

# Combustion Reactivity of Unburned Carbon in Coal Combustion Fly Ashes

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## ABSTRACT

Oxidation reactivity studies are imperative for improving carbon re-burn technologies and using the heat content of unburned carbon within coal combustion ashes. Non-isothermal, thermal gravimetric analysis (TGA) was used to examine the oxidation kinetics of unburned carbon in coal combustion fly ashes having different particle size distributions, the results from which were related to combustion efficiencies as measured in a bench-scale rotary kiln. The activation energy and pre-exponential factor were determined for the chemically-controlled reaction regime; the transition temperatures between chemically-controlled and partially diffusion-controlled combustion regimes were obtained for unburned carbon particles of different sizes. After the oxidation reaction rates were evaluated, the residence time distribution (RTD) of fly ashes in the rotary kiln were experimentally measured and the mean residence times related to process parameters, including the rotating velocity and kiln inclination. By comparing these results with an advective-dispersive model, the axial dispersion coefficient of fly ashes was determined. The reaction rates obtained by thermal analyses and the RTDs were used to predict combustion efficiencies within the kiln. They are related to the efficient oxidation of unburned carbon using various industrial processing options.

## INTRODUCTION

Coal combustion, which is the main source of energy in Italy and in many other countries, produces massive quantities of CCBP (Coal Combustion By-Products): most of these are fly ashes which are made of coal mineral impurities altered by the thermal treatment and unburned carbon. Since unburned carbon content may hinder fly ash re-use in cement and concrete markets, several efforts have been devoted in the last years to develop cost effective processes in order to meet the ASTM and UNI specifications (ASTM C618, UNI – EN 450)<sup>1,2</sup> in USA and EU, respectively. The issue of carbon content in fly ash has risen after the introduction of low-NO<sub>x</sub> burners in utility boilers which cause reactivity loss during combustion and consequential higher amount of unburned carbon in fly ash. Different processes, encompassing physical separation and carbon re-burning, have been developed for reducing unburned carbon in utility fly ash.<sup>3,4</sup> Although different re-burning technologies have been

studied and some of them commercially applied,<sup>4</sup> few studies are available on the kinetic of carbon removal by thermal oxidation in pilot scale reactor related to carbon physical properties and deactivation degree. Three main tasks were carried out in this study, aimed to investigate the best suited setting conditions of a rotary kiln, with reference to basic properties of unburned carbon. First the properties of unburned carbon derived from two large utilities in terms of surface area and reactivity in thermogravimetric (TG) analyses were investigated. Second, motion and axial mixing of ash in a pilot scale rotary kiln were experimentally studied and described with an advective-dispersive model. Finally, kinetic parameters derived from TG measurements and residence time distributions can be used to predict combustion efficiencies within the kiln.

## EXPERIMENTAL

Fly ashes originated from two different coal-fired utility boilers (UB1, UB2) were used in this study. The as-received sample (AR) from UB1 was fractionated by standard dry-sieving techniques, obtaining three samples labeled as SF1 (>150  $\mu\text{m}$ ), SF2 (75-150  $\mu\text{m}$ ) and SF3 (<75  $\mu\text{m}$ ). Three fly ashes (ESP1-3) were collected from the hoppers at different lines of an electrostatic precipitator in UB2 fired with 60/40 blend of Venezuelan/Russian coals; a char was originated by pyrolysis of this coals blend. A thermogravimetric apparatus Netzsch STA 409 was used for coal blend pyrolysis, reactivity measurements by means of non-isothermal analyses for the samples ESP1-3 and isothermal analyses at 550, 600, 700 and 1000° C for samples AR, SF1-3. Surface area of UB1 samples heated at 700° C was measured and assumed as the inorganic fraction contribution. The carbon's contribution to the surface area was calculated from the surface area of the total fly ash less the inorganic contribution. The porosity of all samples was determined via N<sub>2</sub>-adsorption isotherms at 77 K using a Autosorb-1 adsorption apparatus (Quantachrome Instruments, USA). A continuous flow rotary kiln (Lenton furnaces, U.K.) was used either to measure the mean and axial-dispersion coefficient or to carry out combustion experiments with a rotation speed ranging from 2 to 20.7 RPM. A vibratory feeder was manually controlled to provide feed rates with a range of 0.05-1.00 g/s. AR fly ash was heated at 600°C in the kiln for complete carbon removal, so that its color changed from dark gray to light yellow and it was used as tracer during tests carried out to determine residence time distribution (RTD). During combustion experiments the temperature ranged from 525 to 600° C.

## RESULTS AND DISCUSSION

Data collected during non-isothermal thermogravimetric oxidation of ESP1-3 samples were used to obtain model prediction according to a Volumetric Reaction Model (VRM).<sup>5</sup> Figure 1 shows that synthetic char reacts at higher temperature than residual carbon having the same parent coal, hence demonstrating the expected minor reactivity of unburned carbon than char pyrolysed at 950° C.<sup>5</sup> These results are a consequence of thermal annealing whose effects depend on different thermal histories char undergoes. In figure 2 are shown the curves of char conversion rate ( $dX/dt$ ) versus temperature (T) of samples originated from UB1, where X is the char conversion.<sup>5</sup>

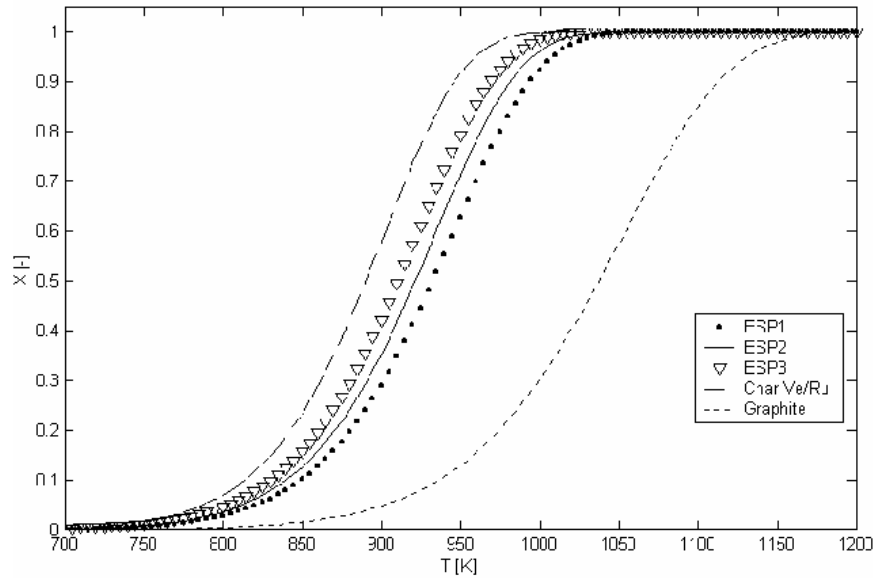


Fig. 1: Oxidation profiles of char, UB2 samples and commercial graphite.

It was observed that the finer samples, with higher total surface areas, oxidize faster. Actually, all the ash samples having different particle sizes have approximately the same specific surface areas, calculated as  $\text{m}^2$  per gram of carbon. Particles of different sizes experience different thermal deactivations (annealing): the coarser the size fraction, the higher the annealing will be.<sup>6</sup> Furthermore, the oxidation profiles of AR and SF3 may indicate that the organic matter in the ash is quite homogeneous, while unburned carbon of SF2 and SF1 samples has two distinct phases with different reactivity, highlighted by two peaks in the curves. The abundance of the less reactive phase grows as the particle size increases, thus explaining the lower reactivity of samples SF1-2. As the as-received ash is mostly ( $\approx 80\%$ ) constituted of fine particles, his reactivity resembles that of sample SF3.

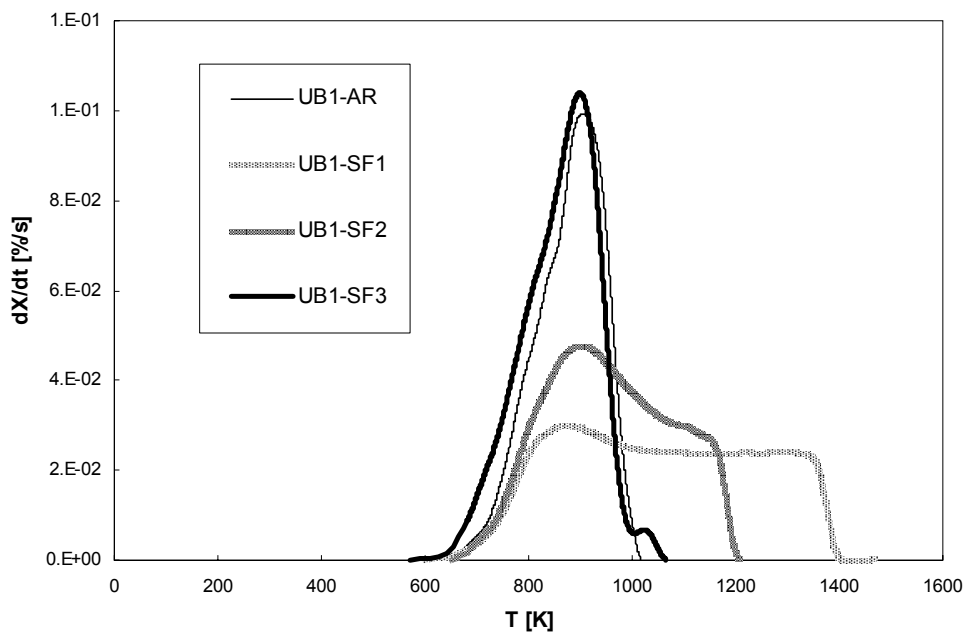


Fig. 2: DTG curves of UB1 samples

Experimentally measured mean residence times were compared with those calculated by a model for particle motion in rotating drums.<sup>7</sup> Fig. 3 shows that plug flow velocity was higher with both increasing rotational speed and slope of the kiln and, on the whole, a good agreement was achieved between experimental data and simulated curves (figure 3).

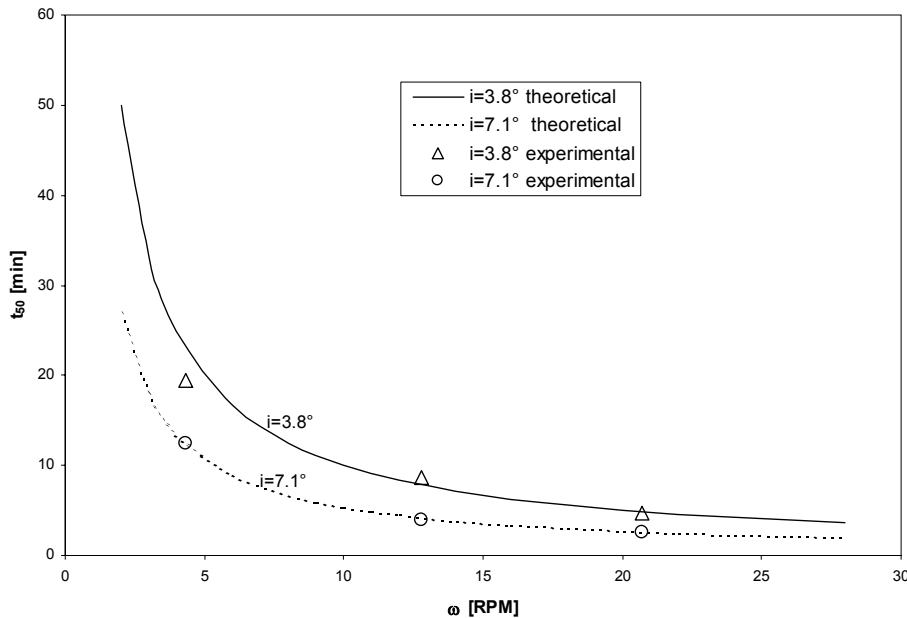


Fig. 3: Mean residence times curves of fly ashes in the rotary kiln

Unburned carbon oxidation data in the pilot scale rotary kiln were described by coupling results of char reactivity obtained in the first part of the study and residence time distribution derived from tracer experiments.<sup>8</sup> In particular, VRM, fitted to results obtained in TG, was used as kinetic model to describe the combustion at constant temperature for a char particle reacting for a given time. The convolution integral used to determine the mean conversion of the exit stream of ash has been calculated by discretizing the function representing the residence time distribution. Experimental and theoretical decreases in LOI after thermal treatments in the rotary kiln are shown in figure 4a and 4b for AR and SF3, respectively.

As expected, both simulated and theoretical curves display lower residual LOI after combustion with increasing either mean residence time or combustion temperature. The differences between experimental and simulated curves are mostly related to the usage of VRM as kinetic model for char combustion in a rotary kiln, since residence time distribution fits perfectly to experimental results and the convolution model has reliable theoretical bases.

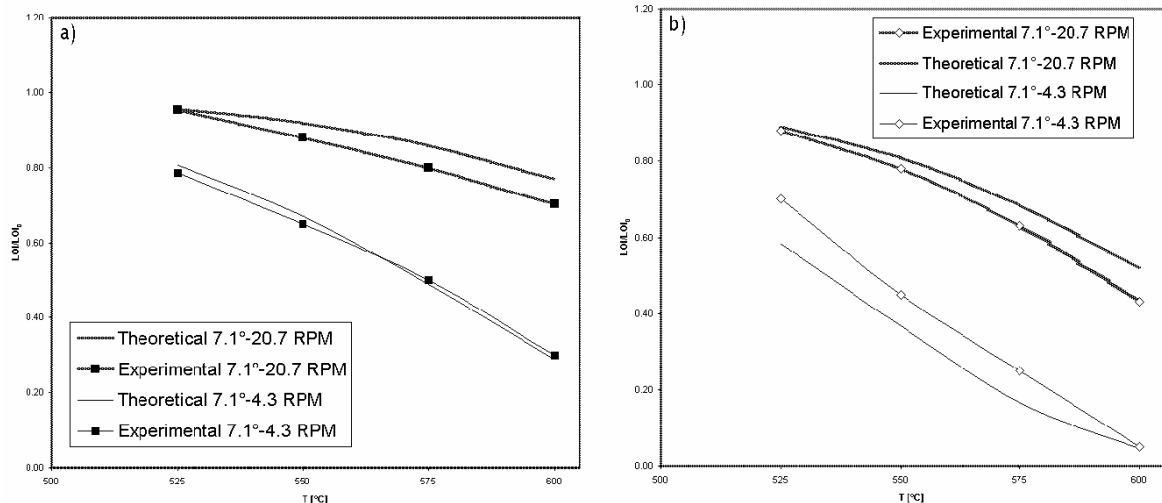


Fig. 4. a) Experimental and theoretical curves of AR sample. b) Experimental and theoretical curves of SF3 sample

## CONCLUSIONS

The experimental and theoretical investigation to study the combustion reactivity of fly ashes of different characteristics was carried out in three phases. TG experiments showed that different degrees of thermal deactivation that carbon particles experience, result in higher loss of reactivity of coarser particle fractions.

Tests performed on the rotary kiln allowed to characterize both the advective and dispersive components of fly ash motion, showing good agreements with theoretical predictions. Results derived from thermal reactivities and residence time distribution studies were coupled to better understand the observed trend. On the whole, experimental data were fairly comparable to model interpretations, although further efforts are required to achieve quantitative reliable predictions and choose appropriate processing conditions.

## ACKNOWLEDGMENTS

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