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# Deliverable D3.4: Fuel conversion phenomena

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# **Table of Contents**

0	PREFACE				
	0.1	Disclaimer	4		
1	INTRO	DUCTION	. 5		
2	RESUI	TS	. 6		
	2.1	How to model char conversion	6		
	2.2	Momentum, mass, and heat transfer for reacting particles	6		
	2.3	Reaction mechanism for conversion of petcoke char	7		
	2.4	The effect of turbulence on char conversion in dilute flows	7		
	2.5	CFD simulations of CLC reactor systems	7		
3	SUM	/ARY	. 8		
APP		۹			
APP	ENDIX	Β			
APP		۵			
APP		D			



## 0 PREFACE

**CHEERS** conforms to the European Horizon 2020 Work Programme 2016 – 2017, 10. 'Secure, Clean and Efficient Energy', under the low-carbon energy initiative (*LCE-29-2017: CCS in Industry, including BioCCS*). The ambition is to improve the efficacy of  $CO_2$  capture in industry, and help ensuring sustainable, secure, and affordable energy.

The action involves a 2<sup>nd</sup> generation chemical-looping technology tested and verified at laboratory scale. Within the framework of CHEERS, the core technology will be developed into a 3 MW<sub>th</sub> system prototype for demonstration in an operational environment. This constitutes a major step towards large-scale decarbonisation of industry, offering a considerable potential for retrofitting industrial combustion processes.

The system prototype is based on a fundamentally new fuel-conversion process synthesised from prior research and development actions over more than a decade. The system will include heat recovery steam generation with CO<sub>2</sub> separation and purification, and it will comply with industrial standards, specifications and safety regulations. Except for CO<sub>2</sub> compression work, the innovative concept is capable of removing 96% of the CO<sub>2</sub> while eliminating capture losses to almost zero.

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## 0.1 Disclaimer

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# 1 Introduction

In the CHEERS project, petcoke is the main fuel to be operated in the 3  $MW_{th}$  CLC fluidised bed demo unit. Petcoke is characterised by a high content of carbon, low amount of volatiles, and therefore a low reactivity. It is necessary to develop a profound understanding of petcoke conversion (devolatilisation, oxidation and gasification) in order to determine the ideal fluidisation and fuel pre-treatment conditions. This is particularly so when the oxygen carriers have limited CLOU effects, which means that there will be only a limited amount of oxygen in the gas phase that can convert the petcoke char. In this work, the understanding of petcoke char conversion is expanded by combining numerical and experimental studies of char under different conditions.

Before we can consider doing numerical simulations of char conversion, it is a pre-requisite to have a numerical simulation tool that produce accurate and reliable results. In section 2.1 we therefore go ahead by presenting various approaches for performing numerical simulations for char conversion. In section 2.2, detailed descriptions of the momentum, mass and heat transfer rates from small particles embedded in a non-stationary fluid is obtained based on fully resolved Direct Numerical Simulations (DNS). In order to accurately model petcoke gasification with steam and carbon dioxide, in addition to oxidation with oxygen, a global reaction mechanism is required, as well as knowledge of the volatile composition. This has been obtained through lab scale experiments and is presented in section 2.3. The effect that turbulence has on the heat and mass transfer to reacting char particles is presented in section 2.4. Finally, results from CFD simulations of various reactor systems are presented in section 2.5.



# 2 RESULTS

# 2.1 How to model char conversion

Depending on the desired accuracy, size of particles, available CPU power and time, numerical conversion of char particles can be handled in a number of different ways. All involving various degrees of modelling and resolution. Together with colleagues at Stanford University we set out to produce a comprehensive review of available numerical approaches that is meant to be a starting point for all researchers and scientists intending to develop numerical codes for simulating char conversion. This review is now under consideration for publication in Progress in Energy and Combustion Science<sup>1</sup>.

# 2.2 Momentum, mass, and heat transfer for reacting particles

In order to be able to provide good models for later use in RANS simulations, detailed numerical studies of momentum, mass and heat transfer are carried out both for actually reacting particles<sup>2,3</sup> and for non-reacting particles with constant outflows, either in isothermal<sup>4</sup> or non-isothermal<sup>5</sup> environments. Knowledge about these phenomena is crucial in order to be able to accurately simulate char conversion in large scale Computational Fluid Dynamic (CFD) simulations. This work has primarily been done by three PhD candidates at Zhejiang University, Silesian University / NTNU and at Luleå University of Technology. The four papers that are already published are attached in Appendix A, three of them are open access articles, and one are reprinted with permission from Elsevier. In addition to these papers, the PhD student at Luleå is currently working on two additional papers. One paper is related to the effect of multiple particles that interact with each other through their wakes, while the other paper is studying reacting particles where the porous reactions are actually accounted for – not just the reactions at the outer surface. By simulating the reactions that occur in the real porous char structure, things like the Thiele modulus and pore size evolution can be accounted for and compared with current models for point particle simulations. This will serve as a good test of the accuracy of such models under various conditions.

<sup>&</sup>lt;sup>1</sup> Haugen, N. E. L., Ka Yan Loong, B. and Mitchell, R. E., Numerical approaches for thermochemical conversion of char, Under review for publication in Progress in Energy and Combustion Science

<sup>&</sup>lt;sup>2</sup> Zhang, H., Luo, K., Haugen, N. E. L., Mao, C. and Fan, J., Drag force for a burning particle, *Combustion & Flame* (2020) **217**, 188-199

<sup>&</sup>lt;sup>3</sup> Karchniwy, E., Haugen, N. E. L. and Klimanek, A., A numerical study on the combustion of a resolved carbon particle, *Combustion & Flame* (2022) **238**, 111880

<sup>&</sup>lt;sup>4</sup> Jayawickrama, T. T., Haugen, N. E. L., Babler, M. U., Chishty, M. A. and Umeki, K., The effect of Stefan flow on the drag coefficient of spherical particles in a gas flow, *Int. J. of Multiphase Flow* (2019) **117**, 130-137

<sup>&</sup>lt;sup>5</sup> Jayawickrama, T. T., Haugen, N. E. L., Babler, M. U., Chishty, M. A. and Umeki, K., The effect of Stefan flow on Nusselt number and drag coefficient of spherical particles in non-isothermal gas flow, *Int. J. of Multiphase Flow* (2021) **140**, 103650



# 2.3 Reaction mechanism for conversion of petcoke char

In order to model petcoke conversion, detailed knowledge about the reactions of pet-coke with oxygen, carbon dioxide and steam at temperatures between 750 and 1100 C is required. The reactivity of these reactions is presented in a paper written by Silesian University of Technology<sup>6</sup> and collaborators. Here, they use a custom-built test rig that enable measurements of the mass loss of the fuel samples and the composition of the released gases. From the measurements, a global reaction mechanism has been developed. The published paper is attached in Appendix B.

# 2.4 The effect of turbulence on char conversion in dilute flows

When performing simulations of the flow dynamics in large-scale combustion facilities, the scale separation between the largest and the smallest spatial scale in the system is so large that it is not possible to resolve the smallest scales. This typically corresponds to the smallest scales of the turbulence, in addition to the internal structure of flames. Therefore, for all RANS simulations, the effect that turbulence has on the heat and mass transfer to reacting char particles must be modelled. For this to be done correctly, two effects of turbulence must be included: 1) the enhancement of the heat and mass transfer due to turbulence-induced relative velocity between particles and fluid and 2) reduction of the heat and mass transfer due to turbulence-induced particle clustering. The effect of these two phenomena is investigated for real burners in the paper of Karchniwy et al.<sup>7</sup>, which is attached in Appendix C.

# 2.5 CFD simulations of CLC reactor systems

CFD simulations of the 3 MW demo unit has been performed by IMFT in Toulouse and the PostDoc candidate Liyan Sun, using the Neptune CFD code. First, the 150kWth CLC pilot unit at SINTEF ER was simulated, with both non-reacting<sup>8</sup> and reacting simulations, using a detailed description of petcoke reactivity. Extensive pressure measurements giving reactor pressure profiles were used to indirectly calculate particle concentrations and inventory throughout the reactor system. The results were then used for model validation. A large cold flow model of the 3 MW demo unit was constructed and operated in the early phase of the project. The CFD model was further validated by comparing simulation results with experimental measurements of this cold flow model. Then, the validated CFD model is used to simulate the 3 MW CLC demonstration unit. One relevant paper is attached in Appendix D. In addition, three more papers are in the pipeline.

<sup>&</sup>lt;sup>6</sup> Korus, A., Klimanek, A., Sladek, S., Szlek, A., Tilland, A., Bertholin, S. and Haugen, N. E. L., Kinetic parameters of petroleum coke gasification for modelling chemical-looping combustion systems, *Energy* (2021) **232**, 120935

<sup>&</sup>lt;sup>7</sup> Karchniwy, E., Haugen, N. E. L., Klimanek, A., Langørgen, Ø. and Sladek, S., The effect of turbulence on mass transfer in solid fuel combustion: RANS model, *Combustion & Flame* (2021) **227**, 65-78

<sup>&</sup>lt;sup>8</sup> Sun, L., Masi, E., Simonin, O., Langørgen, Ø., Saanum, I. and Haugen, N. E. L., Effect of wall boundary conditions on 3D hydrodynamic numerical simulation of a CLC unit with dual circulating fluidized-bed reactors, 13'th International conference on fluidized bed technology CFB-13



## 3 SUMMARY

In task 3.4 of CHEERS, a large number of detailed studies related to conversion of char and petcoke in general, and the relation to CLC units in particular, have been performed. The results from these studies are presented in a number of papers, which are either included as appendices, referenced, in the pipeline of being published or soon to be submitted for publication. An overview of all papers is given in the table below.

No.	Paper	Published	Submitted for publication	To be submitted for publication	Conference proceedings	Attached in Appendix No.
1	Haugen, N. E. L., Ka Yan Loong, B. and Mitchell, R. E., Numerical approaches for thermochemical conversion of char, Under review for publication in Progress in Energy and Combustion Science		x			
2	Zhang, H., Luo, K., Haugen, N. E. L., Mao, C. and Fan, J., Drag force for a burning particle, <i>Combustion &amp; Flame</i> (2020) <b>217</b> , 188-199	x				А
3	Karchniwy, E., Haugen, N. E. L. and Klimanek, A., A numerical study on the combustion of a resolved carbon particle, <i>Combustion &amp; Flame</i> (2022) <b>238</b> , 111880	x				A
4	Jayawickrama, T. T., Haugen, N. E. L., Babler, M. U., Chishty, M. A. and Umeki, K., The effect of Stefan flow on the drag coefficient of spherical particles in a gas flow, <i>Int. J. of Multiphase Flow</i> (2019) <b>117</b> , 130-137	x				A
5	Jayawickrama, T. T., Haugen, N. E. L., Babler, M. U., Chishty, M. A. and Umeki, K., The effect of Stefan flow on Nusselt number and drag coefficient of spherical particles in non-isothermal gas flow, <i>Int. J. of Multiphase Flow</i> (2021) <b>140</b> , 103650	x				A
6	Korus, A., Klimanek, A., Sladek, S., Szlek, A., Tilland, A., Bertholin, S. and Haugen, N. E. L., Kinetic parameters of petroleum coke gasification for modelling chemical-looping combustion systems, <i>Energy</i> (2021) <b>232</b> , 120935	x				В
7	Karchniwy, E., Haugen, N. E. L., Klimanek, A., Langørgen, Ø. and Sladek, S., The effect of turbulence on mass transfer in solid fuel combustion: RANS model, <i>Combustion &amp; Flame</i> (2021) <b>227</b> , 65-78	x				С



8	Sun, L., Masi, E., Simonin, O., Langørgen, Ø., Saanum, I. and Haugen, N. E. L., Effect of wall boundary conditions on 3D hydrodynamic numerical simulation of a CLC unit with dual circulating fluidized-bed reactors, 13'th International conference on fluidized bed technology CFB-13				x	D
9	Sun et al., Three-dimensional unsteady numerical simulation of a 150 kWth full-loop chemical looping combustion pilot with biomass as fuel: a hydrodynamic investigation			x		
10	Sun et al., Reactive simulation of 150 kW CLC unit			х		
11	1 Sun et al., Simulations of 3MW CLC demo unit					
12	Jayawickrama et al., The effect of Stefan flow on the drag coefficient of closely located spherical particles in isothermal gas flow			x		
13	Jayawickrama et al., Reactions in the porous structure of char particles			х		



## APPENDIX A

Four articles are attached in Appendix A, related to chapter 2.2 on momentum, mass, and heat transfer for reacting particles. See summary table in chapter 3 for details.

The first article is reprinted from Combustion & Flame, Vol 217, Zhang, H., Luo, K., Haugen, N. E. L., Mao, C. and Fan, J., Drag force for a burning particle, Pages 188-199, Copyright (2020), with permission from Elsevier.

The three next articles are open access articles.

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# Drag force for a burning particle

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#### ABSTRACT

Fully-resolved simulations of a burning char particle are performed to understand the effects of chemical reactions on the drag force by using the ghost cell immersed boundary method. The momentum, heat and mass transfers at the interface are all considered. Reactive particle with different reaction rates, temperatures and diameters are simulated and compared with a non-reactive adiabatic particle and a particle with an outflow. The results show that both the heterogeneous reactions and the gaseous reactions increase the drag force, which is converse to the effect observed for a non-reactive particle with a pure outflow. This difference indicates that the species and temperature distributions caused by the chemical reactions around the particle play an important role in shaping the drag force. To consider these effects, the Stefan flow Reynolds number and the non-dimensional gaseous reaction rate are introduced to formulate a new drag force correlation for a burning particle based on the fully-resolved simulations. Good performance of the correlation has been demonstrated in the current conditions, and more evaluation might be required for future work.

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## 1. Introduction

In numerical simulations of multiphase flows, accurate description of the momentum, heat and mass exchanges between the carrier phase and the dispersed phase is essential. Therefore, various models have been developed to close the conservation equations. The interphase momentum exchange is usually described by the drag force coefficient, which is generally regarded as a function of the Reynolds number. Numerous researches have studied the drag force and relevant empirical drag correlations for cold-state flows. For instance, Tritton [1] and Dennis and Chang [2] measured the drag force of a circular cylinder at low and high Reynolds number, respectively, and proposed corresponding drag force correlations. The empirical drag force correlation for a spherical particle was proposed by Clift et al. [3]  $(C_D = 24(1 + Re_p^{0.687})/Re_p)$  and has been widely used for multiphase flow simulations. Another widely used drag force correlation was put forward by Schiller and Nauman [4]. These drag correlations are of great importance for describing the momentum transfer in dilute cold multiphase flows [5–7].

However, the above drag correlations are influenced by chemical reactions and usually not applicable for reactive multiphase flows. For a reactive particle, one of the difficulties to draw a gen-

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eral drag correlation is that the wall-normal velocity of the particle is often not zero. As a result, the flow Reynolds number is not enough to represent the drag force. The effect of the non-zero wall-normal velocity has been discussed in the previous studies on porous particles and outflow particles. For a porous particle, the fluid phase can penetrate into the particle, leading to a nonzero velocity [40,41]. The governing equation of the flow inside the porous particle follows the Darcy-Brinkman-Forchheimer extended model [8], and the normal component of the velocity at the rear of the surface is called as "base bleed" [9]. According to the studies of Bhattacharyya et al. [10] and Yu et al. [11], the base bleed at the rear of the cylinder has some interaction with the shear layer, making the recirculation wake detach from or penetrate into the cylinder. Therefore, the surface ratio and particle porosity were used to quantify the effect of the porosity in the drag correlation [12].

A particle with outflow has previously been studied as a simplification of an evaporating droplet or a solid fuel particle with a Stefan flow [13], and the outflow velocity condition was implemented at the surface without considering the effect of the species. A number of studies [13–15] show that the outflow tends to reduce the drag force. To take this effect into consideration, a blowing correlation was introduced in the study of Stöllinger et al. [16]. The Stefan flow Reynolds number was also used in the drag correlation [17]. In the study of Higuera [18], a gasification term was added to the drag force calculation besides the pressure and the friction





terms. Interestingly, the recent study of Luo et al. [19] showed that the chemical reactions might increase the drag force of a reactive particle, compared with a an inert particle. Moreover, the properties of the flow in the vicinity of the particle also influence the drag force. Kurose et al. [20] studied the change in drag force due to the sphere being either heated or cooled. It was found that the temperature difference between particles and the inlet flow influenced the drag force, and a heated particle tends to have a larger drag coefficient. The study of Nagata et al. [21] showed that the temperature changes the drag force mainly by altering the kinematic viscosity coefficient in the vicinity of the sphere.

Several recent researches also involved surface reactions of solid fuels [22–24] (e.g. pulverized coal combustion and biomass combustion) and droplet evaporation [25,26]. However, they all focused on the heat and mass transfer properties on the interface, and up to now, the drag force of reactive particle has not yet been well studied. Heterogeneous reactions influence the drag force not only through the Stefan flow. When the momentum, heat and mass transfer occur simultaneously, the drag force of a reactive particle may show a more complex behavior. To explore this phenomenon, particle-resolved simulations of a single burning char particle are performed with the immersed boundary method in the present work. The influence of the heterogeneous and gaseous reactions on the drag force during the process of char combustion is investigated in detail.

The remainder of this paper is structured as follows. The numerical method and simulation setup are described in Section 2. The mechanism of how reactions influence the drag force is discussed in Section 3. The effects of heterogeneous reactions, the gaseous reaction, and the particle temperature are studied, respectively. A new drag force correlation for a burning char particle is also formulated. The last section is devoted to the conclusions.

#### 2. Numerical approach and simulation setup

#### 2.1. Numerical method

Following the study of Luo et al. [19], a high-order finite difference solver [27,28] is improved and used in the present work. The governing equations of gas phase read

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \boldsymbol{u} = \boldsymbol{0},\tag{1}$$

$$\frac{Du}{Dt} = \frac{1}{\rho} (-\nabla p + \nabla \cdot (2\rho \nu S)), \qquad (2)$$

$$\rho \frac{DY_k}{Dt} = -\nabla \cdot J_k + \dot{\omega}_k,\tag{3}$$

$$\left(c_{p} - \frac{R}{\overline{W}}\right)\frac{D\ln T}{Dt} = \sum_{k} \frac{DY_{k}}{Dt}\left(\frac{R}{W_{k}} - \frac{h_{k}}{T}\right) - \frac{R}{\overline{W}}\nabla \cdot u + \frac{2\nu S^{2}}{T} - \frac{\nabla \cdot q}{\rho T}.$$
(4)

In the above set of equations, $D/Dt = \partial/\partial t + u \cdot \nabla$  represents the convective derivative. The traceless rate of train tensor is given by  $S_{ij} = \frac{1}{2}(\partial u_i/\partial x_j + \partial u_j/\partial x_i) - \frac{1}{3}\delta_{ij}\nabla \cdot u$ , while *J* is the diffusive flux, and  $\dot{\omega}_k$  represents the reaction rate of species *k*. The reaction rates and the diffusive flux are calculated according to the method mentioned in [28]. Although the energy equation uses  $\ln T$  instead of *T*, it can be easily transformed into the commonly used form by modifying  $\frac{D\ln T}{Dt}$  into  $\frac{1}{T}\frac{DT}{Dt}$  and using  $\frac{Dp}{Dt}$  instead of expanding it based on the equation of state [29]. In the energy equation, the enthalpy is given by *h* while *W* is the molar mass of the gas phase and *q* is

the heat flux. The ideal gas equation of state, given by

$$p = \frac{\rho R I}{\overline{W}} \tag{5}$$

is used to close the governing equations.

Because of the heterogeneous reactions at the char particle surface, the velocity, temperature and the species mass fraction at the char surface are affected. It is essential to determine these boundary conditions properly. The mass transfer at the interface is a balance of the convective flux, diffusive flux and heterogeneous reactions, which is given by

$$\bar{n} \cdot \left[ \rho Y_k (\bar{V}_k + u_{Stefan}) \right] = \dot{m}_k \tag{6}$$

where  $\bar{n}$  represents the outward wall-normal unit vector, and  $\dot{m}_k$  is the mass production rate of the *k*th species. The diffusion velocity of the *k*th species is related to the gradient of the species mass fraction as

$$\bar{V}_k = \frac{1}{X_k \overline{W}} \sum_{j \neq k} W_j D_{k,j} \nabla X_j \tag{7}$$

while  $u_{Stefan}$  represents the velocity of the Stefan flow. The total species diffusion flux is zero

$$\sum_{k} V_k Y_k = 0. \tag{8}$$

Based on mass transfer balance at the surface, the Stefan flow velocity can be formulated as

$$\overline{n} \cdot u_{Stefan} = \frac{1}{\rho} \sum_{k=1}^{K_g} \dot{m}_k \ . \tag{9}$$

The boundary velocity of the particle is a combination of particle shrinking velocity and the Stefan flow velocity, which is given by

$$u_{IB} = u_{Stefan} + v_n = u_{Stefan} + \frac{\int_{surf} \dot{m}_c ds}{s\rho_c}.$$
 (10)

Here *s* is the surface area of the particle, and  $\rho_c$  is the density of the char particle.

In this study, the temperature gradient within the particle is neglected. Therefore, the heat transfer at the interface contains the diffusive flux, radiation, reaction heat and the heat conduction from the outside of the particle. The particle energy balance is then given by

$$Vc_{p,C}\frac{dT_p}{d\tau} = \int_{surf} \left( -\sigma \varepsilon (T_p^4 - T_0^4) + \sum_{k=1}^K \dot{m}_k h_k + \bar{n} \cdot \lambda \nabla T_{gas} \right) ds$$
(11)

where *V* is the volume of the particle,  $T_0$  represents the temperature of the incoming flow, and  $c_{p, C}$  is the heat capacity of the char particle. In the radiation term,  $\varepsilon$  is the emissivity coefficient, and  $\sigma$  is the Stefan–Boltzmann constant. Finally,  $\dot{m}_k$  and  $h_k$  are the reaction rate and enthalpy of species *k*, respectively. The right hand side (RHS) of the equation is an integral over the particle surface. In addition, the pressure gradient at the surface should be zero because of the no-penetration condition.

The improved ghost cell immersed boundary method [30] can be used to enforce the boundary conditions of velocity, species concentrations, temperature, and pressure. This method is of a second-order accuracy. For more detailed description and validation of the method for char combustion, please refer to the previous research [19].

#### 2.2. Assumptions and simplifications

In this study, a semi-global heterogeneous reaction mechanism of char conversion and a homogeneous reaction of CO oxidation

Table 1Kinetic Parameters of chemical reactions.

Chemi	cal reaction	В	E (J/mol)	Reference
(R1) (R2)	$\begin{array}{l} 2C(s) + O_2(g) \rightarrow 2CO(g) \\ C(s) + CO_2(g) \rightarrow 2CO(g) \end{array}$	$1.97 \times 10^{7}$ $1.291 \times 10^{5}$	$1.98 \times 10^{5}$ $1.91 \times 10^{5}$	Zhang et al. [31] Zhang et al. [31]
(R3)	$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$	$2.24\times10^{12}$	$1.6742 \ \times \ 10^{5}$	Turns [32]



Fig. 1. Schematic of the computational domain.

are used for the simulation. The heterogeneous reactions are essentially from the study of Zhang et al. [31], which have also been validated in our previous study [19]. The kinetic parameters of chemical reactions are shown in Table 1.

Several simplifications and assumptions are made to simplify the task and focus on the key problem. Firstly, the solver we used is fully transient, but it will take too much time to resolve the whole conversion process of the char particle. Therefore, the pseudo-steady-state (PSS) assumption [33] is utilized, according to which we can use the steady condition to represent the transient burning char particle if the characteristic time scales of the convection and diffusion are much shorter than the conversion time scale of the char particle. As a result, the particle temperature and radius can be fixed, and the simulation can reach the quasi-steady state faster. Secondly, the particle is fixed in the flow field and the inlet flow is uniform, which has been a common assumption in many previous studies [34-37]. Thirdly, the gas phase only contains N<sub>2</sub>, O<sub>2</sub>, CO, and CO<sub>2</sub>, and the effect of water gas shift is neglected. The kinematic viscosity is calculated using Wilke's method [38] which considers the effect of species, instead of the Sutherland's temperature dependence viscosity [39].

The drag force on the particle contains two parts, namely the pressure and the friction contributions, as given by the two terms on the RHS in the equation below

$$F_D = \int_A P dA + \int_A \tau \, dA \ . \tag{12}$$

#### 2.3. Simulation setup

In the simulations, a two-dimensional cylindrical char particle, with diameter  $D_p$ , is fixed in the domain. The computational domain has a size of  $24D_p \times 16D_p$ , and the position of the particle is shown in Fig. 1. The grid resolution is set as  $\Delta x = 1/50D_p$ . The Navier-Stokes Characteristic Boundary Condition (NSCBC) [45] is used at the inlet and outlet boundaries. Meanwhile, periodic boundary conditions are used in the spanwise direction. Parameters of the incoming flow and the char particle are summarized in Table 2. Different cases of particle Reynolds numbers and particle temperatures are analyzed. Here the particle Reynolds number is

ladie 2				
Parameters	of the	simulation	conditions.	

Parameter	Values
p <sub>0</sub>	1.01 × 10 <sup>5</sup> Pa
Y <sub>O2</sub>	23% (diluted by N <sub>2</sub> )
T <sub>inlet</sub>	1500 K
Re	5, 10, 20
T <sub>particle</sub>	1400 K, 1500 K, 1600 K, 1800 K
D <sub>p</sub>	100 μm, 200 μm, 400 μm
B	0.1B <sub>0</sub> , 0.5B <sub>0</sub> , 1.0B <sub>0</sub> , 1.5B <sub>0</sub>

given by

$$Re = \frac{UD_p}{\upsilon}.$$
(13)

Here, *U* and v are the velocity and kinematic viscosity coefficient of the incoming flow. In addition, to analyze the effect of reaction rate, we arbitrarily change the pre-exponential factor (denoted by *B* in Table 2) of the heterogeneous reactions. *B*<sub>0</sub> refers to the original value of pre-exponential factor of the heterogeneous reactions. At an identical Reynolds number, different diameters cause the variation of the time scale of reactions and diffusion. Therefore, cases with different diameters are also simulated. Each case is simulated until it reaches a quasi-steady state.

#### 3. Results and discussion

#### 3.1. Flow pattern

As mentioned in Section 2.1, the heterogeneous reactions at the surface of the particle result in a Stefan flow, leading to a nonzero normal velocity. This nonzero normal velocity will change the structure of the particle boundary layer. As shown in Fig. 2, when positive wall-normal velocity occurs, the stagnation point at the front of the particle becomes detached from the surface. The position of the stagnation point is farther from the surface when the Stefan flow increases.

The specific separation angle at the surface is hard to be determined because of the Stefan flow. Meanwhile, the recirculation wake structure also changes. According to the simulations of Bhattacharyya et al. [10], the critical Reynolds number of a cylindrical particle when the separation point first occurs is about 7. This criterion is no longer valid for a cylindrical reactive particle. The Stefan flow restrains the formation of the recirculation wake so that the recirculation wake is detached from the particle. The critical Reynolds number where the recirculation wake occurs depends on the Stefan flow at the surface.

To quantify the effect of the Stefan flow, an average Stefan flow Reynolds number over the particle surface is defined and will be discussed in the next section, which is given by

$$Re_{stefan} = \frac{D_p \int_{\text{Surf}} \sum_{k=1}^{K_g} \dot{m}_k ds}{\rho \upsilon},$$
(14)

where  $\rho$  and  $\nu$  are the density and kinematic viscosity coefficient of the incoming flow, and  $\dot{m}_k$  is the reaction rate of the *k*th species on the surface (kg/m<sup>2</sup>s).



**Fig. 2.** The vorticity and flow pattern around the particle with different heterogeneous reaction rates ( $T_{particle} = 1500 \text{ K}$ ,  $D_p = 400 \text{ }\mu\text{m}$ , Re = 20).

In Fig. 2, the length of the wake becomes shorter and the front of the wake is further from the particle when reaction rates increase. The so-called 'base bleed' of the porous particle has the analogous effect on the recirculation wake [11]. The formation of the recirculating wake can be explained using Leal and Acrivos's entrainment-detrainment mechanism [9]. According to the mechanism, the wake at the rear of the bluff body is formed because the fluid entrained inside the shear layer gets separated from the shear layer and reverses itself again to meet the entrainment need of the shear layer. But for a burning char particle, the wall-normal velocity meets the entrainment demand of shear layer, hence the recirculating wake is weakened.

### 3.2. Effect of reactions

In the process of char conversion, heterogeneous and gaseous reactions happen simultaneously. Not only the flow pattern is influenced, but also the fluid properties are affected because of the non-uniform temperature and species distribution around the particle. In this section, the effects of heterogeneous and gaseous reactions are analyzed. To simplify the analysis, the particle temperature is set to be equal to the temperature of the incoming flow.

### 3.2.1. Heterogeneous reactions

In several previous studies, the effects of heterogeneous reactions and evaporation are simplified as a pure outflow [15,42]. Hence, the effect of species distribution resulting from relative rate of reaction and diffusion, is neglected. It was reported that the Stefan flow has little influence on the pressure but attenuates the friction, and thus tends to weaken the drag force [13-15,17]. To investigate whether heterogeneous reactions have the same effect, a comparison of particles with heterogeneous reactions and particles with pure outflow is performed. Fig. 3 shows how the drag, pressure and friction coefficients vary with the Restefan for a reacting char particle and a non-reacting particle with outflow. For the reacting char particle, the drag force increases slightly with the increasing reaction rate (increasing the Stefan flow). This is in contrast to what is found for the non-reacting particle with an outflow, in which increase in Restefan results in an obvious decrease in the drag coefficient. At the same Stefan flow Reynolds number, the friction coefficient of the reactive particle is slightly higher than that of the particle with the pure outflow. As a result, the difference in drag force is mainly resultant from the difference in the pressure contribution which is associated with the species profiles caused by the heterogeneous reactions. Hence, it is apparent that a particle with heterogeneous reactions cannot be simplified as just



**Fig. 3.** The comparison of the particle with heterogeneous reactions and the particle with outflow ( $D_p = 400 \ \mu m$ , Re = 5,  $T_{particle} = 1500 \ K$  for the char particle). (a) Drag force coefficient (b) Pressure and friction coefficients.



Fig. 4. Local pressure and friction coefficient distribution of particle with different heterogeneous reaction rates (T<sub>particle</sub> = 1500 K, D<sub>p</sub> = 400 µm, Re = 5).



Fig. 5. Temperature contours in the neighborhood of particles with different reaction rates ( $T_{particle} = 1500$  K,  $D_p = 400$  µm, Re = 5).

a particle with an outflow. The drag force of a particle with heterogeneous reactions might be obviously larger than that of a particle with an outflow.

### 3.2.2. Gaseous reaction

The species distribution and fluid properties are also affected by the gaseous reaction. This effect is little mentioned in previous studies of the particle drag force. According to the above discussion in Section 3.2.1, the effect of species distribution offsets the effect of the outflow on the drag force. Similarly, the gaseous reaction makes this effect more pronounced.

Based on the definition of drag force (as shown in Section 2.2), here we define a local pressure coefficient and a local friction coefficient to describe the distribution of the drag force components;

$$C_{P\_local} = \frac{(p - p_{front})}{1/2\rho U^2}, C_{\tau\_local} = \frac{\nabla \cdot (2\rho \nu S) \cdot \bar{x}}{1/2\rho U^2}$$
(15)

where  $p_{front}$  is the pressure at the front point of the cylinder surface in the streamwise direction, and  $\overline{x}$  is the streamwise unit vector. The density and the streamwise velocity of the incoming flow are given by  $\rho$  and U, respectively. In the following discussions,  $\theta$ 

refers to the surface angle of the cylinder, and  $\theta = 0$  refers to the front of the cylinder toward the incoming flow.

As the left panel of Fig. 4(a) shows, at the rear of the particle, cases with gaseous reactions have larger pressure drops. According to the ideal gas state equation, the pressure is related to the density, molar mass and temperature of the gas phase, but according to the definition of the pressure coefficient, the density term can be roughly reduced. As a result, the variation of the pressure coefficient is mainly associated with the variation of temperature and the molar mass. Fig. 5 shows that since convection dominates the transport in the vicinity of the particle, CO tends to be consumed at the rear, yielding a high temperature region at a certain distance from the particle. However, the temperature difference between the boundary temperature and the particle temperature is less than 1 K (within 0.067% of the particle temperature) according the simulation results. Considering this negligible difference of temperature, one concludes that the non-uniformity of molar mass plays an important role in the remarkable drop of the pressure coefficient at the rear of the particle. Fig. 6 shows that with the reaction rate increasing, the CO concentration increases at the front of the particle. But because of the gaseous reaction, CO is transformed into CO2 at the rear region. This change of species profile around the particle finally alter the density and molar mass



**Fig. 7.** Normalized density and molar mass distribution along the particle surface ( $T_{particle} = 1500$  K,  $D_p = 400 \mu m$ , Re = 5, normalized by the density and molar mass of the incoming flow).

profiles around the particles, as shown in Fig. 7. The molar mass of the gas phase increases at the back side of the particle, which accounts for the increase of the pressure drop.

Meanwhile, Fig. 4(b) shows that the local drag due to friction is slightly different from the non-reactive particle at the front and rear of the particle, but the friction at the side of the particle is almost the same. For 0 <  $\theta$  < 30°, the friction force of a reactive particle is higher than that of a non-reactive particle. To explore the underlying physics, the kinematic viscosity distribution normalized by the parameter of the incoming flow is shown in Fig. 8. It is found that the kinematic viscosity in the boundary layer around the particle is lower than that of the incoming flow and the kinematic viscosity decreases with the increase of the surface angle of the cylinder. This is related to the species change around the particle, especially the accumulation of CO<sub>2</sub> at the rear of the particle. As the viscosity around the reactive particle is lower for  $0 < \theta < 30^{\circ}$ , the velocity gradient must be higher. Actually, because the streamwise velocity component of the Stefan flow in this region is opposite to the incoming flow, the velocity gradient will definitely be higher. For similar reason, in the region of  $150^{\circ} < \theta < 180^{\circ}$ , the reactive particle has a lower velocity gradient, so the friction is lower. Meanwhile, as Fig. 9 shows, the oxidation of CO causes a high temperature region around the particle, and therefore the kinematic viscosity coefficient increases. As a result, the velocity distribution is also different from that of a particle with pure Stefan flow, which influences the friction at the surface too. In addition, it is interesting to find that the normalized temperature and kinematic viscosity peak at around a location with a distance of  $D_p$  from the cylinder, in which gaseous reaction happens.



**Fig. 8.** Kinematic viscosity coefficient distribution around a particle with different reaction rates normalized by the viscosity at the inlet ( $T_{particle} = 1500$  K,  $D_p = 400 \ \mu\text{m}$ , Re = 5).

In many previous studies on the drag force of particle with outflow [13,14], *Re<sub>stefan</sub>* is used as the only variable to describe the change in the drag force. However, when the gaseous reaction is introduced into the system, the situation becomes more complicated. Fig. 10 shows the correlations between the drag force coefficient and other variables. The symbol represents the simulation results, while the solid lines are obtained using quadratic polynomial fitting. When the Reynolds number and particle diameter are fixed,



**Fig. 9.** Normalized temperature and kinematic viscosity coefficient (normalized by the values at the inlet) distribution as a function of normalized radial distance from the particle surface at  $\theta = 90^{\circ}$  ( $T_{particle} = 1500$  K,  $D_p = 400$  µm, Re = 5).



**Fig. 10.** Correlations between drag force coefficient and other variables (a) Variation of drag force coefficient with particle diameter and the Stefan flow Reynolds number when Re = 5 (b) Variation of drag force coefficient with the Reynolds number and the Stefan flow Reynolds number when  $D_p = 400 \mu m$ . (normalized by the drag force of the inert particle at the same Reynolds number).

the drag force has a quadratic dependence on  $Re_{stefan}$ . However, when the diameter of the particle is changed,  $Re_{stefan}$  is no longer enough to describe the drag force, as demonstrated in Fig. 10(a). In addition, it is found that the drag force of the reactive particle with  $D_p$ =100 µm is almost equal to that of the non-reactive particle ( $Re_{stefan}$ =0), indicating that the heterogeneous and gaseous reactions can even be neglected when the diameter is relatively small. The reason is that when the diameter becomes smaller, the time scales of convection  $\tau_{conv} = D_p/U$  and diffusion  $\tau_{diff} = D_p^2/D_{CO}$  both decrease so that the accumulation of products at the rear of the particle is attenuated. Fig. 10(b) confirms that when the particle diameter of 400 µm is fixed, the drag force coefficient correlates well with the Reynolds number and the Stefan flow Reynolds number. The drag force coefficent increases with the Stefan flow Reynolds

number, but decreases with the Reynolds number when the Stefan flow Reynolds number is fixed. This also suggests that the effect of chemical reactions can be weakened by the convection. Fig. 11 presents the contours of  $Y_{CO}$  in the neighborhood of the particle with different diameters at the same Reynolds number. It is clear that the species of CO shows different profiles around the particle. For the particle with a larger diameter, CO is burnt at the surface, and the concentration is lower. The smaller particle shows higher char consumption rate, but CO tends to be transported and burnt far from the particle because of the stronger convection. These results suggest that besides the Reynolds number and the Stefan flow Reynolds number, other parameters related to gaseous reaction also influence the drag force of a burning particle.



**Fig. 11.**  $Y_{CO}$  contours in the neighborhood of the particle with different diameters ( $T_{particle} = 1500$  K, Re = 5,  $B = B_0$ ).



**Fig. 12.** Variation of drag force coefficient of a reactive particles with temperature  $(D_p = 400 \ \mu\text{m}, Re = 5, B = B_0)$ .

### 3.3. Effect of the particle temperature

When the particle temperature is different from the incoming flow, the change of fluid properties must be taken into account. According to the study of Kurose et al. [20], the main factor of influence is the viscosity. While when a reactive particle has a different temperature from the temperature of the incoming flow, not only the viscosity, but also the reaction rates are affected, leading to different characteristics from the heated/cooled non-reactive particle. This effect will be discussed in this section.

Four cases are simulated and the results are presented in Fig. 12. The incoming flow temperature is fixed (1500 K), and the temperatures of reactive particles are 1400 K, 1500 K, 1600 K, and 1800 K, respectively. With the increase of the particle temperature, chemical reactions are expected to be more intense. It can be seen that both the pressure and friction terms linearly increase with the enhancement of the particle temperature. As for local distribution, it was found that the pressure of the heated particle is higher than that of the adiabatic particle in the re-

gion of  $54^{\circ} < \theta < 108^{\circ}$ , while lower at the rear of the particle in the study of Kurose et al. [20]. The reason was attributed to the shift of the separation point. But for a reactive particle here, the effect of separation point is eliminated by the Stefan flow. As a result, this phenomenon could not be observed any more as shown in Fig. 13(a). The higher particle temperature leads to larger pressure drop at the wake region of the particle, similar to Fig. 4(a). For the friction distribution, it is interesting to note that the friction peaks around  $\theta$ =70° and the particle of higher temperature shows larger peak. This indicates that the stronger chemical reactions enhance the velocity gradient there as the kinematic viscosity is not obviously changed (Fig. 14).

#### 3.4. Drag force correlation for a burning particle

According to the analysis above, reactions cause a difference in species and temperature distributions around a burning particle, leading to a shift of drag force. To take this effect into consideration, new drag force correlation needs to be developed.



**Fig. 13.** Local pressure and friction coefficient distribution of particle with different temperatures ( $D_p = 400 \mu m$ , Re = 5,  $B = B_0$ ).



**Fig. 14.** Kinematic viscosity coefficient distribution around the particle with different temperatures ( $D_p = 400 \text{ } \mu \text{m}$ , Re = 5,  $B = B_0$ ).

For a burning char particle, besides the convection, the heat and mass transfer at the solid-fluid interface is related to three other processes, namely the heterogeneous reactions, the gaseous reaction and the diffusion. The effect of heterogeneous reactions is represented by the average char consumption rate on the surface, and the effect of gaseous reaction is described by using the reaction rate CO since only one gaseous reaction is involved in the present study. The process of diffusion is represented by the diffusion coefficient. According to the Buckingham  $\pi$  theorem [43], three more dimensionless variables can be deduced besides the Reynolds number and the temperature ratio. The temperature ratio is usually close to unity when char of pulverized coal particle burns in furnace. As a result, the average Stefan flow Reynolds number, the dimensionless gaseous reaction rate, and the diffusion Damköhler number are of relevance and can be expressed as follows

$$Re_{stefan} = \frac{\dot{m}_c D_p}{\rho \upsilon}, \ m_{CO}^* = \frac{\dot{m}_{CO} D_p}{\rho U}, \ Da_{diff} = \frac{\rho D_{CO}}{D_p^2 \dot{m}_{CO}},$$
(16)

where  $\rho$ , *U*,  $\upsilon$  are the density, streamwise velocity, and kinematic viscosity of the incoming flow, respectively. The char consumption rate is given by  $\dot{m}_c$ , while  $\dot{m}_{CO}$  is the CO reaction rate of the gaseous reaction at the boundary of the particle. For point-particle based simulations [46–48], the char consumption rate can be obtained by using a char combustion model, such as the single-film model [49] or the double-film model [50]. As the present work focuses on the effect of chemical reactions on the drag force, the diffusion Damköhler number will not be discussed in the next analysis.

For a cylindrical particle, the drag force coefficient has been measured for cold flows in previous studies. Here to show the performance of the code, the drag force coefficient of a cold inert cylindrical particle is calculated from the current particle-resolved simulations and compared with the experimental data of Tritton [1]. As show in Fig. 15, the predicted drag force coefficient agrees well with the experimental data. Non-linear least square fitting is further used to obtain the following correlation:

$$C_D = \frac{24}{Re} \left( 0.382 + 0.191 Re^{0.678} \right). \tag{17}$$

To consider the effect of chemical reactions, the average Stefan flow Reynolds number and the dimensionless gaseous reaction rate should be formulated into the correlation. From Fig. 10, it can be seen that  $C_D$  shows an approximately quadric dependence on  $Re_{stefan}$ . Assuming the similar quadratic behavior of  $\dot{m}_{co}$ , the correction for a burning particle can be formulated as below based



Fig. 15. Comparison of simulation data, experimental data [1], and Eq. (17).

on Eq. (17)  

$$C_{D} = \frac{24}{Re} \Big[ \Big( 0.382 + 0.191 Re^{0.678} \Big) + \Big( a_{1} Re_{stefan}^{2} + b_{1} m_{CO}^{*2} + c_{1} Re_{stefan} m_{CO}^{*} + d_{1} Re_{stefan} + e_{1} m_{CO}^{*} \Big) + \Big( a_{2} Re_{stefan}^{2} + b_{2} m_{CO}^{*2} + c_{2} Re_{stefan} m_{CO}^{*} + d_{2} Re_{stefan} + e_{2} m_{CO}^{*} \Big) Re^{0.678} \Big].$$
(18)

For a cold non-reactive particle, both  $Re_{stefan}$  and  $m_{CO}^*$  are 0, and the above equation is reduced to Eq. (17). To determine the constants in the above equation, non-linear least squares fitting of the particle-resolved results is performed. Finally, the correlation becomes

$$C_{D} = \frac{24}{Re} \Big[ (0.382 + 0.191 Re^{0.678}) + (1.373 Re_{stefan}^{2} + 16.715 m_{CO}^{*2} + 6.303 Re_{stefan} m_{CO}^{*} - 0.215 Re_{stefan} + 1.129 m_{CO}^{*}) - (0.144 Re_{stefan}^{2} + 26.530 m_{CO}^{*2} - 1.288 Re_{stefan} m_{CO}^{*} - 0.315 m_{CO}^{*}) Re^{0.678} \Big].$$
(19)

Fig. 16 shows the comparison of the drag force coefficient between the particle-resolved simulations and the fitted correlation at the Reynolds numbers of 5 and 10. The adjusted coefficient of determination  $R^2$  [44] of this correlation is 0.99. For all cases used for fitting, the maximum error occurs at Re = 5 with a value of 0.3%.

To validate the correlation, a posteriori analysis is performed and presented in Fig. 17. Five additional cases at the Reynolds

 Table 3

 Parameters of posterior cases

	-		
Case Re		$D_p \ (\mu m)$	Pre-exponential factor
1	7.5	200	B <sub>0</sub>
2	7.5	400	0
3	7.5	400	$0.5B_0$
4	7.5	400	1.0B <sub>0</sub>
5	7.5	400	$1.5B_0$

number of 7.5 are used. Parameters of these cases are shown in Table 3, including different reaction rates and diameters. Results show that these posterior cases are also in good agreement with the correlation. The maximum error is about 1.5%, which occurs at  $D_n = 200 \text{ }\mu\text{m}$ .

For a cylinder with other orientation, or for a spherical particle, the effect of chemical reactions on the drag force is expected to show similar trends, but the correlation formula will be different because the reaction rates and species distributions will be different for different geometries. Nevertheless, the dimensionless numbers may remain to be the same, which lays a solid foundation for future study. This developed correlation can easily be coupled with point-source based simulations. All parameters required to calculate these dimensionless numbers can be obtained from the classic char combustion models [49,50]. The application and performance evaluation of this new drag force model for a burning particle needs further study in the future.

#### 4. Conclusions

Particle-resolved simulations are performed to analyze the effect of chemical reactions on the drag force of a burning char particle by using the ghost cell immersed boundary method. The effects of heterogeneous reactions, gaseous reactions and the particle temperature are investigated. It is found that the flow patterns are changed due to the Stefan flow induced by the heterogeneous reactions. The recirculation wake becomes shorter and detaches from the particle, which leads to the change of the pressure, friction and drag force. As a result, the reactive particle can not be simplified as a particle with an outflow. The drag force of the reactive particle is obviously higher than the one with an outflow. The gaseous reaction of CO and  $O_2$  also increases the drag force. The CO<sub>2</sub> produced by the gaseous reaction accumulates at the rear of



Fig. 16. Comparison of drag force coefficient between fully-resolved simulations and the fitted formulation (a) Re = 5, (b) Re = 10.



Fig. 17. Comparison of posterior analysis cases and predicted drag force.

the particle and causes a increase of the molar mass, leading to a larger pressure drop. Besides, the drag force is also influenced by the temperature difference between the particle and the incoming flow, not only through the viscosity but also through the chemical reactions. Based on the fully-resolved simulations, a new drag force correlation for a burning particle is developed. Two dimensionless numbers are introduced to represent the effects of the heterogeneous reactions and the gaseous reaction respectively. The correlation shows good performance in the current configurations, and need more evaluation in the future work.

#### **Declaration of Competing Interest**

The authors have no conflicts of interest to declare.

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#### References

- [1] D.J. Tritton, Experiments on the flow past a circular cylinder at low Reynolds numbers, J. Fluid Mech. 6 (1959) 547–567.
- [2] S. Dennis, G.-.Z. Chang, Numerical solutions for steady flow past a circular cylinder at Reynolds numbers up to 100, J. Fluid Mech. 42 (1970) 471–489.
- [3] R. Clift, J. Grace, M. Weber, Bubbles, drops, and particles, Academic Press, New York, 1978, p. 510.
- [4] T.J. Poinsot, S.K. Lelef, A drag coefficient correlation, 1933 Ver. Deut. Ing., 77 318-320.
- [5] T. Hara, M. Muto, T. Kitano, R. Kurose, S. Komori, Direct numerical simulation of a pulverized coal jet flame employing a global volatile matter reaction scheme based on detailed reaction mechanism, Combust. Flame 162 (2015) 4391–4407.
- [6] M. Rieth, A. Kempf, A. Kronenburg, O. Stein, Carrier-phase DNS of pulverized coal particle ignition and volatile burning in a turbulent mixing layer, Fuel 212 (2018) 364–374.

- [7] T. Brosh, D. Patel, D. Wacks, N. Chakraborty, Numerical investigation of localised forced ignition of pulverised coal particle-laden mixtures: a direct numerical simulation (DNS) analysis, Fuel 145 (2015) 50–62.
- [8] P. Nithiarasu, K. Seetharamu, T. Sundararajan, Natural convective heat transfer in a fluid saturated variable porosity medium, Int. J. Heat Mass Transf. 40 (1997) 3955–3967.
- [9] L. Leal, A. Acrivos, The effect of base bleed on the steady separated flow past bluff objects, J. Fluid Mech. 39 (1969) 735–752.
- [10] S. Bhattacharyya, S. Dhinakaran, A. Khalili, Fluid motion around and through a porous cylinder, Chem. Eng. Sci. 61 (2006) 4451–4461.
- [11] S. Yu, P. Yu, T. Tang, Effect of thermal buoyancy on flow and heat transfer around a permeable circular cylinder with internal heat generation, Int. J. Heat Mass Transf. 126 (2018) 1143–1163.
- [12] K. Wittig, P. Nikrityuk, A. Richter, Drag coefficient and Nusselt number for porous particles under laminar flow conditions, Int. J. Heat Mass Transf. 112 (2017) 1005–1016.
- [13] M. Watanabe, J. Yahagi, Effects of nonuniform outflow and buoyancy on drag coefficient acting on a spherical particle, J. Flow Control Meas. Vis. 5 (2017) 99.
- [14] R. Kurose, H. Makino, S. Komori, M. Nakamura, F. Akamatsu, M. Katsuki, Effects of outflow from the surface of a sphere on drag, shear lift, and scalar diffusion, Phys. Fluids 15 (2003) 2338–2351.
- [15] T. Jayawickrama, N. Haugen, M. Babler, K. Umeki, Effect of Stefan flow on drag coefficient of reactive spherical particles in gas flow, ICHMT Digital Library Online, Begel House Inc, 2018.
- [16] M. Stöllinger, B. Naud, D. Roekaerts, N. Beishuizen, S. Heinz, PDF modeling and simulations of pulverized coal combustion-part 1: theory and modeling, Combust. Flame 160 (2013) 384–395.
- [17] T.R. Jayawickrama, N.E.L. Haugen, M.U. Babler, M.A. Chishty, K. Umeki, The effect of Stefan flow on the drag coefficient of spherical particles in a gas flow, Int. J. Multiph. Flow 117 (2019) 130–137.
- [18] F. Higuera, Combustion of a coal char particle in a stream of dry gas, Combust. Flame 152 (2008) 230–244.
- [19] K. Luo, C. Mao, J. Fan, Z. Zhuang, N.E.L. Haugen, Fully resolved simulations of single char particle combustion using a ghost-cell immersed boundary method, AlChE J. 64 (2018) 2851–2863.
- [20] R. Kurose, M. Anami, A. Fujita, S. Komori, Numerical simulation of flow past a heated/cooled sphere, J. Fluid Mech. 692 (2012) 332–346.
- [21] T. Nagata, T. Nonomura, S. Takahashi, Y. Mizuno, K. Fukuda, Direct numerical simulation of flow around a heated/cooled isolated sphere up to a Reynolds number of 300 under subsonic to supersonic conditions, Int. J. Heat Mass Transf. 120 (2018) 284–299.
- [22] C.R. Shaddix, E.S. Hecht, C. Gonzalo-Tirado, B.S. Haynes, The effect of bulk gas diffusivity on apparent pulverized coal char combustion kinetics, Proc. Combust. Inst. 37 (2019) 3071–3079.
- [23] N.E.L. Haugen, J. Krüger, D. Mitra, T. Løvås, The effect of turbulence on mass transfer rates of small inertial particles with surface reactions, J. Fluid Mech. 836 (2018) 932–951.

- [24] S. Farazi, M. Sadr, S. Kang, M. Schiemann, N. Vorobiev, V. Scherer, H. Pitsch, Resolved simulations of single char particle combustion in a laminar flow field, Fuel 201 (2017) 15–28.
- [25] M. Renksizbulut, M. Yuen, Experimental study of droplet evaporation in a high-temperature air stream, J. Heat Transf. 105 (1983) 384–388.
- [26] R.S. Miller, J. Bellan, Direct numerical simulation of a confined three-dimensional gas mixing layer with one evaporating hydrocarbon-droplet-laden stream, J. Fluid Mech. 384 (1999) 293–338.
- [27] A. Brandenburg, W. Dobler, Pencil: finite-difference code for compressible hydrodynamic flows, astrophysics source code library, (2010).
- [28] N. Babkovskaia, N. Haugen, A. Brandenburg, A high-order public domain code for direct numerical simulations of turbulent combustion, J. Comput. Phys. 230 (2011) 1–12.
- [29] G. Lupo, M.N. Ardekani, L. Brandt, C. Duwig, An immersed boundary method for flows with evaporating droplets, Int. J. Heat Mass Transf. 143 (2019) 118563.
- [30] K. Luo, Z. Zhuang, J. Fan, N.E.L. Haugen, A ghost-cell immersed boundary method for simulations of heat transfer in compressible flows under different boundary conditions, Int. J. Heat Mass Transf. 92 (2016) 708–717.
- [31] L. Zhang, K. Liu, C. You, Fictitious domain method for fully resolved reacting gas-solid flow simulation, J. Comput. Phys. 299 (2015) 215–228.
- [32] S.R. Turns, An introduction to combustion, McGraw-Hill, New York, 1996.
- [33] S. Sundaresan, N.R. Amundson, Diffusion and reaction in a stagnant boundary layer about a carbon particle. 6. Effect of water vapor on the pseudo-steady-state structure, Ind. Eng. Chem. Fundam. 19 (1980) 351–357.
- [34] S. Tenneti, R. Garg, S. Subramaniam, Drag law for monodisperse gas-solid systems using particle-resolved direct numerical simulation of flow past fixed assemblies of spheres, Int. J. Multiph. Flow 37 (2011) 1072–1092.
- [35] R.J. Hill, D.L. Koch, A.J. Ladd, The first effects of fluid inertia on flows in ordered and random arrays of spheres, J. Fluid Mech. 448 (2001) 213–241.
- [36] R.J. Hill, D.L. Koch, A.J. Ladd, Moderate-Reynolds-number flows in ordered and random arrays of spheres, J. Fluid Mech. 448 (2001) 243–278.

- [37] M.A. van der, Hoef, R. Beetstra, J. Kuipers, Lattice-Boltzmann simulations of low-Reynolds-number flow past mono-and bidisperse arrays of spheres: results for the permeability and drag force, J. Fluid Mech. 528 (2005) 233–254.
- [38] C. Wilke, A viscosity equation for gas mixtures, J. Chem. Phys. 18 (1950) 517–519.
- [39] W. Sutherland, LII. The viscosity of gases and molecular force, Lond. Edinb. Dublin Philos. Mag. J. Sci. 36 (1893) 507–531.
- [40] P. Yu, Y. Zeng, T. Lee, H. Bai, H. Low, Wake structure for flow past and through a porous square cylinder, Int. J. Heat Fluid Flow 31 (2010) 141–153.
- [41] P. Yu, Y. Zeng, T.S. Lee, X.B. Chen, H.T. Low, Steady flow around and through a permeable circular cylinder, Comput. Fluids 42 (2011) 1–12.
- [42] M. Renksizbulut, M. Yuen, Numerical study of droplet evaporation in a hightemperature stream, J. Heat Transf. 105 (1983) 389–397.
- [43] E. Buckingham, On physically similar systems; illustrations of the use of dimensional equations, Phys. Rev. 4 (1914) 345.
- [44] G. Shieh, Improved shrinkage estimation of squared multiple correlation coefficient and squared cross-validity coefficient, Organ. Res. Methods 11 (2008) 387–407.
- [45] T.J. Poinsot, S.K. Lelef, Boundary conditions for direct simulations of compressible viscous flows, J. Comput. Phys. 101 (1) (1992) 104–129.
- [46] Kun Luo, Yun Bai, Tai Jin, Kunzan Qiu, Jianren Fan, Direct numerical simulation study on the stabilization mechanism of a turbulent lifted pulverized coal jet flame in a heated coflow, Energy & Fuels 31 (8) (2017) 8742–8757.
- [47] Masaya Muto, Kohei Yuasa, Ryoichi Kurose, Numerical simulation of ignition in pulverized coal combustion with detailed chemical reaction mechanism, Fuel 190 (2017) 136–144.
- [48] M. Rieth, A.M. Kempf, A. Kronenburg, O.T. Stein, Carrier-phase DNS of pulverized coal particle ignition and volatile burning in a turbulent mixing layer, Fuel 212 (2018) 364–374.
- [49] W.Z. Nusselt, The process of combustion in powdered coal firing, Ver Z Deut Ing 68 (1924) 124–128.
- [50] H.S. Burke, T.E.W. Schumann, The mechanism of combustion of solid fuel, Proceedings of the International Conference on Bituminous Coal 2 (1932) 485.

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# A numerical study on the combustion of a resolved carbon particle

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#### ABSTRACT

Combustion of a single, resolved carbon particle is studied using a novel numerical approach that makes use of an overset grid. The model is implemented into the framework of a compressible Direct Numerical Simulation (DNS) code. A method to artificially reduce the speed of sound is presented. For Mach numbers lower than  $\sim$ 0.1 this method may dramatically improve numerical efficiency without affecting any physical aspects except for the acoustics. The ability of the model to simulate solid fuel combustion is demonstrated and all parts of the model are validated against experimental and numerical data. A sensitivity of the carbon conversion rate to selected parameters (diffusion coefficients and homogeneous and heterogeneous kinetics) is investigated. A strong dependence on the oxygen diffusivity is observed and explained.

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### 1. Introduction

Solid fuels are among the most important energy sources worldwide. On one hand, some countries, like e.g. China, India or Poland, are still vastly dependent on coal [1]. On the other hand, the contribution to the energy production from solid fuels in the form of biomass and refuse-derived fuel is increasing every year [2]. Due to its strong effect on global warming, emission of carbon dioxide from solid fuels conversion is a serious environmental problem. This, in connection with the global increase in energy demand [3], necessitates development of low-emission and efficient solid fuel-based technologies. Such technologies cannot be designed without a thorough knowledge about fuel properties and understanding of the underlying fuel conversion phenomena. This understanding is currently provided by experiments and by numerical simulations. Experimental investigation of solid fuels combustion is difficult because of complex physical and chemical processes occurring at different scales. As a consequence, information provided by experiments may not be complete. A deeper insight can be gained through detailed numerical simulations, in which all flow scales are resolved on a numerical grid. It should be stressed, however, that both research methods are complementary and equally important.

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version in turbulent systems, particles are commonly represented as point sources. This approach has previously been employed to study different aspects of pulverized coal combustion, for example in jet flames [4–6] and mixing layers [7–9]. The approximation of point particles is applicable only to very small particles, i.e. to particles with diameters smaller than Kolmogorov length scales of turbulence [10]. Also, in such simulations, interactions between the fluid and particles must be modeled using closure expressions. These expressions can be supplied by simulations in which the particle surface and its boundary layer are resolved on the numerical mesh. Even though such resolved simulations are typically limited to one or a few particles, this approach has a great potential to provide an understanding of the solid fuel conversion and gas-particle interactions at a very fundamental level. The resolved particle approach has recently been employed in several numerical investigations of coal or carbon conversion. Devolatilization and ignition stages of the resolved pulverized coal particle were considered by Vascellari et al. [11], whose studies were extended by Tufano et al. [12] to account for different atmospheres and a more accurate description of the volatile yield and composition. The same research group further broadened the focus of their studies on resolved coal particles by considering particle arrays [13], higher particle Reynolds numbers and effects of turbulence [14]. A number of publications neglect the devolatilization and investigate resolved char particle combustion and gasification in steady state. For example, Kestel et al. [15] studied the impact of steam content and

In Direct Numerical Simulation (DNS) studies on solid fuels con-

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Reynolds number on the char oxidation in air, while the effects of the ambient gas temperature, gas velocity and oxygen mass fractions in  $O_2/CO_2$  atmosphere were considered by Richter et al. [16]. A similar analysis was also performed by Safronov et al. [17] who indicated differences in combustion behavior between micro- and milimeter-sized particles. The conversion of a collection of resolved carbon particles was also investigated in a similar way by Schulze et al. [18]. Furthermore, the steady state approach was employed in a few studies [19–21] that attempted to resolve porous particle and understand intrinsic reactivity. It was shown that both porosity and pore structure can affect char conversion.

As demonstrated by the above-mentioned examples, a great deal of understanding can be reached with the steady state assumption. However, all transient phenomena and processes (ignition, volatiles burnout, progress of char conversion, combustion in non-laminar flow) require unsteady approach. The first transient simulations of resolved particle combustion in a non-quiescent (two-dimensional) flow were performed by Lee et al. [22] using the spectral element method. Recently, Farazi et al. [23] used an unsteady approach and a detailed chemical mechanism, and investigated char particle combustion in air and oxy-fuel atmospheres. The combustion characteristics in these two atmospheres were explored, as well as interactions between kinetics and mass transfer. This work was further extended to particle arrays by Sayadi et al. [24]. Another study on the resolved particle conversion in which the governing equations were solved in their unsteady form was done by Luo et al. [6]. In their work, an immersed boundary method and a simple semi-global mechanism were utilized. Finally, Tufano et al. [25] performed the most complete study up to date, in which all stages of the coal particle conversion are considered, i.e. heating, drying, ignition, volatiles combustion and char particle conversion. Moreover, in addition to detailed chemistry, their numerical model accounts for complex features of particle interior, such as time evolution of porosity and tortuosity. Most recently, Nguyen et al. [26] performed unsteady particle-resolved simulations to investigate the evolution of char particle morphology. Based on their results, improved expressions for the mode of burning and the Random Pore Model were proposed.

In the existing literature on resolved particle conversion, very different levels of numerical model complexity are presented. The current trend seems to be towards more and more detailed models and models that are able to capture transient effects. However, high accuracy is achieved at the expense of efficiency. The objective of this work is to propose a novel numerical approach for resolved char particle combustion modeling. Contrary to the present trend in the literature, we aim for the model to be as simple and efficient as possible, while still preserving high accuracy and being able to predict unsteady phenomena. This is accomplished by using structured, overset grids and by introducing carefully verified assumptions and simplifications.

### 2. Governing equations and numerical methods

An open-source, compressible solver called the Pencil Code [27] is used to perform the simulations presented in this work. The Pencil Code uses a 6th order finite difference scheme and a 3rd order Runge–Kutta scheme for spatial and temporal discretization, respectively. One of the main features of the numerical approach employed in this study is the overset grid. The particle is surrounded by a cylindrical body-fitted grid (later also referred to as 'ogrid'), which spans the space between  $r = r_p$  to  $r = 3r_p = r_{ogrid}$ , where r is a radial coordinate and  $r_p$  is the particle radius. The rest of the computational domain is resolved on the Cartesian grid. Such an approach allows one to use very high resolution close to the particle, which is necessary to resolve its boundary layer and the surrounding flame. Further away from the particle, the grid

is much coarser, making the computational effort relatively low. The solution is interpolated between the ogrid and the Cartesian grid using a 4th order, explicit Lagrangian interpolation method, which has been shown to be an optimal choice in connection with a 6th order finite difference scheme [28,29]. In order to avoid spurious oscillations, Padé filtering [30,31] is applied on the cylindrical grid to density, temperature and velocity fields. The details about the implementation of the overset grid and performance of this method can be found in [32,33].

#### 2.1. Fluid equations

The continuity and momentum equations are solved in their non-conservative, compressible form:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = \mathbf{0},\tag{1}$$

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \nabla \cdot \underline{\underline{\tau}} + \boldsymbol{f}, \qquad (2)$$

where  $\rho$  and p are the density and pressure, respectively, and the bold symbols represent the velocity (u) and volumetric force (f) vectors. The stress tensor,  $\underline{\tau}$ , is given by

$$\underline{\underline{\tau}} = \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \underline{\underline{\tau}},$$
(3)

where  $\mu$  stands for the dynamic viscosity and  $\underline{\tau}$  is the identity matrix. The mass fraction of chemical species k, given by  $Y_k$ , obeys the following transport equation

$$\rho \frac{\partial Y_k}{\partial t} + \rho \mathbf{u} \cdot \nabla Y_k = -\nabla \cdot \mathbb{J}_k + \dot{\omega}_k, \tag{4}$$

in which the diffusive flux,  $\mathbb{J}_k$ , is simplified by using the assumption of Fickian diffusion, such that

$$\mathbb{J}_k = -\rho D_k \nabla Y_k,\tag{5}$$

where  $D_k$  is the diffusion coefficient of species k and  $\dot{\omega}_k$  represents the gas phase reaction rate of the same species.

By neglecting viscous heating, the energy equation is expressed in terms of temperature as [34]

$$\rho \frac{\partial T}{\partial t} + \rho \mathbf{u} \cdot \nabla T$$
  
=  $\sum_{k} (\dot{\omega}_{k} - \nabla \cdot \mathbb{J}_{k}) \left( \frac{TR}{c_{\nu}M_{k}} - \frac{h_{k}}{c_{\nu}} \right) - \frac{\rho TR}{c_{\nu}M} \nabla \cdot \mathbf{u} - \frac{\nabla \cdot \mathbf{q}}{c_{\nu}},$  (6)

where *T* represents the temperature,  $c_v$  is the heat capacity at constant volume, *R* is the universal gas constant and *M* is the molar mass for the mixture,  $1/M = \sum_k Y_k/M_k$ . The heat flux,  $\Pi$ , is computed as

$$H = \sum_{k} h_{k} \mathbb{J}_{k} - \lambda \nabla T, \tag{7}$$

where  $\lambda$  represents thermal conductivity and  $h_k = \Delta h_{s,k} + h_{f,k}^0$  is the absolute enthalpy of species k, which is the sum of its sensible enthalpy,  $\Delta h_{s,k}$ , and its heat of formation,  $h_{f,k}^0$ . Finally, to relate density with pressure, the ideal gas equation of state is used,

$$p = \frac{\rho RT}{M}.$$
(8)

### 2.2. Chemical mechanism and boundary conditions

A simplified chemical mechanism that consists of two surface reactions and one reversible gas phase reaction is employed:

$$2C + O_2 \rightarrow 2CO$$
 (R1)

#### Table 1

Kinetic parameters. Here, [*a*] denotes concentration of species *a*,  $k_i$  is given by Eq. (9) and  $r_i$  represents the rate-of-progress variable. Note that for surface reactions units of  $r_i$  are mol/cm<sup>2</sup>/s, while for gas phase reactions it is mol/cm<sup>3</sup>/s.

reaction	B <sub>i</sub>	$E_i[kcal/mol]$	r <sub>i</sub>	source
R1	$\begin{array}{l} 1.97\times 10^9\ cm\ /\ s\\ 1.29\times 10^7\ cm\ /s\\ 3.98\times 10^{14}\ {\left(\frac{cm^3}{mol}\right)^{3/4}}/s\\ 5\times 10^8\ 1/s \end{array}$	47.3	$k_1[O_2]$	[36]
R2		45.6	$k_2[CO_2]$	[36]
R3 (forward)		40.7	$k_{3,f}[CO][H_2O]^{1/2}[O_2]^{1/4}$	[37]
R3 (reverse)		40.7	$k_{3,r}[CO_2]$	[37]

$$C + CO_2 \rightarrow 2CO$$
 (R2)

$$CO + 0.5O_2 \leftrightarrow CO_2$$
 (R3)

It should be noted that the gasification reaction through  $H_2O$  is not considered in the present study, even though water vapor is present in the atmosphere. The reason this reaction was omitted was the very low concentration of  $H_2O$  ( $Y_{H_2O} = 8 \times 10^{-4}$  at the inlet), which has been shown by Kestel et al. [15] to have essentially no effect on the conversion rate. To study cases characterized by higher content of water vapor, the additional gasification reaction and the water-gas shift reaction should be included in the mechanism. The Arrhenius expression for reaction *i* reads

$$k_i = B_i \exp(-E_i/RT). \tag{9}$$

The empirical kinetic parameters: pre-exponential factor  $B_i$ , activation energy  $E_i$  and reaction orders are listed in Table 1. The reaction term for the gas phase reaction in Eq. (4) is computed as

$$\dot{\omega}_k = M_k \sum_{i=1}^{n_{r,gas}} (\nu_{ki}'' - \nu_{ki}') r_i, \tag{10}$$

where  $v'_{ki}$  and  $v''_{ki}$  are the stoichiometric coefficients of gas phase species k in reaction i on the reactant and product side, respectively, while  $n_{r,gas}$  is the number of gas phase reactions, and  $r_i$  is the rate-of-progress variable (adopting terminology from Ch. 4 in [35]), as given in Table 1.

Since the particle interior is not included in the current framework, it is assumed that all contributions to the reaction rate due to internal reactions are accounted for through the apparent kinetic parameters, and that the temperature gradient inside the particle is small enough to be neglected. Also, the particle is assumed to be entirely made of carbon and the model does not incorporate particle shrinkage during its conversion. In reality, the particle size and density are slowly changing as combustion progresses [38]. However, the typical time of our simulations is much shorter than the burnout time of the particle such that the reduction of the particle diameter can be considered negligible.

As stated above, the interior of the particle is not included in the computational mesh. The interaction between the solid and the surrounding gas is therefore incorporated through the particle boundary conditions. We will now continue by describing these boundary conditions. The species balance at the cylinder surface can be expressed as [6]:

$$\rho D_k \frac{\partial Y_k}{\partial r} + \dot{m}_c Y_k + \dot{m}_k = 0, \tag{11}$$

where

$$\dot{m}_{k} = M_{k} \sum_{i=1}^{n_{r,heter}} (\nu_{ki}'' - \nu_{ki}') r_{i},$$
(12)

is the production rate of species k due to heterogeneous reactions, and  $n_{r,heter}$  is the number of heterogeneous reactions. The char conversion rate is given by

$$\dot{m}_{c} = -M_{C}(2k_{1}[O_{2}] + k_{2}[CO_{2}])$$

$$= -(\dot{m}_{O_{2}} + \dot{m}_{CO_{2}} + \dot{m}_{CO}) = -\sum_{k=1}^{n_{s,gas}} \dot{m}_{k},$$
(13)

where the final summation is over all gas-phase species. A detailed deduction of Eq. (11) can be found in Appendix A. It should be noted that both  $\dot{m}_c$  and  $\dot{m}_k$  depend on the species concentration on the surface, which makes it necessary to solve Eq. (11) in an iterative manner. Another possibility is to use species production rates from the previous time step, this can however lead to numerical instabilities and non-physical results. Here, we employ a simple iterative algorithm to simultaneously find solutions for  $Y_{O_2}$  at the surface, while the remaining species are solved for directly.

Mass conservation at the particle surface requires that (see Appendix A)

$$\sum_{k} (\rho Y_k \mathbf{u} + \mathbb{J}_k) \cdot \hat{\mathbf{r}} = \sum_{k} \dot{m}_k = -\dot{m}_c, \tag{14}$$

where  $\hat{\boldsymbol{r}}$  is the vector normal to the particle surface. From the above equation, and since  $\sum_{k} \mathbb{J}_{k} \cdot \hat{\boldsymbol{r}} = 0$ , the boundary condition for velocity becomes:

$$u_r = -\dot{m}_c/\rho,\tag{15}$$

where  $u_r$  is the outward velocity in the radial direction, corresponding to the so called Stefan flow.

Dirichlet boundary condition is employed for the temperature. The intention behind the Dirichlet boundary condition for temperature is to validate the code against the experimental data of Makino et al. [39], where the temperature was maintained constant. The last variable that needs to be defined at the cylinder surface is density, which is solved for directly from the transport equation and does therefore not require any special treatment at the boundary.

### 2.3. Transport properties

In simulations of reacting flows, it is common practice to compute transport coefficients, such as  $\mu_k$ ,  $D_k$  and thermal diffusivity  $D_{th}$ , based on the kinetic theory of gases, as described e.g. in [34]. This approach, while accurate, significantly increases computational cost. This is especially the case for species diffusion coefficients for which binary diffusion coefficients need to be evaluated first. In order to maximize computational efficiency, a simplified approach is employed in this work. At the same time, care is taken not to compromise the accuracy of the results.

The kinetic viscosity is related to temperature through Sutherland's law

$$\nu = \frac{C_1 T^{3/2}}{\rho(T + C_2)} \tag{16}$$

with constants  $C_1 = 1.52 \cdot 10^{-6}$  kg/m/s/K<sup>1/2</sup> and  $C_2 = 110$  K. The above expression is fully applicable to single-component gases. However, if a mixture is dominated by components with similar

Table 2

Polynomial coefficients for heat capacity in the temperature range 1000 K < T < 5000 K.

species	СО	CO <sub>2</sub>	H <sub>2</sub> 0	N <sub>2</sub>	02
<i>a</i> <sub>1</sub>	3.025	4.454	2.672	2.927	3.698
<i>a</i> <sub>2</sub>	$1.443 \cdot 10^{-3}$	$3.140 \cdot 10^{-3}$	$3.056 \cdot 10^{-3}$	$1.488 \cdot 10^{-3}$	$6.135\cdot10^{-4}$
a <sub>3</sub>	$-5.631 \cdot 10^{-7}$	$-1.278 \cdot 10^{-6}$	$-8.730 \cdot 10^{-7}$	$-5.685 \cdot 10^{-7}$	$-1.259 \cdot 10^{-7}$
$a_4$	$1.019 \cdot 10^{-10}$	$2.394 \cdot 10^{-10}$	$1.201 \cdot 10^{-10}$	$1.010 \cdot 10^{-10}$	$1.775 \cdot 10^{-11}$
a <sub>5</sub>	$-6.911 \cdot 10^{-15}$	$-1.669 \cdot 10^{-14}$	$-6.392 \cdot 10^{-15}$	$-6.753 \cdot 10^{-15}$	$-1.136 \cdot 10^{-15}$



**Fig. 1.** Kinetic viscosity as obtained using Sutherland's law (Eq. (16)) and multicomponent approach for the mixture consisting of  $Y_{N_2} = 0.7292$ ,  $Y_{O_2} = 0.05$ ,  $Y_{H_2O} = 0.0008$ ,  $Y_{CO} = 0.02$  and  $Y_{CO_2} = 0.2$ .

properties (as is the case here), Eq. (16) is reduced to a decent approximation. Furthermore, constants  $C_1$  and  $C_2$  were selected such that for a wide range of temperatures and compositions the kinetic viscosity resulting from Eq. (16) is in a good agreement with the kinetic viscosity determined using the multi-component approach (i.e. based on kinetic theory). In Fig. 1, these two methods are compared for a typical composition encountered in the current work. For other compositions that are likely to occur, a deviation from the kinetic theory remains below 7% for the temperature range presented in Fig. 1.

The main assumption allowing us to compute the remaining transport coefficients is that the transport coefficients are proportional to each other, i.e.

$$\nu = \Pr D_{th} = \Pr \operatorname{Le}_k D_k,\tag{17}$$

with the constants of proportionality being the Prandtl (Pr) and Lewis (Le<sub>k</sub>) numbers. Such an assumption of constant Prandtl and/or Lewis numbers has successfully been applied in recent studies on resolved particle devolatilization and combustion [12,23]. Typically, Pr= 0.7 and Le<sub>k</sub> = 1 for all species are assumed. This was shown to have a negligible impact on the devolatilization stage when compared with the complex multi-component approach [12]. However, in some conditions, the combustion rate might be affected by diffusion coefficients, as will be demonstrated in the next section. Therefore, a more careful approach is employed, as described below.

The heat capacity at constant pressure is given by

$$c_p = \sum_k Y_k c_{p,k} = \frac{R}{M} \sum_k Y_k \sum_{i=1}^5 a_i T^{i-1},$$
(18)

where the polynomial coefficients  $a_i$  are taken from Gordon and Mcbride [40] and are listed in Table 2 for the relevant temperature range. The heat capacity at constant volume is related to the heat capacity at constant pressure through the gas constant, such that



**Fig. 2.** Thermal conductivity as obtained using Eq. (17) with Pr = 0.9 and multicomponent approach for the mixture consisting of  $Y_{N_2} = 0.7292$ ,  $Y_{O_2} = 0.05$ ,  $Y_{H_2O} = 0.0008$ ,  $Y_{CO} = 0.02$  and  $Y_{CO_2} = 0.2$ .

Table 3         Selected Lewis numbers.					
species	СО	CO <sub>2</sub>	$H_2O$	$N_2$	02
Lek	0.78	1.01	0.58	0.7	0.78

$$c_p - c_v = R/M. \tag{19}$$

Using the heat capacity given by Eq. (18) and the thermal diffusivity given by Eq. (17), the thermal conductivity, defined as

$$\lambda = c_p \rho D_{\rm th},\tag{20}$$

is shown in Fig. 2 as a function of temperature for the same mixture as used in Fig. 1. In Fig. 2, the thermal conductivity as obtained using the multi-component approach is also presented. The best agreement between these two functions for a wide range of mixtures is achieved by setting the Prandtl number equal to 0.9.

For each species,  $Le_k$  is chosen such that the resulting diffusion coefficient does not differ by more than around 10% from the diffusion coefficient computed based on the multi-component diffusion approach. This was verified for the full range of compositions and temperatures that are likely to appear in the cases we examine. Figure 3 presents a comparison between the diffusion coefficients as a function of temperature as computed from Eq. (17) and as obtained using the multi-component diffusion. The magnitudes of the Lewis numbers leading to these results are listed in Table 3. A good agreement between the two approaches is achieved for all transport coefficients ( $\nu$ ,  $\lambda$  and  $D_k$ ), which justifies the use of the simplified approach for the transport coefficients.

In order to quantify the efficiency gain obtained by simplifying the formulation of the transport coefficients, a one-dimensional flame was simulated for two cases (details regarding the onedimensional flame simulations are given in the next section). In the first case, transport properties were computed according



**Fig. 3.** Diffusion coefficients as obtained using Eq. (17) (referred to as 'simplified') and multi-component approach for the mixture consisting of  $Y_{N_2} = 0.7292$ ,  $Y_{O_2} = 0.05$ ,  $Y_{H_2O} = 0.0008$ ,  $Y_{CO} = 0.02$  and  $Y_{CO_2} = 0.2$ .

to Eqs. (16), (17) and (20), while in the second case, a multicomponent approach was employed. A comparison of the execution time of subroutines responsible for computing transport properties revealed that 7.5 times less computational time was required for the case in which the simplified approach was used. Furthermore, since these subroutines are computationally the most expensive (i.e. their execution takes a large fraction of the simulation time), this corresponds to a reduction in the total execution time by a factor of 3.4. It should also be noted that the efficiency gain is dependent on the number of species present in the simulation. The reason for this is that one additional nested loop over all species must be executed and a significantly larger number of operations have to be performed to compute transport coefficients based on the kinetic theory. In our case, the factor of 7.5 was achieved for 5 species.

#### 2.4. Speed of sound reduction

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Numerical stability of the simulations requires several conditions to be fulfilled. First of all, a requirement due to convection, often called the CFL condition limits the maximum time step to:

$$\Delta t \le \frac{C\Delta x}{\max(c_s + u)},\tag{21}$$

where C is a constant that depends on a numerical scheme (typically  $C \approx 1$ ) and

$$c_{\rm s} = \sqrt{\gamma RT/M} \tag{22}$$

is the speed of sound and  $\gamma = c_p/c_v$ . For reacting flows, the length of the time step and the grid spacing is most often limited by chemical scales. However, it turns out that in the case of flows that are both reacting and compressible, the resolution requirement due to the ratio between viscosity and the speed of sound might be more restrictive. For the particular numerical approach employed in the Pencil Code, it has been shown [41] that the grid spacing is constrained by

$$\Delta x < \frac{\beta \nu}{c_{\rm s}},\tag{23}$$

where  $\beta \sim 50$ . It follows from Eq. (23) that larger grid spacing, and hence less mesh points, may be used if the speed of sound is reduced. A good rule of thumb is that, as long as we are not interested in thermo-acoustics, the results are independent of the Mach number, Ma =  $u/c_s$ , for all Mach numbers below 0.1. In our

Table 4

Initial	conditions	IOL	ID	carbon	monoxide
flame.					

reactant side	product side
0.165	0.0
0.29	0.0
0.0	0.455
0.0008	0.0008
0.544	0.544
298	2000
	reactant side 0.165 0.29 0.0 0.0008 0.544 298

case, the Mach number is typically of the order of  $10^{-3}$ . The speed of sound can therefore be reduced by up to two orders of magnitude while still maintaining Mach-independent results. Since the time step is often limited by the CFL condition, which is typically the case for lower temperatures, a reduction of the speed of sound would also allow us to use larger time steps.

In the previous paragraph we showed that a reduction in the speed of sound could be very beneficial for the CPU consumption of our simulations, and that the effect such a reduction has on the results should be negligible if the Mach number is kept below a certain value. The question now is how the speed of sound can be changed without affecting any other aspect of the results. This is done by dividing the gas constant by a factor  $\alpha^2$ , such that

$$R \to R/\alpha^2,$$
 (24)

which implies that (22)

$$c_s \to c_s/\alpha$$
. (25)

The gas constant is changed consistently for all equations, with the exception of Eq. (9) in which the original magnitude of *R* must be used in order for the reaction rate not to be affected. It should be noted that the reduction of *R* means that  $c_p$ ,  $c_v$  and  $\lambda$  are also reduced by the same factor of  $\alpha^2$ , as can be seen from Eqs. (19) to (20). However, this has no effect on the energy equation as all these reductions cancel out in every term of Eq. (6). The only term that is affected is the pressure gradient term in the momentum equation, since  $\nabla p \sim c_s^2$ , which is as intended.

We will now validate the assumption that a reduction in the speed of sound does not affect the main results, except for the acoustic waves, as long as the Mach number is below 0.1. This is done by simulating reacting flows of a one-dimensional carbon monoxide flame with three different values of  $c_s$ . In the base case, the speed of sound was kept unchanged, which resulted in Ma  $\approx$  0.001, in the other cases the speed of sound was reduced by factors of 10 and 50, which led to Ma  $\approx$  0.01 and Ma  $\approx$  0.05, respectively. The initial conditions for these cases are given in Table 4, while the one-step mechanism given in Section 2.2 governs the flame.

The resulting temperature and species mass fraction profiles at steady state are presented in Fig. 4, from which it can be seen that the results are not affected by the speed of sound reduction. Furthermore, for all three cases, the same flame speed,  $S_L = 14 \text{ cm/s}$ , is obtained. Having verified that the speed of sound can be reduced without affecting the results, this tactic is employed for all cases discussed in the next section, which resulted in a major reduction of CPU power consumption, in particular for those cases where the time-step was not limited by chemical reactions. It is also worth mentioning that the efficiency gain resulting from the speed of sound reduction is very case-dependent. This can be illustrated by subsequently reducing the spatial resolution of the 1D flame simulation in which the speed of sound was reduced by a factor of 10 (corresponding to the green line in Fig. 4). Despite the fact that the maximum grid size, as defined by Eq. (23), is inversely proportional to the speed of sound, it was possible to reduce the resolution only by a factor of  $\sim$ 3 due to the fact that, for stability rea-



Fig. 4. Comparison of temperature and species profiles across the flame obtained before and after the speed of sound reduction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Schematic representation of the analyzed case (not drawn to scale).

sons, a certain number of grid points are required across the flame front. It can be therefore concluded, that the speed of sound reduction allows one to eliminate the grid size/time step requirement due to the speed of sound in low Mach number flows, but the efficiency gain associated with this cannot be quantified in general basis since it depends on other case-specific time and length scales.

#### 2.5. Numerical set-up

The set-up for all simulated cases correspond to the experimental set-up of Makino et al. [39] and can be summarized as follows. A cylindrical particle of 5 mm in diameter is placed in the middle of a 10 cm × 8 cm computational domain. The fluid, which has a composition that is typical for air ( $Y_{N_2} = 0.77$ ,  $Y_{O_2} = 0.23$ ,  $Y_{H_2O} = 0.0008$ ) enters the domain through one side with a velocity of 1 m/s in the *y*-direction. Periodic boundary conditions are specified in the two cross-flow directions. Initially, the temperature inside the domain is everywhere equal to 1280 K. The initial species distribution on the ogrid is such that the oxygen mass fraction decreases exponentially from  $Y_{O_2} = 0.23$  at  $r = r_{ogrid}$  to  $Y_{O_2} = 0$  at the particle surface  $(r = r_p)$ , while carbon dioxide is introduced in place of oxygen, *i.e.*  $Y_{CO_2}(r) = Y_{O_2}(r_{ogrid}) - Y_{O_2}(r)$ . The initial composition on the Cartesian grid is the same as the composition at the inlet. Such initial conditions do not reflect the experimental set-up and were selected purely to improve stability of simulations during the initial stage.

For most cases, a grid resolution of 720 x 896 ( $x \times y$  directions) grid points on the Cartesian grid and 208 x 432 ( $r \times \theta$  directions) on the ogrid was sufficient to accurately resolve all flow features. It should be noted that the ogrid is stretched in a non-linear manner in the radial direction. For the resolution given

above this resulted in  $\Delta r_{\rm min} = 8.3 \cdot 10^{-4}$  cm at the particle surface and  $\Delta r_{\rm max} = 6.8 \cdot 10^{-3}$  cm at the outer edge of the cylindrical grid. A schematic representation of the numerical grid together with initial condition is presented in Fig. 5. If the particle temperature is relatively low ( $T_p \leq 1800$  K) the maximum time-step is limited to  $\sim 10^{-7}$  s by convection, while for higher particle temperatures the time-step needs to be reduced to  $\sim 10^{-8}$  s due to the shorter chemical timescales.

### 3. Results and discussion

#### 3.1. Implementation of chemistry module - validation

Various aspects of the Pencil Code have been validated and tested a number of times and the results have been published in a large number of papers available in the open literature. See [27] for an overview of some relevant papers. In this work, we have, however, implemented several new methods and approximations to speed up the calculations, such as: simplified calculation of transport data, simplified global reaction mechanisms, heterogeneous reactions at the particle surface with the overset grid method, and variable speed of sound. In order to validate the current numerical model beyond the more specific validations presented in the previous section, the experimental set-up of Makino et al. [39] is reproduced numerically. In the experiment of Makino et al., combustion of a graphite rod was studied at different surface temperatures, for different air velocities and temperatures. An important feature of the experiment is that the heat loss from the graphite surface due to radiation is balanced by electrical heating, such that a constant particle surface temperature is maintained at all times. As a result, a quasi-steady state is achieved for a relatively large fraction of the particle conversion time. In the current work, the case characterized by an air temperature of 1280 K and a velocity of 102.5 cm/s is analyzed for a range of particle surface temperatures. This particular selection of experimental conditions was motivated by the fact that the same case was studied numerically by Luo et al. [6], who demonstrated that a good agreement with the experimental results can be obtained using the chemical mechanism given by reactions (R1)–(R3). Despite the fact that Luo et al. also used the Pencil Code, there are two main differences between their approach and the approach used in the current work: (1) Luo et al. used kinetic theory to compute transport coefficients, and (2) their particle was resolved on a Cartesian grid using immersed boundary conditions for the particle surface.

Figure 6 presents the carbon conversion rate obtained with the current numerical approach (green squares) in addition to what was found experimentally by Makino et al. [39] (red circles) and numerically by Luo et al. [6] (blue circles). In fact, what is shown is the conversion rate in the forward stagnation point. Additionally, kinetic (solid blue line) and diffusion (dotted black line) limits for oxidation are also included in Fig. 6. The first limit corresponds to the case of infinitely fast diffusion ( $Y_{O_{2,surface}} = Y_{O_{2,\infty}}$ ), while the latter to the reaction rate being controlled by diffusion ( $\sim T^{1/2}$ ). It can be seen that up to  $T_p = 1200$  K, the carbon conversion rate is governed by kinetics, while around  $T_p = 1600$  K the slope corresponding to the diffusion limit is achieved. There is one more limiting slope included in Fig. 6, which is called 'flame diffusion' limit. This limit arises due to the fact that at around  $T_p = 1700$ K the flame begins to detach from the particle surface. The reason for this detachment is the large CO production at the surface and its subsequent transport by means of the Stefan flow and diffusion. The result is that most of the O<sub>2</sub> is consumed in the gas phase at the position of the flame that is formed away from the surface. As a consequence, mostly CO<sub>2</sub> can diffuse to the surface and the carbon conversion is due to the Boudouard reaction (R2). From the perspective of the oxidation reaction, the oxygen diffuses



**Fig. 6.** Comparison of carbon conversion rates as a function of particle surface temperature. The results for Luo et al. [6] are reproduced from their Fig. 8. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. Effective flame radius in a function of temperature.



Fig. 8. Comparison of temperature profiles along the centerline with and without gas-to-gas radiation model.

now towards the flame surface, not the particle surface. This effective surface grows proportionally to  $T^g$ , where the exponent g can be found by a fitting procedure. This was done in Fig. 7, from which it can be seen that the 'effective radius' scales as  $T^{0.78}$ . Here, the effective radius was computed as the average radial distance from the particle center to the flame, where it was assumed that the flame location corresponds to the grid point in which the gas phase reaction rate is the highest. The carbon conversion rate in



Fig. 9. Contributions to CO production from gasification and oxidation.

the diffusion limit is proportional to the product of the mass transfer coefficient  $(k_i)$  and the effective surface:

$$\dot{m}_c \sim d_{p,eff}^2 k_i, \tag{26}$$

where  $d_{p,eff}$  is the effective diameter of the flame surface. Since the mass transfer coefficient scales as  $k_i \sim D_i/d_{p,eff}$  and  $D_i \sim T^{1/2}$ (see Eqs. (16) and (17)), the conversion rate dependence on temperature becomes:

$$\dot{m}_c \sim d_{p,eff}^2 k_i \sim d_{p,eff} D_i \sim T^{1/2} T^{0.78} = T^{1.28}.$$
 (27)

This is the flame diffusion limit seen in Fig. 6, which is reached for the highest of the studied particle surface temperatures.

Compared to the experimental results, slightly too low conversion is obtained for most temperatures. On the other hand, very similar magnitudes of conversion rates were obtained by Luo et al. [6], which indicates that the difference is most probably caused by the reaction kinetics. It is in fact common that there is no agreement on the reaction kinetics and quite often a number of mechanisms are suggested, resulting in different reaction rates. The influence of heterogeneous kinetics has already been investigated by Nikrityuk et al. [42], who revealed that a factor of 2 or even 3 difference in the carbon consumption rate can be expected between different sets of kinetic parameters that are found in the literature. A set of kinetic parameters for surface reactions was also proposed by Makino et al. [39] based on their experimental results and the conversion rates resulting from these parameters are presented in Fig. 6 (cvan triangles). It can be seen that this vielded a significantly higher carbon conversion rate at high surface temperatures, but did not lead to noticeable difference for  $T_p \leq 1600$  K. This could be expected as the gasification reaction is much faster in Makino's mechanism, while there is only a tiny difference in the oxidation rates when compared with the mechanism given in Table 1.

Another experimental feature that is not captured properly with the current approach is a sudden decrease of the conversion rate for surface temperatures around 1700–1800 K. This decrease is also present in the results shown in Fig. 6 in Luo et al. [6] (although the results in their Figs. 6 and 8 seem to be inconsistent regarding this feature). The main difference between their and the present numerical approach is how the transport coefficients are computed. In that respect, our approach is much simpler and, potentially, less accurate. Therefore, a further validation is essential. Such a validation was performed using the ANSYS Fluent software, in which the same cases were reproduced and the resulting carbon conversion rates are shown as black x-signs in Fig. 6 [add contours here or a plot showing T comparison along centerline]. The Fluent simulations were performed with the diffusion coefficients calculated from kinetic theory, as was also done by Luo et al. [6]. In addition, incompressible and steady state flow was assumed. Both assumptions are valid since the Mach number is low and the change in particle radius is very slow. As can be seen in Fig. 6, almost the same conversion rates were obtained using the complex formulation for the transport coefficients in ANSYS Fluent as for the simplified formulation used in the Pencil Code. In particular, the conversion rates in both cases are monotonically increasing functions, i.e. no reduction of the conversion rate was observed around  $T_p = 1700-1800$  K. This verifies that the simplified approach for the transport is not responsible for this qualitative discrepancy between the experimental results and our numerical results, and allows us to gain confidence in the predictions of our approach.

The case that was set up in ANSYS Fluent was also used to estimate the influence of gas phase radiation, which was omitted in the energy equation in the Pencil Code. While it is not uncommon to omit gas-to-gas radiation in simulations of conversion of resolved char particles, some studies suggest that its effect is nonnegligible. For example, a significant reduction of the char particle surface temperature due to gas phase radiation was observed by Richter et al. [16], especially for cases with high ambient temperature. On the other hand, Tufano et al. [12] showed that the effect of gas-to-gas radiation on ignition is rather weak. In our study, the gas phase radiation was accounted for through the Discrete Ordinates model, and its influence can be seen in Fig. 8, which compares the temperature distribution along the centerline of the reacting particle for the cases with and without radiation. The case with  $T_p = 2000$  K is shown here since the effect of radiation is the highest for cases with high particle temperature. It can be seen that the effect on the gas phase temperature field is certainly nonnegligible in the region behind the particle. Nevertheless, the conversion rate remained unchanged due to the experiment-imitating assumption of constant temperature at the particle surface and virtually no influence of radiation on species concentrations. It should be noted, however, that based on the results presented by Luo et al. [6], it is expected that the particle surface temperature is unlikely to change by more than a few percent for the cases studied in the present paper, even if heat transfer at the particle surface (chemical heat release, conduction, convection and radiation) was accounted for through the particle boundary condition.





Fig. 10. Upper: conversion rates for different diffusion coefficients, lower: contributions from gasification/oxidation to the CO production rate,  $T_p = 1700$  K.

It still remains to be understood why conversion rate obtained with the Pencil Code (and ANSYS Fluent) does not follow the experimental trend when it comes to the dip in carbon conversion rate around  $T_p = 1700$  K. There exist several physical explanations of this trend in the literature, e.g.: it is attributed to the change of the effective reaction zone thickness [43], it is linked with the change of molecular structure of graphite [44,45], it is caused by thermal rearrangement of surface-covering sites, from highly reactive at low temperatures to less reactive at higher temperatures [46,47]. Makino et al. [39] argue that the presence of the dip stems from the fact that the dominant surface reaction shifts from oxidation to gasification around  $T_p = 1700$  K. The reason for this shift is that at low temperatures the oxygen is used to oxidize the carbon directly at the surface, while at high temperatures the oxygen is used to oxidize CO in a CO-flame surrounding the particle, while the carbon conversion proceeds through gasification of CO<sub>2</sub> that diffuse to the surface from the CO flame. This change in the dominant mechanism for CO production at the surface is correctly predicted by the Pencil Code, as can be seen in Fig. 9. However, the shift is gradual and does not result in the non-monotonicity of  $\dot{m}_{\rm C}(T_{\rm p})$  as suggested by Makino et al. [39]. Another plausible explanation for the dip in  $\dot{m}_c$  is that since the shape of the conversion function depends on the gas phase kinetics, as shown in [48], the kinetic parameters we use might not yield the right behavior. While all the above explanations are probable, it is also possible that the results are affected by the measurement method. In the experiment, the surface temperature of the rod was measured using two-color pyrometer [49]. These measurements are used to control the internal heating that is required to maintain a constant temperature of the graphite rod. This method is indirect, it might therefore be difficult to precisely measure the surface temperature without the results being affected by the surrounding flame. At relatively low surface temperatures, the flame remains attached to the surface, so the difference between the flame and the surface temperature is small. However, at temperatures at which the drop in the conversion rate is observed, the flame starts detaching from the rod surface. As such, the flame temperature might be significantly higher, giving a false impression of higher surface temperature. Since the experiment attempts to maintain a constant surface temperature, it is likely that the rod was cooled to lower temperature than intended, which resulted in a sudden decrease of the conversion rate. These are, however, only conjectures, and the reason for the qualitative inconsistency between the experiment and our results might be a combination of several of the abovementioned factors.

### 3.2. Sensitivity analysis

In order to better understand which parameters that control the carbon conversion rate, we have done a series of parameter studies. The first study investigates the effect of species diffusivity. In this respect we varied the diffusivities of  $O_2$ ,  $CO_2$  and CO from half of their original value up to twice the original value, and investigated how this influenced the solid (carbon) conversion rate. For this investigation, we concentrate on the situation where the particle temperature is 1700 K.

From the upper panel of Fig. 10 we see that the solid conversion rate has a strong dependence on diffusivity of  $O_2$ . This is expected since higher diffusivity of  $O_2$  will yield a higher transport rate of  $O_2$  to the solid, which will then be able to convert (oxidize) more solid. From the lower panel of Fig. 10 we see that increasing the oxygen diffusivity results in an increase of both the oxidation and gasification rates of the solid. At first glance, it may look surprising that even the gasification rate increases with increased  $O_2$ 



Fig. 11. Oxygen and carbon dioxide mass fractions and temperature profiles in the particle stagnation region as obtained for different diffusion coefficients.

diffusivity, but the reason is simply that at the surface temperature of 1700 K that we focus on here, we experience a higher surface-fraction of  $CO_2$ , resulting from oxidation of CO very close to the surface.

Let us now move on to the effect of CO diffusivity. We see from the upper panel of Fig. 10 that the solid conversion rate is weakly increasing with increasing diffusivity of CO. This effect is, however, more complicated than that of O<sub>2</sub> diffusivity, as can be seen from the lower panel of Fig. 10, which shows that solid conversion due to oxidation increases with CO diffusivity, while the opposite is true for gasification. To elucidate this behaviour in Fig. 11, we show  $CO_2$  and  $O_2$  concentrations along the y-axis in front of the solid. The dashed vertical line in the figure corresponds to the solid surface. From the left panel we see that lower CO diffusivity yields higher concentration of CO<sub>2</sub> at the surface, which explains why the gasification rate decreases with increasing CO diffusivity. The reason for the increased  $CO_2$  concentration at the surface is that a lower CO diffusivity moves the flame closer to the surface. Since the CO<sub>2</sub> concentration is highest close to where it is produced, which is in the CO flame, this means that the concentration of  $CO_2$  at the surface is also higher. Studying the gradients of  $O_2$  very close to the surface (right panel) we see that the case with higher CO diffusivity has a steeper gradient of O<sub>2</sub> very close to the surface. For a given O<sub>2</sub> diffusivity, a steeper O<sub>2</sub> gradient results in more transport of  $O_2$  to the surface, and, hence, more solid oxidation.

Finally, when increasing the diffusivity of  $CO_2$ , we see from Fig. 10 that the solid conversion rate is actually reduced. This is despite the fact that the solid oxidation rate is independent of the diffusivity of  $CO_2$  (see the lower panel of Fig. 10). The question is therefore why the solid gasification rate is reduced when the  $CO_2$ diffusivity is increased. The answer to that question is that for the current case, which has a solid temperature of 1700 K, the  $CO_2$  is always produced close to the solid surface due to the CO flame not being significantly lifted. Consequently, an increased  $CO_2$  diffusivity will tend to transport  $CO_2$  away from the surface, lowering the surface concentration, and, by that, reducing the gasification rate. Another parameter that can influence the carbon conversion rate is chemical kinetics, both of surface and gas phase reactions. In the following we will proceed by studying the sensitivity of the carbon conversion rate to the chemical reactivity. The reactivity is varied by changing the pre-exponential factor. First, the surface reaction rate is varied. This is done separately for the oxidation (denoted by R1) and gasification (denoted by R2) reactions. The effect of this variation on the conversion rate can be seen in Fig. 12 for two different surface temperatures: 1200 and 1800 K.

For the higher temperature, the conversion rate is almost uninfluenced by changes in the oxidation rate, which is due to the fact that at such high temperatures the reaction is controlled almost purely by diffusion. This is confirmed in the lower panel of Fig. 12, which shows that the oxidation rate (R1) variations have no effect neither on the contribution from oxidation, nor on the contribution from gasification. At the same surface temperature, variations in the gasification rate (R2) have only a weak effect on the solid conversion rate. However, the reason for this is quite different, as in this case both contributions from gasification and oxidation are significantly affected, as can be observed in the lower panel of Fig. 12. These two contributions are affected in such a way that the increase in the carbon conversion rate due to the higher gasification rate is almost exactly balanced by the decrease in the solid conversion rate due to the faster oxidation.

For  $T_p = 1200$  K, the carbon conversion rate is directly proportional to the change of the oxidation rate (R1), but does not depend on the gasification rate (R2). This is expected since at this temperature the surface reaction rates are controlled by kinetics, but the contribution to the solid conversion rate from gasification is around two orders of magnitude smaller than the contribution from oxidation.

The effect of the gas phase kinetics is shown in Fig. 13, from which it is clear that the solid conversion rate is not sensitive to the gas phase reaction rate variations, as long as the surface reactions are controlled by kinetics, i.e. for  $T_p = 1200$  K. At higher particle surface temperatures, the solid conversion becomes faster upon decreasing the gas phase reaction rate. This is consistent



Fig. 12. upper: conversion rates as obtained for modified surface reaction rates, lower: contributions from gasification/oxidation to the CO production rate. R1 and R2 denote oxidation and gasification, respectively, and indicate which reaction has been modified, while ox. and gas. denote contribution from oxidation and gasification to the CO production rate.

with theoretical predictions of Libby and Blake [50] and Makino [51] who showed that the solid conversion rate is highest in the limit of the gas phase reaction rate approaching zero (so called 'frozen mode'), and lowest in the limit of very fast homogeneous reaction rate. This tendency can be linked to the fact that the higher the gas phase reaction rate, the more oxygen is consumed inside the CO-flame before reaching the particle surface, thus, the

contribution to the combustion rate from oxidation decreases (see the lower panel of Fig. 13). Furthermore, the flame characteristics are also directly linked to the gas phase reaction rate. In particular, when the rate is increased, the flame becomes thinner and can detach from the particle surface or shift further from the surface if it was already detached. This situation can be observed in Fig. 14, which presents contours of the CO flame for the cases in



**Fig. 14.** CO flame contours,  $T_p = 1800$  K, left:  $k_{3,f} \rightarrow 0.5k_{3,f}$ , right:  $k_{3,f} \rightarrow 2k_{3,f}$ .



Fig. 13. upper: conversion rates as obtained for modified homogeneous reaction rate, lower: contributions from gasification/oxidation to the CO production rate.



Fig. 15. Oxygen and carbon dioxide mass fraction profiles along the centerline behind the particle as obtained for different gas phase reaction rates.

which the pre-exponential factor of the homogeneous reaction rate was halved and doubled relative to what it was originally. A consequence of the flame moving away from the solid surface is that the gradient of oxygen between the flame and the surface becomes less steep, leading to a slower diffusion of O<sub>2</sub> towards the particle. This can be observed for  $T_p = 1800$  K in Fig. 15, which shows oxygen profiles along the centerline behind the particle. For  $T_p = 1500$ K, the flame is much closer to the solid surface, thus the oxygen profiles further away are almost parallel to each other, and the contribution to the combustion rate from oxidation is affected to a smaller extent, as seen in the lower panel of Fig. 13. The situation is opposite for carbon dioxide, as higher rate of homogeneous reaction means more CO<sub>2</sub> that is produced inside the flame and faster diffusion of this species to the surface. It is also interesting to notice in the right panel of Fig. 15 that for  $T_p = 1500$  K the concentration of CO<sub>2</sub> at the solid surface is almost the same as the concentration inside the flame, which indicates that the gasification rate is still controlled by kinetics. Therefore, the increase of the contribution from gasification is simply caused by the higher mass fraction of CO<sub>2</sub> at the surface, not by the diffusion rate as was the case for  $T_p = 1800$  K.

### 4. Conclusions

The goal of this work was twofold, first to formulate an efficient approach to model resolved solid particle combustion, then to understand the relevant physics and sensitivity. For this purpose, a model within the framework of the Pencil Code was developed and validated against experimental and numerical data. Our model is not as advanced as some approaches proposed in the literature, but it has a great potential to capture the transient nature of char conversion upon further development. Although within this study the laminar flow over a single particle was analyzed, the model can also be employed in turbulent flow situations. In order to achieve high efficiency, an overset grid was used, which allowed us to reduce the computational expense without compromising the accuracy. Other features of the numerical approach that have been proposed for the sake of efficiency are the speed of sound reduction and fitting of the transport coefficients (kinetic viscosity, thermal conductivity and species diffusion coefficients). It was demonstrated that the above mentioned actions did not lead to relevant changes in the results for the range of considered conditions. On the other hand, the results are in general dependent on the chemical mechanism and care must be taken to use a mechanism that represents well the examined situation.

A sensitivity analysis was performed that showed that the solid conversion rate can be affected by different parameters (diffusion coefficients, surface kinetics and gas phase kinetics). Which of these parameters is the most important, depends on whether the conversion is controlled by the reaction kinetics or the reactant diffusion. For most of the studied particle surface temperatures, the conversion was found to be controlled by the oxygen diffusion to the particle (around 1400 <  $T_p$  < 1800 K) and to the effective flame ( $T_p$  > 1800 K) surfaces. Even though in diffusion-controlled conditions the overall solid conversion rate is only weakly dependent on kinetics, the contributions from gasification and oxidation reactions, as well as the flame structure, might be substantially affected.

It is remarkable that the combustion behavior of the solid particle can be explored in such a detailed manner by employing a very simple chemical mechanism. However, a complex mechanism is needed for a more thorough analysis. At the current stage of development, the model presented in this study was validated against quasi-steady experimental results. In order to explore transient phenomena in further studies, it would be necessary to account for the heat transfer at the particle surface, in particular radiation between the particle and the surrounding gas, and for temperature gradients inside the particle. Finally, the reason for the conversion rate to drop around  $T_p = 1700$  K could be explored by including models that account for changes in the molecular structure of the solid.

### **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.

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#### Appendix A. Derivation of boundary conditions for species

Species transport equation,

$$\frac{\partial(\rho Y_k)}{\partial t} + \nabla \cdot (\rho \mathbf{u} Y_k + \mathbb{J}_k) = \dot{\omega}_k, \tag{A.1}$$

can be expressed in integral form as

$$\int_{V} \frac{\partial (\rho Y_k)}{\partial t} dV + \int_{V} \nabla \cdot (\rho \mathbf{u} Y_k + \mathbb{J}_k) dV = \int_{V} \dot{\omega}_k dV.$$
(A.2)

Using the divergence theorem, Eq. (A.2) becomes

$$\int_{V} \frac{\partial (\rho Y_{k})}{\partial t} dV + \int_{S} (\rho u Y_{k} + \mathbb{J}_{k}) \cdot \hat{\boldsymbol{n}} dA = \int_{V} \dot{\omega}_{k} dV, \qquad (A.3)$$

where  $\hat{\mathbf{n}}$  is a unit vector normal to the surface. At the particle surface all volumetric integrals tend to 0 and a source term due to the surface reactions  $(\dot{m}_k)$  appears in the place of the volumetric reaction term  $(\dot{\omega}_k)$ . Also, since the particle is assumed to be perfectly cylindrical  $\hat{\mathbf{n}} = \hat{\mathbf{r}}$ , where  $\hat{r}$  is a unit normal vector in the radial direction. After taking all of the above into account, Eq. (A.3) becomes

$$\int_{S} (\rho \mathbf{u} Y_k + \mathbb{J}_k) \cdot \hat{\mathbf{r}} dA = \int_{S} \dot{m}_k dA.$$
(A.4)

Using the fact that for an arbitrary surface

$$\int_{S} bdA = \int_{S} cdA \Leftrightarrow b = c, \tag{A.5}$$

Eq. (A.4) can be written in a differential form

$$(\rho \mathbf{u} Y_k + \mathbb{J}_k) \cdot \hat{\mathbf{r}} = \dot{m}_k. \tag{A.6}$$

Summing over all gas phase species one obtains

$$\sum_{k} (\rho \mathbf{u} Y_k + \mathbb{J}_k) \cdot \hat{\mathbf{r}} = \rho u_r = \sum_{k} \dot{m}_k = -\dot{m}_C \tag{A.7}$$

where it has been used that  $\sum_{k} \mathbb{J}_{k} \cdot \hat{\mathbf{r}} = 0$ . Here,  $\dot{m}_{C}$  is a carbon consumption rate and  $u_{r}$  is the outward velocity of the species mixture in the radial direction. One can now substitute

$$\mathbb{J}_k = -\rho D_k \nabla Y_k, \tag{A.8}$$

$$\mathbf{u} \cdot \hat{\mathbf{r}} = u_r = -\dot{m}_C / \rho \tag{A.9}$$

and

$$\nabla Y_k \cdot \hat{\boldsymbol{r}} = \frac{\partial Y_k}{\partial r} \tag{A.10}$$

into Eq. (A.6) to arrive at the final form of boundary conditions for species mass fractions at the particle surface,

$$\dot{m}_k + \dot{m}_C Y_k + \rho D_k \frac{\partial Y_k}{\partial r} = 0.$$
(A.11)

#### References

- Coal 2018Technical Report, International Energy Agency, Paris, 2020. www.iea. org/reports/coal-2020
- [2] Renewables 2020Technical Report, International Energy Agency, Paris, 2020. https://www.iea.org/reports/renewables-2020
- [3] World Energy Outlook 2020Technical Report, International Energy Agency, Paris, 2020. https://www.iea.org/reports/world-energy-outlook-2020
- [4] T. Hara, M. Muto, T. Kitano, R. Kurose, S. Komori, Direct numerical simulation of a pulverized coal jet flame employing a global volatile matter reaction scheme based on detailed reaction mechanism, Combust. Flame 162 (12) (2015) 4391–4407, doi:10.1016/J.COMBUSTFLAME.2015.07.027.
- [5] K. Luo, Y. Bai, T. Jin, K. Qiu, J. Fan, Direct numerical simulation study on the stabilization mechanism of a turbulent lifted pulverized coal jet flame in a heated coflow, Energy Fuels 31 (8) (2017) 8742–8757, doi:10.1021/acs. energyfuels.7b01342.
- [6] K. Luo, C. Mao, J. Fan, Z. Zhuang, N. Haugen, Fully resolved simulations of single char particle combustion using a ghost-cell immersed boundary method, AlChE J. 64 (7) (2018) 2851–2863, doi:10.1002/aic.16136.
- [7] M. Muto, K. Yuasa, R. Kurose, Numerical simulation of ignition in pulverized coal combustion with detailed chemical reaction mechanism, Fuel 190 (2017) 136–144, doi:10.1016/j.fuel.2016.11.029.
- [8] M. Rieth, A. Kempf, A. Kronenburg, O. Stein, Carrier-phase DNS of pulverized coal particle ignition and volatile burning in a turbulent mixing layer, Fuel 212 (2018) 364–374, doi:10.1016/J.FUEL.2017.09.096.
- [9] X. Wen, A. Shamooni, O.T. Stein, L. Cai, A. Kronenburg, H. Pitsch, A.M. Kempf, C. Hasse, Detailed analysis of early-stage NOxformation in turbulent pulverized coal combustion with fuel-bound nitrogen, Proc. Combust. Inst. volume 38 (2021) 4111–4119, doi:10.1016/j.proci.2020.06.317. Elsevier
- [10] J.G.M Kuerten, Point-particle DNS and LES of particle-Laden turbulent flow a state-of-the-art review, Flow Turbul. Combust. 97 (3) (2016) 689–713, doi:10. 1007/s10494-016-9765-y.
- [11] M. Vascellari, H. Xu, C. Hasse, Flamelet modeling of coal particle ignition, Proc. Combust. Inst. 34 (2) (2013) 2445–2452, doi:10.1016/j.proci.2012.06.152.
- [12] G.L. Tufano, O.T. Stein, A. Kronenburg, A. Frassoldati, T. Faravelli, L. Deng, A.M. Kempf, M. Vascellari, C. Hasse, Resolved flow simulation of pulverized coal particle devolatilization and ignition in air- and O<sub>2</sub>/CO<sub>2</sub>-atmospheres, Fuel 186 (2016) 285–292, doi:10.1016/j.fuel.2016.08.073.
- [13] G.L. Tufano, O.T. Stein, B. Wang, A. Kronenburg, M. Rieth, A.M. Kempf, Coal particle volatile combustion and flame interaction. Part I: characterization of transient and group effects, Fuel 229 (2018) 262–269, doi:10.1016/j.fuel.2018. 02.105.
- [14] G.L. Tufano, O.T. Stein, B. Wang, A. Kronenburg, M. Rieth, A.M. Kempf, Coal particle volatile combustion and flame interaction. Part II: effects of particle Reynolds number and turbulence, Fuel 234 (2018) 723–731, doi:10.1016/j.fuel. 2018.07.054.
- [15] M. Kestel, P. Nikrityuk, O. Hennig, C. Hasse, Numerical study of the partial oxidation of a coal particle in steam and dry air atmospheres, IMA J. Appl. Math. (Inst. Math. Appl.) volume 77 (2012) 32–46, doi:10.1093/imamat/hxr071. Oxford University Press
- [16] A. Richter, P.A. Nikrityuk, M. Kestel, Numerical investigation of a chemically reacting carbon particle moving in a hot O<sub>2</sub>/CO<sub>2</sub> atmosphere, Ind. Eng. Chem. Res. 52 (16) (2013) 5815–5824, doi:10.1021/ie302770j.
- [17] D. Safronov, M. Kestel, P. Nikrityuk, B. Meyer, Particle resolved simulations of carbon oxidation in a laminar flow, Can. J. Chem. Eng. 92 (10) (2014) 1669– 1686, doi:10.1002/cjce.22017.
- [18] S. Schulze, P. Nikrityuk, F. Compart, A. Richter, B. Meyer, Particle-resolved numerical study of char conversion processes in packed beds, Fuel 207 (2017) 655–662, doi:10.1016/j.fuel.2017.05.071.
- [19] Z. Xue, Q. Guo, Y. Gong, J. Xu, G. Yu, Numerical study of a reacting single coal char particle with different pore structures moving in a hot O<sub>2</sub>/CO<sub>2</sub> atmosphere, Fuel 206 (2017) 381–389, doi:10.1016/j.fuel.2017.06.035.
- [20] Z. Xue, Y. Gong, Q. Guo, Y. Wang, C. Yu, Conversion characteristics of a single coal char particle with high porosity moving in a hot O<sub>2</sub>/CO<sub>2</sub> atmosphere, Fuel 256 (2019) 115967, doi:10.1016/j.fuel.2019.115967.
- [21] A. Richter, M. Kestel, P.A. Nikrityuk, Pore-resolved simulation of char particle combustion/gasification, Gasification Processes: Modeling and Simulation, Wiley-VCH (2014), pp. 243–270.
- [22] J. Lee, A. Tomboulides, S. Orszag, R. Yetter, F. Dryer, A transient twodimensional chemically reactive flow model: fuel particle combustion in a nonquiescent environment, Symp. (Int.) Combust. 26 (2) (1996) 3059–3065, doi:10.1016/S0082-0784(96)80149-4.
- [23] S. Farazi, M. Sadr, S. Kang, M. Schiemann, N. Vorobiev, V. Scherer, H. Pitsch, Resolved simulations of single char particle combustion in a laminar flow field, Fuel 201 (2017) 15–28, doi:10.1016/j.fuel.2016.11.011.
- [24] T. Sayadi, S. Farazi, S. Kang, H. Pitsch, Transient multiple particle simulations of char particle combustion, Fuel 199 (2017) 289–298, doi:10.1016/j.fuel.2017. 02.096.
- [25] G.L. Tufano, O.T. Stein, A. Kronenburg, G. Gentile, A. Stagni, A. Frassoldati, T. Faravelli, A.M. Kempf, M. Vascellari, C. Hasse, Fully-resolved simulations of

coal particle combustion using a detailed multi-step approach for heterogeneous kinetics, Fuel 240 (2019) 75–83, doi:10.1016/j.fuel.2018.11.139.

- [26] C.B. Nguyen, J. Scherer, M. Hartwich, A. Richter, The morphology evolution of char particles during conversion processes, Combust. Flame 226 (2021) 117– 128, doi:10.1016/j.combustflame.2020.11.038.
- [27] A. Brandenburg, A. Johansen, P.A. Bourdin, W. Dobler, W. Lyra, M. Rheinhardt, S. Bingert, N.E.L. Haugen, A. Mee, F. Gent, N. Babkovskaia, C.-C. Yang, T. Heinemann, B. Dintrans, D. Mitra, S. Candelaresi, J. rn Warnecke, P.J. Käpylä, A. Schreiber, P. Chatterjee, M.J. Käpylä, X.-Y. Li, J.K. ger, J. rgen R. Aarnes, G.R. Sarson, J.S. Oishi, J. Schober, R. Plasson, C. Sandin, E. Karchniwy, L.F.S. Rodrigues, A. Hubbard, G. Guerrero, A. Snodin, I.R. Losada, J. Pekkilä, C. Qian, The pencil code, a modular MPI code for partial differential equations and particles: multipurpose and multiuser-maintained, J. Open Source Softw. 6 (58) (2021) 2807, doi:10.21105/joss.02807.
- [28] S.E. Sherer, J.N. Scott, High-order compact finite-difference methods on general overset grids, J. Comput. Phys. 210 (2) (2005) 459–496, doi:10.1016/j.jcp.2005. 04.017.
- [29] J. Chicheportiche, X. Gloerfelt, Study of interpolation methods for highaccuracy computations on overlapping grids, Comput. Fluids 68 (2012) 112– 133, doi:10.1016/j.compfluid.2012.07.019.
- [30] M.R. Visbal, D.V. Gaitonde, High-order-accurate methods for complex unsteady subsonic flows, AIAA J. 37 (10) (1999) 1231–1239, doi:10.2514/2.591.
- [31] M.R. Visbal, D.V. Gaitonde, On the use of higher-order finite-difference schemes on curvilinear and deforming meshes, J. Comput. Phys. 181 (1) (2002) 155–185, doi:10.1006/jcph.2002.7117.
- [32] J.R. Aarnes, N.E.L. Haugen, H.I. Andersson, High-order overset grid method for detecting particle impaction on a cylinder in a cross flow, Int. J. Comput. Fluid Dyn. 33 (1–2) (2019) 43–58, doi:10.1080/10618562.2019.1593385.
- [33] J.R. Aarnes, T. Jin, C. Mao, N.E.L. Haugen, K. Luo, H.I. Andersson, Treatment of solid objects in the pencil code using an immersed boundary method and overset grids, Geophys. Astrophys. Fluid Dyn. 114 (1–2) (2020) 35–57, doi:10.1080/03091929.2018.1492720.
- [34] N. Babkovskaia, N.E. Haugen, A. Brandenburg, A high-order public domain code for direct numerical simulations of turbulent combustion, J. Comput. Phys. 230 (1) (2011) 1–12, doi:10.1016/j.jcp.2010.08.028.
- [35] S.R. Turns, An introduction to combustion: concepts and applications, Second Edition., McGraw Hills International Editions, 2000.
- [36] L. Zhang, K. Liu, C. You, Fictitious domain method for fully resolved reacting gas-solid flow simulation, J. Comput. Phys. 299 (2015) 215–228, doi:10.1016/j. jcp.2015.07.010.
- [37] F.L. Dryer, C.K. Westbrook, Simplified reaction mechanisms for the oxidation of hydrocarbon fuels in flames, Combust. Sci. Technol. 27 (1–2) (1981) 31–43, doi:10.1080/00102208108946970.
- [38] N.E.L. Haugen, R.E. Mitchell, M.B. Tilghman, A comprehensive model for char particle conversion in environments containing O<sub>2</sub> and CO<sub>2</sub>, Combust. Flame 162 (2015) 1455–1463, doi:10.1016/j.combustflame.2014.11.015.
- [39] A. Makino, T. Namikiri, K. Kimura, Combustion rates of graphite rods in the forward stagnation field with high-temperature airflow, Combust. Flame 132 (4) (2003) 743–753, doi:10.1016/S0010-2180(02)00537-0.
- [40] S. Gordon, B. Mcbride, Computer program for calculation of complex chemical equilibrium compositions, NASA Reference Publication, 1971. 1311
- [41] A. Brandenburg, Computational aspects of astrophysical MHD and turbulence, Advances in Nonlinear Dynamos, CRC Press (2003), pp. 269–344, doi:10.1201/ 9780203493137-9.
- [42] P.A. Nikrityuk, M. Gräbner, M. Kestel, B. Meyer, Numerical study of the influence of heterogeneous kinetics on the carbon consumption by oxidation of a single coal particle, Fuel 114 (2013) 88–98, doi:10.1016/j.fuel.2012.10.037.
- [43] R.T. Yang, M. Steinberg, A diffusion cell method for studying heterogeneous kinetics in the chemical reaction/diffusion controlled region. kinetics of c + CO<sub>2</sub> → 2CO at 1200–1600 °c, Ind. Eng. Chem. Fundam. 16 (2) (1977) 235–242, doi:10.1021/i160062a011.
- [44] D.E. Rosner, H.D. Allendor, Comparative studies of the attack of pyrolytic and isotropic graphite by atomic and molecular oxygen at high temperatures, AIAA J. 6 (4) (1968) 650-654, doi:10.2514/3.4558.
- [45] D.E. Rosner, High-temperature gas-solid reactions, Annu. Rev. Mater. Sci. 2 (1) (1972) 573–606, doi:10.1146/annurev.ms.02.080172.003041.
- [46] J. Nagle, R.F. Strickland-Constable, Oxidation of carbon between 1000–2000 °C, Fifth Conference on Carbon, Pergamon (1962), pp. 154–164, doi:10.1016/ B978-0-08-009707-7.50026-1.
- [47] J.R. Walls, R.F. Strickland-Constable, Oxidation of carbon between 1000-2400 °C, Carbon 1 (3) (1964) 333–338, doi:10.1016/0008-6223(64)90288-x.
- [48] A. Makino, N. Araki, Y. Mihara, Combustion of artificial graphite in stagnation flow: Estimation of global kinetic parameters from experimental results, Combust. Flame 96 (3) (1994) 261–274, doi:10.1016/0010-2180(94)90013-2.
- [49] A. Makino, T. Namikiri, N. Araki, Combustion rate of graphite in a high stagnation flowfield and its expression as a function of the transfer number, Symp. (Int.) Combust. volume 27 (1998) 2949–2956, doi:10.1016/S0082-0784(98) 80154-9. Elsevier
- [50] P.A. Libby, T.R. Blake, Theoretical study of burning carbon particles, Combust. Flame 36 (C) (1979) 139–169, doi:10.1016/0010-2180(79)90056-7.
- [51] A. Makino, An approximate explicit expression for the combustion rate of a small carbon particle, Combust. Flame 90 (2) (1992) 143–154, doi:10.1016/ 0010-2180(92)90116-7.
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# The effect of Stefan flow on the drag coefficient of spherical particles in a gas flow



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#### ABSTRACT

Particle laden flows with reactive particles are common in industrial applications. Chemical reactions inside the particle can generate a Stefan flow that affects heat, mass and momentum transfer between the particle and the bulk flow. This study aims at investigating the effect of Stefan flow on the drag coefficient of a spherical particle immersed in a uniform flow under isothermal conditions. Fully resolved simulations were carried out for particle Reynolds numbers ranging from 0.2 to 14 and Stefan flow Reynolds numbers from (-1) to 3, using the immersed boundary method for treating fluid-solid interactions. Results showed that the drag coefficient decreased with an increase of the outward Stefan flow. The main reason was the change in viscous force by the expansion of the boundary layer surrounding the particle. A simple model was developed based on this physical interpretation. With only one fitting parameter, the performance of the model to describe the simulation data were comparable to previous empirical models.

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#### 1. Introduction

Many industrial applications involve particle laden flows with reactive particles, such as combustion of solid fuels, catalytic cracking and drying applications. Unlike ordinary particle-laden flows, reacting particles exchange mass with the surrounding fluid. A Stefan flow, induced by chemical reactions inside or at the surface of the particle, has effects on the gas-solid interaction, i.e. momentum (C<sub>D</sub>-drag coefficient), heat (Nu-Nusselt number) and mass transfer (Sh-Sherwood number) between the particle and the bulk flow (Hayhurst, 2000; Yu and Zhang, 2009; Yu et al., 2013; Kalinchak, 2001). This can be exemplified by gasification and combustion processes, where, upon being released into the hot environment, fuel particles undergo fast devolatilization that results in a pronounced gas stream leaving the particles. Although momentum, heat, and mass transfer could be affected by the Stefan flow, as a first step, we focus on the effect of Stefan flow on  $C_D$  in isolation from the effects of heat and mass transfer in this study.

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Resolved simulations of multiphase reactive flows demand high computational resources due to its complexity and the multi-scale nature of the processes. The smallest scale in such systems typically corresponds to the scale of the particles and their boundary layers  $(10^{-6} - 10^{-3} \text{ m})$ , while the largest scales are set by the entire reactor, which typically contains millions of reactive particles and has a length scale  $(10^{0} - 10^{2} \text{ m})$  that is several orders of magnitudes larger than the particle scale. Therefore, it is impractical to carry out particle resolved simulations for a large domain. Instead, it is useful to develop constitutive models based on the results from particle resolved simulations of single or multiple particles, which can then be implemented in large scale reactor simulations that do not resolve the individual particles. Compared with the many particle-resolved simulations in the literature, only a few studies have used their results to develop models suitable to use in large scale simulations (e.g. models for Stefan flow developed by Miller and Bellan (1999) and Kestel (2016), while models taking into account particle porosity and particle shape are presented in Wittig et al. (2017) and Richter and Nikrityuk (2012), respectively.)

Previous studies on Stefan flow effects mainly investigated droplet evaporation/condensation (Bagchi et al., 2001; Renksizbulut and Yuen, 1983; Dukowicz, 1984) and suction/blowing

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effects (Chuchottaworn et al., 1983; Dukowicz, 1982; Cliffe and Lever, 1985). Models developed for the drag coefficient of evaporating/condensing droplets are based on both experimental and simulation data. Recently, the performance of the model by Renksizbulut and Yuen (1983) was assessed for a char particle during oxy-fuel combustion (Farazi et al., 2016). The model contains a case-specific blowing number and had to be adjusted by introducing a new blowing number. However, some studies have proposed more general models for the drag coefficients of a reacting particle, based on the suction/blowing effect directly. In early models, the mass flux inward/outward (hereafter called Stefan flow) was represented by 'a non-dimensional blowing number  $(\Lambda)$ ', which is the ratio of Stefan flow velocity and slip velocity  $(=U_{sf}/U_{\infty})$ (Cliffe and Lever, 1985). More recently, the Stefan velocity has been non-dimensionalized by the Stefan Reynolds number, Resf, which is based on particle radius (R), Stefan velocity ( $U_{sf}$ ) and fluid viscosity (*v*) (Kestel, 2016):

$$Re_{sf} = \frac{2U_{sf}R}{\nu}.$$
 (1)

Another relevant Reynolds number is the particle Reynolds number, *Re*, which is based on the particle slip velocity  $(U_{\infty})$ ,

$$Re = \frac{2U_{\infty}R}{\nu},\tag{2}$$

such that  $U_{sf,r} = Re_{sf}/Re$ .

Dukowicz (1982) developed an analytical relation for the drag of a spherical solid particle with suction/blowing in creeping flows  $(Re \rightarrow 0)$ . For higher Re, a number of works addressed the effects of Stefan flow on the drag coefficient (Cliffe and Lever, 1985; Miller and Bellan, 1999; Kestel, 2016; Nour et al., 2017). Miller and Bellan (1999) developed an empirical model based on the numerical simulation results of Cliffe and Lever (1985) for an isothermal flow around a sphere. Kurose et al. (2003) has modified the model coefficients of the same model to fit the data for an outflow in a linear shear flow around a solid sphere. Later, another empirical model was introduced by Kestel (2016), which is applicable for the wider range of mass fluxes that appeared in a 200 MW commercial gasifier data. It is apparent that the change of drag coefficient due to Stefan flow cannot be neglected. However, available models are not based on physical observations, and they rely on a number of fitting parameters. In addition, none of the models are suitable for negative Stefan flows (suction).

This study investigates the interaction between a gas flow and an embedded reacting particle that experience a Stefan flow. The main aim is to develop a physics-based simple model describing the change of the drag coefficient due to the Stefan flow for a particle in an isothermal flow. Direct numerical simulations that resolve the boundary layer at the particle surface were carried out for a laminar flow surrounding a stationary particle with either an outgoing or an incoming Stefan flow. Simulation results were analyzed and a model was developed with a physical interpretation from the simulations. The developed model and two previous models from the literature (Miller and Bellan, 1999; Kestel, 2016) were compared with the simulation results. The range of particle Reynolds numbers (*Re*) in this study is limited to the conditions relevant to entrained-flow gasification or pulverized combustion.

#### 2. Methodology

The numerical simulations considered a static particle in a uniform isothermal flow. The generation and consumption of gas in the solid phase were considered as a uniform outgoing or incoming mass flux at the particle surface in the surface-normal direction. In all of the simulations performed here, the Reynolds number is smaller than the critical Reynolds number that yields von Karman oscillations. This means that there are no transients in the flow, and hence, a steady state solver can be used.

#### 2.1. Governing equations

Steady state simulations were carried out under isothermal conditions, with the gas phase assumed to be incompressible. The discrete phase was described as a static spherical particle with constant size. The gas phase is governed by mass conservation,

$$\nabla \cdot \vec{u} = 0, \tag{3}$$

and momentum conservation,

$$(\rho \vec{u} \cdot \nabla) \vec{u} = -\nabla p + \mu \nabla^2 \vec{u}, \qquad (4)$$

where  $\rho$  is the density of the fluid,  $\vec{u}$  is velocity vector, p is pressure and  $\mu$  is dynamic viscosity. Eqs. (3) and (4) were discretized with the finite volume method using second-order schemes.

#### 2.2. Boundary conditions

The slip velocity between the particle and the bulk gas was set as the inlet velocity at the front boundary (left side of the calculation domain in Fig. 1). An 'outflow' boundary condition (i.e. zero velocity gradient) was applied at the back boundary (right side of the calculation domain in Fig. 1). The side boundaries of the domain were treated as 'slip walls'. A 'slip wall' boundary condition enforces both the velocity component normal to the wall and the gradients of the other velocity components in the normal direction to be zero. Boundaries along the symmetry axes were considered as 'symmetric' boundaries, which means that the component of velocity normal to the symmetry plane is zero and that the gradient of all the other properties normal to the plane is zero.

The immersed boundary method (IBM) was used at the surface of the particle. The current work used the discrete forcing approach (Mittal and Iaccarino, 2005), which uses the direct imposition of boundary conditions (Jasak et al., 2014), and the presence of the immersed surface/body is formulated through the boundary conditions. The value of any parameter inside the cells that contain the immersed boundary was calculated by interpolating values at the immersed boundary points and the neighbour cells (Fadlun et al., 2000). To implement Stefan flow, the velocity is fixed (Dirichlet boundary condition) at the immersed boundary normal to the particle surface as:

$$\dot{m} = \rho \oint_{S} (\vec{u}_{sf} \cdot \vec{n}) dS, \tag{5}$$

where integration is over the surface *S* of the particle,  $\vec{n}$  is unit vector in the direction normal to the surface element *dS* and  $\dot{m}$  is mass flow rate due to the Stefan flow. Furthermore, for pressure the gradient is set to zero at the immersed boundary (Neumann boundary condition). The treatment of Dirichlet and Neumann boundary conditions for an immersed boundary method in *foam-extend* is shown in the Appendix A (Jasak et al., 2014).

#### 2.3. Calculation conditions and procedure

In this work, we used the OpenFoam environment, called *foam-extend*-3.2 (Weller et al., 1998). The numerical simulations were carried out using the incompressible, steady-state, immersed boundary solver. The solver uses quadratic interpolation (Jasak et al., 2014) for the reconstruction of the solid phase boundary conditions into the closest fluid cells.

Flow conditions were selected based on practical applications of pulverized combustion and gasification at atmospheric pressure. Four different *Re* were selected by considering particle size (0.1-1.0 mm), slip velocity  $(0.5-3 \text{ m s}^{-1})$ , and gas properties of N<sub>2</sub> at



**Fig. 1.** Computational domain for the simulations, with *D* denoting the particle diameter, and  $\Delta_i$ , i = 1 to 5 representing the coarsest mesh to finest mesh.  $D_{-x,i}$  is the distance from the centre of the sphere to positive x-direction and  $D_{+x,i}$  is the distance from the centre of the sphere to positive x-direction in level *i* (See the Table 1).

 Table 1

 Distance from the centre of the particle

 in diameters (D) in the computational domain (See Fig. 1).

i	$D_{-x,i}$	$D_{+x,i}$	$D_{y,i}, D_{z,i}$	$\Delta_i/D$
1	16	48	16	0.16
2	3	6	3	0.08
3	2	5	2	0.04
4	1.5	3	1.5	0.02
5	1.2	2	1.2	0.01

1400 K. The considered *Re* are: 0.232, 2.32, 6.98, 13.96. The magnitude of the Stefan-flow mass flux was calculated from data relevant for devolatilization and char conversion of biomass (Kreitzberg et al., 2016; Umeki et al., 2012). Since the *Re* was always less than 20 in this study, the flow is steady, axisymmetric and topologically similar (Johnson and Patel, 1999). Therefore, only a quarter of the domain was simulated with symmetric boundaries.

Initially, the domain size and mesh resolution was selected based on previous studies (Constant et al., 2017; Richter and Nikrityuk, 2012) for flow around a sphere. Then, mesh refinement tests were carried out for the highest *Re*. Based on these tests, we arrived at five levels of refinement that were eventually used for the simulations, with the mesh size of the finest refinement being 0.01*D* (see the Fig. 1 and Tab. 1). After the mesh refinement test, domain size tests were carried out for the smallest *Re* and the highest Stefan flow velocity, i.e. because the boundary layer is expected to be the largest under such condition. Based on the results (see Table 2), mesh 2 was selected considering accuracy and econ-

Domain size test for Re = 0.23 at  $Re_{sf} = 2.90$  and 1.45 for different domain sizes.

Table 2

<i>Re<sub>sf</sub></i>	Mesh	Domain size	Refinement levels	C <sub>D</sub>	Error (% of mesh 3)
2.90	mesh 1	$32\times 16\times 16$	4	86.25	19.2
	mesh 2	$64\times32\times32$	4	75.45	4.2
	mesh 3	$128\times 64\times 64$	4	72.38	-
1.45	mesh 2	$64\times32\times32$	4	90.28	2.8
	mesh 3	$128\times 64\times 64$	4	87.85	-

omy of computational resources. The final mesh and domain are shown in Fig. 1, consisting of around 9.6 million cells in total.

For isothermal conditions, the drag coefficient of a particle with no Stefan flow should depend only on *Re*. As preliminary tests, we confirmed this with two different sets of particle diameters and slip velocities at the same *Re*.

#### 2.4. Estimation of the drag coefficient

The drag coefficient can be calculated as

$$C_{D} = \frac{\vec{F}_{P,x} + \vec{F}_{visc,x}}{\frac{1}{2}\rho U_{\infty}^{2}(\pi R^{2})},$$
(6)

when the pressure and viscous forces are given as

$$\vec{F}_{P} = \oint_{S} (P_{sur} - P_{ref}) \vec{n} \, ds, \tag{7}$$

and

$$\vec{F}_{visc} = -\oint_{S} \mu \left( \nabla \vec{u} + \nabla \vec{u}^{t} \right) \vec{n} \, ds, \tag{8}$$

respectively. Here, the integration is over the surface *S* of the particle. In the above,  $P_{sur}$  and  $P_{ref}$  are the interpolated pressure at the particle surface and in the far field, respectively, and  $\vec{n}$  is the unit vector in the surface-normal direction. Only the components  $\vec{F}_{P}$  and  $\vec{F}_{visc}$  in the direction of the mean flow were accounted for when calculating the drag coefficient, since the other components are canceled out due to symmetry.

#### 3. Results and discussion

#### 3.1. Validation

The numerical implementation was validated for the estimated drag coefficient using four *Re* without Stefan flow. The obtained drag coefficient was compared to the empirical formula of Haider and Levenspiel (1989),

$$C_D = \frac{24}{Re} (1 + 0.1806Re^{0.6459}) + 0.4251 \left(1 + \frac{6880.95}{Re}\right)^{-1}, \qquad (9)$$



**Fig. 2.** Drag coefficient as a function of *Re* for the case where there is no Stefan flow. Line: Correlation of Haider and Levenspiel (1989), symbols: numerical simulations.



**Fig. 3.** Normalized drag coefficient  $C_{D,f}/C_{D,0}$  vs normalized Stefan flow velocity  $U_{sf}/U_{\infty}$  at different *Re*. Symbols: simulations, lines: linear regression to the data.

which was derived from 408 experimental data points. Fig. 2 shows that the drag coefficients obtained from our simulations (symbols) are in agreement with this empirical formula (solid line). The data is also listed in Table B.1.

The velocity profile surrounding the particle generated by Stefan flow was validated in a quiescent fluid by comparing it to the analytical solution,

$$\vec{u_d} = \frac{\vec{u_{sf}}R^2}{d^2},\tag{10}$$

where  $\vec{u}_d$  is the velocity vector at a distance *d* from the centre of the sphere, and  $\vec{u}_{sf}$  is the Stefan flow velocity vector at its surface.

#### 3.2. Effects of Stefan flow on drag coefficient

Fig. 3 shows the normalized drag coefficient,  $C_{D,r} = C_{D,sf}/C_{D,0}$ , plotted against the normalized Stefan flow velocity,  $U_{sf,r} = U_{sf}/U_{\infty}$ , for different *Re*. Here,  $C_{D,0}$  and  $C_{D,sf}$  refer to the drag coefficients without and with Stefan flow, respectively, while  $U_{\infty}$  is the inlet velocity. The results show a nearly linear relationships between  $C_{D,r}$  and  $U_{sf,r}$  for every given *Re*, with the slope of the relationship getting steeper with increasing *Re*.

According to Fig. 3, the normalized drag coefficient was as low as 0.7 (for Re=2.32 and  $U_{sf,r} = 1.3$ ), and is expected to decrease



**Fig. 4.** Drag force due to pressure ( $F_p$ , circles) and viscous stress( $F_{visc}$ , squares) on the sphere normalized by the total drag force ( $F_p + F_{visc}$ ) for  $Re_{sf} = 0$ .



**Fig. 5.** Pressure component  $(P_{surf} - P_{ref})\vec{n}_x$  in the flow direction at the surface of the sphere normalized by the characteristic pressure  $\vec{F}_{tot,x}/\pi R^2$  for Re = 13.96 and different  $U_{sf}/U_{\infty}$ .

even further at higher Stefan velocity. This significant reduction in drag shows the relevance of the Stefan flow in entrained flow gasification and combustion applications.

Fig. 4 explores the effect of Stefan flow in more detail by showing the pressure and viscous forces separately. In all cases studied here, both with and without Stefan flow, we found that the viscous force was larger than the pressure force by a factor of roughly two, as is expected for low *Re*. We do see, however, that this factor is decreasing for increasing  $Re_{sf}$ , and for much larger values of  $Re_{sf}$  it can not be excluded that it may even be less than one. The bottom line is that a positive Stefan flow give a significant reduction of the viscous force while the pressure force remains almost constant.

To elucidate the observed effects, the pressure force component in the mean flow direction,  $(P_{surf} - P_{ref})\vec{n}_x$  is shown in Fig. 5 as a function of surface angle from the front of the particle (See schematic in the inset of Fig. 1). The Stefan flow velocity at the surface is given as  $U_{sf}/U_{\infty}$ , where the positive values indicate outgoing flows. The figure confirms the observation from Fig. 4, i.e.; the pressure force is hardly affected by the Stefan flow and it is almost constant for a given *Re*.

On the contrary, Fig. 4 showed that the viscous force decreased with an outgoing Stefan flow and increased with an incoming Stefan flow. To explore this effect, Fig. 6 shows the viscous stress com-



**Fig. 6.** Viscous stress component  $[-\mu(\nabla \vec{U} + \nabla \vec{U}^{\dagger}), \vec{n}]_x$  in the mean flow direction at the surface of the sphere, normalized by the characteristic pressure  $\vec{F}_{tot,x}/\pi R^2$  for Re = 13.96 and different  $U_{sf}/U_{\infty}$ .

ponent in flow direction as a function of the surface angle from the front of the particle. It shows that the viscous stress is actually higher at the front of the particle for the simulations with outgoing Stefan flow. On the other hand, the viscous stress behind the particle is smaller with outgoing Stefan flow. The changes in the viscous stress at the front and the back of the particle cancel each other and have no significant net effect. The shear stress at the side of the particle ( $40 < \theta < 140$ ) is smaller with outgoing Stefan flow. As a result, the overall viscous stress for the particle decreased under the influence of outward Stefan flow. The main factor that affects the viscous force is the velocity gradient as shown in Eq. (8). The observation in Fig. 6 implies that the change in the boundary layer thickness is more significant than the change in velocity difference that appear at the front and back of the particle.

Fig. 7 shows the flow field (i.e. velocity magnitude) with (lower half panel) and without (upper half panel) outward Stefan flow. Comparison of the flow fields showed that the boundary layer thickness increased with outgoing Stefan flow. On the contrary, the boundary layer thickness decreased with incoming Stefan flow. This change in boundary layer thickness due to the Stefan flow is clearly seen by inspecting the velocity magnitude along the y-axis crossing the centre of the sphere, as shown in Fig. 8. For an outgoing Stefan flow (red dashed line in Fig. 8) we observed a slower relaxation of the velocity magnitude to the free stream velocity, while vice versa, a faster relaxation was observed for incoming Stefan flow (green dashed line). This effect can be understood as the boundary layer being pushed away from the particle surface in case of an outward Stefan flow, while it was pulled towards the surface for an inward Stefan flow. This change in boundary layer thickness with the Stefan flow affects the velocity gradient, and hence it explains the observed change in the viscous force and, consequently, also the drag.

#### 3.3. A model for the drag coefficient with Stefan flow

In this section, a simple expression is suggested for the drag coefficient under the influence of Stefan flow for small *Re*. The net drag on a particle is entirely determined by the boundary layer around the particle. Any change to the boundary layer due to the presence of Stefan flow would therefore have an effect on the drag. Indeed, we observed in the previous section that Stefan flow reduced/enhanced the drag coefficient by modifying the

viscous force through the expansion/contraction of the boundary layer. As a first approximation, we assume that the change in the normalized drag coefficient depends on the change in the volume of the boundary layer. By assuming that the volume of boundary layer with Stefan flow simply becomes the sum of its original volume ( $V_B$ ) and the volume of Stefan flow ( $V_{sf}$ ), the normalized drag coefficient can be expressed as

$$C_{D,r} = \frac{V_B}{V_B + V_{sf}}.$$
(11)

Here, the volume of the Stefan flow is defined as the volume of fluid emitted from the particle during a typical flow time-scale,  $\tau_{f}$ , such that

$$V_{sf} = 4\pi R^2 U_{sf} \tau_f, \tag{12}$$

where the flow time-scale is given by

$$\tau_f = \frac{2(R+\delta)}{U_{\infty}},\tag{13}$$

where  $\delta$  is the boundary layer thickness. We can assume  $\delta \gg R$  at small *Re*. Hence,

$$\tau_f \approx \frac{2\delta}{U_{\infty}}.\tag{14}$$

Based on the above, the volumes of the Stefan flow and its approximation at low *Re* are now given by

$$V_{sf} = 8\pi R^2 (R+\delta) \frac{U_{sf}}{U_{\infty}} \approx 8\pi R^2 \delta \frac{U_{sf}}{U_{\infty}}.$$
 (15)

Furthermore, the volume of the boundary layer is given as

$$V_B = \frac{4}{3}\pi (R+\delta)^3 - \frac{4}{3}\pi R^3,$$
(16)

and when  $\delta \gg R$ ,

$$V_B \approx \frac{4}{3}\pi\,\delta^3.\tag{17}$$

Adopting the result from classical boundary layer theory, the boundary layer thickness is given by

$$\delta = \frac{2AR}{\sqrt{Re}},\tag{18}$$

where A is a constant with a value of the order of one. Combining Eqs. (15) and (17) with Eq. (11) yields

$$C_{D,r} = \frac{1}{1 + \frac{3Re_{sf}}{2A^2}}.$$
(19)

Fig. 9 shows the normalized drag coefficient  $C_{D,r}$  for various Re obtained from the simulations as a function of  $Re_{sf}$ , together with the prediction given in Eq. (19) (solid line). The parameter A in Eq. (19) was calculated by fitting to the data for the smallest Re ( $A = 3.25 \pm 0.25$  at Re = 0.232).

Eq. 19 is based on the assumption that *Re* is small enough to satisfy  $\delta \gg R$ , and it is not applicable for higher *Re*.



**Fig. 7.** Velocity magnitude map with contour lines (velocity magnitude step 0.5) surrounding the sphere at Re = 13.96. Upper half without Stefan flow ( $U_{sf}/U_{\infty} = 0$ ) and lower half with Stefan flow ( $U_{sf}/U_{\infty} = 0.208$ ).



**Fig. 8.** Velocity magnitude normalized by  $U_{\infty}$  along the *y*-axis crossing the sphere centre ( $\theta = 90^{\circ}$ ; distance normalized with particle radius, *R*) for Re = 13.96 at different  $U_{sf}/U_{\infty}$ .

Without the assumptions of  $\delta \gg R$ , i.e. keeping the particle radius when estimating the boundary layer volumes using Eqs. (15) and (16), the normalized drag coefficient based on Eq. (11) follows as :

$$C_{D,r} = \frac{1}{1 + f(Re)Re_{sf}},$$
(20)

with

$$f(Re) = \frac{3}{Re} \left( 1 + \frac{2A}{\sqrt{Re}} \right) \frac{1}{\left(\frac{3A}{\sqrt{Re}} + 6\left(\frac{A}{\sqrt{Re}}\right)^2 + 4\left(\frac{A}{\sqrt{Re}}\right)^3\right)},$$
(21)

where  $A = 3.01 \pm 0.13$  as obtained by fitting to the simulation data using the least squares methods. The performance of the model was compared against the previous models by Miller and Bellan (1999) (Eq. (22)) and Kestel (2016) (Eq. (23)); the former reads as:

$$C_D = \frac{24}{Re} \left[ \frac{1 + 0.054Re + 0.1Re^{\frac{1}{2}} (1 - 0.03Re)}{1 + a|Re_{sf}|^b} \right],$$
(22)



Fig. 9. The normalized drag coefficient as a function of the Stefan based Re.

where  $a = 0.09 + 0.77 \exp(0.4Re)$  and  $b = 0.4 + 0.77 \exp(-0.04Re)$ which is valid for  $0 \le Re \le 100$  and  $0 \le Re_{sf} \le 10$  (Miller and Bellan, 1999) and Kestel (2016) model reads as;

$$C_{D,r} = \frac{1}{(1+0.138Re_{sf}^{-1.153})^a},$$
(23)

where  $a = (\frac{1.063}{1+0.223Re})^{0.568}$ , which is valid for  $0 \le Re \le 200$  and  $0 \le Re_{sf} \le 20$ .

Fig. 10 compares the performances of three models with the data from the simulations. All the models are in good agreement with the simulation results for positive *Re*. The maximum error of the current model was less than 6% in the simulated range that is  $0 \le Re \le 14$  and  $(-1) \le Re_{sf} \le 3$ . However, there are two major differences between the current and previous models. First, the previous models contain several fitting parameters without clear physical background. The current model, however, contains only one fitting parameter, which is related to the relationship between *Re* and the boundary layer thickness (Eq. (18)). Moreover, the previous models by Miller and Bellan (1999) and Kestel (2016) are not applicable to negative  $Re_{sf}$  while the current model expands to negative  $Re_{sf}$  and is in good agreement with simulation data, at least down to  $Re_{sf} = (-1)$ . For strongly negative  $Re_{sf}$ ,  $C_{D,r}$  given by Eq. (20) di-



Fig. 10. Drag coefficient as a function of the Re<sub>sf</sub>, for different Re.

verges. However for Re = 0.232,  $Re_{sf}$  has to become as small as (-7) before  $C_{D,r}$  diverges.

#### 4. Conclusions

Fully resolved numerical simulations of flow surrounding a gasemitting particle were carried out to elucidate the effect of Stefan flow on the drag acting on a particle in a uniform flow. The application of this study is limited to steady, axisymmetric flow (Re < 14), and low Stefan flow velocity ( $-1 \le Re_{sf} \le 3$ ).

Results showed that the drag coefficient has a nearly linear relationship with the Stefan flow velocity. An outward Stefan flow lead to a reduction of the drag coefficient, whereas the magnitude of the reduction increases with increasing *Re*. For the Reynolds numbers in this study, the main reason for the reduction/increase in the drag coefficient was the change in viscous force. This was caused by the expansion/contraction of the boundary layer surrounding the particle, rather than the change in relative velocity at the particle surface.

A simple model was developed based on the change in the volume of the boundary layer due to Stefan flow. Although the model contains only one fitting parameter, it showed as good agreement with the simulation data as previous models with several fitting parameters. The proposed model also showed good agreement with the simulation data for negative  $Re_{sf}$  while previous models could not be computed because of non-integer indexes for  $Re_{sf}$ . Similar studies for Nusselt number and Sherwood number would be important for future works.

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## Appendix A. Boundary treatment with immersed boundary (IB) method in *foam-extend* (Jasak et al., 2014)

In the IB method, the mesh is categorized into three types of cells called IB cells, Fluid cells or solid cells, which is shown in the Fig. A.1a.



**Fig. A1.** (a) Different cells around an Immersed boundary(IB), IB cell normals, (b) Extended stencil around an IB and local co-ordinate system for Neumann boundary conditions. adopted from Jasak et al. (2014) with the permission from the authors.

Velocity (Dirichlet boundary condition) of an immersed boundary cell( $\phi_p$ ) is calculated using quadratic interpolation as

$$\begin{split} \phi_p &= \phi_{ib} + C_0 (x_P - x_{ib}) + C_1 (y_P - y_{ib}) \\ &+ C_2 (x_P - x_{ib}) (y_P - y_{ib}) \\ &+ C_3 (x_P - x_{ib})^2 + C_4 (y_P - y_{ib})^2, \end{split} \tag{A.1}$$

and pressure (Neumann boundary condition) of an immersed boundary cell is calculated as

$$\phi_p = C_0 + [n_{ib} \cdot (\nabla \phi)_{ib}] x_P^1 + C_1 y_P^1 + C_2 x_P^1 y_P^1 + C_3 (x_P^1)^2 + C_4 (y_P^1)^2,$$
(A.2)

where the coefficients  $C_0$ ,  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  are calculated using weighted least squares method in the extended stencil shown in Fig. A.1b and  $x^1$  and  $y^1$  are local co-ordinates where  $x^1$  is normal to the point *ib*.

#### Appendix B. Data tables of Figure 2

Table B.1Data tables of Fig. 2.					
Simulations	Model	Difference (% of model value)			
3.431	3.424	0.20			
5.521	5.617	1.71			
13.074	13.562	3.60			
108.490	110.720	2.01			
	s of Fig. 2. Simulations 3.431 5.521 13.074 108.490	s of Fig. 2. Simulations Model 3.431 3.424 5.521 5.617 13.074 13.562 108.490 110.720			

#### Appendix C. Data tables of Figure 10

Table C.1	
Data tables of Fig.	9.

		CD	Current	Kestel	Error of current model
Re	Re <sub>sf</sub>	-simulations	model	model	(% of numerical results)
13.96	2.90	2.82	2.87	2.87	1.6
	0.97	3.19	3.22	3.232	0.7
	0.19	3.38	3.38	3.392	0.02
	0.04	3.42	3.42	3.42	0.01
	0	3.43	-	-	_
	-0.39	3.48	3.52	-	1.2
	-0.97	3.65	3.66	-	0.4
6.98	2.90	4.36	4.53	4.44	4.0
	1.45	4.89	5.02	5.00	2.5
	0.48	5.30	5.40	5.42	1.9
	0.10	5.48	5.58	5.59	1.8
	0	5.52	-	-	-
	-0.20	5.61	5.71	-	1.7
	-0.97	6.00	6.10	-	1.9
2.32	2.90	9.60	10.37	9.90	8.0
	1.93	10.60	11.25	10.98	6.1
	0.97	11.75	12.30	12.25	4.7
	0.20	12.91	13.29	13.34	2.9
	0	13.07	-	-	-
	-0.39	13.61	14.14	-	3.9
	-0.97	14.51	15.12	-	4.2
0.232	2.90	75.45	78.20	74.88	3.7
	1.45	90.28	91.56	91.00	1.4
	0.58	100.80	102.01	102.79	1.2
	0.29	104.57	106.05	106.85	1.4
	0.19	105.80	107.46	108.15	1.6
	0.10	107.09	108.92	109.39	1.7
	0.02	108.27	110.11	110.25	1.7
	0	108.49	-	-	-
	-0.04	108.90	111.02	-	2.0
	-0.97	122.78	127.99	-	4.2

#### References

- Bagchi, P., Ha, M.Y., Balachandar, S., 2001. Direct numerical simulation of flow and heat transfer from a sphere in a uniform cross-Flow. J. Fluids Eng. 123, 347–358. doi:10.1115/1.1358844.
- Chuchottaworn, P., Fujinami, A., Asano, K., 1983. Numerical analysis of the effect of mass injection or suction on drag coefficients of a sphere. J. Chem. Eng. Jpn. 16, 18–24. doi:10.1252/jcej.16.18.
- Cliffe, A., Lever, D., 1985. Isothermal flow past a blowing sphere. Int. J. Numer. Methods Fluids 5, 709–725. doi:10.1002/fld.1650050804.
- Constant, E., Favier, J., Meldi, M., Meliga, P., Serre, E., 2017. An immersed boundary method in OpenFOAM: verification and validation. Comput. Fluids doi:10.1016/ j.compfluid.2017.08.001.
- Dukowicz, J.K., 1982. An exact solution for the drag of a sphere in low Reynolds number flow with strong uniform suction or blowing. Phys. Fluids 25, 1117– 1118. doi:10.1063/1.863875.
- Dukowicz, J.K., 1984. Drag of evaporating or condensing droplets in low Reynolds number flow. Phys. Fluids 27, 1351–1358. doi:10.1063/1.864776.
- Fadlun, E.A., Verzicco, R., Orlandi, P., Mohd-Yusof, J., 2000. Combined immersedboundary finite-Difference methods for three-Dimensional complex flow simulations. J. Comput. Phys. 161, 35–60. doi:10.1006/jcph.2000.6484.
- Farazi, S., Sayadi, T., Pitsch, H., 2016. Numerical analysis of the drag force acting on the reactive single char particle under oxy-fuel condition. In: Proc. of the China National Symposium on Combustion 2016. Ma'anshan
- Haider, A., Levenspiel, O., 1989. Drag coefficient and terminal velocity of spherical and nonspherical particles. Powder Technol. 58, 63–70. doi:10.1016/ 0032-5910(89)80008-7.
- Hayhurst, A.N., 2000. The mass transfer coefficient for oxygen reacting with a carbon particle in a fluidized or packed bed. Combust.Flame 121, 679–688. doi:10.1016/s0010-2180(99)00178-9.
- Jasak, H., Rigler, D., Tukovic, Z., 2014. Design and implementation of Immersed Boundary method with discrete forcing approach for boundary conditions. In: In Proceedings of 6th European Congress on Computational Fluid Dynamics -ECFD VI, pp. 5319–5332. Barcelona, Spain
- Johnson, T.A., Patel, V.C., 1999. Flow past a sphere up to a reynolds number of 300. J. Fluid Mech 378, 19-70. doi:10.1017/S0022112098003206.
- Kalinchak, V., 2001. Influence of Stefan flow and convection on the kinetics of chemical reactions and heat and mass exchange of carbon particles with gases. J. Eng. Phys. Thermophys. 74, 323–330. doi:10.1023/A:1016696203987.

- Kestel, M., 2016. Numerical Modeling of Moving Carbonaceous Particle Conversion in Hot Environments. TU Bergakademie Ph.D. thesis.
- Kreitzberg, T., Pielsticker, S., Gvert, B.M., Kneer, R., 2016. CO2 and H2O Gasification under chemically and diffusion controlled conditions. In: 33rd Annual International Pittsburgh Coal Conference. Cape Town
- Kurose, R., Makino, H., Komori, S., Nakamura, M., Akamatsu, F., Katsuki, M., 2003. Effects of outflow from the surface of a sphere on drag, shear lift, and scalar diffusion. Phys. Fluids 15, 2338–2351. doi:10.1063/1.1591770.
- Miller, R., Bellan, J., 1999. Direct numerical simulation of a confined threedimensional gas mixing layer with one evaporating hydrocarbon-droplet-laden stream. J. Fluid Mech. 384, 293–338. doi:10.1017/S0022112098004042.
- Mittal, R., Iaccarino, G., 2005. Immersed boundary methods. Annu. Rev. Fluid Mech 37, 239–261. doi:10.1146/annurev.fluid.37.061903.175743.
- Nour, Z., Amberg, G., Do-Quang, M., 2017. Kinematics and dynamics of suspended gasifying particle. Acta Mech. 228, 1135–1151. doi:10.1007/s00707-016-1748-5.
- Renksizbulut, M., Yuen, M.C., 1983. Numerical study of droplet evaporation in a high-temperature stream. J. Heat Transf. 105, 389–397. doi:10.1115/ 1.3245591.
- Richter, A., Nikrityuk, P.A., 2012. Drag forces and heat transfer coefficients for spherical, cuboidal and ellipsoidal particles in cross flow at sub-critical reynolds numbers. International Journal of Heat and Mass Transfer 55 (4), 1343–1354. doi:10.1016/j.ijheatmasstransfer.2011.09.005.
- Umeki, K., Kirtania, K., Chen, L., Bhattacharya, S., 2012. Fuel particle conversion of pulverized biomass during pyrolysis in an entrained flow reactor. Ind. Eng. Chem. Res. 51, 13973–13979. doi:10.1021/ie301530j.
- Weller, H.G., Tabor, G., Jasak, H., Fureby, C., 1998. A tensorial approach to computational continuum mechanics using object-oriented techniques. Comput. Phys. 12, 620–631. doi:10.1063/1.168744.
- Wittig, K., Nikrityuk, P., Richter, A., 2017. Drag coefficient and Nusselt number for porous particles under laminar flow conditions. Int. J. Heat Mass Transf. 112, 1005–1016. doi:10.1016/j.ijheatmasstransfer.2017.05.035.
- Yu, J., Zhang, M.C., 2009. Mass transfer coefficients for the combustion of a char particle in O<sub>2</sub>/CO<sub>2</sub>. Energy Fuels 23, 5717–5724. doi:10.1021/ef900481c.
- Yu, J., Zhou, K., Ou, W., 2013. Effects of stefan flow and CO oxidation on char particle combustion in O2/CO2 atmosphere. Fuel 106, 576–585. doi:10.1016/j.fuel.2013. 01.005.

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# The effect of Stefan flow on Nusselt number and drag coefficient of spherical particles in non-isothermal gas flow



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#### ABSTRACT

A Stefan flow can be generated during a phase change or reactions of a particle immersed in a fluid. This study investigates the effect of Stefan flow on the exchange of momentum (drag coefficient ( $C_D$ )) and heat transfer (Nusselt number (Nu)) between the particle and bulk-fluid. Fully resolved simulations were carried out for a flow near a spherical particle immersed in a uniform bulk flow. The immersed boundary method is used for implementing fluid-solid interactions and the particle is considered as a static boundary with fixed boundary conditions. In a non-isothermal flow, the changes in thermophysical properties at the boundary layer played a role in the variation of  $C_D$  and Nu by a Stefan flow further. The previously developed model for the drag coefficient of a spherical particle in a uniform isothermal flow was modified for a uniform non-isothermal flow. The model is developed based on physical interpretation. A new model is developed for the Nusselt number for a spherical particle with a uniform Stefan flow combining available models in literature. The models are validated for Stefan Reynolds number  $-8 \leq \text{Re}_{sf,p} \leq 25$  and particle Reynolds number of  $2 \leq \text{Re}_f \leq 30$  in gas flow (i.e.  $\text{Pr} \approx 0.7$ ).

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#### 1. Introduction

Particle-laden flows have many complexities due to *e.g.* flow separation, particle wakes, multi-particle effects, Stefan flow effects and reactions. Such flows are associated with physical effects that have a wide range of length and time scales. For example, the largest length scale in pulverized boilers (reactor) is  $\mathcal{O}(10^{-1}\text{m})$  while the smallest physical scale (particle boundary layer) is  $\mathcal{O}(10^{-5}\text{m})$  and the smallest chemical scale is  $\mathcal{O}(10^{-10}\text{m})$ . Therefore, it is currently impossible to resolve all scales in any numerical setup of practical relevance. This gap can be bridged by developing models describing the effects occurring at smaller scales (smallest physical/chemical scales). The smallest physical scales ( $\mathcal{O}(10^{-5}\text{m})$ ) can be studied through detailed numerical simulations. In contrast to experimental data, numerical simulations create a virtual environment that is much more versatile to elucidate the relevant transport phenomena and that can be used for

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developing models. In the current study, we investigate the Stefan flow effects in particle-laden flows using numerical simulations.

A Stefan flow is created when there is a net flow of gas/fluid towards or away from a solid surface that is reacting or undergoing a phase change (Murphy and Shaddix, 2003). Some examples are: evaporation, condensation and combustion of droplets as well as pulverized fuel combustion and gasification. The Stefan flow can affect the exchange of mass, momentum and heat between the surface and the bulk fluid in particle-laden flows. Models for Nusselt number (Nu), Sherwood number (Sh) and the drag coefficient ( $C_D$ ) are used to calculate heat, mass and momentum transfer between the particle and the fluid, respectively. However, this study will only consider the Nusselt number and the drag coefficient.

In the past, the Stefan flow effect was considered for droplet evaporation and combustion (Renksizbulut and Yuen, 1983b; 1983a; Abramzon and Sirignano, 1989; Harpole, 1981). Lately, an interest for the effect of the Stefan flow has emerged for coal combustion applications due to high reactive gas concentration in Oxy-fuel combustion ( $O_2/CO_2$ ) compared to air-fuel combustion ( $N_2/O_2$ ). The importance of Stefan flow in Oxy-fuel combustion of coal is emphasized by Yu et al. (2013). According to them, a Ste-

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Nomenclature

Roman Symbols Symbol Description (Units) cross section area (m<sup>2</sup>) Α specific heat capacity (J  $kg^{-1} K^{-1}$ ) C<sub>p</sub> Ď diameter of the particle (m) F force (N) heat transfer coefficient (W  $m^{-2} K^{-1}$ ) h Ĩ identity matrix (1) latent heat of evaporation ( $I kg^{-1}$ ) L ñ unit normal vector (1) pressure (Pa) р R radius (m) S surface area (m<sup>2</sup>) Т temperature (K) t weighting factor (between 0 to 1) (-) U velocity (m  $s^{-1}$ ) velocity vector (m  $s^{-1}$ ) ù volume (m<sup>3</sup>) V Greek Symbols boundary layer thickness (m) δ viscosity (Pa s) μ density (kg m<sup>-3</sup>) ρ time scale (s) τ thermal conductivity (W m<sup>-1</sup> K<sup>-1</sup>) λ Subscripts boiling point (-) b В boundary layer (-) parameters calculated at the far-field condition (-)  $\infty$ parameters calculated at the film condition (when f t = 0.5) (-) 1 liquid (-) with Stefan flow conditions (-) sf parameters calculated at the particle surface (-) р Dimensionless numbers Spalding heat transfer number  $(B_T = \frac{c_p(T_b - T_\infty)}{I})$  $B_T$ Drag coefficient ( $C_D = \frac{F}{0.5\rho U^2 A}$ )  $C_D$ Nusselt number  $(Nu = \frac{hd}{\lambda})$ Peclet number  $(Pe = Re \times Pr)$ Nu Pe Prandtl number (Pr =  $\frac{c_{p\mu}}{\lambda}$ ) Reynolds number (Re =  $\frac{\rho UD}{\mu}$ ) Pr Re

fan flow has a strong influence on the mass transfer rate in Zone II conversion (kinetically and diffusion controlled) while the effect is insignificant in Zone III (diffusion controlled) during burnout period. Still it is not clear from their results when Stefan flow can be neglected.

The main objective of the current paper is to study the effect of Stefan flow on Nusselt number and drag coefficient for nonisothermal conditions (*i.e.* when there is a temperature difference between particle and gas field). Even though the model is generic and meant to be applicable for a variety of conditions, it was developed and validated with a primary interest on entrained-flow biomass gasification. As summarized in the next section, we aim to fill a gap in knowledge and models, especially under the presence of large temperature differences (*i.e.* > 100 K). Hereafter 'temperature difference ( $\Delta T$ )' means the temperature difference between the solid particle (sphere) surface and the far-field of the fluid. Simulations resolving the boundary layer are carried out for a laminar flow surrounding a static spherical particle. Multi-component effects were avoided for the simplicity of work. The applicability of our model for the drag coefficient, developed in our previous work under isothermal conditions (Jayawickrama et al., 2019), is assessed and extended to non-isothermal conditions. In addition, a new model describing the effect of Stefan flow on the Nusselt number is developed.

#### 2. Previous studies

#### 2.1. Nusselt number at high temperature difference

The Nusselt number  $(Nu=hD/\lambda)$  is usually expressed as a function of Reynolds number  $(Re=\rho UD/\mu)$  and Prandtl number  $(Pr=c_p\mu/\lambda)$ . A Nusselt number formula that is applicable for both high and low temperature difference conditions is hard to find in the literature. Two popular models are the models of Whitaker (1972) and the model of Ranz-Marshall Ranz and Marshall (1952). The former reads as:

Nu = 2 + (0.4Re<sup>$$\frac{1}{2}$$</sup> + 0.06Re <sup>$\frac{2}{3}$</sup> )Pr<sup>0.4</sup>  $\left(\frac{\mu_{\infty}}{\mu_{p}}\right)^{\frac{4}{3}}$ , (1)

1

where thermophysical properties (*i.e.*  $\lambda$ ,  $\rho$ ,  $\mu$ , and  $c_p$ ) for the calculation of Nusselt number, Reynolds number, and Prandtl number are based on far-field conditions,  $\mu_{\infty}$  is the viscosity at far-field condition and  $\mu_p$  is the viscosity at particle surface condition. The Ranz-Marshall model Ranz and Marshall (1952) is given as:

$$Nu = 2 + 0.6Re^{\frac{1}{2}}Pr^{\frac{1}{3}},$$
(2)

where thermophysical properties at film condition are used to calculate Nusselt number, Reynolds number and Prandtl numbers, instead of those at far-field conditions. Film condition is defined as the average between the far-field condition and the surface condition, i.e.  $T_f = (T_{\infty} + T_p)/2$  where  $T_{\infty}$  and  $T_p$  are the far-field and surface temperatures, respectively. At low temperature differences and Reynolds numbers ( $\approx 0 < \text{Re} < 100$ ), the Whitaker model (Eq. 1) typically gives predictions that are closer to the actual values (Nikrityuk and Meyer, 2014), while the Ranz-Marshall model (Eq. (2)) can be applied for high temperature differences (1 < Re < 130) (Ellendt et al., 2018).

There are numerous works on developing models for the Nusselt number associated with droplet evaporation. Evaporation at high temperature differences requires consideration of the variation of thermophysical properties, such as thermal conductivity ( $\lambda$ ) and specific heat capacity ( $c_p$ ). This effect can be accounted for through a correction factor for the Nusselt number (Harpole, 1981), or by introducing a reference temperature (Naraslmhan and Gauvin, 1967; Downingm, 1966; Yuen and Chen, 1978). The reference temperature is then calculated as follows:

$$T_t = tT_\infty + (1-t)T_p,\tag{3}$$

where *t* is weight factor.

#### 2.2. Effect of Stefan flow on Nusselt number

Different models for the Nusselt number developed for evaporation of single droplets are summarized by Zhifu et al. (2013). They have categorized the available models into theoretical, numerical and experimental models. According to their comparisons, all the models are deviating from experimental results when the evaporation rates are high. Therefore, they have developed a model with a correction factor that is applicable for high evaporation rates as well. In this model, the Nusselt number is given as:

$$Nu_{Zh} = f_T Nu, \tag{4}$$

$$f_T = (1 + B_{Tp})^{-\frac{2}{3}},\tag{5}$$

where

and

$$Nu = 2 + 0.552 Re^{\frac{1}{2}} Pr^{\frac{1}{3}}.$$
 (6)

Here the Spalding heat transfer number  $(B_{Tp})$  is defined as:

$$B_{Tp} = \frac{c_{p,p}(T_{\infty} - T_b)}{L},\tag{7}$$

where *L* is latent heat of evaporation and  $T_b$  is the boiling point temperature. The Reynolds number is calculated based on properties at the particle surface, while the Prandtl number is calculated based on far-field condition. The Nusselt number is calculated based on properties at the particle surface condition. It is noticed that the model of Zhifu et al. (2013) has no explicit dependence on the Stefan flow. The effect of Stefan flow is accounted for indirectly through the evaporation rate, characterized by the Spalding heat transfer number.

Niazmand and Renksizbulut (2003) used the model developed for droplet evaporation by Renksizbulut & Yuen ( $Nu_{RY}$ ) Renksizbulut and Yuen (1983a) for the generalized case of a Stefan flow:

$$Nu_{RY} = \frac{2 + 0.57 Re^{1/2} Pr^{1/3}}{(1 + B_{T_f})^{0.7}}$$
(8)

where the Reynolds number is calculated based on particle surface conditions, Prandtl number is calculated based on film condition and the Spalding heat transfer number is defined as:

$$B_{T_f} = \frac{\Pr \operatorname{Re}_{sf}}{\operatorname{Nu}},\tag{9}$$

where

$$\operatorname{Re}_{sf} = \frac{\rho U_{sf} D}{\mu},\tag{10}$$

is the Reynolds number based on the Stefan flow velocity (hereafter, called Stefan Reynolds number). The variation of thermophysical properties are neglected for Niazmand and Renksizbulut Niazmand and Renksizbulut (2003) and the selected range of Stefan flows was based on droplet evaporation ( $0.01 \ge \frac{U_{sf}}{U_{\infty}} \ge 0.04$ ). Murphy & Shaddix Murphy and Shaddix (2003) have formulated a Nusselt number ( $Nu_M$ ) correlation, for Stefan flow in a quiescent environment. Assuming constant properties, their expression reads as:

$$Nu_{M} = Nu \frac{(PrRe_{sf})/Nu}{e^{(PrRe_{sf})/Nu} - 1},$$
(11)

where Nu = 2 is the Nusselt number in a quiescent flow without Stefan flow. Recently, Kestel Kestel (2016) developed a new empirical model applicable for the convective flow environment based on his simulation data that gave better accuracy than the other available models. In this model, which is applicable for Re < 200, Re<sub>sf</sub> < 20 and 0.744 < Pr < 1.5, the Nusselt number (Nu<sub>K</sub>) is given as:

$$Nu_{K} = Nu \exp\left(\frac{-0.54 \operatorname{Pr} \operatorname{Re}_{sf}^{1.126}}{\operatorname{Nu}^{1.052}}\right),$$
(12)

where

$$Nu = 2 + 0.39 Re^{0.56} Pr^{0.45}.$$
 (13)

In Eq. 12 and 13, all properties are calculated based on the reference temperature as defined in Eq. (3) when the weight factor is t = 0.9. This model has a large number of fitting parameters and it does agree better with simulation results. However, it does not necessarily represent the physical phenomena.

In summary, most of the currently available models for Nusselt number for particles with Stefan flow in a convective environment are empirical. One of the very few theoretical models (of Eq. 11) (Murphy and Shaddix, 2003) developed for the Nusselt number of particles with Stefan flow is for a *quiescent* environment and is based on a constant property assumption. Therefore, there are no models for Stefan flow in a convective environment based on physical interpretation while considering variation of properties.

#### 2.3. Drag coefficients at high temperature differences.

The drag coefficient is defined as  $C_D = F/(0.5\rho U^2 A)$ , where *F* is the drag force, *A* is the cross-sectional area of the particle,  $\rho$  is the density of the fluid and *U* is the velocity difference between the particle and the fluid. There are many correlations available to calculate fluid drag on a solid spherical object. However, most of these models have been developed for isothermal or close to isothermal conditions. This makes these models fail at high temperature differences, since variations of properties have to be considered in order to accurately calculate the drag. The Schiller-Naumann model Schiller and Naumann (1935) for the drag coefficient, given as:

$$C_D = \frac{24}{\text{Re}} (1 + 0.15 \text{Re}^{0.687}), \tag{14}$$

is a widely used drag model. Recently, Ellendt et al. Ellendt et al. (2018) have suggested a correction factor ( $\phi$ ) for the Schiller-Naumann correlation considering non-isothermal effects:

$$C_{D} = \frac{24}{\text{Re}} (1 + 0.15 \text{Re}^{0.687}) \phi;$$
  

$$\phi = 0.273 (1 - 0.883^{\text{Re}}) \left(\frac{\rho_{\infty}}{\rho_{p}} - 1\right) + 1,$$
(15)

when 1 < Re < 130. Here, the Reynolds number is evaluated at the surface temperature of the sphere,  $\rho_{\infty}$  is the density of the fluid in the far-field and  $\rho_p$  is the density of the fluid at the particle surface. The fluid density entering the expression for the drag coefficient ( $C_D = F/(0.5\rho U^2 A)$ ) is at far-field conditions.

#### 2.4. Effects of Stefan flow on drag coefficients.

Similar to the Nusselt number, the models developed for the combustion and evaporation of sprays are available for the drag coefficient under the influence of a Stefan flow (Yuen and Chen, 1976; Eisenkalam et al., 1967; Renksizbulut and Yuen, 1983b). One common approach is the so-called one-third rule proposed by Yuen and Chen Yuen and Chen (1976). The one-third rule uses ordinary drag models, for example the one of Schiller-Naumann Schiller and Naumann (1935) (see Eq. (14)), for an evaporating droplet, but with the Reynolds number calculated as:

$$\operatorname{Re} = \frac{\rho_{\infty} UD}{\mu_t},\tag{16}$$

where  $\mu_t$  is the dynamic viscosity obtained at the reference temperature, as given by Eq. (3), with a weight factor of t = 1/3. This model is applicable in the range of 1 < Re < 2000 and  $0 < B_T < 3$ . The same result was confirmed by Renksizbulut and Yuen Renksizbulut and Yuen (1983b) for an evaporating droplet from their simulations. However, the approach described above does not include a dependency on the Stefan velocity and is therefore not expected to be suitable unless the Stefan flow velocity is small compared to the velocity of the mean flow.

Studies of the effect of Stefan flow on the drag coefficient for generalized cases have always assumed isothermal conditions as per the authors knowledge. Most recent works are done by Jayawickrama et al. Jayawickrama et al. (2019), Kestel Kestel (2016) and Miller & Bellan Miller and Bellan (1999). The latter two have developed empirical models for the drag coefficient of a spherical object



**Fig. 1.** Computational domain for the simulations.  $\Delta_i$ , i = 1 to 5 representing the coarsest mesh to finest mesh.  $D_{-x,i}$  is the distance from the centre of the sphere to negative x-direction and  $D_{+x,i}$  is the distance from the centre of the sphere to positive x-direction in level *i* (See the Table 2).

with a Stefan flow. Kestel's model is applicable for a wider range of Stefan flows (0 < Re<sub>sf</sub>  $\leq$  20 and Re  $\leq$  200). Both models have several fitting parameters. Jayawickrama et al. (2019) developed a model based on a physical interpretation of the drag that required only one fitting parameter. This model was validated against numerical simulations in the range of  $-1 \leq \text{Re}_{sf} \leq 3$  (a negative Re<sub>sf</sub> means inward Stefan flow) and Re < 14. All three models are applicable for isothermal conditions only. Therefore, it is important to study the effect of a Stefan flow on the drag coefficient including thermal effects as well.

#### 3. Methodology

In the current work, numerical simulations are carried out for a flow around a static, spherical particle with constant size using OpenFOAM. The simulation domain and boundaries are shown in Fig. 1. The incoming gas flow to the simulation domain is uniform and its temperature is kept at 1400 K. A uniform Stefan flow is given as a boundary condition at the particle surface. Different cases are simulated by varying sphere surface temperature, diameter and incoming flow velocity, resulting in a variety of Reynolds numbers. Variation of properties with temperature is considered (See Appendix A for more details.). The Reynolds number is within the limit of steady, axi-symmetric flow (Re < 210) (Johnson and Patel, 2017) and the Mach number of the flow is well below 0.1. Therefore, the flow is essentially in-compressible. The intra-particle heat transfer is not considered and the particle temperature is kept uniform both in space and time. Radiative heat transfer is also neglected. The fluid is governed by the steady, incompressible, laminar flow equations, where mass conservation yields the continuity equation as:

$$\nabla \cdot (\rho \,\overrightarrow{u}\,) = 0,\tag{17}$$

while momentum conservation gives:

$$(\rho \vec{u} \cdot \nabla) \vec{u} = -\nabla p + \nabla \cdot \mu [\nabla \vec{u} + \nabla \vec{u}^{T} - \frac{2}{3} (\nabla \cdot \vec{u}) \vec{l}].$$
(18)

Finally, from energy conservation we get:

$$\nabla \cdot (\rho c_p \vec{u} T) = -\nabla \cdot \lambda \nabla T. \tag{19}$$

Eqs. 17, 18 and 19 were discretized using second-order schemes with the finite volume method.

#### 3.1. Boundary conditions.

The temperature of the inlet boundary is kept at 1400 K. The exit of the domain is considered as an outflow boundary, where the gradients of the velocity and temperature are set to zero. The boundaries at the side of the domain are treated as slip walls. In the slip wall boundary condition, the velocity component normal to the wall is zero. In addition, the gradients of temperature and the other velocity components in the normal direction to the wall are also set to be zero. Along the axis of symmetry, a symmetric boundary condition, the velocity component normal to the symmetric boundary condition, the velocity component normal to the symmetry plane and the gradients of all the other properties normal to the plane are set to zero. Only a quarter of the domain is simulated as the flow is axisymmetric.

A Cartesian mesh is used for the simulation. The immersed boundary method (IBM) was applied for the implementation of the solid boundary. In this work, the discrete forcing approach (Mittal and laccarino, 2005), which directly applies the presence of a solid body through boundary conditions (Jasak et al., 2014), is used. The value of any parameter of a cell that crosses the immersed boundary is calculated by interpolating values between the immersed boundary and neighboring cells (Fadlun et al., 2000). The Stefan velocity is considered as a uniform velocity normal

#### Table 1

Conditions maintained for far-field velocity, particle diameter and particle temperature. Far-field temperature was kept at  $T_{\infty} = 1400$ K.

Condition	Inlet velocity (m/s)	Diameter (mm)	$T_p(\mathbf{K})$	Ref
1	0.5	1.0	400	4.88
			1200	2.66
			1600	2.10
2	3.0	0.5	400	14.64
			1200	7.98
			1600	6.31
3	3.0	1.0	400	29.29
			1200	15.98
			1600	13.74

to the immersed boundary (Dirichlet boundary condition). For an outwardly directed Stefan flow, the temperature of the outflow is equal to the surface temperature of the particle.

The pressure gradient is set to zero at the solid boundary (Neumann boundary conditions). Treatment of Neumann and Dirichlet boundary conditions in the immersed boundary method is explained in Jayawickrama et al. (2019).

#### 3.2. Simulation conditions and procedure

For all the simulations in this work, the fluid (including the fluid of the Stefan flow) was assumed to be pure nitrogen. The inlet velocity, diameter of the particle and temperature range of the fluid and the sphere were selected based on pulverized combustion and gasification applications at atmospheric pressure. The velocity at the inlet varied between 0.5-3 m  $s^{-1}$  and the diameter of the particle is between 0.5-1.0 mm. The range of Stefan flow velocities was selected based on results from Kreitzberg et al. (2016) and Umeki et al. (2012) for devolatilization and char conversion of biomass. The choice of bulk fluid temperature (1400 K) is based on the range of typical bulk fluid temperatures observed in pilot scale experiments of entrained-flow gasification (Sepman et al., 2017). Fuel particles in entrained flow gasifiers are usually colder than the surrounding gas because of predominantly endothermic reactions and the lack of an oxygen rich atmosphere, except for the near burner zone. The particle temperature can, however, exceed the gas temperature by ca. 200 K in pulverized combustion, where oxygen is available for char combustion reactions (Li et al., 2018). Therefore, we selected three different fuel particle temperatures  $(T_p = 400, 1200, and 1600 \text{ K})$ , each representing drying, char gasification, and char oxidation stages, respectively. The particle temperatures and far-field conditions studied in this work are shown in Table 1.

We used the OpenFOAM environment *foam-extend-4.0* (Weller et al., 1998) for the simulations. The immersed boundary solver for incompressible, steady-state conditions was modified to account for non-isothermal, variable density and variable property conditions. The solver uses quadratic interpolation (Jasak et al., 2014) for the reconstruction of the solid phase boundary conditions into the closest fluid cells.

The preliminary domain size and mesh resolution was selected based on previous studies (Jayawickrama et al., 2019; Constant et al., 2017; Richter and Nikrityuk, 2012) for isothermal flow around a sphere. The inlet conditions and Stefan flow velocities are similar to the ones used for the isothermal simulations in our previous work (Jayawickrama et al., 2019). Therefore, the domain size is unchanged for the current non-isothermal simulations ( $64D \times 32D \times 32D$ ). There are, however, two main differences in the non-isothermal cases compared to the isothermal cases.

The first difference is that a reduction (increase) of particle temperature increases (decreases) the Reynolds number (Re), resulting in a thinner (thicker) boundary layer for non-isothermal

#### Table 2

Distance from the centre of the particle in diameters (D) in the computational domain (See Fig. 1).

-					
	(a) l	Mesh I			
	i	$D_{-x,i}$	$D_{+x,i}$	$D_{y,i}, D_{z,i}$	$\Delta_i/D$
Ī	1	16	48	16	0.32
	2	3	6	3	0.16
	3	2	5	2	0.08
	4	1.5	3	1.5	0.04
	5	1.2	2	1.2	0.02
	(b)	Mesh II			
	i	$D_{-x,i}$	$D_{+x,i}$	$D_{y,i}, D_{z,i}$	Delta <sub>i</sub> /D
	1	16	48	16	0.32
	2	6.5	12	6.5	0.16
	3	5.5	10	5.5	0.08
	4	4.5	6	4.5	0.04
	5	3.5	4	3.5	0.02
	(c) l	Mesh III			
	i	$D_{-x,i}$	$D_{+x,i}$	$D_{y,i}, D_{z,i}$	$\Delta_i/D$
	1	16	48	16	0.16
	2	3	6	3	0.08
	3	2	5	2	0.04
	4	1.5	3	1.5	0.02
	5	1.2	2	1.2	0.01

conditions. Mesh refinement tests therefore had to be carried out. The tests were carried out with the highest Reynolds number conditions (condition 3 of Table 1 with particle temperature 400K) and with the smallest possible boundary layer thickness (inward Stefan flow condition). Two mesh refinement levels were tested, as shown in Table 2 (Mesh I and Mesh III).

The other difference between the isothermal and nonisothermal cases is due to the difference between the thermal  $(\delta_{th})$  and the viscous boundary layer thickness  $(\delta_{vis})$ . As the Prandtl number (Pr) is less than 1, the thermal boundary layer thickness is larger than the viscous boundary layer thickness  $(\delta_{th} > \delta_{vis})$ . Therefore, the size of the mesh refinement regions have to be examined. This was carried out for the lowest Reynolds number condition (condition 1 of Table 1 with particle temperature 1600K) with the largest possible boundary layer thickness (highest outward Stefan flow). Two refinement region sizes were tested, which is shown in Table 2 (Mesh I and Mesh II). Difference between Mesh I, II and III were very small in  $C_D$  and Nu and the velocity and temperature fields around the boundary layer were also identical when comparing all the meshes. Therefore, Mesh III was used for the simulations.

Table 3 shows the selection of mesh refinement levels and size of refinement regions used for the simulations in this paper. The final mesh for all the conditions was Mesh III with the highest refinement 0.01*D*.

#### 3.3. Estimation of drag coefficient and Nusselt number

The drag coefficient is a dimensionless quantity used to represent forces acting on the surface of a body immersed in a fluid. For a spherical body with radius *R*, it can be calculated as:

$$C_{D,f} = \frac{\overrightarrow{F}_{P,x} + \overrightarrow{F}_{visc,x}}{\frac{1}{2}\rho_f U_{\infty}^2(\pi R^2)},$$
(20)

where  $\rho_f$  is the fluid density of film condition. The pressure and viscous forces are given as

$$\vec{F}_p = \oint_S p_p \vec{n} \, ds, \tag{21}$$

and

$$\vec{F}_{visc} = -\oint_{S} \mu_{p} (\nabla \vec{u} + \nabla \vec{u}^{T}) \vec{n} \, ds, \qquad (22)$$

#### Table 3

Mesh refinement results and refinement domain size results as explained in section 3.2. The drag  $(C_D)$  and Nusselt number (Nu) calculated at far-field conditions and Stefan Reynolds number  $(\text{Re}_{sf})$  calculated at particle surface condition.

Re <sub>sf</sub>	Mesh	C <sub>D</sub>	Error (% of mesh III or II)	$\mathrm{Nu}_\infty$	Error (% of mesh III or II)
-7.98	mesh I	3.01	10.12	5.40	0.15
	mesh III	3.36	-	5.39	-
2.36	mesh I	10.52	0.25	2.16	2.44
	mesh II	10.55		2.11	-
	mesh III	10.94		2.16	-



**Fig. 2.** Drag coefficient ( $C_D$ ) at film condition for the case where there is no Stefan flow. Lines: Correlations of Ellendt et al. Ellendt et al. (2018) at different particle temperatures (400 K,1200 K,1600 K), symbols: results from our numerical simulations. Green: isothermal. Cyan:  $T_p = 400$  K. Red:  $T_p = 1200$  K. Blue:  $T_p = 1600$  K.

respectively. Here, the integration is over the surface *S* of the particle. In the above,  $p_p$  is the extrapolated pressure at the particle surface. Only the components  $\vec{F}_p$  and  $\vec{F}_{visc}$  in the direction of the mean flow are accounted for when calculating the drag coefficient, since the other components are canceled due to symmetry. The Nusselt number is calculated based on the overall difference in enthalpy flux at the boundaries of the simulation domain. Here, the far-field based Nusselt number is calculated as follows:

$$Nu_{\infty} = \frac{(\rho \,\overline{u} \, c_p T S)_{in} + \overline{u}_{sf} (\rho c_p T S)_{sph} - (\int (\rho \,\overline{u} \, c_p T) \,\overline{n} \, dS)_{out}}{S_{sph} (T_p - T_{\infty})} \times \frac{2R}{\lambda_{\infty}},$$
(23)

where subscripts *in*, *out* and *sph* refers to the conditions at the inlet boundary, the outlet boundary and the particle surface, respectively, and *S* is the surface area of the relevant boundary.

#### 3.4. Validation

In order to validate the code, simulations were carried out to examine if the code reproduces known results both for the drag coefficient and the Nusselt number.

For the validation of the code with respect to the drag coefficient, non-isothermal simulations *without* Stefan flow were carried out. The drag coefficients obtained from the simulations based on Eq. 20 were compared with the model suggested by Ellendt et al. Ellendt et al. (2018) (see Eq. 15). As shown in Fig. 2, the numerical results show good agreement with the model of Ellendt et al. Please note that, when determining the model predictions, the Reynolds number is based on film conditions.

We are interested in the Nusselt number at strongly nonisothermal conditions, i.e., where the temperature difference between the particle surface and the far-field is high (> 100 K). In



**Fig. 3.** Normalized drag  $C_{D,sf}/C_{D,0}$  at film condition and Normalized Stefan flow velocity  $U_{sf}/U_{\infty}$ .  $C_{D,0}$  is the drag coefficient without Stefan flow. Simulation conditions:  $U_{\infty}$ =3.0 m s<sup>-1</sup>,  $T_{\infty}$  = 1400 K, and D=1.0 mm.

order to validate the code with respect to the Nusselt number, simulations were carried out with a strong temperature difference, but without Stefan flow. The results were compared with the Ranz-Marshall model (Eq. 2), which is applicable for strongly non-isothermal conditions (see section 2.1). Table 4 shows a good agreement between the numerical results and the model data.

#### 4. Results and Discussion

## 4.1. The effect of Stefan flow on the drag coefficient under non-isothermal conditions

By comparing the simulation results obtained at isothermal and non-isothermal conditions, it is possible to isolate the physical effects of the Stefan flow (*e.g.* due to the change in boundary layer thickness) from thermal effects (*e.g.* variation of thermophysical properties due to the change in temperature). Figure 3 shows the normalized drag coefficient ( $C_{D,sf}/C_{D,0}$ ) against normalized Stefan flow velocity ( $U_{sf}/U_{\infty}$ ) for both isothermal and non-isothermal conditions (condition 3 of Table 1).

The drag coefficient is normalized by the corresponding drag as obtained *without* a Stefan flow ( $C_{D,0}$ ). Here,  $C_{D,0}$  and  $C_{D,sf}$  are calculated based on film condition (See Eq. 20). As can be seen from the figure, the temperature difference has a significant effect on the slope of the curve, especially for high temperature differences. The drag reduction by the Stefan flow is more significant when the particle temperature is lower than the surrounding gas ( $T_p < T_{\infty}$ ) and vice versa. The same behavior can be observed (not shown here) for conditions 1 and 2 (see Table 1) as well. It means that apart from the physical effects of the Stefan flow, the thermal effect has to be considered to describe the change of  $C_D$  for non-isothermal conditions.

#### Table 4

Comparison of Nusselt numbers (Nu) and the drag coefficient ( $C_D$ ) without Stefan flow from simulations and the Ranz-Marshall model (Eq. 2)), respectively the model of Ellendt et al. (Eq. 15). Far-field temperature ( $T_\infty$ ) is 1400 K for all the cases. Conditions 1-3 are listed in Table 1, while conditions 4-5 are presented in the following: condition 4: D = 1.0 mm and  $U_\infty = 5.94$  m s<sup>-1</sup>, Condition 5: D = 1.0 mm and  $U_\infty = 11.88$  m s<sup>-1</sup>

Condition	T <sub>p</sub> K	Re <sub>f</sub> -	Nu Sim	Model	Error %	C <sub>D, f</sub> Sim	Model	Error %
1	400 1200 1600	4.88 2.66 2.10	3.16 2.84 2.74	3.32 2.89 2.78	4.8 1.7 1.4	5.90 11.39 13.67	6.48 11.53 14 38	8.95 1.22 4.98
2	400 1200	14.65 7.99	4.04 3.57	4.28 3.55	5.6 0.6	2.76 5.01	2.67 4.76	1.34 2.15
3	1600 400 1200	6.31 29.29 15.98	3.41 5.16	3.35 5.23 4.20	1.8 1.3 3 3	5.90 1.74 3.09	5.95 1.68 2.92	0.30 0.92
4 5	1600 1600 1600	12.63 25.0 50.0	4.06 4.95 6.22	3.91 4.69 5.80	3.8 5.5 7.2	3.60	3.64	0.24

The thermal effects of the Stefan flow can be studied by investigating Fig. 4, which shows the variation of the velocity and temperature fields in the boundary layer. Without the Stefan flow (blue lines), the velocity gradient of the non-isothermal case  $(T_n < T_{\infty})$ is slightly larger than that of the isothermal case. Nevertheless, we can see from Fig. 2 that the drag coefficient for  $T_p < T_{\infty}$  (nonisothermal case) is lower than for the isothermal case. This is because the contribution from the change in thermophysical parameters is more significant than the change in boundary layer thickness (Eq. 20). To be more specific: one would expect the drag coefficient to increase when the boundary layer gets thinner (higher velocity gradients), but this effect is more than compensated by the decrease in viscosity due to the lower temperature. In essence, the local Reynolds number is increased when the particle temperature becomes lower than the far-field temperature, and it is clear from Fig. 2 that the drag coefficient decrease with increasing  $\text{Re}_{f}$ .

In contrast, the same non-isothermal case shows a more pronounced expansion of the velocity boundary layer with an outward Stefan flow (red lines) than does the isothermal case. This pronounced change in the velocity is due to the expansion of the gas from the Stefan flow as it is heated. Since it is the velocity of the Stefan flow that is kept constant between different cases, the total mass flux due to the Stefan flow is much higher for the nonisothermal case (since the fluid density is more than three times higher at 400 K than at 1400 K). This means that as the initially cold gas emitted from the particle at 400 K is heated up, it accelerates and pushes the boundary layer outwards. In fact, the normalized temperature plot in Fig. 4b shows the decrease in gas temperature near the particle surface with outward Stefan flow. As for the inward Stefan flow, both velocity and thermal boundary layers showed exactly opposite trends from the outward Stefan flow, i.e. steeper velocity gradient and thinner thermal boundary layer. These observations imply the importance to consider the change in thermophysical parameters when modelling the drag coefficient under non-isothermal conditions. Therefore, the model developed in our previous paper (Jayawickrama et al., 2019), which was based on isothermal simulations, needs to be extended to consider the effect of the variation of thermo-physical properties.

Our previous study under isothermal conditions (Jayawickrama et al., 2019) showed that the drag coefficient changes due to a Stefan flow. This change is primarily caused by a modification of the viscous forces due to the change in boundary layer thickness. Following the idea in Jayawickrama et al. (2019), the current study uses a simple model for the effect of a Stefan flow on the drag coefficient. It is related to the change in the volume of the boundary layer due to the Stefan flow, and is



(b)

**Fig. 4.** (a) Normalized velocity in the mean flow direction  $(U_x/U_\infty)$ ; (b) Normalized temperature  $(T/T_\infty)$ . Both figures are drawn as functions of the normalized distance from the centre of the sphere (y/R) along the *y*-axis ( $\theta = 90^\circ$ ). Simulation conditions:  $U_\infty = 3.0$  m s<sup>-1</sup>,  $T_\infty = 1400$  K, and D=1.0 mm. Solid lines: isothermal and Dashed lines: non-isothermal results ( $T_p = 400$  K).

proposed as:

$$C_{D,sf} = C_{D,0} \times C_{D,r},\tag{24}$$

when  $C_{D,0}$  is the drag coefficient under non-isothermal conditions without a Stefan flow (see e.g. Eq. (15)), and  $C_{D,r}$  is a correction term that accounts for the effects of a Stefan flow, in addition to any thermal effects of this Stefan flow. This correction term takes into account two effects: one is due to the temperature difference between the particle surface and the far-field while the other is due to the variation of the temperature field due to the Stefan flow. Both effects can be accounted for by using a modified temperature  $(\tilde{T})$  based on the volumetric contribution of the Stefan flow ( $V_{sf}$ ) and its temperature ( $T_{sf} = T_p$ ), and the volume of the boundary layer without Stefan flow ( $V_B$ ) and its temperature ( $T_f = \frac{T_\infty + T_p}{2}$ );

$$\tilde{T} = \frac{V_B T_f + V_{sf} T_p}{V_B + V_{sf}},\tag{25}$$

where

$$V_{sf} = 4\pi R^2 U_{sf} \tau \tag{26}$$

is the added volume due to the Stefan flow, with the flow timescale given as:

$$\tau = \frac{2(R+\delta)}{U_{\infty}}.$$
(27)

Furthermore, the volume of the boundary layer is given as:

$$V_B = \frac{4}{3}\pi (R+\delta)^3 - \frac{4}{3}\pi R^3,$$
(28)

when

$$\delta = \frac{2AR}{\sqrt{\text{Re}_f}},\tag{29}$$

is the classical boundary layer thickness, where

. .

$$\operatorname{Re}_{f} = \frac{\rho_{f} U_{\infty} d}{\mu_{f}} \tag{30}$$

and *A* is a model constant. By substituting  $V_{sf}$  and  $V_B$  in Eq. 25 with the corresponding expressions found in Eq. 26 and 28 we obtain:

$$\tilde{T} = \frac{T_f + \frac{U_{sf}}{U_{\infty}} f(\operatorname{Re}_f) T_{sf}}{1 + \frac{U_{sf}}{U_{\infty}} f(\operatorname{Re}_f)},$$
(31)

where

...

$$f(\text{Re}_f) = 3(1 + \frac{2A}{\sqrt{\text{Re}_f}}) \frac{1}{(\frac{3A}{\sqrt{\text{Re}_f}} + 6(\frac{A}{\sqrt{\text{Re}_f}})^2 + 4(\frac{A}{\sqrt{\text{Re}_f}})^3)}.$$
 (32)

Now,  $\tilde{T}$  will be used to calculate the drag coefficient without Stefan flow ( $\tilde{C}_{D,0}$ ) such that the non-isothermal model for  $C_{D,sf}$  becomes:

$$C_{D,sf} = \tilde{C}_{D,0} \times C_{D,r},\tag{33}$$

where  $\tilde{C}_D$  is calculated from the modified Schiller-Naumann equation (Eq. 15) for non-isothermal conditions:

$$\tilde{C}_{D,0} = \frac{24}{\tilde{Re}} (1 + 0.15\tilde{Re}^{0.687})\phi; \qquad \phi = 0.273(1 - 0.883\tilde{Re})(\frac{\rho_{\infty}}{\rho_{p}} - 1) + (34)$$

where  $\tilde{Re}$  is the Reynolds number calculated with properties at  $\tilde{T}$ .  $C_{D,r}$  is calculated based on the model developed from isothermal simulations (Jayawickrama et al., 2019) where:

$$C_{D,r} = \frac{V_B}{V_{sf} + V_B} = \frac{1}{1 + \frac{U_{sf}}{U_{\infty}} f(\text{Re}_f)}.$$
(35)

In the above, the tilde over  $C_D$  is used to highlight that it is based on properties calculated at  $\tilde{T}$ . The constant A is calculated using non-linear least-squares regression to minimize the error between the model and the simulation results (*nlinfit* in MATLAB). The final value of A is 2.93.

Fig. 5, which shows the drag coefficient as a function of the Stefan flow Reynolds number, compares the above model with simulation results. The model is an extension of the previous isothermal model presented in Jayawickrama et al. (2019). This new model captures the effects of non-isothermal, uniform bulk flow and uniform Stefan flow. Model data and simulation results are matching well and it has only one fitting parameter (*A*). The model has a good qualitative performance for both negative and positive Stefan flow conditions, and it is based on a physical interpretation of thermal effects due to property variations and the Stefan flow, and physical effects due to pressure, viscosity and Stefan flow.

The (relative) root-mean-square error (Eq. 36) with all the data in Fig. 5 was 9.6%. The error was relatively high for  $T_p = 400$  K (Fig. 5a), with the maximum value reaching 28%. When only considering the data from the temperature difference of 200 K (Fig. 5b-c), the maximum relative error of the model was 6% and the root-mean-square error was 4.6%. Root-mean-square error (*RMSE*<sub>Cd</sub>) is calculated as follows:

$$RMSE_{C_d} = 100 \times \sqrt{\frac{\left[\sum \left(\frac{C_{d,model} - C_{d,simulations}}{C_{d,simulations}}\right)^2\right]}{n}},$$
(36)

where  $C_{d,model}$  is the value predicted by the model Eq. 33-(35) and  $C_{d,simulations}$  is the value calculated from the simulations and *n* is the number of simulations considered.

The models are tested and validated for the particle Reynolds number range of  $2 \leq \text{Re}_f \leq 30$ , Stefan Reynolds number range of  $-8 \leq \text{Re}_{sf,p} \leq 25$ , and temperature range of  $400K \leq T_p \leq 1600K$  with uniform Stefan flow. The developed model should be applicable for the valid temperature ranges of the modified Schiller-Naumann model (Eq. 34). However, one should be careful when extrapolating the applicability beyond the range of validation conditions. For example, the model might not be valid at higher particle Reynolds number due to flow separation or the change in the relative magnitude between the pressure force and the viscous force.

#### 4.2. Nusselt number with Stefan flow

Murphy & Shaddix Murphy and Shaddix (2003) has developed a theoretical model that accounts for the effect of a Stefan flow when calculating the Nusselt number of a sphere immersed in a quiescent fluid (See Eq. 11). In their model, the Nusselt number is calculated as  $Nu_M = Nu_0 f_{corr}$ , where  $Nu_0 = 2$  is the Nusselt number of a spherical particle with no Stefan flow in a quiescent fluid and  $f_{corr}$  is a correction term that accounts for the effect of the Stefan flow. One way to apply this model directly for the cases with convective flows is to replace the Nusselt number,  $Nu_0$ , with the one with a convective flow, as given by e.g. the Ranz-Marshall model. However, the prediction with this approach does not describe the simulation results. The same observation was discussed by Kestel Kestel (2016), who proceeded to develop an empirical - fhodel with several fitting parameters Eqs. 12-(13).

As discussed in the previous section, the temperature in the boundary layer changes due to the Stefan flow, especially when the temperature differences are significant. This change should be reflected in the characteristic temperature when calculating the Nusselt number. In this work, we apply a multiplication law to describe the effect of a Stefan flow (by Eq. 11) and the effect of a convective flow (Eq. 2), but considering the change in characteristic temperature. This approach in practice calculates the Nusselt



**Fig. 5.** Comparison of the drag coefficient from the model, i.e. Eqs. 31-35, (lines) and the simulations based on  $\tilde{T}$  (symbols). Particle temperature ( $T_p$ ) is (a) 400 K (b) 1200 K or (c) 1600 K. Condition 1:  $U_{\infty}$ =0.5 m s<sup>-1</sup> and D=1.0 mm. Condition 2:  $U_{\infty}$ =3.0 m s<sup>-1</sup> and D=0.5 mm. Condition 3:  $U_{\infty}$ =3.0 m s<sup>-1</sup> and D=1.0 mm.

number based on the thermophysical properties using the volume averaged temperature derived earlier (Eq. 31). The model for the Nusselt number needs to be applicable for convective flows around a sphere with high temperature differences. Here, we have used a Ranz-Marshall type model by parameter fitting the original Ranz-Marshall model with simulation data without Stefan flow, to obtain:

$$\tilde{Nu} = 2 + 0.570\tilde{Re}^{0.537}\tilde{Pr}^{1/3},$$
(37)

where Re and Pr were calculated based on the volume averaged temperature,  $\tilde{T}$ , as given in Eq. 31. Now we can replace the Nusselt number without Stefan flow (Nu) in Murphy & Shaddix model (Eq. 11) with the model presented in Eq. 37, such that the final model for Nu, accounting for non-isothermal effects and Stefan flow reads as:

$$\mathrm{Nu}_{sf,f} = \tilde{\mathrm{Nu}}\frac{q}{e^q - 1},\tag{38}$$

where  $q = \frac{\Pr_f \operatorname{Re}_{sf,p}}{\operatorname{Nu}}$  and  $\operatorname{Nu}_{sf,f}$  calculated based on film condition for the thermal conductivity ( $\lambda_f$ ). The Stefan flow Reynolds number ( $\operatorname{Re}_{sf}$ ) is calculated based on particle surface condition while the Prandtl number ( $\operatorname{Pr}$ ) is calculated based on film condition.

It is clear that the volume averaged temperature must lie between the particle temperature  $(T_p)$  and the far-field temperature  $(T_{\infty})$ . From the definition of the volume averaged temperature, as given by Eq. 25 (respectively Eq. 31), it can be shown that this is not the case when  $V_{sf}/V_B < -0.5$ . (This corresponds to a situation where there is a very strong *inward* Stefan flow.) This means that the expression given by Eq. 25 can not be used to define the volume averaged temperature for such a condition. Therefore, the volume averaged temperature is assumed to be equal to the far-field temperature when  $V_{sf}/V_B < -0.5$ . This means that,

$$\tilde{T} = \begin{cases} \frac{T_f + \frac{U_{sf}}{U_{o}} f(\text{Re}_f) T_{sf}}{1 + \frac{U_{sf}}{U_{o}} f(\text{Re}_f)} & (\text{Eq.31}) & \text{for } V_{sf} / V_B \ge -0.5, \\ T_{\infty} & \text{for } V_{sf} / V_B < -0.5, \end{cases}$$
(39)

for  $V_{sf}/V_B < -0.5$ , (40)

where  $f(Re_f)$  is calculated from Eq. 32 and A = 0.4.

To validate the model, the Nusselt number was calculated from the simulation with the conditions 1, 2, and 3 (see Table 1) including one negative Stefan flow case with  $V_{sf}/V_B < -0.5$ . Fig. 6 depicts the comparison between simulation results (symbols) and the predictions obtained with the model presented in Eq. (38) (lines).

The (relative) root-mean-square error (Eq. 36 after replacing the term  $C_d$  with Nu) with all the data in Fig. 6 was 12.6%. The error was relatively high for  $T_p = 400$  K (Fig. 6a), with the maximum value reaching 73%. When only considering the data from the tem-



**Fig. 6.** The Nusselt number comparison between the model (Eq. 38-lines) and simulation (symbols) data with Stefan flow. Particle temperature ( $T_p$ ) is (a) 400 K (b) 1200 K or (c) 1600 K. Condition 1:  $U_{\infty}$ =0.5 m s<sup>-1</sup>and D=1.0 mm. Condition 2:  $U_{\infty}$ =3.0 m s<sup>-1</sup> and D=0.5 mm. Condition 3:  $U_{\infty}$ =3.0 m s<sup>-1</sup> and D=1.0 mm.

perature difference of 200 K (Fig. 6b-c), the maximum relative error of the model was 9% and the root-mean-square error was 3.8%.

The model is developed for calculating the Nusselt number for a spherical particle with uniform Stefan flow, immersed in a uniform convective flow. It was validated for the Reynolds number ( $\text{Re}_f$ )  $2 \leq \text{Re}_f \leq 30$ , Stefan Reynolds number ( $\text{Re}_{sf,p}$ )  $-8 \leq \text{Re}_{sf,p} \leq 25$  and temperature range 400 K-1600 K for nitrogen gas atmosphere. The parameters for the Nusselt number without Stefan flow (Eq. 37) were estimated by fitting the simulation data presented in this study. Different sets of parameters might be applicable for different Reynolds number and temperature ranges.

The model for the drag coefficient and the Nusselt number were both developed by assuming that the change in temperature inside the boundary-layer occurs due to variations in Stefan flow velocity, Stefan flow temperature and far-field temperature alone. This would not be the case when there are other phenomena that affect the boundary-layer temperature, such as e.g., homogeneous reactions. The model is based on the assumption that the pressure force and the viscous force are of the same order of magnitude and that only the viscous force is affected by the Stefan flow (see Jayawickrama et al. (2019)). This might not be true for higher Reynolds numbers.

#### 5. Conclusions

The effect of a Stefan flow on the drag coefficient and Nusselt number was studied for a uniform flow around a spherical particle. The effect was investigated at non-isothermal conditions using resolved numerical simulations. Particle diameter, slip velocity, particle temperature, and Stefan flow velocity from/to the particle have been varied during the simulations. The range of Stefan Reynolds number of  $-8 \leq \text{Re}_{sf,p} \leq 25$ , Reynolds number of  $2 \leq \text{Re}_f \leq 30$  and particle temperatures ( $T_p$ ) of 400 K, 1200 K and 1600 K were considered in the simulations. The far-field temperature ( $T_{\infty}$ ) was kept constant at 1400 K.

The sensitivity of the drag coefficients on the Stefan flow was significantly different between isothermal and non-isothermal conditions. The effect of variation in thermophysical properties, especially at high temperature differences (between particle and farfield), is emphasized. This difference makes isothermal models less accurate for estimation of the drag coefficient.

Our previous model, developed for the drag coefficient with Stefan flow at isothermal conditions, therefore was modified for non-isothermal conditions. The refined model (presented in Eq. 33) introduced the volume averaged film temperature ( $\tilde{T}$ ) to describe the change of thermophysical parameters in the boundary layer by a Stefan flow under non-isothermal conditions. The model is based on the physical interpretations and shows a good agreement with the simulation data. It kept the number of fitting parameter to one, which represents the relationship between the boundary layer thickness and the particle Reynolds number.

Similarly, a new model (see Eq. (38)) that describes the effect of a Stefan flow on the Nusselt number was developed by using the volume averaged temperature ( $\tilde{T}$ ) in combination with models that describe convective flow effects and Stefan flow effects on the Nusselt number. The model agrees well with the simulation data with a single fitting parameter, which represents the relationship between boundary layer thickness and particle Reynolds number.

#### **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.

#### **CRediT** authorship contribution statement

Thamali R. Jayawickrama: Conceptualization, Methodology, Software, Validation, Formal analysis, Writing - original draft, Visualization. Nils Erland L. Haugen: Conceptualization, Writing review & editing, Supervision, Funding acquisition. Matthaus U. Babler: Writing - review & editing, Supervision, Funding acquisition. M.A. Chishty: Writing - review & editing, Supervision. Kentaro Umeki: Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

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#### Appendix A. Gas properties

Variation of thermal and physical properties of nitrogen  $(N_2)$  with temperature were calculated as follows. Specific heat capacity $(c_p)$  is calculated by NASA polynomials:

$$c_p = R_{c_p}(a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4 + a_5/T + a_6/T^2), \quad (A.1)$$

Table A.5

Coefficients for calculation of heat capacity  $(c_p)$  of gas.

Coefficient	T < 1000  K	T > 1000  K
<i>a</i> <sub>0</sub>	3.29868	2.92664
<i>a</i> <sub>1</sub>	0.00140824	0.00148798
<i>a</i> <sub>2</sub>	$-3.96322 \times 10^{-6}$	$-5.68476 \times 10^{-7}$
<i>a</i> <sub>3</sub>	5.64152×10 <sup>-9</sup>	$1.0097 \times 10^{-10}$
$a_4$	$-2.44486 \times 10^{-12}$	$-6.75335 \times 10^{-15}$
a <sub>5</sub>	-1020	-922.798
<i>a</i> <sub>6</sub>	3.95037	5.98053

where  $a_0$ ,  $a_1$ ,  $a_2$ ,  $a_3$ ,  $a_4$ ,  $a_5$ ,  $a_6$  are one set of constants for T > 1000 K and another set of constants for T < 1000 K.  $R_{c_p}$  (=296.8048) is a constant (Table A.5).

Dynamic viscosity( $\mu$ ) is calculated from Sutherland formula (Sutherland, 1893):

$$\mu = 1.67212 \times 10^{-6} \sqrt{T} / (1 + 170.672/T), \tag{A.2}$$

where  $\mu$  is in Pa.s and *T* is in K. Density ( $\rho$ ) is calculated from state equation with constant pressure;

$$\rho = pM/RT,\tag{A.3}$$

where *M* is the molecular weight (28.01 g/mol), *p* atmospheric pressure (101325 Pa) is and *R* is the gas constant. Thermal conductivity ( $\lambda$ ) is calculated from following model:

$$\lambda = 4.8 \times 10^{-4} T^{0.717},\tag{A.4}$$

where  $\lambda$  is in W/(K.m) and T is in K.

#### References

- Abramzon, B., Sirignano, W.A., 1989. Droplet vaporization model for spray combustion calculations. International Journal Heat Mass Transfer 32 (9), 1605–1618.
- Constant, E., Favier, J., Meldi, M., Meliga, P., Serre, E., et al., 2017. An immersed boundary method in OpenFOAM: Verification and validation. Computers and Fluids doi:10.1016/j.compfluid.2017.08.001.
- Downingm, C.G., 1966. The evaporation of drops of pure liquids at elevated temperatures: Rates of evaporation and wet-bulb temperatures. AIChE Journal 12 (4), 760–766. doi:10.1002/aic.690120424. arXiv:1011.1669v3.
- Eisenkalam, P., Arunachalam, S.A., Westen, J.A., 1967. Evaporation rates and drag resistance of burning drops. In: Eleventh Symposium (International) on Combustion, Vol. 11, pp. 715–728.
- Ellendt, N., Lumanglas, A.M., Moqadam, S.I., M\u00e4dler, L., 2018. A model for the drag and heat transfer of spheres in the laminar regime at high temperature differences. International Journal of Thermal Sciences 133, 98–105. doi:10.1016/j. ijthermalsci.2018.07.009.
- Fadlun, E.A., Verzicco, R., Orlandi, P., Mohd-Yusof, J., 2000. Combined Immersed-Boundary Finite-Difference Methods for Three-Dimensional Complex Flow Simulations. Journal of Computational Physics 161, 35–60. doi:10.1006/jcph.2000. 6484.
- Harpole, G.M., 1981. Droplet Evaporation in High Temperature Environments. Jouranl of Heat Transfer 103, 86–91.
- Jasak, H., Rigler, D., Tukovic, Z., 2014. Design and implementation of Immersed Boundary method with discrete forcing approach for boundary conditions. In: proceedings of 6th European Congress on Computational Fluid Dynamics - ECFD VI, Barcelona, Spain, pp. 5319–5332.
- Jayawickrama, T.R., Haugen, N.E.L., Babler, M.U., Chishty, M.A., Umeki, K., 2019. The effect of Stefan flow on the drag coefficient of spherical particles in a gas flow. International Journal of Multi-phase Flow 117, 130–137. doi:10.1016/ j.ijmultiphaseflow.2019.04.022.
- Johnson, T.A., Patel, V.C., 2017. Flow past a sphere up to a Reynolds number of 300. J. Fluid Mech 378, 19–70. doi:10.1017/S0022112098003206.
- Kestel, M., 2016. Numerical Modeling of Moving Carbonaceous Particle Conversion in Hot Environments. TU Bergakademie Ph.D. thesis.
- Kreitzberg, T., Pielsticker, S., Gvert, B.M., Kneer, R., 2016. CO2 and H2O Gasification under Chemically and Diffusion Controlled Conditions. In: 33rd Annual International Pittsburgh Coal Conference, Cape Town.
- Li, T., Niu, Y., Wang, L., Shaddix, C., Løvås, T., et al., 2018. High temperature gasification of high heating-rate chars using a flat-flame reactor. Applied Energy 227, 100–107. doi:10.1016/j.apenergy.2017.08.075.
- Miller, R.S., Bellan, J., 1999. Direct numerical simulation of a confined three-dimensional gas mixing layer with one evaporating hydrocarbon-droplet-laden stream. J. Fluid Mech 384, 293–338.
- Mittal, R., Iaccarino, G., 2005. Immersed Boundary Methods. Annual Review of Fluid Mechanics 37 (1), 239-261. doi:10.1146/annurev.fluid.37.061903.175743.
- Murphy, J.J., Shaddix, C.R., 2003. Effects of Stefan Flow on Heat Transfer from reacting Carbon particles. Sandia-Report 2003-8720] 1–24.

- Naraslmhan, C., Gauvin, W.H., 1967. Heat and Mass Transfer to Spheres in High Temperature Surroundings. The Canadian journal of Chemical Engineering 45, 181-188
- Niazmand, H., Renksizbulut, M., 2003. Transient three-dimensional heat transfer from rotating spheres with surface blowing. Chemical Engineering Science 58, 3535-3554. doi:10.1016/S0009-2509(03)00191-X.
- Nikrityuk, B., Meyer, P.A., 2014. Gasification Processes Modeling and Simulation, 1 Wilev-VCH.
- Ranz, W.E., Marshall, W.R., 1952. Evaporation from drops. Chemical Engineering
- Progress 48 (3), 141–146. Renksizbulut, M., Yuen, M.C., 1983. Experimental study of droplet evaporation in a high-temperature air stream. Journal of Heat Transfer 105, 384–388.
- Renksizbulut, M., Yuen, M.C., 1983. Numerical Study of Droplet Evaporation in a High-Temperature Stream. Journal of Heat Transfer 105 (2), 389-397. doi:10. 1115/1 3245591
- Richter, A., Nikrityuk, P.A., 2012. Drag forces and heat transfer coefficients for spherical, cuboidal and ellipsoidal particles in cross flow at sub-critical Reynolds numbers. International Journal of Heat and Mass Transfer 55 (4), 1343-1354. doi:10.1016/j.ijheatmasstransfer.2011.09.005.

Schiller, L., Naumann, A., 1935. A drag coefficient correlation. Zeitschrift des Vereins Deutscher Ingenieure 77, 318-320.

Sepman, A., Ögren, Y., Qu, Z., Wiinikka, H., Schmidt, F.M., et al., 2017. Real-time in situ multi-parameter TDLAS sensing in the reactor core of an entrained-flow biomass gasifier. Proceedings of the Combustion Institute 36 (3), 4541-4548. doi:10.1016/j.proci.2016.07.011.

Sutherland, W., 1893. The viscosity of gases and molecular force. Philosophical Magazine 507-531.

- Umeki, K., Kirtania, K., Chen, L., Bhattacharya, S., et al., 2012. Fuel Particle Conversion of Pulverized Biomass during Pyrolysis in an Entrained Flow Reactor. Industrial & Engineering Chemistry Research 51, 13973–13979. doi:10.1021/ie301530j.
- Weller, H.G., Tabor, G., Jasak, H., Fureby, C., 1998. A tensorial approach to compu-tational continuum mechanics using object-oriented techniques. Computers in Physics 12, 620-631. doi:10.1063/1.168744
- Whitaker, S., 1972. Forced Convection Heat Transfer Correlations for Flow in Pipes, Past Flat Plates, Single Cylinders, Single Spheres, and for Flow in Packed Beds and Tube Bundles. AIChE Journal 18, 361–371.
- Yu, J., Zhou, K., Ou, W., 2013. Effects of Stefan flow and CO oxidation on char particle combustion in O2/CO2 atmosphere. Fuel 106, 576-585.
- Yuen, M.C., Chen, L.W., 1976. On drag of evaporating liquid droplets. Combustion Science Technology 14, 147–154.
- Yuen, M.C., Chen, L.W., 1978. Heat-transfer measurements of evaporating liquid droplets. International Journal of Heat and Mass Transfer 21 (5), 537-542. doi:10.1016/0017-9310(78)90049-2.
- Zhifu, Z., Guoxiang, W., Bin, C., Liejin, G., Yueshe, W., 2013. Evaluation of Evapora-tion Models for Single Moving Droplet with a High Evaporation Rate. Powder Technology 240, 95-102. doi:10.1016/j.powtec.2012.07.002.



### APPENDIX B

One article is attached in Appendix B, related to chapter 2.3 on reaction mechanisms for conversion of petcoke char. See summary table in chapter 3 for details.

The article is reprinted from Energy, Vol 232, Korus, A., Klimanek, A., Sladek, S., Szlek, A., Tilland, A., Bertholin, S. and Haugen, N. E. L., Kinetic parameters of petroleum coke gasification for modelling chemical-looping combustion systems, 120935, Copyright (2021), with permission from Elsevier.

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# Kinetic parameters of petroleum coke gasification for modelling chemical-looping combustion systems



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#### ABSTRACT

One of the best low-cost approaches for capturing carbon dioxide from the combustion of solid fuels is chemical looping combustion (CLC) technology, where the processes of fuel oxidation and extraction of oxygen from the air are split in two separate reactors. In order to model the petroleum coke (petcoke) conversion in a CLC method, detailed knowledge about the reactions of pet-coke with  $O_2$ ,  $CO_2$ , and  $H_2O$  at temperatures between 750 and 1100 °C is required. Due to the lack of sufficient literature data, in this paper, the reactivity of these reactions is investigated in a custom-built test rig that enabled measurements of the mass loss of the fuel sample and the composition of the released gases. The Avrami, Random Pore, Shrinking Core, and Hybrid models were applied to the experimental results to determine the kinetic parameters of petcoke gasification. At temperatures up to 1000 °C, the reaction with  $CO_2$  was found to be negligibly slow. An activation energy of 103.91 kJ/mol was obtained for petcoke gasification in 10–40 vol% of H<sub>2</sub>O, while a value of 15.87 kJ/mol was found for oxidation in 2–4 vol% O<sub>2</sub>, as described by best-fitting models, i.e. Hybrid and Random Pore models, respectively.

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#### 1. Introduction

The production of petroleum coke (petcoke), a by-product of the oil refining process, is constantly increasing due to the high demand for oil-derived fuels and chemicals [1]. This highly calorific material can, therefore, be acquired in abundance at a low cost to produce energy or gaseous fuels [2]. The advantage of using petcoke as a feedstock for thermochemical conversion processes is its high heating value, approximately 20% higher than that of coal, and its low ash content (0.1-0.3%) [3].

Due to the need to incorporate carbon capture and sequestration (CCS) into the thermochemical conversion of carbonaceous fuels, chemical looping combustion (CLC) technology has become an attractive alternative to conventional combustion methods. The main reason for this is that the use of oxygen carriers that are transported between the air and the fuel reactors essentially results in an oxy-fuel process without the energy penalty associated with

\* Corresponding author. E-mail address: agnieszka.korus@polsl.pl (A. Korus). the cryogenic oxygen separation process of a regular oxy-fuel process. Although CLC was initially designated for gaseous fuel utilisation, the conversion of solids is also feasible, but it requires a gasifying agent, e.g. H<sub>2</sub>O or CO<sub>2</sub>, to act as the gaseous intermediate between the solids – oxygen carrier and fuel [4,5]. The feasibility studies on large-scale CLC installations have confirmed the low cost of the CO<sub>2</sub> capture integration [5], thus increasing the importance of developing this technology to achieve zero or even negative greenhouse gas emissions. To optimise the CLC reactor design, the detailed kinetic data on solid fuel gasification under the conditions characteristic for this technology must be acquired. Therefore, the purpose of this paper is to obtain accurate kinetic parameters for petcoke gasification through kinetic modelling of experimental data.

No clear correlation between the main physicochemical properties of the petcoke and its conversion rate have been established thus far. The parameters such as the specific surface area or volatile matter content do not vary significantly between various samples and they are not responsible for the different kinetics of petcoke oxidation [6]. However, the metals content in petroleum coke can be relatively diverse and these elements can have a non-negligible,



yet difficult to quantify, catalytic effect on the petcoke conversion [6,7]. Among others, vanadium, iron, or alkali and alkaline earth metals have been reported to have a significant impact on petcoke gasification and combustion kinetics [6,8,9].

The focus of this study is low-sulphur Chinese petcoke selected for testing at the 3 MW CLC reactor designed in the scope of the CHEERS project.<sup>1</sup> Even though some studies of petcoke thermochemical reactivity already exist in the literature [3.8-11], the reactivity of this particular petcoke has not previously been studied. Even more importantly, the kinetic data for CLC conditions, which require high temperatures and low oxygen concentrations, do not exist. Thus, an examination of the thermochemical conversion of the actual material selected for the pilot CLC reactor development, including the exact particle size range and gasification agent concentration, was required to provide accurate data on the apparent kinetic parameters to successfully model the reactor operation. The existing work on petcoke reactions with oxygen typically focuses on combustion, thus the experiments are carried out at lower temperatures (400–600 °C) and higher concentrations of oxidiser (>20 vol%) [7,12] than the experiments performed in this work. E.g., Gajera et al. [13] examined petcoke conversion in pure O<sub>2</sub> flow at temperatures up to 900 C. Gasification tests are also usually performed with undiluted oxidising agent, such as petcoke conversion in TGA in a pure flow of steam performed by Edreis et al. [14]. Some petcoke gasification tests carried out at temperatures above 1000 °C can be found in recently published works [15–19]. However, these reports are often oriented on the fundamental research on the petcoke kinetics, thus comprising thermogravimetric experiments with small sample sizes and the reaction atmosphere limited to pure CO<sub>2</sub>. E.g., Wei et al. [17,20] examined the effects of the addition of biomass leachates and Yu et al. [15] the addition of biomass ash on the petcoke gasification. Meanwhile, the conditions for gasification in a CLC reactor require presence of steam or oxygen. It is also beneficial to conduct the applicationoriented research in a larger scale than the instrumental analysis such as TGA. Lulu et al. [21] examined petcoke gasification with  $O_2$ and H<sub>2</sub>O at 900 °C in a fluidized bed, which represented a CLC reactor, using large sample of 0.75 g. Wei et al. [19] used a horizontal furnace with a 50 mg petcoke sample placed in a quartz boat crucible to examine CO<sub>2</sub> gasification at temperatures up to 1200 °C, while Wang et al. [22] carried out steam gasification tests at 650–750 °C with 20 g sample in a fixed bed reactor. Liu et al. [23] conducted tests in a 30 kW chemical looping combustion unit. However, the experiments carried out in the larger facilities focused mainly on the operational aspects of these reactors, i.e. monitoring the conversion efficiency or the evolved gases composition, etc., and they do not provide any kinetic data. Zhang et al. [24] presented a robust model of petcoke conversion in 15–50 vol% of steam and 0–3 vol% of oxygen based on the experiments in the entrained flow gasifier with a 60 g/h carbon feeding rate. The combined array design methodology allowed for an accurate description of the process, however, these results cannot be directly incorporated into the deterministic models for petcoke conversion. Although the existing research on petcoke conversion is extensive, there is a lack of kinetic parameters determined at the conditions relevant for gasification in chemical looping combustion units, i.e. based on the experimental work performed in the larger reactor, thus comprising more representative samples, and carried out in the oxidising agent concentrations up to 40 vol% at the temperatures up to 1000 °C.

To provide relevant data for the CHEERS project, measurements were conducted in a custom-built test rig that allowed the use of a wider size fraction and higher sample mass than thermogravimetric (TGA) experiments, which typically focus on samples with narrow particles size ranges and lower sample masses <10 mg [8.11.25–27]. The unique construction of the test rig, which has a crucible with a fritted bottom, enables the gas flow through the sample. Improved sample penetration by the oxidising gases reduces the diffusional resistance at high temperatures. Therefore, the kinetic parameters for the conversion not affected by the external diffusion could be obtained for the temperatures as high as 950 °C. The design also allows the use of a larger, more representative, sample size than conventional TGA, and the particle size range wide enough to represent the heterogenous fraction of fuel particles used in the industrial scale applications. Moreover, gasification tests for CO<sub>2</sub> partial pressures <0.1 MPa and steam/CO<sub>2</sub> mixtures were performed to meet the conditions relevant for chemical looping gasification, as opposed to the typical kinetic experiments carried out in atmospheres with a single gasifying agent [8-11,25,26]. The combination of the mass loss measurements and analysis of the gases evolved during gasification in CO<sub>2</sub>,  $H_2O$ ,  $CO_2/H_2O$  and  $O_2$  provide insight into the nature of petcoke conversion. Finally, the kinetic parameters are fitted using the Avrami, Random Pore, Shrinking Core, and Hybrid Model, and the most suitable approximations are identified for each gasification agent. These most common and universal models were chosen to ensure that the obtained kinetics could be easily applied to the global models of the entire gasification installations, e.g. CLC-CCS systems. E.g., the Random Pore Model and the Shrinking Core Model were successfully used to describe thermochemical conversion of petcoke in numerous thermogravimetric experiments [14,16,18,20,28]. The experimental work and following calculations provided the apparent kinetics of petcoke conversion under the conditions and for the particle sizes typical for chemical looping gasification, which is necessary for the design and modelling of the pilot installation yet has not been addressed in the previously published works.

#### 2. Experimental

#### 2.1. Materials

The petroleum coke (petcoke) used for the kinetic studies was a low-sulphur Chinese petcoke, which was also used as the main fuel in the CHEERS project. The reported raw petcoke composition on dry basis is: C - 91.2, H - 4.13, O - 1.44, N - 2.52, and S - 0.51 wt% and ash 0.2 wt% (by diff.).

Particles in the size range 100-300 µm were used in the experiments. Some preliminary tests with a larger fraction (300–500 µm) were also carried out (as presented in the Supplement S1); although the results were similar at lower temperatures and oxidiser concentrations, under the more reactive atmospheres (e.g. 40 vol%  $H_2O$  at 1000 °C) the gasification time increased by 25% when the larger fraction was used. This means that the internal diffusion within the petcoke particles plays a nonnegligible role during conversion under more reactive conditions (high temperatures and oxidiser concentrations). The influence of the external diffusion was limited due to the construction of the test rig (a porous crucible that allows for an unrestrained gas flow through the sample bed) and limitation of the analysis to the temperatures characteristic for the kinetic regime. Thus, the obtained parameters represent the apparent kinetics, which include only internal diffusion, and they are relevant for the examined particle size that was chosen to best represent the fuel used in the CLC unit. Therefore, for the successful utilisation of these results for other

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applications, external diffusion resistance should be incorporated into the presented model, adequately to the conditions in the given reactor.

To avoid contaminating the test rig with released tars, the petcoke was devolatilised prior to the experiments. The material was heated to 600 °C in a N<sub>2</sub> flow with a 10 °C/min heating rate followed by a 30 min isotherm. It was then cooled to ambient temperature and stored in a desiccator. This pre-treatment was also recreated in a TGA instrument, where the petcoke was heated and then cooled down in a N<sub>2</sub> flow, followed by CO<sub>2</sub> gasification. The similarity in the devolatilised and raw petcoke mass loss curves during the gasification step confirmed that the devolatilization and the cooling steps introduced due to the pretreatment did not significantly affect the gasification of the material (Supplement S2). Moreover, the test with the non-devolatilised petcoke was carried out in the main test rig under the most reactive of the studied conditions, and a comparison is presented in Supplement S3. An initial, rapid loss of approximately 10% of the sample mass occurred due to the rapid release of volatiles; however, the further mass loss curve was parallel to that of the devolatilised sample, and the reactivity at 50% conversion  $(R_{50})$  was 0.023 and 0.022 (1/min) for non-devolatilised and devolatilised petcoke, respectively. Therefore, it can be assumed that the relatively slow gasification reaction was not affected by the rapid release of lighter compounds at the beginning of the process and that the devolatilization time was negligibly small compared with the oxidation of the solid residue. Therefore, the applied petcoke pre-treatment should not affect the kinetic parameters obtained in this research.

#### 2.2. The test rig and experimental procedure

Petcoke gasification kinetics were determined from a series of measurements performed in the custom-built test rig for thermochemical fuel conversion studies (Fig. 1). The test rig can operate in two modes, referred to as the gravimetric and evolved gases methods. The main principle of the experiment was to perform the gasification of petcoke under isothermal conditions in a controlled flow of a gaseous mixture with a predetermined composition while registering the mass loss of the sample during the reaction. The decrease in the sample mass was determined by directly measuring the sample's weight during the reaction (gravimetric method). For some tests, the mass loss was validated by calculating the amount of carbon in the gases produced during petcoke gasification in another configuration of the test rig, where the gaseous products were monitored instead of the mass of the sample (evolved gases method).

Pictures of the test rig are shown in Fig. 1. The main part of the rig is comprised of two electrical furnaces fixed on a common panel attached to a vertical rail. An electric motor (1) allows for a rapid (ca. 300 mm/s) movement of the panel along the rail over a distance of 500 mm to quickly heat the sample (ca. 1700 °C/min). The required gas mixture of  $N_2/CO_2/O_2$  was prepared by supplying highpurity (99.999%) gases from gas cylinders into the mixing chamber (2) using thermal mass flow controllers. Since some of the examined gasification parameters requires steam, the gaseous mixture is supplied to the separate quartz tube reactor, the evaporator (3), before entering the reaction zone. If steam is required, a constant water flow is delivered to the evaporator using a syringe pump (4) and a PTFE transfer line, inserted from the bottom of the reactor and nested in a quartz wool plug, in the middle of the heating zone of the evaporator. The temperature in the evaporator is maintained at 300 °C to ensure constant, complete water vaporisation. The gases from the cylinders, now mixed with the steam, are further transferred via a heated line (5) into the main reactor, enclosed in the second furnace (6).

Depending on the selected method, one of the two types of vertical quartz tube reactors can be fixed in the furnace of the test rig. For the gravimetric method, a reactor (i.d. 27 mm) sealed at the top and opened at the bottom was used. The gaseous mixture was continuously supplied to the top of the reactor. Below the open lower end of the tube, a weighing module (7) enclosed in a protective case and purged with a constant  $N_2$  flow was placed. A quartz rod was attached to the weighing plate of the module. The shift of the panel with the furnaces to the lowest position allowed the rod to be inserted into the reactor through its open end. At the end of the rod, in the middle of the reactor heating zone, a quartz



**Fig. 1.** Test rig for petcoke gasification in the gravimetric mode with the furnace in the lower (left) and upper (right) position (1 – electric motor, 2 – gaseous mixture preparation unit, 3 – evaporator, 4 – syringe pump, 5 – heated transfer line, 6 – the main furnace, 7 – weighting module, 8 – sample holder).

sample holder (8) is mounted. The holder is cylindrical with an i.d. of 15 mm and a bottom made of a G3 quartz frit disc to allow the gaseous mixture to pass through the bed of the sample. The gaseous mixture and evolved gasification products exit the reactor through the open end. The sample mass was continuously measured, with the accuracy of 0.1 mg, throughout the experiment.

The second method, involving analysis of the released gases, required an air-tight gas outlet from the reactor; thus, it is impossible to register sample mass during this measurement. In this mode, a quartz tube (i.d. 20 mm) sealed on both ends is used, and the gaseous mixture is also supplied to the top of the reactor. It passes through a fixed bed of sample that is placed in the middle of the heating zone and is supported by a quartz wool plug. Through the sealed bottom end of the reactor, a thermocouple enclosed in a protective guartz tube is inserted to monitor the temperature of the bed. The evolved gases are transferred from the reactor through a cleaning line directly to the sampling loop of a gas chromatograph with a thermal conductivity detector (GC-TCD). The cleaning line includes an isopropanol impinger to remove condensable species, a particular matter filter, and a moisture trap. Gases, which constantly purged the sampling loop of the GC-TCD, were analysed every 10 min by switching the 6-way valve, which introduced the current contents of the sampling loop into the capillary column. The analysis was performed with an Agilent 6890 N gas chromatograph with a TCD detector, with the 100 ppm limit of quantitation. The samples were separated on a capillary J&W GS-CarbonPLOT 30 m  $\times$  0.53 mm x 3  $\mu m$  column followed by J&W HP-PLOT 30 m  $\times$  0.53 mm x 25  $\mu m$  molecular sieves. For the duration of CO<sub>2</sub> elution, the latter was bypassed using a 6-way valve.

The measurement principles of both methods are detailed in Fig. 2. In the gravimetric method, 300 mg of the sample (20 mg in tests with  $O_2$  to limit diffusion resistance) was weighted into the crucible attached to the rod connected to the weighing module, while the furnace panel was in the upper position, so that the reactor was above the sample holder. The experiment can be carried out with either a low or high heating rate. In the former case, the furnace panel is lowered prior to heating, and the sample is therefore enclosed inside the reactor purged by a N<sub>2</sub> flow. The furnace is then heated to the selected temperature at a rate of 20 °C/ min. The atmosphere is then switched to the predefined gaseous mixture and the gasification process is initiated. The mass loss in time is registered, providing the process kinetics data. A high heating rate of *ca.* 1700 °C/min could be achieved by lowering the

pre-heated furnace so that it rapidly enclosed the sample that was waiting in the ambient atmosphere. However, only preliminary tests are carried out using the fast heating, while the main experiments used for kinetic calculations were performed using the slow heating. The comparison of tests at both heating rates (presented in Supplement S4) revealed that, although the initial mass loss of the sample slightly increased during rapid heating, the average reactivity ( $R_{50}$ ) during conversion was not significantly affected by the sample heating time, due to the relatively long total gasification time.

In the gas evolution method, the gasification products are determined using GC-TCD analysis. The test rig setup included a sealed gas-tight reactor (Fig. 2). A 500 mg sample was enclosed in the reactor prior to the experiment and purged with N<sub>2</sub>, while the reactor was heated with a controlled, low heating rate (20 °C/min) up to the desired temperature. The N<sub>2</sub> flow was then switched to the gasification mixture and the online analysis of the gasification products, in 10 min intervals, was initiated.

The parameters for the petcoke conversion tests were selected to represent the conditions in a commercial CLC gasification unit. Therefore, the experiments were carried out under atmospheric pressure at temperatures in the range of 750–1100 °C and the oxidising agent concentrations set to: 2 and 4 vol% for O<sub>2</sub>; 10 and 40 vol% for CO<sub>2</sub>; and 10, 20 and 40 vol% for H<sub>2</sub>O.

#### 2.3. Calculations

Kinetic parameters are calculated only from the mass loss curves obtained from the gravimetric method. The evolved gases mode was mainly used to evaluate the reaction products; however, the mass loss of petcoke during steam gasification is also estimated from the carbon balance, based on all detected carbon-containing species, i.e. CO, CO<sub>2</sub>, and CH<sub>4</sub>. The remaining relative mass of the sample is expressed as

$$m_{\rm rel}(t) = 1 - \frac{(n_{\rm CO}(t) + n_{\rm CO2}(t) + n_{\rm CH4}(t))M_{\rm C}}{m_{\rm i}x_{\rm c}}$$
(1)

where  $n_i$  is the integrated molar amount of carbon (in mmol) in the *i*-th reaction product released in the time interval from t = 0 to t = t,  $M_C$  is the carbon molar mass (in mg/mmol),  $m_i$  is the initial mass of petcoke (in mg), and  $x_c$  is the mass fraction of C in petcoke (in mg C/mg).

The recorded mass losses during the gravimetric method are



Fig. 2. The principle of petcoke gasification with the a) gravimetric and b) evolved gases methods.

used to calculate the carbon conversion, which is defined as

$$X(t) = \frac{m_0 - m(t)}{m_0 - m_\infty}$$
(2)

where m,  $m_0$  and  $m_\infty$  are the instantaneous, initial and final masses of the sample, respectively (in mg). In the experiments where full conversion was not reached, the final mass was assumed based on the residual mass obtained in the tests with complete sample conversion.

A general form of the apparent rate of conversion for gas-solid reactions is given by

$$\frac{dX}{dt} = kf(X)p_{ox}^n \tag{3}$$

where  $p_{ox}$  is the partial pressure of the oxidizer (Pa), n is the reaction order, k is the apparent reaction rate coefficient (in  $1/(s \cdot Pa^n)$ ) and f(X) is a model function. The apparent reaction rate coefficient k takes into account the changes in temperature introduced in the Arrhenius form

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{4}$$

where *A* is the pre-exponential factor (in  $1/(s \cdot Pa^n)$ ), *E* is the activation energy (kJ/mol), *R* is the universal gas constant (in kJ/(mol·K)) and *T* is the temperature (in K). The model function f(X) takes into account variations in the physical and chemical properties of the sample as the reaction proceeds. Four model functions are tested within this study. First is the uniform conversion model [29], also known as homogeneous [30] or Avrami model (AVRAMI) [31], which is given by

$$f(X) = (1 - X) \tag{5}$$

The second examined function is the Random Pore Model (RPM) [31,32] expressed as

$$f(X) = (1 - X)\sqrt{1 - \psi \ln(1 - X)}$$
(6)

where  $\psi$  is the pore structure parameter, which can be determined using

$$\psi = \frac{2}{2\ln(1 - X_{max}) + 1} \tag{7}$$

where  $X_{max}$  is the conversion at maximum reaction rate, which is determined using the condition

$$\frac{d(dX/dt)}{dX} = 0 \tag{8}$$

The third considered model function is the Shrinking Core Model (SCM) [31].

$$f(X) = (1 - X)^m \tag{9}$$

where m = 2/3 for spheres is assumed. The last function analysed is called the Hybrid Model (HM) [31] which is identical to Eq. (9), but the exponent m is treated as a parameter and is adjusted during data fitting.

The experimental data is analysed using a series of scripts written in Matlab. As mentioned earlier, the measurements are done for petcoke reactions with  $O_2$ ,  $H_2O$  and  $CO_2$ . For all reactants, the reaction orders *n* were determined first, by analysing the conversion rates obtained for various partial pressures of the reactants.

Then, the obtained reaction orders were kept constant and the reaction rate coefficients were determined by fitting the conversion rates with functions (5)–(9). Finally, the kinetic parameters A and E from Eq. (4) were determined using Arrhenius plots. The results of the analyses are presented in section 3.2.

#### 3. Results and discussion

#### 3.1. Results of the petcoke gasification experiments

#### 3.1.1. Gas evolution profiles

Gases released during the gasification of petcoke in 10 and 40 vol% of steam in N2 were measured online with a gas chromatograph coupled with a thermal conductivity detector (GC-TCD). The evolution profile for the test performed at 1000 °C in 40 vol% of steam in N<sub>2</sub> is presented in Fig. 3 as an example; the main released gases were CO and H<sub>2</sub>, while the CO<sub>2</sub> and CH<sub>4</sub> yields were an order of magnitude lower. The delayed increase in the CO<sub>2</sub> evolution profile suggests that the water-gas shift (WGS) reaction was intensified during gasification. This could be due to either the catalytic effect of metals exposed by the initial carbon consumption with steam or as a result of a local increase in the steam concentration in the particle's surrounding, which occurred as the main steam gasification reaction, responsible for CO formation, slowed after 50 min. Another explanation for the delayed release of CO<sub>2</sub> might be its chemisorption on the petcoke surface at the initial stage of the process. For all examined cases, the maximum H<sub>2</sub> and CO yield occurred around the 0.1 conversion, and reaching even this early stage of petcoke gasification required residence times too long to be considered in operating commercial reactors. However, the experiments with steam as a sole oxidising agent were performed for the purpose of kinetic parameters determination that will be implemented in the modelling of a real gasifier. Due to the low reactivity of the sample, and the limited duration of the experiment (480 min), the carbon conversion, X, in the tests with the lower steam concentration reached only 0.5-0.75, depending on the applied temperature. Thus, the composition of the gaseous products was averaged only for the first half of the petcoke conversion (up to X = 0.5), and the result is presented in Fig. 4. As can be seen from the figure, CO and H<sub>2</sub> were the main gasification products, and their yields peaked at the beginning of the process and then decreased continuously with the carbon burnout. The molar ratios of the cumulative amounts of H<sub>2</sub> and CO  $(n_{H2}/n_{CO})$  released during carbon conversion up to X = 0.5 at temperatures up to 1000 °C were between 1.2 and 1.4 for the gasification with steam. The CO<sub>2</sub> concentration in the gasification products (i.e. excluding N<sub>2</sub> and H<sub>2</sub>O) was below 5 vol%. The composition of the obtained syngas was similar to the values reported by Trommer et al. [33] for two petcoke samples gasified in 10 vol% steam in a plug flow reactor.



Fig. 3. Gas evolution profiles for petcoke gasification in 40 vol% of steam in  $N_2$  at 1000  $^\circ C.$ 



**Fig. 4.** Composition of the gaseous reaction products from petcoke steam gasification averaged for the conversion X = 0 to X = 0.5 (labels: *steam concentration in vol%/reaction temperature in* °*C*).

However, more CO<sub>2</sub> was formed under the most reactive conditions, i.e. 40 vol% of steam and 1100 °C. Wu et al. [9] stated that during petcoke gasification with steam in a fixed-bed reactor the water-gas shift reaction (WGS) shown in equation (10) will not reach equilibrium.

$$CO + H_2O = CO_2 + H_2 \tag{10}$$

Since the WGS reaction rate increases rapidly above 1000 °C, at 1100 °C the WGS reaction is intensified, despite its exothermic character, while the rate of the heterogenous reaction is constrained by the available surface of the petcoke particles, which increases  $CO_2$  and decreases CO yield. Another possible explanation for the observed increase in the  $CO_2$  formation is the rapid increase in the catalytic activity of the metal M-C-O conformations in petcoke, which are known to increase selectivity towards  $CO_2$  formation, at the expense of CO yield [9,34].

$$C + H_2 O = CO + H_2$$
 (11)

As can be seen from Fig. 5, the reaction rate of petcoke gasification with  $CO_2$  was extremely slow. The measurement time was arbitrarily limited to 480 min and negligible conversion was achieved during these tests. Gasification with  $CO_2$  gradually increased the porosity of petcoke, resulting in an increase in the CO yield. Even under the most reactive condition, i.e. 40 vol% of  $CO_2$  at 1000 °C, the reaction rate did not reach its maximum even after 480 min of measurements, while, in the same concentration of



steam, the petcoke bed reached full conversion in less than 240 min. Therefore, the role of CO<sub>2</sub> during petcoke gasification below 1000 °C could be considered negligible and it does not have any applicable commercial value. Since the petcoke conversion with CO<sub>2</sub> was so slow, realistic kinetic parameters could not be obtained.

In contrast, petcoke gasification in 4 vol% of  $O_2$  was very rapid. In the temperature range of 750–1000 °C total conversion was reached in less than 15 min. Since the online gas analysis with GC-TCD was performed in 10 min intervals, no evolution profiles could be determined from these tests. The kinetic parameters of oxygen conversion were, therefore, determined based on the gravimetric tests. The only detected reaction product was  $CO_2$ , which suggest that the combustion of petcoke was complete.

#### 3.1.2. The results of the gravimetric and evolved gases experiments

Gravimetric analysis of petcoke gasification in steam and in oxygen was used to calculate kinetic rate parameters for the heterogeneous reactions. In addition, for steam gasification, gas evolution profiles were also used to determine the corresponding mass loss curves. This was done based on the amount of carbon in the gaseous reaction products (Eq. (1)). The comparison of the mass loss functions obtained with both methods is presented in Fig. 6 and Fig. 7 for experiments performed in 10 vol% and 40 vol% of steam, respectively.

At the lower steam concentration, and thus a lower reaction rate, the curves were similar, but some discrepancies can be seen for the reactions carried out under more reactive conditions. For those cases where full conversion was reached within the time frame of the experiment, i.e. where dX/dt = 0 at the end of the experiment, the final conversion found from the EV method is 0-0.1 larger than for the GR method. This discrepancy may be because not all gases were correctly captured and integrated using the EV method. For these cases, the final conversion of the EV method is normalised by the one obtained using the GR method. A relatively good agreement between the mass loss plots obtained with EV and GR methods suggests that the former provides valid data on the composition of released gases and can be applied to study the petcoke gasification mechanisms and kinetics. As no solid deposits were observed in the experiments, the differences between the methods may result from the larger uncertainties of the indirect mass loss determination approach of the EV method; thus, the data from the GR method was used for the kinetic parameter calculations. This observation indicates that no such limitation occurs at lower temperatures, thus the kinetics calculated from the petcoke gasification experiments up to 950 °C can be attributed to the chemical reaction rates and increase in the surface area of the particles, rather than diffusional limitations of a fixed bed.

The mass loss curves from the gravimetric tests of petcoke gasification with 2 and 4 vol% of  $O_2$  are presented in Fig. 8. As expected, the reaction occurs more rapidly at higher temperatures.  $CO_2$  is the only detected product, and the higher oxygen concentration significantly shortens the reaction times.

#### 3.1.3. Petcoke gasification in a mixture of steam and $CO_2$

The reaction of petcoke with  $CO_2$  was significantly slower than steam gasification; nonetheless, a possible contribution of  $CO_2$ during petcoke conversion under the more complex gasification atmosphere was examined by performing tests in a mixture of 40 vol% of H<sub>2</sub>O in CO<sub>2</sub>. The results were compared with the steam gasification measurements using inert N<sub>2</sub> as the carrier gas, as presented in Fig. 9. The mass loss registered during the 480 min conversion tests in 40 vol% of CO<sub>2</sub> in N<sub>2</sub> are also provided as a reference. It can be noted that, up to 1000 °C, the curves of the petcoke mass loss during reactions with 40 vol% of steam were not



Fig. 6. Mass loss curves from gravimetric (GR) and evolved gases (EV) analysis of petcoke gasification in 10 vol% of steam in N2.

affected by changing the carrier gas from N<sub>2</sub> to CO<sub>2</sub>. This finding confirmed the dominating role of H<sub>2</sub>O over CO<sub>2</sub> in the petcoke gasification process at these temperatures. However, the reaction with CO<sub>2</sub> became significant at 1100 °C. At the same time, since full conversion was reached for steam gasification (after about 160 min), almost 1/3 of the sample was converted when H<sub>2</sub>O was substituted with CO<sub>2</sub>. The same non-negligible role of CO<sub>2</sub> at high temperatures was confirmed by the enhanced petcoke conversion when N<sub>2</sub> was substituted with CO<sub>2</sub> for the measurement at 1100 °C. Therefore, for high-temperature petcoke gasification the presence of CO<sub>2</sub> should be accounted for, while it can be disregarded under less-reactive conditions.

Petcoke gasification measurements in 20 vol% steam in CO<sub>2</sub> were also carried out at temperatures up to 1000 °C. From these results, the assumption that the type of the carrier gas does not affect the kinetics of the steam gasification of petcoke in this temperature range was confirmed by comparison with corresponding measurements in  $H_2O/N_2$  atmospheres.

Moreover, using 20 vol% of steam for these additional tests allowed validation of the results of the models applied for the conversion in 10 and 40 vol%. The mass loss of petcoke in 40, 20 and 10 vol% of steam (in either  $N_2$  or  $CO_2$ ) is presented in Fig. 10. Steam concentration had a strong impact on the petcoke gasification, and when a higher steam content was used, the total conversion times were shorter, regardless of the applied temperature. At 900 °C, the gasification reaction was significantly slower for all examined steam concentrations. However, the offset between the mass loss curves at 950 and 1000 °C was less pronounced and decreased with the reaction time. Surprisingly, after reaching 0.6 and 0.9 conversions with 20 and 10 vol% of steam, respectively, the remaining mass of petcoke was lower at 950 °C than at 1000 °C, possibly due to diffusional limitations at 1000 °C.

#### 3.2. Calculation of the kinetic parameters of petcoke gasification

#### 3.2.1. Reaction with $O_2$

Petcoke oxidation experiments in an  $O_2/N_2$  mixture were performed for two  $O_2$  concentrations of 2 and 4 vol% and three temperatures of 750, 850, and 950 °*C*. The obtained conversion curves are presented in Fig. 11. To determine the reaction order the reaction rates (dX/dt) vs. conversion (X) were limited to the regions of  $X_{\mathcal{E}} < 0.2, 0.8 >$  in which straight lines were fitted to the data, as presented in Fig. 12, following the procedure described by Gartner et al. [31]. The reaction orders were then determined from a plot of  $\ln(dX/dt)$  vs.  $\ln(p_{O2})$  for each conversion X, and based on the obtained results, a mean reaction order was calculated. For the reaction with  $O_2$  the determined mean reaction order is n = 0.55. It should be stressed, however that variations in the reaction order nwith conversion X were observed, in the range from 0.42 to 0.66.

The mean reaction order was then used to calculate the apparent reaction rate coefficient k (and m for HM) by fitting the experimental data with the models defined in Eqs (5)–(9). In Fig. 13, the f(X) function models fitted to the experimental data are compared. As can be seen, the best fit was obtained for the Hybrid Model (HM), which was confirmed by comparison of the sum of squared residuals *SSR* defined as

$$SSR = \sum_{i=1}^{N} (\varepsilon_i)^2$$
(12)

where  $\varepsilon_i$  is the residual (the difference between experimental data and model) and *N* is the number of data points. The *SSR* for each model for all temperatures, as presented in Fig. 13, are: AVRAMI *SSR* = 4.0 · 10<sup>-6</sup>, RPM *SSR* = 1.4 · 10<sup>-6</sup>, SCM *SSR* = 1.7 · 10<sup>-6</sup>, HM





Fig. 7. Mass loss curves from gravimetric (GR) and evolved gases (EV) analysis of petcoke gasification in 40 vol% of steam in N2.



Fig. 8. Mass loss curves from gravimetric analysis of petcoke gasification in 2 and 4 vol% of O2 in N2.



Fig. 9. Mass loss of petcoke during gasification in 40 vol% of H<sub>2</sub>O with N<sub>2</sub> and CO<sub>2</sub> as the carrier gas and in 40 vol% of CO<sub>2</sub> in N<sub>2</sub>.



Fig. 10. Mass loss of petcoke during gasification in 40, 20 and 10 vol% of steam at 900, 950 and 1000  $^{\circ}\text{C}.$ 

 $SSR = 1.8 \cdot 10^{-7}$ .

Finally, the calculated apparent reaction rate coefficients k were used to determine the pre-exponential factor A, and the activation energy E, by fitting the plotted  $\ln(k)$  vs. 1/T data, as presented in Fig. 14. The fitted linear functions predicted the obtained rate coefficients well, suggesting that the reactions occurred in the kinetic regime, as required by the tested models. The determined model parameters are summarised in Table 1. The obtained model parameters were then used to verify the model predictions by



Fig. 11. Experimentally determined fuel conversion vs. time for two different mole fractions of oxygen.

integrating the conversion rates (dX/dt) for the various models and comparing the results with the experimentally determined conversions. The comparison is presented in Fig. 15. The AVRAMI model was excluded, as it gave the poorest predictions. All models predicted the experimentally-determined petcoke conversion vs.



Fig. 12. Linear fits to the experimental data for reaction order determination.

time. In some instances, the models slightly overpredicted the conversion, which is associated with the observed initial time delay of the conversion due to initial sample heating up not captured by the models. In general, the best predictions were obtained for the Energy 232 (2021) 120935



Fig. 14. Determination of the pre-exponential factor A and activation energy.E

Hybrid Model (HM), which is confirmed by the lowest residuals. The calculated sums of squared residuals (SSR) were: RPM *SSR* =  $1.3 \cdot 10^{-5}$ , SCM *SSR* =  $2.2 \cdot 10^{-5}$ , HM *SSR* =  $1.2 \cdot 10^{-5}$ . Therefore, it is recommended to use the Hybrid Model (HM) for reactions with O<sub>2</sub>. It should be also stressed that the models are valid in the kinetic regime.



**Fig. 13.** Comparison of fitted model functions f(X) for the reaction with O<sub>2</sub> ( $x_{02} = 0.04$ ).

## Table 1 Summary of the model parameters determined for the reaction of petcoke with O2.

Model	Equation <sup>a</sup> $\frac{dX}{dt} = Aexp(-E/RT)f(X)p_{O_2}^n$	$\frac{A}{1/(\mathrm{sPa}^n)}$	E kJ/mol	n	m	ψ
AVRAMI	f(X) = (1 - X)	1.004e-4	16.44	0.548	_	_
RPM	$f(X) = (1 - X)\sqrt{1 - \psi \ln(1 - X)}$	6.595e-5	16.85	0.548	-	2.963
SCM	$f(X) = (1 - X)^m$	8.660e-5	16.70	0.548	0.667	_
HM <sup>b</sup>	$f(X) = (1-X)^m$	5.875e-5	15.87	0.548	0.266	-

 $p_{02}$  in Pa, T in K.

<sup>b</sup> Recommended model.



Fig. 15. Comparison of experimental data (EXP) and predictions of the subsequent models.

It was reported by Afrooz et al. [35] that the activation energy of petcoke oxidation decreased from 124 to 35.3 kJ/mol (determined with SCM), and from 124.8 to 31.3 kJ/mol (determined with RPM) when heating rate in the TGA program was increased from 10 to 20 K/min. In this work, the sample was already at the reaction temperature when the oxidising agent was introduced, thus, it is plausible, that the lack of the heating step further decreased the activation energy to the values calculated hereby.

#### 3.2.2. Reaction with H<sub>2</sub>O

The same procedures for determining the kinetic parameters as described above for  $O_2$  were applied for the reaction with  $H_2O$ ,

where the petcoke was gasified in a  $H_2O/N_2$  mixture for the two  $H_2O$  concentrations of 10 and 40 vol%. In Fig. 16, the experimentally-determined fuel conversion vs. time is presented. As can be seen, the conversion lines cross for the high temperature tests. These phenomena are attributed to the reaction rate reduction due to diffusion at high temperature. Furthermore, not full conversion was obtained at the  $H_2O$  concentrations of 10 vol% due to very long reaction times. It should be however stressed that both concentrations ( $x_{H2O} = 0.1 \text{ mol/mol}$  and  $x_{H2O} = 0.4 \text{ mol/mol}$ ) and all temperatures were used to determine the reaction order. For the determination of the kinetic parameters, only data for low temperatures and high  $H_2O$  concentrations ( $x_{H2O} = 0.4 \text{ mol/mol}$ ) were



Fig. 16. Experimentally-determined fuel conversion vs. time.

used. In general, large variations in the reaction orders with temperature was observed, and a mean value of n = 0.9 was calculated and used. Another choice would be to take the orders for low temperatures ( $n \sim 0.86$ ). Since the value was close to the one for all

temperatures and the fitted model predictions with an order of 0.9 were satisfactory, this approach was used, and four models (AVRAMI, RPM, SCM and HM) were tested as previously. In Fig. 17, a comparison of the fitted model functions f(X) to the experimental data is presented. As can be seen for the highest temperature of 1000 °*C*, the reaction rate is initially the highest, however at conversions greater than 0.5, the reaction rate decreases below that of the 950 °*C* plot.

In Fig. 18 the  $\ln(k)$  vs. 1/T plots of the four models are presented, which also show the calculated pre-exponential factor A and activation energy E. In this figure, the data for all temperatures are presented; however, due to the visible reduction in the reaction rate due to diffusion in pores at the highest temperature, the data at 1000 °C was excluded from the analysis. Comparing Figs. 13 and 14 with Figs. 17 and 18 shows that the reaction rate in O<sub>2</sub> is an order of magnitude greater than that in H<sub>2</sub>O. The model parameters were determined and used to verify the predictions by comparing the results with the experimentally-determined conversions, and the comparison is presented in Fig. 19. The model predictions are satisfactory for all the temperatures. As expected, at the highest temperature of 1000 °C the reaction rate is limited by reactant diffusion, thus these datapoints were excluded from the analysis and the model parameters were not determined at this temperature. The sums of squared residuals (SSR) were also similar to each other for all models: RPM SSR =  $2.0 \cdot 10^{-7}$ , SCM SSR =  $3.6 \cdot 10^{-7}$  and HM SSR =  $3.1 \cdot 10^{-7}$ . It was also observed that for the Hybrid Model



**Fig. 17.** Comparison of fitted model functions f(X) for reaction with  $H_2O$ 



Fig. 18. Determination of the pre-exponential factor A and activation energy.E

(HM) the power m (model parameter) changed considerably with temperature. In the results presented in Figs. 17–19, a constant mean value was used. It was therefore verified if the HM model

predictions could be improved by introducing a linear dependence on temperature in the m parameter. Indeed, such a modification allowed reduced the sum of squared residuals of the HM model to HM  $SSR = 3.1 \cdot 10^{-7}$  and improved the model predictions in the temperature range of the conducted experiments; however, the m(T) function became negative at lower temperatures, which may lead to incorrect predictions at these temperatures and was therefore excluded from this analysis. The determined parameters of all the models are summarised in Table 2, where a recommendation on the best model for reactions with H<sub>2</sub>O is also given. Activation energy determined from the thermogravimetric experiments performed by Edreis et al. [14] was slightly higher, i.e. 165.54 kJ/mol modeled with SCM. However, their experiments were carried out as a temperature program with a low heating rate of 10 K/min, whereas in these tests, the reaction was initiated with the samples already heated up.

To further validate the developed models (data from Table 2), they were used to predict conversions vs. time for a set of experimental data obtained for petcoke gasification in H<sub>2</sub>O/CO<sub>2</sub> at 900 and 950 °*C* and water vapor mole fractions  $x_{H20}$  of 0.2 and 0.4. Similar to the previous comparison, the AVRAMI model was excluded from the analysis. The comparison is shown in Fig. 20, where the conversions vs. time are presented. The kinetic data obtained for H<sub>2</sub>O/N<sub>2</sub> mixtures predicted the experimentally-determined conversions in H<sub>2</sub>O/CO<sub>2</sub> mixtures well. Therefore, as



Fig. 19. Comparison of experimental data and model predictions for H<sub>2</sub>O/N<sub>2</sub> mixture.

#### A. Korus, A. Klimanek, S. Sładek et al.

Table 2		
Summary of the determined model	parameters for the reaction	of petcoke with $H_2O$ .

Model	Equation <sup>a</sup> $\frac{dX}{dt} = A \exp(-E/RT) f(X) p_{H_2O}^n$	A 1/(sPa <sup>n</sup> )	E kJ/mol	n	m	ψ
AVRAMI	f(X) = (1 - X)	9.01e-4	109.57	0.9	-	-
RPM <sup>b</sup>	$f(X) = (1 - X)\sqrt{1 - \psi \ln(1 - X)}$	2.92e-4	103.91	0.9	-	3.612
SCM	$f(X) = (1 - X)^m$	4.97e-4	105.63	0.9	0.667	_
HM	$f(X) = (1-X)^m$	1.65e-3	119.50	0.9	0.445	_

 $p_{H2O}$  in Pa, T in K.

<sup>b</sup> Recommended model.



Fig. 20. Comparison of the experimental data for H<sub>2</sub>O/CO<sub>2</sub> mixture and model predictions.

stated before, it can be concluded that the role of  $CO_2$  in the process is minor, and, as will be shown in the next section, the reaction with  $CO_2$  in the context of this analysis can be neglected if the temperature does not significantly exceed 1000 °*C*.

#### 3.2.3. Reaction with CO<sub>2</sub>

The petcoke gasification experiments in a  $CO_2/N_2$  atmosphere ( $x_{CO2} = 0.4 \text{ mol/mol}$ ) were conducted at three temperatures, i.e. 900, 950, and 1000 °*C*. In Fig. 21, the conversion vs. time is presented. The reaction of petcoke with  $CO_2$  is an order of magnitude

lower than that with  $H_2O$ , and decreases further as the reaction proceeds. It took approximately 6 h to convert 10% of the sample at 1000 °C; thus, the conversion rate is below practical considerations under the analysed conditions. Therefore, no model was proposed here, since for practical systems operating at the temperatures considered in this analysis, the reaction rate can be assumed to be 0. Some literature reports describe the relatively rapid CO<sub>2</sub> gasification of petcoke with activation energies of approximately 150 kJ/ mol (e.g. 142 kJ/mol reported by Kumari et al. [16] and 159 kJ/mol reported by Wei et al. [17]). However, those thermogravimetric



Fig. 21. Conversion vs. time for a reaction with.CO<sub>2</sub>

experiments were performed under the atmosphere of pure  $CO_2$  at temperatures above 1000 °C, i.e. conditions significantly more reactive than the ones applied in this study.

#### 4. Conclusions

In this article, the kinetic parameters for petcoke gasification were calculated based on the experimental data from laboratory tests dedicated to the material selected for the CHEERS project, to enable modelling of the 3 MWth prototype of chemical looping combustion (CLC) system with inherent carbon capture.

The tests revealed that the rate of petcoke gasification at 10 and 40 vol% of CO<sub>2</sub> was negligible at temperatures below 1100 °C. The tests allowed the determination of the kinetic parameters for petcoke gasification in steam and oxygen at temperatures up to 950 °C. At higher temperatures, the conversion was limited by diffusion. The kinetic parameters of petcoke gasification were best described by:

- the Hybrid Model for gasification in 2–4% O<sub>2</sub> ( $E_a = 15.87 \text{ kJ/mol}$ );
- the Random Pore Model for gasification in 10–40 vol%  $H_2O(E_a = 103.91 \text{ kJ/mol})$ .

Moreover, at the temperatures up to 1000  $^{\circ}$ C, conversion in CO<sub>2</sub> was negligible and it did not affect the reaction rate, when CO<sub>2</sub> was added to the steam gasification of petcoke.

The apparent kinetic parameters determined in this work include the internal diffusion within the particles; thus, to make the obtained results more universal, the continuation of this research, to account for different particles sizes, will be considered in the future.

#### Credit author statement

Agnieszka Korus: Investigation, Methodology, Visualization, Data curation, Writing – original draft, Writing – review & editing; Adam Klimanek: Methodology, Visualization, Data curation, Formal analysis, Software, Writing – original draft, Writing – review & editing; Sławomir Sładek: Investigation, Methodology, Visualization, Software; Andrzej Szlęk: Conceptualization, Methodology, Writing – review & editing, Supervision; Airy Tilland: Investigation, Methodology; Stéphane Bertholin: Conceptualization, Writing – review & editing, Supervision; Nils Erland L. Haugen: Conceptualization, Writing – review & editing, Supervision

#### **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.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.energy.2021.120935.

#### References

- Karasu S, Altan A, Bekiros S, Ahmad W. A new forecasting model with wrapper-based feature selection approach using multi-objective optimization technique for chaotic crude oil time series. Energy 2020;212:118750. https:// doi.org/10.1016/j.energy.2020.118750.
- [2] Wang J, Anthony EJ, Abanades JC. Clean and efficient use of petroleum coke for combustion and power generation. Fuel 2004;83:1341-8. https://doi.org/ 10.1016/j.fuel.2004.01.002.
- [3] Murthy BN, Sawarkar AN, Deshmukh NA, Mathew T, Joshi JB. Petroleum coke gasification: a review. Can J Chem Eng 2014;92:441-68. https://doi.org/ 10.1002/cjce.21908.
- [4] Leion H, Mattisson T, Lyngfelt A. The use of petroleum coke as fuel in chemical-looping combustion. Fuel 2007;86:1947–58. https://doi.org/ 10.1016/j.fuel.2006.11.037.
- [5] Lyngfelt A, Linderholm C. Chemical-looping combustion of solid fuels status and recent progress. Energy procedia, vol. 114. Elsevier Ltd; 2017. p. 371–86. https://doi.org/10.1016/j.egypro.2017.03.1179.
- [6] Commandré JM, Salvador S. Lack of correlation between the properties of a petroleum coke and its behaviour during combustion. Fuel Process Technol 2005;86:795–808. https://doi.org/10.1016/j.fuproc.2004.08.001.
- [7] Tyler RJ. Intrinsic reactivity of petroleum coke to oxygen. Fuel 1986;65: 235-40. https://doi.org/10.1016/0016-2361(86)90012-8.
- [8] Liu X, Zhou Z, Hu Q, Dai Z, Wang F. Experimental study on Co-gasification of coal liquefaction residue and petroleum coke. Energy Fuels 2011;25. https:// doi.org/10.1021/ef200402z. 3377-81.
- [9] Wu Y, Wang J, Wu S, Huang S, Gao J. Potassium-catalyzed steam gasification of petroleum coke for H2 production: reactivity, selectivity and gas release. Fuel Process Technol 2011;92:523–30. https://doi.org/10.1016/ i.fuproc.2010.11.007.
- [10] Malekshahian M, Hill J M. Kinetic analysis of CO2 gasification of petroleum coke at high pressures. Energy Fuels 2011;25. https://doi.org/10.1021/ ef2009259. 4043-8.
- [11] Zou JH, Zhou ZJ, Wang FC, Zhang W, Dai ZH, Liu HF, et al. Modeling reaction kinetics of petroleum coke gasification with CO2. Chem Eng Process Process Intensif 2007;46:630–6. https://doi.org/10.1016/j.cep.2006.08.008.
  [12] Walsh DE, Green GJ. A laboratory study of petroleum coke combustion: ki-
- [12] Walsh DE, Green GJ. A laboratory study of petroleum coke combustion: kinetics and catalytic effects. Ind Eng Chem Res 1988;27:1115–20. https:// doi.org/10.1021/ie00079a005.
- [13] Gajera ZR, Verma K, Tekade SP, Sawarkar AN. Kinetics of co-gasification of rice husk biomass and high sulphur petroleum coke with oxygen as gasifying medium via TGA. Bioresour Technol Reports 2020;11:100479. https://doi.org/ 10.1016/j.biteb.2020.100479.
- [14] Edreis EMA, Li X, Atya AHA, Sharshir SW, Elsheikh AH, Mahmoud NM, et al. Kinetics, thermodynamics and synergistic effects analyses of petroleum coke and biomass wastes during H2O co-gasification. Int J Hydrogen Energy 2020;45:24502–17. https://doi.org/10.1016/j.ijhydene.2020.06.239.
- [15] Yu J, Gong Y, Wei J, Ding L, Song X, Yu G. Promoting effect of biomass ash additives on high-temperature gasification of petroleum coke: reactivity and kinetic analysis. J Energy Inst 2020;93:1364–72. https://doi.org/10.1016/ j.joei.2019.12.006.
- [16] Kumari N, Saha S, Sahu G, Chauhan V, Roy R, Datta S, et al. Comparison of CO2 gasification reactivity and kinetics: petcoke, biomass and high ash coal.
Biomass Convers Biorefinery 2020:1-14. https://doi.org/10.1007/s13399-020-00882-z.

- [17] Wei J, Guo Q, Gong Y, Ding L, Yu G. Effect of biomass leachates on structure evolution and reactivity characteristic of petroleum coke gasification. Renew Energy 2020;155:111–20. https://doi.org/10.1016/j.renene.2020.03.132.
- [18] Yang H, Song H, Zhao C, Hu J, Li S, Chen H. Catalytic gasification reactivity and mechanism of petroleum coke at high temperature. Fuel 2021;293:120469. https://doi.org/10.1016/j.fuel.2021.120469.
- [19] Wei R, Ren L, Geng F. Gasification reactivity and characteristics of coal chars and petcokes. J Energy Inst 2021;96:25–30. https://doi.org/10.1016/ j.joei.2020.07.012.
- [20] Wei J, Ding L, Gong Y, Guo Q, Wang Y, Yu G. High-temperature char gasification of anthracite/petroleum coke: using biomass leachate as cheap-effective additive. Asia Pac J Chem Eng 2020;15:e2454. https://doi.org/10.1002/ apj.2454.
- [21] Lulu W, Laihong S, Shouxi J, Tao S. Chemical looping gasification with potassium-catalyzed petroleum coke for enhanced production of H2 and H2S. Chem Eng J 2020;397:124631. https://doi.org/10.1016/j.cej.2020.124631.
- [22] Wang Z, Ouyang P, Cui L, Zong B, Wu G, Zhang Y. Valorizing petroleum coke into hydrogen-rich syngas through K-promoted catalytic steam gasification. J Energy Inst 2020;93:2544–9. https://doi.org/10.1016/j.joei.2020.09.001.
- [23] Liu L, Li Z, Wu S, Li D, Cai N. Conversion characteristics of lignite and petroleum coke in chemical looping combustion coupled with an annular carbon stripper. Fuel Process Technol 2021;213:106711. https://doi.org/10.1016/ j.fuproc.2020.106711.
- [24] Zhang J, Hou J, Feng Z, Zeng Q, Song Q, Guan S, et al. Robust modeling, analysis and optimization of entrained flow co-gasification of petcoke with coal using combined array design. Int J Hydrogen Energy 2020;45:294–308. https:// doi.org/10.1016/j.ijhydene.2019.10.153.
- [25] Fermoso J, Arias B, Pevida C, Plaza M, Rubiera F, Pis J. Kinetic models comparison for steam gasification of different nature fuel chars. J Therm Anal Calorim 2008;91:779–86. https://doi.org/10.1007/s10973-007-8623-5.

- [26] Zhan X, Zhou ZJ, Wang F. Catalytic effect of black liquor on the gasification reactivity of petroleum coke. Appl Energy 2010;87:1710–5. https://doi.org/ 10.1016/j.apenergy.2009.10.027.
- [27] Yoon SJ, Choi Y-C, Lee S-H, Lee J-G. Thermogravimetric study of coal and petroleum coke for co-gasification. Kor J Chem Eng 2007;24:512–7. https:// doi.org/10.1007/s11814-007-0090-y.
- [28] Ren L, Wei R, Xin J. Co-gasification mechanism and kinetics of petcoke with lignite. Energy Fuels 2020;34:1688–97. https://doi.org/10.1021/ acs.energyfuels.9b04144.
- [29] Ye DP, Agnew JB, Zhang DK. Gasification of a South Australian low-rank coal with carbon dioxide and steam: kinetics and reactivity studies. Fuel 1998;77: 1209–19. https://doi.org/10.1016/S0016-2361(98)00014-3.
- [30] Molina A, Mondragón F. Reactivity of coal gasification with steam and CO2. Fuel 1998;77:1831-9. https://doi.org/10.1016/S0016-2361(98)00123-9.
- [31] Gartner JK, Garcia-Perez M, Van Wie BJ. Investigation of biomass char gasification kinetic parameters using a novel miniaturized educational system. BioResources 2019;14:3594–614. https://doi.org/10.15376/biores.14.2.3594-3614.
- [32] Everson RC, Neomagus HWJP, Kaitano R. The random pore model with intraparticle diffusion for the description of combustion of char particles derived from mineral- and inertinite rich coal. Fuel 2011;90:2347–52. https:// doi.org/10.1016/j.fuel.2011.03.012.
- [33] Trommer D, Noembrini F, Fasciana M, Rodriguez D, Morales A, Romero M, et al. Hydrogen production by steam-gasification of petroleum coke using concentrated solar power - I. Thermodynamic and kinetic analyses. Int J Hydrogen Energy 2005;30:605–18. https://doi.org/10.1016/ j.ijhydene.2004.06.002.
- [34] Wang J, Jiang M, Yao Y, Zhang Y, Cao J. Steam gasification of coal char catalyzed by K2CO3 for enhanced production of hydrogen without formation of methane. Fuel 2009;88:1572–9. https://doi.org/10.1016/j.fuel.2008.12.017.
- [35] Afrooz IE, Ching DLC. A modified model for kinetic analysis of petroleum coke. Int J Chem Eng 2019;2019. https://doi.org/10.1155/2019/2034983.



# APPENDIX C

One article is attached in Appendix C, related to chapter 2.4 on the effect of turbulence on char conversion in dilute flows. See summary table in chapter 3 for details.

Contents lists available at ScienceDirect





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# The effect of turbulence on mass transfer in solid fuel combustion: RANS model



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#### ABSTRACT

In this paper, a kinetic-diffusion surface combustion model is examined. The model is modified such that two effects of turbulence are included: 1) enhancement of the mass transfer due to relative velocity between particles and fluid and 2) reduction of the mass transfer due to turbulence-induced particle clustering. Details of the implementation are discussed and the influence of parameters such as air-fuel ratio, particle number density, particle diameter, turbulence intensity and characteristic length scales are studied theoretically. A simplified numerical model of a combustion chamber is created to explore the effects of the combustion model predictions. Finally, the model is incorporated into simulations of an industrial-scale boiler to investigate the effect of turbulence on the net surface reaction rate in a real system. The study shows that although on average this effect is rather minor, there exist regions in which the carbon conversion rate is either decreased or increased by turbulence.

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#### 1. Introduction

Modelling of solid fuels combustion and gasification requires taking into account several important processes occurring during fuel conversion. A solid fuel particle injected into a hot environment is first heated up and dried. In the next stage devolatilization starts, which is a complex decomposition process associated with the release of multiple gaseous products. During the last stage of conversion, the remaining char is converted through reactions with the surrounding gas. In reality, a distinct separation between the processes can typically not be distinguished, and the drying and devolatilization, as well as devolatilization and char surface reactions overlap [1,2], in particular for large particles. The devolatilization is much faster than the char conversion, especially in gasification systems, where slow endothermic reactions are responsible for the char conversion rate. Many parameters affect the devolatilization process leading to different volatile compositions, total yield and reaction rate. A range of models have previously been developed, differing considerably by their complexity and accuracy, see

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[2-5] for more detailed information on the process and its modelling.

The final stage of fuel conversion, i.e. the char conversion process, is affected by: the diffusion of reactants from the surrounding fluid to the particle surface, diffusion within particle pores, heterogeneous reactions at external and internal particle surfaces (including reactant gas adsorption and desorption), evolution of the char internal structure of pores, ash inhibition and thermal annealing [6]. Several approaches to char conversion modeling have been proposed in the literature. Among the most commonly used is the kinetic-diffusion surface reaction rate model [7,8] according to which the overall reaction rate can be influenced both by the reaction kinetics and the reactant diffusion. This model uses global kinetics and is computationally very efficient but it does not explicitly account for processes such as evolution of the char intrinsic surface area and pore diffusion, nor does it consider changes in particle diameter and density, variations in the particle reactivity [9], thermal deactivation or ash inhibition. A much more detailed approach that includes all of the above-mentioned processes is the Carbon Burnout Kinetics (CBK) model proposed by Hurt et al. [10] and further extended to oxidation and gasification at elevated pressure by Niksa et al. [11] and Liu & Niksa [12]. The CBK model was developed specifically to correctly predict char burnout and is able to capture a lower reactivity of chars at the final stage of

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conversion. However, the computational expense makes the model impractical to use in large-scale simulations [6]. More recently, groups at Stanford University and SINTEF have developed a model similar to the CBK model [13–15]. This model has a more accurate description of the size and density evolution of the char, together with a detailed intrinsic reaction mechanism. Annealing is, however, not included in this model.

Solid fuel combustion in industrial-scale facilities most often occurs under turbulent conditions. From the processes involved in char conversion mentioned above, turbulence primarily affects the efficiency of the reactant transport towards the particle surface. This effect of turbulence has been a subject of several recent studies [16-19]. Using Direct Numerical Simulations (DNS) and a simplified case in which a passive scalar (reactant) was consumed isothermally, the authors of [16,17] showed that turbulence might have two effects that counteract each other. Krüger et al. [16] demonstrated that the overall conversion rate can be reduced if the turbulent flow promotes particle clustering. This is related to the rapid oxidizer depletion due to increased concentration of particles in the clusters. These studies were extended by Haugen et al. [17] who showed that, in addition to particle clustering, turbulence can also increase the rate of heterogeneous reactions through velocity fluctuations that intensify the reactant transfer towards the particle surface. Furthermore, Haugen et al. [17] formulated a model that modifies the mass transfer coefficient to account for the two effects of turbulence and verified the model against their DNS results. These investigations were further extended to more realistic, non-isothermal conditions [18] and systems of polydisperse particles [19].

In the current study, we focus on the effects of turbulence on the mass transfer from the bulk gas to the particle surface. We discuss the model developed by Haugen et al. [17] and apply it to realistic combustion cases by utilizing the Reynolds Averaged Navier-Stokes (RANS) approach. Both main effects are considered: the enhancement of mass transfer through velocity fluctuations and the mass transfer rate reduction due to turbulence-induced particle clustering. We study the parameters affecting the process and show how the two effects of turbulence influence the char conversion in a jet of particles and in an industrial-scale boiler.

#### 2. Theory

The reactant consumption rate of a fuel particle can be defined as the normalized quantity relating the rate of change of particle mass,  $m_{p,0}$ , and its initial mass,  $m_{p,0}$ .

$$\Theta = -\frac{1}{m_{p,0}} \frac{dm_p}{dt} \tag{1}$$

In order to reduce complexity of the analysis we limit our discussion to the context of char burnout. We apply a simple kineticdiffusion model, with apparent rate kinetics. It should be stressed, however, that the analysis can be easily extended to more detailed models.

#### 2.1. Kinetic-diffusion model

One of the most frequently used approaches in CFD modelling of solid fuels combustion and gasification is to apply the kineticdiffusion model, given by

$$\Theta = \frac{\pi d_p^2 p_{ox}}{m_{p0}} \frac{1}{1/R_{dif} + 1/R_{kin}},$$
(2)

where  $d_p$  is the particle diameter,  $p_{ox}$  is the partial pressure of oxidizer,  $R_{dif}$  is the reaction rate due to diffusion defined as

$$R_{dif} = \frac{C}{d_p} \left(\frac{T+T_p}{2}\right)^{3/4} \tag{3}$$



**Fig. 1.** The kinetic-diffusion model for  $T_p = T$ ,  $\rho_p = 800 \text{ kg/m}^3$ ,  $d_p = 500 \text{ }\mu\text{m}$ , A = 0.002 s/m, E = 79 kJ/mol,  $C = 5 \cdot 10^{-12} \text{ sK}^{-3/4}$ .

and  $R_{kin}$  is the kinetic reaction rate, which is often written in the Arrhenius form

$$R_{kin} = A \exp\left(-\frac{E}{RT_p}\right). \tag{4}$$

In the above equations C is a constant,  $T_p$  and T are the temperatures of the particle and of the gas surrounding the particle, respectively, A is the pre-exponential factor, E is the activation energy, and R is the universal gas constant. The kinetic rate  $R_{kin}$  is the apparent rate, therefore the intrinsic reactivity and pore diffusion is already accounted for in parameters A and E. The model can be extended to account for these effects explicitly, see for example [20–22]. The kinetic-diffusion model, as given in Eq. (2), was derived with the assumption that the reaction is first order with respect to the oxidizer ox, see Smith [20] for details. In Fig. 1 the prediction of the kinetic-diffusion model is plotted as a function of temperature for a given condition. The effects of pure chemical kinetics  $(R_{dif} = \infty)$  and pure diffusion  $(R_{kin} = \infty)$  are also shown. As can be seen, the chemical reactions are slow at low temperatures and limits the overall reaction rate (Zone I). At high temperatures, the chemical reactions are fast, and the overall reaction rate is limited by the transport of oxidizer to the particle surface (Zone III). Between zones I and III, an intermediate temperature range exists (Zone II) in which both chemical kinetics and diffusion are important in determining the overall reaction rate.

#### 2.2. The effect of mean gas-particle velocity difference

The constant *C* entering Eq. (3) incorporates all the effects responsible for mass transfer to the particle surface, i.e. the stoichiometry of the reaction, diffusion to the particle surface and the effect of convection. Chen et al. [23] proposed that for the *i*th reaction

$$C_i = s_i \frac{M_C}{M_i} \frac{\overline{M}}{RT_0^{7/4}} \frac{p_0}{p} \text{Sh}D_{i,0}.$$
(5)

This is an extension of a formula derived by Baum et al. [7] for a single oxidation reaction. Here,  $s_i$  is the ratio of the stoichiometric coefficients of carbon and reactant (e.g.  $s_i = 1$  for  $C + O_2 \rightarrow CO_2$ ;  $s_i = 2$  for  $2C + O_2 \rightarrow 2CO$ ),  $M_C$  and  $M_i$  are the molecular weights of carbon and the reactant of reaction *i*, respectively,  $\overline{M}$  is the mean molecular weight of the gas in the particle boundary layer, Sh is the Sherwood number,  $D_i$  is the diffusion coefficient of the gaseous

reactant of reaction i, p is pressure and subscript 0 denotes the reference state. Assuming that the particles can be treated as spheres, the Sherwood number can be determined from the Ranz-Marshall formula [24]

$$Sh = 2.0 + 0.6 Re_p^{1/2} Sc^{1/3},$$
(6)

where  $Sc = \nu/D$  is the Schmidt number, and  $Re_p$  is the particle Reynolds number defined as

$$\operatorname{Re}_{p} = \frac{|u_{p} - u|d_{p}}{\nu},\tag{7}$$

where *u* is the mean gas velocity,  $u_p$  is the particle velocity and  $\nu$  is the kinematic viscosity. It has frequently been argued [20], that for fine pulverized fuel particles the relative particle-gas velocity is small, and thus  $\text{Re}_p \rightarrow 0$  and  $\text{Sh} \rightarrow 2$ . However, the particle Reynolds numbers can become higher for pressurized systems such as entrained-flow gasification reactors [25]. Also, for larger particles, characterized by larger Stokes numbers, the effect can become important as well.

In modelling of dilute, particulate flows, the effect of turbulence on particle dispersion is often included. One of the most frequently used approaches is to apply a stochastic tracking method. In such a case the particle trajectory is computed based on the instantaneous fluid velocity, which is a sum of the mean fluid velocity and its fluctuating component,

$$u' = \zeta \sqrt{2k/3},\tag{8}$$

where  $\zeta$  is a normally distributed random number and k is the turbulent kinetic energy. Even though this method may produce realistic particle dispersion, it gives rise to unphysically large relative velocity differences between particle and fluid. Remember that even tracer particles will experience this unphysical relative velocity, even though they in reality will always follow the fluid in which they are embedded. This is because it is the unresolved turbulent eddies that transport the particles. In turn, such an exagerated relative velocity gives too large Sherwood number and hence too high transport rate of mass between fluid and particle. Therefore, in the following, we use a constant value of the Sherwood number when calculating *C* from Eq. (5), and include the effect of turbulence by applying a correction factor  $\tilde{\alpha}$ , as will be explained below.

#### 2.3. The effect of turbulence and particle clustering

In practical systems the burning particle is exposed to rapid gas velocity fluctuations occurring due to turbulence. The turbulent motion can be responsible for considerable increase of oxidizer transport to the particle surface due to the induced velocity difference between the particle and the surrounding fluid, as discussed in the former section. However, the particles can also form clusters due to turbulence, which can lead to local oxidizer depletion and reduction of the reaction rate. These effects were studied by Direct Numerical Simulation in [16–19] and the following model was formulated for the turbulence correction factor

$$\tilde{\alpha} = \frac{\mathrm{Sh}_{mod}}{2} = \frac{\mathrm{Sh}}{2} \underbrace{\frac{B}{B + \mathrm{DaSt}/2}}_{=\alpha_{\mathrm{cluster}}}$$
(9)

where  $\frac{1}{2}Sh$  is the part corresponding to the effect of the relative velocity between the particles and the fluid, while  $\alpha_{\text{cluster}}$  is the part that corresponds to clustering. The model parameter *B* was shown by Haugen et al. [17] to vary with Stokes number as

B = 0.08 + St/3.(10)

Apart from the average Sherwood number,  $\overline{Sh}$ , two dimensionless numbers enter Eq. (9), namely the Stokes number (St) and the

Damköhler number (Da). They are defined as

$$St = \tau_p / \tau_L, \tag{11}$$

$$Da = \tau_L / \tau_c, \tag{12}$$

where  $\tau_p$  is the particle response time,  $\tau_L$  is the integral time scale of turbulence and  $\tau_c$  is the chemical time scale, related to the combustion time. The particle response time is defined by the Stokes time

$$\tau_p = \frac{\rho_p d_p^2}{18\rho\nu},\tag{13}$$

where  $\rho_p$  is the particle (material) density and  $\rho$  is the gas density. The integral time scale can be written as

$$\tau_L = \frac{2}{3} \frac{k}{\varepsilon} \tag{14}$$

and the chemical time scale is defined as

$$1/\tau_c = n_p A_p \frac{\mathrm{Sh}}{D} d_p, \tag{15}$$

where  $A_p = \pi d_p^2$  is the particle external surface area and

$$n_p = \frac{6\rho_s}{\rho_p \pi d_p^3} \tag{16}$$

is the particle number density with  $\rho_s$  being the solids density in the mixture. Please note that  $\rho_p$  is the material (or apparent) density of the particle, which is very different from the solid density in the mixture,  $\rho_s$ . For example, the solid density of char in air at 1000 K and stoichiometric conditions is around 0.03 kg/m<sup>3</sup>. This corresponds to nearly one hundred 100 µm-sized char particles per cubic centimeter for char particles with an apparent density of 600 kg/m<sup>3</sup>.

In the following, the physical reasoning on which Eq. (9) was derived will be described. If the lifetime of a particle cluster ( $\tau_{cluster}$ ) is short relative to the chemical time scale ( $\tau_c$ ), the reactant concentration can be assumed to be uniform across the cluster and equal to the concentration outside the cluster. In this case, the relevant reactant consumption rate is given by Eq. (15), which is valid for homogeneous distributions of particles and reactant. For clusters with long lifetimes compared to the chemical time scale, the reactant concentration inside the cluster is reduced. This means that the overall consumption rate becomes dependent on cluster characteristics, such as cluster dimension and particle number density. The resulting reactant consumption rate (r) is therefore limited both by the rate due to Eq. (15) ( $r_{uniform} = 1/\tau_c$ ) and the cluster-characteristic rate ( $r_{cluster} = 1/\tau_{cluster}$ ). This means that the reactant consumption rate, which equals the mass transfer rate, can be written as:

$$r = \frac{r_{uniform}r_{cluster}}{r_{uniform} + r_{cluster}}.$$
(17)

Therefore, when the above formulation is normalized using the reactant consumption rate from Eq. (15) with  $\overline{Sh} = 2$ , denoted as  $r_{uniform,\overline{Sh}=2}$ , one obtains a factor by which the mass transfer rate is altered relative to the rate typically used in RANS simulations:

$$\tilde{\alpha} = \left(\frac{r_{uniform}r_{cluster}}{r_{uniform} + r_{cluster}}\right) / r_{uniform,\overline{Sh}=2}.$$
(18)

Using Eqs. (12) and (15), and after some rearranging, Eq. (9) can be recovered with  $B = r_{cluster}\tau_L St/2 = r_{cluster}\tau_p/2$ . Since  $r_{cluster}$  is unknown, an approximate expression for the parameter B was found using DNS (see Eq. (10)). The details on the fitting procedure are given in [17].

Previous studies [16,17] showed that the intensified transport of oxidizer towards the particle surface is the dominating effect of turbulence at relatively low Da. However, as the Damköhler number gets larger, the impeded reactant transport associated with the particle clustering becomes the major phenomenon controlling the overall surface reaction rate. It was also found that the effect of clustering is strongest when the Stokes number is of the order of unity. The reason for that is that such conditions (i.e. similar magnitudes of particle and flow time scales) are the most conducive to the formation of relatively long-lived clusters. (It is well known that particle clusters at the Kolmogorov scale, which are due to particles with Kolmogorov based Stokes numbers around unity, are the strongest and sharpest, but these clusters typically have too short lifetimes to have any relevance for the reactant transport.)

The Sherwood number  $\overline{Sh}$  entering Eq. (9) can still be determined from Eq. (6), however, the particle Reynolds number should now be calculated as

$$\operatorname{Re}_{p} = \frac{u_{rel}d_{p}}{\nu} \tag{19}$$

such that the effect of turbulent velocity fluctuations is taken into account through the relative velocity,  $u_{rel}$ . Based on physical arguments, Haugen et al. [17] proposed the following expression for the average relative velocity difference caused by the turbulence:

$$u_{rel} = \beta u_{rms} \sqrt{\frac{\mathrm{St}k_L^{-2/3} - k_\eta^{-2/3}}{k_L^{-2/3} - k_\eta^{-2/3}}},$$
(20)

where  $\beta = 0.41$  is a model constant,  $k_L$  and  $k_\eta$  are the integral and Kolmogorov scale wavenumbers, respectively. The wave numbers can be linked to the turbulent kinetic energy k, its dissipation rate  $\varepsilon$ , and kinematic viscosity  $\nu$  as

$$k_L = 2\pi \varepsilon \left(\frac{3}{2k}\right)^{3/2} \tag{21}$$

$$k_{\eta} = 2\pi \left(\frac{\varepsilon}{\nu^3}\right)^{1/4}.$$
(22)

The main assumption behind Eq. (20) is that the relative velocity is induced only by those turbulent eddies that have turnover times,  $\tau_{eddy}$ , that are shorter than the particle response time,  $\tau_p$ . In this way, the relative velocity is proportional to the square root of the kinetic energy ( $E(\kappa)$ ) of the corresponding eddies, such that:

$$u_{rel} \sim \left(\int_{k_{\eta}}^{k_{eddy}} E(\kappa) dk\right)^{1/2} \sim \left(\int_{k_{\eta}}^{k_{eddy}} \varepsilon^{2/3} \kappa^{-5/3} dk\right)^{1/2}$$
(23)

where  $k_{eddy} = 2\pi/\tau_{eddy}u_{eddy}$ . Furthermore, Kolmogorov scaling for the inertial sub-range was assumed in order to relate  $k_{eddy}$  with  $k_L$ , while the model constant,  $\beta$ , was obtained by fitting the model with a large variation of highly accurate direct numerical simulations. It should be mentioned that for very small Stokes numbers the numerator of Eq. (20) might become negative. However, at these conditions no significant relative velocity between particles and fluid can exist. Therefore, if this is the case, we assume that  $u_{rel} = 0$ . This will result in a tiny discontinuities in the model prediction that will be visible in figures presented in Section 3.2.

By calculating the particle Reynolds number based on the relative velocity obtained from Eq. (20), the Ranz-Marshall model (see Eq. (6)) can now be used to find the *average* Sherwood number,  $\overline{Sh}$ . As can be seen from Eqs. (19) and (20), the Sherwood number  $\overline{Sh}$ is affected by the turbulence only. The reaction rate due to diffusion given by Eq. (3) can now be modified to take into account the effect of turbulence and particle clustering as

$$R_{dif} = \tilde{\alpha} \frac{C}{d_p} \left(\frac{T+T_p}{2}\right)^{3/4}.$$
(24)

The model can therefore incorporate the effect of mean gasparticle velocity through Eqs. (5)-(7), as well as the effect of turbulence and particle clustering through Eqs. (9)-(15). As mentioned

**Table 1** The value of  $\gamma_{st}$  for some mixtures.

Mixture	Reaction	γst
Char particles in air	$C + O_2 \rightarrow CO_2$	11.4
Char particles in 100% CO <sub>2</sub>	$C + CO_2 \rightarrow 2CO$	3.7
Char particles in 100% O <sub>2</sub>	$C + O_2 \rightarrow CO_2$	2.7
Char particles in steam	$C+H_2O \rightarrow CO+H_2$	1.5
Ilmenite particles in air	$4FeTiO_3+O_2\rightarrow 4TiO_2+2Fe_2O_3$	0.225

above, care should be taken when applying Eqs. (5)–(7) with the stochastic tracking method. It should also be stressed that Eqs. (9)–(15) are suitable to be applied in RANS models, and their form allows to determine all the required variables during the simulation. In this study, the model was implemented into ANSYS Fluent by means of a User Defined Function (UDF) mechanism. The UDF is provided as a supplementary file to this paper.

#### 3. Model sensitivity

In this section, numerical examples are presented in which the model applicability and the influence of the main model parameters is presented. The first two examples are just general calculations, while the last one is a simplified CFD simulation. This enables us to examine the potential conditions in which the effect of turbulence can be significant in practical systems.

#### 3.1. Numerical example 1

Eq. (11) can be re-organized to yield the following expression for the integral time scale:

$$\tau_L = \frac{\rho_p d_p^2}{18\rho \nu \text{St}}.$$
(25)

The Damköhler number is then given as

$$Da = \frac{\tau_L}{\tau_c} = \frac{\tau_L 2Dn_p A_p}{d_p} = \frac{\rho_p d_p^2 2Dn_p A_p}{18\rho \nu St d_p},$$
(26)

where, for the considerations in this section, it has been assumed that  $\overline{Sh} = 2$ . Furthermore, the solids density in the domain can be expressed as

$$\rho_{\rm s} = \rho_g / \gamma_{\rm st},\tag{27}$$

where  $\rho_g$  is the gas density in the gas-solid mixture and  $\gamma_{st}$  is the stoichiometric air-fuel ratio. The value of  $\gamma_{st}$  for some mixtures is given in Table 1. Apart from char-based mixtures, ilmenite was also included due to its possible application since the ilmenite particles can serve as oxygen carriers in Chemical Looping Combustion. The particle number density can now be expressed as

$$n_p = \frac{6\rho_g}{\pi d_p^3 \rho_p \gamma_{st}}.$$
(28)

The intrinsic density of the gas,  $\rho$ , is, however, almost the same as the gaseous density of the mixture,  $\rho_g$ , as long as the solid volume fraction is low. From the above, and by using that  $A_p = \pi d_p^2$ , it can be shown that

$$\mathsf{Da} = \frac{\rho_p d_p^2 12 D \rho_g \pi d_p^2}{18 \rho_v \mathsf{St} \pi d_p^3 \rho_p \gamma_{\mathsf{st}} d_p} = \frac{2 \rho_g}{3\mathsf{ScSt} \gamma_{\mathsf{st}} \rho} \approx \frac{2}{3\mathsf{ScSt} \gamma_{\mathsf{st}}}.$$
 (29)

In Fig. 2, the Damköhler number, as calculated from Eq. (29), is shown as a function of Stokes number for the same cases as listed in Table 1. Clustering is expected to slow down the reactions for Damköhler numbers around or greater than unity [17]. From Fig. 2, it can be seen that for carbon oxidation in air the Damköhler number is larger than unity only for Stokes numbers smaller than 0.1.



**Fig. 2.** Damköhler number at stoichiometric conditions as a function of Stokes number for the cases listed in Table 1. Here, the Schmidt number is set to Sc = 0.7.



Fig. 3. Effect of clustering ( $\alpha_{cluster}$ ) as a function of Stokes number for the cases listed in Table 1.

For oxidation of ilmenite in air, however, the Damköhler number is above 4 even for Stokes number as large as one. Using Eqs. (10) and (29) the part due to clustering can be expressed as

$$\alpha_{\text{cluster}} = \frac{B}{B + \text{DaSt}/2} = \frac{0.08 + \text{St}/3}{0.08 + \text{St}/3 + 1/(3\text{Sc}\gamma_{\text{st}})}.$$
 (30)

The value of  $\alpha_{cluster}$  as a function of Stokes number is shown in Fig. 3, from which it is clear that the potential to reduce the reaction rate highly depends on the composition of the mixture. At stoichiometric conditions the reaction rate due to clustering can be reduced up to 35% in the case of char combustion in air, while for char combustion in pure O<sub>2</sub> or H<sub>2</sub>O the effect of clustering can be twice as large. Finally, for oxidation of ilmenite in air, the reduction due to clustering is dramatic.

#### 3.2. Numerical example 2

In this example we discuss the influence of selected model parameters on  $\tilde{\alpha}$ . The magnitudes of the studied parameters and other essential model parameters are presented in Table 2. They were selected such that they reflect, to some extent, conditions typically found in industrial scale facilities (reactors and combustion chambers). The required turbulence parameters, as would be known in a RANS simulation, were estimated.



**Fig. 4.** The influence of parameters from Table 2 on  $\tilde{\alpha}$  for char particles in air ( $\rho_p = 800 \text{ kg/m}^3$ ,  $\gamma_{st} = 11.4$ ). The legend included in the bottom panels apply to the entire figure.

**Table 2**Studied model input parameters.

Name	Symbol	Unit	Value
Mean gas velocity	и	m/s	10
Turbulence intensity	Ι	-	10 <sup>-2</sup> ; 10 <sup>-1</sup>
Domain length scale	L	m	1; 10
Particle number density	$n_p$	m <sup>-3</sup>	$10^4 - 10^7$
Gas density	ρ	kg/m <sup>3</sup>	0.35
Gas kinematic viscosity	ν	m <sup>2</sup> /s	$10^{-4}$
Diffusion coefficient	D	m <sup>2</sup> /s	10-4
Particle (material) density	$ ho_p$	kg/m <sup>3</sup>	800

In order to calculate the turbulence kinetic energy k and its dissipation  $\varepsilon$  the following expressions were used

$$u_{rms} = uI, \tag{31}$$

$$k = \frac{3}{2}u_{rms}^2,\tag{32}$$

$$\varepsilon = C_{\mu}^{3/4} \frac{k^{3/2}}{l},\tag{33}$$

where *l* is the integral length scale, approximated as l = 0.07L [26], and  $C_{\mu} = 0.09$  [27]. It should be noted that by using such a definition of *l* for large systems, the integral length scale is likely to be overestimated, which in turn leads to unrealistically high turbulent viscosity since

$$\mu_t = \rho C_\mu \frac{k^2}{\varepsilon} = \rho C_\mu^{1/4} k^{1/2} l.$$
(34)

Nevertheless, in the absence of problem-specific details, we stick to the above estimation.

The particle time scale  $\tau_p$ , the time scale of the integral scale eddies  $\tau_L$  and the chemical time scale  $\tau_c$  are calculated from Eqs. (13)–(15), respectively. These time scales are then used to calculate St and Da, and the mean Sherwood number Sh is calculated using Eqs. (19)–(22) together with Eq. (6). The results, in the form of  $\tilde{\alpha}(d_p)$  for selected particle number densities, are presented in Fig. 4 for the case of char particles in air. In the two upper panels, cases with low turbulence intensity (I = 1%) are presented, whereas for the lower panels I = 10%. Furthermore, the results shown in the left-hand side panels differ from those on the right side by the turbulence length scale, as stated in the title of the figure. There are four black lines in Fig. 4. The line with circle-shaped markers divides the figure into regions of rich (below the



**Fig. 5.** The influence of  $\tilde{\alpha}$  on the reactant consumption rate for  $\rho_p = 800 \text{ kg/m}^3$ ,  $d_p = 500 \text{ }\mu\text{m}$ , A = 0.002 s/m, E = 79 kJ/mol,  $C = 5 \cdot 10^{-12} \text{ sK}^{-3/4}$ .

line) and lean (above the line) conditions, while the line with xshaped markers corresponds to the packing limit of particles, i.e. the maximum volume fraction of the particles. For spherical particles, the volume fraction at the packing limit is assumed to be equal to 0.63, which is a typical limit for randomly packed, spherical particles of the same size. The remaining two lines encompass the region inside which the air-fuel ratio,  $\gamma$ , is between 0.1 and 10. It is expected that conditions in real systems correspond to the region limited by these two lines. Details regarding the derivation of the packing limit line and the stoichiometric line can be found in Appendix A.

From Fig. 4 it is clear that for the range of examined particle number densities, the turbulence do not have any effect on the mass transfer if the particles are too small. This is because particles for which  $\tau_p << \tau_\eta$  immediately follow the motion of the fluid, so it is not possible for them to form clusters or for the turbulence to enhance the mass transfer due to any relative velocity between fluid and particle. (Please note that for  $d_p$  of the order of  $10^{-5} - 10^{-4}$  Eq. (20) yields negative number inside the square root and in this region  $u_{rel} = 0$  was assumed.) For larger particles, which have longer response times, both effects of turbulence can be observed. The largest mass transfer enhancement is, as expected, observed for the high turbulence intensity cases (lower panels of Fig. 4), in which  $\tilde{\alpha}$  becomes greater than 1 if the particle number density is sufficiently low. For all cases above a certain  $n_p$ , the effect of particle clustering becomes dominant ( $\tilde{\alpha} < 1$ ). This decrease in the reactant transfer rate is particularly strong for the low turbulence intensity cases (upper panels of Fig. 4) and it is more intense in larger facilities (right panels). It is also worth noticing that both scenarios are probable around the stoichiometric conditions, i.e. we can expect both effects of turbulence to be observed in real systems.

Finally, the influence of  $\tilde{\alpha}$  on the reactant consumption rate  $\Theta$ , as given by Eq. (2) in which  $R_{\text{diff}}$  is found from Eq. (24), is presented in Fig. 5 as a function of temperature. Resorting also to the results shown in Fig. 4, a factor of 2 enhancement of reaction rate due to turbulence ( $\tilde{\alpha} > 1$ ) can be expected at favorable flow conditions and high temperatures. The reduction of the rate ( $\tilde{\alpha} < 1$ ) can potentially be much stronger. In the following, we will investigate how  $\tilde{\alpha}$  may vary in more realistic applications.

#### 3.3. Numerical example 3

In order to visualize and quantify the effect of turbulence on pulverized char conversion, a simplified CFD model was developed.

Table 3Stoichiometric coefficients for reaction(36) and volatiles composition.

$C_kH$	$_{l}O_{m}N_{n}S_{o}$	$\nu_i$	
k	1.034	02	1.258
1	2.682	CO	1.034
т	0.899	$H_2O$	1.341
п	0.0274	SO <sub>2</sub>	0.0034
0	0.0034	N <sub>2</sub>	0.0137



Fig. 6. Schematics of the geometry and boundary conditions.

The geometry of the model was selected to be a  $2m \times 2m \times 8m$  cuboid to which coal particles are introduced through a square (4cm  $\times$  4cm) inlet together with a co-flowing hot air. Inside the domain the particles form a jet and undergo devolatilization and char combustion. The main features of the numerical approach are as follows. The Navier-Stokes equations are solved in a steady-state and incompressible form, turbulence is modelled using the standard  $k - \varepsilon$  model, radiation is accounted for with the Discrete Ordinates model and the particles are tracked in a Lagrangian reference frame. For simplicity, and since the focus of the paper is on char conversion, the devolatilization rate is assumed constant (=50 1/s). A single surface reaction is considered:

$$C + O_2 \to CO_2 \tag{35}$$

where the corresponding Arrhenius parameters are A = 0.002 s/m,  $E = 7.9 \cdot 10^7 \text{ J/kmol}$  and the diffusion constant from Eq. (3) is given by  $C = 5 \cdot 10^{-12} \text{ s/K}^{-3/4}$ , while the combustion rate of volatiles is computed using the Finite-Rate/Eddy-Dissipation model, according to the reaction:

$$C_{k}H_{l}O_{m}N_{n}S_{o} + \nu_{O_{2}}O_{2} \rightarrow \nu_{CO}CO + \nu_{H_{2}O}H_{2}O + \nu_{SO_{2}}SO_{2} + \nu_{N_{2}}N_{2},$$
(36)

where the stoichiometric coefficients  $v_i$  and the composition of the fictitious volatiles species  $C_k H_l O_m N_n S_o$  are given in Table 3. A schematic representation of the geometry and boundary conditions are given in Fig. 6, coal properties are given in Table 4, and the main model parameters are presented in Table 5. The selection of this particular configuration was motivated by the fact that it reflects typical conditions for fuel supply to the combustion cham-



**Fig. 7.** Distribution of Da, St and  $\tilde{\alpha}$  inside the jet.

Table 4Coal properties.

Proximate anal	ysis	Ulti	mate analysis (daf)
Moisture	0.107	С	0.674
Volatiles	0.446	Н	0.05
Fixed carbon	0.357	0	0.267
Ash	0.09	Ν	0.007
HCV (AR)	22.5 MJ/kg	S	0.002

Table 5

CFD model input parameters.

Name	Symbol	Unit	Value
Coal mass flow rate Transport air mass flow rate Transport air temperature Coflow air mass flow rate Coflow air temperature Turbulence intensity Viscosity ratio Coal (material) density	$ \begin{array}{c} m_f \\ m_{air,1} \\ T_{air,1} \\ m_{air,2} \\ T_{air,2} \\ I \\ \mu_t/\mu \\ \rho_p \end{array} $	kg/s kg/s K kg/s K - - kg/m <sup>3</sup>	$\begin{array}{c} 1.5\cdot 10^{-2}\\ 0.0056\\ 1000\\ 7.0\\ 1000\\ 10^{-2}\\ 50\\ 1400\\ \end{array}$
Coal particle diameter	$d_p$	m	$2.5 \cdot 10^{-4}$

ber. Moreover, the input parameters are chosen such that this setup corresponds (to a certain degree) to the upper, left-hand side panel of Fig. 4, which means that the turbulence is most likely to reduce the mass transfer rate. The right panel of Fig. 7 shows the distribution of  $\tilde{\alpha}$  in a cross section inside the jet. Please note that: 1) no interpolation (no smoothing between cell values) is used to produce contours of  $\tilde{\alpha}$  in order to avoid a false impression of low  $\tilde{\alpha}$  at the edges of the jet; 2) only regions with burning particles are displayed. From the figure it can be seen that, for the configuration considered, the effect of clustering is significant. In fact,  $\tilde{\alpha}$  is of the order of  $10^{-1}$  for the most part of the jet. An intensification in the mass transfer is predicted only at the edges of the jet, where the particle number density is lower and the turbulence intensity is highest. The reason the effect of turbulence is so strong can be understood by inspecting the Damköhler and Stokes numbers inside the jet. These two dimensionless numbers are shown in the left and middle panels of Fig. 7. Even though St decreases by 2-3



**Fig. 8.** Char conversion as a function of distance from the inlet - effect of fuel mass flow rate (in all cases  $d_p = 2.5 \cdot 10^{-4}$  m).

orders of magnitude along the particle jet, Da remains sufficiently high (of the order of 1) in the entire volume of the jet to yield  $\tilde{\alpha} < 1$ . It should also be noted that, based on Fig. 4, for  $\tilde{\alpha}$  to decrease below 0.5 the local conditions must correspond to very rich mixture. For the case we study here, a relatively high fuel mass flow rate ( $m_f = 1.5 \cdot 10^{-2} \text{ kg/s}$ ) was chosen to obtain such conditions but in reality the existence of large volumes with rich mixture is rather unlikely and mostly restricted to regions next to the fuel supply. Therefore, in the following we attempt to verify if the effect of turbulence still remains significant for lower fuel mass flow rates.

In Fig. 8 char conversion along the jet for three different fuel mass flow rates is presented. For each mass flow rate, two cases are shown. In the first, the baseline case, the effect of turbulence was not accounted for in the numerical model. In the second case, the effect of turbulence was introduced through the User Defined Function (UDF). This was done by modifying the reaction rate due to diffusion according to Eqs. (9), (10) and (24). In order to produce



Fig. 9. Contours of temperature (in K) inside the particle jet, from left to right:  $m_f = 1.5 \cdot 10^{-2}$  kg/s,  $m_f = 1.5 \cdot 10^{-3}$  kg/s and  $m_f = 1.5 \cdot 10^{-4}$  kg/s.

Fig. 8 the domain was divided into *N* segments along its height. For each such segment an average carbon conversion  $(\overline{X})$  was computed for particles within the given section as

$$\overline{X} = \frac{1}{n_{part}} \sum_{i=1}^{n_{part}} X_i = \frac{1}{n_{part}} \sum_{i=1}^{n_{part}} \left( 1 - \frac{m_c}{m_{c,0}} \right).$$
(37)

In the above,  $n_{part}$  is the number of particles passing through the given segment,  $m_c$  and  $m_{c,0}$  are the current and initial particle char masses, respectively. The selected fuel mass flow rates can be thought of as rich ( $m_f = 1.5 \cdot 10^{-2} \text{ kg/s}$ ), around-stoichiometric  $(m_f = 1.5 \cdot 10^{-3} \text{ kg/s})$  and lean  $(m_f = 1.5 \cdot 10^{-4} \text{ kg/s})$  mixtures, although we deliberately do not provide the exact magnitudes of air-fuel ratio  $(\gamma)$  as it varies significantly from cell to cell. It can be seen that turbulence has only a very weak positive effect on the conversion rate if the mass flow rate is very low or, in other words, if  $\gamma >> \gamma_{st}$ . The reason for that is a very low particle number density, and hence low Damköhler number. In regions with low Da, no dense clusters can be formed, so there is no reduction of the reaction rate due to clustering, but a weak increase due to turbulence ( $\tilde{\alpha} > 1$ ). This behavior is also in agreement with the results presented in Fig. 4. In the cases with higher fuel mass flow rates in Fig. 8 (red and green lines), the particle number densities in the core of the jet are much higher, and a strong effect due to particle clustering can be observed as the conversion is much slower in the cases where the reaction rate is modified by the UDF. The conversion profiles are similar in both cases, but the conversion begins further downstream for the case with the highest mass flow rate.

It should be stressed that the results presented in Fig. 8 are strongly affected by the temperature. Even though the same boundary conditions were used, the cases with lower fuel mass flow rates are characterized by lower temperatures in the system due to the smaller amounts of released and burned volatiles. This is confirmed in Fig. 9, where the contours of temperature are presented. The consequence of higher temperature is higher reaction rate. This can be observed by comparing the slopes of the conversion profiles in Fig. 8, i.e. the higher the mass flow rate, the

steeper the slope. At the same time, as the temperature increases, the diffusion rate becomes more important in the overall reaction rate, and thus the observed effect of turbulence is stronger. The difference in the reaction rates is more clearly visible in Fig. 10, which shows contours of the relative rate difference, defined as  $(\Theta-\Theta_0)/\Theta_0,$  where  $\Theta$  is the modified rate including the effect of turbulence, and  $\Theta_0$  is the unmodified rate. The highest relative rate difference is observed for the highest mass flow rate, and it is smaller for the lower flow rate. It can be seen that the differences occur mostly in the core of the jet, where the particle number density, and hence the Damköhler number, are the highest, and thus the rate is considerably reduced. However, also regions of increased reaction rate are observed further away from the jet core. For the smallest mass flow rate the relative rate difference is not reduced in the center of the jet. Instead a slightly increased reaction rate can be observed at the jet outskirts, where the turbulence is strongest and the particle number density is quite low. Based on the results discussed above, we can conclude that the effect of particle clustering can be significant for a quite wide range of fuel mass flow rates or, in other words, for a wide range of stoichiometric conditions.

Another important parameter that influences how strong the effect of turbulence is, is the particle size. We examine this parameter by changing the particle diameter, but keeping the mass flow rate constant and equal to  $1.5 \cdot 10^{-3}$  kg/s, corresponding to roughly stoichiometric conditions, for all cases. The particle sizes were chosen such that the particle number density  $n_p$  is decreasing by a factor of 10 as the particle diameter increases  $(n_p \sim d_p^{-3})$ . As can be seen in Fig. 11, for the smallest particles (red lines) the effect of turbulence amounts to essentially no difference when the total conversion is considered (i.e. the distance from the inlet to the point at which full conversion rate is actually of the same magnitude for all particle sizes. The reason the decreased reaction rate does not affect the total conversion time for the smallest particles is depletion of the available oxygen, seen as a flattening of the



**Fig. 10.** Contours of relative rate differences  $(\Theta - \Theta_0)/\Theta_0$  inside the particle jet, from left to right:  $m_f = 1.5 \cdot 10^{-2}$  kg/s,  $m_f = 1.5 \cdot 10^{-3}$  kg/s and  $m_f = 1.5 \cdot 10^{-4}$  kg/s.



**Fig. 11.** Char conversion as a function of distance from the inlet – effect of particle diameter (in all cases  $m_f = 1.5 \cdot 10^{-3} \text{ kg/s}$ ).

'without UDF' profile at the final stage of conversion. As the particle size becomes larger, particles travel further downstream before they reach a complete burnout. This is because these larger particles are less affected by fluid motions. Also, on average, they burn in lower temperatures as they still undergo conversion long after they have passed the regions of highest temperature, i.e. regions of volatile burning. For these larger particles, the effect of turbulence is more pronounced, e.g. particles with  $d_p = 2.5 \cdot 10^{-4}$  m (dark blue lines) need to travel around 50% longer to reach complete burnout when the effect of turbulence is accounted for. This is opposite to what can be expected based on Fig. 4, since for a given stoichiometric condition  $\tilde{\alpha}$  increases for larger particle sizes. Nevertheless, the degree to which the conversion rate is reduced depends not only on  $\tilde{\alpha}$  but also on the relative magnitudes of  $R_{kin}$  and  $R_{dif}$ . As the particle diameter increases the conversion rate be

comes more diffusion-controlled since  $R_{dif} \sim 1/d_p$  (see Eq. (3)). At the same time, the rate due to kinetics varies only slightly. The resulting shift towards diffusion-controlled regime outweighs the effect of higher  $\tilde{\alpha}$  and leads to the conversion rate being reduced by the same amount, irrespective of the particle size. Finally, it should be noted that for even larger particles, at some point  $\tilde{\alpha} \ge 1$  (see Fig. 4), such that no reduction in the conversion rate due to clustering will be possible, even for a fully diffusion-controlled reaction. This was observed for particles with  $d_p \sim 1 \cdot 10^{-3}$  m but was not shown in Fig. 11 due to much longer time scale required to reach even a fractional burnout.

The degree to which the turbulence influences the surface reaction rate might also depend on the characteristics of the turbulence itself, such as turbulence intensity or the viscosity ratio,  $\mu_t/\mu$ , as they are linked to turbulence kinetic energy and its dissipation. These two parameters can affect the integral time scale, and thus, the Damköhler and Stokes numbers. Their influence is shown in Fig. 12 from which it can be seen that the conversion rate is affected in almost exactly the same way for all parameter combinations that we study. The only difference is that a sufficiently strong turbulence causes the particles to be converted slightly faster as a result of enhanced mixing.

Finally, we observed that the effect of clustering weakens if the jet velocity (velocity at which the transport air and particles are introduced) is increased, as shown in Fig. 13. This is due to the Damköhler number being reduced as the jet velocity increases. At even higher jet velocity, the only effect of turbulence would be to increase the conversion rate as a result of enhanced mass transfer to the particle surface.

#### 4. Application to an industrial scale boiler

In the previous section we explored potential conditions in which turbulence can enhance or decrease the surface reactions through the mass transfer rate. As shown by Haugen et al. [17] these conditions can be reduced to only two dimension-



**Fig. 12.** Char conversion as a function of distance from the inlet – effect of inlet turbulence  $(d_p = 2.5 \cdot 10^{-4} \text{ m}, m_f = 1.5 \cdot 10^{-2} \text{ kg/s}, T_{air} = 600 \text{ K}).$ 



**Fig. 13.** Char conversion as a function of distance from the inlet – effect of jet inlet velocity  $(d_p = 1.2 \cdot 10^{-4} \text{ m}, m_f = 1.5 \cdot 10^{-3} \text{ kg/s})$ 

less numbers, the Stokes number and the Damköhler number. This implies that, in theory, one should be able to predict the effect of turbulence on the mass transfer rate in practical systems, such as large scale boilers, by a simple estimation of Da and St characterizing the given system. This is however not so straight forward since one has to deal with a certain range of these two parameters, often varying by several orders of magnitude. Thus, in order to verify how our theoretical considerations translate into reality, we examine a real-scale industrial boiler OP-430. This is a middle size boiler fired with a pulverized coal and producing 430 tones of steam per hour (at 532 °C, 12.7 MPa). Tangential firing is applied in the boiler, i.e. the burners are located in each of four corners of the furnace. A detailed description of the boiler geometry and operating conditions can be found in Adamczyk et al. [28]. A similar numerical approach to that described in Section 3.3 is utilized here, the main differences being: 1) lower devolatilization rate (=13 1/s), 2) slightly more accurate chemistry and 3) a different coal type. The considered reactions are:

$$C + \frac{1}{2}O_2 \to CO \tag{38}$$

$$CO + \frac{1}{2}O_2 + H_2O \to CO_2 + H_2O$$
(39)

Table 6

Stoichiometric coefficients for reaction (36) and volatiles composition.

C <sub>k</sub> H	$_{l}O_{m}N_{n}S_{o}$	$\nu_i$	
k	1.19	02	1.54
1	4.41	CO	1.35
т	0.58	$H_2O$	2.17
п	0.068	SO <sub>2</sub>	0.018
0	0.0027	N <sub>2</sub>	0.040

Table 7	
Coal prop	oerties.

Proximate analysis		Ultimate analysis (daf)	
Moisture	0.022	С	0.803
Volatiles	0.290	Н	0.056
Fixed carbon	0.48	0	0.118
Ash	0.208	Ν	0.012
HCV (AR)	24.7 MJ/kg	S	0.011

Table 8	5					
Kinetic	parameters	for	reactions	(38)	and	(39)

Reaction	А	E [J/kmol]	$C [s/K^{-3/4}]$
(38)	0.001	$7.9\cdot 10^7$	$5\cdot 10^{-12}$
(39)	$2.239 \cdot 10^{12}$	$1.7\cdot 10^8$	-



Fig. 14. Contours of temperature in the boiler central cross section. Arrows indicate elevations of fuel injection ports.

and the combustion of volatiles follow reaction (36) with the coefficients given in Table 6. The coal properties are listed in Table 7 and kinetic parameters given in Table 8.

In order to observe any effect of turbulence on the overall reaction rate it is required that the conditions inside the boiler correspond to zones II or III conversion. Otherwise, the conversion rate is fully limited by the reaction kinetics and the turbulence-affected mass transfer rate will have no influence on the process. Conditions in zones II and III are characterized by relatively high temperatures. Figure 14 shows the temperature distribution in the boiler central cross section. Four elevations at which coal is injected are also shown and marked with arrows. The pockets of low temperature located symmetrically close to the walls coincide with coal and air injections (pockets in the lower part) and overfire air ports (pockets in the upper part). The highest temperature can be observed around the particle injections and in the central part of the



Fig. 15. Contours of the Stokes number. Arrows indicate elevations of fuel injection ports.



Fig. 16. Contours of the Damköhler number. Arrows indicate elevations of fuel injection ports.

boiler. These are the regions in which we can expect the conversion rate to be influenced by the turbulence.

The distribution of the Stokes and Damköhler numbers in the boiler cross section is shown in Figs. 15 and 16, respectively. In both figures, white zones in the central part correspond to regions in which there are no particles undergoing char combustion. The much higher density of particles in the vicinity of the boiler walls is caused by the specific design of injections, i.e. the particles are injected from the corners in a way that induces a spiraling motion (see Fig. 17, which shows pathlines in the injection area and locations at which the coal is injected). It can be seen that close to the walls in the lower part of the boiler both Da and St are relatively high. These conditions are favorable to particle clustering, thus, it is expected that the conversion process will slow down in these regions. This is in agreement with Fig. 18 which shows that  $\tilde{\alpha}$  for these areas can be significantly less than one. On the other hand, in the upper part of the boiler, the Damköhler number is much lower. This is because of the particle number density, which is lower by around 2-3 orders of magnitude. In such regions the only effect turbulence can have is to intensify the reactant transport towards the particle surface, which is equivalent to saying that  $\tilde{\alpha} > 1$ , as can be seen in Fig. 18.



**Fig. 17.** Pathlines in the plane of injection 3 coloured by temperature [K]. Black arrows indicate locations and directions at which particles are introduced.



**Fig. 18.** Distribution of  $\tilde{\alpha}$  in the boiler central cross section. Arrows indicate elevations of fuel injection ports.

To investigate the effect of turbulence in this particular boiler, we compared the degree of carbon conversion along the boiler height in Fig. 19. These results were obtained in an equivalent way to Fig. 8. The four panels in the figure correspond to the four levels of particle injections as they are located at different heights in the boiler, as marked in Fig. 18. The points at which carbon conversion is lowest reveals where the particles are injected. Please note that the coal is introduced through all four injections simultaneously so the particles from different injections influence each other; it is only for clarity that we follow particles introduced through each injection separately and divide the results into four panels. It can be seen that for particles spiraling up the boiler the effect of turbulence on the conversion rate is rather insignificant, there is only a slight increase in the conversion rate for most injections, except for the injection 4 which is located the highest in the boiler. The situation changes for particles that travel down the boiler, i.e. the particles that are introduced mostly by injections 1 and 2. There, a clear reduction in the conversion rate can be observed which means that in these regions the conditions are just right for turbu-



Fig. 19. Char conversion as a function of boiler height as predicted for the baseline case and the case with the UDF.



**Fig. 20.** Probability distribution of  $\tilde{\alpha}$  inside the boiler.

lence to cause particle clustering. This is consistent with Fig. 18 in which  $\tilde{\alpha}$  is smallest in the lower part of the boiler.

It should be noted that from Fig. 19 it is still not possible to deduce to what extent the overall conversion rate is affected and what fraction of particles has their conversion rate affected by clustering. This important information can be conveyed through Fig. 20, which presents probability distribution of  $\tilde{\alpha}$  inside the boiler. From the figure, it can be seen that for majority (79.2%) of reacting particles  $\tilde{\alpha} < 1$  and that on average  $\tilde{\alpha} = 0.825$ . Taking into account results in Fig. 18, it can be concluded that the particle concentration is much higher in the lower part of the boiler

where  $\tilde{\alpha} < 1$ . However, despite the fact that such a large fraction of particles is affected by the effect of clustering, the global rate reduction given by

Rate reduction = 
$$1 - \left(\sum_{i=1}^{n_{part}} \frac{m_{c,0,i}}{t_{c,i}}\right)_{withUDF} / \left(\sum_{i=1}^{n_{part}} \frac{m_{c,0,i}}{t_{c,i}}\right)_{w/oUDF}$$
(40)

is equal to 2.02% (in the above,  $t_c$  is a total combustion time). The reason that the global rate reduction is so low for this particular boiler, is that it is relatively cold in the volumes where  $\tilde{\alpha}$  is small, which is typically in the bottom part of the boiler. This means that the conversion rate is largely controlled by kinetics in the same areas where the clustering happens to be slowing down the mass transfer. Hence, the effect of the slow mass transfer is diminished.

Overall, for this boiler, the influence of turbulence on the conversion rate is weaker than what could be anticipated based on our theoretical predictions. This highlights that many variables and the interplay between them are relevant when predicting the effect of turbulence on the char conversion rate. It also shows that it is difficult to determine a priori if this effect needs to be accounted for. Based on what we have learned from this study, we do believe that the effect of char clustering may have significantly more effect on other applications or boiler geometries.

#### 5. Conclusions

It has recently been shown that turbulence may both increase and decrease the mass transfer rate to reacting pulverized particles. More specifically, turbulence may *decrease* the fluid-particle mass transfer rate when the life time of turbulence induced particle clusters is comparable to the consumption rate of any gaseous reactant. If particle clustering is not important, the mass transfer rate to the particles may be *increased* due to turbulence induced relative velocity between particle and fluid. Both of these effects are accounted for in a natural manner if all relevant turbulent scales are resolved on the numerical mesh. This is the case for DNS and potentially also for well resolved large eddy simulations (LES), but it is *not* the case for RANS simulations. Naively, one may think that the classical turbulence particle dissipation model that is commonly used in many RANS simulations may accurately account for the relative velocity between particle and fluid. This is, however, not the case. Instead they are grossly overpredicting the relative velocity between particles and fluid and, hence, the mass transfer rate. This is particularly the case for smaller particles.

In the present work, we use the numerical model that was developed by Haugen et al. [17] to assess the effect of turbulence on the char conversion rate for two realistic cases. The first case is a simplified jet burner while the other is an industrial scale boiler. In addition, several theoretical examples are given to show the influence of the selected parameters. The most promising conditions to observe the effect of turbulence on the conversion rate were found to include relatively large particles, large-scale facilities, fuel-rich conditions, moderate turbulence intensity and a low stoichiometric air-fuel ratio.

From the simplified jet burner, we show that the effect of turbulence can be significant for a quite wide range of parameters, such as fuel mass flow rates, particle sizes and jet velocities. It is, however, crucial to consider how the selected parameters influence not only the mass transfer rate ( $\tilde{\alpha}$ ), but also the ratio of the diffusion and kinetic rates. The reason for this is that for low temperatures, where the reactions are kinetically dominated, a reduction in the mass transfer rate will not have any effect on the conversion rate of char. Nevertheless, for some of the cases studied, the distance where full conversion of char was achieved was increased by 50% when proper account was made for the effect of turbulence.

The industrial scale boiler was studied as an example of a real practical system in which the turbulence can play a role. Inside the boiler, we did observe regions where the char conversion rate was both increased and decreased due to the turbulence. However, the density of particles in this kind of boiler is typically too low to observe a strong decrease in the global conversion rate of char. Similarly, the effect associated with relative velocity differences is rather minor. We expect this effect to show a greater importance in systems characterized by larger particles (higher Stokes numbers) since small particles quickly adjust to fluid motions without any significant relative velocity between them and the fluid.

Even though the effect of turbulence is not very dramatic in the industrial boiler studied here, we know from the example with the simplified burner that for certain conditions it will indeed have a strong effect. One should therefore always include the effect of turbulence in RANS simulations used for accurate predictions of char burnout.

In the future one should also study how turbulence affect the reaction rates of solid particles in other industrial facilities, such as char conversion in e.g. gasifiers or MILD combustors. Another interesting application would be oxidation of ilmenite in the air reactor of a Chemical Looping Combustion (CLC) system.

#### **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.

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# Appendix A. Derivation of the stoichiometric number density $n_{p,st}$ and packing limit

The gas and solids volume fractions sum up to unity

$$\epsilon_s + \epsilon_g = \frac{V_s}{V} + \frac{V_g}{V} = 1 \tag{A.1}$$

$$\rho_s = \frac{m_s}{V} = n_p m_p = n_p \rho_p \frac{\pi d_p^3}{6} = \epsilon_s \rho_p \tag{A.2}$$

$$\rho_g = \frac{m_g}{V} = \rho \epsilon_g \tag{A.3}$$

$$\epsilon_s + \epsilon_g = \frac{\rho_s}{\rho_p} + \frac{\rho_g}{\rho} = 1 \tag{A.4}$$

$$\frac{1}{\rho_p} + \frac{\rho_g}{\rho_s \rho} = \frac{1}{\rho_s} \tag{A.5}$$

Taking the ratio of gas to solids such that it is stoichiometric

$$\gamma_{st} = \frac{\rho_g}{\rho_s} \tag{A.6}$$

and using Eqs. (A.2) and (A.5) becomes

$$\frac{1}{\rho_p} + \frac{\gamma_{st}}{\rho} = \frac{6}{n_{p,st}\rho_p \pi d_p^3} \tag{A.7}$$

$$n_{p,st} = \frac{6}{\rho_p \pi d_p^3} \frac{\rho \rho_p}{\gamma_{st} \rho_p + \rho} = \frac{6}{\pi d_p^3} \frac{1}{\gamma_{st} \frac{\rho_p}{\rho} + 1}$$
(A.8)

which for  $\frac{\rho_p}{\rho} \gg 1$  becomes

$$n_{p,st} \approx \frac{6}{\pi \, d_p^3} \frac{\rho}{\gamma_{st} \, \rho_p} \tag{A.9}$$

For a given  $\gamma_{st}$ ,  $n_{p,st}$  is the stoichiometric particle number density, for which  $\tilde{\alpha}$  can be determined. The relation between the particle number density  $n_p$  and solids volume fraction  $\epsilon_s$  is

$$n_p = \frac{6}{\pi d_p^3} \epsilon_s. \tag{A.10}$$

Thus, for a given particle number density, the maximum diameter the particle can have without exceeding the packing limit can be computed from

$$d_{p,max} = \left(\frac{6\epsilon_{s,max}}{\pi n_p}\right)^{1/3}.$$
(A.11)

The relation between the density ratio  $\gamma_{st}$  and solids volume fraction  $\epsilon_s$  is

$$\epsilon_s = \frac{1}{\gamma_{st}\frac{\rho_p}{\rho} + 1} \tag{A.12}$$

From the above the solids volume fraction at stoichiometric conditions can be determined, i.e. for  $\gamma_{st}$  from Table 1.

#### Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2020.12. 040.

#### References

- H. Thunman, K. Davidsson, B. Leckner, Separation of drying and devolatilization during conversion of solid fuels, Combust. Flame 137 (1) (2004) 242–250, doi:10.1016/j.combustflame.2004.02.008.
- S. Saxena, Devolatilization and combustion characteristics of coal particles, Prog. Energy Combust. Sci. 16 (1) (1990) 55–94, doi:10.1016/0360-1285(90) 90025-X.
- [3] R.C. Borah, P. Ghosh, P.G. Rao, A review on devolatilization of coal in fluidized bed, Int. J. Energy Res. 35 (11) (2011) 929–963, doi:10.1002/er.1833.
- [4] J. Yu, J.A. Lucas, T.F. Wall, Formation of the structure of chars during devolatilization of pulverized coal and its thermoproperties: a review, Prog. Energy Combust. Sci. 33 (2) (2007) 135–170, doi:10.1016/j.pecs.2006.07.003.
- [5] M. Vascellari, R. Arora, M. Pollack, C. Hasse, Simulation of entrained flow gasification with advanced coal conversion submodels. Part 1: pyrolysis, Fuel 113 (2013) 654–669, doi:10.1016/j.fuel.2013.06.014.
- [6] M. Vascellari, R. Arora, C. Hasse, Simulation of entrained flow gasification with advanced coal conversion submodels. Part 2: char conversion, Fuel 118 (2014) 369–384, doi:10.1016/j.fuel.2013.11.004.
- [7] M. Baum, P. Street, Predicting the combustion behaviour of coal particles, Combust. Sci. Technol. 3 (5) (1971) 231–243, doi:10.1080/00102207108952290.
- [8] M.A. Field, Rate of combustion of size-graded fractions of char from a low-rank coal between 1 200°K and 2 000°K, Combust. Flame 13 (3) (1969) 237–252, doi:10.1016/0010-2180(69)90002-9.
- [9] R.H. Hurt, M.M. Lunden, E.G. Brehob, D.J. Maloney, Statistical kinetics for pulverized coal combustion, Symp. (Int.) Combust. 26 (2) (1996) 3169–3177, doi:10.1016/S0082-0784(96)80162-7.
- [10] R. Hurt, J.-K. Sun, M. Lunden, A kinetic model of carbon burnout in pulverized coal combustion, Combust. Flame 113 (1) (1998) 181–197, doi:10.1016/ S0010-2180(97)00240-X.
- [11] S. Niksa, G.S. Liu, R.H. Hurt, Coal conversion submodels for design applications at elevated pressures. Part I. Devolatilization and char oxidation 29 (5) (2003) 425–477, doi:10.1016/S0360-1285(03)00033-9.
- [12] G.S. Liu, S. Niksa, Coal conversion submodels for design applications at elevated pressures. Part II. Char gasification 30 (6) (2004) 679–717, doi:10.1016/j. pecs.2004.08.001.

- [13] N.E.L. Haugen, M.B. Tilghman, R.E. Mitchell, The conversion mode of a porous carbon particle during oxidation and gasification, Combust. Flame 161 (2014) 612–619, doi:10.1016/j.combustflame.2013.09.012.
- [14] N.E.L. Haugen, R.E. Mitchell, M.B. Tilghman, A comprehensive model for char particle conversion in environments containing O<sub>2</sub> and CO<sub>2</sub>, Combust. Flame 162 (2015) 1455–1463, doi:10.1016/j.combustflame.2014.11.015.
- [15] M.B. Tilghman, N.E.L. Haugen, R.E. Mitchell, A comprehensive char-particle gasification model adequate for entrained-flow and fluidized-bed gasifiers, Energy Fuels 31 (2015) 2164–2174, doi:10.1021/acs.energyfuels.6b02148.
- [16] J. Krüger, N. Haugen, T. Løvås, D. Mitra, The effect of turbulence on the reaction rate of particles with heterogeneous surface reactions, Proc. Combust. Inst. 36 (2017) 2333–3240, doi:10.1016/j.proci.2016.06.187.
- [17] N. Haugen, J. Krüger, D. Mitra, T. Løvås, The effect of turbulence on mass transfer rates of small inertial particles with surface reactions, J. Fluid Mech. 836 (2018) 932–951, doi:10.1017/jfm.2017.820.
- [18] J. Krüger, N.E.L. Haugen, T. Løvås, Correlation effects between turbulence and the conversion rate of pulverized char particles, Combust. Flame 185 (2017) 160–172, doi:10.1016/j.combustflame.2017.07.008.
- [19] E. Karchniwy, A. Klimanek, N. Haugen, The effect of turbulence on mass transfer rates between inertial polydisperse particles and fluid, J. Fluid Mech. 874 (2019) 1147–1168, doi:10.1017/jfm.2019.493.
- [20] I. Smith, The combustion rates of coal chars: a review, Symp. (Int.) Combust. 19 (1) (1982) 1045–1065, doi:10.1016/S0082-0784(82)80281-6.
- [21] D.D. Toporov, Combustion of Pulverised Coal in a Mixture of Oxygen and Recycled Flue Gas, Elsevier Insights, Elsevier, 2015, doi:10.1016/C2013-0-19301-4.
- [22] A. Hayhurst, The mass transfer coefficient for oxygen reacting with a carbon particle in a fluidized or packed bed, Combust. Flame 121 (2000) 679–688, doi:10.1017/jfm.2017.820.
- [23] L. Chen, S.Z. Yong, A.F. Ghoniem, Oxy-fuel combustion of pulverized coal: characterization, fundamentals, stabilization and CFD modeling, Prog. Energy Combust. Sci. 38 (2) (2012) 156–214, doi:10.1016/j.pecs.2011.09.003.
- [24] W. Ranz, W. Marshall, Evaporation from drops, part I, Chem. Eng. Prog. 48 (3) (1952) 141–146.
- [25] S. Kriebitzsch, A. Richter, LES simulation of char particle gasification at Reynolds numbers up to 1000, Combust. Flame 211 (2020) 185–194, doi:10. 1016/j.combustflame.2019.08.028.
- [26] W. Rodi, Turbulence Models and Their Application in Hydraulics a State of the Art Review, NASA STI/Recon Technical Report A, 1980.
- [27] B.E. Launder, D.B. Spalding, The numerical computation of turbulent flows, Comput. Methods Appl. Mech. Eng. (3) (1974) 269–289.
- [28] W.P. Adamczyk, B. Isaac, J. Parra-Alvarez, S.T. Smith, D. Harris, J.N. Thornock, M. Zhou, P.J. Smith, R. Zmuda, Application of LES-CFD for predicting pulverized-coal working conditions after installation of NOx control system, Energy 160 (2) (2018) 693–709, doi:10.1016/j.energy.2018.07.031.



# APPENDIX D

One conference proceeding is attached in Appendix D, related to chapter 2.5 on CFD simulations of CLC reactor systems. See summary table in chapter 3 for details.

# EFFECT OF WALL BOUNDARY CONDITIONS ON 3D HYDRODYNAMIC NUMERICAL SIMULATION OF A CLC UNIT WITH DUAL CIRCULATING FLUIDIZED-BED REACTORS

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# Abstract

3D unsteady numerical simulations of a chemical looping combustion (CLC) unit constructed at SINTEF Energy Research (Trondheim, Norway) are performed with the goal to investigate the effect of the particle-wall boundary conditions on the CLC flow behavior. Simulations are carried out using NEPTUNE\_CFD, a simulation tool based on a two-fluid modelling approach. Three types of boundary conditions are used for the solid phase: free-slip, no-slip and friction conditions. Comparison between predictions shows that the dominant frictional effect on the particle phase velocity is due to the long-time frictional contact of the particles with the wall. Results show that different boundary conditions may have an effect on the pressure distribution because of the modification of the flow behavior inside the reactors. Noteworthy is the effect that such a modification entails on the different parts of the system because of their coupling.

## Introduction

Chemical looping combustion (CLC) allows to control CO<sub>2</sub> emissions by CO<sub>2</sub> separation from the combustion products with a very low energy penalty (Lyngfelt et al. 2011). It is now a wellestablished technology, intended for use on an industrial scale. New processes based on this technology are being developed and they need as much information as possible to design units that ensure efficiency along with low costs. In this regard, the three-dimensional (3D) numerical simulations may help in both the development and scale-up stages, especially when understanding the instantaneous and local behavior of the flow is crucial for optimizing some parts of the CLC system. In present work, a multiphase computational-fluid-dynamics (CFD) strategy is used to investigate the flow behavior of an existing CLC pilot constructed at SINTEF Energy Research (Trondheim, Norway). Such a strategy uses a two-fluid model approach which is well known to allow numerical simulations at larger scales. This approach relies on the modeling of the particulate flows inside the flow as well as at the wall. The present study aims at investigating the effect of the particle-wall boundary conditions (BC) on the CLC predictions. Three different BC are tested: free-slip, no-slip and friction conditions, with a given set of particle/wall interaction parameters. Results are mainly analyzed on the basis of the time-averaged relative pressure predictions comparing with experimental measurements.

## **Mathematical models**

The two-fluid model implemented in NEPTUNE\_CFD has been used to predict the local and instantaneous behavior of both the gas and solid phases under isothermal conditions. Details about the whole modeling may be found in previous works (see, for example, Hamidouche et al. 2019). The present study is focusing on the effect of particle-wall BC on the hydrodynamic of the dual circulating fluidized bed reactor systems. The wall BC for the particle phase consist in the modelling of the mean particle tangential momentum and random kinetic energy fluxes

at the wall, namely at a particle center distance  $d_p/2$ , where  $d_p$  is the particle diameter. Particlewall BC may be written in the very general form as

$$\left(\mu_p \frac{\partial U_{p,\tau}}{\partial n}\right)_{wall} = \Sigma_{w,\tau n} \tag{1}$$

$$\left(\lambda_p \frac{\partial q_p^2}{\partial n}\right)_{wall} = \phi_w \tag{2}$$

where  $\Sigma_{w,\tau n}$  and  $\phi_w$  represent, respectively, the mean particle tangential momentum and random kinetic energy fluxes transferred by the particle assembly to the wall. The unit vector normal to the wall, **n**, is directed towards the flow, and the unit vector tangent to the wall, **r**, is given as colinear to the projection of the particle velocity on the wall. Accordingly, the tangential particle velocity component is written as  $U_{p,\tau} = |\mathbf{U}_{p} \cdot (\mathbf{U}_{p}, \mathbf{n})\mathbf{n}|$ . In Eqs. (1) and (2),  $\mu_p$ and  $\lambda_p$  are the particle dynamic viscosity and random kinetic energy diffusivity which account for the transport within the particle assembly due to kinetic, collisional and frictional effects.

 $\Sigma_{w,\tau n}$  and  $\phi_w$  depend on how the discrete particles interact with the wall and, in particular, may be a function of the elastic normal and tangential restitution coefficients, of the friction coefficient, as well as of the wall roughness. In the simplest case, the BC may be derived by assuming pure elastic frictionless bouncing of the particles on a flat wall and are written as

$$\left(\mu_p \frac{\partial U_{p,\tau}}{\partial n}\right)_{wall} = 0 \tag{3}$$

$$\left(\lambda_p \frac{\partial q_p^2}{\partial n}\right)_{wall} = 0 \tag{4}$$

These boundary conditions are referred to as free-slip BC in this work.

In practical flow configurations,  $\Sigma_{w,\tau n}$  takes positive value and increases with the particle-wall friction and wall roughness effect. However, according to Fede et al. (2016), the flux transferred by the particles towards the wall is limited by the transport effect within the particle assembly, accounted for by using the viscosity assumption, and such a maximum value is obtained for a zero particle tangential velocity condition at the wall. Therefore, the corresponding BC are

$$\left(U_{p,\tau}\right)_{wall} = 0 \tag{5}$$

$$\left(\lambda_p \frac{\partial q_p^2}{\partial n}\right)_{wall} = 0 \tag{6}$$

These BC are referred to as no-slip BC in this study.

Finally, as pointed out by Johnson and Jackson (1987),  $\Sigma_{w,\tau n}$  may be written as the sum of a collisional and frictional contributions:  $\Sigma_{w,\tau n} = \Sigma_{w,\tau n}^{col} + \Sigma_{w,\tau n}^{fr}$ . The first contribution corresponds to the frictional effect due to the short particle contacts with the wall occurring when particles are in a wide space and bounce off the wall. The second contribution corresponds to the effect of particle contacts with the wall sustained for long times, which may occur when particles are very close to each other and slide together along the wall.

In the case of Coulomb's law for full sliding collisions on a flat surface with a friction coefficient  $\mu_w^{col}$ ,  $\Sigma_{w,\tau n}^{col}$  may be written as (Sakiz and Simonin, 1999):

$$\Sigma_{w,\tau n}^{col} = \mu_w^{col} \left( \alpha_p \, \rho_p \, \frac{2}{3} \, q_p^2 \right)_{wall} \tag{7}$$

 $\Sigma_{w,\tau n}^{fr}$  may then be written as the product of a Coulomb friction coefficient,  $\mu_w^{fr}$ , and the wallnormal component of the particle-wall frictional stresses,  $\Sigma_{w,nn}^{col}$ . In practice,  $\Sigma_{w,nn}^{col}$  is assumed to be nearly identical to the inter-particle frictional pressure  $P_p^{fr}(\alpha_p)$  given as an empirical function of the particle volume fraction  $\alpha_p|_{wall}$  computed at particle center distance  $d_p/2$  from the wall (Johnson and Jackson, 1987; Srivastava and Sundaresan, 2003). Finally, the particlewall BC accounting for friction are written as

$$\left(\mu_p \frac{\partial U_{p,\tau}}{\partial n}\right)_{wall} = \mu_w^{col} \left(\alpha_p \rho_p \frac{2}{3} q_p^2\right)_{wall} + \mu_w^{fr} P_p^{fr} \left(\alpha_p \big|_{wall}\right)$$
(8)

$$\left(\lambda_p \frac{\partial q_p^2}{\partial n}\right)_{wall} = 0, \tag{9}$$

where the two Coulomb coefficients are depending on the particle and wall properties.

We may point out that the second term on the right-hand side of Eq. (8) is the dominant contribution in the dense regions of the system. In contrast, the frictional pressure is taken equal to zero for particle volume fraction less than  $\alpha_{p,min} = 0.55$  and the only remaining contribution to particle friction at the wall is the collisional contribution which is proportional to the particle volume fraction  $\alpha_p$  and to the random kinetic energy  $q_p^2$ .

### Experimental system and simulation setup

The CLC system reproduced by the unsteady 3D numerical simulation is a 150 kW<sub>th</sub> pilot operating at SINTEF Energy Research (Trondheim, Norway). A schematic diagram of the unit is given in Fig. 1. It is composed of two reactors, the air reactor (AR) and the fuel reactor (FR), each connected with its own cyclone and loop seal, and a lifter allowing the particles to flow from FR to AR according to the CLC design. AR dimensions are 23 cm in diameter and 6 m in height, and FR dimensions are 15.4 cm in diameter and 6.7 m in height (including lifter). In the experiments, the oxygen carrier is ilmenite from Titania A/S in Norway. Particle mean diameter ( $D_{50}$ ) and bulk density are 90  $\mu$ m and 2600 kg/m<sup>3</sup>, respectively. In the numerical simulations, spherical particles with same mean properties are used, and a total mass inventory of 125.9 kg, estimated by the experiments, is imposed. Gas properties are computed at the temperature of 1273 K, which represents a mean temperature value of the CLC system at such operating point. Mass flow rates are chosen according to the experimental conditions, with the exception of the FR inlet, which is supplemented by the amount of volatiles released by the biomass during the pyrolysis, estimated by the proximate analysis. Mass flow rates are given in Table 1. Pressure boundary conditions at the two cyclone outlets are estimated from the experiments.

Item	Value (kg/h)	ltem	Value (kg/h)
Primary gas of AR	146.67	AR loop seal, inlet leg	2.23
Secondary gas of AR, G1	17.04	AR loop seal, outlet leg	3.21
Secondary gas of AR, G2	29.16	FR loop seal, inlet leg	2.15
Inlet of FR	27.82	FR loop seal, outlet leg	1.73
Inlet of Lifter	2.27		

Table 1. Gas inlet flow rates

Table 2. Parameters for particle-wall boundary conditions

		$\mu_{\scriptscriptstyle W}^{\scriptscriptstyle col}$	$\mu_{\scriptscriptstyle W}^{{\scriptscriptstyle fr}}$
Case 1	No-slip BC		
Case 2	Free slip BC	(0.0)	(0.0)
Case 3	Friction BC	0.5	0.5
Case 4	Friction BC	0.5	0.0

Numerical simulations are performed using NEPTUNE\_CFD, which is a multiphase CFD code based on a cell-center type finite volume method and a first order temporal scheme (Neau et al., 2020). The CLC geometry is modeled by a mesh of about 0.76 million cells. Simulations are performed using 144 cores (4 nodes) corresponding to a mean computational cost of about 278 hours per second of physical time. A multiphase version of the k- $\varepsilon$  model is used to predict the gas turbulence accounting for the effect of the particulate phase on the fluid flow. This model is coupled with an uncorrelated collision model for the particle random kinetic energy prediction. More details can be found in Hamidouche et al. (2019). In order to study the effects

of the particle-wall BC, different BC are used. Table 2 gives the corresponding parameters for each test case.

# **Results and discussion**

Fig. 1 (first on the left) shows the distribution of the time-averaged relative pressure in the CLC system for Case 3, as an example. In the numerical simulation, pressure is taken at the center of the reactors (but it was found radially uniform inside). In the experiments, pressure was measured by transmitters (Fuji Electric, model FKCW33V5AKCYYAU, 0 – 320 mbar, 4 – 20 mA signal), mounted together on a skid / panel with 10 or 12 mm pipes to their respective pressure measurement points. They are differential pressure transmitters, but the reference pressure is to the atmosphere (the low-pressure entrance of the transmitter is open to the atmosphere) (Bischi et al. (2013)). The pressure is minimum at the top of the reactors and maximum at the bottom of the lifter, as expected. The pressure is much larger in the bottom part of the FR than in the bottom part of the AR, corresponding to a much larger solid inventory, about three times larger for Case 3 (using frictional BC as shown by Table 1). The distribution of the instantaneous solid volume fraction predicted by using frictional BC is shown by Fig. 1 (second on the left). The corresponding time animations show that in the AR, operating in a circulating regime, solids are transported by the fluidization gas to be separated by the cyclone. Then, these particles are sent to the FR through a loop seal. In the FR, solids are transported downward and injected in the AR through the Lifter, but some particles are also transported upward towards the cyclone, to be separated and reinjected in the AR through the loop seal. Results show that the solid volume fraction is higher in the FR than in the AR due to the different fluidization gas velocity, but the solid mass flow rate transported in FR to the cyclone represents only a small part of the total solid circulation rate (about 10%).



Fig. 1. From the left to the right: time-averaged relative pressure, instantaneous solid volume fraction, time-averaged solid volume fraction, for frictional wall BC (Case 3), schematic diagram of the CLC.

Fig. 2 shows the vertical profiles of time-averaged relative pressure predicted by using different BC. Results are globally in a good agreement with experimental data. However, significant differences in the mean pressure predictions may be observed between simulation results according to the wall BC used for the particle phase velocity. Fig. 2 (left) shows a comparison of the different boundary conditions in the AR. The figure shows a more rapid development of the linear pressure profile and less accumulation of solid in the bottom part of the reactor for no-slip than for free-slip BC. Fig. 2 shows that the pressure profiles obtained with partial friction BC corresponding to Case 4 ( $\mu_w^{col} = 0.5$ ,  $\mu_w^{fr} = 0$ ) are nearly identical to the free-slip BC predictions, meaning that the BC representing only the short-time frictional collision with a flat wall has a negligible effect on the flow behavior, as also shown in dense fluidized bed configuration by Fede et al. (2016). In contrast, Fig. 2 shows that the full friction BC ( $\mu_w^{col} = 0.5$ ,  $\mu_w^{fr} = 0.5$ ) has an effective effect on the mean pressure profiles but it is more difficult to analyze. As a matter of fact, according to the values of the solid volume fraction

predicted in the AR along the wall ( $\alpha_p < 0.2$ ), the long-time friction BC contribution represented by  $\mu_w^{fr} = 0.5$  should not have any influence in this part of the system. Indeed, Fig. 2 (left) shows that the corresponding pressure profile in AR has a very similar shape than the pressure profile obtained in the free-slip case in terms of the height of the acceleration region and the extension of the linear pressure profile region, but the total mass and flow rate in the AR are smaller than in the free-slip case (see Fig. 4 and 5). So we may expect that the differences observed between the predictions of Case 3 (full friction) and those of Case 2 (free-slip) and Case 4 (partial friction) are mainly due to the effect of the long-time friction effect in the Lifter and in the FR, but also in the connecting pipes, which leads to modify the coupling conditions with the AR in the bottom region and to reduce the global circulation rate.



Radial profiles of time-averaged vertical solid velocity in AR and FR are displayed in Fig. 3 at a height far from connections. Particles flow up in the center and flow down near the wall. Negative velocities are detected in both the AR and FR in the region near the wall. As shown by the figure, in the AR, the time-averaged vertical velocities predicted using frictional BC are close to the one of simulation using free-slip BC, in the center. However, the asymmetry at the wall leads to conclude that these results are not statistically converged. In the FR, such differences are smaller.



Fig. 3. Time-averaged vertical solid velocity. AR: left; FR: right.

The simulated flow rates of solids leaving the reactors from the top, based on different BC, are shown in Fig. 4. A substantial amount of solids leave the AR from the top, because it operates as a circulating fluidized bed. For the FR, most particles leave from bottom and enter the AR through the Lifter. The mass distributions in the different parts of the CLC, obtained using different BC, are shown in Fig. 5. The solid mass obtained in the FR based on free-slip and partial frictional BC ( $\mu_w^{fr}$  = 0) are very similar. While, the mass based on a full frictional model ( $\mu_w^{fr}$  = 0.5) is similar to that obtained with no-slip BC. In the Lifter and in the AR, the mass inventory is decreasing with the increase of the frictional effect, from free-slip to no-slip BC, and this effect is depending on the amount of solid inventory in the connecting parts of the system (cyclones, loop seals, pipes).

## Conclusions

3D unsteady numerical simulations of a CLC system were carried out using the NEPTUNE CFD multiphase code based on a two-fluid model approach. Several BC modeling assumptions were tested on a dual fluidized bed configuration corresponding to a pilot operating at SINTEF, Trondheim, Norway. The predicted time-averaged vertical pressure profiles were analyzed and compared with the experimental measurements. Radial profiles of the time-averaged solid vertical velocity, as well as the solid mass distribution and flow rate were also shown for various BC models. The analysis pointed out the dominant particle-wall frictional effect of the long-time contacts in the Lifter and in the FR and the negligible particle-wall frictional effect of short-time collisions in the AR. The friction model is particularly suitable for prediction of systems with complex structures and different flow regimes. Further study should be carried out to analyze the effect of the wall roughness or irregular particle shape which may increase the particle-wall friction particularly in the dilute configuration of the AR.







Fig. 5. Time-averaged distribution of solids in the different parts of the CLC.

### References

- Bischi, A., Langørgen, Ø., Bolland, O. Double loop circulating fluidized bed reactor system for two reaction processes, based on pneumatically controlled divided loop-seals and bottom extraction/lift. Powder Technol. 2013. 246, 51-62.
- Fede, P., Simonin, O., Ingram, A. 3D numerical simulation of a lab-scale pressurized dense fluidized bed focussing on the effect of the particle-particle restitution coefficient and particle–wall boundary conditions. Chem. Eng. Sci. 2016. 142, 215-235.
- Hamidouche, Z., Masi, E., Fede, P., Simonin, O., Mayer, K., Penthor, S. Unsteady threedimensional theoretical model and numerical simulation of a 120-kW chemical looping combustion pilot plant. Chem. Eng. Sci. 2019. 193, 102-119.
- Johnson, P. C., Jackson, R. Frictional-collisional constitutive relations for granular materials, with application to plane shearing. J. Fluid Mech. 1987. 176, 67–93.
- Lyngfelt, A., Leckner, B., Mattisson, T. A fluidized-bed combustion process with inherent CO2 separation; application of chemical-looping combustion. Chem. Eng. Sci. 2001. 56, 3101–3113.
- Neau, H., Pigou, M., Fede, P., Ansart, R., Baudry, C., Mérigoux, N., Laviéville, J., Fournier, Y., Renon, N., Simonin, O. Massively parallel numerical simulation using up to 36,000 CPU cores of an industrial-scale polydispersed reactive pressurized fluidized bed with a mesh of one billion cells. Powder Technol. 2020. 366, 906–924.
- Sakiz, M., Simonin, O. Development and validation of continuum particle wall boundary conditions using Lagrangian simulation of a vertical gas/solid channel flow. Proc. 8th Int. Symp. on Gas-Particle Flows, ASME Fluids Engineering Division Summer Meeting. 1999.
- Srivastava, A., Sundaresan, S. Analysis of a frictional-kinetic model for gas-particle flow. Powder Technol. 2003. 129, 72–85.