygen uncoupling mechanism (-)
$\dot{m}_{OC}$	solids circulation rate ($\text{kg}\cdot\text{s}^{-1}$)
$\dot{m}_{SF}$	solid fuel rate fed ($\text{kg}\cdot\text{s}^{-1}$)
m	mass of oxygen carrier (kg)
m_{bix}	mass of the oxygen carrier in the bixbyite form (kg)
m_{mw}	mass of the oxygen carrier in the mangano-wüstite form (kg)
m_{sp}	mass of the oxygen carrier in the spinel form (kg)
P_i	partial pressure of gas i (atm)
Q_{AR}	air reactor heat flow withdrawn or supplied (W)
R_{OC}^g	oxygen transport capacity between spinel and mangano-wüstite (kg oxygen per kg of oxygen carrier)
R_{OC}^{ou}	oxygen transport capacity between bixbyite and spinel (kg oxygen per kg of oxygen carrier)
R_{OC}^t	total oxygen transport capacity between bixbyite and mangano-wüstite (kg oxygen per kg of oxygen carrier)
T	temperature (K)

X_j^g	conversion in reaction j between spinel and mangano-wüstite (-)
X_j^{ou}	conversion in reaction j between bixbyite and spinel (-)
X_j^t	total solids conversion for reaction j between mangano-wüstite and bixbyite (-)

Greek symbols

$ \Delta E_{Air\ flow} $	energy penalty due to the air excess increase (percentage points)
$ \Delta E_{Oxygen\ demand} $	energy savings due to the decrease in the oxygen demand (percentage points)
$\Delta \dot{H}_j$	balance in the enthalpy flow for one reactor j ($j = AR$ or FR) (W)
$\Delta H_{f,i}$	formation enthalpy for the compound i ($J \cdot mol^{-1}$)
$\Delta H_{f,k}$	formation enthalpy for one pure compound k ($k =$ bixbyite, spinel or mangano-wüstite) ($J \cdot mol^{-1}$)
$\Delta H_{f,i}^p$	formation enthalpy in a stream formed by one mixture of i phases under p conditions ($p = ou$ or g) ($J \cdot mol^{-1}$)
ΔT_{FR-AR}	thermal gradient between the fuel and the air reactors (K)
ΔX_s^t	difference on solids conversion between air and fuel reactors (-)
ϕ	oxygen carrier to fuel ratio (-)
η_{comb}	combustion efficiency in a CLC unit (-)
λ	air excess ratio supplied to the air reactor (-)
Ω_{SF}	oxygen demand of the solid fuel (kg oxygen per kg solid fuel fed)

Subscripts

AR	air reactor
FR	fuel reactor
in	reactor inlet
o	oxidation
out	reactor outlet
r	reduction
ref	reference conditions

Acronyms

CLaOU	Chemical Looping <i>assisted by</i> Oxygen Uncoupling
CLC	Chemical Looping Combustion
CLOU	Chemical Looping with Oxygen Uncoupling
iG-CLC	<i>in-situ</i> Gasification Chemical Looping Combustion

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