Industry-scale production of a perovskite oxide as oxygen carrier material in chemical looping

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Abstract

How to upscale the production of oxygen carrier particles from laboratory level to industrial level is still challenging in the field of chemical looping. The upscaled oxygen carrier must maintain its physical and chemical properties. In the present contribution, a spray drying granulation protocol was developed to produce a perovskite oxygen carrier ($CaMn_{0.5}Ti_{0.375}Fe_{0.125}O_{3-\delta}$) at an industrial scale. The micro-fluidized bed thermogravimetric (MFB-TGA) experiments were performed to measure the oxygen uncoupling and redox reaction kinetics under the fluidization state with enhanced heat and mass transfer, and the obtained experimental data at different temperatures were fitted by a fluidized-bed reactor coupled with a semi-empirical kinetic model. The physical and chemical properties of granulates were compared with those of the same perovskite composition

prepared at the laboratory level. The results show the volume fraction of particle size at 75-500 μm is >90% for the upscaled granulats, and the particles show no degradation in reactivity and no agglomeration for more than 20 redox cycles at high temperatures. The heterogeneous reaction rates are high enough, especially for the oxidization, e.g. it only spent ~5 s to achieve full oxidization. Low attrition index of 3.74 wt% was found after the five-hour attrition test. The industrial-scale particles possess similar chemical and physical properties as the laboratory-scale particles with regards to the reaction kinetics, attrition index, crystalline phase, etc. The required bed inventories and fan energy consumption were finally estimated and found to be lower than other oxygen carriers reported in the literature.

Key words: Large scale production; Chemical looping; Oxygen carrier material (OCM); Perovskite; Spray granulation; Kinetics; MFB-TGA

Abbreviations

CLC	Chemical looping combustion
CLOU	Chemical Looping with Oxygen Uncoupling
CMTF_Ind	$CaMn_{0.5}Ti_{0.375}Fe_{0.125}O_{3-\delta}$ prepared at an industrial level
CMTF_Lab	$CaMn_{0.5}Ti_{0.375}Fe_{0.125}O_{3-\delta}$ prepared at a laboratory level
MFB-TGA	Micro-fluidized bed thermogravimetric analysis
OCM	Oxygen carrier material

1. Introduction

Chemical Looping Combustion (CLC) is considered as a cost-effective technology with inherent CO_2 capture during the fossil fuel conversion for heat and power generation [1]. A general CLC system contains an air reactor and a fuel reactor. In the fuel reactor, solid fuels, coal, biomass,

petroleum coke, etc., firstly experience an endothermic devolatilization step at a high temperature, followed by an endothermic gasification step of char to produce syngas, CO and H_2 , and the reducing pyrolysis gas and syngas are finally converted to CO_2 and H_2O by the solid oxygen carrier material (OCM) in the form of endothermic or exothermic gas-solid reactions. In the air reactor, the reduced OCM is oxidized and regenerated by air, generating a large amount of heat. The OCM mainly takes charge of heat and oxygen transports between the air reactor and the fuel reactor. During the solid fuel-fired CLC process, the char gasification is the rate-controlling step [1,2], which easily causes some unconverted char particles to flow into the air reactor with the OCM streams, and the carbon capture efficiency will decrease due to the char escape. To enhance the char conversion in the fuel reactor, one strategy is to employ an OCM with a capacity of releasing gaseous O_2 in a relatively low oxygen partial pressure (e.g. inert atmosphere) to combust the char in the fuel reactor, as referred to as the Chemical Looping with Oxygen Uncoupling (CLOU) put forward by Mattisson et al. [3,4]. Operation with the OCMs possessing CLOU property has shown higher fuel conversion or gas combustion efficiency in different-scale CLC pilots, such as 1.5 kWth [5], 10 kWth [6,7], 100 kWth [8,9], 120 kWth [10,11] and 1 MWth [12] at various spots.

Cu-based [13,14], Mn-based [15,16] and Co-based [17] metal oxides, are provided with suitable thermodynamics for oxygen uncoupling in a low oxygen partial pressure atmosphere, and are therefore proposed as the OCMs for CLOU applications. However, physical and chemical stability could be a serious issue for the above-mentioned OCMs due to phase change, agglomeration, inactivation and attrition during the redox cycles. An OCM must possess high reactivity and suitable thermodynamics, high resistance towards attrition, stable chemical and physical performances in multiple redox cycles. Perovskite oxides (formula as ABO_3), such as

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$CaMnO_{3-\delta}$, have shown acceptable thermodynamics for oxygen uncoupling and high reactivity for reducing gases conversion [18,19], high stability under a wide range of oxygen partial pressures and fast oxygen ionic diffusion in the bulk phase [20]. The performances of fast oxygen diffusion and exchange without phase change make some perovskite-based OCMs promising for CLOU using solid fuels. In addition, doping different metal elements on B sites could further increase reactivity and the structural stability, such as $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ [19] and $CaMn_{0.875}Ti_{0.125}O_3$ [21] designed as OCMs for both CLOU and CLC applications. In the previous contribution, the perovskite, $CaMn_{0.5}Ti_{0.375}Fe_{0.125}O_{3-\delta}$ (CMTF), was developed for enhancing the stability via Ti addition and reactivity via Fe addition [22]. This perovskite possesses much faster oxygen uncoupling and redox kinetics than Cu- [13] and Mn-based oxygen carriers [23], and other reported perovskite oxygen carriers [19,24]. Currently, most investigations of synthetic OCMs are prepared in lab scales, with few reported large-scale fabrication [Ref, Larring]. However, the upscaling is still a big challenge to be solved when it comes to the CLC demonstration and industrial applications.

In the present work, the main objective was to address the perovskite oxygen carrier particle preparation issue at a tonne level to reach the industry-scale production of $CaMn_{0.5}Ti_{0.375}Fe_{0.125}O_{3-\delta}$ (CMTF_Ind). Since accurate heterogeneous oxygen uncoupling and redox kinetics is crucial to determining the solid residence time and bed inventories in CLC reactor design and process optimization, we therefore measured the reaction kinetics by means of the microfluidized bed thermogravimetric analysis (MFB-TGA) based on the on-line track of mass change [23,25]. We finally evaluate the properties and performance of CMTF_Ind ($CaMn_{0.5}Ti_{0.375}Fe_{0.125}O_{3-\delta}$ prepared at industrial level) and compare them with those of CMTF_Lab ($CaMn_{0.5}Ti_{0.375}Fe_{0.125}O_{3-\delta}$ prepared at laboratory level).

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2.Larring, Y., Pishahang, M., Tolchard, J., Lind, A.M., Sunding, M.F., Stensrød, R.E., Jacobs, M., Snijkers, F., van der Kolk, T., Albertsen, K. "Fabrication process parameters significantly affect the perovskite oxygen carriers materials (OCM) performance in chemical looping with oxygen uncoupling (CLOU)" J Therm Anal Calorim. 140 **(2020)** 577–589 10.1007/s10973-018-7903-6

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2. Experimental

2.1. Oxygen carrier preparation

To produce the CMTF_Ind particles, commercial $Ca(OH)_2$ (Guanghui, China), Mn_3O_4 (Zhonggang, China), TiO_2 (Yuxing, China) and Fe_2O_3 (Changli, China) powders were selected as the raw materials, and the compositions and purities of these raw materials measured by X-ray Fluorescence (XRF) are listed in Table 1; their size distributions are illustrated in Fig. 1. The average diameters (d_{50}) are 3.18 μm for $Ca(OH)_2$, 2.83 μm for Mn_3O_4, 0.99 μm for TiO_2, and 4.44 μm for Fe_2O_3. The maximum diameter for all raw materials is within 20 μm, fine enough for the synthesis in the next stage.

Table 1. Compositions of the raw materials used for the CMTF_Ind particles production

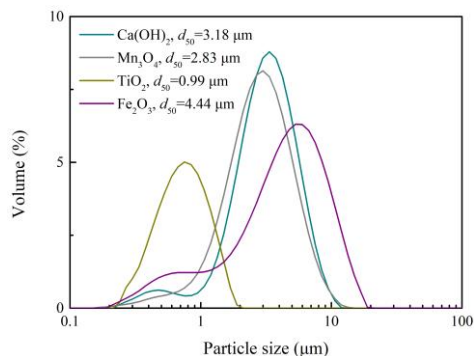| Source	Compositions (wt%)								
Mn_3O_4	Mn	Zn	Fe	Si	Gd	Mg	Cl	Lu	O*
	75.79	0.17	0.13	0.08	0.06	0.05	0.03	0.02	23.67
Fe_2O_3	Fe	Zn	Dy	Cl	Na	Mn	Se	Tm	O*
	67.81	0.97	0.26	0.22	0.14	0.13	0.12	0.14	30.21
TiO_2	Ti	Al	Na	Si	V	Zn	P	Zr	O*
	54.25	1.48	1.34	0.81	0.19	0.22	0.07	0.06	41.58
$Ca(OH)_2$	Ca	Mg	Sn	Pb	O*				
	51.17	1.90	0.01	0.01	46.91				

* Oxygen calculation by difference

Fig.1. Size distribution of the raw materials used for the CMTF_Ind particles production

Fines of $Ca(OH)_2$, Mn_3O_4, TiO_2 and Fe_2O_3 were filled in a propeller blade mixer, according to the corresponding stoichiometric ratio of the metal elements in $CaMn_{0.5}Ti_{0.375}Fe_{0.125}O_{3-\delta}$. Plenty of water was added into the mixer, to maintain a solid-water ratio of 2:1. After continuous stirring for two hours, binder was added to increase the suspension viscosity, followed by one-hour stirring. To eliminate the bubbles generated during the stirring process, a small fraction of the defoamer was employed. A small amount of dispersant and lubricant was then used to improve the rheology and liquidity of the suspension. The total mass fraction of the binder, defoamer, dispersant and lubricant is 1.20 wt%. The technical support of the binder, defoamer, dispersant and lubricant is from Dingsheng Spray Co., Ltd, China. Finally, the suspension was obtained for the next-step particle production.

CMTF_Ind particles were fabricated by utilizing a pressure-spray drying granulation device. The maximum water evaporation of the device is ~2800 kg/h. Prior to granulating, the spray device was heated to 180 °C, and the gauge pressure inner the spray device was operated at ~ -80 Pa via an induced draft fan. The granulation process is demonstrated in Fig. 2. The prepared suspension, from the mixer, was pressed to 3.5 MPa and was pumped to single-fluid high-pressure nozzles located at the top of the spray device. The suspension was sprayed downward and was atomized into droplets

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through the single-fluid high-pressure nozzles, following the droplets moved down due to the gravity and hot air. In the process of droplets falling, the water was quickly evaporated, which causing spherical particles formation due to surface tension. Finally, the dry particles were continuously collected at the bottom of the spray drying device. The particles were continuously manufactured at a production scale of ~2500 kg/h, and ~1000 kg particles were synthesized within half an hour at present.
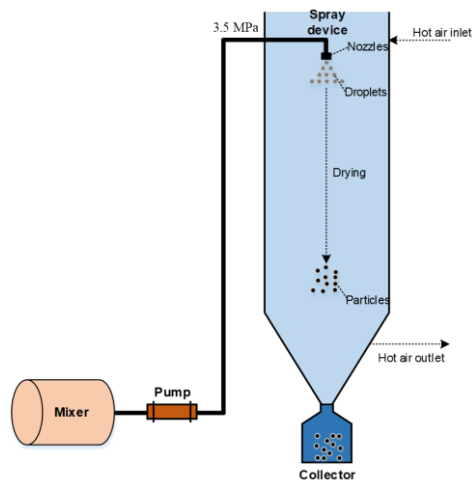

Fig. 2. Process flow diagram for the spray drying granulation

The parameters, nozzle pressure, nozzle size, suspension rheology, drying temperature, etc., were adjusted, to obtain a reasonable particle size range. It can be seen from Fig. 3 that the volume fraction of the particle size at 75-500 μm is ~ 90%, and the average diameter (d_{50}) of the prepared CMTF_Ind particles is 195 μm.
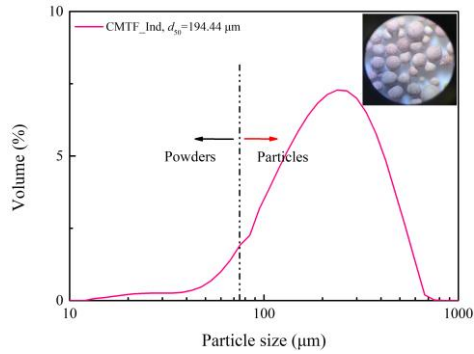
Fig. 3. Size distribution of the CMTF_Ind particles

Finally, calcination was performed in air at 1350 °C for 8 hours, to obtain CMTF_Ind particles with the desired crystalline phases and with sufficient mechanical strength. The total cost for the CMTF_Ind particle production is ~2000 US$/ton-OCM, containing the raw materials, spray drying granulation, and calcination. The detailed cost estimation can be found in the supporting information.

After calcination, CMTF_Ind was characterized X-ray Fluorescence (XRF), and its compositions were compared with CMTF_Lab, see Table 2. It can be seen that the oxide constitutions of CMTF_Ind are very close to that of CMTF_Lab,. For example,the mass factions of MnO are 29.06 wt% for CMTF_Lab and 30.29 wt% for CMTF_Ind.

Table 2. Comparison of compositions between CMTF_Lab and CMTF_Ind

Composition (wt%)	CaO	MnO	TiO_2	Fe_2O_3
CMTF_Lab	40.82	29.06	19.16	8.27
CMTF_Ind	39.04	30.29	19.54	8.07

2.2. Micro-fluidized bed thermogravimetric analysis (MFB-TGA)

The isothermal kinetic experiments of the manufactured CMTF_Ind particles, including oxygen uncoupling, oxidization and reduction reactions, were performed by using a micro-fluidized

bed thermogravimetric analysis technology (MFB-TGA) [23,25,26]. As shown in Fig. 4(a), the MFB-TGA mainly contains a furnace, a fluidized-bed reactor with an inner diameter of 30 mm, a gas supply system, and a measuring system, of which the fluidized-bed reactor is the core of the MFB-TGA,. The reactor is made of quartz, and a porous quartz plate is used as the gas distributor. The bed temperature above the gas distributor was recorded by a K-type thermocouple, and the pressure drop of the fluidized-bed reactor was measured by a differential pressure sensor.
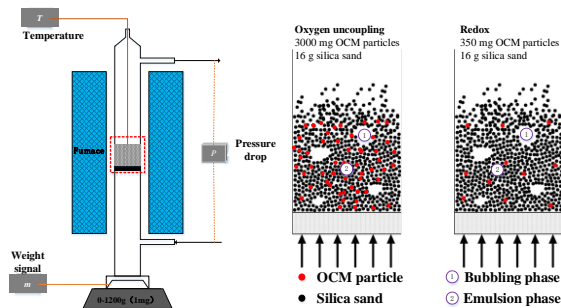

Fig. 1. Schematic diagrams of (a) the MFB-TGA apparatus and (b) the solid particles in the

bubbling bed reactor

The flow rates of fluidizing agents were controlled by well-calibrated mass flowmeters. The gas flowed into the bottom of the micro-fluidized bed reactor through switching well-connected magnetic valves. A mass transducer with a measurement accuracy of 1 mg was applied to measure the whole weight including the reactor and bed materials. The measurement error of the MFB-TGA is within ±1 mg, which guarantees that the mass change is mainly caused by the gas-solid reaction between samples and gas phases [22]. More details about this technique can be found elsewhere [23,25,26].

For the oxygen uncoupling kinetic tests, ~ 16 g silica sand (300-350 μm) was filled in the reactor as the bed material; the reactor with a 21 vol% O_2 fluidizing gas of 1.2 L/min (STP) was

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heated to 800-930 °C; ~ 3000 mg fully oxidized CMTF_Ind particles (180-250 μm) were added into the reactor; once mass and temperature signals were stable, to eliminate the initial effect produced by calcination stage 6 redox cycles were performed by switching the fluidizing agents between 10 vol% H_2 and 21 vol% O_2, before least 3 isothermal O_2 release and uptake cycles were carried out to measure the oxygen uncoupling kinetics by switching the fluidizing gases between 100 vol% N_2 and 21 vol% O_2. For the oxidization and reduction kinetic tests, ~ 16 g silica sand (300-350 μm) was filled as the bed material, before ~ 350 mg CMTF_Ind particles (180-250 μm) was added, the reactor was heated to 750-900 °C, and a 21 vol% O_2 was introduced to act as the fluidizing gas; isothermal redox cycles were performed by switching the fluidizing gases between 21 vol% O_2 and 10 vol% H_2, or 21 vol% O_2 and 10 vol% CH_4; to prevent direct mixing of the reducing and oxidizing gases, 100 vol% N_2 was introduced for 30 s between the reduction stage and oxidization stage. The gas flowrates of the fluidizing agents were controlled at 1.2-1.5 L/min (STP), corresponding to a superficial velocity of 3-5 U_{mf}. The reactor was hence operated at the bubbling state. The gas switch was realized through the well-connected magnetic valves. Therefore, the mass change is only arisen from the gas-solid reactions between solid CMTF_Ind particles and gas phases. The active lattice oxygen in CMTF_Ind would be lost during the oxygen release and reduction, causing the particle mass to decrease, while the reduced CMTF_Ind obtained the lattice oxygen again during the oxidization, causing the particle mass to increase. The principle of the MFB-TGA is to monitor the mass change in real-time, to obtain the reaction kinetics close to the real fluidization condition with enhanced heat and mass transfer.

2.3. Particle characterization and Data evaluation

X-ray Diffraction (XRD, Rigaku D/max-2550@3-70°) analysis was conducted to determine

the crystal phases of the fresh CMTF_Lab, fresh CMTF_Ind, and tested CMTF_Ind. The mercury intrusion method (AutoPore IV 9500, Micromeritics) was applied to measure the porosity, and the nitrogen adsorption experiments (Micromeritics ASAP 2460) were performed at 77 K to obtain the BET surface area and BJH pore diameter. The morphology of the CMTF_Ind particle and cross-section was characterized by a scanning electron microscope (Zeiss Merlin, 0.8nm@15kV).

The online mass signals, $m(t)$, are collected by the mass transducer during the oxygen uncoupling and redox experiments. The conversion level of the oxygen uncoupling reactions can be described as Eq. (1), and the conversion levels for the reduction (X_r) and oxidization (X_o) reactions were described as Eqs. (2) and (3). The numerator in Eqs. (1)-(3) refers to the mass change caused by the heterogeneous gas-solid reactions.

$$X_{ou}(t) = \frac{m_o - m(t)}{R_{oc,ou} m_{oc}} \tag{1}$$

$$X_r(t) = \frac{m_o - m(t)}{R_{o,t} m_{oc}} \tag{2}$$

$$X_o(t) = \frac{m(t) - m_r}{R_{o,t} m_{oc}} \tag{3}$$

where m_o is the total mass of the reactor and bed materials (silica sand and fully oxidized CMTF_Ind particles), m_r is the total mass of the reactor and bed materials (silica sand and fully reduced CMTF_Ind particles), m_{oc} is the mass of CMTF_Ind particles added into the reactor. The oxygen transfer capacity for oxygen uncoupling ($R_{oc,ou}$) is 0.88 wt% for 850 °C, 0.82 wt% for 900 °C, and 0.70 wt% for 930 °C, according to the theoretical calculation [22], while the total oxygen transfer capacity ($R_{oc,t}$) was determined by the experiments.

3. Models

3.1. Model for oxygen uncoupling reaction

The CMTF_Ind particles release gaseous O_2 in the bubbling-bed reactor at the pure N_2 condition during the oxygen uncoupling reaction. It is well known that the bed zone in the reaction can be divided into two phases, of which the bubble phase stores the majority of fluidizing gases, and the emulsion phase contains almost all particles. Therefore, the CMTF_Ind particles mainly release gaseous O_2 in the emulsion phase, and the driving force is (C_{eq,O_2}-C_{e,O_2}). The released O_2 will firstly diffuse to the emulsion phase through the external mass transfer around the particle, then to the bubble phase due to the concentration gradient. An O_2 concentration profile along the axial direction will be produced in the emulsion phase and the bubble phase. The released O_2 finally leaves the reactor. A reactor model should be used to describe the O_2 transfer process in the reactor.

The simplified two-phase model, derived from the classic Kunii and Levenspiel model (K-L model) [27], could relate the reaction and the gas diffusion between the bubble phase and the emulsion phase [22,23], see Eq. (4). The simplified K-L model is based on the mass balance with the assumptions that there are no solids in the bubble phase. The first equation in Eq. (4) describes the O_2 concentration profile in the emulsion phase, affected by the oxygen uncoupling reaction and interphase gas exchange. The second equation in Eq. (4) describes the O_2 concentration profile in the bubble phase, only affected by the O_2 transfer from the emulsion phase.

$$\begin{cases} -(1-\theta)U_{mf}\dfrac{dC_{e,O_2}}{dz} = -f_a(1-\theta)(1-\varepsilon_{mf})K_r\left(C_{eq,O_2}-C_{e,O_2}\right)+\theta K_{be}(C_{e,O_2}-C_{b,O_2}) \\ -U_b^*\dfrac{dC_{b,O_2}}{dz} = -K_{be}(C_{e,O_2}-C_{b,O_2}) \end{cases} \tag{4}$$

where C_{b,O_2} (mol/m^3) and C_{e,O_2} (mol/m^3) stand for the O_2 concentrations in the bubble phase and

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the emulsion phase respectively, C_{eq,O_2} (mol/m³) refers to the equilibrium O_2 concentration. U_b^* (m/s) and U_{mf} (m/s), are the effective gas velocity in the bubble phase and the minimum fluidization gas velocity. The parameters, f_a and θ, are the volume fraction of the CMTF_Ind particles in all solid volume and the bubble fraction. All the coefficients can be calculated, see the supporting information. The only undefined parameter is the reaction rate constant (K_r, s⁻¹), which can be expressed as

$$\begin{cases} K_r = \dfrac{1}{\dfrac{1}{K_{ri}} + \dfrac{d_p}{6k_g}} \\ K_{ri} = \dfrac{R_{OC,ou}\rho_s}{2M_O}\left\{ k_{chem}(\psi X_e - X_{chem})^{2/3} + k_{diff}[(1-\psi)X_e - X_{diff}]^{2/3} \right\} \\ k_g = \left(Sh \cdot D_{O_2} \right)/d_p \end{cases} \quad (5)$$

where k_g (m/s) refers to the external mass transfer coefficient, and Sh is the Sherwood number. K_{ri} (s⁻¹) refers to the comprehensive reaction rate constant of the particle, which can be obtained with the given rate constants (k_{chem} and k_{diff}) and the ratio of the conversion level at the first reaction stage to the total conversion level (ψ). The value of K_r is then calculated from Eq. (5). A semi-empirical model [22] with two equations was employed to describe the conversion vs. time, see Eq. (6). The kinetic model includes two independent equations, where the former and the latter are used to fit the experimental data in the first reaction stage and the second reaction stage respectively. The total conversion (X) is the sum of the first stage conversion (X_{chem}) and the second stage (X_{diff}).

$$\begin{cases} \dfrac{dX_{chem}}{dt} = k_{chem}(\psi X_e - X_{chem})^{2/3}\left(C_{eq,O_2} - C_{e,O_2} \right) \\ \dfrac{dX_{diff}}{dt} = k_{diff}[(1-\psi)X_e - X_{diff}]^{2/3}\left(C_{eq,O_2} - C_{e,O_2} \right) \\ X = X_{chem} + X_{diff} \end{cases} \quad (6)$$

The rate constants (k_{chem} and k_{diff}) and the ratio (ψ) can be written as Arrhenius expressions,

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$$k_{\text{chem}} = A_{0,\text{chem}} \exp\left(-\frac{E_{\text{chem}}}{RT}\right) \tag{7}$$

$$k_{\text{diff}} = A_{0,\text{diff}} \exp\left(-\frac{E_{\text{diff}}}{RT}\right) \tag{8}$$

$$\psi = A_{0,\text{L}} \exp\left(-\frac{E_{\text{L}}}{RT}\right) \tag{9}$$

3.2. Model for oxidation and reduction reactions

Different from the oxygen uncoupling, the mass transfer direction is opposite for the oxidization and reduction reactions. The reaction gases initially exist in the bubble phase, then diffuse to the emulsion phase through the interphase gas exchange, further transfer to the oxygen carrier particle surface through the external mass transfer. The chemical reactions finally occur. To analyze the experimental data from the MFB-TGA, the simplified K-L model was also used to describe the chemical reaction and the mass transfer between the phases:

$$\begin{cases} -U_b^* \dfrac{dC_{b,i}}{dz} = K_{\text{be}}(C_{b,i} - C_{e,i}), (i = \text{O}_2, \text{H}_2, \text{CH}_4) \\ -(1-\theta)U_{\text{mf}} \dfrac{dC_{e,i}}{dz} = -\theta K_{\text{be}}(C_{b,i} - C_{e,i}) + f_a(1-\theta)(1-\varepsilon_{\text{mf}})K_r\left(C_{e,i} - C_{\text{eq},i}\right), (i = \text{O}_2, \text{H}_2, \text{CH}_4) \end{cases} \tag{10}$$

How to calculate the parameters in Eq. (10) has been introduced in Section 3.1. K_r (s^{-1}) couples the reaction term and the external mass transfer term, as

$$\begin{cases} K_r = \dfrac{1}{\dfrac{1}{K_{\text{ri}}} + \dfrac{d_p}{6k_g}} \\ K_{\text{ri}} = \dfrac{R_{\text{o,t}}\rho_s}{\alpha M_{\text{O}}}\left\{k_{\text{chem}}(\psi X_e - X_{\text{chem}})^{2/3} + k_{\text{diff}}[(1-\psi)X_e - X_{\text{diff}}]^{2/3}\right\} \\ k_g = (Sh \cdot D_i)/d_p, \ (i = \text{O}_2, \text{H}_2, \text{CH}_4) \end{cases} \tag{11}$$

The above semi-empirical model including the two stages was also used to fit the conversion curves of the oxidation and reduction reactions, see Eq. (12). The rate constants (k_{chem} and k_{diff}) and the ratio (ψ) can be written as Arrhenius expressions.

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$$\begin{cases} \dfrac{\mathrm{d}X_{\mathrm{chem}}}{\mathrm{d}t} = k_{\mathrm{chem}}(\psi X_{\mathrm{e}} - X_{\mathrm{chem}})^{2/3}\left(C_{\mathrm{e},i} - C_{\mathrm{eq},i}\right), \quad (i = \mathrm{O_2, H_2, CH_4}) \\ \dfrac{\mathrm{d}X_{\mathrm{diff}}}{\mathrm{d}t} = k_{\mathrm{diff}}[(1-\psi)X_{\mathrm{e}} - X_{\mathrm{diff}}]^{2/3}\left(C_{\mathrm{e},i} - C_{\mathrm{eq},i}\right), \quad (i = \mathrm{O_2, H_2, CH_4}) \\ X = X_{\mathrm{chem}} + X_{\mathrm{diff}} \end{cases} \qquad (12)$$

4. Results and discussions

4.1. Multiple redox cycles and typical test

The redox multicycles at 900 °C of the prepared CMTF_Ind are shown in Fig. 2. The reduction and oxidization reactions were performed in 10 vol% H_2 and 21 vol% O_2. The first cycle was carried out with the longest reduction time (300 s) and oxidization time (120 s), to measure the total oxygen transfer capacity ($R_{\mathrm{OC,t}}$) of CMTF_Ind. It can be seen that the mass continuously decreased during the reduction, since the active oxygen in CMTF_Ind was taken away in the form of H_2O. The final mass loss is 5.71 wt%, and the lost mass was fully gained during the following oxidization, implying that the total oxygen transfer capacity ($R_{\mathrm{OC,t}}$) is 5.71 wt%. For the 2nd – 4th cycles, the reduction time was stayed at 300 s, whereas the oxidization time was halved (60 s). The mass change is still 5.71 wt% during the redox cycles, and the reduced CMTF_Ind can be fully regenerated after oxidization. Furthermore, the oxidization time was unchanged, while the reduction time was decreased to 180 s. The mass change was stabilized at 5.71 wt% as well. The redox period was finally shortened to 90 s for reduction and 30 s for oxidization, to compete the whole multiple cycles test. It can be observed that neither the oxygen transfer capacity nor the chemical performance has been influenced. The shortest redox period indicates CMTF_Ind possesses fast lattice oxygen exchange ability with the reacting gases. The measured oxygen transfer capacity (5.71 wt%) is exactly equal to that of CMTF_lab [22]. A combination of the pressure drop curves (Fig. 2) and the real-time fluidization video (supporting video) demonstrates that agglomeration did not occur during the redox, showing

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that the synthesized CMTF_Ind particles possess acceptable fluidization property.
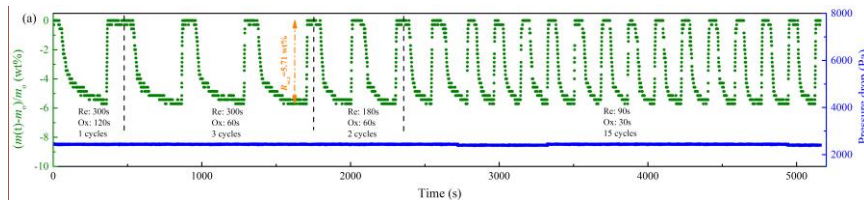

Fig. 2. Mass variation during the multiple redox cycles in the MFB-TGA at 900 °C (oxidization by

21 vol% O_2 and reduction by10 vol% H_2)

A typical redox cycle is shown in Fig. 3. The weight of OCM was decreasing after altering the

fluidizing gas to 10 vol% H_2. Once full oxygen capacity of CMTF_Ind was consumed, the OCM

was fully reduced, and the weight of OCM was unchanged. The weight loss is 20 mg, corresponding

to a total oxygen transfer capacity of 5.71 wt%. The oxidization step fully regenerated the lattice
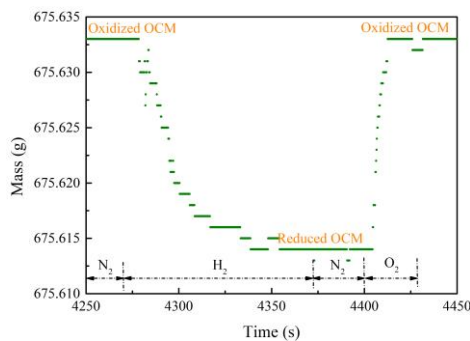
oxygen.

Fig. 3. A typical redox cycle in the MFB-TGA at 900 °C (oxidization by 21 vol% O_2 and reduction

by10 vol% H_2)

4.2. Comparison of heterogeneous reaction kinetics

The measured heterogeneous reaction rates of CMTF_Ind were compared with CMTF_lab at

900 °C, see Fig. 4. The whole process of the oxygen uncoupling reaction of CMTF_Ind includes

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two stages: one is the first fast O_2 release stage, and the other is the second slow O_2 release stage. It will take ~20 s to reach the critical conversion level of 0.35, as seen in Fig. 4(a). There are similar oxygen uncoupling rates between CMTF_Ind and CMTF_Lab. The oxidization will be fully completed within ~5 s, whether it is CMTF_Ind or CMTF_Lab (Fig. 4(b)), indicating an ultrafast oxidization rate. When CMTF_Ind is reduced by 10 vol% H_2, the reaction consists of a fast reduction stage and a slow reduction stage, and the reduction rate decreases with the conversion at the slow stage, as shown in Fig. 4(c). The full reduction will be finished within ~30 s. The reduction rate of CMTF_Ind is very close to that of CMTF_Lab. The reaction rate with CH_4 is apparently ~8 times slower than that with H_2, see Fig. 4(d). The reduction can also be divided into an initial fast stage followed by a slow stage, and the required time for reaching the critical conversion is ~100 s. From the above comparisons, the heterogeneous reaction rates of CMTF_Ind are similar to those of CMTF_Lab, implying the upscaling granulation is successful from the view of chemical performance.
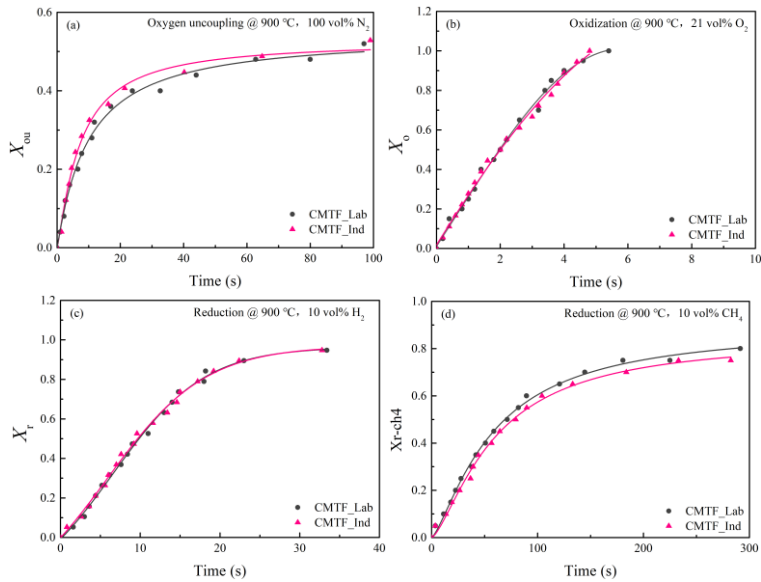
Fig. 4. Comparison of the heterogeneous reaction kinetics between CMTF_Ind and

CMTF_Lab. (a) oxygen uncoupling reaction; (b) oxidization reaction; (c) reduction reaction with

H_2; (c) reduction reaction with CH_4

4.3. Kinetics determination for heterogeneous reaction

Reaction kinetic parameters are significantly important to determine the solid bed inventory and solid residence time in the air reactor and the fuel reactor. In this work, the oxygen uncoupling and redox kinetics were measured by using the MFB-TGA technology.

4.3.1. Oxygen uncoupling reactions

The oxygen uncoupling kinetics was measured in the temperature range of 850-930 ºC, see Fig. 5. The oxygen uncoupling rate increases with the rising temperature. For any temperature, the kinetic curve contains an initial fast O_2 release stage followed by a slower stage. The critical conversion decreases from 0.4 to 0.3 when the reaction temperature decreases from 930 ºC to 850 ºC.
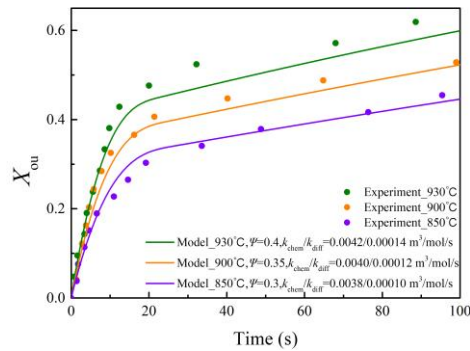

Fig. 5. Experimental and model results of oxygen uncoupling reaction at 850-930 ºC

Now that the oxygen uncoupling rates are similar between CMTF_Ind and CMTF_Lab, we used the same kinetic parameters (pre-exponential factors and activation energies) as CMTF_Lab, see Table 3 [22]. The rate constants (k_{chem} and k_{diff}) and the ratio (Ψ) at different temperatures can

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be further calculated according to Eqs. (7)-(9). Introduced the calculated rate constants (k_{chem} and k_{diff}) and the ratio (Ψ) into the reactor model coupled with the kinetic model, the kinetic curves predicted by the model can be obtained, and the model results are illustrated in Fig. 5. It can be seen that the model could fit the experimental data well.

Table 3. Kinetic parameters for the oxygen uncoupling reaction [22]

Parameter	E_L	E_{chem}	E_{diff}	$A_{0,L}$	$A_{0,chem}$	$A_{0,diff}$
Unit	kJ/mol	kJ/mol	kJ/mol	n.a.	m^3/mol/s	m^3/mol/s
Value	37.86	12.36	45.12	17.33	1.43×10^{-2}	1.25×10^{-2}

4.3.2. Oxidization and reduction reactions

The oxidization kinetics in the temperature range of 750-900 ºC were measured, see Fig. 6. Like CMTF_Lab [22], the oxidization rate is ultrafast and the required time to achieve complete oxidization is ~5 s. The oxidation only consists of a fast reaction stage. The oxidization is insensitive to the reaction temperatures, like CMTF_Lab [22] and some other oxygen carriers [19,24].

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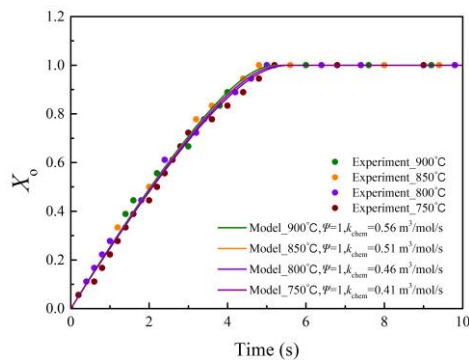

Fig. 6. Experimental and model results of oxidization reaction at 750-900 ºC

The measured reduction reaction kinetics with 10 vol% H_2 and 10 vol% CH_4 are shown in Fig.

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7. The conversion vs time curves of reduction by H_2 and CH_4 are composed of an initial fast reduction stage and a second slow reduction stage. The reduction rates with H_2 and CH_4 could be enhanced with the increaseing temperature. The difference is the reduction rates with H_2 are significantly faster than the reduction rates with CH_4, and the temperature effect is stronger for the reduction by CH_4. The needed time for full reduction with H_2 is ~30 s at 900 $^{\circ}$C, and the reduction with CH_4 is ~8 times longer than that with H_2 at 900 $^{\circ}$C.
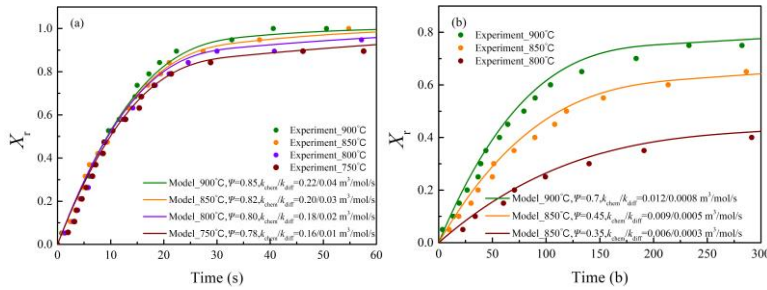

Fig. 7. Experimental and model results of reduction reactions with (a) H_2 and (b) CH_4

According to section 4.2, there are similar oxidization and reduction rates between CMTF_Lab and CMTF_Ind, so are the pre-exponential factors and activation energies of the rate constants (k_{chem} and k_{diff}) and the ratio (Ψ), see Table 4 [22]. Employing the kinetic parameters in the below table, the rate constants (k_{chem} and k_{diff}) and the ratio (Ψ) can be obtained according to the Arrhenius equations (Eqs. (7)-(9)). Inputting the values of k_{chem}, k_{diff} and Ψ into the simplified two-phase model coupled with the two-stage kinetic model, the model predicted results can be obtained, see Fig. 6 and Fig. 7. The model could reproduce the experimental data and describe the two-stage behavior well. The accurate kinetics should be obtained under enough reacting gases, to avoid diffusion control. The analysis of mass transfer resistance has been done for the redox of CMTF_Lab [22]. Since the used model and experimental conditions are the same as the previous work [22], the effect of interphase gas diffusion and external gas diffusion can be found in the kinetics determination of

CMTF_Lab [22]. All in all, the mass transfer rate is high enough for the chemical reactions, therefore the measured kinetic parameters in MFB-TGA are reliable.

Table 4. Kinetic parameters for the oxidization and reduction reactions [22]

Parameter	E_L	E_{chem}	E_{diff}	$A_{0,chem}$	$A_{0,chem}$	$A_{0,diff}$
Unit	kJ/mol	kJ/mol	kJ/mol	n.a.	m³/mol/s	m³/mol/s
O_2	n.a.	18.77	n.a	n.a.	3.80	n.a
H_2	5.86	27.62	78.13	1.55	3.86	1.01×10^2
CH_4	72.19	72.67	102.63	1.10×10^2	20.98	29.74

4.4. Particle characterization

4.4.1. Attrition test and particle analysis

The particle attrition tests of CMTF_Lab and CMTF_Ind were performed and compared. The attrition resistance was measured by applying an air jet attrition apparatus, and the test method strictly followed procedures in the ASTM D5757 standard [28]. The size of the air jet attrition apparatus and more details about the attrition test can be found elsewhere [29,30]. The particle size used for the test is 120-200 μm，and 50 g particles were filled in the air jet attrition apparatus, where the fines were produced from the frequent collision among the particles. By weighing the amount of fines collected, the attrition index results can be obtained, and plotted in Fig. 8. The five-hour attrition tests show the attrition index of CMTF_Lab and CMTF_Ind are almost the same (3.70 wt% for CMTF_Lab and 3.74 wt% for CMTF_Ind). According to Cabello etal. [29], when the value of the attrition test is < 5%, the particle lifetimes usually can reach > 2000 h. For comparison, the $CaMn_{0.9}Mg_{0.1}O_{3-\delta}$ oxygen carrier has an attrition index of 14.1 wt% [29], and its lifetime was

evaluated to be 12000 h in a 10 kW$_{th}$ CLC unit [6]. Therefore, the CMTF_Ind particle is expected to possess an even longer lifetime.
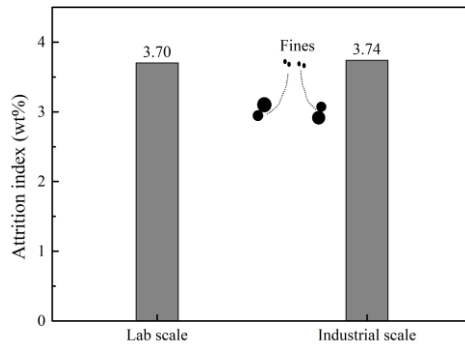

Fig. 8. Attrition test results of CMTF_Lab and CMTF_Ind

Other physical properties, such as BET surface area, particle pore diameter, porosity, etc., are listed in Table 5. According to the nitrogen intrusion results, the BET surface area and BJH pore diameter of the fresh CMTF_Ind are 0.15 m^2/g and 2.11 nm, which is lower than that of the fresh CMTF_Lab. The mercury intrusion results show that the fresh CMTF_Ind has a particle porosity of 0.45, which is slightly high than the fresh CMTF_Lab porosity of 0.48. According to the helium intrusion results, the true densities of the fresh CMTF_Ind and CMTF_Lab are 4227 kg/m^3 and 4488 kg/m^3, respectively. After multi redox cycles, all the above mentioned physical parameters of CMTF_Ind increase except for true density. For example, the BET surface area and porosity of the tested CMTF_Ind increase slightly to 0.31 m^2/g and 0.50, respectively.

Table 5. Physical properties of the fresh CMTF_Lab, fresh CMTF_Ind and tested CMTF_Ind

	BET (m^2/g)	BJH pore diameter(nm)	Porosity	True density (kg/m^3)
Fresh CMTF_Lab	0.21	7.56	0.48	4488
Fresh CMTF_Ind	0.15	2.11	0.45	4227

22

Commented [ZL29]: Lei: pls specify the time for such a mass lowss if you do not use it in y-axis

Commented [ll30R29]: It is 3.74wt% fines was attrited in the 5 hour test, means the attrion index id 3.74 wt%, rather than the attrition rate (3.74/5 wt%)

Commented [ZL31R29]: OK

Commented [ZL32]: Lei: what do you want to mean here for such increased properties? Does this mean that such a degradation is acceptable?

Commented [YL33R32]: True density is conctant, but sureface area increased from 0.15 to 0.31 is not detrimental, often a factor of 10 and above is seen if you get swelling/recrystallisation. This number will only give a slghtly higher activity which is good.

Commented [ll34R32]: Thanks for the commets!

Commented [ZL35R32]: I think the reactivity is alsmot constant form redox cycles.

Tested CMTF_Ind	0.31	7.25	0.50	4115

4.4.2. Crystalline phase analysis

The XRD patterns of the prepared CMTF_Ind and CMTF_Lab show a pure phase has been obtained. After a long-term redox test, the position of XRD peaks of the tested CMTF_Ind is unchanged, indicating the crystalline phases kept unchanged. No phase separation or phase change occurs, indicating very good chemical stablilty of upscaled CMTF_Ind under harsh redox cycles.
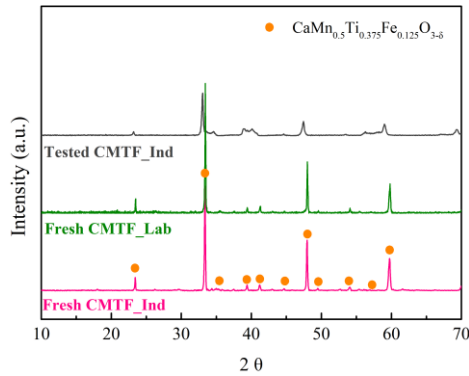

Fig. 9. Crystalline phase analysis of the fresh CMTF_Lab, fresh CMTF_Ind and tested CMTF_Ind

4.4.3. Particle morphology

The morphology of particle surface and cross-section of the fresh CMTF_Ind and the tested CMTF_Ind is demonstrated in Fig. 10. The fresh CMTF_Ind particle is almost spherical, and the particle is quite integral. The particle contains plenty of grains, and the grain boundaries on the particle surface are significantly clear. The integration of the fresh CMTF_Ind particle is also shown in the morphology of the cross-section inside the particle. There are some macro-pores existing inside the particle, but the solid structure is very dense around the macro-pores. For the tested CMTF_Ind particle, apparent cracks are formed on the particle. During the multiple redox test, the

CMTF_Ind particle continuously collided with other CMTF_Ind particles and silica sand particles, which may be the cause of the crack formation. The obvious grain boundaries can also be found on the particle surface, the distinction is the grain surface becomes more rough, resulting in an increase in the specific surface area as listed in Table 5. Apart from the macro-pores inside the particle, amounts of micro-pore formed after the test. The newly formed porosity could promote gas diffusion inside the particle.
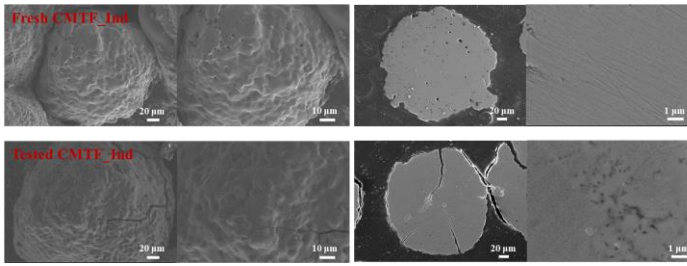

Fig. 10. Particle surface and cross-sectional SEM morphology of the fresh and tested

CMTF_Ind

5. Applications to a CLC unit

The obtained kinetic parameters were then applied to acquire the design and operatrion criteria for CLC reactors, such as the solid bed inventory in each reactor, and energy consumption of fan to overcome the bed pressure, etc. According to the oxygen mass balance, the minimum solid inventories can be calculated as Equation (13) for the air reactor and Equation (14) for the fuel reactor [31].

$$m_{OC,AR} = \frac{10^3 m_O}{H_{fuel} R_{OC,t}} \frac{1}{[dX_o/dt]_{\bar{x}_{O_2,AR}}} \tag{13}$$

$$m_{OC,FR} = \frac{10^3 m_O}{H_{fuel} R_{OC,t}} \frac{1}{[dX_r/dt]_{\bar{x}_{H_2,FR}}} \tag{14}$$

where m_O (kg-O_2/kg-fuel) is the oxygen mass required for full combustion per kg of solid fuel,

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H_{fuel} (kJ/mol) is the low heat value (LHV) of the solid fuel. $m_{\text{OC,AR}}$ (kg/MW$_{\text{th}}$) and $m_{\text{OC,FR}}$ (kg/MW$_{\text{th}}$) are the minimum solid inventories in the air reactor and the fuel reactor, respectively. $\bar{x}_{\text{O}_2,\text{AR}}$ (vol%) and $\bar{x}_{\text{H}_2,\text{FR}}$ (vol%) are the average O_2 and H_2 concentrations in the air reactor and the fuel reactor, respectively. In the fuel reactor, only H_2 was considered: for the solid fuel-fired CLC, the main reducing gases are H_2 and CO from the devolatilization and gasification, the CH_4 has a low concentration value and can be further converted to H_2 via steam reforming; the reactivity of H_2 and CO mixtures are similar to that of H_2 [32]. The average H_2 concentration ($\bar{x}_{\text{H}_2,\text{FR}}$) is 5 vol% according to Adanez et al.[31,33].

The seclected solid fuel is lignite, and its proximate analysis and ultimate analysis results are listed in Table 4. The ilmenite [31], managanese ore [23], and CuO@TiO$_2$-Al$_2$O$_3$ [34] oxygen carriers were seclected for comparison. The minimum solid inventories for the four oxygen carriers are illustrated in Fig. 11. For CuO@TiO$_2$-Al$_2$O$_3$, the needed solid inventories in the air reactor are 95 kg/MW$_{\text{th}}$, which is far higher than the other oxygen carriers, due to the slow oxidization rate. The required solid inventories in the air reactor is only 13 kg/MW$_{\text{th}}$ for CMTF_Ind due to the ultrafast oxidization rate. In the fuel reactor, the required minimum bed inventories are 65 kg/MW$_{\text{th}}$ for CMTF_Ind, which is far lower than 191 kg/MW$_{\text{th}}$ for CuO@TiO$_2$-Al$_2$O$_3$, 212 kg/MW$_{\text{th}}$ for ilmenite, and 274 kg/MW$_{\text{th}}$ for manganese ore. The total bed inventories are minimum, implying the sizes of the reactors can be reduced a lot. The cost of erecting the CLC unit and oxygen carrier production is promisingly reduced as well.

Table 4. Proximate analysis and utimate analysis of lignite [35]

Utimate analysis (wt%)		Proximate analysis (wt%)	
C$_{\text{ar}}$	45.4	Mositure$_{\text{ar}}$	12.6
H$_{\text{ar}}$	2.5	Volatile matter$_{\text{ar}}$	28.6
N$_{\text{ar}}$	0.6	Fixed carbon$_{\text{ar}}$	33.6
S$_{\text{ar}}$	5.2	Ash$_{\text{ar}}$	25.2

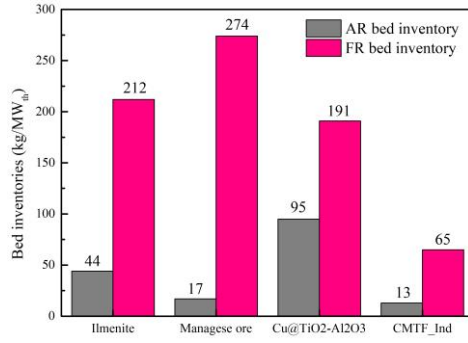|			
O_{ar}	8.5*		
m_O (kg-O_2/kg-fuel)	1.2	H_{fuel} (kJ/kg)	16250

*oxygen to balance

Fig. 11. Required minimum solid inventories for different oxygen carriers (AR: air reactor;

FR: fuel reactor)

The bed pressure drops in the air reactor (Δp_{AR}, Pa/MW$_{th}$) and the fuel reactor (Δp_{FR},

Pa/MW$_{th}$) are given by

$$\Delta p_{AR} = \frac{m_{OC,AR} g}{A_{AR}} \tag{15}$$

$$\Delta p_{FR} = \frac{m_{OC,FR} g}{A_{FR}} \tag{16}$$

where A_{AR} (m^2) and A_{FR} (m^2) are the cross sectional areas of the air reactor and the fuel reactor,

respectively.

In the actual operation, the energy consumption of fans is a crucial index affecting the CLC

power plant efficiency. The fan power should overcome the pressur drops in the air reactor and the

fuel reactor. The fan powers for the air reactor ($\Delta P_{AR,fan}$, W) and the fuel reactor ($\Delta P_{FR,fan}$, W)

can be calculated as

$$\Delta P_{AR,fan} = \frac{n}{n-1} \frac{p_{am} \dot{V}_{g,AR}}{\eta_{fan}} \left[\left(\frac{p_{am} + \Delta p_{bed,AR}}{p_{am}} \right)^{\frac{n-1}{n}} - 1 \right] \tag{17}$$

26

$$\Delta P_{FR,fan} = \frac{n}{n-1}\frac{p_{am}\dot{V}_{g,FR}}{\eta_{fan}}\left[\left(\frac{p_{am}+\Delta p_{bed,FR}}{p_{am}}\right)^{\frac{n-1}{n}}-1\right] \tag{18}$$

where n refers to the isentropic coefficient, p_{am} (Pa) is the fan inlet pressure (assumed to be ambient). $\dot{V}_{g,AR}$ (m³/s) and $\dot{V}_{g,FR}$ (m³/s) are the fan volume flowrates of the air reactor and the fuel reactor at ambient temperature, which are equal to the needed flowrates of fluidizing gases for the reactors. η_{fan} is the fan efficiency. $\Delta p_{bed,AR}$ (Pa) and $\Delta p_{bed,FR}$ (Pa) are bed pressure drops of the he air reactor and the fuel reactor.

For a 1000 MW$_{th}$ CLC designed by Lyngfelt and Leckner [36], The chosen or assumed parameter values are listed in Table 5. The estimated fan powers for the air reactor and the fuel reactor are showed in Fig. 12 for above different oxygen carriers. It can be seen than the total fans power is 989 kW when using the prepared CMTF_Ind as oxygen carrier, the value is 3.0 to 3.6 times lower than the total fans power when using ilmenite, manganese ore and $CuO@TiO_2-Al_2O_3$. It will be create a great gain in efficiency for a CLC power plant.

Table 5. Chosen or assumed parameter values

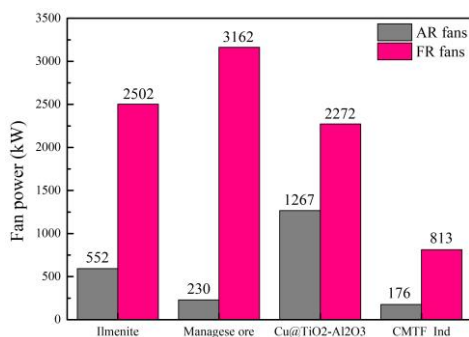|	A_i (m²)	$\dot{V}_{g,i}$ (m³/s)	n	η_{fan}
AR	198	260	1.4	0.95
FR	77	96	1.4	0.95

Fig. 12. Esitimated fan energy consumption when using different oxygen carriers (AR: air

reactor; FR: fuel reactor)

Conclusions

The spray drying granulation method was employed to produce the perovskite $CaMn_{0.5}Ti_{0.375}Fe_{0.125}O_{3-\delta}$ particles at an industrial scale (CMTF_Ind). The fine raw materials are manufactured to CMTF_Ind particles after the spray drying granulation and the calcination. More than 90% of the prepared CMTF_Ind particles are in the diameter range of 75-500 μm. The physical and chemical properties were compared with the perovskite prepared at laboratory scale (CMTF_Lab). Microfluidized bed thermogravimetric analysis (MFB-TGA) experiments were conducted to obtain oxygen uncoupling and redox kinetics of CMTF_Ind at a wide temperature range. The redox multicycles show that CMTF_Ind shows no degradation in reactivity and no agglomeration after more than 20 redox cycles. Kinetic experiments, conducted at 900 ºC, found that the required time for full oxygen release at the firstly fast stage is ~20 s, the full oxidation of CMTF_Ind can be finished within ~5 s, and full reduction with H_2 can be completed within ~30 s. The experimental data of the oxygen uncoupling and redox reactions from the MFB-TGA were well fitted by the simplified two-phase reactor model coupled with a two-stage kinetic model, using the same pre-exponential factors and activation energies as CMTF_Lab. The comparison of kinetics,

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attritionindex and crystalline phase shows CMTF_Ind shows similar chemical and physical properties as CMTF_Lab. ***Therefore, the upscaling preparation of the perovskite particles at an industrial scale was successfully realized in this work***. Based on the measured kinetics, the required bed inventories are 13 kg/MW$_{th}$ in the air reactor and 65 kg/MW$_{th}$ in the fuel reactor when using the prepared CMTF_Ind as the oxygen carrier. Comparing with ilmenite, manganese, $CuO@TiO_2$-Al_2O_3, the bed inventories are quite low. Moreover, the fan powers to overcome the bed pressures were estimated, and the total fan power is 3.0 to 3.6 times lower than the total fan power when using other oxygen carriers.

Acknowledgments

Nomenclature

$A_{0,chem}$ pre-exponential factor of the fast reaction stage, m^3/mol/s

$A_{0,diff}$ pre-exponential factor of the slow reaction stage, m^3/mol/s

$A_{0,L}$ pre-exponential factor of the critical conversion

A_i cross sectional areas of the air reactor or fuel reactor, m^2

Ar Archimedes number

$c_{p,OC}$ specific heat capacity of oxygen carrier, J/kg/K

$C_{b,i}$	concentration of gas i in the bubble phase, mol/m^3
$C_{e,i}$	concentration of gas i in the emulsion phase, mol/m^3
$C_{eq,i}$	equilibrium concentration of gas i, mol/m^3
d_p	diameter of the oxygen carrier particle, m
D_i	gas i molecular diffusivity, m^2/s
E_{chem}	activation energy of the fast reaction stage, kJ/mol
E_{diff}	activation energy of the slow reaction stage, kJ/mol
E_L	activation energy of the critical conversion, kJ/mol
f_a	volume fraction of oxygen carrier particles in all solid volume
H_{fuel}	low heat value (LHV) of the solid fuel, kJ/kg
H_{mf}	bed height in the bubbling bed reactor, m
k_{chem}	reaction rate constant of the fast reaction stage, m^3/mol/s
k_{diff}	reaction rate constant of the slow reaction stage, m^3/mol/s
k_g	external mass transfer coefficient, m/s
K_{be}	interchange coefficient between the bubble and emulsion phase, s^{-1}
K_r	reaction rate constant of particles in the emulsion phase, s^{-1}
K_{ri}	reaction rate constant of particles, s^{-1}
$m(t)$	mass measured by the weight transducer at time t, g
m_o	whole mass of the reactor and oxidized oxygen carrier samples, g
m_O	oxygen mass required for full combusting per kg of solid fuel, kg-O$_2$/kg-fuel
m_{OC}	mass of the added oxygen carrier samples, g
$m_{OC,i}$	required minimum solid inventories in the air reactor or fuel reactor, kg/MW$_{th}$

m_r whole mass of the reactor and reduced oxygen carrier, g

M_i molar mass of i, kg/mol

n isentropic coefficient

p_{am} fan inlet pressure

Δp_i bed pressure drops in the air reactor or fuel reactor, Pa/MW$_{th}$

$\Delta P_{i,fan}$ fan powers of the air reactor or fuel reactor, W

R_e Reynolds number

R_g ideal gases constant, J/mol/K

$R_{OC,ou}$ oxygen transport capacity for oxygen uncoupling, wt.%

$R_{OC,t}$ total oxygen transport capacity, wt.%

Sh Sherwood number

T temperature in Kelvin, K

U_0 superficial gas velocity, m/s

U_b bubble rise velocity, m/s

U_b^* effective gas velocity in the bubble phase, m/s

U_{mf} minimum fluidization velocity, m/s

$\dot{V}_{g,i}$ fan volume flowrates of air reactor or fuel reactor at ambient temperature, m^3/s

$\bar{x}_{j,i}$ average gas j concentration in the air reactor or fuel reactor, vol%

X conversion level of oxidation or reduction reaction at time t

X_{chem} conversion level of the fast reaction stage at time t

X_{diff} conversion level of the slow reaction stage at time t

X_e equilibrium conversion level of an oxygen carrier

X_o	conversion level of oxidation reaction at time t
X_{ou}	conversion level of oxygen uncoupling reaction at time t
X_r	conversion level of reduction reaction at time t
α	stoichiometric coefficient
ρ_s	particle density of oxygen carrier, kg/m^3
ε_{mf}	voidage of fluidized bed
θ	fraction of the bubble phase
η_{fan}	fan efficiency
δ	amount of lattice oxygen
γ	amount of lattice oxygen
ψ	ratio of the conversion level at the fast reaction stage to the conversion level

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