Extension and evaluation of a macroscopic model for syngas-fueled chemical looping combustion

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Abstract

Syngas-fueled Chemical Looping Combustion (syngas-CLC) which can be integrated to *ex-situ* gasification of coal possesses the advantages over direct use of coal in CLC: (i) no requirement for carbon stripper, (ii) no requirement for oxygen demand, (iii) no interaction of oxygen carrier with coal ash, (iv) no losses of oxygen carrier with the draining stream of ash. Fuel reactor in syngas-CLC determines the performance of combustion and thus important to the increase of CO₂ capture efficiency. This work carries out a modeling of the fuel reactor of a continuous 500 W_{th} CLC system with syngas as fuel and a Cu-based material (Cu14Al-I) as oxygen carrier. Shrinking core model (SCM) using summation rate for single gases (CO and H₂) was evolved for the description of reaction kinetics for syngas (CO+H₂) and Cu14Al-I oxygen carrier. Considering the reaction kinetics, the fluid dynamics and the mass balance in fuel reactor, a mathematical fuel reactor model was established using MATLAB[®] codes. This model was then validated against experiments obtained from the same 500 W_{th} facility in literature. Various operation parameters including syngas composition, temperature, solids circulation rate and solids inventory were changed during the modeling process to analyze their effects on combustion performance of syngas. Water-Gas Shift (WGS) reaction was also evaluated for its relevance in syngas-CLC. Finally, operation regions for 99.9% combustion of syngas were mapped, which could be applied for the optimization, design and scale-up of syngas-CLC systems.

Keywords: Fluidized bed reactor model; Chemical looping combustion; Syngas; Cu-based oxygen carrier; Shrinking core model; CO₂ capture

1. Introduction

The dependence on fossil fuel for production of energy cannot be substituted by other alternatives including renewable energies before they become mature to supply most of demanded energy [1]. During the utilization of fossil fuels, emission of CO₂ is crucial because of its effect on global warming, thus strategies for CO₂ removal must be developed [2]. Among them, Chemical Looping Combustion (CLC) has been suggested among the best options for CO₂ capture with low costs [3]. CLC concept is based on the rationale of pure CO₂ generation patented by Lewis and Gilliland [4], which was first proposed by Ishida et al. [5]. In CLC technology, conventional combustion is split into two steps: oxygen required for fuel combustion is provided by solid oxygen carrier, a type of metal oxide; and then air is used as regeneration agent for the oxygen carrier. The most common form of CLC operation is realized with interconnected fluidized bed reactors, where oxygen carrier circulates between them [6]. In one reactor, so-called fuel reactor, the fuel (C_nH_{2m}) combusts with oxygen source from oxygen carrier (MeO_x), being the oxygen carrier reduced to MeO_{x-1}, as shown in reaction (1). In the second reactor, so-called air reactor, the previously reduced oxygen carrier MeO_{x-1} is oxidized back to the original form MeO_x by reacting with gaseous oxygen in air via reaction (2). It can be seen that CO₂ can be inherently separated in reaction (1) after simple condensation of H₂O steam. In this sense, CLC technology gives a prospective technical pathway to address the increase of global CO₂ emission.

Fuel reactor

Air reactor

64 For the application to coal combustion, CLC technology was extensively investigated during the
65 past decades [7, 8]. Due to the extremely low rate of solid-solid reaction between coal and oxygen
66 carrier particles [9], several technologies including syngas-fueled Chemical Looping Combustion
67 (syngas-CLC) [10, 11], *in-situ* Gasification Chemical Looping Combustion (*iG*-CLC) [12] and
68 Chemical Looping with Oxygen Uncoupling (CLOU) [13] were proposed. The syngas-CLC process
69 would have several advantages compared to *iG*-CLC and CLOU, namely: no requirement for the
70 carbon stripper, no requirement for the oxygen demand, no interaction of oxygen carrier with coal
71 ash and no losses of oxygen carrier with the draining stream of ash. In this sense, syngas-CLC is
72 simpler and straightforward to be implemented for energy generation from coal or even biomass.
73 The syngas-CLC can be easily accomplished by integrating with existing Integrated Gasification
74 Combined Cycle (IGCC) process [10, 14]. According to the simulation works of Jin et al. [10] and
75 Wolf et al. [15], efficiency of the IGCC process can be improved by 5-10% if conventional CO₂
76 capture technology was replaced by syngas-CLC. Nevertheless, this high improvement is
77 achievable when the CLC unit would operate at pressurized conditions and at temperatures above
78 1473 K in order to take advantages of the high efficient gas turbine [16-18]. However, these
79 conditions are not reachable with the state of the art for CLC technology. More indeed, when
80 surplus heat of the CLC unit is only considered for steam generation at super-critical or ultra
81 super-critical conditions, a limited increase in the net efficiency of plant would be expected for
82 pressurized conditions [19, 20]. Therefore, operation of CLC at atmospheric pressure would be
83 recommended. The prospect of syngas-CLC at atmospheric pressure was demonstrated with
84 continuous CLC units ranged from 0.3 to 120 kW_{th} by using Mn-, Fe-, Ni- and Cu-based oxygen
85 carriers [11, 21-26]. The use of syngas as fuel with Mn-, Fe- and Ni-based oxygen carriers resulted
86 in much higher combustion efficiency in comparison to methane fuel [11, 21, 22], which suggests

87 the higher reactivity of syngas. Moreover, oxygen carriers including low-cost materials [25, 26] and
88 synthetic particles [23, 24, 27, 28] displayed different reactivity with syngas during the continuous
89 tests. In comparable experiments performed with a 500 W_{th} plant [23, 24], it was found that the
90 Ni-based material must circulate fast enough to give an oxygen carrier-to-fuel ratio $\phi > 5$ to reach
91 maximum combustion of syngas at 1073 K [23]. However, in the case of Cu-based material, $\phi > 1.5$
92 already assured the complete combustion of syngas at the same temperature [24], indicating higher
93 reactivity of the Cu-based oxygen carrier than the Ni-based material. Furthermore, it can also be
94 speculated that Cu-based materials are more reactive than Mn- and Fe-based oxygen carriers [27,
95 28].

96
97 In order to give better performance of a CLC system, modeling of reactors would be helpful for the
98 optimization, design and scale-up of the process. For these purposes, mathematical and multiphase
99 Computational Fluid Dynamics (CFD) models were developed in the range of 5 kW_{th}-1 MW_{th}
100 during the latest years, mainly for CH₄ [29-32] or coal combustion [33-37]. Simulations under
101 steady or unsteady conditions were conducted mainly focused on fuel reactor with different fuels,
102 from which temperature was identified as the most important parameter affecting the performance
103 of CLC system. Later, modeling results were successfully validated [29, 35] and applied to the
104 design and optimization of 10-100 MW_{th} CLC plants by Abad et al. [38, 39]. However, few
105 modeling works were carried out for the syngas-CLC system. In these cases, modeling with Fe- or
106 Cu-based oxygen carriers in batch bubbling fluidized bed reactors have been performed using
107 macroscopic [40] or CFD models [41-43]. Less are the works focused on the performance of
108 continuously operated syngas-CLC units [44, 45]. In general, the effect of several operating
109 conditions, such as particle size, gas velocity, solids inventory, temperature or pressure, has been

110 evaluated, and it has been determined that the CO conversion is lower than the H₂ conversion. Most
111 of these models did not consider solids in the freeboard, although it has been determined that this
112 region is highly relevant to achieve a high conversion of the fuel [29, 44]. In addition, validation of
113 syngas-CLC models against experimental results is still pending, and optimized conditions to reach
114 complete syngas combustion has not been determined.

115

116 The objective of this work is to develop a fuel reactor model based on the geometry of a 500 W_{th}
117 continuous CLC plant erected at “Instituto de Carboquímica” (ICB-CSIC, Spain), which is then
118 used to evaluate the effects of operation conditions and to evolve useful information for the
119 optimization, design and scale-up of syngas-CLC systems. With this aim, reaction kinetics model
120 for combustion of syngas (CO+H₂) and a Cu-based oxygen carrier was developed based on its
121 respective reactivity with H₂ and CO involved in syngas. Considering the fluidization pattern in the
122 bubbling fluidized bed, i.e. dense bed and freeboard, and the mass balance over the reactor, a fuel
123 reactor model was built with MATLAB[®] codes. Then, the model was validated against the
124 experimental data obtained from the 500 W_{th} CLC plant in literature. Subsequently, influence of
125 operation conditions including syngas composition, temperature, solids circulation rate, solids
126 inventory and WGS reaction was evaluated. Finally, operation regions for 99.9% combustion of
127 syngas were identified, which could be used for the optimization, design and scale-up of
128 syngas-CLC systems.

129

130 **2. Fuel reactor model**

131

132 **2.1. Reaction kinetics model**

133 The oxygen carrier reacted with syngas is a previously tested Cu-based material in Forero et al. [24],
 134 which is composed of CuO, CuAl₂O₄, CuAlO₂ and α -Al₂O₃ components, and thus denoted as
 135 Cu14Al-I. The main properties of Cu14Al-I are shown in Table 1, from which it can be seen that
 136 this material contains 13.5 wt.% of active component. As a consequence, the oxygen transport
 137 capacity of Cu14Al-I is $R_{OC}=0.027$ being calculated as $R_{OC}=(m_{ox}-m_{red})/m_{ox}$. Here, m_{ox} and m_{red}
 138 represent the masses of fully oxidized and fully reduced oxygen carriers, respectively. Reaction
 139 kinetics model that can be used to describe the reduction of Cu14Al-I by syngas is a prerequisite for
 140 the formulation of fuel reactor model in this work. Several reaction kinetics models were developed
 141 for the reduction of Cu-based oxygen carriers by CH₄, CO and H₂ [29, 46, 47]. However, none of
 142 them can be directly applied to syngas combustion with Cu14Al-I according to our preliminary
 143 study, due to they were developed for single gas but not syngas. In this sense, reaction kinetics
 144 model must be formed for the combustion of syngas.

145
 146 It is noticed that in the morphology analysis performed by Gayán et al. [48] spherical grains of CuO
 147 inside a similar Cu-based oxygen carrier to Cu14Al-I were observed. Consequently, a spherical
 148 grain shrinking core model (SCM) developed by Abad et al. [46] for single gas (CO and H₂) is
 149 employed for the development of reaction kinetics model for syngas combustion with Cu14Al-I
 150 oxygen carrier. Dominated by the chemical reaction in grain of Cu14Al-I, the reaction kinetics
 151 model can be written as Eqs. (3)-(5).

$$152 \quad \frac{t}{\tau_i} = 1 - (1 - X_s)^{1/3} \quad (3)$$

$$153 \quad \tau_i = \frac{r_{g,CuO}}{b_i V_{M,CuO} k_i C_i^n} \quad (4)$$

154 where τ_i represents the time required for complete reduction of oxygen carrier particles by single
 155 component i ($i=CO$ or H_2) and X_s is the reduction conversion of oxygen carrier, calculated as

156 $X_s=(m_{ox}-m)/(R_{OC}\cdot m_{ox})$ being m the instantaneous mass of oxygen carrier. In Eq. (4), b_i is the
 157 stoichiometric factor in the reaction with gas i , $r_{g,CuO}$ and $V_{M,CuO}$ referring to the radius and molar
 158 volume of CuO grain, respectively; C_i represents the concentration of gas i in the stream and n is the
 159 reaction order.

160 The rate constant k_i in Eq. (4) follows Arrhenius type dependence with temperature, see Eq. (5).

$$161 \quad k_i = k_{0,i} \exp\left(-\frac{E_i}{R_g T}\right) \quad (5)$$

162 Values of the kinetics parameters involved in Eqs. (3)-(5) are gathered in Table 2. Accordingly, the
 163 reduction conversion of oxygen carrier X_s can be obtained as a function of time t .

164

165 With regard to syngas, CO and H₂ coexist in the same gas stream. In this case, few works were
 166 carried out for the determination of reaction kinetics of syngas where CO and H₂ react
 167 simultaneously with oxygen carrier [49]. Generally, there are two options for the derivation of
 168 global reaction rate of syngas: (i) using the more reactive component (CO or H₂) to represent syngas
 169 combustion, (ii) using the summation of rate for single gas as the rate of syngas combustion.

170 Preliminary study of this work found that option (ii) can give better predictions of experimental
 171 results. In this sense, option (ii) is selected to describe the rate of syngas combustion by Cu14Al-I,
 172 that is, the time for complete reduction of oxygen carrier by syngas, τ_{syn} , was calculated from the
 173 formulation $1/\tau_{syn} = 1/\tau_{CO} + 1/\tau_{H_2}$. For validation purposes, the syngas used in thermogravimetric
 174 analyzer (TGA) by Forero et al. [24], i.e. Syngas 1 with ratio CO/H₂=1 and Syngas 3 with ratio
 175 CO/H₂=3 shown in Table 3, is used in the reaction kinetics model. In both syngas, H₂O and CO₂
 176 were introduced during TGA tests to fulfill the Water-Gas Shift (WGS) equilibrium as shown in
 177 Table 3 and Forero et al. [24]. Fig. 1 displays a comparison of model predictions and experimental
 178 results, where the reduction conversion X_s in the cases of Syngas 1 and Syngas 3 can be adequately

179 replicated with the reaction kinetics model presented in Eqs. (3)-(5) and the corresponding values of
 180 kinetics parameters in Table 2. To this end, the reaction kinetics model developed by Abad et al. [46]
 181 is further evolved for the description of reaction between Cu14Al-I oxygen carrier and syngas,
 182 which is also validated against experimental data.

183

184 **2.2. Average reactivity of gas**

185

186 Prior to applying the above reaction kinetics model to fluidized bed, gas concentration on the active
 187 surface of oxygen carrier particles must be calculated. In fluidization condition, fuel component in
 188 bulk flow must pass through the gas film surrounding particles to reach the active surface of oxygen
 189 carrier. To obtain actual gas concentration on the active surface of an oxygen carrier particle, a mass
 190 balance to the whole particle is performed, as seen in Eq. (6).

$$191 \quad \frac{1}{b_i} \rho_{m,p} \left(\frac{1}{6} \pi d_p^3 \right) \frac{dX_s}{dt} = k_{g,i} \pi d_p^2 (C_z - C_{ex}) \quad (6)$$

192 where the left term indicates consumption of component i ($i=CO, H_2$) in fuel gas during the reaction
 193 on a particle with a diameter of d_p and a molar density of $\rho_{m,p}$. This consumption is simultaneously
 194 compensated by the same component flowing from bulk gas, as described in right term of Eq. (6).
 195 Accordingly, concentration of fuel component on the active surface of oxygen carrier particle C_{ex}
 196 can be calculated using bulk concentration C_z at height z of the reactor. Mass transfer coefficient in
 197 the gas film $k_{g,i}$ for component i in dense bed and freeboard, shown in Eq. (6), can be calculated
 198 according to Palchonok et al. [50] and Chakraborty et al. [51], respectively.

199

200 In fluidized bed reactor, a distribution of solids conversion of the particles can be found. To
 201 characterize the consumption of oxygen carrier, an average reaction rate of particles in Eq. (7) is

202 used.

$$203 \quad (-\bar{r}_{s,i}) = \rho_{m,p} (1 - \varepsilon_z) \int_0^\tau \frac{dX_s}{dt} E(t) dt \quad (7)$$

204 where ε_z means the bed porosity at position z of the reactor, determined according to solids

205 concentration. The residence time distribution of particles inside fuel reactor $E(t)$ can be described

206 using Eq. (8) by assuming perfect mixing of solids.

$$207 \quad E(t) = \frac{1}{t_{mr}} e^{-t/t_{mr}} \quad (8)$$

208 being t_{mr} the mean residence time of particles inside fuel reactor.

209

210 Finally, the average reaction rate of gas component i ($i=\text{CO}, \text{H}_2$), $(-\bar{r}_{g,i})$, in the gas flow can be

211 calculated with Eq. (9), which will be used in the fuel reactor model to account for the consumption

212 of gas components due to gas-solid reactions.

$$213 \quad (-\bar{r}_{g,i}) = \frac{(-\bar{r}_{s,i})}{b_i} \quad (9)$$

214

215 **2.3. Fluid dynamics and mass balance**

216

217 The mathematical model in this work is similar to that developed by Abad et al. [29] for CLC of

218 CH_4 in a 10 kW_{th} facility; however, herein it is evolved for syngas combustion in a 500 W_{th} CLC

219 plant. Fuel reactor geometry of the 500 W_{th} facility is shown in Table 4, which is a fluidized bed

220 with height of 0.6 m and inner diameter of 0.05 m. A distributor with 17 nozzles is located at the

221 entry of reactor to give good gas distribution. In order to obtain gas distribution inside the reactor,

222 equations on fluid dynamics and mass balances must be established and then solved simultaneously.

223

224 *2.3.1. Fluid dynamics in dense bed*

225 The dense bed is composed of emulsion and bubble phases, where the oxygen carrier particles are
 226 all assumed to be distributed in emulsion phase and thus no oxygen carrier is considered in bubbles.
 227 In emulsion, the oxygen carrier particles are under minimum fluidization condition, from which the
 228 excessive gas over minimum fluidization is transferred to bubbles. A modified two-phase model
 229 proposed by Johnsson et al. [52] is applied to obtain flow structure of the dense bed. Accordingly,
 230 the total gas velocity u_0 is shared by minimum fluidization velocity u_{mf} , visible bubble velocity u_{vis}
 231 and throughflow velocity u_{tf} , as shown in Eq. (10).

$$232 \quad u_0 = (1 - \delta_b)u_{mf} + u_{vis} + u_{tf} \quad (10)$$

233 The minimum fluidization velocity u_{mf} is calculated via Wen and Yu correlation [53]. In Eq. (10), δ_b
 234 represents the bubble fraction in the dense bed, which can be calculated through Eq. (11).

$$235 \quad \delta_b = \frac{u_{vis}}{u_{vis} + 0.71\sqrt{gd_b}} \quad (11)$$

236 where the bubble diameter d_b is obtained using the correlation proposed by Darton et al. [54].

237 The velocities u_{vis} and u_{tf} are calculated according to the Eqs. (12) and (13), respectively.

$$238 \quad u_{vis} = \psi(u_0 - u_{mf}(1 - \delta_b)) \quad (12)$$

$$239 \quad u_{tf} = (1 - \psi)(u_0 - u_{mf}(1 - \delta_b)) \quad (13)$$

240 where ψ , the ratio of u_{vis} and $(u_{vis} + u_{tf})$, is calculated according to Johnsson et al. [52].

241

242 2.3.2. Fluid dynamics in freeboard

243

244 The top of dense bed begins freeboard, where the solids concentration C_s is decreasing with reactor
 245 height [55].

$$246 \quad \frac{dC_s}{dz} = -aC_s \quad (14)$$

247 being a the decay factor of solids concentration in freeboard.

248 2.3.3. Mass balance

249

250 All reactants and products, including Cu14Al-I, CO, CO₂, H₂ and H₂O, are considered to the mass
 251 balance. For gas-solid interaction, the following reactions (15) and (16) for syngas combustion are
 252 used for mass balance, which is consistent to the fact obtained with this kind of materials in
 253 literatures [29, 46].

256 In addition, because WGS equilibrium was experimentally observed as a dominant intermediate
 257 step for syngas combustion in the 500 W_{th} plant [24], it is assumed to be reached immediately
 258 during reactions and used to mass balance for gases.

260

261 In dense bed, oxygen carrier particles can react directly with gases in emulsion or react with gases
 262 transferred from bubbles. However, no gas-solid reaction is involved inside bubbles, because no
 263 oxygen carrier particles are considered there. The mass balances for emulsion and bubble phases in
 264 dense bed can be expressed as Eqs. (18) and (19), respectively.

265 Emulsion phase

$$266 \quad \frac{dF_{e,i}}{dV} = \frac{d((1-\delta_b)u_{mf}C_{e,i})}{dz} \quad (18)$$

$$= -(1-\delta_b)\sum(-\bar{r}_{g,i})_e - \delta_b k_{be}(C_{e,i} - C_{b,i}) - y_{e,i} \frac{dF_{exc}}{dV} - \frac{dF_{WGS}}{dV}$$

267 Bubble phase

$$268 \quad \frac{dF_{b,i}}{dV} = \frac{d((u_{vis} + u_{tf})C_{b,i})}{dz} = \delta_b k_{be}(C_{e,i} - C_{b,i}) + y_{e,i} \frac{dF_{exc}}{dV} - \frac{dF_{WGS}}{dV} \quad (19)$$

269 being k_{be} - the exchange coefficient of gas i (CO, CO₂, H₂ and H₂O) between emulsion (with a

270 concentration of $C_{e,i}$) and bubble (with the concentration of $C_{b,i}$) - calculated by Sit and Grace [56]
 271 and F_{exc} - containing $y_{e,i}$ of component i - the excessive flow over minimum fluidization.
 272 In freeboard, although there is no constraint limiting gas exchange from bubbles, the gas-solid
 273 reactions are influenced by a contact efficiency ξ_{g-s} . Therefore, the mass balance for this region can
 274 be written as Eq. (20).

$$275 \quad \frac{dF_{f,i}}{dV} = \frac{d(u_0 C_{f,i})}{dz} = -\sum \xi_{g-s} (-\bar{r}_{g,i})_f - \frac{dF_{WGS}}{dV} \quad (20)$$

276 The contact efficiency, ξ_{g-s} , between gases and solids in freeboard is calculated with the equation
 277 proposed by Furusaki et al. [57].

$$278 \quad \xi_{g-s} = 1 - 0.75 \left(\frac{C_s}{C_{s,b}} \right)^{0.4} \quad (21)$$

279 where $C_{s,b}$ is the solids concentration at the upper limit of dense bed.

280

281 The fluid dynamics model and mass balance equations were formulated with MATLAB[®] codes,
 282 which were solved simultaneously with Runge-Kutta method.

283

284 **2.4. Input and output of reactor model**

285

286 The inputs to reactor model are mainly the properties of Cu14Al-I oxygen carrier in Table 1 and the
 287 operation conditions in Table 4. The size and density of particles shown in Table 1 are used to
 288 determine average reactivity of gas and fluid dynamics in fuel reactor. As seen in Table 4, the fuel
 289 reactor is operated at atmospheric pressure with a total inlet gas molar flow of $F_{in}=3.2 \cdot 10^{-3} \text{ mol} \cdot \text{s}^{-1}$
 290 which includes CO, H₂, CO₂ and N₂ as balance gas. According to the tests in Forero et al. [24], full
 291 oxidation of Cu14Al-I oxygen carrier in air reactor was noticed, thus the oxidation conversion of
 292 Cu14Al-I at fuel reactor inlet is fixed to $X_{o,in}=1$, see Table 4. The other operation parameters

including pressure drop, temperature, bed mass, solids circulation rate and thermal power are varied in some ranges as inputs to the model for better evaluation purposes.

With variation of operation conditions, the oxygen carrier-to-fuel ratio ϕ , defined as the ratio of available oxygen in solids stream to that for complete combustion of syngas, can also changes, which is obtained by Eq. (22).

$$\phi = \frac{R_{OC} \cdot \dot{m}_s}{3600 \cdot M_O \cdot (x_{CO} + x_{H_2})_{in} \cdot F_{in}} \quad (22)$$

where M_O is molar weight of oxygen and $(x_i)_{in}$ refers to molar fractions of component i ($i=CO$ and H_2) in the gas stream F_{in} entering fuel reactor.

Because of the use of different bed masses and thermal powers in fuel reactor, the solids inventory m_{FR} , defined as oxygen carrier mass per MW_{th} fuel, would be varied, which can be calculated using Eq. (23).

$$m_{FR} = \frac{m_s}{P_{th}} \cdot 10^6 \quad (23)$$

The outputs of reactor model are distributions of gases and oxygen carrier particles, as well as gas flow rates along the height of fuel reactor.

According to gas distribution, combustion efficiency η_C , defined as the ratio between the oxygen taken by gas leaving reactor over the oxygen required for complete syngas combustion, is calculated as Eq. (24).

$$\eta_C = \frac{(2x_{CO_2} + x_{CO} + x_{H_2O})_{out} \cdot F_{out} - (2x_{CO_2} + x_{CO})_{in} \cdot F_{in}}{(x_{CO} + x_{H_2})_{in} \cdot F_{in}} \quad (24)$$

where F_{out} is the molar flow of gas stream at fuel reactor exit, $(x_i)_{out}$ means the molar fraction of component i ($i=CO_2$, CO and H_2O) in F_{out} . Here it is necessary to note that H_2O is not fed to the reactor.

3. Results and discussions

3.1. Gas distribution

As an example, Fig. 2 shows gas distribution, combustion efficiency η_C and solids fraction ε_s as a function of fuel reactor height for the case using syngas with $\text{CO}/\text{H}_2=3$, oxygen carrier-to-fuel ratio $\phi=1.2$, solids circulation rate $\dot{m}_s=3 \text{ kg}\cdot\text{h}^{-1}$ and bed mass $m_s=0.2 \text{ kg}$ at 1073 K. According to solids fraction ε_s , the fuel reactor is composed of a dense bed with height of 0.1 m and a freeboard above, as identified by the vertical dash line in Fig. 2. After the introduction of syngas, the WGS equilibrium is reached immediately, resulting in 27 vol.% CO, 9 vol.% H₂, 12 vol.% CO₂ and 4 vol.% H₂O at location close to the inlet of fuel reactor. Similarly, at each height of fuel reactor the WGS equilibrium is reached during the reaction. Despite this, different behaviors are seen for dense bed and freeboard. In the dense bed, the reaction becomes slower at higher position because: (i) the bubble, formed by gas bypass, increases its size with the height of the reactor, which derived an insufficient contact between syngas fuel and oxygen carrier particles, (ii) the concentrations of CO and H₂ are decreased gradually with the reactor. Because of the consumptions of CO and H₂ in syngas, higher concentrations of CO₂ and H₂O are achieved at higher height but keeping the WGS equilibrium. As a result, higher combustion efficiency is observed at higher position of dense bed. In the freeboard, bubbles from dense bed are broken which resulted in better contact of gas and oxygen carrier particles. In this sense, a higher rate of syngas combustion can be seen in freeboard, which leads to faster increase of concentrations of CO₂ and H₂O, and thus the combustion efficiency. In the case of Fig. 2, incomplete combustion of syngas is encountered, thereby around 3 vol.% CO and 1 vol.% H₂ are observed. The incomplete combustion is ascribed to the low oxygen

338 carrier-to-fuel ratio used, in this case $\phi=1.2$, which limits the average reactivity of oxygen carrier
339 particles [58]. However, when higher oxygen carrier-to-fuel ratios are applied, better combustion
340 behaviors can be observed.

341

342 **3.2. Fuel reactor model validation**

343

344 Experimental results used for the validation of the reactor model are from Forero et al. [24], where
345 continuous tests of Cu14Al-I and syngas were carried out in a 500 W_{th} CLC plant. Fig. 3 compares
346 modeling results and experimental data in terms of combustion efficiency η_C and concentrations of
347 CO and H₂ for the combustion of syngas at 1073 K. With the increase of oxygen carrier-to-fuel ratio
348 ϕ , the concentrations show decreases but the combustion efficiency rises gradually to 100%.

349 Despite the complicated reaction conditions are involved, it can be seen that the concentrations of
350 CO and H₂ are well predicted by the mathematical model, independent to the oxygen carrier-to-fuel
351 ratio ϕ or syngas composition. In this sense, the combustion efficiency of syngas η_C agrees well
352 with the experimental results. As a consequence, good agreements of experiments and modeling are
353 achieved, thus the fuel reactor model stated above is validated.

354

355 **3.3. Effect of operation condition**

356

357 *3.3.1. Effect of CO/H₂ ratio*

358

359 Industrial syngas has various compositions within the ratios of CO/H₂=1-3, which could affect the
360 combustion performance. In order to evaluate the effect of syngas composition, CO/H₂ ratio is

361 varied in the range of 1-3 while other parameters including temperature, bed mass, solids circulation
362 rate, oxygen carrier-to-fuel ratio ϕ and fuel flow are kept constant.

363

364 Fig. 4 shows the effect of CO/H₂ ratio under the condition of $T=1073$ K, $m_s=0.2$ kg, $\dot{m}_s=6$ kg·h⁻¹ and
365 $\phi=1.5$. It can be observed that higher CO/H₂ ratio results in more CO moles in the reacting
366 environment, thus higher concentration of this component in Fig. 4. On the contrary, although less
367 H₂ moles are contained at higher CO/H₂ ratios, the H₂ concentration at fuel reactor exit shows some
368 increases, ascribing to the joint influence of CO/H₂ ratio and WGS equilibrium. On the one hand, an
369 increase of CO/H₂ ratio directly reduces H₂ concentration. On the other hand, more CO in the gas
370 stream at higher CO/H₂ ratio forces WGS equilibrium in Eq. (17) to the direction with more
371 generations of CO₂ and H₂. In this sense, more CO and H₂ are found in Fig. 4 for higher CO/H₂
372 ratio. The increase of CO/H₂ ratio also leads to a slight reduction of oxygen carrier inventory m_{FR} ,
373 which is attributable to the slight higher heating value of CO combustion than H₂, albeit the total
374 fraction and flow of CO and H₂ are unchanged. Higher concentrations of unburnt CO and H₂ as well
375 as slight lower m_{FR} at higher CO/H₂ ratios lead to some decreases of combustion efficiency η_C and
376 oxygen carrier conversion X_s .

377

378 3.3.2. *Effect of operation temperature*

379

380 In order to evaluate the effect of fuel reactor temperature on combustion performance of syngas
381 with Cu14Al-I oxygen carrier, the operation temperature is varied in the range of $T=973-1173$ K,
382 while other parameters are maintained as constants. Fig. 5 shows the effect of operation temperature
383 on gas concentration, combustion efficiency and solids conversion, using $m_s=0.2$ kg, $\dot{m}_s=6$ kg·h⁻¹

384 and $\phi=1.5$ for the combustion of syngas with $\text{CO}/\text{H}_2=3$. Similar to most findings in other researches,
385 higher temperature is favorable for the combustion of syngas due to faster reaction kinetics. When
386 the temperature is increased from 973 to 1173 K, concentrations of CO and H_2 are reduced by
387 64.0% and 80.0%, respectively, which results in 1.5% increase of X_s and 3.0% increase of η_C in Fig.
388 5. At $T=1173$ K, the concentrations of CO and H_2 can reach as low as 0.6 vol.% and 0.2 vol.%,
389 respectively, whereas the combustion efficiency can be as high as $\eta_C=99\%$.

390

391 3.3.3. *Effect of solids circulation rate*

392

393 Oxygen carrier materials, circulating between fuel and air reactors, are responsible for the transport
394 of oxygen source for fuel combustion, which can affect the performance of fuel conversion. To
395 study the influence of this operation parameter, the solids circulation rate of oxygen carrier is varied
396 within the interval of $\dot{m}_s=3\text{-}8\text{ kg}\cdot\text{h}^{-1}$, while the other parameters including temperature, bed mass
397 and CO/H_2 ratio are kept constant. With the variation of $\dot{m}_s$, oxygen carrier-to-fuel ratio ϕ is also
398 changed, because the fuel flow, thermal power and CO/H_2 ratio are fixed. As shown in Fig. 6, ϕ
399 increases linearly from 0.8 to 2.1 as the $\dot{m}_s$ rises from 3 to $8\text{ kg}\cdot\text{h}^{-1}$. Faster circulation of oxygen
400 carrier particles results in shorter residence time of solids in the fuel reactor, which produces less
401 solids conversion in Fig. 6 and higher average reactivity of oxygen carrier, see Eqs. (7) and (8). As a
402 consequence, at higher solids circulation rate faster conversion of syngas could be foreseen. In this
403 sense, lower concentrations of CO and H_2 as well as higher combustion efficiency η_C are seen in Fig.
404 6 for higher solids circulation rate. In the case of Fig. 6, solids circulation rate $\dot{m}_s>7\text{ kg}\cdot\text{h}^{-1}$ would be
405 adequate for complete combustion of syngas.

406

3.3.4. Effect of solids inventory

408

409 For fixed thermal power and solids circulation rate, solids inventory in the fuel reactor determines
410 combustion time and contact chance of oxygen carrier particles and fuel gas. Fig. 7 shows the
411 influence of solids inventory m_{FR} on gas concentration, combustion efficiency and solids conversion
412 using bed mass of $m_s=0.05-0.8$ kg, $\dot{m}_s=6$ kg·h⁻¹, $\phi=1.5$ and CO/H₂=3 at $T=1173$ K. With the increase
413 of m_s , the solids inventory m_{FR} calculated by Eq. (23) is raised from 100 to 1500 kg·MW_{th}⁻¹. As seen
414 in Fig. 7, during the increase of m_{FR} from 100 kg·MW_{th}⁻¹ to higher than 1000 kg·MW_{th}⁻¹, the
415 concentrations of unburnt CO and H₂ decline gradually to zero from 3 vol.% and 0.7 vol.%,
416 respectively. In contrast, the combustion efficiency η_C and solids conversion X_s are increased
417 gradually from 94% and 0.8 to 100% and 0.85, respectively, as the m_{FR} rises in the range of
418 100-1500 kg·MW_{th}⁻¹. This behavior is attributed to that higher m_{FR} means higher dense bed height
419 in the range of $H_b=0.025-0.4$ m which results in longer reaction time and more opportunities for
420 gas-solids contact. In the case of Fig. 7, the minimum oxygen carrier inventory for full combustion
421 of syngas is around $m_{FR}=1100$ kg·MW_{th}⁻¹.

422

3.3.5. Effect of joint variation of solids circulation rate and fuel flow

424

425 During the operation of a continuous CLC system, solids circulation rate and fuel flow can be
426 changed simultaneously. In this case, there would be a condition that ϕ is a constant. Despite this,
427 combustion characteristics can be varied under different $\dot{m}_s$ and fuel flows. In order to evaluate the
428 effect of this condition, $\dot{m}_s$ and fuel flow are changed in the range of 3-8 kg·h⁻¹ and $3.2 \cdot 10^{-4}-2.7 \cdot 10^{-3}$
429 mol·s⁻¹ (corresponding thermal power $P_{th}=80-700$ W_{th}), respectively, while temperature, bed mass,

oxygen carrier-to-fuel ratio and CO/H_2 are kept as constants. Here, the joint variation of $\dot{m}_s$ and fuel flow (or thermal power) is to obtain a fixed ϕ , in this case $\phi=1.5$. Fig. 8 shows the effect of varying $\dot{m}_s$ and fuel flow at the same time on gas concentration, combustion efficiency, solids conversion and solids inventory for the case of $T=1173\text{ K}$, $m_s=0.2\text{ kg}$, $\dot{m}_s=2\text{--}8\text{ kg}\cdot\text{h}^{-1}$, $\phi=1.5$ and $\text{CO}/\text{H}_2=3$. As stated above in *section 3.3.3*, higher $\dot{m}_s$ leads to shorter residence time of oxygen carrier particles inside the fuel reactor, thus higher average reactivity of oxygen carrier, see Eqs. (7) and (8). This enhances combustion in the case of *section 3.3.3*, however, it is different for Fig. 8 because the opposite effect is seen here. In Fig. 8, higher $\dot{m}_s$ leads to increase of CO and H_2 concentrations and decrease of η_C and X_s . The explanation of this phenomenon is that the rising of $\dot{m}_s$ is associated by higher fuel flow (or thermal power) to maintain ϕ , which causes the dramatic decrease of m_{FR} leading to shorter combustion time and less chance for the contact between oxygen carrier particles and gases. In this sense, the influence of m_{FR} is more relevant than average reactivity of oxygen carrier for the combustion in the case of Fig. 8. For the joint variation of $\dot{m}_s$ and fuel flow, if a fixed ϕ is desired during the operation, low solids circulation rate can only assure the complete combustion of low flow of fuel with low thermal power. For syngas with high flow rate, the increase of ϕ could be recommended as a straightforward measure to reach full combustion.

3.4. Relevance of WGS reaction

In Figs. 4-8, gas concentration, combustion efficiency and solids conversion are all plotted for excluding and including WGS reaction in the reactor model. In the case of excluding WGS, the results are plotted with dash lines in these figures. Generally, lower CO concentration, higher H_2 concentration but little changes of combustion efficiency and solids conversion can be expected

while WGS is excluded from the model, despite scarce influence on the variation trend of these parameters is noticed. This behavior is due to the WGS equilibrium in reaction (17) is positive for more generation of CO, that is, WGS can convert the gas product CO_2 of syngas-CLC to CO. This influence is more obvious for high CO/H_2 ratios, as indicated in Fig. 4. For $\text{CO}/\text{H}_2 > 2$ in Fig. 4, CO concentration is higher in the case of including WGS than excluding WGS, however, the opposite is found for $\text{CO}/\text{H}_2 < 2$. Additionally, for better evaluation, the concentrations of CO and H_2 and combustion efficiency for excluding WGS are subtracted by that for including WGS, which are then divided by the latter to get variation degrees. Fig.9 shows the variation degrees for gas concentrations and combustion efficiency as a function of CO/H_2 ratio at different temperatures. It can be seen that the variation degrees for H_2 concentration and η_C are always positive or negative for all CO/H_2 ratios focused; however, it is not the case for CO concentration due to the reasons stated above for CO concentration in Fig. 4. The temperature also shows some impacts on the variation degrees. Normally, higher temperature leads to higher variation degrees of CO and H_2 concentrations, but with little influence on η_C . In Figs. 4-9, although the concentrations of CO and H_2 are changed to some extent, there is little difference in the values of η_C and X_s for both cases while WGS is included or not in the reactor model. Consequently, the WGS reaction can impose some variations on the composition of gas products but shows negligible effects on combustion efficiency and oxygen carrier conversion for syngas-CLC in this work.

471

472 **3.5. Operation regions for 99.9% combustion**

473

Complete combustion of fuel is always desirable in CLC system, which can be affected by the selection of operation conditions. As discussed above in *sections 3.3.4 and 3.3.5*, one of the most

475

476 important parameters for full combustion is the solids inventory m_{FR} inside fuel reactor. For a fixed
 477 thermal power, an increase of m_{FR} results in more time of reaction, and thus higher combustion
 478 efficiency, which is illustrated in Figs. 7 and 8 and demonstrated by the works of Abad et al. [59]
 479 and Mei et al. [60]. In this sense, there is a minimum value of m_{FR} corresponding to 100%
 480 combustion of fuel. To facilitate the evaluation, the value of m_{FR} for 99.9% combustion of syngas is
 481 considered as a reference in the present work. For per MW_{th} thermal power of fuel, Fig. 10 maps the
 482 operation regions for 99.9% combustion of syngas with $CO/H_2=3$ and Cu14Al-I oxygen carrier,
 483 where the specific m_{FR} , ϕ and X_s at various temperatures are shown as a function of solids
 484 circulation. As seen, the ϕ and X_s are never affected by reaction temperature. Despite this, ϕ and X_s
 485 are directly related to solids circulation per MW_{th} fuel, thus higher values of them are observed for
 486 faster circulation of oxygen carrier. Moreover, higher average reactivity of oxygen carrier is reached
 487 at lower X_s , thereby lower values of m_{FR} for 99.9% combustion are found at higher solids
 488 circulation for all temperatures. Within the range of $T=973-1173$ K, the specific m_{FR} varies from
 489 1250 to 50 $kg \cdot MW_{th}^{-1}$ as the increase of solids circulation from 3.4 to 6.6 $kg \cdot s^{-1} \cdot MW_{th}^{-1}$. It can also
 490 be observed that lower values of m_{FR} would be achieved at higher temperatures. Especially, at 1173
 491 K the m_{FR} can reach as low as 50 $kg \cdot MW_{th}^{-1}$ for solids circulations higher than 5 $kg \cdot s^{-1} \cdot MW_{th}^{-1}$,
 492 which is then hardly affected by even higher solids circulation. At other temperatures, the similar
 493 behavior can also be expected. Although the lowest and stable m_{FR} for $T=973$ and 1023 K are not
 494 shown in Fig. 10, the similar $m_{FR}=50$ $kg \cdot MW_{th}^{-1}$ to that of $T=1073$, 1123 and 1173 K can be
 495 speculated in these cases, if solids circulation higher than 6.6 $kg \cdot s^{-1} \cdot MW_{th}^{-1}$ can be used. In this
 496 sense, higher temperature and faster solids circulation can both be considered as effective measures
 497 for reducing oxygen carrier inventory. For the use of syngas with $CO/H_2 < 3$, even lower m_{FR} would
 498 be expected due to higher reactivity of those syngas than that for $CO/H_2=3$.

Information in Fig. 10 can be applied to the optimization of existing CLC systems and to the design of new CLC systems. As an example, for the operation of the 500W_{th} CLC system focused in this work, the optimized solids circulation per MW_{th} fuel at each temperature can be readable from Fig. 10. For instance, if the temperature is $T=1123$ K, solids circulation higher than $5.5 \text{ kg}\cdot\text{s}^{-1}\cdot\text{MW}_{\text{th}}^{-1}$, i.e. $\dot{m}_s > 9.9 \text{ kg}\cdot\text{h}^{-1}$ associated with $\phi > 2.6$ and $X_s < 0.5$, must be used to assure the best combustion of syngas. Furthermore, in the case of designing new CLC systems, data in Fig. 10 can also be referred. For example, in the design of a 1 MW_{th} syngas-CLC plant, $T > 1073$ K could give good reaction kinetics. In this case, solids circulation higher than $6 \text{ kg}\cdot\text{s}^{-1}\cdot\text{MW}_{\text{th}}^{-1}$ is sufficient for optimized combustion. Geometry of fuel reactor for the new 1 MW_{th} syngas-CLC system must be adjusted for the above identified solids circulation rates.

509

510 **4. Conclusions**

511

Based on the geometry of a 500 W_{th} CLC plant, a mathematical model for a bubbling fluidized bed to describe the combustion behavior of syngas in the fuel reactor was developed and validated against experimental data. The reaction process of syngas and the Cu14Al-I oxygen carrier can be represented by a spherical grain shrinking core model using summation rate of CO and H₂ in the fuel. In the dense bed, the combustion rate of syngas was a bit lower than that in the freeboard, due to the limit of gas transfer from bubbles. However, better contact between oxygen carrier particles and gases was observed in the freeboard where no existence of bubbles. The operation conditions of the fuel reactor exhibited influences on the combustion behavior. Higher concentration of CO in the syngas is disadvantageous for complete combustion, due to the lower reactivity of this gas. On the contrary, higher temperature is helpful to fast reaction kinetics, which thus be beneficial to complete

522 combustion of syngas. Faster circulation of oxygen carrier particles can lead to higher combustion
523 efficiency of the syngas at a fixed fuel power. The WGS reaction although can change the
524 composition of gas products, cannot impose significant influence on the combustion efficiency of
525 the system. Considering all the main influencing factors, a mapping of operation regions to assure
526 99.9% combustion of syngas was developed. Accordingly, in order to minimize the solids inventory,
527 high temperature and solids circulation are recommendable for the operation. The operation regions
528 can be referred for optimization, design and scale-up purposes of syngas-CLC systems.

529

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531

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535

536

537 **Nomenclatures**

538

539 a decay factor of solids concentration in the freeboard

540 b_i stoichiometric factor for the reaction of CuO and component i (i =CO or H₂) in the syngas, mol

541 CuO per mol of gas

542 C_{ex} concentration of gas component at the active surface of oxygen carrier particle, mol·m⁻³

543 C_i concentration of fuel component i (i =CO or H₂), mol·m⁻³

544 $C_{j,i}$ concentration of component i (i =CO, CO₂, H₂ or H₂O) in bubble (j =b), emulsion (j =e) or
545 freeboard (j =f), mol·m⁻³

546 C_s solids concentration, kg·m⁻³

547 $C_{s,b}$ solids concentration at the upper limit of the dense bed, kg·m⁻³

548 C_z bulk gas concentration at height z of the fuel reactor, mol·m⁻³

549 d_j diameter of bubble (j =b) or particle size (j =p), m

550 D_r inner diameter of the fuel reactor, m

551 E_i activation energy for the reaction with component i (i =CO or H₂) in syngas, J·mol⁻¹

552 F_{exc} excessive gas molar flow over minimum fluidization, mol·s⁻¹

553 F_j gas molar flow at the inlet (j =in) or outlet (j =out) of fuel reactor, mol·s⁻¹

554 $F_{j,i}$ molar flow of component i (i =CO, CO₂, H₂ or H₂O) in bubble (j =b), emulsion (j =e) or
555 freeboard (j =f), mol·s⁻¹

556 F_{WGS} gas molar flow due to WGS reaction, mol·s⁻¹

557 g acceleration of gravity, 9.8 m·s⁻²

558 H_j height of dense bed (j =b) or the entire fuel reactor (j =r), m

559 k_{be} coefficient for gas exchange between bubble and emulsion, s⁻¹

560 $k_{g,i}$ mass transfer coefficient of component i ($i=\text{CO}$ or H_2) in the gas film surrounding oxygen
561 carrier particles, $\text{m}\cdot\text{s}^{-1}$

562 k_i rate constant of the reaction between component i ($i=\text{CO}$ or H_2) and oxygen carrier,
563 $\text{mol}^{1-n}\cdot\text{m}^{3n-2}\cdot\text{s}^{-1}$

564 $k_{0,i}$ pre-exponential factor of the rate constant for the reaction between component i ($i=\text{CO}$ or H_2)
565 and oxygen carrier, $\text{mol}^{1-n}\cdot\text{m}^{3n-2}\cdot\text{s}^{-1}$

566 m instantaneous mass of oxygen carrier, kg

567 m_{FR} solids inventory per MW_{th} fuel, $\text{kg}\cdot\text{MW}_{\text{th}}^{-1}$

568 m_j mass of fully oxidized ($j=\text{ox}$) or reduced ($j=\text{red}$) oxygen carrier, kg

569 M_{O} molar weight of oxygen carrier, $\text{kg}\cdot\text{mol}^{-1}$

570 $\dot{m}_{\text{s}}$ solids circulation rate, $\text{kg}\cdot\text{h}^{-1}$

571 m_{s} bed mass of oxygen carrier in fuel reactor, kg

572 n reaction order

573 N_{nz} number of nozzle in the gas distributor of fuel reactor

574 p pressure at the outlet of fuel reactor, Pa

575 P_{th} thermal power, W_{th}

576 R_{g} universal gas constant, $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

577 $r_{\text{g,CuO}}$ radius of CuO grain in the oxygen carrier, m

578 $(-\bar{r}_{\text{g},i})$ average reaction rate of gas component i ($i=\text{CO}$ or H_2), $\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$

579 $(-\bar{r}_{\text{g},i})_j$ average reaction rate of gas component i ($i=\text{CO}$ or H_2) in emulsion ($j=\text{e}$) or freeboard ($j=\text{f}$),
580 $\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$

581 R_{OC} oxygen transport capacity

582 $(-\bar{r}_{\text{s},i})$ average reaction rate of oxygen carrier particles during the oxidation of component i ($i=\text{CO}$

583 or H_2) in the syngas, $\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$

584 t reaction time, s

585 T temperature, K

586 t_{mr} mean residence time of oxygen carrier particles in fuel reactor, s

587 u_j velocity corresponding to total gas flow ($j=0$), minimum fluidization flow ($j=\text{mf}$), throughflow
588 ($j=\text{tf}$) or visible bubble flow ($j=\text{vis}$), $\text{m}\cdot\text{s}^{-1}$

589 V fuel reactor volume, m^3

590 $V_{\text{M,CuO}}$ molar volume of CuO grain in the oxygen carrier, $\text{m}^3\cdot\text{mol}^{-1}$

591 $(x_i)_j$ molar fraction of component i ($i=\text{CO}, \text{CO}_2, \text{H}_2$ or H_2O) in the gas stream at the inlet ($j=\text{in}$) or
592 outlet ($j=\text{out}$) of the fuel reactor

593 $X_{\text{o,in}}$ oxidation conversion of oxygen carrier at the inlet of fuel reactor

594 X_s solids conversion during reduction

595 $y_{e,i}$ volume fraction of component i ($i=\text{CO}, \text{CO}_2, \text{H}_2$ or H_2O) in the excessive gas over minimum
596 fluidization

597 z axial position in the fuel reactor, m

598 *Greek Symbols*

599 Δp pressure drop over fuel reactor, Pa

600 δ_b bubble fraction in the dense bed

601 ε_s solids fraction in fuel reactor

602 ε_z bed porosity at position z of the fuel reactor

603 η_C combustion efficiency

604 $\xi_{\text{g-s}}$ contact efficiency between gas and solids in freeboard

605 $\rho_{\text{m,p}}$ molar density of CuO in the oxygen carrier particles, $\rho_{\text{m,p}}=y_{\text{CuO}}/V_{\text{MCuO}}$, being y_{CuO} the volume

606 fraction of CuO in the oxygen carrier, $\text{mol}\cdot\text{m}^{-3}$

607 ρ_p particle density, $\text{kg}\cdot\text{m}^{-3}$

608 τ_i time required for complete reduction of oxygen carrier by gas i ($i=\text{CO}$, H_2 or syn for syngas), s

609 ψ ratio of u_{vis} and $(u_{\text{vis}}+u_{\text{tf}})$

610 ϕ oxygen carrier-to-fuel ratio

611 *Acronyms*

612 BET Brunauer-Emmett-Teller

613 CFD computational fluid dynamics

614 CLC chemical looping combustion

615 IGCC integrated gasification combined cycle

616 syngas-CLC syngas-fueled chemical looping combustion

617 SCM shrinking core model

618 TGA thermogravimetric analyzer

619 WGS water-gas shift

620 XRD x-ray diffraction

621

622

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624

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780 **Figure Captions**

781 Fig. 1. Comparison of reaction kinetics model predictions (—) and experimental results (○, □, taken
782 from [24]) for Syngas 1 (CO/H₂=1, blue color) and Syngas 3 (CO/H₂=3, red color) at 1073 K

783 Fig. 2. Distribution of gas concentration (H₂, CO, H₂O and CO₂), combustion efficiency η_C and
784 solids fraction ε_s along reactor height during the combustion of syngas for the condition of $T=1073$
785 K, $m_s=0.2$ kg, $\dot{m}_s=3$ kg·h⁻¹, $\phi=1.2$ and CO/H₂=3

786 Fig. 3. Comparison of CO and H₂ concentrations and combustion efficiency η_C between modeling
787 (void symbols: □ ○) and experimental (filled symbols: ■ ● taken from [24]) results obtained in 500
788 W_{th} plant for the combustion of syngas with CO/H₂=1 (cubic symbols: ■ □) and syngas with
789 CO/H₂=3 (circle symbols: ● ○) at 1073 K

790 Fig. 4. Effect of CO/H₂ ratio on gas concentration (H₂ and CO), combustion efficiency η_C , oxygen
791 carrier conversion X_s and solids inventory m_{FR} for the condition of $T=1073$ K, $m_s=0.2$ kg, $\dot{m}_s=6$
792 kg·h⁻¹, and $\phi=1.5$, including (solid lines) or excluding (dash lines) WGS reaction

793 Fig. 5. Effect of temperature on gas concentration (H₂ and CO), combustion efficiency η_C and
794 oxygen carrier conversion X_s for the condition of $m_s=0.2$ kg, $\dot{m}_s=6$ kg·h⁻¹, $\phi=1.5$, CO/H₂=3 and
795 $P_{th}=500$ W_{th}, including (solid lines) or excluding (dash lines) WGS reaction

796 Fig. 6. Effect of solids circulation rate on gas concentration (H₂ and CO), combustion efficiency η_C ,
797 oxygen carrier conversion X_s and oxygen carrier-to-fuel ratio ϕ for the condition of $T=1173$ K,
798 $m_s=0.2$ kg, CO/H₂=3 and $P_{th}=500$ W_{th}, including (solid lines) or excluding (dash lines) WGS
799 reaction

800 Fig. 7. Effect of solids inventory on gas concentration (H₂ and CO), combustion efficiency η_C and
801 oxygen carrier conversion X_s for the condition of $T=1173$ K, $m_s=0.05-0.8$ kg, $\dot{m}_s=6$ kg·h⁻¹, $\phi=1.5$,
802 CO/H₂=3 and $P_{th}=500$ W_{th}, including (solid lines) or excluding (dash lines) WGS reaction

803 Fig. 8. Effect of joint variation of solids circulation rate and fuel flow on gas concentration (H_2 and
804 CO), combustion efficiency η_C , oxygen carrier conversion X_s and solids inventory m_{FR} for the
805 condition of $T=1173$ K, $m_s=0.2$ kg, $\dot{m}_s=2-8$ kg $\cdot$ h $^{-1}$, $\phi=1.5$, and $CO/H_2=3$ with fuel flow varying from
806 $3.2\cdot 10^{-4}$ to $2.7\cdot 10^{-3}$ mol $\cdot$ s $^{-1}$ ($P_{th}=80-700$ W $_{th}$), including (solid lines) or excluding (dash lines) WGS
807 reaction

808 Fig. 9. Variation degrees of gas concentrations (H_2 and CO) and combustion efficiency at different
809 temperatures of 973-1173 K with $\dot{m}_s=6$ kg $\cdot$ h $^{-1}$, $\phi=1.5$, as a function of CO/H_2 ratio; positive data
810 means the values of parameters increased when WGS reaction is excluded from the model in
811 comparison to that while WGS is included

812 Fig. 10. Operation regions for 99.9% combustion of per MW $_{th}$ syngas with $CO/H_2=3$ at $T=973-1173$
813 K: distributions of minimum oxygen carrier inventory m_{FR} , oxygen carrier-to-fuel ratio ϕ and
814 oxygen carrier conversion X_s at different solids circulation rates per MW $_{th}$ fuel

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842 Fig. 5. Effect of temperature on gas concentration (H_2 and CO), combustion efficiency η_C and
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848 Fig. 6. Effect of solids circulation rate on gas concentration (H_2 and CO), combustion efficiency η_c ,
849 oxygen carrier conversion X_s and oxygen carrier-to-fuel ratio ϕ for the condition of $T=1173$ K,
850 $m_s=0.2$ kg, $CO/H_2=3$ and $P_{th}=500$ W_{th} , including (solid lines) or excluding (dash lines) WGS
851 reaction

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878 oxygen carrier conversion X_s at different solids circulation rates per MW_{th} fuel

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882 **Table Captions**

883 Table 1. Main properties of the Cu₁₄Al-I oxygen carrier

884 Table 2. Values of parameters in the reaction kinetics model

885 Table 3. Volume fractions of CO (vol.%) and H₂ (vol.%) and CO/H₂ ratios in Syngas 1 and Syngas
886 3 used by Forero et al. [24]

887 Table 4. Fuel reactor geometry and operation condition

888

889

890 Table 1. Main properties of the Cu14Al-I oxygen carrier

XRD phase	CuO, CuAl ₂ O ₄ , CuAlO ₂ , α Al ₂ O ₃
Content of active material (wt.%)	13.5
Oxygen transport capacity R_{OC} (-)	0.027
Particle size (mm)	0.3-0.5
Particle density (kg·m ⁻³)	1900

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893 Table 2. Values of parameters in the reaction kinetics model

Symbols	CO	H ₂	Units
$r_{g, \text{CuO}}$	$2 \cdot 10^{-7}$	$2 \cdot 10^{-7}$	m
$V_{M, \text{CuO}}$	$12.4 \cdot 10^{-6}$	$12.4 \cdot 10^{-6}$	$\text{m}^3 \cdot \text{mol}^{-1}$
b_i	1	1	-
n	0.6	0.8	-
$k_{0,i}$	0.01	1.0	$\text{mol}^{1-n} \text{m}^{3n-2} \text{s}^{-1}$
E_i	25000	60000	$\text{J} \cdot \text{mol}^{-1}$

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895

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	CO	H ₂	H ₂ O	CO ₂	CO/H ₂ ratio
Syngas 1	7.5	7.5	10	11	1
Syngas 3	11.2	3.8	10	33	3

898

899

900 Table 4. Fuel reactor geometry and operation condition

	Symbols	Values	Units
<i>Reactor geometry</i>			
Reactor height	H_r	0.6	m
Inner diameter	D_r	0.05	m
Nozzle number	N_{nz}	17	
<i>Operation condition</i>			
Pressure at outlet	p	101325	Pa
Gas molar flow at inlet	F_{in}	$3.2 \cdot 10^{-3}$	$\text{mol} \cdot \text{s}^{-1}$
Pressure drop	Δp	250-4000	Pa
Temperature	T	973-1173	K
Bed mass	m_s	0.05-0.8	kg
Solids circulation rate	$\dot{m}_s$	2-8	$\text{kg} \cdot \text{h}^{-1}$
Dense bed height	H_b	0.025-0.4	m
Thermal power	P_{th}	80-700	W_{th}
Oxidation conversion	$X_{o,in}$	1	

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