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# Oxy-fuel combustion of millimeter-sized coal char: Particle temperatures and NO formation

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## HIGHLIGHTS

- Combustion of millimeter sized char particles in fixed bed reactor.
- Combustion in $O_2/N_2$ and $O_2/CO_2$ atmospheres up to 80 vol.% $O_2$.
- Particle temperatures determined by CCD camera.
- NO yields from char combustion determined.

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## ABSTRACT

In this work, differences in particle temperature and NO yield during char oxidation in $O_2/N_2$ and $O_2/CO_2$ atmospheres, respectively, have been examined. A laboratory scale fixed bed reactor, operated isothermally at 1073 K, was used for combustion of millimeter-sized lignite and bituminous coal char particles in 5–80 vol.% $O_2$. Experiments were carried out with both single particles of different sizes (1.3–543 mg) and multiple particles (30–50 mg). Particle temperatures and structural changes were recorded by a Charged Coupled Device (CCD) camera during the experiments. The particle surface temperatures increased with mass loading, by as much as 700 K above the furnace set point. The formation of NO from lignite char was not influenced by the change from $N_2$ to $CO_2$ whereas the NO yield from bituminous coal char was considerably lower in $O_2/CO_2$ compared $O_2/N_2$. For both chars the conversion to NO decreased as the $O_2$ concentration or the particle size increased. However, for the bituminous coal char, a peak in NO yield was observed at an intermediate particle size of 0.1–0.2 g. The differences in the effect of gas atmosphere, $O_2$ concentration, and particle mass on the NO yield from oxidation of bituminous coal char and lignite char, respectively, cannot be fully explained. Char/NO interactions appear to be quite complex, and mineral catalysis and release to the gas-phase of volatile N-species such as HCN, either from secondary pyrolysis or as a product of the char–N + $O_2$ reaction, may play a role.



## 1. Introduction

The focus in recent years on anthropogenic $CO_2$ emissions and their effect on the earth's climate has lead to research programs that aim at reducing the $CO_2$ emission from fossil fueled heat and power production. An interesting technology in this context is oxy-fuel combustion, where recycled flue gas is mixed with $O_2$ before the boiler entrance. The oxy-fuel technology yields a plant exit stream with a high $CO_2$ concentration, facilitating subsequent capture and sequestration [1,2].

The change from $N_2$ to $CO_2$ as the dominant gaseous species alters the characteristics of NO formation and reduction and facilitates lower emissions of NO [1–11]. Even though mechanisms of NO formation and reduction have been extensively studied [12–14], questions remain unanswered, making interpretation of results obtained under oxy-fuel conditions difficult. In their recent study of NO formation during oxy-fuel combustion, Hashemi et al. [11] identified char/N interactions at high $CO_2$ conditions as an area of uncertainty. Oxidation of char–N and the reaction between char and NO have been studied extensively [14–29], but little is known about char/N interactions under oxy-fuel conditions. Questions relate to the effect of mineral catalysis [30–32], coal rank [23] and CO concentration [30,33,34] in heterogeneous NO reduction. Recent results indicate that the homogeneous kinetics of NO under oxy-fuel conditions, which change significantly compared to combustion in air, are fairly well described [8,9,35]. However, in order to utilize the potential of reduced NO emissions in

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oxy-fuel combustion through primary measures, knowledge of especially char–NO formation is necessary.

The objective of the present work is to investigate the effect of $O_2$ and $CO_2$ concentrations, representative of oxy-fuel combustion, on particle temperature and formation of NO in char oxidation. The experiments are conducted in a laboratory fixed-bed reactor with millimeter-sized lignite and bituminous coal char particles, for both single particles of different sizes and multiple particles. The reactor temperature is maintained at 1073 K, while the $O_2$ mole fraction is varied between 5% and 80%. A CCD camera is used for continuous monitoring of the particle temperature and structure. The results are discussed in terms of mechanisms for NO formation from char nitrogen oxidation.

## 2. Experimental

### 2.1. Equipment

The experiments were carried out in the laboratory scale fixed bed reactor shown schematically in Fig. 1. The reactor consisted of an inner and outer quartz tube heated by three electrical heating elements. In all experiments the reactor was operated isothermally at 1073 K, showing fluctuations of less than 10 K through its centerline. The reactor inlet gas was preheated in the annulus between the inner and outer tube before it flowed through the inner tube where it made contact with the particle, cf. Fig. 1. After the gas exited the reactor, it was sent for analysis for CO, $CO_2$, $O_2$ and NO (not shown in Fig. 1). The time delay from the reactor exit to the gas analyzers was measured prior to experiments. The delay, which was constant in all experiments, was used for correction of the gas analysis signals to real time. In all experiments the particle rested on a 5 mm bed of 300–355 μm sand particles on top of a quartz frit to ensure its fixation during combustion and to protect the frit. Gaseous atmospheres were created by mixing bottled gases and the volumetric flow was 1 Nl $min^{-1}$ in all experiments. Oxygen concentrations ranged between 5% and 80% in either $N_2$ or $CO_2$. Here and elsewhere in the manuscript, "%" is on volume basis, unless otherwise noted. The majority of the experiments were conducted with single particles, weighing between 1.3 and 543 mg, but a series of experiments with 5, 10, 15 and 20 particles (each about 30–50 mg) in both $O_2/N_2$ and $O_2/CO_2$ has also been carried out to investigate the effect of particle concentration.

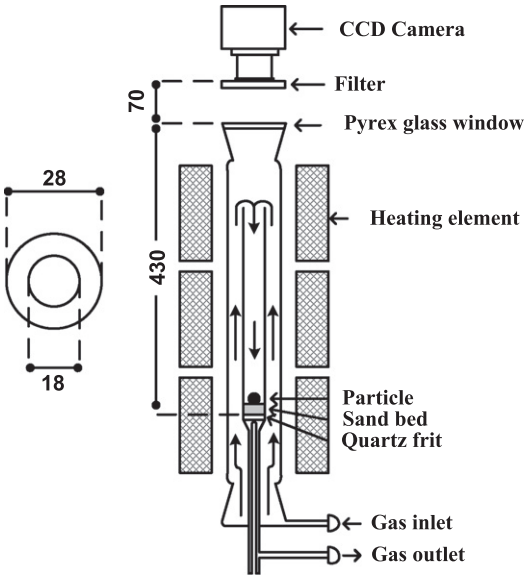


**Fig. 1.** Experimental setup. The inlet gas is mixed from bottled gases. The product gas is sent for analysis for CO, $CO_2$, $O_2$ and NO. Length scale is millimeters.

A pyrex glass window was mounted on top of the reactor, directly above the bed, through which a 16 bit CCD camera measured the intensity of the Near Infra Red (NIR) radiation emitted by the particle. To ensure pure NIR measurements and to avoid saturation of the camera's light sensor, a filter was placed in front of the lens.

#### 2.1.1. CCD camera and temperature measurements

The CCD camera used was a Stingray F033 from Allied Vision Technologies and had a 14 bit analog to digital converter. An extra 2 bit of unsigned resolution was achieved by averaging a series of shutter intervals thereby providing a total of $2^{16} = 65{,}536$ digital levels that could be detected by the camera. The digital level is a measure of the photon radiation intensity. The maximum digital level corresponds to a saturation of the detector and its processing system and it therefore relates to the maximum measurable particle temperature. A filter that allows radiation only in the wavelength interval 710–1100 nm (NIR) to reach the sensor was placed in front of the camera. The camera was calibrated with the filter in the temperature interval 1023–1873 K using a black body source. This temperature interval was adequate for the experiments presented here. The filter served two purposes: It avoided saturation of the camera at each temperature and it reduced the influence of scatter caused by background radiation. The relationship between particle temperature and camera response was modeled by integration of Planck's law over the wavelength interval of the filter. Constants accounting for the emissivity of the radiating source, the transmittance of the filter and optics and the camera sensitivity were established during calibration. With proper calibration and for well defined materials, the accuracy of the temperature measurement was better than ±10 K, but for the chars investigated here we estimate an uncertainty of ±50 K. The sensitivity of the temperature measurements towards potential changes in source emissivity, e.g. ash layer formation during combustion, were tested and found negligible (changes were a few K). Data acquisition during the experiments was done using a LabVIEW program developed specifically for this setup and output were given both as movies made up from still images and data files.

It is important to emphasize that because the camera was recording the NIR radiation from the part of the particles surface that was positioned in its view field, reported temperatures are surface temperatures of this area. It is unlikely that the particle temperatures are uniform, especially for the larger particles where internal temperature gradients are likely to exist. Throughout the text the term "Maximum Particle Temperature" refers to the highest temperature measured during an experiment.

### 2.2. Fuels and char preparation

Experiments have been conducted using chars from a bituminous coal (El Cerrejón) and a German lignite. Proximate and ultimate analyses of these coals are shown in Table 1. To prepare the chars, coals were dried at 378 K for app. 22 h. Then the dry coals were sieved into the size intervals 0.7–2 mm, 2–4 mm, 4–7 mm and >7 mm. A size fraction of 1.7–2.4 mm bituminous coal particles was also prepared and used for experiments with several particles present in the reactor. Each of the size fractions were pyrolysed in a muffle furnace at 1173 K for 2 h in $N_2$ to ensure that volatiles would not interfere with gas analysis during the experiments. During the pyrolysis no swelling was observed; the size intervals remained intact. Chars from pyrolysis in $CO_2$ at 1173 K were not used for combustion experiments, as gasification caused additional weight losses of 8–20 wt.% for bituminous coal and total conversion of the lignite.