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# 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 with ex-situ gasification of coal has advantages over the direct use of coal in CLC: (*i*) no requirement of carbon stripper, (*ii*) no interaction of oxygen carrier with coal ash, (*iii*) no loss of oxygen carrier with the draining stream of ash. Few works on simulation of syngas-CLC were performed, although experimental investigations were extensively carried out. In this work, a macroscopic fuel reactor model is extended to a lab-scale 500 W<sub>th</sub> reactor. The model based on fluid dynamics, mass balance and reduction kinetics is solved with MATLAB<sup>\*</sup> codes and validated against experiments. Influences of various operation parameters are evaluated to study the flexibility of this model. It is shown that the model can give satisfactory predictions for fuel reactor of a syngas-CLC system, independent on the operation conditions. Variations of syngas composition, temperature, solids circulation and oxygen carrier inventory show different effects on flue gas composition and combustion efficiency. After thorough simulation, a region for a combustion efficiency of  $\eta_C = 99.9\%$  is proposed, with which the optimized conditions for the 500 W<sub>th</sub> reactor are established. An oxygen carrier inventory as low as 50 kg/MW<sub>th</sub> can assure the complete syngas combustion.

# 1. Introduction

The dependence on fossil fuel for energy production cannot be substituted by other alternatives including renewable energies before they become mature to supply most of the demanded energy [1]. CO<sub>2</sub> emission during the utilization of fossil fuels is considered as one of the major contributors to global warming, thus different strategies for CO<sub>2</sub> removal are developing [2]. Among them, Chemical Looping Combustion (CLC) has been suggested among the most promising technologies for low-cost CO<sub>2</sub> capture [3]. CLC concept is based on the rationale of pure CO<sub>2</sub> generation patented by Lewis and Gilliland [4], which was first proposed by Ishida et al. [5]. In CLC, the conventional combustion is split into two steps: oxygen required for fuel combustion is provided by a solid oxygen carrier, a type of metal oxide; and then air is used to regenerate the oxygen carrier. The most common configuration for CLC is realized by circulating oxygen carrier particles inside interconnected fluidized bed reactors [6]. In the fuel reactor, fuel (CnH2m) combusts with lattice oxygen of oxygen carrier  $(MeO_x)$ , while the oxygen carrier

is reduced to  $\text{MeO}_{x-1}$  as shown in reaction R1. In the air reactor, the previously reduced oxygen carrier  $\text{MeO}_{x-1}$  is oxidized back to its original form  $\text{MeO}_x$  by reacting with gaseous oxygen of air via Reaction (R2). It can be seen that CO<sub>2</sub> can be easily separated in Reaction (R1) after a simple condensation of H<sub>2</sub>O steam. In this sense, CLC technology provides a prospective technical pathway to address the increase of global CO<sub>2</sub> emission.

$C_nH_{2m} + (2n + m)MeO_x \rightarrow (2n + m)MeO_{x-1} + nCO_2 + m$
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$$MeO_{x-1} + 1/2O_2 \rightarrow MeO_x$$
 (R2)

For the application to coal combustion, CLC technology was extensively investigated during the past decades [7,8]. Due to the extremely low rate of solid-solid reaction between coal and oxygen carrier particles in fluidization condition [9], several technologies including syngas-fueled Chemical Looping Combustion (syngas-CLC) [10,11], insitu Gasification Chemical Looping Combustion (*iG*-CLC) [12] and Chemical Looping with Oxygen Uncoupling (CLOU) [13] were proposed. Syngas-CLC has several advantages over *iG*-CLC and CLOU,

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#### Nomenclatures

- Decay factor of solids concentration in the freeboard а
- Archimedes number Ar
- Stoichiometric factor for the reaction of CuO and compo $b_i$ nent i (i = CO or H<sub>2</sub>) in the syngas, mol CuO per mol of gas
- Concentration of gas component at the active surface of  $C_{\rm ex}$ oxygen carrier particle,  $mol m^{-3}$
- Concentration of fuel component i (i = CO or H<sub>2</sub>), mol  $C_i$  $m^{-3}$
- Concentration of component i ( $i = CO, CO_2, H_2$  or  $H_2O$ ) in  $C_{i,i}$ bubble (i = b), emulsion (i = e) or freeboard (i = f), mol m<sup>-</sup>
- Solids concentration, kg m $^{-3}$  $C_{\rm s}$
- Solids concentration at the upper limit of the dense bed,  $C_{\rm s,b}$ kg m⁻
- $C_{\rm z}$ Bulk gas concentration at height z of the fuel reactor,  $mol\,m^{-3}$
- Diameter of bubble (j = b) or oxygen carrier particle  $d_i$ (j = p), m
- Diffusivity of gas component i ( $i = CO, CO_2, H_2$  or  $H_2O$ ),  $D_{q,i}$  $m^{2}s^{-1}$
- $D_r$ Inner diameter of the fuel reactor, m
- Activation energy for the reduction of oxygen carrier by Ei component *i* (*i* = CO or H<sub>2</sub>) in the syngas,  $J \mod^{-1}$
- $F_{\rm exc}$ Excessive gas molar flow over minimum fluidization,  $mol s^{-1}$
- Fi Gas molar flow at the inlet (j = in) or height z (j = z) of fuel reactor or caused by the WGS reaction (j = WGS),  $mol s^{-1}$
- $F_{j,i}$ Molar flow of component i ( $i = CO, CO_2, H_2$  or  $H_2O$ ) in bubble (i = b), emulsion (i = e) or freeboard (i = f),  $mol s^{-}$
- Acceleration f gravity,  $9.8 \,\mathrm{m \, s^{-2}}$ g
- Height of dense bed (j = b) or the entire fuel reactor Hi (j = r), m
- Coefficient for gas exchange between bubble and emul $k_{\rm be}$ sion,  $s^{-1}$
- Mass transfer coefficient of component i ( $i = CO \text{ or } H_2$ ) in k<sub>g,i</sub> the gas film surrounding oxygen carrier particles, m s<sup>-</sup>

Rate constant of the reaction between component *i* k<sub>i</sub>  $(i = CO \text{ or } H_2)$  and oxygen carrier, mol<sup>1-n</sup> m<sup>3n-2</sup> s<sup>-1</sup>

Pre-exponential factor of the rate constant for the reaction  $k_{0,i}$ between component i (i = CO or H<sub>2</sub>) and oxygen carrier,  $mol^{1-n}m^{3n-2}s^{-1}$ 

K<sub>WGS,eq</sub> Equilibrium constant for WGS reaction

- Instantaneous mass of oxygen carrier, kg т
- Solids inventory per MW<sub>th</sub> fuel, kg MW<sub>th</sub>  $m_{\rm FR}$
- Mass of fully oxidized (j = ox) or reduced (j = red) oxygen m carrier, or the bed mass of oxygen carrier in the fuel reactor (i = s), kg

- 1

- $M_{\rm O}$ Molar weight of oxygen carrier, kg mol $^{-1}$ Solids circulation rate, kg  $h^{-1}$ ṁs
- Reaction order n
- Nnz Number of nozzle in the gas distributor of fuel reactor
- Pressure at the outlet of fuel reactor, Pa р
- $P_{\rm th}$ Thermal power, W<sub>th</sub>
- Re<sub>D</sub> Reynolds number

Universal gas constant, 8.314 J mol<sup>-1</sup> K<sup>-1</sup> Rg

namely: no requirement for the carbon stripper, no interaction of oxygen carrier with coal ash and no loss of oxygen carrier with the draining stream of ash. In this sense, syngas-CLC is simpler and more straightforward to be implemented for energy generation from coal.

Radius of CuO grain in the oxygen carrier, m  $r_{\rm g,CuO}$ 

- Average reaction rate of gas component i (i = CO or H<sub>2</sub>),  $(-\bar{r}_{g,i})$  $mol m^{-3} s^{-1}$
- $(-\bar{r}_{g,i})_j$ Average reaction rate of gas component i (i = CO or H<sub>2</sub>) in emulsion (*i* = e) or freeboard (*i* = f), mol m<sup>-3</sup> s<sup>-1</sup> Oxygen transport capacity

R<sub>OC</sub>

- Average reaction rate of oxygen carrier particles during  $(-\bar{r}_{s,i})$ the oxidation of component i  $(i = CO \text{ or } H_2)$  in the syngas,  $mol m^{-3} s^{-1}$
- Sc Schmidt number
- Reaction time, s t
- Т Temperature, K
- Mean residence time of oxygen carrier particles in fuel t<sub>m</sub>r reactor, s
- Velocity corresponding to total gas flow (j = 0), minimum u<sub>i</sub> fluidization flow (j = mf), through flow (j = tf) or visible bubble flow (i = vis), m s<sup>-1</sup>
- V Fuel reactor volume, m<sup>3</sup>
- Molar volume of CuO grain in the oxygen carrier, V<sub>M.CuO</sub>  $m^3 mol^{-1}$
- Molar fraction of component i ( $i = CO, CO_2, H_2$  or  $H_2O$ ) in  $(x_i)_i$ the gas stream at the inlet (j = in) or height z (j = z) of the fuel reactor
- Oxidation conversion of oxygen carrier at the inlet of fuel  $X_{o,in}$ reactor
- $X_{\rm s}$ Solids conversion during reduction
- Molar fraction of component i ( $i = CO, CO_2, H_2$  or  $H_2O$ ) in  $y_{e,i}$ the excessive gas over minimum fluidization z
- Axial position in the fuel reactor, m

# Greek Symbols

$\Delta p$	Pressure drop over fuel reactor, Pa
$\delta_{ m b}$	Bubble fraction in the dense bed
$\varepsilon_{\rm mf}$	Bed porosity at minimum fluidization
$\varepsilon_{\rm s}$	Solids fraction in fuel reactor
$\varepsilon_{\rm z}$	Bed porosity at position z of the fuel reactor
$\eta_{\rm C}$	Combustion efficiency
ξg-s	Contact efficiency between gas and solids in freeboard
ρ <sub>m,p</sub>	Molar density of CuO in the oxygen carrier particles,
	$\rho_{m,p} = y_{CuO}/V_{MCuO}$ , being $y_{CuO}$ the volume fraction of CuO
	in the oxygen carrier, $mol m^{-3}$
ρ <sub>p</sub>	Particle density, kg m $^{-3}$
$\tau_i$	Time required for complete reduction of oxygen carrier by
	gas $i$ ( $i$ = CO, H <sub>2</sub> or syn for syngas), s
ψ	Ratio of $u_{\rm vis}$ and $(u_{\rm vis} + u_{\rm tf})$
$\phi$	Oxygen carrier-to-fuel ratio
Acronyms	

CFD	Computational fluid dynamics		
CLC	Chemical looping combustion		
IGCC	Integrated gasification combined cycle		
syngas-CLC Syngas-fueled chemical looping combustion			
SCM	Shrinking core model		
TGA	Thermogravimetric analyzer		
WGS	Water-gas shift		
XRD	X-ray diffraction		

Syngas-CLC can be easily integrated with Integrated Gasification Combined Cycle (IGCC) process [10,14]. According to the simulations of Jin et al. [10] and Wolf et al. [15], system efficiency of IGCC process can be improved by 5-10% if the conventional CO<sub>2</sub> capture technology

was replaced by syngas-CLC. Nevertheless, this improvement is only achievable when the CLC unit is operated under pressurized conditions and at temperatures above 1473 K in order to take advantages of the high efficient gas turbine [16-18]. However, these conditions are difficult to be reached with the state of the art for CLC technology. More indeed, when surplus heat of the CLC unit is only considered for steam generation at super-critical or ultra super-critical conditions, a limited increase in the net efficiency would be expected for pressurized conditions [19,20]. Therefore, the operation of CLC at atmospheric pressure would be recommended for industrial application. The prospect of syngas-CLC at atmospheric pressure was demonstrated by using continuous CLC units with thermal powers of 0.3–120 kW<sub>tb</sub> [11,21–26]. In these results, a much higher combustion efficiency for syngas than that for methane was reached by using Mn-, Fe- and Ni-based oxygen carriers [11,21,22], which suggests a higher reactivity of syngas. In comparison to the Ni-based material, a much lower oxygen carrier-to-fuel ratio  $\phi$  for Cu-based material can assure the complete combustion [23,24]. This indicates a higher reactivity of the Cu-based oxygen carrier than the Ni-based material. Furthermore, it can also be found that the Cu-based material is more reactive than Mn- and Fe-based oxygen carriers [27,28].

Modeling of reactors is important to the development of CLC technology. Different mathematical and multiphase Computational Fluid Dynamics (CFD) models were developed for CLC reactors with the thermal powers of  $5 \, kW_{th}$ – $1 \, MW_{th}$  in recent years, but mainly for  $CH_4$ [29-32] or coal combustion [33-38]. In these investigations, temperature was identified as the most important parameter affecting the performance of CLC systems. Later, some modeling results were successfully validated [29,39] and applied to the design and optimization of 10-100 MW<sub>th</sub> CLC plants by Abad et al. [39,40]. However, in the case of syngas-CLC, modeling work is lacking. Despite a few works used macroscopic [41] or CFD models [42-44] for batch bubbling fluidized bed reactors, little investigation was focused on the simulation of continuous syngas-CLC units [45,46]. More indeed, most of these models did not consider solids in freeboard, although it has been determined that this region is highly relevant to achieve a high conversion of fuel [29,45]. In addition, the validation of syngas-CLC models against experiments is still pending, and the optimized conditions to reach complete syngas combustion have not been determined.

The objective of this work is to extend a macroscopic model to the fuel reactor of a 500  $W_{th}$  continuous CLC facility at "Instituto de Carboquímica" (ICB-CSIC, Spain), and then use various operation conditions to check its flexibility. With this aim, reaction kinetics model for the combustion of syngas (CO + H<sub>2</sub>) and a Cu-based oxygen carrier is developed based on its individual reactivity with CO and H<sub>2</sub>. The macroscopic model for bubbling fluidized bed is built with MATLAB<sup>®</sup> codes and validated against experimental data from the 500 W<sub>th</sub> CLC fuel reactor. Subsequently, influence of operation conditions including syngas composition, temperature, solids circulation rate, solids inventory and WGS reaction is evaluated to examine the flexibility of this reactor model. Finally, the optimized operation conditions for the 500 W<sub>th</sub> fuel reactor are proposed to accomplish almost full combustion of syngas with the lowest oxygen carrier inventory.

# 2. Fuel reactor model

#### 2.1. Reaction kinetics model

The oxygen carrier is a previously tested Cu-based material in Forero et al. [24], which is composed of CuAl<sub>2</sub>O<sub>4</sub>, CuAlO<sub>2</sub>,  $\alpha$ Al<sub>2</sub>O<sub>3</sub> and minor CuO and denoted as Cu14Al-I. The main properties of Cu14Al-I are shown in Table 1, from which it can be seen that this material contains 13.5 wt.% of active component. Thus, the oxygen transport capacity of Cu14Al-I is  $R_{\rm OC} = 0.027$  calculated by  $R_{\rm OC} = (m_{\rm ox} - m_{\rm red})/m_{\rm ox}$ . Here,  $m_{\rm ox}$  and  $m_{\rm red}$  represent the masses of fully oxidized and fully reduced oxygen carriers, respectively. Because of minor presence of

CuO, which is an active component for gaseous oxygen release and uptake, the Cu14Al-I cannot be considered as a CLOU effective material. Thus, this work only focused on its CLC properties.

Reaction kinetics model describing the reaction of Cu14Al-I and syngas is a prerequisite for the formulation of fuel reactor model. In literatures, several reaction kinetics models were developed for the reduction of Cu-based oxygen carriers by  $CH_4$ , CO and  $H_2$  [29,47,48]. However, none of them can be directly applied to syngas and Cu14Al-I according to our preliminary study, due to they were developed for single gas but not syngas. It is noticed that in the morphology analysis performed by Gayán et al. [49] a similar Cu-based oxygen carrier to Cu14Al-I possessed spherical CuO grains inside the material. According to this physical property and the chemical composition of Cu14Al-I, a spherical grain shrinking core model (SCM) for single gas (CO and  $H_2$ ) [47] is used to develop the reaction kinetics model for syngas. Dominated by chemical reaction in the grains, the reaction kinetics model can be written as Eqs. (1)–(3).

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

$$r_i = \frac{r_{\rm g,CuO}}{b_i V_{\rm M,CuO} k_i C_i^n} \tag{2}$$

where  $\tau_i$  represents the required time for complete reduction of oxygen carrier by single component *i* (*i* = CO or H<sub>2</sub>) and X<sub>s</sub> is the reduction conversion of oxygen carrier calculated as  $X_s = (m_{ox} - m)/(R_{OC}m_{ox})$ , being *m* the instantaneous mass of oxygen carrier. In Eq. (2),  $b_i$  is the stoichiometric factor for the reaction with gas *i*,  $r_{g,CuO}$  and  $V_{M,CuO}$  refer to the radius and molar volume of CuO grain, respectively, and  $C_i$  represents the concentration of gas *i* in the stream and *n* is the reaction order.

The rate constant  $k_i$  in Eq. (2) follows the Arrhenius-type dependence as a function of temperature, as seen in Eq. (3).

$$k_i = k_{0,i} \exp\left(-\frac{E_i}{R_g T}\right) \tag{3}$$

Values of the kinetics parameters involved in Eqs. (1)–(3) are adapted from Abad et al. [47] and gathered in Table 2.

Few works were carried out for reaction kinetics model of syngas [50]. Generally, there are two options, developed from experimental observations, for the derivation of global reaction rate of syngas: (*i*) using the more reactive component (CO or H<sub>2</sub>) to represent syngas combustion, (*ii*) using the summation of rates for single gas as the rate of syngas combustion. Preliminary study of this work found that option (*ii*) can give a better prediction of experimental results. Consequently, option (*ii*) is used to describe the rate of syngas combustion with Cu14Al-I, that is, the time for complete reduction of oxygen carrier by syngas,  $\tau_{syn}$ , is calculated with the formulae  $1/\tau_{syn} = 1/\tau_{CO} + 1/\tau_{H2}$ .

For validation purposes, the two syngas used by Forero et al. [24] in a thermogravimetric analyzer (TGA), i.e. Syngas 1 with ratio CO/  $H_2 = 1$  and Syngas 3 with ratio CO/ $H_2 = 3$  shown in Table 3, are applied to check the reaction kinetics model. In both syngas,  $H_2O$  and  $CO_2$ were introduced during TGA tests to fulfill the Water-Gas Shift (WGS) equilibrium, as shown in Table 3 and in Forero et al. [24]. It can be observed in Fig. 1 the reduction conversion  $X_s$  for Syngas 1 and Syngas 3 can be adequately replicated with the reaction kinetics model

# Table 1

Main properties of the Cu14Al-I oxygen carrier.

XRD phase	$CuAl_2O_4$ , $CuAlO_2$ , $CuO^a$ , $\alpha Al_2O_3$	
Content of active material	13.5	wt.%
Oxygen transport capacity $R_{\rm OC}$	0.027	-
Particle diameter	0.3-0.5	mm
Particle density	1900	kg m <sup>-3</sup>

<sup>a</sup> Minor amount.

 Table 2

 Parameter values in the reaction kinetics model from Abad et al. [47].

Symbols	СО	H <sub>2</sub>	
$r_{g, CuO}$	2·10 <sup>-7</sup>	2:10 <sup>-7</sup>	m
$V_{M, CuO}$	12.4·10 <sup>-6</sup>	12.4:10 <sup>-6</sup>	m <sup>3</sup> mol <sup>-1</sup>
$b_i$	1	1	-
n	0.6	0.8	-
$k_{0,i}$	0.01	1.0	mol <sup>1-n</sup> m <sup>3n-2</sup> s <sup>-1</sup>
$E_i$	25,000	60,000	J mol <sup>-1</sup>

Table 3

Volume fractions (vol.%) of CO,  $H_2$ ,  $H_2O$  and  $CO_2$ , and  $CO/H_2$  ratios in Syngas 1 and Syngas 3 used by Forero et al. [24].

	CO	$H_2$	$H_2O$	$CO_2$	CO/H <sub>2</sub> ratio
Syngas 1	7.5	7.5	10	11	1
Syngas 3	11.2	3.8	10	33	3



**Fig. 1.** Comparison of reaction kinetics model predictions (—, —) and experimental results ( $\bigcirc$ ,  $\square$ , taken from Forero et al. [24]) for Syngas 1 (CO/H<sub>2</sub> = 1, blue color) and Syngas 3 (CO/H<sub>2</sub> = 3, red color) at 1073 K (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

presented in Eqs. (1)–(3) and the values of kinetics parameters in Table 2. To this end, the reaction kinetics model for single gas (CO or  $H_2$ ) is evolved for Cu14Al-I oxygen carrier and syngas (CO +  $H_2$ ), which is also validated against experiments.

#### 2.2. Reactivity on particle surface

Prior to applying the above reaction kinetics model to a fluidized bed, gas concentration on the active surface of oxygen carrier particles must be calculated. In fluidization condition, fuel component in bulk flow must pass through the gas film surrounding oxygen carrier particles to react with the active surface. To obtain the actual gas concentration on the active surface, the mass balance to a whole particle is performed, as seen in Eq. (4).

$$\frac{1}{b_i} \rho_{\rm m,p} \left( \frac{1}{6} \pi d_p^3 \right) \frac{dX_{\rm s}}{dt} = k_{\rm g,i} \pi d_p^2 (C_{\rm z} - C_{\rm ex})$$
(4)

where the left term represents the consumption of component i (i = CO, H<sub>2</sub>) on the surface of a particle with a diameter of  $d_p$  and a molar density of  $\rho_{m,p}$ . This consumption is simultaneously compensated by the same component flowing from bulk gas, as described in right term of Eq. (4). Accordingly, the concentration of fuel component on the active

surface,  $C_{ex}$ , can be calculated using bulk concentration  $C_z$  at height z of the reactor. In this case, the concentration  $C_z$  of component *i* is equal to that in emulsion phase for dense bed and that in bulk flow for freeboard, depending on the height position. Mass transfer coefficient  $k_{g,i}$  for component *i* in dense bed and freeboard in Eq. (4), can be calculated as Eqs. (5) and (6) according to Palchonok et al. [51] and Chakraborty et al. [52], respectively, which were extensively checked for their feasibility in the use of CLC fluidized bed reactors [29,33,34,38,47].

$$\frac{k_{g,i}d_p}{D_{g,i}} = 2\varepsilon_{mf} + 0.117Ar^{0.39}Sc^{1/3}$$
(5)

$$\frac{k_{g,i}d_p}{D_{g,i}} = 2\varepsilon_z + 0.69 \operatorname{Re}_p^{1/2} Sc^{1/3}$$
(6)

where  $D_{g,i}$  is the diffusivity of component *i* calculated according to Fuller et al. [53],  $e_{mf}$  is the bed porosity under minimum fluidization calculated with the method used by Hannes et al. [54],  $e_z$  means the bed porosity at position z of the reactor, determined according to the solids concentration. The symbols of *Ar*,  $Re_p$  and *Sc* represent Archimedes number, Reynolds number and Schmidt number, respectively.

In stabilized fluidized bed reactors, e.g. the 500  $W_{\rm th}$  reactor in this work, a stable oxygen carrier conversion at each location of reactor can be predicted. For a position z of the reactor, the average reaction rate of oxygen carrier can be calculated.

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

The assumption of perfect mixing of solids in the reactor showed reasonability in the previous work of Abad et al. [29]. Thus, this assumption is also applied to the present work. In this case, the residence time distribution of particles inside fuel reactor E(t) can be described as Eq. (8).

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

being  $t_{\rm mr}$  the mean residence time of particles in fuel reactor.

The average reaction rate of gas component *i* (*i* = CO, H<sub>2</sub>) at each height of reactor,  $(-\bar{r}_{g,i})$ , can be calculated with Eq. (9). This equation is then used in the reactor model to account for the gas consumption due to gas-solid reactions.

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

# 2.3. Fluid dynamics and mass balance

The macroscopic model is similar to that developed by Abad et al. [29] for CLC of  $CH_4$  in a 10 kW<sub>th</sub> facility; however, herein it is extended for syngas combustion in a 500 W<sub>th</sub> CLC reactor. Fuel reactor geometry of the 500 W<sub>th</sub> facility is shown in Table 4, which is a bubbling fluidized bed reactor with a height of 0.6 m and an inner diameter of 0.05 m. A distributor with 17 nozzles is located at the entrance of bed to give good gas distribution, which is also used to calculate the bubble diameter in dense bed. A schematic dynamic description of the fuel reactor is shown in Fig. 2. The bubbling fluidized bed is composed of dense region and freeboard (zone 3), of which the dense region contains a bubble phase (zone 2) and an emulsion phase (zone 1). As shown in Fig. 2, different behaviors can be seen in these regions. In order to obtain gas distribution as a function of reactor height, equations on fluid dynamics and mass balances for the entire reactor must be established and solved simultaneously.

#### 2.3.1. Fluid dynamics in dense bed

The dense bed is composed of emulsion and bubble phases, where the oxygen carrier particles are all assumed to be distributed in emulsion phase and thus no oxygen carrier is included in bubbles, as seen in

#### Table 4

Fuel reactor geometry and operation condition.

	Symbols	Values	Units
Reactor geometry			
Reactor height	$H_{ m r}$	0.6	m
Inner diameter	$D_{\rm r}$	0.05	m
Nozzle number	N <sub>nz</sub>	17	-
Operation condition			
Pressure at outlet	р	101,325	Pa
Gas molar flow at inlet	Fin	$3.2 \cdot 10^{-3}$	$mol s^{-1}$
Pressure drop	$\Delta p$	250-4000	Pa
Temperature	Т	973-1173	K
Bed mass	m <sub>s</sub>	0.05-0.8	kg
Solids circulation rate	$\dot{m}_{ m s}$	2-8	kg h <sup>-1</sup>
Dense bed height	$H_{\rm b}$	0.025-0.4	m
Thermal power	$P_{\rm th}$	80-700	W <sub>th</sub>
Oxidation conversion	$X_{o,in}$	1	-



**Fig. 2.** Characteristics and dynamic description of the bubbling fluidized bed with zone 1: emulsion phase, zone 2: bubble phase and zone 3: freeboard.

Fig. 2. In emulsion, the oxygen carrier particles are assumed to be under minimum fluidization condition. However, in practice several times of minimum fluidization velocity are always used to get good fluidization. Therefore, the excessive gas over minimum fluidization of emulsion phase is assumed to be transferred to bubbles or passed through bubbles, see zone 2 of Fig. 2. A modified two-phase model proposed by Johnsson et al. [55] is applied to obtain flow structure of the dense bed. Accordingly, the total gas velocity  $u_0$  is shared by the minimum fluidization velocity  $u_{mfr}$  the visible bubble velocity  $u_{vis}$  and the throughflow velocity  $u_{tfr}$  as shown in Eq. (10). Here, the throughflow  $u_{tf}$  can be understood as a stream of gas passing through bubbles, which in combination with the visible bubbles were treated as a bubble phase in the following reactor model.

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

The minimum fluidization velocity  $u_{\rm mf}$  is calculated via Wen and Yu correlation [56]. In Eq. (10),  $\delta_{\rm b}$  represents the bubble fraction in the dense bed, which can be calculated through Eq. (11).

$$\delta_{\rm b} = \frac{u_{\rm vis}}{u_{\rm vis} + 0.71\sqrt{{\rm g}d_{\rm b}}} \tag{11}$$

where the bubble diameter  $d_b$  is obtained as a function of bed height z and nozzle number  $N_{nz}$  using Darton correlation [57].

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

 $u_{\rm vis} = \psi(u_0 - u_{\rm mf}(1 - \delta_{\rm b})) \tag{12}$ 

 $u_{\rm tf} = (1 - \psi)(u_0 - u_{\rm mf}(1 - \delta_{\rm b})) \tag{13}$ 

where  $\psi$ , the ratio of  $u_{vis}$  and  $(u_{vis} + u_{tf})$ , is calculated according to Johnsson et al. [55].

#### 2.3.2. Fluid dynamics in freeboard

The top of dense bed begins freeboard as seen in Fig. 2, where the solids concentration  $C_s$  is decreasing with reactor height [58].

$$\frac{dC_{\rm s}}{dz} = -aC_{\rm s} \tag{14}$$

being *a* the decay factor of solids concentration in freeboard, calculated with the correlation  $a = 4 \cdot u_t / u_g$  proposed by Johnsson et al. [55], which was recently validated for its application in small-scale CLC fuel reactors [34,38].

#### 2.3.3. Mass balance

All reactants and products, including Cu14Al-I, CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O, are considered to the mass balance. For gas-solid interaction, the following Reactions (R3) and (R4) for syngas combustion are used for mass balance, which is consistent to the fact obtained with this kind of materials in literatures [29,47].

$$CO + CuO \rightarrow Cu + CO_2$$
 (R3)

$$H_2 + CuO \rightarrow Cu + H_2O$$
 (R4)

In addition, because WGS equilibrium was experimentally observed as an intermediate step for syngas combustion in the 500  $W_{\rm th}$  reactor [24], this equilibrium is assumed to be reached immediately for the gas products. This assumption was also used in the works of Abad et al. [29,47], where satisfactory simulation results were attained.

$$CO + H_2 O \leftrightarrow CO_2 + H_2$$
 (R5)

In dense bed, oxygen carrier particles can react directly with gases in emulsion or react with gases exchanged from bubbles. However, no gas-solid reaction is involved inside bubbles, because no oxygen carrier particles are included there as observed in Fig. 2. The mass balances for emulsion phase and bubble phase ( $u_{vis} + u_{rf}$ ) in dense bed can be expressed as Eqs. (15) and (16), respectively.

# 2.3.3.1. Emulsion phase.

$$\frac{dF_{e,i}}{dV} = -(1 - \delta_{b})\sum_{i}(-\bar{r}_{g,i})_{e} - \delta_{b}k_{be}(C_{e,i} - C_{b,i}) - y_{e,i}\frac{dF_{exc}}{dV} - \frac{dF_{WGS}}{dV}$$
(15)

#### 2.3.3.2. Bubble phase.

$$\frac{dF_{b,i}}{dV} = \frac{d((u_{vis} + u_{tf})C_{b,i})}{dz} = \delta_b k_{be}(C_{e,i} - C_{b,i}) + y_{e,i}\frac{dF_{exc}}{dV} - \frac{dF_{WGS}}{dV}$$
(16)

being  $k_{be}$  - the exchange coefficient of gas *i* (CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O) between emulsion (with a concentration of  $C_{e,i}$ ) and bubble (with the concentration of  $C_{b,i}$ ), depicted in zone 2 of Fig. 2 - calculated through Eq. (17) by Sit and Grace [59] and  $F_{exc}$  - containing  $y_{e,i}$  molar fraction of component *i* – the excessive flow over minimum fluidization. Here, it is noted that  $F_{exc}$  decides the part of gas flow higher than the minimum fluidization, which must be transferred to bubble phase to maintain the minimum fluidization of emulsion, as seen in zone 2 of Fig. 2.  $F_{WGS}$ denotes the gas molar flow caused by WGS reaction, which is limited by an equilibrium constant  $K_{WGS,eq}$  calculated as Eq. (18).

$$k_{be} = \frac{1}{d_b} \left( 2u_{mf} + 12 \left( \frac{D_{g,i} \varepsilon_{mf} u_{\text{vis}}}{\pi d_b \delta_b} \right)^{0.5} \right)$$
(17)

$$K_{\rm WGS,eq} = \exp\left(-3.296 + \frac{3.144 \cdot 10^3}{T} + \frac{4.980 \cdot 10^5}{T^2}\right)$$
(18)

In freeboard, although there is no constraint limiting gas exchange from bubbles, the gas-solid reactions are influenced by a contact efficiency  $\xi_{g,s}$ , as shown in zone 3 of Fig. 2. Therefore, the mass balance for

this region can be written as Eq. (19).

$$\frac{dF_{f,i}}{dV} = \frac{d(u_0 C_{f,i})}{dz} = -\sum \xi_{g-s} (-\bar{r}_{g,i})_f - \frac{dF_{WGS}}{dV}$$
(19)

The contact efficiency,  $\xi_{g-s}$ , between gases and solids in freeboard is calculated with the equation proposed by Furusaki et al. [60].

$$\xi_{\rm g-s} = 1 - 0.75 \left(\frac{C_{\rm s}}{C_{\rm s,b}}\right)^{0.4} \tag{20}$$

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

The fluid dynamics model and mass balance equations are formulated with MATLAB<sup>\*</sup> codes, which are solved simultaneously with the Runge-Kutta method.

#### 2.4. Input and output of reactor model

The inputs to reactor model are the properties of Cu14Al-I oxygen carrier in Table 1, reactor geometry and the operation conditions in Table 4. The diameter and density of particles shown in Table 1 are used to determine average reactivity. Geometry of reactor in Table 4 is used in the model to obtain fluid dynamics and to limit the calculation boundary. As seen in Table 4, the fuel reactor is operated at atmospheric pressure with a total inlet gas molar flow of  $F_{\rm in} = 3.2 \cdot 10^{-3}$ mol s<sup>-1</sup> which includes CO, H<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub> as balance gas. According to Forero et al. [24], the Cu14Al-I oxygen carrier can be fully oxidized in air reactor, thus the oxidation conversion of Cu14Al-I at the fuel reactor inlet is fixed to  $X_{o,in} = 1$ , see Table 4. The other operation parameters including pressure drop  $\Delta p$ , temperature T, bed mass  $m_s$ , solids circulation rate  $\dot{m}_{s}$  and thermal power  $P_{th}$  are varied in some ranges for better evaluation purposes. It is noted that the pressure drop  $\Delta p$  is a dependent variable, which was changed according to the bed mass  $m_s$  and the reactor geometry, as described by Abad et al. [39].

With the variation of operation conditions, the oxygen carrier-tofuel ratio  $\phi$ , 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. (21).

$$\phi = \frac{R_{\rm OC} \cdot \dot{m}_{\rm s}}{3600 \cdot M_{\rm O} \cdot (x_{\rm CO} + x_{\rm H_2})_{\rm in} \cdot F_{\rm in}}$$
(21)

where  $M_0$  is the molar weight of oxygen and  $(x_i)_{in}$  refers to the molar fractions of component *i* (*i* = CO and H<sub>2</sub>) in the gas stream  $F_{in}$  entering fuel reactor.

Because of the use of different bed masses  $m_{\rm s}$  and thermal powers  $P_{\rm th}$  in the fuel reactor, the solids inventory  $m_{\rm FR}$ , defined as oxygen carrier mass per MW<sub>th</sub> fuel, would be varied according to Eq. (22).

$$m_{\rm FR} = \frac{m_{\rm s}}{P_{\rm th}} \cdot 10^6 \tag{22}$$

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

According to the gas distribution, combustion efficiency  $\eta_c$ , defined as the ratio between the oxygen taken by gas products over the oxygen required for complete syngas combustion, is calculated as Eq. (23).

$$\eta_{\rm C} = \frac{(2x_{\rm CO_2} + x_{\rm CO} + x_{\rm H_2O})_z \cdot F_z - (2x_{\rm CO_2} + x_{\rm CO})_{\rm in} \cdot F_{\rm in}}{(x_{\rm CO} + x_{\rm H_2})_{\rm in} \cdot F_{\rm in}}$$
(23)

where  $F_z$  is the molar flow of gas stream at height z of fuel reactor,  $(x_i)_z$  means the molar fraction of component *i* (*i* = CO<sub>2</sub>, CO and H<sub>2</sub>O) in  $F_z$ .

#### 3. Results and discussions

## 3.1. Gas distribution

As an example, Fig. 3 shows gas distribution, combustion efficiency

 $\eta_{\rm C}$  and solids fraction  $\varepsilon_{\rm s}$  as a function of fuel reactor height for the case of using syngas with CO/H<sub>2</sub> = 3, oxygen carrier-to-fuel ratio  $\phi = 1.2$ , solids circulation rate  $\dot{m}_{\rm s} = 3 \,{\rm kg} \,{\rm h}^{-1}$  and bed mass  $m_{\rm s} = 0.2 \,{\rm kg}$  at  $T = 1073 \,{\rm K}$ . According to solids fraction  $\varepsilon_{\rm s}$ , the fuel reactor is composed of a dense bed with a height of 0.1 m and a freeboard above, as identified by the vertical dash line in Fig. 3.

After the introduction of syngas, the WGS equilibrium is reached immediately, resulting in 27 vol.% CO, 9 vol.% H<sub>2</sub>, 12 vol.% CO<sub>2</sub> and 4 vol.% H<sub>2</sub>O at the 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 reaction behaviors are seen for dense bed and freeboard. In dense bed, the reaction becomes slower at higher positions because: (i) the bubble, formed by gas over minimum fluidization, increases its size with the height of the reactor, which results in an insufficient contact between syngas and oxygen carrier particles, (ii) the concentrations of CO and H<sub>2</sub> are decreased gradually with the reactor height. Because of the consumptions of CO and H<sub>2</sub> in syngas, higher concentrations of CO2 and H2O are achieved at higher heights but keeping the WGS equilibrium. The similar phenomenon was also noticed by Abad et al. [29,47] for CH<sub>4</sub> combustion, meanwhile immediate WGS equilibrium was regarded as a proper assumption according to experiments [24] and model validations [29,47]. Because of the conversion of syngas, higher combustion efficiency is observed at a higher position of dense bed. In the freeboard, bubbles from dense bed are broken which results in a better contact of gas and oxygen carrier particles, see also Fig. 2. Therefore, in Fig. 3 a higher rate of syngas combustion is seen in freeboard, which leads to a faster increase of CO<sub>2</sub> and H<sub>2</sub>O concentrations, and thus the combustion efficiency. In the case of Fig. 3, incomplete combustion is encountered, thereby around 3 vol. % CO and 1 vol.% H<sub>2</sub> are observed at fuel reactor exit. The incomplete combustion is ascribed to the low oxygen carrier-to-fuel ratio  $\phi$  used, in this case  $\phi = 1.2$ , which limits the average reactivity of oxygen carrier particles [61]. However, when higher oxygen carrier-to-fuel ratios are applied, better combustion behaviors can be observed.

#### 3.2. Fuel reactor model validation

Experimental results used for the validation of the reactor model are from Forero et al. [24], where continuous tests of Cu14Al-I and syngas were carried out in the same 500 W<sub>th</sub> CLC facility. Fig. 4 compares modeling results and experimental data in terms of the concentrations of CO and H<sub>2</sub> and the combustion efficiency  $\eta_C$  obtained at temperatures of 1073 and around 1173 K. With the increase of oxygen carrierto-fuel ratio  $\phi$ , the concentrations show decreases but the combustion efficiency rises gradually to 100%. Despite the complicated reaction conditions are involved, it can be seen that the concentrations of CO and H<sub>2</sub> are well predicted by the model, independent on the oxygen carrier-to-fuel ratio  $\phi$  or syngas composition. In this sense, the



**Fig. 3.** Distribution of gas concentration (H<sub>2</sub>, CO, H<sub>2</sub>O and CO<sub>2</sub>), combustion efficiency  $\eta_{\rm C}$  and solids fraction  $\varepsilon_{\rm s}$  along reactor height during the combustion of syngas for the condition of T = 1073 K,  $m_{\rm s} = 0.2$  kg,  $\dot{m}_{\rm s} = 3$  kg h<sup>-1</sup>,  $\phi = 1.2$  and CO/H<sub>2</sub> = 3.



combustion efficiency  $\eta_C$  of syngas agrees well with the experimental results obtained at 1073 and around 1173 K. As a consequence, good agreements of experiments and modeling are achieved, thus the fuel reactor model stated above is validated.

#### 3.3. Flexibility of the macroscopic model

#### 3.3.1. Variation of CO/H<sub>2</sub> ratio

Industrial syngas has various compositions within the ratios of CO/ H<sub>2</sub> = 1–3, which could affect the combustion performance. In order to evaluate the effect of syngas composition, CO/H<sub>2</sub> ratio is varied in the range of 1–3 while the other parameters including temperature *T*, bed mass  $m_{\rm s}$ , solids circulation rate  $\dot{m}_{\rm s}$ , oxygen carrier-to-fuel ratio  $\phi$  and fuel flow are kept constant.

Fig. 5 shows the effect of CO/H<sub>2</sub> ratio under the condition with temperature T = 1073 K, bed mass  $m_s = 0.2$  kg, solids circulation rate  $\dot{m}_{\rm s} = 6 \, \text{kg} \, \text{h}^{-1}$  and oxygen carrier-to-fuel ratio  $\phi = 1.5$ . It can be observed that a higher CO/H<sub>2</sub> ratio results in more CO moles at the outlet of fuel reactor. On the contrary, although less moles of H<sub>2</sub> are used at higher CO/H<sub>2</sub> ratios, H<sub>2</sub> concentration at fuel reactor exit shows some increases, which is ascribed to the combined influences from CO/H<sub>2</sub> ratio and WGS equilibrium. On the one hand, an increase of CO/H<sub>2</sub> ratio directly reduces H<sub>2</sub> concentration. On the other hand, more CO in the gas stream at higher  $CO/H_2$  ratios forces WGS in Reaction (R5) to the direction with more generations of CO<sub>2</sub> and H<sub>2</sub>. Therefore, more CO and H<sub>2</sub> are found in Fig. 5 for higher CO/H<sub>2</sub> ratios. The increase of CO/  $H_2$  ratio also leads to a slight decrease of oxygen carrier inventory  $m_{\rm FR}$ per MW<sub>th</sub> fuel, which is attributable to the slightly higher heating value of CO combustion than H<sub>2</sub>, albeit the total fraction and flow of CO and H<sub>2</sub> are unchanged. Higher concentrations of unburnt CO and H<sub>2</sub> as well as slightly lower  $m_{\rm FR}$  at higher CO/H<sub>2</sub> ratios lead to some decreases of combustion efficiency  $\eta_{\rm C}$  and oxygen carrier conversion  $X_{\rm s}$ .

#### 3.3.2. Variation of temperature

The operation temperature is varied in the range of T = 973-1173 K, while the other parameters are maintained as constants. It is necessary to note that the temperatures considered here are in the range for CLC operations of this type of Cu-based oxygen carriers, i.e. the reaction rate is adequate for gaseous fuel combustion and agglomeration can be avoided [29,49]. Moreover, the CLOU effect of Cu14Al-I is irrelevant because of the minor content of CuO in the oxygen carrier as stated above in Section 2.1.

Fig. 6 shows the effect of operation temperature on gas concentration, combustion efficiency and solids conversion, using bed mass  $m_s = 0.2$  kg, solids circulation rate  $\dot{m}_s = 6$  kg h<sup>-1</sup> and oxygen carrierto-fuel ratio  $\phi = 1.5$  for the combustion of syngas with CO/H<sub>2</sub> = 3. Similar to most findings elsewhere, higher temperatures are favorable for syngas combustion due to the faster reaction kinetics. When the temperature is increased from 973 to 1173 K, concentrations of CO and H<sub>2</sub> at fuel reactor outlet are reduced by 64.0% and 80.0%, respectively, which results in a 1.5% increase of  $X_s$  and a 3.0% increase of  $\eta_C$ . At

**Fig. 4.** Comparison of CO and H<sub>2</sub> concentrations and combustion efficiency  $\eta_{\rm C}$  between modeling (void symbols:  $\Box \Diamond \rangle$ ) and experimental (filled symbols:  $\blacksquare \bullet \bullet$  taken from Forero et al. [24]) results obtained in 500 W<sub>th</sub> plant for the combustion of syngas with CO/H<sub>2</sub> = 1 (cubic symbols:  $\blacksquare \Box$ ) and syngas with CO/H<sub>2</sub> = 3 (circle symbols:  $\bullet \bigcirc$  diamond symbols:  $\bullet \bigcirc$ ) at 1073 K (in black and red) and around 1173 K (in blue) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

T = 1173 K, the concentrations of CO and H<sub>2</sub> at fuel reactor exit can be as low as 0.6 vol.% and 0.2 vol.%, respectively, meanwhile the combustion efficiency can be as high as  $\eta_{\rm C} = 99\%$ .

# 3.3.3. Variation of solids circulation rate

The solids circulation rate is varied within the interval of  $\dot{m}_{\rm s} = 3-8 \, {\rm kg \, h^{-1}}$  calculated based on the fully oxidized oxygen carrier, i.e.  $X_{\rm o,in} = 1$  as shown in Table 4, while the other parameters including temperature, bed mass and CO/H<sub>2</sub> ratio are kept constant. With the variation of  $\dot{m}_{\rm s}$ , the oxygen carrier-to-fuel ratio  $\phi$  is also changed, because the fuel flow, thermal power  $P_{\rm th}$  and CO/H<sub>2</sub> ratio are fixed.

As shown in Fig. 7, oxygen carrier-to-fuel ratio  $\phi$  increases linearly from 0.8 to 2.1 as the solids circulation rate  $m_s$  rises from 3 to 8 kg h<sup>-1</sup>. A faster circulation of oxygen carrier particles results in a shorter residence time of solids, which leads to a lower solids conversion in Fig. 7 and a higher average reactivity of oxygen carrier, see Eqs. (7) and (8). As a consequence, at higher solids circulation rates faster conversion of syngas could be foreseen. In this sense, lower concentrations of CO and H<sub>2</sub> as well as higher combustion efficiency  $\eta_C$  are seen in Fig. 7 for higher solids circulation rates. In the case of Fig. 7, solids circulation rate  $\dot{m}_s > 7 \text{ kg h}^{-1}$  would be adequate for the complete combustion of syngas, which can be realized in the 500 W<sub>th</sub> reactor illustrated by Forero et al. [24].

# 3.3.4. Variation of solids inventory

For fixed thermal powers and solids circulation rates, solids inventory in the fuel reactor determines dense bed height and thus combustion time and contact chance between oxygen carrier particles and fuel gas. Fig. 8 shows the influence of solids inventory  $m_{\rm FR}$  on gas concentration, combustion efficiency  $\eta_{\rm C}$  and solids conversion  $X_{\rm s}$  using bed mass of  $m_{\rm s} = 0.05-0.8$  kg, solids circulation rate  $\dot{m}_{\rm s} = 6$  kg h<sup>-1</sup>, oxygen carrier-to-fuel ratio  $\phi = 1.5$  and CO/H<sub>2</sub> = 3 at T = 1173 K, where the dense bed surface and fuel reactor outlet are focused.

With the increase of bed mass  $m_{\rm s}$ , the solids inventory  $m_{\rm FR}$ 



**Fig. 5.** Effect of CO/H<sub>2</sub> ratio on gas concentration (H<sub>2</sub> and CO), combustion efficiency  $\eta_{C}$ , oxygen carrier conversion  $X_s$  at fuel reactor outlet and solids inventory  $m_{FR}$  for the condition of T = 1073 K,  $m_s = 0.2$  kg,  $\dot{m}_s = 6$  kg h<sup>-1</sup>, and  $\phi = 1.5$ , including (solid lines) or excluding (dash lines) WGS reaction.



**Fig. 6.** Effect of temperature on gas concentration (H<sub>2</sub> and CO), combustion efficiency  $\eta_{\rm C}$  and oxygen carrier conversion  $X_{\rm s}$  at fuel reactor outlet for the condition of  $m_{\rm s} = 0.2 \,\rm kg$ ,  $\dot{m}_{\rm s} = 6 \,\rm kg \,h^{-1}$ ,  $\phi = 1.5$ , CO/H<sub>2</sub> = 3 and  $P_{\rm th} = 500 \,\rm W_{th}$ , including (solid lines) or excluding (dash lines) WGS reaction.



**Fig. 7.** Effect of solids circulation rate on gas concentration (H<sub>2</sub> and CO), combustion efficiency  $\eta_{\rm C}$ , oxygen carrier conversion  $X_{\rm s}$  at fuel reactor outlet and oxygen carrier-to-fuel ratio  $\phi$  for the condition of T = 1173 K,  $m_{\rm s} = 0.2$  kg, CO/H<sub>2</sub> = 3 and  $P_{\rm th} = 500$  W<sub>th</sub>, including (solid lines) or excluding (dash lines) WGS reaction.

calculated by eq 22 is raised from 100 to 1500 kg MW<sub>th</sub><sup>-1</sup>. As seen in Fig. 8 (a), during the increase of  $m_{\rm FR}$  from 100 kg MW<sub>th</sub><sup>-1</sup> to higher than 1000 kg MW<sub>th</sub><sup>-1</sup>, the concentrations of unburnt CO and H<sub>2</sub> at fuel reactor exit decline gradually to zero from 2.9 vol.% and 0.8 vol.%, respectively. In contrast, the combustion efficiency  $\eta_{\rm C}$  and solids conversion  $X_{\rm s}$  are increased gradually in the ranges of 94–100% and 0.8–0.85, respectively. For the dense bed, as shown in Fig. 8 (b), the concentrations of CO and H<sub>2</sub>, combustion efficiency and oxygen carrier conversion also show similar behaviors. This behavior is attributed to that a higher  $m_{\rm FR}$  means a higher dense bed height in the range of  $H_{\rm b} = 0.025$ –0.4 m which results in longer reaction time and more



**Fig. 9.** Effect of joint variation of solids circulation rate and fuel flow on gas concentration (H<sub>2</sub> and CO), combustion efficiency  $\eta_{\rm C}$ , oxygen carrier conversion  $X_{\rm s}$  at fuel reactor outlet and solids inventory  $m_{\rm FR}$  for the condition of T = 1173 K,  $m_{\rm s} = 0.2$  kg,  $\dot{m}_{\rm s} = 2-8$  kg h<sup>-1</sup>,  $\phi = 1.5$ , and CO/H<sub>2</sub> = 3 with fuel flow varying from  $3.2 \cdot 10^{-4}$  to  $2.7 \cdot 10^{-3}$  mol s<sup>-1</sup> ( $P_{\rm th} = 80-700$  W<sub>th</sub>), including (solid lines) or excluding (dash lines) WGS.

opportunities for gas-solids contact. In the case of Fig. 8, the minimum oxygen carrier inventory for full combustion of syngas at fuel reactor outlet is around  $m_{\rm FR} = 1100 \, \text{kg MW}_{\text{th}}^{-1}$ .

# 3.3.5. Joint variation of solids circulation rate and fuel flow

During the operation of a continuous CLC system, solids circulation rate and fuel flow can be changed simultaneously. In this case, there would be a condition with  $\phi$  as a constant. Despite this, combustion characteristics can be varied under different solids circulation rate  $\dot{m}_s$ and fuel flows. In this part, solids circulation rate  $\dot{m}_s$  and fuel flow are changed in the ranges of  $3-8 \text{ kg h}^{-1}$  and  $3.2 \cdot 10^{-4} - 2.7 \cdot 10^{-3} \text{ mol s}^{-1}$ (corresponding to thermal powers of  $P_{\text{th}} = 80-700 \text{ W}_{\text{th}}$ ), respectively, while temperature, bed mass  $m_s$ , oxygen carrier-to-fuel ratio  $\phi$  and CO/ H<sub>2</sub> are kept constant. Here, the simultaneous variations of solids circulation rate  $\dot{m}_s$  and fuel flow (or thermal power  $P_{\text{th}}$ ) are to maintain a fixed  $\phi$ , in this case  $\phi = 1.5$ .

Fig. 9 shows the effect of varying  $\dot{m}_{\rm s}$  and fuel flow at the same time on gas concentration, combustion efficiency  $\eta_{\rm C}$ , solids conversion  $X_{\rm s}$ and solids inventory  $m_{\rm FR}$  for the case of using temperature T = 1173 K, bed mass  $m_{\rm s} = 0.2$  kg, solids circulation rate  $\dot{m}_{\rm s} = 2-8$  kg h<sup>-1</sup>, oxygen carrier-to-fuel ratio  $\phi = 1.5$  and CO/H<sub>2</sub> = 3. As stated above in Section 3.3.3, a higher solids circulation rate  $\dot{m}_{\rm s}$  leads to a shorter residence time of oxygen carrier particles inside the fuel reactor, thus a higher average reactivity of oxygen carrier, see Eqs. (7) and (8). This enhances the combustion in the case of Section 3.3.3, however, it is different here for Fig. 9 where the opposite is found. A higher solids circulation rate  $\dot{m}_{\rm s}$  leads to the increases of CO and H<sub>2</sub> concentrations and decreases of  $\eta_{\rm C}$  and  $X_{\rm s}$  in Fig. 9. This is because that to maintain  $\phi = 1.5$  the increase of  $\dot{m}_{\rm s}$  must be associated by proportionally rising fuel flow (or thermal power in MW<sub>th</sub>), which directly reduces the solids inventory  $m_{\rm FR}$  with the unit kg/MW<sub>th</sub>. Furthermore, the decrease of  $m_{\rm FR}$  leads to a lower

**Fig. 8.** Effect of solids inventory on gas concentration (H<sub>2</sub> and CO), combustion efficiency  $\eta_{\rm C}$  and oxygen carrier conversion  $X_{\rm s}$  at (a) fuel reactor outlet and (b) dense bed surface for the condition of T = 1173 K,  $m_{\rm s} = 0.05-0.8$  kg,  $\dot{m}_{\rm s} = 6$  kg h<sup>-1</sup>,  $\phi = 1.5$ , CO/H<sub>2</sub> = 3 and  $P_{\rm th} = 500$  W<sub>th</sub>, including (solid lines) or excluding (dash lines) WGS.



dense bed height and less chance for the contact between oxygen carrier particles and gases. In this sense, the influence of  $m_{\rm FR}$  is more relevant than the average reactivity of oxygen carrier during combustion. For the joint variation of solids circulation rate  $\dot{m}_{\rm s}$  and fuel flow, if a fixed  $\phi$  is desired during the operation, a low solids circulation rate can only assure the complete combustion of syngas with low values of flow rate and thermal power. For syngas with a high flow rate, the increase of oxygen carrier-to-fuel ratio  $\phi$  could be recommended as a more straightforward measure to reach full combustion.

# 3.4. Relevance of WGS reaction

In Figs. 5–9, gas concentration, combustion efficiency  $\eta_C$  and solids conversion  $X_s$  at fuel reactor exit 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, a lower CO concentration and a higher H<sub>2</sub> concentration at fuel reactor exit can be expected while WGS is excluded from the model, but little changes of combustion efficiency  $\eta_C$  and solids conversion  $X_s$  are seen. This behavior is due to the WGS equilibrium in Reaction (R5) is positive for more generation of CO. That is, WGS reaction in this case can increase the conversion of CO<sub>2</sub> to CO, thus increases the CO concentration at fuel reactor exit, which is more obvious for higher CO/H<sub>2</sub> ratios. As indicated in Fig. 5, CO/H<sub>2</sub> = 2 is a critical point for concentrations of unburnt CO and H<sub>2</sub>. For CO/H<sub>2</sub> > 2, the CO concentration is higher in the case of including WGS than that excluding WGS, however, the opposite is found for CO/H<sub>2</sub> < 2.

Additionally, for better evaluations, the concentrations of CO and  $H_2$  and combustion efficiency  $\eta_C$  at fuel reactor exit for excluding WGS are subtracted by that for including WGS, which are then divided by the latter to get the variation degrees. Fig. 10 shows the variation degrees for gas concentrations and combustion efficiency  $\eta_{\rm C}$  as a function of CO/H<sub>2</sub> ratio at different temperatures. It can be seen that the variation degrees for H<sub>2</sub> concentration and  $\eta_{\rm C}$  are always positive or negative for all CO/H<sub>2</sub> ratios; however, it is not the case for CO concentration, due to the reasons stated above in Section 3.3.1 for Fig. 5. The temperature also shows some impacts on the variation degrees. Normally, a higher temperature leads to a higher variation degree of CO and H<sub>2</sub> concentrations, but with little influence on  $\eta_{\rm C}$ . It is important to note that in Figs. 5–10 although the concentrations of CO and  $H_2$  are changed to some extent, there are little changes in the values of  $\eta_{\rm C}$  and  $X_{\rm s}$  while WGS is included or not. Consequently, the WGS reaction can impose some variations on the composition of gas products but has negligible effects on combustion efficiency and oxygen carrier conversion for syngas-CLC in this work.

#### 3.5. Optimized condition for fuel reactor

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 important parameters for full combustion is the solids inventory  $m_{\rm FR}$ . For a fixed



**Fig. 11.** Operation regions for 99.9% combustion of one MW<sub>th</sub> syngas with CO/ H<sub>2</sub> = 3 at T = 973-1173 K: distributions of minimum oxygen carrier inventory  $m_{\rm FR}$ , oxygen carrier-to-fuel ratio  $\phi$  and oxygen carrier conversion  $X_{\rm s}$  at different solids circulation rates per MW<sub>th</sub> fuel.

thermal power, an increase of  $m_{\rm FR}$  results in a higher dense bed height, thus more reaction time and higher combustion efficiency, which is illustrated in Figs. 8 and 9 and demonstrated by the tests of Abad et al. [62] and Mei et al. [63]. To facilitate the evaluation, the value of  $m_{\rm FR}$ for 99.9% combustion of syngas is considered as a reference in the present work. For one MW<sub>th</sub> thermal power of fuel, Fig. 11 maps the operation regions for 99.9% combustion of syngas with  $CO/H_2 = 3$ using Cu14Al-I as oxygen carrier, where the oxygen carrier inventory  $m_{\rm FR}$ , oxygen carrier-to-fuel ratio  $\phi$  and oxygen carrier conversion  $X_{\rm s}$  at various temperatures are shown as a function of solids circulation per  $MW_{th}$  fuel. As seen, oxygen carrier-to-fuel ratio  $\phi$  and oxygen carrier conversion  $X_s$  are always the same for different reaction temperatures, because they are preset as those values. Despite this,  $\phi$  and  $X_s$  are directly related to solids circulation per  $MW_{th}$  fuel, thus higher values of  $\phi$ and lower values of  $X_s$  are observed for faster circulations of oxygen carrier. Moreover, a higher average reactivity of oxygen carrier is reached at a lower  $X_s$ , thereby lower values of oxygen carrier inventory  $m_{\rm FR}$  for 99.9% combustion are found at higher solids circulations for all temperatures. Within the range of T = 973-1173 K, the oxygen carrier inventory  $m_{\rm FR}$  varies from 1250 to 50 kg·MW<sub>th</sub><sup>-1</sup> as the increase of solids circulation from 3.4 to 6.6 kg s<sup>-1</sup> MW<sub>th</sub><sup>-1</sup>. It can also be observed that lower values of  $m_{\rm FR}$  would be achieved at higher temperatures. Particularly, at T = 1173 K the  $m_{\rm FR}$  can reach as low as  $50 \text{ kg MW}_{\text{th}}^{-1}$  for solids circulations higher than  $5 \text{ kg s}^{-1} \text{ MW}_{\text{th}}^{-1}$ , which is then hardly affected by even higher solids circulations. At the other temperatures, the similar behavior can also be expected. Although the lowest and stable  $m_{\rm FR}$  for T = 973 and 1023 K are not shown in Fig. 11, the similar  $m_{\rm FR} = 50$  kg MW<sub>th</sub><sup>-1</sup> to that for T = 1073, 1123 and 1173 K can be estimated in these cases, if solids circulation higher than  $6.6 \text{ kg s}^{-1} \text{ MW}_{\text{th}}^{-1}$  were used. In this sense, higher temperatures and faster solids circulations can both be considered as effective measures for the reduction of oxygen carrier inventory. For the use of syngas with CO/H<sub>2</sub> < 3, an even lower  $m_{\rm FR}$  would be expected, due to their higher reactivity than that for  $CO/H_2 = 3$ .



**Fig. 10.** Variation degrees of gas concentrations (H<sub>2</sub> and CO) and combustion efficiency at fuel reactor outlet for different temperatures of 973–1173 K with  $\dot{m}_s = 6 \text{ kg h}^{-1}$ ,  $\phi = 1.5$ , as a function of CO/H<sub>2</sub> ratio; positive data means the values of parameters increase when WGS reaction is excluded from the model in comparison to that while WGS is included.

Information in Fig. 11 can be applied to the optimization of the syngas-CLC systems. As an example, for operating the 500 W<sub>th</sub> CLC system, the optimized solids circulation per MW<sub>th</sub> fuel at each temperature can be readable in Fig. 11. For instance, if the temperature is T = 1123 K, a solids circulation higher than 5.5 kg s<sup>-1</sup> MW<sub>th</sub><sup>-1</sup> associated with an oxygen carrier-to-fuel ratio  $\phi > 2.6$  and an oxygen carrier conversion  $X_s < 0.5$ , should be used to assure the best combustion of syngas.

# 4. Conclusions

A macroscopic model for bubbling fluidized bed is successfully extended to the simulation of a syngas-CLC fuel reactor with a thermal power of 500 Wth. Good agreements between modeling results and experiments under various conditions confirm the reliability of the reactor model. Different behaviors are observed in dense bed and freeboard. The rate of syngas combustion in dense bed is lower than that in the freeboard, due to the limited rate of gas transfer from bubbles. Simulations are carried out under various operation conditions by changing fuel composition, temperature, oxygen carrier circulation rate and solids inventory. It is found that the model has a high flexibility for using in the fuel reactor simulation under different environments of syngas-CLC. After thorough simulation, operation regions for 99.9% syngas combustion are developed. Accordingly, for one  $\mathrm{MW}_{\mathrm{th}}$  fuel in syngas-CLC, solids circulations higher than  $6\,kg\,s^{-1}\,MW_{th}{}^{-1}$  are enough for optimal combustion at T > 1073 K. In this case, the oxygen carrier inventory can be as low as  $m_{\rm FR} = 50 \text{ kg MW}_{\rm th}^{-1}$ .

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