Oxy-coal combustion in an entrained flow reactor: Application of specific char and volatile combustion and radiation models for oxy-firing conditions

L. Álvarez¹, C. Yin², J. Riaz¹, C. Pevida¹, J.J. Pis¹, F. Rubiera^{1*}

¹ Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo, Spain

² Department of Energy Technology, Aalborg University, 9220 Aalborg East, Denmark

Abstract

The deployment of oxy-fuel combustion in utility boilers is one of the major options for CO₂ capture. However, combustion under oxy-firing conditions differs from conventional air-firing combustion, e.g., in the aspect of radiative heat transfer, coal conversion and pollutants formation. In this work, a numerical study on pulverised coal combustion was conducted to verify the applicability and accuracy of several sub-models refined for oxy-fuel conditions, e.g., gaseous radiative property model, gas-phase combustion mechanism and heterogeneous char reaction model. The sub-models were implemented in Computational Fluid Dynamics (CFD) simulations of combustion of three coals under air-firing and various oxy-firing (21-35% vol O₂ in O₂/CO₂ mixture) conditions in an entrained flow reactor (EFR). The predicted coal burnouts and gaseous emissions were compared against experimental results. A good agreement between the simulations and experiments was achieved, indicating a good applicability and reliability of the refined sub-models and suitability of use of the experimentally derived kinetic data in coal devolatilisation and char oxidation sub-models. The sub-models and the practices implemented in this work can be used in large-scale oxy-fuel combustion processes for reliable design and optimization.

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* Corresponding author: Tel.: +34 985 118 975; Fax: +34 985 297 662
E-mail address: frubiera@incar.csic.es

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Nomenclature

$a_{e,i}$	emissivity weighting factors (-)
A	pre-exponential factor for coal devolatilisation (s^{-1})
A_p	projected area of the particle (m^2)
$b_{e,i,j}$	emissivity gas temperature polynomial coefficients (-)
C_d	drag coefficient (-)
c_p	heat capacity of the particle ($J\ kg^{-1}\ K^{-1}$)
C_1	mass diffusion limited rate constant (-)
C_2	kinetic rate constant (-)
D_0	bulk molecular diffusion rate coefficient ($m^2\ s^{-1}$)
E_a	activation energy for coal devolatilisation ($J\ kmol^{-1}$)
f_h	fraction of heat absorbed by char face during its combustion (-)
h	convective heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
h_{fg}	heat release due to coal devolatilisation ($J\ kmol^{-1}$)
H_{reac}	heat release due to char reaction ($J\ kmol^{-1}$)
$I(\mathbf{r}, \mathbf{s})$	radiation intensity at position $\mathbf{r}$ in direction $\mathbf{s}$ ($W\ m^{-2}$)
I_b	total blackbody intensity ($W\ m^{-2}$)
J_i	diffusion flux of species i ($kg\ m^{-2}\ s^{-1}$)
k_i	pressure absorption coefficient ($atm^{-1}\ m^{-1}$)

K	devolatilisation constant rate (s^{-1})
L	path length (m)
m_p	mass of the particle (kg)
$M_{w,i}$	molecular weight of species i ($kg\ kmol^{-1}$)
p_{ox}	partial pressure of the oxidant (Pa)
S_c	char burnout rate ($kg\ s^{-1}$)
S_i	rate of creation of species i ($kg\ m^{-3}\ s^{-1}$)
S_{Φ_k}	source term for the scalar Φ_k ((unit of Φ_k) $\cdot kg/(m^3\cdot s)$)
T_g	local temperature (K)
T_p	temperature of the particle (K)
T_{∞}	local temperature of the continuous phase (K)
u_i	gas velocity ($m\ s^{-1}$)
u_f	fluid velocity ($m\ s^{-1}$)
u_p	particle velocity ($m\ s^{-1}$)
V	cell volume (m^3)
W	mass of the volatiles (kg)
R_i	net rate of production of species i ($kg\ m^{-3}\ s^{-1}$)
$\Re$	chemical rate of the char ($kg\ m^{-2}\ Pa^{-1}\ s^{-1}$)
X_i	local mole fraction of species i (-)
Y_i	local mass fraction of species i (-)
ε	total emissivity of the gas mixture (-)

ε_p	particle emissivity (-)
κ_a	absorption coefficient (m^{-1})
θ_R	radiation temperature (K)
ρ	density of gas mixture (kg m^{-3})
ρ_f	fluid density (kg m^{-3})
η	mass conversion factor of char-N to NO (-)
σ	Stefan-Boltzmann constant ($5.67 \cdot 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$)
Γ_k	effective diffusion coefficient for scalar k
Φ_k	scalar k

1. Introduction

Oxy-coal combustion is considered to be one of the most promising CO₂ capture technologies since it can be adapted to both existing and new steam power plants. During oxy-fuel combustion, coal is burnt in a mixture of oxygen and recycled flue gas (mainly CO₂ and H₂O), to yield a rich stream of CO₂. The successful implementation of oxy-coal combustion depends on a full understanding of the difficulties that arise as a result of replacing nitrogen by CO₂ in the oxidiser stream. For instance, the change of inert nitrogen to reactive CO₂ will affect coal devolatilisation and, as a consequence, this may lead to changes in char reactivity and affect the product distribution between char and volatiles [1]. Oxy-fuel conditions will also strongly enhance radiative heat transfer, as a result of the much higher levels of CO₂, H₂O, and in-flame soot, as well as the different CO₂/H₂O ratio compared to air-firing combustion [2]. Other aspects of

combustion, such as the combustion of volatiles, flame ignition and stability, or pollutant formation, may also be affected [3, 4].

Computational Fluid Dynamics (CFD) models have been widely used to simulate combustion in coal-fired utility boilers in power stations [5-7]. Some of the sub-models integrated in a CFD model were originally developed for air-firing conditions, e.g., homogeneous and heterogeneous combustion, and gaseous radiative properties. On the basis of the accumulated knowledge of the fundamental differences between air-fuel and oxy-fuel combustion, much effort has been devoted to developing and validating sub-models for the new combustion environment. For example, considerable progress has been made recently in the modelling of radiative heat transfer in oxy-fuel combustion systems, for example, different Weighted-Sum-of-Gray-Gases-Models (WSGGMs) refined for oxy-fuel combustion modelling [8-10]. In the case of char combustion, Gil et al. [1] found that the oxidation kinetics of chars obtained in a CO₂ atmosphere were slightly different to those of chars obtained in a N₂ atmosphere. Furthermore, the mathematical model for char oxidation needs to reflect the effects of the slower oxygen diffusion and the gasification reactions in a CO₂-rich atmosphere. Also the global reaction rates of gas phase reactions in a rich CO₂ environment are likely to be different from those under conventional air-fuel conditions due to the chemical effects of CO₂. Global mechanisms have been refined for oxy-fuel conditions, based on comparisons with predictions made with a detailed chemical kinetic mechanism [11].

The aim of this study was to develop a CFD modelling methodology which would adequately describe overall combustion behaviour under oxy-firing conditions and can be used for reliable modelling of industrial oxy-coal combustion processes. In order to achieve this goal, several modifications were introduced in the char and volatile

combustion sub-models, and in the radiative heat transfer sub-models in order to adapt them to oxy-fuel combustion conditions and the refined sub-models are demonstrated in CFD simulations of oxy-coal combustion in a lab-scale entrained flow reactor.

2. Experimental procedure

The combustion experiments of this study were performed in a down-fired entrained flow reactor (EFR), which has been reported in detail elsewhere [12]. Here only a very brief description of the experimental procedure is given. Figure 1 shows a schematic diagram of the EFR. The EFR has an internal diameter of 4 cm and a height of 200 cm. For the experiments reported in this work a reaction zone of 140 cm was used.

-Fig 1 here-

Four different combustion atmospheres were employed, air-firing (21%O₂/79%N₂), and three oxy-firing in different O₂-CO₂ mixtures (21%O₂/79%CO₂, 30%O₂/70%CO₂ and 35%O₂/65%CO₂). The EFR was electrically heated and the preheated gases were introduced through flow straighteners placed on the top of the reactor to ensure laminar flow conditions. The experiments were performed at a heated furnace temperature of 1273 K. The gas flow was adjusted to 22.4 L/min, in order to ensure a residence time of 2.5 s, which would be sufficiently low to simulate the residence time in the hot zone of pf boilers and sufficiently high to ensure high burnout degrees. The excess oxygen was set to 25%. Three coals of different ranks, i.e., an anthracitic coal, a semi-anthracitic coal and a high-volatile bituminous coal, were employed in the combustion experiments. The coals were ground and sieved to obtain a 75-150 µm particle size fraction. The proximate and ultimate analyses of the coals are presented in Table 1.

-Table 1 here-

Coal was introduced from the top of the EFR through a cooled injector into the reaction zone. The reaction products were quenched by aspiration inside a stream of nitrogen using a water-cooled probe. The probe was inserted into the reaction chamber from the bottom, as shown in Fig.1. Particles were removed by means of a cyclone and a filter. The coal burnout was determined by means of the ash tracer method [13]. The experimental error in the burnout determinations was on the order of $\pm 1\%$. The exhaust gases were monitored using a battery of analysers (O_2 , CO, CO_2 , SO_2 , and NO). Their experimental error range was on the order of $\pm 5\%$.

The experimental findings for coal burnout and NO emissions have been reported in detail elsewhere [14]. All the experimental results were compared against the CFD simulations in this study, in order to derive useful guidelines or practices on how to reliably simulate oxy-fuel combustion.

3. CFD modelling

In combustion modelling, several coupled processes, such as gas and particle phase dynamics, turbulence, heat transfer, heterogeneous and homogeneous reactions, and pollutant formation must be considered and integrated. In this study, the simulations were performed using a commercial CFD package, Ansys Fluent version 13 [15]. The refined sub-models were implemented into Ansys Fluent via User-Defined Functions (UDF).

3.1. Mesh and boundary conditions

Because of the symmetrical conditions at two perpendicular mid-planes, only a quarter of the total reaction zone of the EFR (4cm i.d. $\times$ 140cm height) was used in the simulations, which was meshed using $\sim 75,000$ hexahedral cells. It was a structured mesh, in which the upper zone was locally refined to enhance the prediction of the

devolatilisation and initial combustion steps of the coal particles. The grid density was found to be sufficient to obtain grid independent solutions [16]. The 12 different combustion tests (i.e., three coals under four different compositions of combustion atmospheres, respectively) performed in the experimental study were numerically simulated here. The coal feed and mass flow rates for each test case are shown in Table 2. The reactor wall temperature was 1273 K and the injector wall temperature was 373 K.

-Table 2 here-

3.2. Gas flow simulation

The CFD model was formulated using the Eulerian-Lagrangian frame of reference. The appropriate transport equations were solved for the continuous phase and the trajectories of the particles were computed through the calculated gas field. For the gas flow, the mass, momentum, energy, and species can be solved from the following general transport equation, Eq (1):

$$\underbrace{\frac{\partial \rho \Phi_k}{\partial t}}_{\text{transient}} + \underbrace{\frac{\partial (\rho u_i \Phi_k)}{\partial x_i}}_{\text{convective}} = \underbrace{\frac{\partial}{\partial x_i} \left(\Gamma_k \frac{\partial \Phi_k}{\partial x_i} \right)}_{\text{diffusive}} + \underbrace{S_{\Phi_k}}_{\text{source}} \quad k = 1, \dots, N \quad (1)$$

In this study, steady simulations were performed for all the cases and therefore, the transient term was not included. In the general transport equation, the scalar, Φ_k , represents the k -th scalar under simulation, which is 1 for continuity equation, u_i for i -th momentum equation, turbulent kinetic energy (k) and dissipation rate (ε) in turbulence model, mass fraction of species j (Y_j) in species transport equation, and temperature (T) in energy equation. Γ_k is the effective diffusion coefficient for Φ_k , which is a summation of both laminar and turbulent contributions. S_{Φ_k} represents the

source term in the transport equation of Φ_k . When pulverized coal particles are injected into the EFR, they will travel through the gas, interact with the gas, and undergo different conversion processes (i.e., heating up and drying, devolatilisation and char oxidation), creating sources for gas-phase transport equation. The sources from the particle phase, together with sources due to gas-phase combustion, will make up S_{Φ_k} for different scalar Φ_k . The effect of turbulence was accounted for by the RNG k- ϵ turbulence model with default parameters [17]. Although this model was developed for turbulent flows, it has been successfully employed for low Reynolds-number flows [18]. The different combustion environments (e.g., air-fuel or oxy-fuel combustion) have no impact on the general transport equation and the way to solve it.

3.3. Radiative heat transfer

In a pulverised-fuel combustion chamber, radiation is the dominant mode of heat transfer and plays an important role in the source term in energy equation. In earlier effort on CFD simulation of oxy-fuel combustion, improving radiative heat transfer did not gain sufficient concerns. For example, the approach of modelling coal combustion in air was directly extended to oxy-coal combustion with no modification [19], in which the authors believed that the model would be naturally adjusted to give the proper radiative properties of the new medium based on the concentration of CO, H₂O and the substantially higher amount of CO₂. Recently, much effort was made to refine the gaseous radiative property models and implement them into CFD simulation of oxy-fuel combustion in order to greatly improve the accuracy of CFD predictions. For instance, CFD simulation of oxy-coal combustion was done through an optimized weighted sum

of gray gases model, in which the gas flame temperatures were found to be better predicted by the optimized parameters than by the air-fired parameters [20].

The radiative transfer equation (RTE) for an absorbing, emitting, and scattering medium is as follows,:

$$\frac{dI(\mathbf{r}, \mathbf{s})}{ds} = \kappa_a(\mathbf{r})[I_b(\mathbf{r}) - I(\mathbf{r}, \mathbf{s})] + \sigma_s(\mathbf{r}) \left[\frac{1}{4\pi} \int_{4\pi} I(\mathbf{r}, \mathbf{s}') \phi(\mathbf{s}' \Rightarrow \mathbf{s}) d\omega' - I(\mathbf{r}, \mathbf{s}) \right] \quad (2)$$

where $I(\mathbf{r}, \mathbf{s})$ denotes the radiative intensity at position $\mathbf{r}$ in direction $\mathbf{s}$, s represents the path length and I_b is the total blackbody radiative intensity ($=\sigma T_g^4/\pi$). $\sigma_s(\mathbf{r})$ and $\frac{\sigma_s(\mathbf{r})}{4\pi} \int_{4\pi} I(\mathbf{r}, \mathbf{s}') \phi(\mathbf{s}' \Rightarrow \mathbf{s}) d\omega'$ represent the local scattering coefficient and in-scattering gain, respectively. When particle-radiation interaction is negligible (e.g., in gaseous fuel combustion) or not considered (e.g., low particle loading in solid fuel combustion), the in-scattering gain (i.e., the 2nd term on the right hand side) will be removed from Eq. (2).

There are two key issues in the modelling of radiative heat transfer in combustion. The first is how to calculate radiative intensity at different locations, along different directions from the RTEs. A review of the various radiation models used in combustion systems for CFD applications to solve the RTE equation can be found in [21]. In all the simulations conducted in this study, the Discrete Ordinates radiation model was employed, as it is the only model which allows non-gray radiation to be computed.

The second is how to evaluate the local absorption coefficient $\kappa_a(\mathbf{r})$ and scattering coefficient $\sigma_s(\mathbf{r})$. It is comparatively easy to handle the local scattering coefficient, which is zero for gas mixture and assumed to be a constant for particles. Efforts in literature were mainly on the local gas mixture radiation properties. For the air-coal

combustion modelling, the gray formulation of the Smith et al. air-fuel WSGGM [22] was adopted to evaluate the gas mixture radiation properties. It has been widely used in air-fuel combustion modelling in the literature and it is implemented by default in the database of the commercial Ansys Fluent program. In the gray approach, constant radiative properties were assumed over the entire wavelength spectrum. The radiative intensity I represents the total intensity and κ_a denotes the gray absorption coefficient evaluated from Eq. (3). Therefore, only one single RTE per direction is solved for the entire spectrum. Thus:

$$\kappa_{a,gray} = -1/L \cdot \ln(1 - \varepsilon) \quad (3)$$

where ε represents the total emissivity of the gas mixture which was calculated from the Smith et al. air-fuel WSGGM.

Treating an oxy-coal flame as gray may lead to inaccuracies in the calculation of radiation due to the increased concentrations of CO₂ and H₂O. The combustion products have strong absorption and emission bands caused by transitions between energy levels of CO₂ and H₂O molecules at wavelengths important in combustion. Hence they exhibit spectral properties that a gray model cannot account for. In non-gray approach spectral variations are taken into account to some extent. The entire spectrum is divided into a small number of interval fractions, and one RTE per direction is solved for each interval or fraction. As shown in Eq. 4, the RTE of the i -th interval is

$$\frac{dI_i}{ds} = \kappa_{a,i} \left(a_i \frac{\sigma T_g^4}{\pi} - I_i \right) \quad (4)$$

where a_i denotes the percentage of the total blackbody radiation that corresponds to the i -th spectral fraction. For the calculation of the absorption coefficient of the gas mixture at different i -th intervals ($\kappa_{a,i}$) the Yin et al. oxy-fuel WSGGM [9] was implemented in

Ansys Fluent via UDF (User Defined Functions) subroutines. The WSGGM postulates that the total emissivity may be represented by the sum of the emissivities of N hypothetical gray gases weighted by temperature-dependent factors. In this concept, $N-1$ are the participating gray gases, each of which has a constant temperature absorption coefficient, k_i . One is clear gas, with $k_0=0$. The total emissivity is calculated from Eq. 5:

$$\varepsilon = \sum_{i=0}^N a_{\varepsilon,i}(T_g)(1 - e^{-k_i L}) \quad (5)$$

where $a_{\varepsilon,i}(T_g)$ denotes the emissivity weighting factors for the i -th gray gas based on gas temperature. For a gas mixture, P , is the sum of the partial pressures of the participating gases. The weighting factors are calculated from Eq. 6:

$$a_{\varepsilon,i} = \sum_{j=1}^J b_{\varepsilon,i,j} \left(\frac{T_g}{T_{ref}} \right)^{j-1} \quad i = 1, \dots, N \quad a_{\varepsilon,i} > 0 \quad (6)$$

The values for the coefficients k_i and $b_{\varepsilon,i,j}$, and the validation of the model, against experimental results have been reported in [9].

For oxy-fuel combustion, the importance of non-gray-gas effects has been well demonstrated in the modelling of a large-scale oxy-fuel combustion of natural gas and it was concluded that non-gray formulation of an appropriate oxy-fuel WSGGM needed to be used in order to improve the modelling of oxy-fuel combustion [23]. Therefore, non-gray calculation of the Yin et al. oxy-fuel WSGGM was performed in this study to evaluate the gaseous radiative properties in the modelling of oxy-coal combustion. This did not significantly compromise computational efficiency when compared to the conventional gray calculation of the Smith et al. air-fuel WSGGM, and was found to improve the simulations of oxy-fuel combustion processes at all scales.

3.4. Coal particles: Motion and conversion

3.4.1. Coal particle motion

The trajectories of coal particles were computed using the discrete phase model, by assuming spherical particles and retaining only the drag and gravity forces in the equation of motion of the particles. The motion equation for a representative coal particle is given by Eq. (7).

$$m_p \frac{d\vec{u}_p}{dt} = \frac{1}{2} C_D \rho_f A_p |\vec{u}_f - \vec{u}_p| (\vec{u}_f - \vec{u}_p) \quad (7)$$

The initial density of the particles was assumed to be 1550 kg/m³ for the anthracitic coals and 1400 kg/m³ for the high-volatile bituminous coal. A specific heat of 1.68J/(kg·K) was used for all the coals involved. These values were included in Ansys Fluent material database and had been determined for a wide variety of coals. The size distribution of the coal particles was fitted to a Rosin-Rammler distribution, in which the minimum, mean and maximum particle diameters are 75, 115 and 150 µm, respectively, spread parameter is unity and 5 size groups are considered. The particle sizes are sufficiently small for isothermal condition to hold, i.e., the intra-particle thermal gradients are negligible and individual fuel particles can be assumed under uniform temperature. The effect of turbulence on particle dispersion was taken into account using the discrete random walk model. When travelling through gas in the reactor, the coal particles heat up, release the volatiles, and undergo char oxidation, creating source for gas-phase combustion.

3.4.2. Coal devolatilisation

Devolatilisation is an inseparable intermediate process of combustion, which not only affects the yields of volatiles, tars and char but also determines the split of fuel nitrogen into volatiles and char. Therefore, devolatilisation has a great impact on the combustion process and a correct description of the devolatilisation process is crucial in CFD

modelling of coal combustion. The characteristics of the devolatilisation process are dependent on the type of fuel and operation conditions (temperature, heating rate, devolatilisation atmosphere). The mechanism of coal pyrolysis and product yield has been reviewed in the literature [24].

The simplest approaches for understanding the devolatilisation process are empirical and employ global kinetics, where Arrhenius expressions are used to correlate the rates of weight loss with temperature. Other approaches, such as the Kobayashi model, consider two competitive rates that control devolatilisation over different temperature ranges [25]. Network pyrolysis codes, which are based on coal structural network description, constitute one of the best means to determine the correct devolatilisation parameters compared to standard devolatilisation models [26], such as the FG-DVC (Functional Group-Depolymerisation Vaporisation Cross-linking), the FLASHCHAIN and the CPD (Chemical Percolation Devolatilisation) models. In this study the devolatilisation rate of coal was modelled using a single step first-order Arrhenius reaction. The devolatilisation law is applied to a combusting particle when the temperature of the particle reaches the vaporization temperature, T_{vap} , and remains effective as long as the mass of the particle, m_p , exceeds the mass of the non-volatiles in the particle. The rate expression for the release of volatiles can be expressed as follows:

$$-\frac{1}{W} \frac{dW}{dt} = K = A e^{-E_a / RT} \quad (8)$$

Knowledge of the kinetic values is the key point of the devolatilisation sub-model. These values (i.e., the pre-exponential factor, A , and the activation energy, E_a) can be obtained from the literature, estimated by network pyrolysis codes, or determined experimentally. Table 3 shows a summary of the different devolatilisation approaches found in the literature.

- Table 3 here-

The pre-exponential factor (A) and the activation energy (E_a) used in the present work are shown in Fig. 4 and were estimated for each of the coals by means of the FG-DVC code [37] at a temperature of 1273 K and a heating rate of 10^5 K/s under an inert atmosphere. These kinetic values were employed in both air-coal and oxy-coal combustion modelling, because the release of volatiles was not significantly affected by the devolatilisation atmospheres [38]. The comparison of coal pyrolysis in N_2 and CO_2 devolatilisation atmospheres conducted in a thermogravimetric apparatus (heating rate of 15 K/min) as illustrated in Fig. 2 also shows some evidence of this. Before devolatilisation was finished at around 1150 K, the mass loss curves in the N_2 and CO_2 atmospheres followed a similar trend. The additional mass loss in the CO_2 atmosphere above 1200 K was mainly due to the char- CO_2 reaction.

- Fig. 2 here –

-Table 4 here-

The particle heat balance during the devolatilisation process includes contributions from convection, radiation and the heat consumed during devolatilisation, as shown in Eq. 9:

$$m_p c_p \frac{dT_p}{dt} = h A_p (T_\infty - T_p) + \frac{dm_p}{dt} h_{fg} + \varepsilon_p A_p \sigma (\theta_R^4 - T_p^4) \quad (9)$$

If particle-radiation is not taken into account (due to, e.g., low particle loading), only the convection and reaction heat effects (i.e., the first two terms on the right hand side in Eq. 9) contribute to particle temperature evolution.

3.4.3. Combustion of the released volatiles

To describe the gas composition in the EFR, the species transport approach was used, together with the Eddy-Dissipation Concept for the turbulence-chemistry interaction

[39]. For the air-coal combustion cases, six species were defined as follows: CH_yO_x , O_2 , H_2O , CO , CO_2 , and N_2 . The compositions of the volatiles of each coal were derived from the FG-DVC predictions, as listed in Table 5. In the CFD simulations, the volatile gases were lumped into one single “artificial” species, CH_yO_x . The artificial volatile species and its formation enthalpy are also given in Table 5. The conservation equation for chemical species was solved in order to predict the local mass fraction of each species, Y_i . This conservation equation takes the following general form:

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\rho \mathbf{u} Y_i) = -\nabla \cdot \mathbf{J}_i + R_i + S_i \quad (10)$$

where R_i is the net rate of production of species i by chemical reaction and S_i is the rate of creation by addition from the dispersed phase. An equation of this form was solved for $N-1$ species where N is the total number of gas species present in the system. Since the mass fraction of the species must sum to unity, the N^{th} mass fraction is determined as one minus the sum of the $N-1$ solved mass fractions. To minimize numerical error, the N^{th} species is the one with the overall largest mass fraction. It is N_2 and CO_2 for air-coal combustion and oxy-coal combustion, respectively.

- Table 5 here -

Simplified global combustion mechanisms are almost exclusively used in industrial air-fuel or oxy-fuel combustion modelling. For instance, the original 2-step mechanism [40] was used oxy-coal combustion modelling [19], and an adapted 3-step global mechanism was used in modelling of oxy-coal combustion in a 100 kW_{th} chamber [20]. In this study, a 4-step global reaction mechanism was employed for gas-phase combustion of the released volatiles for both air-fuel and oxy-fuel combustion modelling. The reactions involved are given as follow [41]:

-Table 6-

The original 4-step mechanism was used for air-coal combustion. Because it was intended for air-firing conditions, it is not expected to work as well under oxy-fuel conditions. For this reason, a refined 4-step mechanism with the kinetics adapted for oxy-fuel combustion conditions [11] was employed for the various oxy-coal cases. The reaction rate expressions and kinetic parameters of both the original and the refined mechanisms are shown in Table 6. In comparison with the original multi-step mechanism, the refined mechanism provides a better description of the CO-CO₂ reactions (R2) thereby improving prediction of the major species concentration. This refined mechanism was also implemented in the CFD modelling of a 0.8 MW oxy-natural gas flame, and the predicted gas species (e.g., CO₂, O₂, CO and H₂) and gas temperature showed good agreement with the experimental results [42].

It is important to point out that although this global mechanism is a simplification, it has been widely used in combustion simulation. CFD modelling of industrial combustion applications is a computationally demanding task, so it is necessary to apply simplified reaction mechanisms in order to alleviate the computing task. These computationally cheap mechanisms do provide adequate results if only the concentrations of the main species and the temperature picture are of interest. For instance, predictions made with the multi-step mechanism employed in this work were contrasted against reference calculations conducted with a detailed chemical kinetic mechanism (DCKM) [11]. The DCKM, which takes into account the effect of a high level of CO₂ on the combustion of

volatiles, included 60 species and 424 reactions, and it was validated against oxy-fuel experiments in a reactor with an internal diameter of 70 mm and a length of 70 cm [43]. When the DCKM was implemented in Ansys Fluent for the EFR of the present work, the simulations were very significantly slowed down and no converged solution was obtained within acceptable time.

3.4.4. Heterogeneous reactions of char

After the volatile component of the particle had completely evolved, a surface reaction begins which consumes the combustible fraction, f_{comb} , of the particle. The multiple-surface-reaction model was applied to model char reactions, i.e., char oxidation and char gasification with CO_2 . At high temperatures as in this EFR, CO is the dominant product in char oxidation, $\text{C(s)} + \text{O}_2 \rightarrow \text{CO/CO}_2$ [29]. Therefore, only reaction (R5) was considered for the modelling of char oxidation. The CO formed in (R5) will undergo further reactions as shown in (R2) and (R3).

The global char combustion kinetic rate of (R5), was represented by Arrhenius expressions as given in Eq 11. As already mentioned, the devolatilisation step has a great influence in subsequent stages, such as char combustion, the kinetics of which are greatly affected not only by the operation conditions, but also by the composition of the fuel. Table 3 gives an overview of the different options for estimating the combustion kinetics. The activation energies and pre-exponential factors employed in this work are those related to the combustion of chars previously obtained in an entrained flow reactor in N_2 and CO_2 at 1273 K [1], and their values are summarized in Table 7. Equation 11 takes the form of:

$$r = -A_p P_{ox} \frac{D_0 \Re}{D_0 + \Re} \quad (11)$$

where the diffusion and kinetic rate coefficients are $D_0 = C_1((T_p + T_\infty)/2)^{0.75}/d_p$ and $\Re = C_2 e^{-E/(RT_p)}$, respectively. A more detailed multi-step model could be employed, although this would be very time consuming.

- Table 7 here -

At elevated gas temperature and CO₂ concentrations, char CO₂ gasification shows an increasingly important effect. Therefore, char CO₂ gasification was also considered in the modelling study,

The global char combustion kinetic rate of (R5), was represented by Arrhenius expressions (Eq 12). The kinetic data of (R6) were based on previous works [44, 45]: $A=192 \text{ s}^{-1} \cdot \text{atm}^{-1}$, $E_a=210 \text{ kJ mol}^{-1}$, and order of reaction with respect to CO₂, $n=0.6$.

$$r = k y_{\text{CO}_2}^n = A e^{-E_a/RT} y_{\text{CO}_2}^n \quad (12)$$

The surface reaction consumes the oxidant species (O₂) in the gas phase, i.e., it supplies a negative source term during the computation of the transport equation for this species. Similarly, the surface reaction is a source of species in the gas phase (CO, CO₂). The surface reaction also consumes or produces energy in an amount determined by the heat of reaction. The particle heat balance during the surface reaction is:

$$m_p c_p \frac{dT_p}{dt} = h A_p (T_\infty - T_p) - f_h \frac{dm_p}{dt} H_{\text{reac}} + \varepsilon_p A_p \sigma (\theta_R^4 - T_p^4) \quad (13)$$

where H_{reac} is the heat released by the surface reaction. Only a portion $(1-f_h)$ of the energy produced by the surface reaction appears as a heat source in the gas-phase energy equation: the surface absorbs a fraction f_h of this heat directly. In the case of coal combustion f_h is set to 1.0 if the char burnout product is CO. Similarly, the radiation contribution will be removed in Eq. (13) if particle-radiation interaction is not included.

The intrinsic model was also tested. However, it was not finally used due to the uncertainties with respect to model parameters, e.g., the specific internal surface area. This area varies during char combustion and is greatly influenced by the pyrolysis conditions [29]. Assuming a constant value for the internal surface area is common practice, but it can give rise to considerable errors.

For the multiple-surface-reaction model, the effectiveness factor (η) is the only parameter that needs to be determined, apart from char combustion kinetics. It is defined as the ratio of the diffusion rate to the maximum diffusion rate and used as a measure of the penetration of the oxidant into the char matrix. High values for η indicate the dominance of surface reaction over diffusion as the controlling mechanism in char combustion. The classical method to determine the effectiveness factor is via the Thiele modulus as calculated by Gharebaghi et al. [46] for a large number of defined oxy-fuel combustion cases.

3.5. NO_x formation

As NO_x is a trace species, its presence does not affect the calculation of the combustion solution. Therefore, the post-processing NO_x model was used. NO can be formed via the thermal, prompt and fuel-NO mechanism. Prompt-NO was not considered in this work since preliminary computation tests showed its contribution was negligible. Thermal-NO was only considered for air-firing conditions, for which the Zeldovich mechanism was assumed along with the partial equilibrium approach for radical O and OH concentrations, which are expressed as follows:

At near-stoichiometric conditions and in fuel-rich mixtures, a third reaction contributes:

When there is sufficient oxygen available a quasi-steady state is established and the rate of NO formation via R7-R9 becomes:

$$\frac{d[NO]}{dt} = 2k_{f,1}[O][N_2] \frac{\left(1 - \frac{k_{r,1}k_{r,2}[NO]^2}{k_{f,1}[N_2]k_{f,2}[O_2]}\right)}{\left(1 + \frac{k_{r,1}[NO]}{k_{f,2}[O_2] + k_{f,3}[OH]}\right)} \quad (R10)$$

where all the concentrations (NO, N₂, O, OH) have units of kmol/m³. In the above expression, k_{f,1}, k_{f,2} and k_{f,3} are the rate constants for the forward reactions and k_{r,1}, k_{r,2} and k_{r,3} are the respective reverse rate constants. The expressions for these rate coefficients are those given by Hanson and Salimian [47].

The fuel-NO is formed from the oxidation of molecular nitrogen organically bound within the fuel. Fuel-bound nitrogen can either be released during devolatilisation (referred to as volatile-N), or it can be retained in the char (referred to as char-N). Fuel nitrogen is distributed between the volatiles and the char. Since there is no reason to assume that N is equally distributed, the fraction of N in the volatiles and the char should be specified separately. Studies carried out by Chui et al. [48] have shown that NO predictions are quite dependent on an adequate estimation of the fuel nitrogen partitioning between the char and the volatiles. This distribution can be estimated by pyrolysis network codes, determined experimentally or obtained from the literature, as shown in Table 8.

- Table 8 here -

In this work, the partitioning of the fuel-bound nitrogen between the char and volatiles was determined experimentally during the devolatilisation of the coals in N₂ and CO₂ in the EFR (see Table 8). HCN and NH₃ are often assumed to be the dominant NO_x

precursors evolved as volatile-N. HCN and NH₃ are competitively oxidised and reduced to form NO and N₂, respectively, with the following reaction rates according to DeSoete's scheme [49]:

The governing equations for the production of HCN and NH₃ can be written as,

$$S_{HCN} = S_{vol,HCN} + S_{HCN-1} + S_{HCN-2} = M_{w,HCN} \left(\frac{S_{vol} Y_{N,vol}}{M_{w,N} V} - R_1 \frac{p}{RT} - R_2 \frac{p}{RT} \right) \quad (R15)$$

$$S_{NH_3} = S_{vol,NH_3} + S_{NH_3-3} + S_{NH_3-4} = M_{w,NH_3} \left(\frac{S_{vol} Y_{N,vol}}{M_{w,N} V} - R_3 \frac{p}{RT} - R_4 \frac{p}{RT} \right) \quad (R16)$$

where $S_{vol,HCN}$ is the source of HCN, $Y_{N,vol}$ the mass fraction of nitrogen in the volatiles, V the cell volume and S_{vol,NH_3} the source of NH₃. In this work, the evolution of volatile-N into HCN and NH₃ was based on the predictions made by Álvarez et al. [50].

The governing equations for the formation of fuel-NO can be written as follows:

$$S_{NO} = S_{NO-1} + S_{NO-3} + S_{NO-char} = M_{w,NO} \left(R_1 \frac{p}{RT} + R_3 \frac{p}{RT} + \frac{S_c Y_{N,char} \eta}{M_{w,N} V} \right) \quad (R17)$$

Char-N was assumed to be heterogeneously oxidised to NO, mainly as a desorption product from the oxidised char nitrogen atoms [51]. The fraction of char nitrogen converted to NO is roughly proportional to the char burnout rate, S_c , the mass fraction of

nitrogen in the char, $Y_{N,char}$, and the conversion factor, η . Knowledge of the empirical factor η for the conversion of char-N to NO is the key point in this formulation. In this work we have employed the value of 20% mass reported by Jones et al. [52]

4. Results and discussion

The main results of the present work are discussed in detail below. Also, Table 9 presents a comparison between the highlights of the present work and other oxy-fuel combustion modeling works.

-Table 9 here-

4.1. Temperature profiles

Combustion simulations were performed for the three coals in four different atmospheres (i.e., one air-fuel and three oxy-fuel conditions). Fig. 3 shows the CFD-predicted axial profiles of the area-weighted average gas temperature, from the top to the bottom of the EFR. For all the coals, the trend is quite similar. After the coal-oxidizer stream is fed into the EFR at a distance of 0.015 m, it is heated up rapidly. Along the centerline of the EFR, the stream temperature can rise from the inlet temperature of 373 K to over 1000 K, at about 0.1 m downstream of the feeding point. Significant devolatilisation starts quickly, releasing all the volatiles in a short distance span. The intensive combustion of volatiles in a comparatively small volume leads to a further increase in local temperature, which in turn spurs remarkable char oxidation. The temperature peaks on the EFR centerline are located at a distance of 0.15-0.3 m downstream of the coal feeding point, depending on the coal rank and firing conditions. After the volatiles have quickly burned out, char oxidation continues throughout the lower part of the EFR, resulting in a more uniform but comparatively lower temperature

profile. A monotonic increase in temperature was observed along the EFR centerline before a temperature peak was reached, followed by a monotonic, slow decrease in temperature. The local fluctuations in the area-weighted average temperature profiles around the location where the coal stream is ignited, as shown in Fig. 3, are due to the different lateral profiles of jet temperatures spread over each cross-section. The different lateral temperature profiles around the ignition location are clearly illustrated in Fig. 4.

- Fig. 3 here -

-Fig. 4 here-

Fig 4 shows the temperature contours in the mid plane of the EFR for its whole length (140 cm) and for its first 40 cm. These results correspond to the combustion of coal HVN (high rank coal) and coal SAB (low rank coal) in air-firing and oxy-firing conditions. It can be seen that higher temperatures are reached in the upper part of the reactor, where the intensive combustion of volatiles occurs and remarkable char oxidation starts. After the volatiles have rapidly burned out in a small volume in the upper part of the reactor, char oxidation continues at relatively low rates throughout the lower part of the reactor until the exit of the reactor. As a result, the temperatures are comparatively low and more uniform in the lower part of the reactor. There is also a significant decrease in the temperature contours when air is replaced by 21%O₂/79%CO₂ (see Fig. 3). CO₂ has a higher specific heat capacity than N₂. When N₂ is replaced by CO₂ for the same oxygen concentration, the specific heat capacity of the gases increases, leading to lower flame and gas temperatures. Both Fig. 3 and Fig. 4 indicate that the oxygen content in the O₂-CO₂ mixture needs to be around 30% for the low-rank coal, and around 35% for the high-rank coal, in order to obtain a similar temperature distribution under oxy-firing conditions relative to that under air-firing conditions. These temperature predictions are in good agreement with the experimental

findings observed by other researchers and summarized in [4] (i.e., in oxy-firing conditions to obtain gas temperatures similar to those in air-coal combustion, the oxygen mole fraction needs to be between 28-35% depending on the rank of the coal).

For the simulations in the oxy-fuel atmosphere with the highest CO₂ content (i.e., 21%O₂/79%CO₂) non-gray oxyfuel WSSGGM and air-fuel WSGGM calculations were both performed. Since the reactor under simulation is small (in terms of beam length), using new gaseous radiation properties led to little differences in CFD predictions. The deviations in temperature profiles for both cases were less than $\pm 1\%$. For solid fuel combustion, particle radiation plays an important role. Simulations with and without enabling particle-radiation interaction were also performed; the deviations in temperature profiles for both cases were less than $\pm 2\%$. For that reason, in the final simulations particle-radiation interaction was not taken into account due to the low particle loading.

4.2. Char oxidation and burnout

Char burnout is a key issue in the study of oxy-coal combustion, e.g., [56]. It has also been investigated in this work, both experimentally and numerically. Table 10 shows the experimental and predicted coal burnouts, as well as the deviations between them. As can be observed, this deviation is in most of the cases lower than $\pm 1\%$, i.e., lower than the experimental error associated with the determination of burnout. Thus, the predicted burnouts showed a good degree of fit with the experimental results.

- Table 10 here -

In our previous work, simulations of oxy-coal combustion were also performed [57]. Although these simulations correctly reproduced the trend of the experimental results, a more accurate description of the combustion kinetics for oxy-coal conditions was

considered to be necessary in order to achieve an improvement of the simulation results. In addition, the applicability and accuracy of some sub-models or combustion mechanisms in oxy-fuel combustion were not tested or verified. In the present work, the effects of the devolatilisation atmospheres and coal rank on char reactivity were taken into account by experimentally determining the combustion kinetics for each char. The use of the experimentally derived kinetic data, together with some special sub-models and combustion mechanisms refined for oxy-fuel conditions, significantly improved the modelling of oxy-coal combustion, including the predicted char burnouts.

- Fig. 5 here -

Figure 5 shows the predicted char reaction rates for coal HVN and SAB combustion under air and oxy-firing conditions. Basically, a similar tendency can be observed for both the coals. In the temperature range of this EFR, char combustion occurs in Regime II, where both the kinetics and diffusion play an important role. When changing from air-firing to 21%O₂/79%CO₂ oxy-firing, the temperatures in the reactor remarkably decrease, resulting in a reduced char reaction rate. When changing to 30%O₂/70%CO₂ oxy-firing, similar temperatures to those of air-firing are obtained, and the increased O₂ concentration favours a faster rate of char oxidation. When further increasing O₂ to 35% in oxy-firing conditions, both the higher O₂ concentration and the resulting higher temperatures favour an even faster rate of char oxidation. Under each of the four firing conditions, the char reaction rates are higher in the upper part of the EFR where the gas temperature peaks are located. In the two heterogeneous char reactions considered, char oxidation (R5) completely overwhelms the char CO₂ gasification (R6) in the total char burning rate. The reaction rate of the former is a few orders of magnitude higher than the latter in the temperature ranges in this EFR. As a result, the char CO₂ gasification may be neglected in this modelling study. The predicted effect of the various

combustion conditions on the overall char oxidation rate is well in line with the conventional theory expressed in terms of the so-called effective reaction rate. In combustion engineering, a simple one-step model is often employed, whose reaction rate is given by Eq (11). The effective reaction “order”, n , varies with temperature: increasing from zero at low temperatures (below 500 °C) to unity at high temperatures (above 2000 °C) [58].

4.3. Gaseous emissions

Table 11 shows the experimentally measured and CFD predicted oxygen concentrations at the outlet of the EFR, as well the deviations between them. In this case, the degree of fit between the predictions and experimental results is not as good as in the case of coal burnout. But in any case, as the experimental error is $\pm 5\%$, and most of the deviations between the predictions and experimental results are within a range of $\pm 1-10\%$, the degree of fit can be considered as acceptable. As can be seen, the oxygen values in the flue gas for combustion in 35%O₂/65%CO₂ are very high, especially for coal SAB. The 35%O₂/65%CO₂ atmosphere is an extreme oxy-fuel option, which is very unlikely to be used at industrial scale. The 30%O₂/70%CO₂ atmosphere seems to be a more attractive option, since it is enough to ensure similar burnouts to those achieved in air-firing conditions, and there is less oxygen in the flue gas. Improvement of CO₂ capture efficiency lies in the further treatment of the inert stream (O₂, N₂, Ar). For instance, Air Products are currently working on pilot scale O₂ separation by selective PRISM membrane [59]. Moreover, similar radiative heat transfer fluxes to those of air-firing conditions are achieved when the oxygen content in oxy-firing conditions is $\sim 27-30\%$ [56].

- Table 11 here -

These results are in agreement with those of Yin et al. [42] in their study of the effect of the global combustion mechanism on the species and flame temperature in air and oxy-firing conditions. Gas phase combustion mechanisms play a more important role in oxy-fuel combustion modelling than in air-fuel modelling. Therefore, mechanisms applicable to oxy-fuel combustion need to be implemented for reliable simulations of oxy-fuel combustion processes.

- Table 12 here -

Table 12 compares the experimental and predicted NO emissions for all the coals studied in air and oxy-firing conditions as well as the deviations between them. In most of the cases the deviation is lower than $\pm 5\%$, which is the value of the experimental error. Therefore, the degree of fit can be considered to be good, at least better than that of the oxygen prediction. Given the higher nitrogen content of the high-volatile bituminous coal (SAB) and its higher burnout value (i.e., greater char-N conversion to NO), one might expect the NO emissions to be the highest of the three coals studied. However, the NO emissions of SAB (both experimental and predicted) are in fact lower than those of the semi-anthracite (HVN), which has a slightly lower nitrogen content and a much lower burnout value. This can be attributed to the higher volatile matter content of SAB which may have contributed to the formation of a reducing atmosphere. A higher concentration of volatiles would lead to the formation of a large amount of NH_3 and HCN, which favor the reduction of the formed NO to N_2 via reactions (R12) and (R14). In general, a good agreement was found between the experimental and predicted results, as can be seen in Table 11, which also verifies the use of the nitrogen conversion chemistry as well as other combustion sub-models employed in this study.

-Fig 6 here-

Fig. 6 shows the predicted NO concentration profiles at the mid plane of the EFR. It can be observed that higher amounts of NO were produced close to the injection zone, especially for SAB and in oxy-firing conditions with a high oxygen content. However, some of the NO formed was later reduced to N₂ through reactions (R12) and (R14). In the lower part of the EFR where devolatilisation is finished and all the released volatiles are completely burned out, only the heterogeneous conversion of char-N to NO occurred. Also there was a decrease in NO emissions during combustion in the 21%O₂/79%CO₂ atmosphere in comparison with the air-firing conditions. This can be explained by the lower burning rate and consequently the lower char-N conversion to NO observed in the oxy-fuel atmosphere. Under oxy-firing conditions, higher oxygen concentrations result in an increase in the char burning rate and, as a consequence, the char-N conversion to NO is enhanced.

5. Conclusions

Reliable CFD modelling capability of oxy-fuel combustion was successfully demonstrated in this paper through our original efforts on refining key sub-models and making them applicable to oxy-fuel conditions, experimentally determining the required input data (e.g., devolatilization and char oxidation kinetics, volatile composition and fuel-nitrogen partitioning), and generating high-quality mesh. The refined sub-models were derived based on more general but more computationally demanding models. For instance, the gaseous radiative property model and global gas-phase combustion mechanism were refined by using the Exponential Wide Band Model and the detailed chemical kinetic mechanism as reference, respectively. Therefore, the refined sub-models can be implemented in CFD simulation of any oxy-fuel combustion process. The CFD results of coal combustion under air-firing and various oxy-firing conditions in an EFR (4 cm i.d. x 140 cm height) were found to have a good agreement with the

measured coal burnouts and gaseous emissions from the reactor. The refined sub-models and the overall modeling methodology will be used soon in a CFD analysis of an industrial 20 MW_{th} oxy-coal pf boiler.

More specifically, the refined multi-step mechanism for gas-phase combustion is recommended for oxy-fuel modelling since it better predicts gas species combustion and also improves flame temperature prediction. For gaseous radiative property modelling, though the non-gray calculation of the oxy-fuel WSGGM was not found to make significant difference from the gray calculation of the air-fuel WSGGM in the simulations of such a small reactor, non-gray calculation of an appropriate oxy-fuel WSGGM is still recommended. It does not significantly compromise computational efficiency and improves the simulations of oxy-fuel combustion processes at all scales.

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Table 1. Proximate and ultimate analyses of the coals

Sample	AC	HVN	SAB
Origin	Spain	Spain	S. Africa
Rank	an	sa	hvb
Proximate analysis (wt %)			
Moisture	2.2	1.1	2.4
Volatile matter (db)	3.6	9.2	29.9
Ash (db)	14.2	10.7	15.0
Fixed carbon ^a (db)	82.2	80.1	55.1
Ultimate analysis (wt %, daf)			
C	94.7	91.7	81.5
H	1.6	3.5	5.0
N	1.0	1.9	2.1
S	0.7	1.6	0.9
O ^a	2.0	1.3	10.5
High heating value (kcal/kg, db)	8130	8330	7820

an: anthracite; sa: semi-anthracite; hvb: high-volatile bituminous coal

db: dry basis; daf: dry and ash free basis

^a Calculated by difference

Table 2. Inputs of the CFD code for the gases and coal feed rates

Atmosphere	Gas inlet	Coal mass flow rate (g/min)		
	(g/min)	AC	HVN	SAB
21%O ₂ /79%N ₂	1.548	0.099	0.110	0.105
21%O ₂ /79%CO ₂	2.118	0.099	0.110	0.105
30%O ₂ /70%CO ₂	2.058	0.138	0.157	0.147
35%O ₂ /65%CO ₂	2.016	0.160	0.182	0.175

Table 3. Summary of research on devolatilisation, char combustion and NO formation sub-models

Authors	Sub-model	Observations
Solomon [27]	Devolatilisation	Overview on formation of pyrolysis products, kinetic rates and mechanisms of coal devolatilisation
Smith [28]	Char combustion	Overview on experimental kinetics for a wide number of coals of different rank
Laurendeau [29]	Char combustion	Overview on heterogeneous kinetics of coal char combustion
Hill [30]	NO formation	Overview of NO formation and destruction processes, and on the nitrogen pollutant formation and destruction sub-models used in combustion codes
Glarborg [31]	NO formation	Overview of the chemical and physical processes that govern formation and destruction of NO
Chen [4]	Various	Summary of CFD simulations and their sub-models for oxy-fuel combustion
Jovanovic [26]	Devolatilisation	Sensitive analysis of different sub-models (experimental, single rate model, Kobayashi model, CPD model and FG model) on ignition prediction
Backreedy [32]	Devolatilisation	Volatile composition and release rate derived from FG-DVC code
Williams [33]	Char combustion	Comparison of different sub-models (Baum and Street model, and intrinsic model) Improvements to char sub-models by taking into account coal char characterisation
Jones [34]	Devolatilisation	Comparison of different sub-models (FG-DVC, Kobayashi, SANDIA and Ubhayakar)
	NO formation	Fuel nitrogen partitioning between char and volatiles predicted by FG-DVC code
Nikolopoulos [35]	Devolatilisation	Single-step first order Arrhenius, kinetics derived from the literature
	Char combustion	Three-step semi global intrinsic kinetic law mechanism
	NO formation	Fuel nitrogen distribution gathered from the literature
Holtmeyer [36]	Devolatilisation	Single-step first order Arrhenius, kinetics derived from thermogravimetric analysis
	Char combustion	Multiple-surface reaction char model with kinetics derived from the literature
	NO formation	Fuel nitrogen distribution gathered from the literature
This work	Devolatilisation	Kinetics derived from FG-DVC code and contrasted against experimental results
	Char combustion	Kinetics derived from isothermal thermogravimetric analysis of chars obtained in N ₂ and CO ₂
	NO formation	Fuel nitrogen partitioning determined for chars after their devolatilisation in the EFR in N ₂ and CO ₂

Table 4. Devolatilisation data inputs for the CFD code

Coal	A (s ⁻¹)	Ea (kJ/kmol)
AC	3.07 10 ¹⁴	228.6±1.5
HVN	3.60 10 ¹⁴	229.7±1.8
SAB	4.68 10 ¹¹	155.9±2.6

Table 5. Composition (wt%) of the volatiles determined by FG-DVC and volatiles formation enthalpies (kJ/kmol)

Coal	CH ₄	CO ₂	CO	H ₂	CH _y O _x	ΔH _f
AC	73.4	4.7	9.0	12.9	CH _{6.21} O _{0.11}	-86×10 ³
HVN	84.5	8.5	6.1	0.9	CH _{3.87} O _{0.11}	-42×10 ³
SAB	67.9	10.9	12.2	9.0	CH _{3.56} O _{0.47}	-540×10 ³

Table 6. Kinetic rate data of the reactions involved (Units in m, s, kmol, J and K)

No.	Rate equation	A	b	E
<i>Original multi-step global combustion mechanism [41]</i>				
1	$(d[CH_yO_x]/dt) = AT^b e^{-E/RT} [CH_yO_x]^{0.2} [O_2]^{1.3}$	$2.119 \cdot 10^{11}$	0	$2.027 \cdot 10^8$
2	$(d[CO]/dt) = AT^b e^{-E/RT} [CO][O_2]^{0.25} [H_2O]^{0.5}$	$2.239 \cdot 10^{12}$	0	$1.702 \cdot 10^8$
2r	$(d[CO_2]/dt) = AT^b e^{-E/RT} [CO_2]$	$5.8 \cdot 10^8$	0	$1.702 \cdot 10^8$
3	$(d[CO]/dt) = AT^b e^{-E/RT} [CO] [H_2O]$	$2.75 \cdot 10^9$	0	$8.36 \cdot 10^7$
4	$(d[H_2]/dt) = AT^b e^{-E/RT} [H_2]^{0.25} [O_2]^{1.5}$	$6.8 \cdot 10^{15}$	-1	$1.67 \cdot 10^8$
4r	$(d[H_2O]/dt) = AT^b e^{-E/RT} [H_2]^{-0.75} [O_2][H_2O]$	$1.255 \cdot 10^{17}$	-0.877	$4.096 \cdot 10^8$
<i>Revised multi-step global combustion mechanism under oxy-fuel conditions [11]</i>				
1	$(d[CH_yO_x]/dt) = AT^b e^{-E/RT} [CH_yO_x]^{0.7} [O_2]^{0.8}$	$5.03 \cdot 10^{11}$	0	$2.00 \cdot 10^8$
2	$(d[CO]/dt) = AT^b e^{-E/RT} [CO][O_2]^{0.25} [H_2O]^{0.5}$	$2.24 \cdot 10^6$	0	$4.18 \cdot 10^7$
2r	$(d[CO_2]/dt) = AT^b e^{-E/RT} [CO_2][H_2O]^{0.5} [O_2]^{-0.25}$	$1.10 \cdot 10^{13}$	-0.97	$3.28 \cdot 10^8$
3	$(d[CO]/dt) = AT^b e^{-E/RT} [CO] [H_2O]$	$2.75 \cdot 10^9$	0	$8.36 \cdot 10^7$
4	$(d[H_2]/dt) = AT^b e^{-E/RT} [H_2]^{0.25} [O_2]^{1.5}$	$5.69 \cdot 10^{11}$	-1	$1.465 \cdot 10^8$
4r	$(d[H_2O]/dt) = AT^b e^{-E/RT} [H_2]^{-0.75} [O_2][H_2O]$	$1.255 \cdot 10^{17}$	-0.877	$4.096 \cdot 10^8$

Table 7. Char combustion kinetic parameters employed

Coal	Char obtained in N ₂		Char obtained in CO ₂	
	A (s ⁻¹)	Ea (kJ/kmol)	A (s ⁻¹)	Ea (kJ/kmol)
AC	1.20 10 ⁴	122×10 ³	7.44 10 ³	119×10 ³
HVN	5.09 10 ⁴	127×10 ³	8.10 10 ³	117×10 ³
SAB	9.48 10 ⁴	120×10 ³	2.31 10 ⁵	125×10 ³

Table 8. Nitrogen content (wt%) in char and volatiles after coal devolatilisation in the EFR in N₂ and CO₂

Coal	Char obtained in N ₂		Char obtained in CO ₂	
	N-char	N-volatile	N-char	N-volatile
AC	0.98	6.52	0.97	5.90
HVN	1.93	1.94	1.9	2.31
SAB	2.38	2.64	2.26	2.70

Table 9. Overview on oxy-fuel combustion modelling

Authors	Device	Observations
Park [53]	100 MW _e front- wall-fired furnace	Focus on the effect of combustion conditions on the wall heat flux Coal devolatilisation was predicted by a network model (FLASHCHAIN). Gas phase and char reactions kinetics taken from literature Radiation was accounted by the Yin et al. [9] oxy-fuel WSGGM model The numerical approach was not validated against experimental data. Further studies are required.
Black [54]	500 MW _e subcritical coal-fired utility boiler	Radiation was accounted by the Smith et al. [22] air-fuel WSGGM model Coal devolatilisation was predicted by a network model (FG-DVC). A two-step mechanism was used for volatile combustion and the intrinsic sub-model for char combustion [28] The simulations were validated under air-coal conditions against experimental data, but not for oxy-coal conditions CFD was used as a predictive tool to highlight the effects of different fuel and environments in an industrial boiler. However to asses the results quantitatively an update on sub-models such as radiation or char reactions will be needed
Edge [55]	0.5 MW _t combustion test facility	To determine oxy-fuel radiation properties a spectral method (FSK) was used A two-step mechanism was used for volatiles combustion and the intrinsic sub-model for char combustion [28] Focus on the effect of using Large Eddy Simulation (LES) on flow, energy and species predictions Predictions were compared against experimental measurements
Nikolopoulos [35]	330 MW _e lignite-fired power plant	For determine oxy-fuel radiation properties an Exponential Wide Band Model (EWBM) was used Char and volatile combustion kinetics obtained from literature The scope of the work was to simulate the operation conditions of a retrofitted boiler
Holtmeyer [36]	30kW _t horizontally-fired combustor	To determine oxy-fuel radiation properties an Exponential Wide Band Model (EWBM) was used Coal devolatilisation was predicted by a network model (CPD). Char and volatile combustion kinetics gathered from oxy-fuel combustion literature The numerical predictions were contrasted against experimental results
This work	Entrained flow reactor	Radiation was accounted by the Yin et al. [9] oxy-fuel WSGGM model Coal devolatilisation was predicted by a network model (FG-DVC). Volatiles combustion mechanism and kinetics, and char combustion kinetics were based on data from oxy-fuel combustion literature [1, 8] Predicted results were compared against experimental measurements Focus on the suitability of the modified sub-models for oxy-fuel combustion

Table 10. Experimental and predicted coal burnouts (%) for the three coals studied in air and oxy-fuel atmospheres (21-35%vol O₂)

	21%O ₂ /79%N ₂			21%O ₂ /79%CO ₂			30%O ₂ /70%CO ₂			35%O ₂ /65%CO ₂		
	Exp	Pred	DEV%	Exp	Pred	DEV%	Exp	Pred	DEV%	Exp	Pred	DEV%
AC	76.8±0.8	76.0	1.0	69.0±0.7	73.1	5.9	79.7±0.8	79.9	0.3	81.6±0.8	82.4	1.0
HVN	79.5±0.8	79.5	0.0	77.1±0.8	77.1	0.0	81.0±0.8	80.8	0.2	82.9±0.8	82.3	0.5
SAB	92.5±0.9	92.3	0.2	90.2±0.9	89.7	0.6	93.9±0.9	92.7	1.3	94.7±0.9	94.6	0.1

Table 11. Experimental and predicted oxygen concentrations (%vol) at the outlet of the EFR for the three coals studied in air and oxy-fuel atmospheres (21-35%vol O₂)

	21%O ₂ /79%N ₂			21%O ₂ /79%CO ₂			30%O ₂ /70%CO ₂			35%O ₂ /65%CO ₂		
	Exp	Pred	DEV%	Exp	Pred	DEV%	Exp	Pred	DEV%	Exp	Pred	DEV%
AC	9.1±0.5	10.2	12.1	11.1±0.6	11.0	0.9	13.7±0.7	14.1	2.9	15.4±0.8	16.6	7.8
HVN	8.5±0.4	8.6	1.2	9.0±0.5	8.3	7.8	10.0±0.5	10.6	6.0	13.4±0.7	13.2	1.5
SAB	8.7±0.4	8.6	1.1	9.5±0.5	8.8	7.4	13.0±0.6	11.0	15.4	23.5±1.2	20.3	13.6

Table 12. Experimental and predicted NO emissions (ppm, vol basis) at the outlet of the EFR for the three coals studied in air and oxy-fuel atmospheres (21-35%vol O₂)

	21%O ₂ /79%N ₂			21%O ₂ /79%CO ₂			30%O ₂ /70%CO ₂			35%O ₂ /65%CO ₂		
	Exp	Pred	DEV%	Exp	Pred	DEV%	Exp	Pred	DEV%	Exp	Pred	DEV%
AC	247±12	242	2.0	223±11	210	5.8	275±14	287	4.4	372±19	324	12.9
HVN	384±19	390	1.6	360±18	362	0.6	578±29	573	0.9	626±31	613	2.1
SAB	400±20	388	3.0	359±18	360	0.3	498±25	504	1.2	474±24	527	11.2

Figure captions

Fig. 1. Schematic diagram of the entrained flow reactor (EFR) used in the combustion experiments.

Fig. 2. Mass loss rate for the three coals studied during devolatilisation tests in N_2 and CO_2 (TG apparatus, heating rate of 15 K/min).

Fig 3. Predicted area-weighted average temperature during combustion in air and oxy-fuel atmospheres (21-35% O_2) for the three coals studied.

Fig. 4. Predicted temperature (K) inside the entrained flow reactor during coal combustion for each atmosphere: air and O_2/CO_2 (21-35% O_2). Length scale is 140 and 40 cm respectively.

Fig. 5. Predicted char reaction rate (kg/s) inside the entrained flow reactor during coal combustion for each atmosphere: air and O_2/CO_2 (21-35% O_2). Length scale is 140 and 40 cm respectively.

Fig. 6. Predicted NO concentration (ppm, vol basis) inside the entrained flow reactor during coal combustion for each atmosphere: air and O_2/CO_2 (21-35% O_2). Length scale is 140 and 40 cm respectively.

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