Application of particle-scale modelling to the combustion of a char particle in a fluidised bed of CLOU particles

K.Y. Kwong *, J.S. Dennis, E.J. Marek

Department of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive, CB3 0AS Cambridge, United Kingdom

A R T I C L E   I N F O

Keywords:
Chemical looping combustion
Fluidised bed
Biomass
BECCS
Oxygen carrier
Modelling

A B S T R A C T

This research concerns the combustion of a biomass char in a fluidised bed of either inert silica particles or particles of a material capable of supporting combustion using chemical looping oxygen uncoupling (CLOU). An analytical solution for combustion using CLOU was developed, accounting for the chemical reactions occurring within a mass-transfer boundary layer of a finite thickness, surrounding a char particle. The reactions considered were: (1) combustion of char with oxygen to CO and CO₂, (2) homogenous reaction of CO with O₂, and (3) oxygen release from CLOU particles. The thickness of the boundary layer, γ, was evaluated using correlation in the literature and the combustion of the char particle was modelled as a shrinking particle. Results from the model were compared with experiments performed by combusting char from birch-wood and activated carbon in a fluidised bed (i.d. 30 mm) of either particles capable of CLOU (CuO supported on mayenite) or inert silica sand. Both types of experiments were undertaken with a partial pressure of oxygen, pO₂, close to the equilibrium pressure of O₂ over CuO at 1173 K, i.e. ~0.016 bar of O₂. The results from the analytical model agreed with the experimental observations from both beds.

In addition to the analytical solution, fuller, numerical models were developed, in which a char particle and its surroundings were discretised in 1D to solve the mass balance equations and to assess the validity of the assumptions made in the analytical solution. To establish the range of conditions in which the analytical solution is valid, various cases were simulated. For example, char combustion and gasification in a bed of CuO-particles fluidised by CO₂-rich gas. Hence, besides the validation of the analytical solution, the results of the numerical solutions provided insight into the importance of char gasification with CO₂ on the overall particle conversion in CLOU at the industrial scale.

1. Introduction

The concentration of CO₂ in the atmosphere continues to increase, having reached 419 ppm in July 2022 [1]. The Paris agreement mandated that the mean rise in global temperatures, resulting from the anthropogenic emission of greenhouse gases, should be kept well below 2 °C above the pre-industrial baseline temperature [2]. However, almost none of the signatory countries are on track with their nationally-determined contributions for achieving the Paris agreement [3]. The International Panel on Climate Change has emphasised the need for so-called ‘negative emission technologies’ (NETs) to remove CO₂ from the atmosphere [4]. Among NETs, chemical looping combustion (CLC) with biomass is a promising option because of the low cost of capturing CO₂ [5].

Chemical looping combustion (CLC) utilises solid materials, commonly referred as oxygen carriers (OC), to transport oxygen between two interconnected reactors: the fuel reactor (FR), where the combustion takes place, usually in a fluidised bed arrangement, and the air reactor (AR), where the OCs are regenerated with air. In CLC, the transfer of oxygen involves only the transport of the particles of oxygen carrier; hence, the air and the fuel never mix. Consequently, the flue gas from the FR is “capture-ready”, containing primarily CO₂. Depending on the OC used, two CLC approaches can be employed for solid fuels: in-situ gasification chemical looping combustion (iG-CLC) and chemical looping combustion with oxygen uncoupling (CLOU) [6–8].

Under a CLOU arrangement, the oxygen carriers are additionally capable of releasing gaseous O₂ by thermal decomposition. The gaseous O₂ can react directly with the fuel char. Otherwise, the solid fuel has to be firstly gasified by a gasifying agent, e.g. CO₂, as in an iG-CLC arrangement. The syngas produced from gasification then reacts...
heterogeneously with the oxygen carrier [9]. The CLOU approach is advantageous compared to iG-CLC because the rate of char oxidation by gaseous O\(_2\) is much faster than the rate of gasification, and hence, implementing CLOU helps increase the rate of fuel conversion [10].

Previous research on CLOU has focused mainly on exploring and assessing suitable CLOU materials, as reviewed by others, e.g. [8,9,11]. Copper-based materials, utilising the transition between CuO and Cu\(_2\)O, have received particular attention because of Cu\(_2\)O’s large gravimetric capacity to release oxygen and its fast redox kinetics. A number of studies have focused on understanding the behaviour of copper-based oxygen carriers, both experimentally and theoretically, e.g. using particle-scale models. Hu et al. [12] investigated the kinetics of oxygen uncoupling of CuO supported on magnesites with a thermogravimetric method and validated the kinetics in a fluidised bed. To develop a universal expression for the intrinsic kinetics of oxygen uncoupling for Cu-based oxygen carriers, Clayton and Whitby [13] determined the rate of decomposition for CuO supported on a MgO-stabilised ZrO\(_2\) or TiO\(_2\)-support, using a thermogravimetric analyser. A near mono-layer of particles with small diameters (<45 μm) was investigated to mitigate the influence of the intra- and inter-particle mass transfer. The rate obtained was then used to model the thermal decomposition of a third Cu-based oxygen carrier, CuO-supported on silica. The proposed rate expression derived from the first two carriers helped predict the rate of decomposition of the third oxygen carrier, suggesting the possibility of extending the expression to any Cu-based oxygen carrier. However, the observed agreement in the rate of oxygen uncoupling among particles of CuO supported on different materials could also be due to the influence of the experimental arrangement, e.g. mass transfer of gases within the sample pan in the thermogravimetric analyser. Recently, Su et al. [14] have undertaken a study of the kinetics of oxygen uncoupling of CuO, incorporating external mass transfer of gases, diffusion of defects in the external layer of the CuO particle, and the surface reaction at a gas–solid interface. They revealed that the external gaseous mass transfer and the effect of sintering could limit the rate of oxygen uncoupling. Hence, an agreement on the rate of oxygen uncoupling between different Cu-based OC materials could arise if the CLOU behaviour were influenced by the external mass transfer of O\(_2\).

Besides the rate of oxygen uncoupling, an important parameter for optimising the performance in CLOU is the rate of combustion of solid fuels, reflected by the magnitude of the burnout time. The rates of combustion and burnout time of solid fuels under different operating conditions have been investigated both experimentally and theoretically using particle-scale models. Recently, High et al. [15] have investigated the combustion of coals with a copper-based oxygen carrier via CLOU and iG-CLC in a fluidised bed. The experiments were conducted over the temperature range between 1123 and 1258 K, with either pure N\(_2\) or a 25.6 vol% H\(_2\)O balance in N\(_2\) as fluidising gas. While the Cu-based carrier released gaseous O\(_2\) throughout the whole combustion process at temperatures below 1173 K (a CLOU arrangement), at 1258 K the rate of release is much higher and so the copper in the carrier was rapidly converted to CuO and stopped releasing gaseous O\(_2\). The experiments at 1258 K, therefore, concern an iG-CLC arrangement. Under the CLOU arrangement (<1173 K), despite the presence of a gasifying agent in the fluidising gas, i.e. 25.6 vol% H\(_2\)O, the burnout time of the solid fuels was similar to that in a scenario where pure N\(_2\) gas was used as the fluidising gas. The experimental observations, thus suggested that, during CLOU, the contribution of gasification reactions to the overall fuel conversion was insignificant for temperatures <1173 K. However, with the same content of steam in N\(_2\), the gasification reaction became significant when increasing the bed temperature to 1258 K. To study the conversion of char in a CLOU arrangement, Su et al. [16,17] developed a numerical model of a single, spherical, porous particle of coal charcombusting in a bed of CLOU particles. However, in their model, two heterogeneous reactions, namely combustion of CO on the surface of CuO and oxygen uncoupling, were neglected; therefore, the models developed were actually simulating oxy-fuel combustion in a diluted O\(_2\) environment. Particle-scale models of char combusting in a CLOU arrangement and in an inert fluidised bed have been developed by Kwong et al. [18] based on a film model to describe mass transfer external to a char particle. The reactions occurring in the mass transfer film around the char particle were considered in the models. However, to obtain analytical solutions, the effect of the thickness of the film around a fuel particle was ignored. In Kwong et al.’s [18] models, gas was essentially treated as stagnant; thus, mass transfer proceeded solely by molecular diffusion. However, errors arising from this simplification could be significant when assessing CLOU under industrial conditions, for example, at high fluidisation velocities in beds of large particles. In such a case, the assumptions about the infinite film thickness would be incorrect, because the thickness of the film layer around a fuel particle depends on the gas velocity. Problems would not be limited to CLOU and active beds because, as presented in [18], in an inert bed of SiO\(_2\), the model developed was also unable to predict the burnout time of a single particle of char, with the over-prediction associated again to the simplifications applied in the film model.

The main objective of the present paper is to develop a model for describing the combustion of a single particle of biomass char in a CLOU arrangement where particles of CuO are used in a fluidised bed arrangement. Here, the models have been developed to explore the impact of the thickness of the mass transfer film surrounding the char particle on the overall rate of char conversion, allowing for mass transfer and chemical reactions in the external film, e.g. homogeneous combustion of CO or oxygen uncoupling from the CLOU particles. An underlying assumption is that mass transfer occurs across a film in which transport is solely by diffusion, viz. surface-renewal approaches have not been taken. Three models have been developed, namely:

1. a numerical model, which explicitly accounts for both intra-particle mass transfer in the char and mass transfer in the boundary layer around the char particle (here, referred to as inter-particle mass transfer),
2. a simplified numerical model with the inter-particle mass transport described explicitly, but the intra-particle mass transport simplified assuming Regime II combustion, and
3. an analytical solution, but one employing a finite thickness of external mass transfer film, thus, extending the model of Kwong et al. [18].

The results from the above models were compared with the experimental results to establish the validity of the models. A comparison of results from the models helped assess the range of conditions for which the analytical solution is valid. The numerical models were also used to explore the factors omitted from the analytical solution, e.g. the influence of gasification by CO\(_2\) and the temperature rise within the combusting char particle.

2. Materials and methods

2.1. Materials

Two fuels were used in the combustion experiments, an activated carbon (supplied by Haycarb plc, granular activated carbon, derived from coconut shell) and a birch char. The latter fuel was prepared by pyrolyzing, individually, a 6 mm diameter spheres of birch wood in an empty quartz reactor (i.d. 40 mm), in a continuous flow of N\(_2\) at 723 K. Each particle was held in the reactor for 4 min, and then retrieved with an intermediate step of cooling in a flow of cold N\(_2\) for 2 min to prevent the char from combusting. Both fuels were crushed and sieved to 1140 – 1400 μm. These fuels were also used in our previous studies [18,19], where the results of proximate, ultimate analysis, BET area and BJH mean pore size are presented.

Two bed materials were used for experiments in a fluidised reactor: inert silica sand or active CLOU particles (60 wt% CuO supported on
mayenite). Silica sand (David Ball Group Ltd.) was sieved to the size range of 250–300 μm. The CLOU particles were prepared using wet impregnation, as described by Hu et al. [12], and sieved to 250 – 425 μm. The composition of the synthesised OC was confirmed using X-ray powder diffraction. The stability of the CLOU particles during repeated oxygen uncoupling and coupling was investigated in a thermogravimetric analyser (TGA). With a fixed pO2 in the TGA, ~ 0.045 bar of O2 in N2, the temperature in TGA was cycled from 1073 K to 1273 K at a rate of 2 K min−1 for 3 – 5 cycles. The results of the characterisation of the CLOU particles have been presented elsewhere [18,20], confirming that the CuO-carrier both released and took up oxygen consistently over the number of redox CLOU cycles employed for the experiments.

2.2. Experimental

A quartz reactor (i.d. 30 mm), with a porous alumina disc (grade 1), used as a gas distributor and located 110 mm from the gas inlet, was used as a fluidised bed reactor. The reactor was heated electrically by a tubular furnace with the temperature controlled by a K-type thermocouple inserted into the reactor and located ~1 cm above the porous disk. Air was mixed with pure N2 (BOC) such that the combined O2 concentration was ~1.6 vol% and was used to fluidise the bed with U/Umf ~ 3, where the superficial, minimum fluidising velocity, Umf, was determined experimentally. The concentration of O2 used here (1.6 vol %) is the equilibrium concentration of O2 over CuO at 1173 K. Experiments were carried out at 1023, 1098 and 1173 K. For clarity, the equilibrium concentrations of O2 over CuO at 1023 K and 1098 K are lower than the O2 concentration of fluidising gas used, 1.6 vol% O2. In a typical experiment, a batch of fuel with known mass (0.05, 0.075, 0.1 g) was dropped into a bed of either silica sand (SiO2) or CLOU particles. Around 30 mL of bed materials was used, giving an unfluidised height of ~4 cm. Concentrations of O2, CO and CO2 in the outlet gases were measured with an ABB EL3020 equipped with a non-dispersive infra-red analyser and paramagnetic cell. The burnout time here was determined as the time taken for the concentration of CO2 in the off-gas to drop to 0.030 vol%. Below that value, the measurement was deemed inaccurate because it was close to the analyser’s accuracy of 0.015 vol%. A detailed description of the experimental apparatus has been presented elsewhere [18].

3. Theory

The chemical reactions expected in CLOU with a char particle are depicted in Fig. 1(a) and also listed here:

- **R1. Heterogeneous combustion of char with O2(g):**

  \[
  \frac{2(ξ + 1)}{ξ + 2} C + O_2 \rightarrow \frac{2ξ}{ξ + 2} CO + \frac{2}{ξ + 2} CO_2
  \]  

- **R2. Homogeneous combustion of CO with O2(g):**

  \[
  CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)
  \]  

- **R3. Heterogeneous thermal decomposition of CuO to release O2(g):**

  \[
  4 CuO(s) \rightarrow 2 Cu_2O(s) + O_2(g)
  \]  

- **R4. Heterogeneous reaction of CO with CuO:**

  \[
  CuO(s) + CO(g) \rightarrow Cu(s) + CO_2(g)
  \]  

- **R5. Gasification of char particle, e.g. with CO2:**

  \[
  C(s) + O_2(g) \rightarrow 2CO(g)
  \]  

In reaction R1, ξ is the proportion of carbon combusting to either CO or CO2 at the surface of the char particle. For the two fuels used here, the values of ξ were determined experimentally using a thermogravimetric method [19]. For example, at 1173 K and pO2 of ~0.01 bar, values of ξ for the birch char and activated carbon were 2.0 and 2.5, respectively.

While R1-[R5] are expected in the CLOU arrangement, if the bed material were instead composed of inert particles, e.g. SiO2, only reactions R1, R2 and R5 are expected.

Since the CLOU particles in the fluidised bed considered here are in excess compared to the loadings of char (i.e. the mass ratio of CLOU particles to char ~280), the overall conversion of the CuO bed considered here can be assumed negligible. Hence, to analyse combustion, only a model of a char particle and the surrounding boundary gas layer was required. The following assumptions were made in the new model of a combusting char particle: (a) the temperature across the boundary layer, γ, surrounding the char particle was uniform, (b) char particles were immersed in a uniform sea of particulate phase, i.e. the bed voidage, ε, is constant, (c) the fuel particles were spherical and only made up of carbon, (d) the char particles were combusted following a shrinking particle model (justified later in Section 4.2), (e) a pseudo-steady state of gas concentration profile, (f) the gases follow ideal gas behaviour, (g) the mass transfer is assumed to occur according to a film mass transfer model, i.e. the concentration in the film changes, from a bulk concentration, c0 at the surface of the film to a value at the surface of char particle, while the rest of the bed is kept uniform at c0, (h) mass transfer in the film involves only diffusion, (i) the impact of fragmentation on the conversion of char was neglected because of the lack of information on the fragmentation characteristics needed to assess the number and size of fragments [21], (j) the effect of the gasification reaction with CO2 on the overall char conversion is negligible. The effect of including gasification with CO2, [R5], and the change in temperature of the particle are discussed in Sections 4.5 and 5.3, respectively.

An analytical solution for CLOU has been previously developed by

![Fig. 1. Chemical reactions involving a char particle with radius, r, and gas species in the boundary layer thickness, γ. Here, J represents fluxes of gaseous components. Reactions in a bed of (a) CLOU particles, and (b) inert particles.](image-url)
Kwong et al. [18], assuming that combustion proceeded in Regime II and that the concentrations of active species were low, i.e. a dilute mixture. With combustion under Regime II, the intra-particle diffusion of O₂ was not explicitly modelled but simplified by expressing the rate of combustion at the nominal surface of the char particle. Then, for a dilute mixture of gas, Fick’s law was applied to describe mass transport. Additionally, as noted earlier, the thickness of the mass transfer film around the char particle was assumed to be infinite. While these simplifications are valid for describing the experimental arrangement in dilute mixtures, they might not be applicable in other cases, e.g. for industrial applications, where the fluidising gas contains high concentrations of CO₂. In a system with high concentrations of active species and non-equimolar diffusion, the assumption of Fickian diffusion would lead to inaccuracies. To explore the combusting behaviour of a char particle under more practical operating conditions, e.g. combusting char in a CLOU arrangement with pure CO₂ as a fluidising gas, improved models are needed. Thus, as noted in the introduction, three different models are presented here: two numerical models (a ‘full numerical model’ and a ‘simplified numerical model’) and an analytical solution. As the ‘full numerical model’ accounted for more physical details, it was used to assess the validity of the assumptions made in the ‘simplified numerical model’ and the analytical solution. The ‘simplified numerical model’ and analytical solution are computationally cheaper than the ‘full numerical solution’, and hence, more viable for conducting various case studies of CLOU.

3.1. Kinetics of reactions

The kinetic parameters of the reactions used here are summarised in Table 1. The concentration of each species is written as $c_i$ ($i = 1 = CO, 2 = CO_2, 3 = O_2$ and $4 = N_2$). $S_p$ is the effective pore surface area for combustion per unit volume of char particle, and $c_{eq}$ is the equilibrium concentration of oxygen over CuO at the operating temperature and pressure.

Activated carbon is typically less reactive than biomass or coal chars [24], so, the applicability of the same kinetic parameters as birch char might be questionable. The set of kinetic constants for the activated carbon was consequently derived from combustion experiments, carried out in a fluidised bed of SiO₂. The value for the intrinsic kinetic constant, $k_i$, was fitted to match the experimental burnout time, as presented in the Supplementary Information (SI), Section 1. At 973 K, the value of $k_f$ for the activated carbon was found to be ~400 times smaller than that for the value obtained by Smith [22].

### Table 1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate (mol m⁻² s⁻¹)</th>
<th>Value</th>
<th>Eqn.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[R1] $\frac{r}{R} \cdot k_i c_i S_p$</td>
<td>$A_i \exp(-E_i/RT) S_p c_i$</td>
<td>$E_i = 179$ kJ mol⁻¹</td>
<td>(1) For BIC: [22]</td>
<td></td>
</tr>
<tr>
<td>[R2] $R_0 = k_i c_i^{1/2} c_o^{1/2}$</td>
<td>$A_i \exp(-E_i/RT) c_i^{1/2} c_o^{1/2}$</td>
<td>$A_i = 1.75T_p$ m⁻¹ s⁻¹</td>
<td>(2) For ACC: refer to SI, Section 1</td>
<td></td>
</tr>
<tr>
<td>[R3] $R_0 = k_i (c_{eq} - c_o)$</td>
<td>$A_i \exp(-E_i/RT) (c_{eq} - c_o)$</td>
<td>$E_i = 59.7$ kJ mol⁻¹</td>
<td>(3) For ACC: refer to SI, Section 1</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Full numerical model (Stefan-Maxwell transport equations with CPIM)

3.2.1. Intra-particle mass transfer

To model the intra-particle mass transfer explicitly, the diffusive and advective transport within the char particle was described using the Cylindrical Pore Interpolation Method (CPIM), which is a multicomponent flux model based on the Stefan-Maxwell equations, modified by a momentum balance [25] and introduced specifically to deal accurately with situations where both molecular and Knudsen diffusivity could have comparable influences.

Within a spherical particle of char, the component balances for species $i$ at steady-state, (where $i = 1, 2, 3, 4$ for CO, CO₂, O₂, N₂, respectively) are:

$$\frac{dJ_i}{dr} = -\frac{2}{r} J_i + \frac{2}{\xi} k_i S_p c_i$$

$$\frac{dJ_i}{dr} = -\frac{2}{r} J_i + \frac{2}{\xi} k_i S_p c_i$$

$$\frac{dJ_i}{dr} = -\frac{2}{r} J_i - k_i S_p c_i$$

$$\frac{dJ_i}{dr} = -\frac{2}{r} J_i$$

Using the CPIM model, the mass transport of the gaseous species within the pores of the particle of char can be described by:

$$\frac{dP}{dr} = \sum_{i=1}^{4} J_i \sqrt{M_i}$$

where $M_i$ is the molecular mass of species $i$, then, $\xi$, and $r_p$ are the tortuosity and porosity of the char particle, respectively, and $P$ is the total pressure. The parameters $\xi_{p,i}$ and $A_i$ were evaluated by interpolating between the extremes of continuum ($\xi \to 0$) and Knudsen flow ($\xi \to \infty$) using the equations proposed by Young and Todd [25]:

$$\frac{1}{\xi_{p,i}} = \frac{1}{\xi_{K,i}} + \frac{1}{\xi_{M}}$$

$$\frac{1}{A_{k,i}} = \frac{1}{A_{k,i}} + \frac{1}{A_{M}}$$

where $\xi_{K,i}$ and $\xi_{M,i}$ are the Knudsen diffusivity and the molecular diffusivity coefficients, respectively, with $\xi_{M,i}$ calculated using the equation of Reid et al. [26]. The Knudsen diffusivities were evaluated using the kinetic theory of gases:

$$\xi_{K,i} = \frac{2R_{pore}}{3} \frac{M_i}{\pi M}$$

In eqn. (11) the parameters $A_{k,i}$ and $A_{M,i}$ are the coefficients in the pressure gradient equations in the continuum and Knudsen regimes, respectively, given by:

$$A_{k,i} = \frac{3}{4R_{pore}} \left( \frac{RT}{2} \right)^{1/2}$$

$$A_{M,i} = \frac{S_{pore} RT}{P R_{pore} \sum_{i=1}^{4} M_i}$$

where $R_{pore}$ is the mean radius of the pores, as determined from the measurement of BJH pore size and $S_{pore}$ is the effective viscosity of the mixture of gases. In this work, the combustion of char can occur in an
atmosphere with either $N_2$ (in experiments) or $CO_2$ (in the industrial application of CLOU, and in the modelling scenarios considered) as the dominant species. For the main species present in such environments, $CO_2$ and $N_2$, the dynamic viscosities are $4.41 \times 10^{-5}$ and $4.61 \times 10^{-5}$ Pa s (at 1173 K), respectively. The values of these viscosities are similar to each other and previous work on combustion by Saucedo [27] has demonstrated that the mass transfer described with a CPIM model is relatively insensitive to the variation in the viscosity of the separate components. Hence, the value of $\mu_{N_2}$ in $AC_c$ was taken as a constant and equal to either the value of $\mu$ for $N_2$ or $CO_2$, depending on whether the system was balanced with $N_2$ or $CO_2$.

The mole fractions and fluxes of the gaseous species $i$ and the total pressure within the particle of char in eqns. (4 – 9) were solved using the boundary conditions:

\begin{equation}
At \ r = 0 : J_i = 0 \ where \ i = 1, 2, 3, 4
\end{equation}

\begin{equation}
At \ r = r_p : J_i = J_{i,b}, \ P = P_i, \ where \ i = 1, 2, 3, 4
\end{equation}

where $J_{i,b}$ and $P_i$ are the molar flux of $i$ and the total pressure at the surface of the particle.

### 3.2.2. Mass transfer in the boundary layer around the particle (inter-particle mass transfer)

The component balance for species $i$ over a differential volume of gas surrounding the fuel particle, i.e. from $r = r_p$ to $r = r_p + y$, under pseudo-steady conditions, can be written as:

\begin{equation}
\frac{1}{r^2} \frac{d(r^2 J_i)}{dr} = z_k R_0 \ \text{for inert bed material (i.e. SiO2)}
\end{equation}

\begin{equation}
\frac{1}{r^2} \frac{d(r^2 J_i)}{dr} = z_k R_0 + z_k \eta_{\text{CuO}} D_i R_0 \ \text{for CLOU material (i.e. CuO)}
\end{equation}

here, $J_i$ is the molar flux per unit area of species $i$ and $x_k, x_{i0}$ are the stoichiometric coefficients for reactions [R2] and [R3], for example, $x_k = 1$ for $CO$, $x_{i0} = 1$ for $CO_2$, $x_k = -\frac{1}{2}$ for $O_2$ and $x_{i0} = 0$ for $N_2$. In eqn. (18), an apparent rate for [R3], i.e. the product of the intrinsic rate, $R_0$, and the effectiveness factor, $\eta_{\text{CuO}}$, was used to account for the influence of intraparticle mass transfer within the oxygen carrier. Here, $\eta_{\text{CuO}} = \frac{K_{\text{CuO}}}{x_{\text{CuO}}}$, where Thiele Modulus, $K_{\text{CuO}} = \frac{4 \sqrt{\eta_{\text{CuO}}}}{3 \sqrt{\text{CuO}}}$ [28]. Here, $K_{\text{CuO}}$ is the equilibrium constant for [R3]; the effective intraparticle diffusivity of $O_2$ through the oxygen carrier particle, $\eta_{\text{CuO}}$, was taken as $\eta_{\text{CuO}}^{0.5}$. The porosity of the oxygen carrier, $\rho_{\text{CuO}}$, and the tortuosity factor, $\tau_{\text{CuO}}$, were taken as 0.6 and 2, respectively.

The thickness of the boundary layer around the char particle, $y$, was determined from the Sherwood number, $Sh = Sh_0 \left( 1 + \frac{y}{\xi} \right)$, where $Sh_0 = 2 \ v_{\text{eff}}$ for a fluidised bed, with $v_{\text{eff}}$ being the voidage of the bed at the incipience fluidisation [29]. For the case with equimolar counter diffusion, i.e. $J_{i0} = -J_{CO_2}$, the Sherwood number in a fluidised bed, $Sh_{EMCD}$, can be evaluated as [30]:

\begin{equation}
Sh_{EMCD} = 2 \ v_{\text{eff}} + 0.69 \left( \frac{U_{\text{eff}} R_p}{v_{\text{eff}}} \right)^{0.5} \left( \frac{v}{\xi} \right)^{0.4}
\end{equation}

where $U_{\text{eff}}$ is the minimum fluidisation velocity, $v$ is the kinematic viscosity of the gas, $\xi$ is the molecular diffusivity of the gas, $\eta$, is the diffusion of the predominant species, $N_2$. When a char particle combusters producing a mixture of $CO$ and $CO_2$, the diffusion is not equimolar, but, for dilute cases, the Sherwood number can be still approximated with $Sh_{EMCD}$ [29]. Because the combustion experiments in this work were strongly influenced by external mass transfer and were conducted in a dilute $O_2$ environment, $Sh$ was, thus, approximated as $Sh_{EMCD}$.

Diffusion in the boundary layer can be described with the Stefan-Maxwell equations as [25]:

\begin{equation}
\frac{dy}{dr} = \frac{RT}{F \sum_{i=1}^{4} \left( J_i \eta_{\text{EMCD}} \frac{\partial J_i}{\partial y} \right)}
\end{equation}

where $y_i$ is the mole fraction of species $i$, and $\partial J_i$ is the effective diffusivity calculated by $\eta_{\text{EMCD}}$. Here, $\eta$ is the voidage of the particulate phase and the $\partial J_i$ are the molecular diffusivities. Tortuosity is not overtly present in $\partial J_i$ because the tortuosity has been accounted for in the Sherwood number. Pressure in eqn. (20) was taken to be constant, because the permeability of the bed is large, and hence, the pressure gradients due to the diffusion are small in comparison to the absolute pressure [31]. Generalised boundary conditions for the solutions of eqns. (17 – 20) are:

\begin{equation}
At \ r = r_p : J_i = J_{i,b} \ where \ i = 1, 2, 3, 4
\end{equation}

\begin{equation}
At \ r = r_p + y : y_i = y_{i,b} \ where \ i = 1, 2, 3, 4
\end{equation}

The boundary conditions at the boundary with the bulk flow in eqn. (22) are taken as for the mixture of the gases fed into the reactor, $y_i = y_{i,b}$.

The above transport equations inside and external to the fuel particles were discretised into 801 nodes and solved using the MATLAB solver, bvp4c, by providing an initial guess for $J_i$ and $y_i$. The number of nodes used was considered adequate on the basis that the percentage difference of the simulated fluxes of $O_2$ at $r = r_p$, between the cases where the number of nodes was halved and doubled, e.g. 1601 and 401 nodes, were <0.007 %.

### 3.3. Simplified numerical model (Stefan-Maxwell transport equations with Regime II combustion)

Under Regime II combustion, when the combustion occurs within an infinitesimally thin, external shell of the char particle, i.e. expected in the experiments carried out here, a simplified approach in describing the intra-particle mass transport can be applied [18]. In this simplification, the rate of consumption of $O_2$ per unit nominal external surface area of char particle, $R_0$ (mol m$^{-2}$ s$^{-1}$), can be calculated as $k_B C_3$, where $k_B$ is $(k_{B} s_{\text{EMCD}})^{0.5}$ [22] and the exponent 0.5 accounts for the effect of intra-particle mass transfer. Also, $\eta_{\text{EMCD}}$ is the effective diffusivity of $O_2$ in the particle, equal to $\partial O_2/y_{i,b} R_0^2$.

An implication of this simplified approach is the avoidance of modelling the intra-particle mass transport explicitly; hence, only the inter-particle mass transport (external to the char particle) was modelled explicitly using the Stefan-Maxwell equations, as given in eqns. (17 – 20). The diffusion and reaction within the char particle were incorporated as the boundary conditions at the surface of the particle of char, $r = r_p$:

\begin{equation}
at \ r = r_p : J_i = \frac{2 \ v_{\text{eff}} R_p}{v_{\text{eff}}} \frac{2}{\xi} \left( k_{B} C_3 \right)^{2} J_1 = \frac{2}{\xi} \left( k_{B} C_3 \right)^{2} J_1 = -k_B C_3 J_1 = 0
\end{equation}

where, as noted earlier, $\xi$ is the proportion of carbon combusting to either $CO$ or $CO_2$ at the surface of the char particle.

The boundary conditions at the boundary with the bulk flow, i.e. at $r = r_p + y$, are given in eqn. (22). The thickness of the boundary layer around the char particle, $y$, was again calculated using eqn. (19). As noted above, only the gas phase in the film surrounding the particle of char was modelled in the simplified numerical model because the combustion of char was assumed to occur only at the external surface of the char particle, as captured in the boundary condition in eqn. (23). Therefore, instead of discretising the transport equations spatially into 801 nodes, as in the full numerical model (Section 3.2), only 201 nodes were used here to model the film layer around a char particle. The 201 nodes were deemed adequate because the percentage difference of the simulated fluxes of $O_2$ at $r = r_p$, between the cases where the number of
nodes was halved and doubled, e.g. 401 and 101 nodes, were <0.005 %. Inter-particle mass transport, described by eqns. (17 – 20), with the boundary conditions, eqn. (22 – 23), was solved for numerically, again, using MATLAB solver bvp4c.

The overall rate of combustion, \( Q_c \) (mol s\(^{-1}\)) was calculated as the product of the external surface area of the fuel particle with the flux of \( O_2 \) at \( r = r_p \):

\[
Q_c = \left. \frac{2(\xi + 1)}{\xi + 2} \cdot 4\pi r^2 \rho c \right|_{r=r_p} = 4\pi r^2 \rho c \frac{dr_p}{dt} \tag{24}
\]

As noted earlier, a shrinking particle model was implemented, relating the rate of combustion, \( Q_c \), to the rate of change of the particle size, \( \frac{dr_p}{dt} \). In eqn. (24), \( \rho c \) is the molar density of the carbon particle and the term \( \frac{2(\xi + 1)}{\xi + 2} \) arises from the stoichiometric coefficient for \( O_2 \) in [R1]. Rearranging eqn. (24) shows that the burnout time of the particle, \( t_{burn} \), can be evaluated numerically from the area under the curve of the plot of \( \frac{4\pi r^2}{Q_c} \) against \( r_p \), when \( r_p \) changes form the initial radius, \( a_0 \), to complete burnout, \( r_p = 0 \). An example of the values of the rate of combustion, \( Q_c \), in Fig. 2 is 200 s.

3.4. Analytical solution with finite thickness of the gas film, \( \gamma \)

The combustion of char in a CLOU arrangement was also simulated using an analytical approach, aiming at providing a model for quick estimates of key combustion parameters, e.g. the burnout time, without the complication of constructing the numerical model. To solve the particle-scale model analytically, assumptions additional to those given in Section 3.3 were made: (a) the active species was assumed to be dilute and so Fick’s law was applied to describe the mass transport external to the fuel particle, (b) a single diffusivity, \( \mathcal{D}_m \), was used for all the gaseous species, (c) the non-linear dependence of the rate of reaction [R2], \( R_b \), with respect to the concentration of \( O_2 \) was simplified with an average value of \( c_3 = c_{3,bulk}/2 \), as previously employed in Kwong et al. [18], i.e. \( k_B = k_B (c_{3,bulk}/2)^{1/2} \cdot \exp(-2m) \). As noted previously, the combustion of char itself was modelled to occur at the particle surface by assuming Regime II combustion.

For the pseudo-steady state, the component balance of species \( i \) (CO, CO\(_2\), \( O_2 \)) surrounding the fuel particle in eqns. (17) and (18) can be written as:

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) c_i = \pm \frac{1}{r} \left( c_i \frac{d}{dr} c_i \right) = \nu_i \Omega_i c_i \tag{25}
\]

with the same boundary conditions as presented for the simplified numerical model in Section 3.3, eqn. (22 – 23). While the governing equations (25) and (26) are the same as in Kwong et al. [18], the boundary conditions account for a finite thickness of the mass transfer film around the char particle. Therefore, this analytical model gives a more realistic representation of the system, compared to the model in [18].

3.4.1. Combustion in an inert bed of SiO\(_2\) particles

With a finite thickness of the boundary layer, which was again calculated using eqn. (19), the solutions for different species in an inert bed, i.e. from eqn. (25), are:

\[
\begin{align*}
\frac{d}{dr} \left( r^2 \frac{d}{dr} \right) c_1 & = \frac{2(\xi + 1)}{\xi + 2} \cdot \frac{3}{2} \cdot \frac{k_B r_p \cdot \exp\left(m(r_p - r)\right)}{m_B (1 + \exp(-2m))} - \frac{m_B (1 + \exp(-2m))}{\exp(-2m)} \cdot \frac{r_p}{r} \\
\frac{d}{dr} \left( r^2 \frac{d}{dr} \right) c_2 & = \frac{2(\xi + 1)}{\xi + 2} \cdot \frac{k_B r_p \cdot \exp\left(m(r_p - r)\right)}{m_B (1 + \exp(-2m))} - \frac{m_B (1 + \exp(-2m))}{\exp(-2m)} \cdot \frac{r_p}{r}
\end{align*}
\]

\[
\begin{align*}
\frac{d}{dr} \left( r^2 \frac{d}{dr} \right) c_3 & = \frac{2(\xi + 1)}{\xi + 2} \cdot \frac{k_B r_p \cdot \exp\left(m(r_p - r)\right)}{m_B (1 + \exp(-2m))} - \frac{m_B (1 + \exp(-2m))}{\exp(-2m)} \cdot \frac{r_p}{r} + \frac{2(\xi + 1)}{\xi + 2} \cdot \left( \frac{r_p}{r_p + \gamma} \right)^{1/2} \cdot \frac{r_p}{r_p + \gamma} \\
& \quad \times \left( \frac{r_p}{r_p + \gamma} \right)^{1/2} \cdot \frac{r_p}{r_p + \gamma}
\end{align*}
\]
\[
I_{\text{burn}} = \frac{\rho_{\text{a}} a_o}{k_{p,C_1,b}} \left( \frac{1}{2(\xi + 1)} + \frac{\rho_r}{\mathcal{D}_e} \right) \left( a_o - \gamma \ln \left( \frac{1}{r} \right) \right) + \frac{a_o}{\gamma} \right) - \frac{\xi}{2(\xi + 1)} \frac{\rho_r}{\mathcal{D}_e} \right) m_o a_o - \ln(1 + m_o a_o) \right) \right) \right) \right)
\]  
(31)

For a stagnant system, \( r \to 0 \), the burnout time expression in eqn. (31) simplifies to:

\[
I_{\text{burn}} = \frac{\rho_{\text{a}} a_o}{k_{p,C_1,b}} \left( \frac{1}{2(\xi + 1)} + \frac{\rho_r}{\mathcal{D}_e} \right) \left( a_o - \gamma \ln \left( \frac{1}{r} \right) \right) + \frac{a_o}{\gamma} \right) - \frac{\xi}{2(\xi + 1)} \frac{\rho_r}{\mathcal{D}_e} \right) m_o a_o - \ln(1 + m_o a_o) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right)
\]  
(32)

consistent with the expression for burnout time published earlier [18], when no oxygen uncoupling occurs, i.e. \( m_o \to 0 \).

3.4.2. Combustion in an active bed of CLOU particles

With a finite boundary thickness, the solutions for different species in the bed of CLOU particles, i.e. eqn. (26), are:

\[
c_1 = \alpha c_1 \frac{2 \xi + 2}{\mathcal{D}_e} \frac{k_{r,p,C_1}}{\mathcal{D}_e} m_r \left( 1 + \exp(-2m_r) \right) + 1 - \exp(-2m_r) \frac{r}{r} \]
\]  
(33)

\[
c_2 = \alpha c_1 \frac{2 \xi + 2}{\mathcal{D}_e} \frac{k_{r,p,C_1}}{\mathcal{D}_e} m_r \left( 1 + \exp(-2m_r) \right) \]
\]  
(34)

\[
c_3 = \frac{\exp(-m_r, r)}{r} \frac{\exp(m_r, r - 2r - 2\gamma)}{r} \left( \frac{z - 1}{c_1, \gamma} \frac{( r + \gamma) \exp(m_r, r - r - \gamma)}{r} \right)
\]  
(35)

where \( m_o^2 = \frac{b_o p_o}{r} \) and \( z = c_{2b} / c_{3r} \). In the experiments in the fluidised bed of CuO-particles, \( c_{2b} \) was fixed at 1.6 vol.\%, which is \( c_{3r} \) of CuO at 1173 K; hence, \( z = 1 \) at 1173 K, and \( z > 1 \) at temperatures below 1173 K; higher temperatures were not investigated experimentally. The constant \( F \) in eqn. (35) can be expressed as:

\[
F = -F_1 c_{1,b} + F_2 c_{1,b}
\]  
(36)

where:

\[
F_1 = \left( \frac{b_o p_o}{r} \right) \left( 1 + \frac{2 \xi + 2}{\mathcal{D}_e} \right) m_r \exp(m_r, r)
\]  
(37)

\[
F_2 = \frac{(m_r, r - 1)(r + \gamma) \exp(m_r, r - r)}{m_r, r + 1 \exp(-2m_r)}
\]  
and

\[
\alpha = \frac{F_1 \exp(-2m_r) \exp(m_r, r)}{m_r, r + 1 \exp(-2m_r)} + \frac{1 - \exp(-2m_r)}{m_r, r + 1 \exp(-2m_r)}
\]  
(38)

\[
A_1 = 2c_2 \frac{2 \xi + 2}{\mathcal{D}_e} \frac{k_{r,p,C_1}}{\mathcal{D}_e} m_r, r \]
\]  
(39)

\[
A_2 = 0.
\]

When \( r \to 0 \) and \( z = 1 \), the constants in eqn. (37) become:

\[
F_1 = \frac{k_{r,p,C_1}}{\mathcal{D}_e} \left( 1 + \frac{2 \xi + 2}{\mathcal{D}_e} \right) \frac{m_r \exp(m_r, r)}{1 + m_r, r} ; F_2 = 0 ; \]
\]  
(40)

\[
\alpha = \frac{1}{1 + \frac{2 \xi + 2}{\mathcal{D}_e} \frac{k_{r,p,C_1}}{\mathcal{D}_e} m_r, r + 1 \exp(-2m_r)} + \frac{1 - \exp(-2m_r)}{m_r, r + 1 \exp(-2m_r)}
\]  
(41)

where \( A_1 = c_{1,b} \frac{2 \xi + 2}{\mathcal{D}_e} \frac{k_{r,p,C_1}}{\mathcal{D}_e} m_r, r + 1 \exp(-2m_r)
\]  
(42)

which is the same solutions as for a stagnant system, presented in [18].

4. Results

4.1. Results from fluidised bed experiments

During combustion in a fluidised bed influenced by interphase mass transfer between bubbles and particulate phase, the product of the O\(_2\) concentration at the reactor inlet, \( c_{O_2, in} \), and the burnout time, \( t_{burn} \), in an inert bed, yields a straight line with a positive gradient [32]. The results of the product of \( c_{O_2, in} \) and experimentally-determined, \( t_{burn} \), are presented in Fig. 3 for various masses of activated carbon and birch char.

In Fig. 3, all results gave positive gradients, except for the experiments in the active bed of CLOU particles at 1173 K, where interphase mass transfer was not the rate limiting factor, as discussed below. The burnout times of the activated carbon in Fig. 3(a) are longer than \( t_{burn} \) for a more reactive fuel, a birch char, in Fig. 3(b), combusted at the same conditions. The \( y \) – intercepts of the lines in Fig. 3 represent the burnout time of a single particle, i.e. without the effect of the interphase mass transfer, and are provided later in Table 2, in Section 4.4 as \( t_{burn} \) from experiments—AGC or -BIC. For the active bed, despite positive gradients at 1023 and 1098 K, the two-phase theory, and hence, Turnbull et al.’s [32] approach, cannot be directly applied, because the presence of the CLOU particle evo out the spatial distribution of O\(_2\) by accelerating the interphase mass transfer of O\(_2\) via the reduction [R4] and reoxidation of oxygen carrier. Therefore, the burnout time of a single particle of a fuel combusting in the active bed cannot be obtained by the method described by Turnbull et al. [32], except for the experiment at 1173 K, when the burnout time was independent of the mass added.

4.2. Results from numerical models (CPIM versus simplified numerical model)

Results from the full numerical model, which included the CPIM for mass transfer (described in Section 3.2), and results from the simplified model, where intra-particle mass transfer was simplified to solely Regime II combustion (described in Section 3.3), are shown in Fig. 4 for the combustion of a particle of birch char, radius 0.64 mm, at 1173 K. With this size of the char particle, the boundary thickness, \( r = 1.5 \times r_p \) and 1.3 \( \times r_p \) in a bed of CLOU particles and inert particles, respectively.

As shown in Fig. 4, in the presence of the CLOU particles, the O\(_2\) concentration remains equal to the equilibrium concentration from the edge of the boundary layer to a radial position closer to the char particle than with other cases, i.e. \( r = r_p \) of ~1.5. With a higher concentration of O\(_2\) at the surface of the char, the rate of combustion of char in the bed of CLOU particles was greater than in an inert fluidised bed, as revealed in Fig. 4(b) and (d), resulting in a higher concentration of CO and CO\(_2\) produced at the char surface. The full numerical model with CPIM (dashed lines) showed that the variation in the mole fractions and molar fluxes of the active species with radius within the char particle were
negligible, confirming the assumption that the particle combusted in Regime II and the combustion followed the shrinking particle model, i.e. combustion only occurred close to the external surface. Therefore, even when the intra-particle mass transport was not modelled explicitly, as in the simplified numerical model (solid lines), the results agreed well with the results from the more accurate numerical model with CPIM. A further estimate of the particle size of char to during transition between Regime I and II combustion is presented in SI, Section 2, showing that with the contribution of Regime I to overall burnout is insignificant for the experimental arrangement used in this work. As the combustion occurred only close to the external surface, the pressure variation within the particle was minimal, e.g. for the particle of birch char in a bed of CLOU particles at 1173 K, the pressure variation was < 3 Pa. This implies that the intra-particle mass transport can be modelled ignoring the pressure variation, i.e. eqn. (10), thus, reducing the computational efforts substantially. A simulation with the full numerical model with CPIM took ~8200 s using an Intel® Core™ i7-3370 CPU@3.40 GHz, 16 GB memory, whereas a simulation with simplified numerical model, neglecting the pressure variation and imposing Regime II simplification took <1 s, using the same machine.

Table 2
Burnout times for a single particle of birch char (BIC) and activated carbon (ACC) in a bed of inert particles and CLOU particles at various temperatures, obtained from experiments, predicted by the analytical model with finite γ (Section 3.4) and predicted by the analytical model with infinite γ by Kwong et al. [18].

<table>
<thead>
<tr>
<th>Temperature (K) and Bed</th>
<th>t_{burn} from experiments (s)</th>
<th>Prediction of t_{burn} with finite γ (s)</th>
<th>Prediction of t_{burn} for stagnant system, i.e. infinite γ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BIC  ACC</td>
<td>BIC  ACC</td>
<td>BIC  ACC</td>
</tr>
<tr>
<td>1023 (Inert)</td>
<td>700 989</td>
<td>500 980</td>
<td>872 2780</td>
</tr>
<tr>
<td>1098 (Inert)</td>
<td>475 653</td>
<td>424 666</td>
<td>761 1940</td>
</tr>
<tr>
<td>1173 (Inert)</td>
<td>325 513</td>
<td>388 522</td>
<td>621 1490</td>
</tr>
<tr>
<td>1173 (CLOU)</td>
<td>174 390</td>
<td>200 340</td>
<td>194 348</td>
</tr>
</tbody>
</table>

Fig. 3. Product of $t_{burn}$ with $c_{in,\text{o}_2}$ against the mass of (a) activated carbon and (b) birch char, added into the fluidised bed of inert materials (squares) and CLOU particles (crosses) at different experimental temperatures. The dashed and dotted lines represent the best fit to the experimental results, solely to guide eyes. Three replicates were carried out, and the error bars based on the range of the experimental result are plotted but overlap with the data markers. The results for the birch char are reproduced with permission from [18].

Fig. 4. Simulated profiles of mole fraction and mole fluxes of different species involved in the conversion of a particle of birch char with $r_p = 0.64$ mm in a bed of (a, b) SiO$_2$ particles and (c,d) CuO particles at 1173 K fluidised by 1.6 vol% O$_2$ in N$_2$ balance. The dashed lines represent results from the numerical model with CPIM described in Section 3.2, while solid lines correspond to the simplified numerical model described in Section 3.3.
analytical solution with finite on the obtained results. The simplification of a stagnant system, evaluated at 1173 K and compared with the results from the simplified numerical, as shown in Fig. 5. Additionally, the analytical solution with the simplification of a stagnant system, i.e. \( \gamma \to \infty \), from [18], was also included to study the effect of this simplification of the stagnant system on the obtained results.

The profiles of the mole fraction and molar fluxes, obtained from the analytical solution with finite \( \gamma \), agreed with the simplified numerical simulation, both in the inert and active beds, confirming that the additional assumptions made in the analytical solution, i.e. the applicability of Fick’s law for describing mass transport, as well as the simplification in the rate of homogeneous combustion of CO (i.e. \( c_1 = c_{1, \text{bulk}}/2 \), as described in Section 3.4), and the use of the single coefficient of diffusion, \( \mathcal{D} \), are sufficient for simulating the CLOU and inert combustion at the operating conditions used here. The slight differences observed for the mole fraction of CO \( \text{in Fig. 5(a)} \) and (c) were caused by the difference in the values of the diffusivity used in the numerical model and analytical solution, as confirmed by a closer agreement in the profiles between these two models when a single diffusivity, \( \mathcal{D} \), was used in the simplified numerical model (not shown here).

For an inert bed, as presented in Fig. 5(b), O\(_2\) diffuses to the surface of the char particle with a lower flux for the stagnant case (\( \gamma \to \infty \)) compared with the active bed of CuO-particles [18]. The same influx of O\(_2\) to the surface of the char resulted in the same effluxes of CO and CO\(_2\) from the particle surface from the two analytical models, as shown in Fig. 5(d). With the same fluxes of CO and CO\(_2\), a smaller boundary thickness led to a lower concentration of CO and CO\(_2\) at the surface of the char, as shown in Fig. 5(c). With the same concentration and influx of O\(_2\) at the surface of char, the same values for the rate of combustion, \( Q \), of 0.92 \( \mu \text{mol s}^{-1} \) were obtained, regardless of the boundary layer thickness. The prediction of burnout times for birch char obtained with the simplified numerical model and analytical solution for a finite value of \( \gamma \) were both 200 s, which is similar to the result from the analytical solution from [18] with the infinite \( \gamma \), 194 s.

### 4.3. Results from the analytical model

The analytical solutions for the concentration profiles of gaseous species around a burning particle of birch char in a bed of CLOU particles, eqns. (33 – 35), and in a bed of silica sand, eqns. (27 – 29), were evaluated at 1173 K and compared with the results from the simplified numerical, as shown in Fig. 5. Additionally, the analytical solution with the simplification of a stagnant system, i.e. \( \gamma \to \infty \), from [18], was also included to study the effect of this simplification of the stagnant system on the obtained results.

The profiles of the mole fraction and molar fluxes, obtained from the analytical solution with finite \( \gamma \), agreed with the simplified numerical simulation, both in the inert and active beds, confirming that the additional assumptions made in the analytical solution, i.e. the applicability of Fick’s law for describing mass transport, as well as the simplification in the rate of homogeneous combustion of CO (i.e. \( c_1 = c_{1, \text{bulk}}/2 \), as described in Section 3.4), and the use of the single coefficient of diffusion, \( \mathcal{D} \), are sufficient for simulating the CLOU and inert combustion at the operating conditions used here. The slight differences observed for the mole fraction of CO \( \text{in Fig. 5(a)} \) and (c) were caused by the difference in the values of the diffusivity used in the numerical model and analytical solution, as confirmed by a closer agreement in the profiles between these two models when a single diffusivity, \( \mathcal{D} \), was used in the simplified numerical model (not shown here).

For an inert bed, as presented in Fig. 5(b), O\(_2\) diffuses to the surface of the char particle with a lower flux for the stagnant case (\( \gamma \to \infty \)) compared with the active bed of CuO-particles [18]. The same influx of O\(_2\) to the surface of the char resulted in the same effluxes of CO and CO\(_2\) from the particle surface from the two analytical models, as shown in Fig. 5(d). With the same fluxes of CO and CO\(_2\), a smaller boundary thickness led to a lower concentration of CO and CO\(_2\) at the surface of the char, as shown in Fig. 5(c). With the same concentration and influx of O\(_2\) at the surface of char, the same values for the rate of combustion, \( Q \), of 0.92 \( \mu \text{mol s}^{-1} \) were obtained, regardless of the boundary layer thickness. The prediction of burnout times for birch char obtained with the simplified numerical model and analytical solution for a finite value of \( \gamma \) were both 200 s, which is similar to the result from the analytical solution from [18] with the infinite \( \gamma \), 194 s.

### 4.4. Comparison between the models and the experiments

Table 2 presents the results of burnout time from the combustion experiment and the predictions from the analytical solution for the combustion of a single particle of activated carbon and birch char in a bed of CLOU particles and inert materials at different temperatures. Predictions of \( t_{\text{burn}} \) in the active bed of CuO-particles for temperatures below 1173 K closely follow the results obtained in the inert bed, hence, are not shown in Table 2. The lack of difference between active and inert beds arises because the models developed focused on a single fuel...
particle and so were incapable of capturing the influence of the interphase mass transfer, which should be faster in a bed of CLOU particles than in the SiO₂ bed, as noted earlier.

As shown in Table 2, the simulated results in SiO₂ indicate the significant influence of the finite boundary thickness around the char particle. In the model where γ → ∞, the burnout times were significantly overpredicted, while here, the simulation results for a finite γ agree with the experimental values of $\phi_{\text{burn}}$. Interestingly, for CLOU, the analytical model developed assuming γ → ∞, agreed with experimental results for both fuels. The agreement arose because O₂ consumed in the combustion was constantly replenished by the CLOU particles; hence, $\phi_{\text{burn}}$ remained constant except in the vicinity of the combusting particle, as shown in Fig. 5(c). Therefore, in a CLOU arrangement, assuming γ to be infinite does not change the actual distribution of O₂ at the surface of a char particle, compared to assuming finite γ. However, for inert beds generally, assuming a stagnant system (γ → ∞) in the simplified model causes a significant over-estimation of the burnout time of a single fuel particle.

4.5. Effect of char gasification with CO₂

So far, all models developed in Section 3 have neglected the gasification of the carbon particles with CO₂, viz.

$$\text{CO}_2(g) + C(s) \rightarrow 2\text{CO}(g)$$ [R5]

Ergun [33] proposed that the overall rate of carbon conversion by gasification, $R_p$ (mol s⁻¹ g⁻¹) be described with a Langmuir-Hinshelwood expression:

$$R_p = \frac{\varepsilon k_3 p_{\text{CO}} - \frac{\rho_p}{\varepsilon_{\text{gas}}}}{p_{\text{CO}} + (k_1/k_2) + (k_3/k_1)p_{\text{CO}}}$$

(39)

where $\varepsilon$ is the concentration of active centres on the surfaces of a fuel particle per unit mass of fuel; $k_1$, $k_2$, $k_3$ are rate constants; $K_{\text{gas}}$ is the equilibrium constant for reaction [R5]; the expressions for rate and equilibrium constants are presented in Table 3. Here, the kinetic parameters for modelling [R5] were taken from Marek et al. [24], who obtained them from experiments with coal chars. This set of parameters was selected because studies of the kinetics of gasification of biomass chars are still lacking. Nevertheless, to demonstrate the effect of gasification on the predictions of the models, the accuracy of the selected kinetic parameters was deemed sufficient. Salinero et al. [34] has previously employed gasification kinetics derived from a coal char for predicting the combustion performance of a char derived from beech wood in an oxy-fuel combustion arrangement. The predicted burnout time from their model agreed with the experimental results, i.e. deviated for <15% of the burnout time determined from experiments.

The rate of gasification, $R_p$, in eqn. (39) was incorporated into the full numerical model, which contained the CPIM model, Section 3.2, by modifying the component balances for CO and CO₂ in eqns. (4 - 5), viz.

$$\frac{dJ_1}{dr} = -\frac{2}{r}J_1 + \frac{2}{r}k_3 p_{\text{CO}} + 2R_p \rho_p$$

(40)

Simulations using the full numerical model with CPIM were computationally expensive. Therefore, the simplified numerical model from Section 3.3 was also extended by adding the gasification reaction. The accuracy of the simplified numerical model with gasification reaction was examined using the results from the full numerical model with CPIM.

For the simplified numerical model, the rate of gasification was incorporated into the boundary conditions at the surface of the char particle, and eqn. (23) changed to:

$$\text{At } r = r_p: J_1 = \frac{2}{r}k_3 p_{\text{CO}} + 2 \eta_{\text{gas}} \frac{R_p C_{\text{gas}}}{2} J_2 = \frac{2}{r}k_3 p_{\text{CO}} + \eta_{\text{gas}} \frac{R_p C_{\text{gas}}}{2}$$

(41)

$J_1 = -k_p c_1$; $J_1 = 0$

(42)

where $\eta_{\text{gas}}$ is the effectiveness factor for gasification, introduced to account for the effect of the intra-particle mass transport of CO₂ and CO on the overall gasification reaction. As shown by Saucedo et al. [31], the limitations arising from the intra-particle diffusion are insignificant for coal chars at temperatures below 1123 K, hence, $\eta_{\text{gas}} = 1$. However, at $T > 1173$ K, the effect of internal mass transfer should not be ignored [31] in an atmosphere of ~80 vol% CO₂. Here, $\eta_{\text{gas}}$ was estimated numerically using an analytical expression proposed by Roberts and Satterfield [35] and modified by Sundaram [36], as shown in the SI, Section 3, e.g. $\eta_{\text{gas}}$ for a char with radius, $r_p$ of 0.64 mm, when fluidised in the mixture with 1.6 vol% O₂ at 1173 K, was calculated to be 0.71. Results from simulations with the full numerical model with CPIM, and the simplified numerical model with $\eta_{\text{gas}}$ are shown in Fig. 6, which presents mole fractions and molar fluxes during the combustion of birch char in CLOU particles fluidised by 1.6 vol% O₂ in N₂ balance, or fluidised, in a hypothetical scenario, by a mixture of 1.6 vol% O₂ in CO₂ balance.

The profiles in Fig. 6 showed a small difference between the results from the full and simplified numerical models and, hence, confirmed the validity of using the simplified numerical model to model char combustion with gasification, for two fluidising mixtures, i.e. 1.6 vol% O₂ balance in N₂ and 1.6 vol% O₂ balance in CO₂. The agreement between these two numerical models also indicated that the value of $\eta_{\text{gas}}$ determined from modified Roberts and Satterfield’s [35] expression was reasonable, for a char particle with radius of 0.64 mm at a bed temperature of 1173 K. The accuracy of $\eta_{\text{gas}}$ at other particle sizes and bed temperatures, determined using modified Roberts and Satterfield’s [35] expression was investigated by comparing with $\eta_{\text{gas}}$ estimated from the numerical model, as discussed in the SI, Section 3. In both mixtures, the concentration of O₂ drops to 0 close to the surface of the char ($r/r_p = 1$), revealing the limited penetration of O₂ into the char matrix. Within the particle, the concentration of CO₂ decreased towards the centre of the particle because of gasification with CO₂. To illustrate the effect of gasification on the gaseous profile, the results of the simplified numerical model in Fig. 6 were plotted with the results from the same model when gasification was ignored, for a birch char particle in a bed of CuO₂ fluidised by 1.6 vol% O₂ balance by N₂ or CO₂, as shown in Fig. 7.

From Fig. 7(a) and (b), for the cases with combustion in 1.6 vol% O₂ balance in N₂, the effect of gasification on the gaseous profiles, and hence, on the conversion of char, was insignificant. The negligible effect of gasification with CO₂ arises because of the low concentration of CO₂ in the system. However, for a hypothetical fluidising medium of 1.6 vol% O₂ in CO₂ balance, the effect of gasification was significant, as shown by the gas profiles in Fig. 7(c) and (d). The overall rate of char conversion was determined from the product of the external surface of the char particle with the molar fluxes of CO and CO₂ at the surface of char particle, i.e. $4\pi r_p^2 (J_1 + J_2)$. Thus, the rate of overall char conversion predicted from the simplified numerical model was $2.12 \times 10^{-6}$ mol s⁻¹, when including gasification [R5], which is ~2.4 times faster than when [R5] was neglected, i.e. $9.00 \times 10^{-7}$ mol s⁻¹. Therefore, for an industrial
Fig. 6. Simulated gas profiles of different species involved in the conversion of birch char particle, with $r_p = 0.64$ mm, at 1173 K in CuO particles fluidised by 1.6 vol % O$_2$ in (a,b) N$_2$ balance and (c,d) CO$_2$ balance. Dashed lines represent the simulation with full numerical model, which accounts for intra-particle mass transport at pseudo-steady state explicitly (CPIM). Solid lines represent the results from the simplified numerical model, assuming Regime II combustion and $\eta_{\text{gas}}$ in eqn. (42).

Fig. 7. Simulated gas profiles of different species involved in the conversion of a birch char particle, with $r_p = 0.64$ mm, at 1173 K in CuO particles fluidised by 1.6 vol% O$_2$ in (a,b) N$_2$ balance and (c,d) CO$_2$ balance. The results obtained from the simplified numerical model. The dashed lines represent the case when gasification was ignored, while the solid lines correspond to the case with gasification [R5].
application of CLOU where flue gas, rich in CO$_2$, will be recycled from the fuel reactor and used as the fluidising medium, gasification should not be ignored.

5. Discussion

5.1. The influence of $\gamma$ on the burnout time of char in an inert fluidised bed

In addition to the analytical solution developed in this work, i.e. eqn. (31), the burnout time of a single particle of char in an inert fluidised bed was also estimated using a 'modified Turnbull' expression, viz.

$$\xi + 2\frac{\rho_{sa}^2}{2(\xi + 1)} \left[ \frac{\rho_{so}}{Sh\gamma_{so}} \right]$$

(43)

The first term in eqn. (43) represents the contribution from the intrinsic kinetics and is identical to eqn. (31). As the fluidising velocity changes, Sherwood number, $Sh$, and the thickness of the boundary layer, $\gamma$, change; hence, the contribution of the external mass transfer to the overall burnout time in eqn. (43) and eqn. (31) will change, as evaluated and illustrated in Fig. 8.

As shown in Fig. 8, the mass transfer term for both eqns. (43) and (31) collapsed into the same expression, i.e. $\frac{\rho_{sa}^2}{2(\xi + 1)}$, when $\gamma \to \infty$, which is identical to a stagnant system. As $\gamma \to 0$, e.g. when char is combusting in a system with a very high fluidising flowrate, $\gamma_{so} - \gamma^2 \ln \left( 1 + \frac{\gamma}{\gamma_{so}} \right) \to 0$; hence, the mass transfer term in eqn. (31) is 0, as shown in Fig. 8. Increasing the value of $\gamma$ resulted in an increase in the burnout time. Additionally, the contribution of mass transfer to the overall burnout predicted by eqn. (31) was always larger than that from eqn. (43), with a maximum difference of ~50 s. This difference can be rationalised both mathematically and physically. Mathematically, the ratio of the gradient for the results from eqn. (31) to the gradient from eqn. (43), presented in Fig. 8, changed from 2 at $\gamma \to 0$ to 2/3 at $\gamma \to \infty$; therefore, with the same limiting values for $\gamma$, the curve from eqn. (31) must lie above eqn. (43). As discussed in Section 3.4, eqn. (31) was derived with a constant value of $\gamma$, even when $r_p$ varied from the initial radius, $a_0$, to 0, i.e. complete burnout. Therefore, during combustion, $\gamma$ in eqn. (31) was always greater than in eqn. (43), leading to a stronger influence of the inter-

![Fig. 8. Contribution of the external mass transfer term to the overall burnout time of a single char particle in an inert bed at 1173 K, fluidised by 1.6 vol% O$_2$ (N$_2$ balance) when CO$_2$ is the only product from the carbon combustion, by eqns. (43) and (31). The prediction based on a stagnant system, is also included.](image)

![Fig. 9. Simulated gas profiles of different species involved in the conversion of birch char particle, with $r_p = 0.64$ mm, at 1223 K in CuO particles fluidised by 4.9 vol % O$_2$ in (a,b) N$_2$ balance and (c,d) CO$_2$ balance. Dashed lines represent the simulation with full numerical model, which accounts for intra-particle mass transport at pseudo-steady state explicitly (CPIM). Solid lines represent the results from the simplified numerical model, assuming Regime II combustion and $\eta_{gas}$ in eqn. (42).](image)
particle mass transfer in the improved analytical solution, eqn. (31), compared to that from Kwong et al. [18].

5.2. Combustion under different operating conditions

The numerical models were used to simulate combustion at operating conditions other than those used in experiments, e.g. at a higher temperature, 1223 K, and with a higher concentration of O$_2$, 4.92 vol% O$_2$ in both N$_2$ and CO$_2$. The value of 4.92 vol% O$_2$ was selected because it is the equilibrium concentration of CuO at 1223 K. The simulated results from the full numerical model with CPIM and the simplified numerical model are plotted in Fig. 9 (a – d).

With a higher temperature and higher concentration of O$_2$, the rate of char conversion was greater, as shown by a greater magnitude of fluxes in Fig. 9 in comparison to those in Fig. 6 at 1173 K and 1.6 vol% O$_2$. For instance, overall rates of conversion of char fluidised in a bed of CLOU particles by N$_2$ at 1173 K and 1223 K were 9.44 x 10$^{-7}$ mol s$^{-1}$ and 3.34 x 10$^{-6}$ mol s$^{-1}$, respectively. When changing the operating temperature from 1173 K (pO$_{2,eq}$ of 0.0157 bar) to 1223 K (pO$_{2,eq}$ of 0.0492 bar), the pO$_{2,eq}$ increased by ~3 times. The combustion reaction over this temperature range was influenced by inter-particle mass transfer instead of intrinsic kinetics, as revealed from the low value of O$_2,eq$.

The influence of inter-particle mass transfer, the rate of char conversion, increased by ~3 times. The combustion reaction on the fluxes of CO and CO$_2$ increased by ~3 times. The decrease in the diffusivity with temperature (26), the change in the diffusivity with temperature (26). Under the influence of inter-particle mass-transfer, the rate of char conversion, Q$_c$ is proportional to pO$_{2,eq}$. The fact that the rate of char conversion also increased by ~3 times indicates that pO$_2$ has a stronger influence on the combustion of char (as the gasification was negligible in N$_2$) than the temperature, at these operating conditions. When fluidised by CO$_2$ at 1223 K, similar to the case at 1173 K, the influence of the gasification reaction on the fluxes of CO and CO$_2$ was significant, as shown in Fig. 9 (d). However, the relative contribution of gasification to the overall char conversion was smaller at 1223 K than 1173 K, owing to a more significant limitation from the intra-particle mass transfer (i.e. the lower value of η$_{gas}$) and a higher rate of combustion due to a higher concentration of O$_2$. This result contrasts with the previous study on the effect of gasification in CLOU, where gasification was also assessed numerically but without accounting for the possible influence of temperature on pO$_{2,eq}$ [37].

Using the simplified numerical model, the rate of char combustion, Q$_{comb}$ was calculated as the product of the surface area of the char with the flux of O$_2$ at the surface of the char, i.e. eqn. (24). The conversion rate of char by gasification, Q$_{gas}$, was determined similarly as the product of the surface area of the char with the fluxes of gasification at the surface and the effectiveness factor, η$_{gas}$, viz.

\[ Q_{comb} = 4 \pi r^2 \eta_{gas} R_{\text{char}} |_{r=r_i} \]

(44)

The conversion of char at 1173 K and 1223 K, by both combustion and gasification, at different concentrations of CO$_2$, were simulated using the simplified numerical model and are plotted as Fig. 10(a) and (b). Higher concentrations of CO$_2$ resulted in a greater rate of gasification and, consequently, a higher rate of char conversion. The rate of conversion due to combustion alone decreased slightly for higher CO$_2$ concentrations in the fluidising gas because the diffusion coefficients of the active species in CO$_2$ were smaller than the diffusion coefficients in N$_2$. In comparison with the 1173 K case, Fig. 10(b) shows that the relative contribution of the gasification to the overall char conversion at 1223 K was lower for the same concentration of CO$_2$, owing to a higher rate of combustion and lower value of η$_{gas}$ at 1223 K.

5.3. Temperature of a char particle

When a char particle is combusted in a bed fluidised by air (~21 vol % O$_2$), the temperature at the centre of the char particle can increase by 150 to 200 K above the bed temperature [38]. In searching for optimal operating conditions of CLOU plants, the temperature of the char particle is an important parameter, because the excess heating from the combusting char could cause the CLOU particles to sinter. Additionally, ash melting, and, hence, agglomeration of particles of the bed material also depend on the temperature of the combusting char.

In the combustion experiments discussed here, where the particles of birch char and activated carbon were ~1.2 mm diameter, the temperature of the char particle, T$_p$ can be estimated by a heat balance during steady state combustion, assuming: (a) the temperature within the char particle is uniform (the validity of this assumption is demonstrated in the SI, Section 5), (b) the solid matrix of char and the gas within the char pores are always in thermal equilibrium, (c) the contribution of transpiration to the overall heat transfer is small, (d) the rate and enthalpy of reaction are calculated based on the bed temperature instead of particle temperature (the validity of this assumption is discussed in the SI, Section 6). Then, the energy balance can be written as:

\[ Q_{comb} \left( \frac{\Delta H_1}{\Delta H_2} + 1 \right) + Q_{gas} \Delta H_2 = 4\pi r^2 \eta_{gas} (T_{bed} - T_p) + \varepsilon a (T_{bed} - T_p^\text{char}) \]

(45)

where $Q_{comb}$ and $Q_{gas}$ are the rates of combustion and gasification of a single particle of char, determined using eqn. (24) and eqn. (44), respectively, as presented in Fig. 10. Also, ΔH$_2$ is the enthalpy of reaction [R1] producing only CO, and equals ~110 kJ mol$^{-1}$ at 298 K; ΔH$_2$ is

![Fig. 10. Simulated conversion of char (r$_i$ = 0.64 mm) by gasification (dashed), combustion (dashed-dotted) and combination of both gasification and combustion (solid) surrounded by CuO particles at (a) 1173 K and (b) 1223 K when fluidised by different concentration of CO$_2$.](image-url)
Fig. 11. Simulated maximum temperature rise of the particle using heat balance at steady state for different cases studies: (a) the effect of gasification: minimum influence of gasification when fluidised by pO2,eq in N2 balance (solid line) and maximum influence of gasification when fluidised by pO2,eq in CO2 balance (dashed line) on a char with radius of 0.64 mm; (b) effect of different radius of char particle when fluidised by pO2,eq in N2 balance.

The gasification reaction, [R5], is endothermic, and hence, under the consideration of the reaction [R1] producing only CO2, equal to \(-393 \text{ kJ mol}^{-1}\) at 298 K; \(\Delta H_2\) is the enthalpy of reaction [R5], \(+173 \text{ kJ mol}^{-1}\) at 298 K; the value of \(\Delta H_1\), \(\Delta H_2\), and \(\Delta H_3\) in eqn. (45) were adjusted to allow for the reactions occurring at \(T_g\) rather that 298 K; \(h_{eff}\) is the heat transfer coefficient in the fluidised bed, calculated using correlations obtained by Parmar and Hayhurst [39]; \(\epsilon\) is the Stefan-Boltzmann constant. The calculation of \(h_{eff}\) is included in the SI, Section 4, being, typically, \(-400 \text{ W m}^{-2} \text{ K}^{-1}\) for a char particle with a radius of 0.64 mm in a bed of 1173 K.

The gasification reaction, [R5], is endothermic, and hence, under the same operating conditions, e.g. bed temperature and particle size, the temperature of the char would be the lowest when the bed was fluidised by pure CO2 corresponding to the highest rate of gasification at a given temperature. The rises in temperature of char with a radius of 0.64 mm fluidised by N2 and CO2 at various bed temperatures were evaluated and plotted in Fig. 11(a).

As shown in Fig. 11(a), when fluidised in N2 as the balance, the temperature of the char was always higher than the temperature of the bed. As \(T_b\) increased, the concentration of O2 in the bulk phase (pO2,eq of CuO rose, which led to a higher rate of combustion, and hence, a greater value of \(\Delta T_p\). When fluidised in CO2 as the balance, the temperature of the char was lower than the temperature of the bed for \(T_b\) below 1198 K, due to the significant influence of the gasification reaction. Indeed, the rate of gasification at \(T_b = 1173 K\) when fluidised by CO2 was greater than the rate of combustion, as revealed in Fig. 10. At \(T_b\) above 1198 K, the temperature of the char was higher than that of the bed and the difference in those two temperatures, \(\Delta T_p\), increased with \(T_b\). The trend of the increase in \(\Delta T_p\) with the increase in \(T_b\) was expected because the relative contribution of the gasification to the overall char conversion dropped with \(T_b\), as shown in Fig. 10.

The effect of the size of the char particle, \(r_p\), on the rise in the temperature of char, \(\Delta T_p\), at various bed temperatures, \(T_b\), when fluidised by pO2,eq in N2 balance, is plotted is Fig. 11(b). The size of the particle of char has only a weak influence on \(\Delta T_p\), especially at a low \(T_b\). In a hypothetical scenario where \(h_{eff}\) was a constant (e.g. 500 W m\(^{-2}\) K\(^{-1}\)), \(r_p\) would have a stronger influence on \(\Delta T_p\), as shown in the SI, Fig. S3. However, from the correlation of Parmar and Hayhurst [39], as \(r_p\) increased, \(h_{eff}\) decreased (as illustrated in the SI, Fig. S2). Consequently, although a decrease in \(r_p\) led to a greater heat generation per unit volume of char, an increase in \(h_{eff}\) improved the convective heat transfer; hence, the generation of heat by combustion was still balanced by the loss of heat by convection, even when \(r_p\) varied. As a result, \(\Delta T_p\) had a weak dependence on \(r_p\).

5.4. Model limitations and future work

Several phenomena were neglected in developing the models. For example, the oxidation of CO at the surface of CLOU particles, [R4], and the catalytic effect of the oxygen carrier on the homogeneous combustion of CO, [R2]. The exact contribution of [R4] to the char conversion could not be determined simply by including the rate constant of [R4] in the expression for \(m\) in the analytical solution, because the effective rate of [R4] would be affected by the CLOU phenomenon, which induced an advective flux of gaseous O2 within the particle of oxygen carrier. However, the analytical solution could be modified to incorporate [R4] alongside [R2] in a system where the oxygen carrier without oxygen uncoupling is used, e.g. in Oxygen Carrier Aided Combustion (OCAC) [41]. For an OCAC system, the main gas medium for fluidisation is air, and the particle of char is combusted by the gaseous O2 into a mixture of CO and CO2. The CO can then be converted into CO2 via both homogeneous combustion with gaseous O2 (R2) and heterogeneous reduction of oxygen carrier (R4). Chuang et al. [42] found that the rate of reduction of Cu-based oxygen carrier per unit volume of the oxygen carrier, \(R_c\), was first order with respect to the concentration of CO, i.e. \(R_c = k_c c_1\) where \(k_c\) is the rate constant. With both rates of reaction [R2] and [R4] being first order in \(c_1\), the analytical solution, i.e. eqns. (33 – 35), can be modified to describe the conversion of char by letting \(m_c\rightarrow0\) and \(m^2 = k_c (1 - \eta) h_{eff} \), where \(\eta\) is the effectiveness factor for reaction [R4] and \((1 - \eta_{eff})\) is the volume fraction of the solid in the particulate phase. The effectiveness factor can be estimated using the same equation as the oxygen uncoupling reaction described in the Section 3.2 but with a different expression for the Thiele modulus, \(\phi_{O2}\). For a first-order irreversible reaction, \(\phi_{O2} = \frac{D_{O2}}{2} \sqrt{\frac{k_{O2}}{\eta_{eff}}} \). Here, \(\phi_{1,CO2}\) represents the effective diffusion coefficient of CO in the particle of the oxygen carrier. With the above modification, the catalytic effect of oxygen carrier on homogeneous combustion, reflected by the magnitude of \(k_c\), might be determined, provided the value of \(k_c\) is known (e.g. from Chuang et al. [42]).

6. Conclusions

An analytical solution and two numerical models for a particle of char combusting in a bed of CLOU and inert particle were developed, accounting for a finite mass transfer film thickness and using the shrinking particle model. The models agreed with the burnout times determined in combustion experiments using birch char and activated carbon. The analytical solutions in this work showed a significant improvement in predicting the burnout time of particles of char in an
inert bed compared to the previous model assuming infinite boundary thickness. In operating condition outside the range investigated experimentally, the agreement between the numerical models (full numerical model and simplified numerical model) showed that the intra-particle mass transport of a particle of char residing in a bed of CLOU particles can be simplified by assuming Regime II combustion and the use of $\Delta t_{\text{char}}$. The development of the simplified numerical model reduced the computational cost substantially, without significant loss in predictive capability.

The simplified numerical model was then used to investigate various parameters, such as the rate of char conversion and the temperature rise in the char during conversion, at various operating conditions, e.g. bed temperature, and $p_{\text{O}_2}$, concentration of $\text{CO}_2$ in the fluidising gas. For industrial applications of CLOU, where fluidising gas of high $\text{CO}_2$ concentration would typically be used, the simplified numerical model shows that gasification is significant, i.e. when the concentration of $\text{CO}_2 > 70 \text{ vol}\%$ at 1173 K. The model also showed that during CLOU, while the temperature increase in the char particle, $\Delta T_p$, in a bed of 1173 K was insignificant, i.e. $\sim 40 \text{ K}$, $\Delta T_p$ at a higher bed temperatures could be significant ($>200 \text{ K}$), owing to a higher $p_{\text{O}_2}$ at $\text{CuO}$.

CRediT authorship contribution statement

K.Y. Kwong: Conceptualization, Methodology, Investigation, Writing – original draft. J.S. Dennis: Conceptualization, Methodology, Investigation, Writing – review & editing. Supervision. E.J. Marek: Conceptualization, Methodology, Investigation, 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.

Data availability

Data will be made available on request.

Acknowledgements

K.Y. Kwong acknowledges the financial support from Cambridge International Scholarship from Cambridge Trust and Gonville and Caius College. Dr Francisco Garcia Labiano, Prof. Henrik Leion, Prof. Fabrizio Scala and Prof Alberto Gomez Barea are thanked for helpful discussions and advice during FBC24. For the purpose of open access, the author has applied a Creative Commons Attribution (CC BY) licence to any Author Accepted Manuscript version arising from this submission.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2023.127902.

References


