

1 **A novel air reactor concept for chemical looping combustion systems**

2 **operated at high pressure**

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7 **Abstract**

8 We analyse the viability of a novel reactor concept for chemical looping combustion applications with
9 CO₂ capture. The reactor consists of a packed bed of reduced oxygen carrier particles traversed by a
10 series of empty conducts oriented in the axial direction. These conducts are made of permeable but
11 non-selective porous walls, through which air diffuses towards the region of reacting solids. The
12 diffusion flux of air through the orifices, which is perpendicular to the main bulk flow of gas along the
13 conducts, imposes very long oxidation times for all the reacting particles and a quasi-steady heating
14 up of the air flow. The conducts designed to have a very high length/diameter ratio (i.e. above 50)
15 allow a large bypass of pressurized air through the reactor without coming into direct contact with the
16 solids, resulting in a modest pressure drop of the gas (i.e. below 5% at the reactor exit). A preliminary
17 reactor design example is described for a case using Fe/Fe₂O₃ pellets as oxygen carrier, which are
18 packed into a reactor (L=100 m, I.D.=2 m) traversed by air conducts (I.D.=0.05 m) with a wall 2 mm
19 thick and orifices occupying an area fraction of 0.12. The reactor can initially generate 100 MW_{th}, with
20 a gas flow at the exit at close to 1050°C and 19 atm, and it could be used intermittently for more than
21 9 hours as the main heater in a highly efficient Brayton cycle.

22

23 **Introduction**

24 Chemical looping combustion (CLC) technology is widely recognised to have potential for CO₂ capture
25 with negligible energy penalties [1-4]. Recent reviews on CLC report on the substantial progress made
26 in recent decades on the development of oxygen carriers, pilot plant operation and process variants
27 [5-15]. For power plant applications using clean fuel gases, high energy conversion efficiencies require
28 the air reactor to operate at high pressures and at the highest possible temperature to avoid functional
29 and/or structural damage to the materials [1, 4, 16-18]. Interconnected fluidized-bed reactors are the
30 main configuration proposed to carry out CLC processes. The efficient mixing of gas and solids in these
31 reactors facilitates the control of the temperature during the fast and energy-intensive redox reactions
32 characteristic of CLC systems [10,15]. However, interconnected fluidized-beds at high pressure still
33 face serious challenges, such as the necessity to maintain a stable solids circulation between the
34 reactors and the need for high-T and high-P filtering devices to remove fine particles from the gas that
35 could otherwise affect the performance of downstream turbines [19,20]. Pressurized packed-bed
36 reactors have been proposed to overcome these limitations. However, they have to deal with high
37 temperature profiles caused by sharp reaction fronts that appear in the bed [21-25]. Different heat
38 management strategies have been investigated to control the fluctuations in temperature, especially
39 during the highly-exothermic oxidation stage of CLC systems. One alternative is to use oxygen carriers
40 with low active phase contents. The heat released during the oxidation reaction is then absorbed by a
41 large amount of inert solid, thereby moderating the temperature in the reaction front, but at the
42 expense of having to use larger reactors for a given fuel input [26,27]. Packed-bed reactors loaded with
43 high proportion of active oxygen carrier can be operated by recirculating a fraction of the product gas.
44 The dilution of the gaseous feed allows the displacement of both reaction and heat transfer fronts to
45 be controlled along the bed without exceeding the temperature limits. A configuration of this type
46 allows more compact reactor designs but it involves greater energy demand and higher equipment
47 cost because of the large gas recirculation [28,29]. CLC packed-bed reactors can also be operated by
48 periodically reversing the direction of the gas flow. Preliminary studies have revealed that the frequent

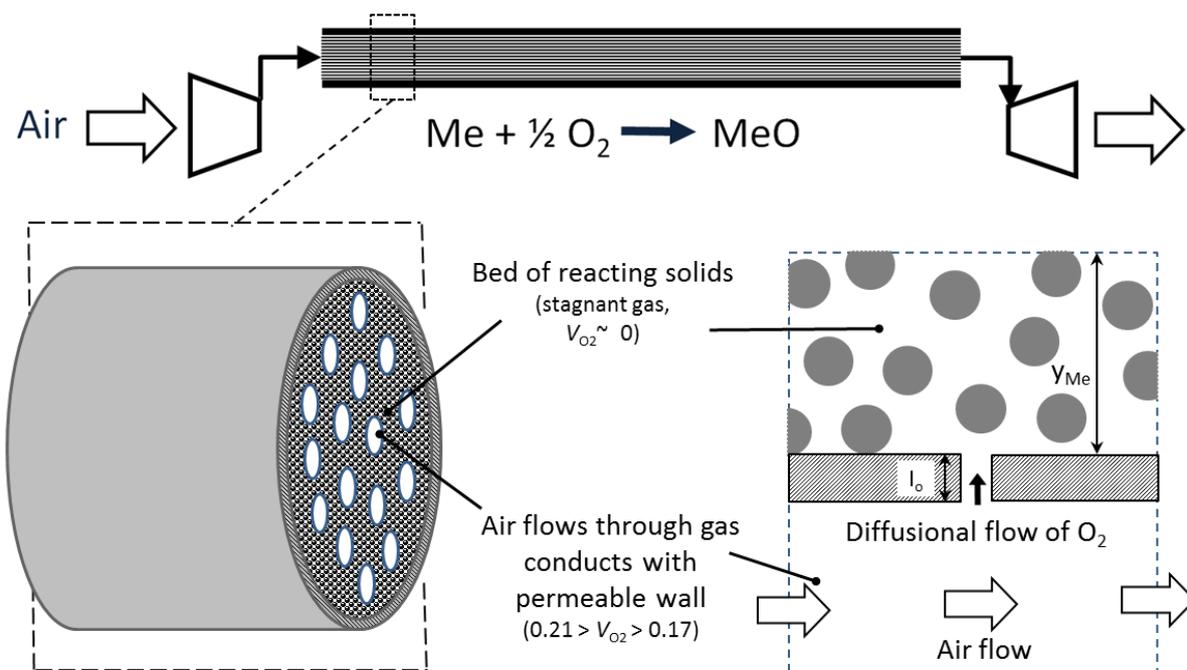
49 switching of reducing and oxidizing feed enhances the heat management inside the bed leading to
50 more uniform solids conversions and temperature profiles [30]. Another novel configuration consists
51 of a rotating bed that spins round while fuel and air are introduced radially. The rapid switching
52 between the oxidation and reduction stages should prevent the development of severe temperature
53 profiles inside the bed [31,32]. However, this reactor design entails possible gas leakages between the
54 reaction zones and requires complex balance of plant. Finally, honeycomb-structured CLC reactors
55 offer larger surface areas than conventional fixed-beds for an enhanced gas-solid contact. Therefore,
56 efficient fuel conversions are feasible with higher gas velocities throughout the bed with a moderate
57 pressure drop, which also help to maintain moderate temperature profiles inside the reactor [33].

58 In this short communication, we examine the basic design and performance of a new packed-bed
59 reactor concept [34] that attempts to overcome the main limitations of previous high pressure air
60 reactors by permitting a slow diffusional control of the solids oxidation in the air reactor.

61 **Reactor concept and case example**

62 The main service of a CLC power generation system is to exploit the thermal power released during
63 the oxidation of the oxygen carrier with air. Ideally, the air reactor should be integrated within a
64 Brayton cycle (Fig. 1, top) so that compressed air is heated up by the exothermic oxidation reaction of
65 *Me* to *MeO* and then expanded in a turbine. The nominal inlet temperatures of modern high-efficient
66 gas turbines are around 1400°C, but the maximum temperatures delivered by CLC fired systems cannot
67 exceed the 1000-1200°C range due to the constraints imposed by the oxygen carrier properties [5, 14].
68 Several process schemes propose the use of an additional combustor situated downstream of the CLC
69 reactors to heat the gas entering the gas turbine up to temperatures that would result in maximum
70 energy conversion efficiency, at the expense of certain carbon leakage when the fuel gas contains
71 carbon [16, 35]. The typical conditions of air fed into these CLC systems are about 500 °C and 20 atm
72 [26-29], so that a temperature increase in the air reactor of between 500 and 700 °C is a reasonable
73 compromise for design calculations. Moreover, oxidation enthalpies are very high for most oxygen

74 carriers (e.g. $\Delta H_{273K} = -553.7$ kJ/molO₂ for Fe/Fe₂O₃, which is the pair of solids used in the example
 75 below). An overall heat balance in the air reactor represented in Fig. 1 (top) shows that modest
 76 conversions of O₂ in the pressurized air that lead to about 0.17-0.18 of O₂ volume fraction at the reactor
 77 exit are sufficient to heat up the circulating air to over 1100 °C, assuming adiabatic conditions.
 78 Therefore, the main design challenge for the air reactor is to ensure a low O₂ conversion when it enters
 79 into contact with a highly reactive oxygen carrier (Me), while maintaining a reasonably low pressure
 80 drop of about 5% [26-29] in the gas subsequently expanded in the turbine for power generation. The
 81 bottom part of Fig. 1 illustrates the gas-solid contact mode adopted in the proposed air reactor to fulfill
 82 these two major constraints.



83

84 **Fig. 1.** Schematic representation of the novel air reactor set-up.

85 The overall reactor set-up is conceptually similar to that proposed by Kusano et al. in a seminal patent
 86 for the desulfurization of flue gas [36], in which a large flow of gas passes through a vessel containing
 87 bags of solid sorbent to remove SO₂. Perforated sheets or nets separate the bed of solids from the
 88 circulating gas. SO₂ then flows by diffusion through the orifices from the flue gas towards the interior
 89 of the bags, where the gas remains in a stagnant state. In the reactor proposed in this work, the same

90 principle is used to reduce by several orders of magnitude the oxidation rate of the oxidizing particles
91 in the packed bed and achieve the desired modest conversion of O₂. As shown in Fig. 1, the packed bed
92 of solids (containing the oxygen carrier in its reduced form, Me) is traversed in axial direction by
93 conducts free of solids through which air flows at high velocity. These conducts are made of porous
94 walls with small orifices that allow a non-selective diffusion of gas. A diffusion flow of air is established
95 through them, perpendicular to the bulk flow of gas along the conduct. When O₂ reacts with the
96 oxidizing solids, the heat generated is transferred through the wall of the conducts and heats up the
97 main air stream. Despite the great reactivity of the solid particles with oxygen under CLC conditions, it
98 is possible to impose very long oxidation times (i.e. hours), since the solids are forced to share the
99 limited oxygen arriving from the oxygen-rich region of the air conducts. This controlled oxidation
100 process will proceed throughout the reactor volume, thereby generating a steady axial temperature
101 profile along the reactor without hot spots and sharp axial reaction fronts characteristic of the reactor
102 designs mentioned above.

103 To illustrate with a quantitative example the viability and performance of the proposed air reactor, the
104 basic design rules that govern the O₂ diffusional fluxes in the reactor are described below for a
105 particular case where iron oxide (i.e. Fe/Fe₂O₃) is used as oxygen carrier.

106 The fraction of gas conduct wall occupied by orifices and the effective length of these orifices are
107 critical design parameters for limiting the oxidation rate of the solids in the packed bed. The high
108 temperature conditions existing in the air reactor will allow sufficiently fast oxidation kinetics of the
109 oxygen carrier to ensure that the O₂ partial pressure in the voids between the particles of the packed
110 bed remains close to zero. In these conditions, the overall reaction rate will be controlled by the flux
111 of O₂ through the orifices of the wall (F_{O_2} , mol/s O₂ per m² of gas conduct wall), which is given by Fick's
112 diffusion law, according to equation (1).

$$113 \quad F_{O_2,z} = \frac{D_{O_2,z} \varepsilon_w C_{O_2,z}}{l_o} \quad (1)$$

114 where D_{O_2} is the local value of the diffusivity of oxygen in air, ϵ_w is the fraction of gas conduct wall area
115 occupied by the orifices, $C_{O_2,z}$ is the local molar concentration of O_2 and l_o is the effective length of the
116 orifices.

117 The orifices are assumed to be uniformly distributed in the gas conduct wall. Their diameter should be
118 sufficiently small to prevent the entrance of particles from the packed bed section to the air conducts
119 and sufficiently large to reduce Knudsen diffusion effects, that would impose further limitations on the
120 effective flux of oxygen through the wall. In steady state conditions, the initial power output from the
121 oxidation of Me to MeO will be the local product of the flux of O_2 through the orifices and the oxidation
122 enthalpy (i.e. $F_{O_2} \cdot \Delta H_{r,O_2}$), which only depends on the diffusion properties of the gas through the orifices
123 in the wall, and not on the properties of the reacting solids or their degree of conversion.

124 As can be seen below, similar values of F_{O_2} throughout the air reactor are feasible even with large
125 differences in axial temperatures. This is because the fluxes of oxygen along the reactor at a given time
126 t are only linked to the variability in the diffusivity and concentration of O_2 with the local operating
127 conditions (see equation 1) once the design has been fixed (i.e. once the variables affecting the porous
128 wall have been defined). For example, the fact that temperature has opposite effects on diffusivity and
129 concentration of O_2 makes the oxygen fluxes to be remarkably close even at the extremely different
130 local temperature conditions found along the reactor. In the case of pressure, this is even more
131 pronounced as the diffusivity varies inversely proportional to pressure while concentration
132 dependency to this variable is directly proportional. This means that O_2 fluxes, and therefore reaction
133 rates and heat generation rates, are not affected by pressure when all other conditions are maintained.
134 As a result, control possibilities of the oxygen fluxes for a fixed reactor design (and thus, of the thermal
135 output) are very limited since the fluxes of oxygen barely change within the range of temperatures
136 expected. A heat balance in an elemental volume of the reactor under adiabatic and steady state
137 conditions allows the axial temperature profile in the reactor to be calculated by taking into account
138 the difference in temperature between the wall ($T_{w,z}$) and air ($T_{gas,z}$), as follows:

$$\frac{d(m_{gas,z} C_{p_{gas,z}} T_{gas,z})}{dz} = A_w h_{w,z} (T_{w,z} - T_{gas,z}) = A_w F_{O_2,z} \Delta H_{r,O_2} \quad (2)$$

139 where $m_{gas,z}$ is the local mass flow rate of gas, $c_{p_{gas,z}}$ is heat capacity of the gas, A_w is the total inner area
 140 of the air conduct walls and $h_{w,z}$ is the local wall-gas heat transfer coefficient. Both temperature axial
 141 profiles $T_{w,z}$ and $T_{gas,z}$ can then be obtained from the known initial conditions at $z=0$ by solving equations
 142 (1) and (2).

143 As the particles of the oxygen carrier are progressively converted from Me to MeO, additional
 144 resistances to the reaction may appear, in addition to that of the extreme resistance imposed by the
 145 diffusion of oxygen through the porous wall. As a consequence, there may be a gradual decrease in
 146 the overall oxidation reaction rate and hence, in the power output, from a maximum value at the
 147 beginning of the operation (i.e. when the molar fraction of Me in the packed bed, X_{Me} , is equal to 1) to
 148 a minimum when the solids approach total oxidation (i.e. when $X_{Me}=0$ and $X_{MeO}=1$). In the absence of
 149 experimental information on particular materials and reactor set-ups, two extreme cases have been
 150 considered:

151 1. The only controlling step is the diffusion through the orifices (equation 1) and the process is not
 152 affected by the progressive conversion of the solids. This implies some kind of mass transport
 153 mechanism (for example, gas convection promoted by local temperature profiles at particle level)
 154 in the inter-particle voids of the volume associated with each orifice (represented on the right-
 155 hand side of Fig. 1). In this case, the power output will remain constant during the oxidation of
 156 the full batch of solids in the reactor and only change drastically to zero once the solids have
 157 reached full oxidation.

158
 159 2. An oxidation front moves away from each orifice in perpendicular direction to the air flow in the
 160 conducts (i.e. a bed of MeO located at a distance “ y ” from the wall is growing at the expense of
 161 the initial bed of Me). In this case, the same oxygen diffusion mass balance yields Equation 3

162 (assuming the gas diffusivity of O₂ to be the same in the orifices and in the voids between the
 163 particles), which shows that the oxygen flux (and thus, the overall oxidation reaction rate)
 164 decreases with time as the reaction front advances in the solids bed:

$$165 \quad F_{O_2,z,t} = \frac{D_{O_2,y,z,t} \varepsilon_w (C_{O_2,z,t} - C_{O_2,z,w,t})}{I_o} = \frac{D_{O_2,y,z,t} \varepsilon_{MeO} C_{O_2,z,w,t}}{y_{z,t}} \quad (3)$$

166 where $C_{O_2,z,w,t}$ is the local concentration of O₂ on the side of the air conduct wall in contact with the
 167 solids bed and $y_{z,t}$ is the position of the oxidation reaction front at that point in time and reactor length.
 168 The advance of the oxidation front away from the conduct wall with time can be estimated from the
 169 overall conversion of Me to MeO ($X_{MeO,t}$) and the effective thickness of the initial packed bed of solids
 170 allocated to each air conduct (y_{Me}). Assuming Cartesian dimensions (i.e. for flat air conducts or thin
 171 packed beds per cylindrical air conduct), it can be calculated as follows:

$$172 \quad y_{z,t} = X_{MeO,z,t} y_{Me} \quad (4)$$

173 As noted above, fluxes of oxygen will not change much in the axial direction, which means that an
 174 average value of $X_{MeO,t}$ can be adopted for the entire reactor at any given time. This, combined with
 175 equation (3), yields for a given time and level of conversion of the solids:

$$176 \quad F_{O_2,z,t} = \frac{(D_{O_2,y,z,t} \varepsilon_w C_{O_2,z,t})/I_o}{\left(1 + \frac{X_{MeO,t} y_{Me} \varepsilon_w}{I_o \varepsilon_{MeO}}\right)} \quad (5)$$

177 The average conversion of the solids at any time ($X_{MeO,t}$) can be calculated from the oxygen mass
 178 balance in the solid phase associated with each orifice, which states that the oxygen that has diffused
 179 through the porous walls from time 0 to t must be in the form of MeO:

$$180 \quad b X_{MeO,t} y_{Me} (1 - \varepsilon_{MeO}) L_r \rho_{MeO} = \int_{t=0}^{t=t} \int_{z=0}^{z=L_r} F_{O_2,z,t} dt dz \quad (6)$$

181 where b are the moles of O₂ reacted per mol of MeO, ρ_{MeO} is the molar density of MeO (mol/m³) and
 182 L_r is the total length of the reactor (m).

183 A preliminary conceptual design with Fe/Fe₂O₃ as oxygen carrier has been calculated assuming a
 184 reactor 100 m long, with an inner diameter of 2 m and traversed axially by air conducts with diameter
 185 of 0.05 m. The air reactor is able to generate a maximum power of 100 MW_{th} with the gas at the exit
 186 flowing at 1048 °C and 18.9 atm. Dynamic temperature changes to achieve pseudo-steady states have
 187 been ignored for the sake of simplicity, because the thermal ballast associated with temperature
 188 changes in the mass of the reactor is much smaller than the total energy density stored in the reactor
 189 (3100 kWh/m³ in the example). Moreover, no temperature profiles in the bed in a direction
 190 perpendicular to the air flow have been considered due to the modest depth of the solids bed
 191 associated with a single orifice (i.e. 0.02 m in the example). The correlations for calculating the
 192 diffusivity of oxygen and other transport properties at different temperatures have been obtained
 193 from Perry's handbook [37]. Table 1 summarizes the reactor characteristics and the input operating
 194 conditions chosen for the case study with Fe/Fe₂O₃ and Table 2 shows the results obtained once the
 195 previous set of equations are solved.

196 **Table 1.** Reactor characteristics and operating conditions corresponding to the reference case study.

| Parameters | Values |
|---|--------|
| Target thermal power output (MW) | 100 |
| Reactor length, L _r (m) | 100 |
| Effective internal diameter of each air conduct, D _i (m) | 0.05 |
| Thickness of air conduct walls = diffusion length through the wall (m), l _o | 0.002 |
| Fraction of air conduct wall occupied by orifices, ε _w | 0.12 |
| Effective thickness of packed bed of iron solids around an air conduct (m), y _{Me} | 0.02 |
| Initial vol. fraction of Fe (iron sponge) in the packed bed around air conducts, (1-ε _{Me}) | 0.3 |
| Inlet air pressure, P _{in} (atm) | 20 |
| Inlet air temperature, T _{in} (°C) | 500 |
| Inlet air velocity in the interior of the air conduct (m/s) | 20 |
| Enthalpy of oxidation of Fe to Fe ₂ O ₃ (kJ/mol O ₂) | 553.7 |

| | |
|--|-----------|
| Maximum conversion of Fe to Fe ₂ O ₃ | 1 |
| Fe/Fe ₂ O ₃ solid densities (kg/m ³) | 7874/5250 |

197

198 **Table 2.** Calculated parameters at the beginning of the oxidation period in the air reactor, for the
 199 operating conditions listed in Table 1 and assuming steady operation of the reactor.

| Parameters | Value ₂₀₀ |
|--|-------------------------|
| Effective total internal diameter of the reactor, (m) | 1.97 |
| Number of air conducts or pipes, N _a | 438 |
| Air conduct wall-air heat transfer coeffic., h, at reactor inlet (outlet) (W/m ² K) | 480 (615) ¹ |
| Diffusivity of O ₂ in N ₂ , D _{O_{2,z}} at inlet (outlet) (m ² /s x 10 ⁻⁶) | 5.4 (11.9) ² |
| Initial flux of oxygen trough the wall, inlet (outlet) of the reactor, (mol O ₂ /m ² s) | 0.182 (0.219) |
| Fanning factor at inlet | 0.00545 ³ |
| Temperature of the gas at the reactor exit, (°C) | 1048 |
| O ₂ volume fraction at the reactor exit | 0.185 |
| Gas velocity at the reactor exit, (m/s) | 33.13 |
| Pressure at the reactor exit, (atm) | 18.93 |
| Minimum time to complete the oxidation of the solids in the reactor, (hours) | 9.22 |
| Average energy density stored in the full reactor at t=0 (kWh/m ³ reactor) | 3099 |

201 ¹ Nu=0.023·Re^{0.8}Pr^{0.4}; ² D_{O_{2,z}}=0.113·(T+273)^{1.724}/P (m²/s x 10⁻⁸); ³ f_F=0.04/Re^{0.16}

202 Under these controlled oxidation conditions, and for the case 1 noted above, it would take more than
 203 9 hours for the oxygen to oxidize the entire packed bed. It should be mentioned that the operation of
 204 the reactor in a subsequent reduction cycle (i.e. Fe₂O₃ to Fe) involving the feeding of a fuel gas is
 205 considered outside the scope of this work. In general, the operation of this fuel reactor will entail less
 206 challenging reaction conditions and time scales, since fuel flow rates are typically one order of
 207 magnitude lower than the air flows in the air reactors, reduction enthalpies are lower than oxidation

208 enthalpies and the operation times can also be much longer (in particular when the air reactor is used
209 only as back-up power system).

210 As mentioned above, the calculated flux of O₂ through the orifices of the wall is very similar along the
211 air reactor despite the large difference in temperatures between the inlet and outlet of the axial
212 conducts. In fact, this phenomenon makes the axial heat generation rate and temperature profiles
213 virtually linear, as can be seen in Fig. 2a (solid lines). These temperature profiles are very sensitive to
214 design decisions that determine such oxygen fluxes.

215 In addition, for the case 2 described around equation 3, additional resistances to O₂ diffusion in the
216 orifice will appear in the bed, resulting in a drop in temperatures at the reactor exit (see dotted line
217 Fig. 2a, for a constant mass flow at the inlet). In this case study, when almost all the iron present in the
218 bed has been converted into Fe₂O₃, the temperature of the gas leaving the reactor would be around
219 660 °C.

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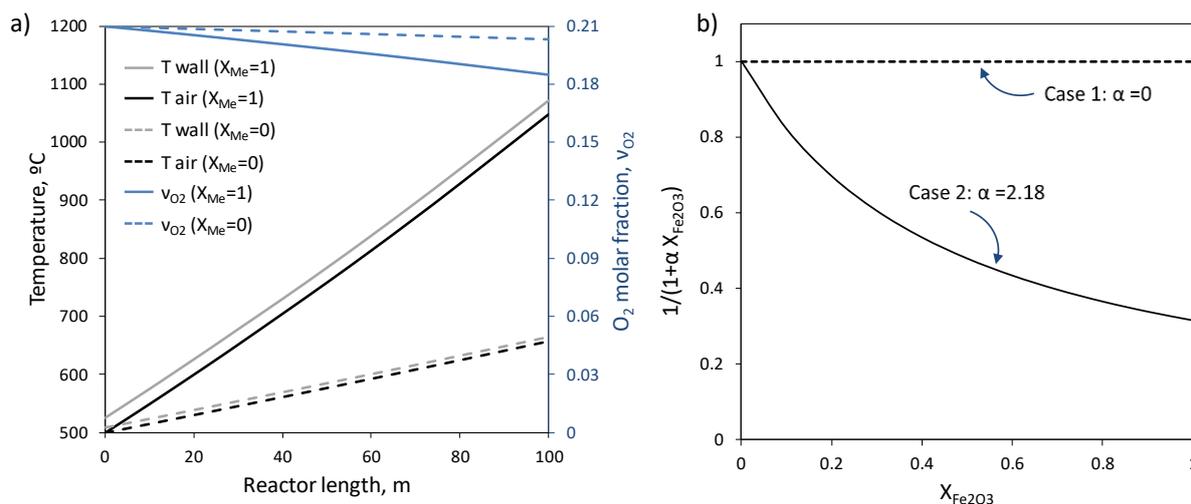
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228 **Fig. 2.** a) Axial temperature and oxygen profiles (right axis) of air and conducts wall at the beginning of
 229 the oxidation stage (solid lines) and when the solids bed is approaching full oxidation (dotted lines); b)
 230 Fall in oxygen fluxes and reactor power output as a function of the conversion of Fe to Fe₂O₃ for cases
 231 1 and 2 (using the data listed in Table 1 to calculate $\alpha=2.18$).

232 Figure 2b shows the decay in power output during the operation under the mode described in case 2.
 233 As can be seen, the term " $\alpha = y_{Me} \epsilon_w / l_o \epsilon_{MeO}$ " in equation (5) entails critical design decisions, since the
 234 fact that bringing it towards zero to maintain the production of power stable will involve much thinner
 235 layers of oxygen carrier per each associated air conduct (i.e. more air conducts for a given amount of
 236 solids), much longer reactors to operate with smaller fraction of air conduct wall occupied by orifices
 237 (ϵ_w), or larger wall thicknesses with a more loosely packed bed of solids (l_o).

238 The decay in power output of the proposed air reactor due to the additional diffusional resistance as
 239 the conversion of the solids progresses may be unavoidable, but this should not be a showstopper for
 240 the use of this diffusion controlled reactor in applications where a steady power supply is demanded.
 241 A straightforward solution to ensure steady outputs has already been mentioned above: this consists
 242 in burning a minor flow of fuel gas at the reactor exit (or at turbine entrance) to top up temperatures,
 243 and consequently, the efficiency of the Brayton cycle [16, 35]. Therefore, the proposed reactor could
 244 be of practical use for wide range of applications, including mobile applications (e.g. boats) and other

245 systems that could accommodate high L/D aspect ratios. However, clearly more theoretical and
246 experimental work is needed to proof the concept.

247 **References**

248 [1] M. Ishida, H. Jin, A new advanced power-generation system using chemical looping combustion,
249 Energy 19 (1994) 415–422.

250 [7] A. Lyngfelt, B. Leckner, T. Mattisson, A fluidized-bed combustion process with inherent CO₂
251 separation; application of chemical-looping combustion, Chem. Eng. Sci. 56 (2001) 3101–3113.

252 [3] M. Ishida, M. Yamamoto, T. Ohba, Experimental results of chemical-looping combustion with
253 NiO/NiAl₂O₄ particle circulation at 1200 degrees C, Energ. Conv. Manag., 43 (2002) 1469-1478.

254 [4] O. Brandvoll, O. Bolland, Inherent CO₂ capture using chemical looping combustion in a natural gas
255 fired power cycle, J. Eng. Gas Turbines Power 126 (2004) 316–321.

256 [5] J. Adanez, A. Abad, F. Garcia-Labiano, P. Gayan, L.F. de Diego, Progress in chemical-looping
257 combustion and reforming technologies, Prog. Energy Combust. Sci. 38 (2012) 215–282.

258 [6] L.S. Fan, L. Zeng, W. Wang, S. Luo, Chemical looping processes for CO₂ capture and carbonaceous
259 fuel conversion – prospect and opportunity, Energ. Environ. Sci. 5 (2012) 7254–7280.

260 [7] A. Lyngfelt, Chemical-looping combustion of solid fuels – Status of development, App. Energ. 113
261 (2014) 1869–1873.

262 [8] S. Banerjee, R.K. Agarwal, Review of recent advances in process modeling and computational fluid
263 dynamics simulation of chemical-looping combustion, 18 (2017) 1-37.

264 [9] M Matzen, J. Pinkerton, X. Wang, Y. Demirel, Use of natural ores as oxygen carriers in chemical
265 looping combustion: A review, Int. J. Greenh. Gas Con. 65 (2017) 1-14.

- 266 [10] J. Adanez, A. Abad, T. Mendiara, P. Gayan, L.F. de Diego, F. Garcia-Labiano, Chemical looping
267 combustion of solid fuels, *Progress in chemical-looping combustion and reforming technologies*, *Prog.*
268 *Energy Combust. Sci.* 65 (2018) 6-66.
- 269 [11] T. Song, L. Shen, Review of reactor for chemical looping combustion of solid fuels, *Int J. Greenh.*
270 *Gas Con.* 76 (2018) 92-110.
- 271 [12] T. Mattisson, M. Keller, C. Linderholm, P. Moldenhauer, M. Ryden, H. Leion, A. Lyngfelt, Chemical-
272 looping technologies using circulating fluidized bed systems: Status of development, *Fuel Proces.*
273 *Technol.* 172 (2018) 1-12.
- 274 [13] Z. Chen, L. Qin, J.A Fan, L.S. Fan, New Insight into the Development of Oxygen Carrier Materials
275 for Chemical Looping Systems, *Engineering*, 4 (2018) 343-351.
- 276 [14] J. Hu, V.V. Galvita, H. Poelman, G.B. Marin, Advanced chemical looping materials for CO₂
277 utilization: A review, *Materials*, 11 (2018) 1187-1219.
- 278 [15] A. Lyngfelt, A. Brink, O. Langorgen, T. Mattisson, M. Ryden, C. Linderholm, 11,000 h of chemical-
279 looping combustion operation—Where are we and where do we want to go? *Int. J. Greenh. Gas Con.*
280 88 (2019) 38-56.
- 281 [16] R. Naqvi, O. Bolland, Multi-stage chemical looping combustion (CLC) for combined cycles with CO₂
282 capture. *Int J Greenh. Gas Con.* 1 (2007) 19-30.
- 283 [17] H.M. Kvamsdal, K. Jordal, O. Bolland, A quantitative comparison of gas turbine cycles with CO₂
284 capture, *Energy* 32 (2007) 10-24.
- 285 [18] R. Naqvi, J. Wolf, O. Bolland, Part-load analysis of a chemical looping combustion (CLC) combined
286 cycle with CO₂ capture, *Energy* 32 (2007) 360-370

- 287 [19] R. Xiao, Q. Song, M. Song, Z. Lu, S. Zhang, L. Shen, Pressurized chemical-looping combustion of
288 coal with an iron ore-based oxygen carrier, *Combust. Flame* 157 (2010) 1140-1153.
- 289 [20] A. Bischi, O. Langørgen, I. Saanum, J. Bakken, M. Seljeskog, M. Bysveen, J.X. Morin, O. Bolland,
290 Design study of a 150kWth double loop circulating fluidized bed reactor system for chemical looping
291 combustion with focus on industrial applicability and pressurization, *Int. J. Greenh. Gas Con.* 5 (2011)
292 467-474.
- 293 [21] S. Noorman, M. van Sint Annaland, H. Kuipers, Packed bed reactor technology for chemical-
294 looping combustion, *Ind. Eng. Chem. Res.* 46 (2007) 4212-4220.
- 295 [22] S. Noorman, F. Gallucci, M. van Sint Annaland, H. Kuipers, Experimental investigation of a
296 CuO/Al₂O₃ oxygen carrier for chemical-looping combustion. *Ind. Eng. Chem. Res.* 49 (2010) 9720-9728.
- 297 [23] S. Noorman, F. Gallucci, M. van Sint Annaland, J.A.M Kuipers, A theoretical investigation of CLC in
298 packed beds. Part 2: Reactor model. *Chem. Eng. J.* 167 (2011) 369-376.
- 299 [24] V. Dupont, A.B. Ross, E. Knight, I. Hanley, M.V. Twigg, Production of hydrogen by unmixed steam
300 reforming of methane, *Chem. Eng. Sci.* 63 (2008) 2966-2979.
- 301 [25] A. Antzara, E. Heracleous, A.A. Lemonidou, Energy efficient sorption enhanced chemical looping
302 methane reforming process for high-purity H₂ production: Experimental proof-of-concept, *App. Energ.*
303 180 (2016) 457-471.
- 304 [26] V. Spallina, F. Gallucci, M.C. Romano, P. Chiesa, G. Lozza, M. van Sint Annaland, Investigation of
305 heat management for CLC of syngas in packed bed reactors. *Chem. Eng. J.* 225 (2013) 174-191.
- 306 [27] V. Spallina, P. Chiesa, E. Martelli, F. Gallucci, M.C Romano, G. Lozza, M. van Sint Annaland,
307 *Reactor design and operation strategies for a large-scale packed-bed CLC power plant with coal*
308 *syngas*. *Int. J. Greenh Gas Con.* 36 (2015) 34-50.

- 309 [28] J.R. Fernandez, J.C. Abanades, Conceptual design of a Ni-based chemical looping combustion
310 process using fixed-beds, *App. Energ.* 135 (2014) 309-319.
- 311 [29] J.R. Fernandez, J.M. Alarcon, Chemical looping combustion process in fixed-bed reactors using
312 ilmenite as oxygen carrier: Conceptual design and operation strategy, *Chem. Eng. J.* 264 (2015) 797-
313 806.
- 314 [30] L. Han, G.M. Bollas, Chemical-looping combustion in a reverse-flow fixed bed reactor. *Energy* 102
315 (2016) 669–81.
- 316 [31] S.F. Håkonsen, R. Blom, R., Chemical looping combustion in a rotating bed reactor – Finding
317 optimal process conditions for prototype reactor. *Environ. Sci. Technol.* 45 (2011) 9619-9626.
- 318 [32] Z. Zhao, T. Chen, A.F. Ghoniem, Rotary bed reactor for chemical-looping combustion with carbon
319 capture. Part 1: reactor design and model development. *Energy Fuel* 27 (2012) 327–343.
- 320 [33] H. Zhang, H. Hong, Q. Jiang, Y. Deng, H. Jin, Q. Kang, Development of a chemical-looping
321 combustion reactor having porous honeycomb chamber and experimental validation by using
322 NiO/NiAl₂O₄, *App. Energ.* 211 (2018) 259-268.
- 323 [34] J.C. Abanades, Reactor for heating a gas and uses thereof, Patent Application to the European
324 Patent Office PCT/EP2019/063643, 2019.
- 325 [35] S. Consonni, G. Lozza, G. Pellicia, S. Rossini, F. Saviano, Chemical-looping combustion for combined
326 cycles with CO₂ capture, *J. Eng. Gas Turb. Power* 128 (2006) 525–534.
- 327 [36] K. Kusano, H. Ando, T. Kagami, A. Uchida, N. Akiyama, Y. Ueda, Y. Akiba, Apparatus for facilitating
328 contact between solid particles and fluid, Patent GB1467277A, 1974.
- 329 [37] R.B. Perry, D.W. Green, *Perry's Chemical Engineers' Handbook*, McGraw-Hill, 1999.