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# Oxy-fuel combustion kinetics and morphology of coal chars obtained in $N_2$ and $CO_2$ atmospheres in an entrained flow reactor

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ABSTRACT

The thermal reactivity and kinetics of four coal chars (HVN, UM, SAB and BA) in an oxy-fuel combustion atmosphere (30%$O_2$–70%$CO_2$) were studied using a thermobalance. The coal chars were obtained by devolatilization in an entrained flow reactor (EFR) at 1000 °C for 2.5 s under 100% $N_2$ and $CO_2$ atmospheres. The reactivity tests were carried out by isothermal thermogravimetric analysis at different temperatures in a kinetically controlled regime. Three *n*th-order representative gas–solid models – the volumetric model (VM), the grain model (GM) and the random pore model (RPM) – were employed in order to describe the reactive behaviour of the chars during oxy-fuel combustion. From these models, the kinetic parameters were determined. The RPM model was found to be the best for describing the reactivity of the HVN, UM and BA chars, while VM was the model that best described the reactivity of the SAB char. The reactivities of the chars obtained in $N_2$ and $CO_2$ in an oxy-fuel combustion atmosphere with 30% of oxygen were compared using the kinetic parameters, but no differences were observed between the two devolatilization atmospheres. The apparent volatile yield after the coal devolatilization under $CO_2$ in the EFR was greater than under $N_2$ for all the coals studied. According to the scanning electron microscopy (SEM) images of the chars, those obtained in the $CO_2$ atmosphere experienced a greater degree of swelling, some particles showing partially reacted surfaces indicative of reaction between the char and $CO_2$.

## 1. Introduction

The use of coal in power plants generates a large amount of $CO_2$, which is the chief contributor to global climate change. However, coal is the most abundant and geographically the most widely distributed fossil fuel. The stability of its supply and its relatively low cost will ensure its inclusion in the energy mix in the foreseeable future [1]. Several strategies for the reduction and capture of $CO_2$ from large-scale stationary power plants are being studied. The main problem is that the concentration of $CO_2$ in a conventional coal-air combustion flue gas stream is low (typically 15% by volume), rendering it unsuitable for direct sequestration in a supercritical state via compression which requires a high concentration of $CO_2$ [2]. As an alternative, the oxy-fuel combustion process has been proposed as a promising technology for $CO_2$ capture from fossil fuel power plants. This technology involves the combustion of coal in a mixture of oxygen (instead of air) and recycled flue gas (RFG), which consists mainly of $CO_2$ and $H_2O$ [3]. In this process, the net volume of flue gas is reduced and a highly concentrated $CO_2$ (95%) flue gas is produced, which after purification [4,5] can be directly stored in a supercritical state by means of compression.

The combustion of coal in the $O_2/CO_2$ atmosphere of an oxy-coal combustion boiler can be expected to be different from that of an $O_2/N_2$ atmosphere of a conventional coal-air combustion boiler, because $CO_2$ has a larger specific molar heat than $N_2$, and the coal may be gasified by the $CO_2$ [6]. The use of $CO_2$ instead of $N_2$ may also cause a reduction in the propagation speed, stability of the flame and gas temperature profile or lead to an increase in the unburned carbon content. During the oxy-fuel combustion process, these problems can be overcome by increasing the oxygen concentration in the oxidizer (up to approximately 30%) in order to match the combustion performance achieved in air.

In addition, oxy-coal combustion can be used as retrofit technology in conventional pulverized coal boilers to capture and store carbon. However, the successful implementation of $O_2/CO_2$ technology in conventional pulverized coal boilers requires a full understanding of the changes that occur when $N_2$ is replaced by $CO_2$ in a combustion atmosphere [7]. A precise knowledge of char reactivity and kinetics under a $CO_2$ atmosphere is essential for designing and modelling oxy-fuel combustion at industrial scale. In modelling studies related to oxy-coal combustion, coal pyrolysis during oxy-coal combustion is usually assumed to be the same as in air [8]. According to Naredi and Pisupati [9], it is necessary to establish whether the pyrolysis of coal particles in $CO_2$ will produce different results from pyrolyzing them in an inert gas medium. Knowledge of coal pyrolysis under a $CO_2$ atmosphere is

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essential for understanding the process of oxy-fuel combustion [10].

The aim of the present work is to study the oxy-fuel combustion (30%$O_2$–70%$CO_2$) reactivity and kinetic behaviour of four coal chars obtained under $N_2$ and $CO_2$ atmospheres. For this purpose, three mathematical models – the volumetric model (VM), the grain model (GM) and the random pore model (RPM) – were used to determine the kinetic parameters which best represent the oxy-fuel combustion characteristics of the coal chars obtained in $N_2$ and $CO_2$ under an oxygen–carbon dioxide atmosphere. The morphology of the coal chars was compared by scanning electron microscopy (SEM).

## 2. Experimental

### 2.1. Fuel samples

Four coals of different rank were used: a semi-anthracite (HVN), a medium-volatile bituminous coal (UM) and two high-volatile bituminous coals (SAB and BA). The samples were ground and sieved to obtain a particle size fraction of 75–150 μm. The results of the proximate and ultimate analyses and high heating values of the samples are shown in Table 1.

### 2.2. Char preparation

The chars were prepared by devolatilizing the raw coals in an electrically heated entrained flow reactor (40 mm internal diameter, 1400 mm length) in streams of 100% $N_2$ or 100% $CO_2$ (4.79 N L $min^{-1}$). The experimental device has been described elsewhere [11,12]. The devolatilization experiments were carried out at a reactor temperature of 1000 °C and a particle residence time of 2.5 s. After the experiments, the chars were cooled down under a flow of nitrogen to room temperature. A water-cooled collecting probe was inserted into the reaction chamber from below to collect the char samples. The external morphology of the coal chars was examined by means of scanning electron microscopy (SEM).

### 2.3. Oxy-fuel combustion reactivity tests of the chars

Thermogravimetric analysis (TGA) is one of the most commonly used techniques to investigate and compare thermal events and kinetics during the combustion and pyrolysis of solid raw materials, such as coal and woods [13–17]. The reactivity tests were conducted in a thermobalance (Setaram TAG24) at atmospheric pressure. Approximately 5 mg of char sample was placed in a crucible of height 2 mm with a circular base 5 mm in diameter. A thermocouple was located close to the platinum basket to monitor the temperature and to close the control loop. In this work, all the experiments were performed under isothermal conditions at different temperatures (400–600 °C). These temperatures were chosen in order to avoid diffusion problems and consequently apply the Arrhenius plot for calculating the kinetic parameters. The total flow rate of the reactive gas introduced into the thermobalance during the oxy-fuel combustion experiments was 50 N mL $min^{-1}$, the gas consisting of 30% $O_2$ and 70% $CO_2$. The char conversion, $X$, and the reaction rate, $dX/dt$, were calculated.

**Table 1**
Proximate and ultimate analyses and high heating value of the coals.

| Sample<br>Origin<br>Rank | HVN<br>Spain<br>sa | UM<br>Mexico<br>mvb | SAB<br>South Africa<br>hvb | BA<br>Spain<br>hvb |
|---|---|---|---|---|
| *Proximate analysis*[a] | | | | |
| Moisture content (wt.%) | 1.1 | 0.4 | 2.4 | 1.2 |
| Ash (wt.%, db) | 10.7 | 21.1 | 15.0 | 6.9 |
| VM (wt.%, db) | 9.2 | 23.7 | 29.9 | 33.9 |
| *FC* (wt.%, db)[b] | 80.1 | 55.2 | 55.1 | 59.2 |
| *Ultimate analysis (wt.%, daf)*[a] | | | | |
| C | 91.7 | 86.2 | 80.8 | 88.5 |
| H | 3.5 | 5.5 | 5.0 | 5.5 |
| N | 1.9 | 1.6 | 2.0 | 1.9 |
| S | 1.6 | 0.8 | 0.9 | 1.1 |
| O[b] | 1.3 | 5.9 | 11.3 | 3.0 |
| *HHV* (MJ/kg, db) | 31.8 | 27.8 | 27.8 | 33.1 |

sa: Semi-anthracite; mvb: medium-volatile bituminous coal; hvb: high-volatile bituminous coal.
db: Dry basis and daf: dry and ash free bases.
[a] The proximate analysis was conducted in a LECO TGA-601, and the ultimate analysis in a LECO CHNS-932.
[b] Calculated by difference.

## 3. Kinetic models

A general kinetic expression for the overall reaction rate in gas–solid reactions can be expressed as follows [18]:

$$dX/dt = k(P_g, T)f(X) \tag{1}$$

where $k$ is the apparent combustion reaction rate, which includes the effect of temperature ($T$) and the effect of the reactive gas partial pressure ($P_g$), and where $f(X)$ describes the changes in the physical or chemical properties of the sample as the combustion proceeds. Assuming that the partial pressure of the reactive gas remains constant during the process, the apparent combustion reaction rate will be dependent on the temperature and can be expressed using the Arrhenius equation, as follows:

$$k = k_0 \exp^{-E/RT} \tag{2}$$

where $k_0$ and $E$ are the pre-exponential factor and activation energy, respectively.

In this work, three $n$th-order models were applied in order to describe the reactivity of the chars studied: the volumetric model (VM), the grain model (GM) and the random pore model (RPM). These models give different formulations of the term $f(X)$, with $X$ representing the degree of char conversion on a dry ash-free basis.

The VM assumes a homogeneous reaction throughout the particle and a linearly decreasing reaction surface area with conversion [19]. The overall reaction rate is expressed by:

$$dX/dt = k_{VM}\ (1 - X) \tag{3}$$

The GM or shrinking core model, proposed by Szekely and Evans [20], assumes that a porous particle consists of an assembly of uniform nonporous grains and that the reaction takes place on the surface of these grains. The space between the grains constitutes the porous network. The shrinking core behaviour applies to each of these grains during the reaction. In a regime of chemical kinetic control and, assuming that the grains have a spherical shape, the overall reaction rate can be expressed as:

$$dX/dt = k_{GM}\ (1 - X)^{2/3} \tag{4}$$

This model predicts a monotonically decreasing reaction rate and surface area because the surface area of each grain is receding during the reaction.

The RPM model considers the overlapping of the pore surfaces, which reduces the area available for reaction [21]. The basic equation for this model is:

$$dX/dt = k_{RPM}\ (1 - X)[1 - \psi \ln(1 - X)]^{1/2} \tag{5}$$

This model is able to predict a maximum value of reactivity as the reaction proceeds, as it considers the competing effects of pore growth during the initial stages of combustion and the destruction of the pores due to the coalescence of neighbouring pores during the reaction. The RPM model employs two parameters, the