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Full Length Article Coal-fueled chemical looping gasification: A CFD-DEM study

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ABSTRACT

Chemical looping gasification (CLG) is an emerging technology for reducing greenhouse gas emissions, yet the complex physical-thermal-chemical behaviour in the CLG unit has not been well understood. This work developed a high-fidelity computational fluid dynamics-discrete element method (CFD-DEM) reactive model considering four heat transfer modes (e.g., conduction, convection, radiation, and reaction heat) and complex heterogeneous and homogeneous reactions. The hydrodynamics and thermochemical characteristics in a CLG unit operating under several key operating parameters are numerically studied. The contribution from each heat transfer mode is quantified and the relationship between particle-scale behaviour and mesoscale bubble structures is quantitatively illuminated. The results show that the solids vertical dispersion coefficient is one order of magnitude larger than the horizontal one. At a low solid holdup, the interphase drag force plays a dominant role and particles in the bubble phase have higher vertical slip velocities. The ratio of particle-averaged heating rates for char particles through conduction, convection, radiation, and reaction take 5.41%, 14.91%, 14.39%, and 65.29%, and that for oxygen carriers take 7.77%, 23.46%, 20.33%, and 48.44%, respectively. For char particle and oxygen carriers, the reaction heat dominates the heat transfer process. Increasing gas inlet velocity promotes particle mixing, alleviates dead zone, and finally increases gas products while increasing the char to oxygen carrier mass ratio decreases gas products. The present work provides a cost-effective tool for the in-depth understanding of heat and mass transfer mechanisms in the CLG process.

1. Introduction

Global warming urges advanced measures to reduce greenhouse gas emissions. The chemical looping process was first proposed in the 1950s and was initially designed for the production of CO₂ [1]. As an energyefficient oxy-fuel method, chemical looping combustion (CLC) is an emerging technology that thermochemically converts solid or gas fuels into high-concentration CO2 for the convenience of carbon capture and storage [2-4]. In contrast, chemical looping gasification (CLG) in this work is defined as a thermochemical process with the aim to produce syngas (e.g., H₂, CO). Fig. 1 shows a typical CLG unit composed of a fuel reactor (FR) and an air reactor (AR). The FR is used for fuel gasification and the AR is used for oxygen carrier (OC) regeneration. Circulating between two reactors, OC can transport the oxygen from the AR to the FR, avoiding direct contact of fuels and air. Recently, solid fuels (e.g., coal, biomass) have been increasingly employed in the CLG process due to the advantage of wide fuel flexibility [5,6]. Many experiments have been conducted focusing on the oxygen carriers characterization, pressure drop, gas species distribution, etc. [7-12]. A CLG unit is a dense gas-solid reaction system involving complex in-furnace phenomena such as multiphase flow and multi-physics processes. However, experiments cannot quantify the contribution from each heat transfer mode (i. e., conduction, radiation, convection, and reaction heat) in the CLG unit, hindering reactor optimization. Besides, experiments cannot illuminate the relationship between thermochemical characteristics with local gas-solid structures (e.g., bubble, cluster), suppressing process intensification [13]. Moreover, the trials and errors of the experiments are time-consuming and costly.

As an alternative, computational fluid dynamics (CFD) provides an efficient and cost-effective method for studying the hydrodynamic and thermochemical details in the CLG or CLC unit [14,15]. Alobaid et al. [16] did a comprehensive review of the development of CFD mathematical models and their applications in various fluidized-bed systems. Based on the fundamental assumptions (gas–solid, particle–particle, and particle–wall interactions) of the dense gas–solid flow, the numerical methods can be generally divided into the Eulerian-Eulerian and Eulerian-Lagrangian frameworks [16,17]. The main difference between these two methods lies in the solid phase treatment. The two-fluid model (TFM) under the Eulerian-Eulerian framework regards both gas and

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Nomencl	lature
$A_{p,i}$	Surface area of particle i , m ²
$C_{p,q}$	Specific heat capacity of gas phase, $J \cdot kg^{-1} \cdot K^{-1}$
C_{ni}	Specific heat capacity of particle <i>i</i> , $J \cdot kg^{-1} \cdot K^{-1}$
$D_n^{\mu,\nu}$	Diffusion coefficient of species $n, m^2 \cdot s^{-1}$
d	Thickness of gas layer, m
d _{n i}	Particle diameter, m
E	Activation energy, kJ/mol
e _{n i}	Emissivity of particle <i>i</i>
$\mathbf{f}_{c,i}$	Contact force exerted on a specific particle, N
\mathbf{f}_{di}	Gas force exerted on a specific particle, N
f _{ct ii}	Tangential contact forces between particle <i>i</i> and <i>j</i> , N
g	Gravitational acceleration, $m \cdot s^{-2}$
$h_{pg,i}$	Convective heat transfer coefficient, $W \cdot m^{-2} \cdot K^{-1}$
I_i	Moment of inertia of a specific particle, $kg \cdot m^2$
I _{om}	Inter-phase momentum exchange rate, $N \cdot m^{-3}$
k_0	Pre-exponential factor of the rate constant
Ĺ	Distance from contact point to particle center, m
l _{ij}	Distance between particle <i>i</i> and <i>j</i> , m
m _i , m _{eff}	Particle mass and effective particle mass, kg
n _{ij}	Normal unit vector between particle <i>i</i> and <i>j</i>
Ng	Number of gaseous species
N_p	Particle number
$N_{p,\Omega}$	Particle number in the domain Ω
Nu _{p,i}	Nusselt number of particle <i>i</i>
N_{x}, N_{y}, N_{y}	z Grid number along x, y, and z directions
Pr	Prandtl number
Q_{gp}	Volumetric heat release rate due to convection, $W{\cdot}m^{-3}$
$q_{gp,i}$	Heating rate due to gas-particle convection, W
$q_{pgp,i}$	Heating rate due to particle-gas-particle conduction, W
$q_{pp,i}$	Heating rate due to particle-particle conduction, W
q rad,i	Heating rate due to radiation, W
$R_{c,ij}$	Radius of contact region, m
Re _{p,i}	Particle Reynold number
R _{in} , R _{out}	Lower and upper bounds of conductive heat transfer
	region, m
$R_{p,i}, R_{p,j}$	Diameters of particle <i>i</i> and <i>j</i> , m
R _{gn}	Volumetric generation rate of n^{th} species, kg·m ⁻³ ·s ⁻¹
R _{sn}	Comsumption of production rate of species n due to the
	mass exchange, $kg \cdot s^{-1}$
t	Time instant, s



Fig. 1. Schematic diagram of chemical looping gasification (CLG).

aal	
$t_{n,ij}^{col}$	Collision time, s
T_{env}	Temperature of environment, K
T_g	Temperature of gas phase, K
$T_{g,\Omega}$	Temperature of gas phase in the domain Ω , K
Т _{р, і} , Т _{р, ј}	Temperatures of particle <i>i</i> and <i>j</i> , K
ug	Velocity vector of gas phase, $m \cdot s^{-1}$
\mathbf{v}_i	Velocity vector of particle <i>i</i> , $m \cdot s^{-1}$
V_c	Volume of computational cell, m ³
$V_{p,i}$	Volume of particle i , m ³
Greek sym	ibols
Eg	Void fraction
β	Inter-phase momentum exchange coefficient, kg·m ⁻³ ·s ⁻¹
ΔH_{rg}	Volumetric heat release rate of gas phase due to chemical reaction. $W \cdot m^{-3}$
ΔH_{rs}	Generated or comsumed rate due to chemical reaction. W
Κα	Gas thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$
Kni. Kni	Thermal conductivity of particle <i>i</i> and <i>i</i> , $W \cdot m^{-1} \cdot K^{-1}$
μ	Friction coefficient
, μ _σ	Gas viscosity, $kg \cdot m^{-1} \cdot s^{-1}$
ρ_{g}, ρ_{n}	Gas and particle density, $kg \cdot m^{-3}$
ω_p	Particle angular velocity, s^{-1}
Subscripts	
g I	Gas phase
i	Particle <i>i</i>
ü	Interactions between particle <i>i</i> and <i>j</i>
i	Particle <i>i</i>
n	Variables in normal direction
Acronvms	
AR	Air reactor
BFB	Bubbling fluidized bed
CFD	Computational fluid dynamics
CLC	Chemical looping combustion
CLG	Chemical looping gasification
CFL	Coutant-Friedrich-Lewy
DEM	Discrete element method
FR	Fuel reactor
LSD	Linear spring dashpot
MI	Mixing index

3D Three-dimensional

solid phases as a continuum and simplifies inter-particle collisions. This method has the advantage of computational convenience and has been widely used to explore the hydrodynamic and thermochemical characteristics of dense gas-solid reaction flow. For example, Lin et al. [18] numerically investigated the gas-solid flow behaviour and reaction characteristics in the FR with different mass ratios of NiO/CuO in the OC using the TFM. Li et al. [19] numerically studied the syngas production and sulfur conversion mechanisms during the CLG process using the Eulerian-Eulerian method. The model can reasonably predict the timevarying outlet concentration of major gas products. However, the Eulerian-Eulerian method cannot obtain particle-scale information, e.g., particle conduction, particle shrinkage, particle residence time, and particle size distribution, prohibiting its application in exploring the fundamental physics of heat and mass transfer during the CLG process [20]. In contrast, under the Eulerian-Lagrangian framework, the CFD-DEM approach truly resolves inter-particle collisions by a soft-sphere contact model and tracks each particle. Besides, it can finely integrate multi-physics processes (e.g., heat transfer, particle shrinkage) and multi-scale effects (e.g., size distribution, non-spherical particle, particle rotation) [21,22]. The CFD-DEM model featuring the corresponding

heat transfer modes and reaction kinetics is known to become a costeffective tool for the investigation of dense gas-solid reaction flow in various reactors. Due to the high-fidelity feature, this approach has emerged to explore the CLC process [16]. For example, Zhang et al. [23] simulated the cold multi-phase flow in a coal-direct CLC process and the results showed great agreement with the experimental data. Peng et al. [24] simulated a lab-scale CLC unit and captured the gas-solid flow patterns, solid distributions, and solid circulation rate. Luo et al. [2] simulated the alumina encapsulated Ni/NiO methane-air CLC system and found that the transient solid circulation rate fluctuated around a fixed value. Banerjee and Agarwal [25] simulated a coal-directed CLC process and found the fluidization performance strongly depended on the density of bed materials. Lin et al. [15] studied a two-dimensional coal-direct CLC process and found that finer oxygen carriers promoted the conversion of intermediate gas products into CO₂ and H₂O, therefore improving the combustion efficiency. Nevertheless, most of the above studies are focused on the cold flow in the CLC unit. The rest of the existing studies on the reaction flow in the CLC unit neglected the fundamental understanding of underlying thermochemical mechanisms, especially the relationship with the local gas structures, e.g., bubble evolution. Moreover, to the best of our knowledge, the CFD-DEM simulation of the CLG process has not been reported in the open literature.

To fill the knowledge gap, the present work has the following novelty: (i) development of a high-fidelity CFD-DEM reactive model considering four heat transfer modes (e.g., conduction, convection, radiation, and reaction heat) and complex heterogeneous and homogeneous reactions; (ii) quantitative analysis of the contribution of each heat transfer mode in the CLG process and the relationship between particle-scale physical-thermal-chemical behaviour and mesoscale bubble evolution. The present work is structured as follows: Section 2 details the governing equations, and heat and mass transfer models. Section 3 gives the numerical settings, followed by the model validation and flow patterns presented in section 4.1. Section 4.2 presents the particle mixing and dispersion characteristics, followed by the dimensionless analysis of heat transfer contribution in sections 4.3 and 4.4, respectively. Section 4.5 shows the chemical reactions involving gas species distribution. Conclusions are drawn in Section 5.

2. Mathematical model

In the present work, the gas phase is assumed as a continuum and solved under the Eulerian framework. The solid phase is regarded as a dispersed phase and is solved under the Lagrangian framework. The coal and oxygen carriers are both assumed as spherical with uniform size and density. Thermochemical sub-models are integrated to denote heat and mass transfer. The governing equations of gas–solid phases, interphase interactions regarding momentum, energy, and species, and chemical reaction kinetics are outlined below.

2.1. Governing equations for gas and solid phases

The gas phase is governed by mass, momentum, energy, and species conversation equations as follows [22]:

$$\frac{\partial(\varepsilon_{g}\rho_{g})}{\partial t} + \nabla(\varepsilon_{g}\rho_{g}\mathbf{u}_{g}) = \sum_{n=1}^{N_{g}} R_{gn}$$
(1)

$$\frac{\partial \left(\varepsilon_{g} \rho_{g} \mathbf{u}_{g}\right)}{\partial t} + \nabla \cdot \left(\varepsilon_{g} \rho_{g} \mathbf{u}_{g} \mathbf{u}_{g}\right) = \nabla \cdot \overline{\overline{S}}_{g} + \rho_{g} \varepsilon_{g} \mathbf{g} - \sum_{m=1}^{M} \mathbf{I}_{gm}$$
(2)

$$\frac{\partial \left(\varepsilon_{g} \rho_{g} C_{p,g} T_{g}\right)}{\partial t} + \nabla \cdot \left(\varepsilon_{g} \rho_{g} \mathbf{u}_{g} C_{p,g} T_{g}\right) = \nabla \cdot \left(\varepsilon_{g} \kappa_{g} \nabla T_{g}\right) + Q_{gp} - \Delta H_{rg}$$
(3)

$$\frac{\partial \left(\varepsilon_{g}\rho_{g}X_{n}\right)}{\partial t}+\nabla\cdot\left(\varepsilon_{g}\rho_{g}\mathbf{u}_{g}X_{n}\right)=\nabla\cdot\left(\varepsilon_{g}\rho_{g}D_{n}\nabla X_{n}\right)+R_{gn}$$
(4)

where ε_{g} , ρ_{g} , \mathbf{u}_{g} are the gas volume fraction, density, and velocity, respectively. \mathbf{I}_{gm} is the momentum exchange term between the gas and the m^{th} type of solid phase. Q_{gp} is the gas-particle convective heat transfer rate and ΔH_{rg} is the heat source of gas phase due to chemical reaction. R_{gn} is the volumetric generation rate of n^{th} species. The gas phase is coupled with the solid particles via the above quantities, which are given by:

$$\varepsilon_{g} = 1 - \frac{1}{V_{c}} \sum_{i=1}^{N_{p}} V_{p,i}; \ \mathbf{I}_{gm} = \frac{1}{V_{c}} \sum_{i=1}^{N_{p}} \mathbf{f}_{d,i}; \ \mathcal{Q}_{gp} = \frac{1}{V_{c}} \sum_{i=1}^{N_{p}} q_{gp,i}; \ \mathcal{R}_{gn} = \frac{1}{V_{c}} \sum_{i=1}^{N_{p}} \mathcal{R}_{gn,i}$$
(5)

where V_c and $V_{p,i}$ are the volume of the current computational cell and i^{th} particle, respectively. $\mathbf{f}_{d,i}$ is the gas force exerted on the i^{th} particle; $q_{gp,i}$ is the heating rate between the gas phase and the i^{th} particle; $R_{gn,i}$ is the generation or consumption rate of i^{th} particle due to heterogeneous reactions.

Newton's second law of motion is used to describe the solid phase by considering heat and mass transfer. Each particle is tracked individually, and the position, temperature, and species of i^{th} particle are given by [22]:

$$m_i \frac{d\mathbf{v}_i}{dt} = m_i \mathbf{g} + \mathbf{f}_{d,i} + \mathbf{f}_{c,i}$$
(6)

$$I_{i}\frac{d\boldsymbol{\omega}_{i}}{dt} = \sum_{j=1, j \neq i}^{k} \left(L\mathbf{n} \times \mathbf{f}_{ct, jj} \right)$$
(7)

$$m_i C_{p,i} \frac{dT_{p,i}}{dt} = q_{gp,i} + q_{pp,i} + q_{pgp,i} + q_{rad,i} - \Delta H_{rs}$$
(8)

$$\frac{dm_i}{dt} = \sum_{n=1}^{N_p} R_{sn} \tag{9}$$

where \mathbf{v}_i , $\boldsymbol{\omega}_i$, $\mathbf{f}_{c,i}$, and $T_{p,i}$ are the translational velocity, rotational velocity, collision force, and temperature of *i*th particle, respectively. In Eq. (8), q means the source term due to different heat transfer modes (i.e., particle-gas convection, particle-particle conduction, particle-gasparticle conduction, and radiation), having a unit of J/s (i.e., W) [26–28]. ΔH_{rs} is the generation (or consumption) rate of heat acting on the i^{th} particle due to chemical reactions. R_{sn} is the comsumption or production rate of species *n* due to the mass exchange of i^{th} particle. N_p is the total number of species in the i^{th} particle. The gas force $\mathbf{f}_{d,i}$ exerted on i^{th} particle considers the pressure gradient force and drag force. The drag force is calculated by the correlation proposed by Gidaspow [29]. The inter-particle collision force $f_{c,i}$ is evaluated by a linear spring-dashpot (LSD) model, which can guarantee high numerical accuracy and efficiency [20]. Furthermore, the particle-turbulence interaction is neglected due to the high particle-to-gas density ratio ($\rho_p/\rho_g \sim 10^3$) used in the following simulation cases [30,31].

2.2. Heat transfer sub-models

In the present work, four heat transfer modes are considered, i.e., convection, conduction, radiation, and heat of reaction. The heating rate of each mode is given below.

The heating rate through convection between gas and i^{th} particle is given by [32,33]:

$$q_{gp,i} = h_{pg,i} A_{p,i} \left(T_g - T_{p,i} \right)$$
(10)

$$h_{pg,i} = \frac{\mathrm{Nu}_{p,i}\kappa_{\mathrm{g}}}{d_{p,i}} \tag{11}$$

Table 1

Proximate and ultimate analysis of coal char (dry basis) [37].

Proximate analysis			Ultimate analysis					Heating value
(wt-%)			(wt-%)					(MJ/kg)
Fixed carbon	Volatiles	Ash	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	27.9
80.94	4.34	14.72	76.70	1.84	2.55	1.65	2.48	

Table 1	2
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Parameters of the char gasification rate [41].

	Pre-exponential factor	Activation energy (kJ/mol)
$k_{\rm CO_2}$	$3.96 imes 10^{-4}$ (1/s)	109
$K_{\rm CO_2}$	$8.37 imes 10^{-5}$ (1/Pa)	16
Kco	$1.90 imes 10^{-5}$ (1/Pa)	_
$k_{\rm H_2O}$	22.10 (1/s)	212
$K_{\rm H_2O}$	$9.54 imes 10^{-2}$ (1/Pa)	69
$K_{ m H_2}$	$9.36 imes 10^{-5}$ (1/Pa)	_

Table 3

Kinetic parameters for gas compositions [38].

Parameters	H ₂	CH4	СО
$k_0 (\text{mol}^{1-n} \cdot \text{m}^{3n-2} \cdot \text{s}^{-1})$	$2.3 imes10^{-3}$	$8 imes 10^{-4}$	$6.2 imes10^{-4}$
$E (kJ \cdot mol^{-1})$	24	49	20
b	3	12	3
n	0.8	1.3	1

$$Nu_{p,i} = 2.0 / \left(1 - \left(1 - \varepsilon_{g} \right)^{1/3} \right) + 0.69 Re_{p,i}^{0.5} Pr^{0.33}$$
(12)

where particle Nusselt number $Nu_{p,i}$ is calculated by combining the particle Reynolds number $Re_{p,i}$ and Prandtl number $Pr(=\mu_g C_{p,g}/\kappa_g)$. In this work, the calculation of $Nu_{p,i}$ proposed by Leckner which considers

the voidage for the fluidized bed is adopted [32].

The conduction mode can be divided into two parts, the particle–particle conduction $q_{pp,i}$ and the particle-gas-particle conduction $q_{pgp,i}$. The latter can be calculated by assuming the heat is transferred through a gas layer with a default thickness of $0.2d_p$ wrapped around two neighbouring particles. These two heat transfer modes are given by [34,35]:

$$q_{pp,ij} = 4 \frac{\kappa_{p,i} \kappa_{p,j}}{\kappa_{p,i} + \kappa_{p,j}} R_{c,ij} (T_{p,j} - T_{p,i})$$
(13)

$$R_{c,ij} = \sqrt{R_{p,j}^2 - \left(\frac{R_{p,j}^2 - R_{p,i}^2 + l_{ij}^2}{2l_{ij}}\right)^2}$$
(14)

$$q_{pgp,ij} = \kappa_g \left(T_{p,j} - T_{p,i} \right) \int_{R_{in}}^{R_{out}} \frac{2\pi r}{l_{ij} - \left(\sqrt{R_{p,i}^2 - r^2} + \sqrt{R_{p,j}^2 - r^2} \right)} dr$$
(15)

$$R_{in} = R_{c,ij} = \begin{cases} 0 & l_{ij} > (R_{p,i} + R_{p,j}) \\ \sqrt{R_{p,j}^2 - \left(\frac{R_{p,j}^2 - R_{p,i}^2 + l_{ij}^2}{2l_{ij}}\right)^2} & l_{ij} \leq (R_{p,i} + R_{p,j}) \end{cases}$$
(16)



Fig. 2. Schematic representation of the coupling scheme of the CFD-DEM reactive model.



Fig. 3. (a) Time-evolution of gas products concentration at the outlet; (b) comparison of the gas composition at the outlet between the experiment and simulation.



Fig. 4. (a) Experiment test-rig [37]; (b) geometry configuration of the investigated reactor.

$$R_{out} = R_{f,ij} = \sqrt{\left(R_{p,j} + d\right)^2 - \left(\frac{\left(R_{p,j} + d\right)^2 - R_{p,i} + l_{ij}^2}{2l_{ij}}\right)^2}$$
(17)

where $R_{c,ij}$ and l_{ij} are the particle contact radius and distance between two particles, respectively. R_{in} and R_{out} are lower and upper bounds for integrating the contact region, respectively.

In the fluidized bed reactor, the CLG process is operated under high temperatures, thus the radiative heat transfer between a specific particle and its surrounding particles in a sub-domain should be considered. This heat transfer mode is calculated by considering the environmental temperature T_{env} and the particle properties (e.g., emissivity $e_{p,i}$) in a sub-domain. In this work, the sub-domain is defined as a spherical region with a default diameter of $1.5d_p$ and T_{env} is defined as the combination of mean particle temperature and gas temperature in this sub-domain [28]. The detailed calculation equations are [33]:

$$q_{rad,i} = e_{p,i}A_{p,i}\sigma\left(T_{env}^4 - T_{p,i}^4\right)$$
(18)

$$T_{env} = \varepsilon_g T_{g,\Omega} + \left(1 - \varepsilon_g\right) \frac{1}{N_{p,\Omega}} \sum_{j=1, j \neq i}^{N_{p,\Omega}} T_j$$
(19)

where σ is the Stefan-Boltzmann constant. $T_{g,\Omega}$ and $N_{p,\Omega}$ are the gas

temperature and the number of particles in the spherical sub-domain, respectively. $e_{p,i}$ is the effective emissivity in the radiative heat exchange between the receiving particle "i" and its surrounding "*env*". This is usually modelled as the interchange between two concentric spheres of almost the same size (this means it is approximated as two infinite parallel plates). However, even if the emissivity of all particles is assumed to be equal (as in the present work) they differ, because a suspension of particles is always darker than the particles themselves. This is called the Hohlraum effect (the cavity effect) and has been evaluated by many different methods [36]. More accurate radiation models will be implemented into the reactive CFD-DEM framework in our future work.

The heat of formation is calculated based on Kirchoff's law, by relating the enthalpy with the heat capacity change of each reaction. Specifically, the heat of reaction for the gas phase (ΔH_{rg}) is calculated from the enthalpy difference between the gaseous products and reactants. The heat of reaction (ΔH_{rs}) for the solid phase is calculated as the enthalpy difference between the solid products and reactants. They are generally given by:

$$\Delta H_r = \sum H_{n,products} - \sum H_{n,reactants}$$
⁽²⁰⁾

where the enthalpy change for n^{th} species at temperature *T* is given by:

Table 4

Details of operating parameters and thermophysical properties.

Parameters	value	Unit
Bed dimension (<i>x</i> , <i>y</i> , <i>z</i>)	0.038, 0.45, 0.00144	m
Cell Number (N_x , N_y , N_z)	19, 225, 1	-
Initial bed temperature (T_b)	1223	K
Initial height of oxygen carriers (H_0)	0.1	m
Particle phase		
Material	OC/Char	-
Particle density (ρ_p)	3734/1540	kg·m ⁻³
Particle diameter (d_p)	0.00048/0.00048	m
Particle spring stiffness (k_n)	1000/1000	$N m^{-1}$
Particle restitution coefficient (e)	0.9/0.9	-
Particle friction coefficient (μ_p)	0.1/0.1	-
Particle emissivity (e_p)	0.7/0.7	-
Gas phase		
Gas density (ρ_g)	Equation of state	-
Gas viscosity (μ_g)	Thermo. Database ^a	kg·m ⁻¹ ·s ⁻¹
Gas thermal conductivity (κ_g)	Thermo. Database ^a	$W \cdot m^{-1} \cdot K^{-1}$
Gas specific heat capacity $(C_{p,g})$	Thermo. Database ^b	J [·] kg ⁻¹ ·K ⁻¹
Gas inlet velocity (U_0)	0.24	$m \cdot s^{-1}$
Outlet gas pressure (P_0)	1.013×10^{5}	Ра

Note: marked a and b represent the data calculated according to the thermo database referring to Bird et al. [47] and Burcat and Ruscic [48], respectively.

Table 5

Boundary conditions for gas phase in the simulation.

Boundaries	Velocity	Pressure	Temperature
Gas inlet (bottom)	Fixed flow rate	Zero gradient	Fixed value
Outlet (top)	Zero gradient	Fixed value	Zero gradient
Walls	No slip	Zero gradient	Fixed value

Table 6

Operating parameters in this work.

Case	U (m/s)	Char/OC (kg/kg)
Base case	0.24	2.4:100
Flow inlet velocity	0.28	2.4:100
	0.32	2.4:100
	0.36	2.4:100
Char to oxygen carrier mass ratio	0.24	1.8:100
	0.24	3.0:100
	0.24	3.6:100

$$H_n(T) = H_n^o(T_{ref}) + \int_{T_{ref}}^T C_{pn} dT$$
(21)

where $H_n^o(T_{ref})$ is the formation enthalpy for n^{th} species at the reference temperature T_{ref} . The change of enthalpy caused by the temperature change can be calculated by integrating the specific heat capacity (C_{pn}) from T_{ref} to T.

2.3. Chemical reaction model

The CLG process in a bench-scale reactor is studied in the present work, which refers to the experimental work of Chen et al. [37]. Coal char is used as the solid fuel while the mixture of Fe_2O_3 and Al_2O_3 is used as oxygen carriers. The proximate analysis and ultimate analysis of coal char are listed in Table 1.

Char combustion is commonly dominated by both reaction resistance and diffusion resistance, as suggested in the open publication. However, in this work, the coal char and oxygen carriers have tiny diameters. Moreover, the oxygen carriers have dense structures and small internal pores. Thus, only the reaction resistance is considered, and the kinetics for the combustion and gasification reactions have been widely used in the simulation of the CLG process including char and oxygen carrier reactions, with reasonable prediction results obtained [38–40]. In future work, we will combine experiments to further quantify the intensity of reaction and diffusion resistances using high-resolution numerical methods (e.g., particle-resolved direct numerical simulation, PR-DNS) for coal char and oxygen carriers. The char gasification reactions during the CLG process are given by [6]:

$$Char + CO_2 \rightarrow 2CO + 0.0365H_2 + 0.026H_2O$$
 (R1)

$$Char + H_2O \rightarrow 1.073H_2 + CO + 0.026H_2O$$
 (R2)

The reaction kinetics proposed by Everson et al. [41] is used to describe char gasification processes:

$$\dot{m}_{Char} = \rho_p \varepsilon_p \frac{A_p}{1 - \varepsilon_0} r_n \left(1 - X_p\right)^{2/3}$$
⁽²²⁾

For these two gasification reactions, the reaction rates are given by:

$$r_{\rm CO_2} = \frac{k_{\rm CO_2} K_{\rm CO_2} P_{\rm CO_2}}{1 + K_{\rm CO_2} P_{\rm CO_2} + K_{\rm CO} P_{\rm CO}}$$
(23)

$$r_{\rm H_2O} = \frac{k_{\rm H_2O} K_{\rm H_2O} P_{\rm H_2O}}{1 + K_{\rm H_2O} P_{\rm H_2O} + K_{\rm H_2} P_{\rm H_2}}$$
(24)

 P_{CO2} , P_{CO} , $P_{\text{H}_2\text{O}}$, and P_{H_2} are the partial pressure of CO₂, CO, H₂O, and H₂ in the gas mixture, respectively. K_{CO_2} and K_{H_2} O are the reaction rate constants. K_{CO_2} , K_{CO} , $K_{\text{H}_2\text{O}}$, and K_{H_2} are the equilibrium constants. The Arrhenius form is adopted to express these constants. Detailed parameters are listed in Table 2.

The water-gas-shift reaction during the CLG process is given by:

$$CO + H_2O \rightarrow H_2 + CO_2$$
 (R3)

The reaction rate for the water–gas-shift reaction is given by [40]:

$$\dot{W}_{\text{WGS}} = -k_0 \left(e^{-E/RT} C_{\text{H}_2}^{0.5} C_{\text{CO}_2} - \frac{1}{\exp(-4.33 + 4577.8/T)} e^{-E/RT} C_{\text{H}_2\text{O}} C_{\text{CO}} \right)$$
(25)

where C_{H_2} , C_{CO_2} , C_{H_2O} , and C_{CO} are the mole concentrations of H₂, CO₂, H₂O, and CO, respectively. ($k_0 = 2.17 \times 10^7 \text{ mol}^{-0.5} \cdot \text{L}^{0.5} \cdot \text{s}^{-1}$, E = 192.9 kJ/mol) [42].

The metal oxide reduction reactions during the CLG process are given by:

$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$
 (R4)

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O \tag{R5}$$

The kinetic parameters for the metal oxide reduction reactions are given by [43]:

$$m_{\rm CO} = \frac{k_{\rm CO} R_0}{2M_{\rm O_2}} \rho_p \varepsilon_p \left(X_{\rm Fe_2O_3} + X_{\rm Fe_3O_4} \times \frac{3M_{\rm Fe_2O_3}}{2M_{\rm Fe_3O_4}} \right) (1 - \xi)^{2/3} M_{\rm CO}$$
(26)

$$m_{\rm H_2} = \frac{k_{\rm H_2} R_0}{2M_{\rm O_2}} \rho_p \varepsilon_p \left(X_{\rm Fe_2O_3} + X_{\rm Fe_3O_4} \times \frac{3M_{\rm Fe_2O_3}}{2M_{\rm Fe_3O_4}} \right) (1 - \xi)^{2/3} M_{\rm H_2}$$
(27)

where R_0 is the carrying capacity of oxygen carriers. ξ represents the conversion degree of oxygen carriers. They are given by:

$$R_0 = \frac{m_{oxy} - m_{red}}{m_{oxy}}, \quad \xi = \frac{m_{oxy} - m}{m_{oxy} - m_{red}}$$
(28)

The kinetic parameter k_{gi} is given by [38]:



Fig. 5. Time-evolution flow patterns in the reactor (coloured by particle species).



Fig. 6. Time-evolution bubble structures in the reactor (coloured by voidage).

$$k_{gi} = \frac{3b_i k_{0i} e^{-E_i/RT}}{\rho_m r_0} C_{gi}^{n_i}$$
(29)

where ρ_m is the molar density of the reactant. r_0 represents the grain radius of the reactant. The details of kinetic parameters are summarized in Table 3.

2.4. Numerical scheme

Through the exchange of mass, momentum, and energy, gas-solid flows can be coupled with chemical reactions in a conservation manner, as shown in Fig. 2. Specifically, the DEM solver updates the particle

quantities (e.g., position, velocity, species) using the initial settings and then transfers these data to the CFD solver to evaluate the void fraction, inter-phase momentum, energy, and species exchange items for the discretizing governing equations of the gas phase. The gas phase governing equations are discretized on the base of the finite volume method (FVM). A first-order implicit Euler scheme discretizes the transient term. A first-order upwind scheme discretizes other spatial terms, such as momentum, mass fraction, energy, and pressure. The governing equations involving particle physical and thermochemical properties are integrated explicitly by a first-order scheme. The SIMPLE algorithm is used to solve the coupling of the gas velocity and pressure. Thus, the velocity, pressure, temperature, and species of the gas phase in each



Fig. 7. Time-evolution profiles of mixing indices under different operating parameters: (a) gas inlet velocity; (b) char to oxygen carrier mass ratio.



Fig. 8. Dispersion coefficients of char particles and oxygen carriers under different operating parameters: (a) gas inlet velocities; (b) char to oxygen carrier mass ratio.

computational node are obtained, which are used by the DEM solver for the next loop to update the particle information. Chemical ordinary differential equations of the homogeneous reactions are solved with a stiff, sparse ODE solver.

The time step of the gas phase (Δt_{CFD}) is determined by the Coutant-Friedrich-Lewy (CFL) condition from the CFD part [39].

$$CFL = \Delta t_{CFD} \max\left(\frac{|\mathbf{u}_f|}{\Delta x}\right) \left\langle 1 \right\rangle$$
(30)

where Δx represents the characteristic size of the grid. To guarantee the numerical stability of multiple collisions, the time step of the solid phase should be smaller than a critical value. In this work, the time step of the solid phase is specified as 1/50 of the minimum collision time ($t_{n,ij}^{col}$) [44]:

$$t_{n,ij}^{col} = \pi \left(\frac{k_{n,ij}}{m_{eff}} - \frac{\eta_{n,ij}^2}{m_{eff}^2} \right)^{-1/2}$$
(31)

where k_n and η_n are the spring constant and damping coefficient, respectively. m_{eff} is the effective mass of particles *i* and *j* in a collision pair. All simulation cases run on a cluster with 32 CPU processors.

2.5. Model validation

The present study focuses on the hydrodynamics (especially bubble dynamics) and thermochemical behaviour of dense gas-solid reaction flow in the CLG unit. Thus, the developed model should be validated against experimental data in terms of flow dynamics, heat transfer, and chemical reactions.



Fig. 9. Time-evolution of dimensionless number (Re_p , Nu_p) for char particles (a) and oxygen carriers (b).



Fig. 10. Relationship between dimensionless number and particle concentration: (a) char particles; (b) oxygen carriers. (Re_p is labeled by blue colour, Nu_p is labeled by pink colour; the size of points indicates the magnitude of particle slip velocity). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The developed model is first validated with the experiment from Patil et al. [45] in terms of the bubble dynamics and particle cooling process in a fluidized bed. The dimension of the bed is 8 cm, 1.5 cm, and 25 cm in width, depth, and height, respectively. The particles with a diameter of 1 mm are initially packed in the bed at 90 °C. The cold gas flow is introduced into the bed from the bottom distributor with a gas velocity of 1.2 m/s and 1.54 m/s at 20 °C. Detailed computational setups are summarized in Table S1 of the Supporting Information. As shown in Fig. S1 of the Supporting Information, the spatial distribution and evolution of bubbles are well captured, with the observation of a narrow low-temperature zone in the centre bottom of the bed. Moreover, the predicted mean particle temperature over time is comparable to the experimental data, as shown in Fig. S2 of the Supporting Information.

The developed model is further validated by the experiment from Chen et al. [37] in terms of gas compositions in the CLG unit. The detailed numerical settings are given in the following section. Fig. 3a shows the time evolution of gas products at the reactor exit. The gas species escape from the reactor exit after 1 s. From 1 s to 5 s, all gas species undergo a dramatic change. As the main gas products, the concentrations of CO₂ and H₂O increase sharply with time. The concentration of the H₂ and CO increases sharply in the period of 1 s to 2 s and then decreases after 2 s. After 5 s, the concentration of each gas composition varies gently. After 10 s, the reactor reaches a dynamic equilibrium state, and the concentration of each gas composition fluctuates around a fixed value. Fig. 3b compares the predicted gas species with the experimental data. The model can successfully capture the mole fraction of each gas composition, and the slight discrepancies may come from the simplification of geometry and chemical reactions. Thus, the present model can predict the thermochemical behaviour of gas–solid flow in the reactor.

Although the in-furnace phenomena of the large-scale fluidized bed reactor (i.e., the apparatus at a meter scale) are distinct from that of the small-scale fluidized bed reactor (i.e., the apparatus at a centimetre scale), the mathematical models governing the gas–solid motion, heat transfer, and chemical reactions in the fluidized bed reactors with different scales are consistent. Therefore, the well-validated mathematical model is reasonable to be applied to simulate dense gas–solid reaction flow in multi-scale fluidized bed reactors.



Fig. 11. Histogram distributions of Re_p and Nu_p at t = 20 s: (a, b) char particles; (c, d) oxygen carriers.



Fig. 12. Time-averaged dimensionless number distribution under different gas inlet velocity (a) and different char to oxygen carrier mass ratios (b).

3. Numerical settings

The simulation refers to the experimental work by Chen et al. [37] regarding a solid-fueled chemical-looping gasification system, as shown in Fig. 4(a). A quasi-3D simulation of the reactor is established based on

the experimental unit. Compared with a full-3D simulation, a quasi-3D simulation contains fewer particles and consumes fewer computational resources, which has also been proven to be reliable in dense gas-solid hydrodynamics simulation [22,46]. Fig. 4(b) shows the geometry configuration of the investigated reactor, which has 0.038 m in



Fig. 13. Time-evolution profiles of the contributions of different heat transfer modes: (a) char particles, (b) oxygen carriers, $T_b = 1223$ K.

width and 0.45 m in height. The computational domain is divided into structural grids with an average size of 2 mm and the total number of grids is 4275. The coal particles and oxygen carriers have a diameter of 0.48 mm. The density of the coal particles and oxygen carriers are 1540 kg/m³ and 3734 kg/m³, respectively. Initially, the oxygen carriers are packed in the bed at a height of 0.1 m and the coal particles are generated above the oxygen particles. The gas mixture of H₂O/N₂ with a molar ratio of 1:1 is introduced from the bottom distributor. The gas–solid parameters and operating conditions are detailed in Table 4.

The inlet is set as the velocity inlet boundary and the outlet is set as the pressure outlet boundary. The walls are set as the no-slip boundary. Meanwhile, the temperatures of walls are assigned the same value as the initial bed temperature. The boundary conditions for gas phase are detailed in Table 5. The time-step of the gas phase is initially set as 1.0×10^{-5} s and can be automatically adjusted based on the CFL number. Table 6 gives the operating parameters investigated in the present work. Four sets of gas inlet superficial velocities (i.e., 0.24 m/s, 0.28 m/s, 0.32 m/s, and 0.36 m/s) are set to investigate the influence on gas–solid hydrodynamics. Besides, four sets of char to oxygen carrier mass ratios (i.e., 1.8:100, 2.4:100, 3.0:100, and 3.6:100) are assigned to explore their influence on reactor performance. Each simulation case runs for 30 s and the last 20 s are adopted to conduct post-processing statistics.

4. Results and discussion

4.1. Particle motion and bubble evolution

In the CLG process, gas–solid hydrodynamics shows a remarkable influence on particle heat and mass transfer behaviour. Fig. 5 and Fig. 6 illustrate the time evolution of flow patterns in the reactor. At the initial stage, oxygen carriers and char particles are packed in the upper and lower parts of the bed, respectively. As the gas mixture is introduced into the bed, small bubbles are generated and rise along with the bed height, and then coalesce into large bubbles. Large bubbles continue to rise in the bed and burst when reaching the bed surface. Following the bubble burst behaviour, a lot of particles are thrown into the freeboard. These particles fall to the bed after reaching the maximum height. The bubble behaviour can greatly promote the gas–solid mixing process and therefore enhance the heat and mass transfer efficiency. In the corner, oxygen carriers don't participate in internal circulation, forming a dead zone.

4.2. Particle mixing and dispersion

Mixing behaviour significantly influence the heat and mass transfer of the solid fuel [33,46]. A good particle mixing process can promote reactor performance. The Lacey mixing index (MI) is used to describe the particle mixing process between the char particle and oxygen carriers [49]:

$$MI = \frac{\sigma_0^2 - S^2}{\sigma_0^2 - \sigma_r^2}$$
(32)

$$\sigma_0^2 = \overline{c}(1-\overline{c}); \quad \sigma_r^2 = \overline{c}(1-\overline{c})/\overline{n}; \quad S = \sqrt{\frac{1}{N-1}\sum_{i=1}^N \left(\overline{c} - c_i\right)^2}$$
(33)

where σ_0^2 and σ_r^2 are the variance of the entire separation and entire mixing of particles, respectively. \bar{c} and \bar{n} are the average solid concentration and the average number of particles. *S* is the deviation of the present particle mixing state. The MI ranges from 0 to 1. MI = 0 represents those different kinds of particles that are fully separated. MI = 1 represents that the particles in the system are entirely mixed.

Fig. 7 and Fig. S3 of the Supporting Information illustrate the mixing process under different gas inlet velocities and char to oxygen carrier mass ratios. With the increase of gas inlet velocity, larger bubbles generate and the bed height increases. The mixing indices rapidly increase to maximum values and fluctuate around the mean values. The mean MI under four different gas inlet velocities is 0.6278, 0.8152, 0.8579, and 0.8859, respectively. Increasing gas inlet velocity significantly promotes the particle mixing process in the bed. Meanwhile, the higher the gas inlet velocity, the faster the system reaches the fully mixing state. Particles in the corner don't participate in the mixing process, which is known as the dead zone. Increasing gas inlet velocity promotes the mixing of particles in the corner and decreases the dead zone. As shown in Fig. S3a of the Supporting Information, several char particles move to the left and right corners in the mixing process when the gas inlet velocity is 0.36 m/s. There are no char particles in the corner under 0.24 m/s. The mean MI under different char to oxygen carrier mass ratios is 0.5596, 0.6278, 0.5408, and 0.5099, respectively. With the increase of the char to oxygen carrier mass ratio, the mean MI first increases and then decreases, reaching a maximum value at the ratio equal to 2.4:100. When the char to oxygen carrier mass ratio is around 2.4:100, the CLG system reaches a better mixing state. Fig. S3b of the Supporting Information shows the instantaneous particle mixing state under different char to oxygen carrier mass ratios. Changing the



Fig. 14. Time-evolution profiles of the contributions of different heat transfer modes for char particle, id = 15000: (a) conduction, (b) convection, (c) radiation, (d) reaction.

char to oxygen carrier mass ratio has an insignificant influence on particle mixing.

The dispersion property is commonly used to illuminate the mixing characteristics from a microscopic perspective. For a single particle, the dispersion coefficient (D_i) is defined as [50]:

$$D_i = \frac{(\Delta r_i)^2}{2\Delta t}$$
(34)

where Δr_i represents the displacement of particle *i* in the time interval Δt . To evaluate the total particle dispersion in the system, the average solids dispersion coefficient is defined as:

$$D = \frac{1}{N_P} \sum_{i=1}^{N_P} \frac{(\Delta r_i)^2}{2\Delta t} = \frac{1}{N_P} \sum_{i=1}^{N_P} \frac{(r_i - r_{i0})^2}{2\Delta t} \quad (i = 1, 2, ..., N_P)$$
(35)

where N_p is the number of particles in the system.

The time evolution of solids dispersion coefficients is presented in Fig. S4 of the Supporting Information. After reaching the dynamic

equilibrium state, the horizontal dispersion coefficients (Dx) for char particles and oxygen carriers fluctuate around the mean values of 1.31 \times $10^{-4}~m^2/s$ and 6.67 \times $10^{-5}~m^2/s,$ respectively. The magnitude difference in dispersion coefficient between these two particle species lies in their distinct densities. Char particles with a smaller density are easier to fluidize, while oxygen carriers with a larger density are harder to fluidize. As illustrated in Fig. S4b of Supporting Information, the vertical solids dispersion coefficient (Dy) for char particles and oxygen carriers rapidly reaches peak values around 0.005 m²/s at the initial startup process and then reaches the dynamic equilibrium state in which the solids dispersion coefficients fluctuate around the mean values. The mean Dy for char particles and oxygen carriers are 3.51×10^{-4} m²/s and $2.11 \times 10^{-4} \text{ m}^2/\text{s}$, respectively. The Dy is two times the Dx for the char particles while the Dy is more than one order of magnitude larger than the Dx. This demonstrates that the introduced gas flow plays a dominant role in determining bed hydrodynamics.

Fig. 8 presents the mean solids dispersion coefficients under different operating parameters. Increasing gas inlet velocity significantly



Fig. 15. Time-evolution profiles of the contributions of different heat transfer modes for oxygen carrier, id = 10000: (a) conduction, (b) convection, (c) radiation, (d) reaction.

increases the dispersion coefficient, especially for the Dy. When the gas inlet velocity increases from 0.24 m/s to 0.36 m/s, Dy is two times larger than the Dx of both char particles and oxygen carriers. As the char to oxygen carrier mass ratio increases, the dispersion coefficients for char particles and oxygen carriers both first increase and then decrease. For the char particles, the Dx reaches the peak value with the char to oxygen carrier mass ratio of 3.0:100. However, for the oxygen carrier mass ratio of 2.4:100. When the ratio of char to oxygen carrier is 2.4:100, the Dy of the char particles and oxygen carriers reaches the maximum value, and the particles in the system achieve a better mixing extent.

4.3. Dimensionless number analysis

Particle Reynolds number (Re_p) is the ratio of the inertial force to the viscous force which can be used to characterize the fluid flow. Particle

Nusselt number (Nu_p) is the ratio of convection to conduction under the same conditions. These dimensionless numbers are closely related to the hydrodynamics and thermal behaviour in the CLG process. Fig. 9 shows the time evolution of the dimensionless number of char particles and oxygen carriers. The average dimensionless numbers Re_p and Nu_p are 0.96 and 2.66 for the char particles while 0.92 and 2.65 for the oxygen carriers, respectively. These two dimensionless numbers have a similar trend for both particle species.

Fig. 10 illustrates the relationship between the dimensionless number and the solid holdup of two particle species. According to the solid holdup and particle vertical slip velocity, particles can be divided into three different phases, i.e., a bubble phase, an intermedia phase, and an emulsion phase. With a lower solid holdup, the inter-phase drag force plays a dominant role thus particles in the bubble phase have higher vertical slip velocities. Particles in the emulsion phase with a higher solid holdup have smaller vertical slip velocities as they are dominated



Fig. 16. Contribution of different heat transfer modes under different gas inlet velocities: (a) char particles; (b) oxygen carriers.



Fig. 17. Contribution of different heat transfer modes under different char to oxygen carrier mass ratios: (a) char particles; (b) oxygen carriers.

by the inter-particle collision force. Gas-solid momentum exchanges can be significantly influenced by flow regimes and different Re_p can be observed. Although the movement and evolution of bubbles in the fluidized bed have been studied in previous studies, this work first characterized the relationship between bubbles and dimensionless numbers in a CLG system. With the increase of solid holdup and the decrease of the particle vertical slip velocity, the Re_p shows a gentle decrease. Gassolid momentum exchange also influences the heat and mass transfer, the investigation of which guides people to strengthen the heat and mass transfer in CLG systems.

Fig. 11 shows the frequency distribution of Re_p and Nu_p of two particle species. Most char particles with small and medium Re_p are distributed in the emulsion and intermedia phases, respectively. Large Re_p in the bubble phase occupies a small proportion. Similar to the Re_p , Nu_p shows a similar frequency distribution. The particle averaged Re_p and Nu_p of char particles are 0.90 and 2.64, respectively. Oxygen carriers in the bubble phase have the largest Re_p and Nu_p , and oxygen carriers in the emulsion phase have the smallest Re_p and Nu_p . The particle averaged Re_p and Nu_p for oxygen carriers are 0.79 and 2.60, respectively.

Fig. 12 illustrates the time-averaged dimensionless number distribution under different gas inlet velocities and different char to oxygen carrier mass ratios. Increasing gas inlet velocity promotes the slip velocity between gas and particles, thus increasing the time-averaged Re_p and Nu_p . As shown in Fig. 12b, for char particles, Re_p and Nu_p have the largest values with the char to oxygen carrier mass ratio of 2.4:100. In this ratio, the particles in the system can be better mixed. Increasing or decreasing this ratio, both Re_p and Nu_p decrease. For oxygen carriers, Re_p and Nu_p are much higher under the ratio of 3.0:100 and 3.6:100. Under the conditions with the ratio of 1.8:100 and 2.4:100, the particle-averaged Re_p and Nu_p are smaller than that with the ratio of 3.0:100 and 3.6:100.

4.4. Heat transfer contribution

The heat transfer of each particle bridges the hydrodynamics and





(c)

Fig. 18. Mass fraction distributions of gas species in the reactor: (a) H₂, (b) CO, (c) CO₂.

chemical reactions of dense gas-solid reaction flow. For example, a faster heat transfer rate leads to a faster temperature increase or decrease rate, further enhancing or inhibiting the heterogeneous reactions. Besides, a faster chemical reaction results in increasing gas generation or consumption, further enlarging or decreasing the local gas velocity and bed hydrodynamics. Thus, the heat transfer of bed particles plays a vital role in determining the hydrodynamics and chemical reactions in fluidized bed reactors. Fig. 13 shows the contribution of different heat transfer modes of char particles and oxygen carriers, with the absolute value of each heat transfer mode presented. The particleaveraged heating rate is divided by particle number. For char particles, the heating rates fluctuate around fixed values, which is caused by many factors such as bubble dynamics and inter-particle/phase interactions. The total particle-averaged heating rate is 0.0074 W and the heating rates from the four heat transfer modes are 0.0004 W, 0.0011 W, 0.0011 W, and 0.0048 W, respectively. The proportion of four heating rates in the total heating rate is 5.41%, 14.91%, 14.39%, and 65.29%, respectively. The heat of reactions dominates the heat transfer process of char particles. The convection and radiation perform weak influences and the influence of conduction is negligible. For the oxygen carriers, the total particle-averaged heating rate is 0.0019 W and the heating rates from the four heat transfer modes are 0.00015 W, 0.00045 W,

0.00039 W, and 0.00092 W, respectively. Similarly, the heat of reactions exerts the main influence on the heat transfer process with a contribution of 48.44%. The convection and radiation perform weak influences with the contribution of 23.46% and 20.33%, respectively. The conduction also performs the weakest influence with a concentration of 7.77%.

Fig. 14 and Fig. 15 show the contribution of different heat transfer modes of a specific char particle (id = 15000) and a specific oxygen carrier (id = 10000). Note that "id" represents the identification number of a specific particle, which is allocated at the initial simulation for the sake of tracking the trajectory and thermochemical evolution of this particle. In the CLG system, the conduction, convection, and radiation heating rate have positive and negative values for both the char particle and oxygen carrier. The positive value of heating rate corresponds to the heat absorption of the particle while the negative value of heating rate corresponds to the heat loss from the particle. However, for the heating rate of rection, the char particle always has the negative value, and the oxygen carrier always has the positive value. Thus, in current considers reactions, the char particle is cooled while the oxygen carrier is heated.

Fig. 16 presents the effects of gas inlet velocity on the heat transfer contribution. As shown in Fig. 16a, for char particles, changing gas inlet velocity has a slight influence on the four heat transfer modes.



Fig. 19. Mean mass fraction of gas species under different operating conditions: (a) gas inlet velocity; (b) char to oxygen carrier mass ratio.

Increasing the gas inlet velocity weakens the four heat transfer modes. For the oxygen carriers, increasing gas inlet velocity weakens conductive heat transfer. With the increase of gas inlet velocity, the heating rates from convection, radiation, and reaction first increase and then decrease and show the maximum values at the gas inlet velocity of 0.28 m/s. Fig. 17 shows the effects of the char to oxygen carrier mass ratio on the heat transfer contribution. Varying char to oxygen carrier mass ratio has a slight influence on the heat transfer of char particles and oxygen carriers. At the char to oxygen carrier mass ratio of 2.4:100, the heat contribution from conduction, radiation, and reaction for the char particles and oxygen carriers shows the minimum value. Although the proportion of each heat transfer mode (i.e., conduction, convection, and radiation) in fluidized beds without chemical reactions has been investigated in many studies [26,28], this work first quantified the contribution of each heat transfer mode (i.e., conduction, convection, radiation, and reaction) in a reactive CLG system.

4.5. Gas species

Fig. 18 shows the mass fraction distribution of H_2 , CO, and CO₂. A similar distribution of H_2 and CO can be observed. In the dense region, the H_2 and CO are mainly generated from the char gasification reactions R(1) and R(2). In the freeboard region, the H_2 and CO are mainly generated from the water–gas-shift reaction (R3). The char particles have a higher concentration near the wall, leading to the H_2 and CO concentrating in this region. The CO₂ is mainly generated from the water–gas-shift reaction R(3) and metal oxide reduction reactions R(4) and R(5). Good mixing of char particles and oxygen carriers promotes the reactions. Thus, the CO₂ is mainly generated in the upper part of the dense region where the two species have a good mixing performance. The wall restriction effect at the macro-scale and the rheology of the solid phase at the micro-scale lead to the asymmetrical distribution of gas particles and solid species in the reactor [21,28,51].

Fig. 19 shows the mean mass fraction of gas species under different gas inlet velocities and char to oxygen carrier mass ratios. As the gas inlet velocity increases, the concentration of CO, CO₂, and H₂ decreases. Increasing the gas inlet velocity promotes the coalescence between bubbles and enlarges the bubble volume, which decreases the gas-particle contact efficiency and weakens the gas–solid reactions (e.g., R1, R2, R3, and R4). As the char to oxygen carrier mass ratio increases, the concentration of gas products increases. The increase of char leads to

the increase of reactants concentration, which intensifies the reactions and increases the concentration of CO, CO_2 , and H_2 . At the ratio of 3.6:100, the concentration of CO_2 decreases, indicating the excess of the char. The excessive char enhances gas–solid reactions (e.g., R1 and R2) and more CO_2 can be converted into CO.

Fly ash generated in the char gasification process may deposit the surface of the oxygen carrier, blocking the pore structure and further decreasing the specific surface area, especially in high temperatures [52–54]. Neglection of the ash deposition in the current CFD-DEM framework is a trade-off between implementation convenience and model sophistication. In future work, it is necessary to design new reactors to alleviate ash deposition within appropriate temperatures and develop a more comprehensive model considering ash deposition.

5. Conclusions

In this work, a high-fidelity CFD-DEM reactive model is developed in which the multiphase flow, heat transfer (e.g., conduction, convection, radiation, and reaction heat), and chemical reactions (e.g., water–gas-shift, char gasification, metal oxide reduction) are all considered. The heat and mass transfer behaviour of the coal-based CLG process are numerically studied by the integrated model. The relationship between solid transport (e.g., mixing, dispersion) and thermochemical characteristics (e.g., heat transfer contribution) is analyzed at the particle scale. Conclusions can be drawn as follows:

- 1) The model developed in this work is confirmed to be reliable and reasonable in modelling the CLG process operating in a bubbling fluidization regime. The char particles have a higher concentration near the wall, leading to a higher concentration of H_2 and CO in this region. CO_2 is mainly generated in the upper part of the bed where the two particle species have a good mixing. As the gas inlet velocity increases, the concentration of CO, CO_2 , and H_2 decreases. As the char to oxygen carrier mass ratio increases, the concentration of gas products increases.
- 2) Increasing gas inlet velocity promotes particle mixing in the bed and avoids the formation of the dead zone. The vertical solids dispersion coefficients are much larger than the horizontal ones. The introduced gas flow plays a dominant role in determining the bed hydrodynamics. The average dimensionless numbers Re_p and Nu_p are 0.96 and 2.66 for char particles while 0.92 and 2.65 for oxygen carriers.

At a low solid holdup, the interphase drag force plays the dominant influence thus particles in the bubble phase have higher vertical slip velocities. The gas inlet velocity and char to oxygen ratio show weak influences on Re_{p} and Nu_{p} .

3) Conduction, convection, radiation, and reaction are the main heat transfer modes in the CLG process. The ratio of four heat transfer modes is respectively 5.41%, 14.91%, 14.39%, and 65.29% for char particles and 7.77%, 23.46%, 20.33%, and 48.44% for oxygen carriers. For the two species, the heat of reaction dominates the heat transfer process. Increasing the gas inlet velocity weakens the four heat transfer modes for the char particles. For the oxygen carriers, with the increase of gas inlet velocity, the conduction is weakened, but the convection, radiation, and heat of reaction first increase and then decrease, with the maximum values appearing at the gas inlet velocity of 0.28 m/s. Changing the char to oxygen carriers. With the char to oxygen carrier mass ratio of 2.4:100, the conduction, radiation, and heat of reaction for the char particles and oxygen carriers have the minimum values.

The present work provides a cost-effective tool for the in-depth understanding of heat and mass transfer mechanisms in the CLG process.

CRediT authorship contribution statement

Jiahui Yu: Data curation, Investigation, Methodology, Software, Writing - original draft. Shuai Wang: Conceptualization, Supervision, Writing - review & editing. Dali Kong: Software, Visualization. Kun Luo: Project administration, Conceptualization, Supervision, Writing review & editing. Jianren Fan: Funding acquisition, Supervisions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2023.128119.

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