Ignition and Combustion of Pulverized Coal and Biomass under Different Oxy-fuel O₂/N₂ and O₂/CO₂ Environments

A Thesis Presented

by

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Dedication

To my family and my parents
Abstract

This work studied the ignition and combustion of burning pulverized coals and biomasses particles under either conventional combustion in air or oxy-fuel combustion conditions. Oxy-fuel combustion is a ‘clean-coal’ process that takes place in O2/CO2 environments, which are achieved by removing nitrogen from the intake gases and recirculating large amounts of flue gases to the boiler. Removal of nitrogen from the combustion gases generates a high CO2-content, sequestration-ready gas at the boiler effluent. Flue gas recirculation moderates the high temperatures caused by the elevated oxygen partial pressure in the boiler. In this study, combustion of the fuels took place in a laboratory laminar-flow drop-tube furnace (DTF), electrically-heated to 1400 K, in environments containing various mole fractions of oxygen in either nitrogen or carbon-dioxide background gases.

The experiments were conducted at two different gas conditions inside the furnace: (a) quiescent gas condition (i.e., no flow or inactive flow) and, (b) an active gas flow condition in both the injector and furnace. Eight coals from different ranks (anthracite, semi-anthracite, three bituminous, subbituminous and two lignites) and four biomasses from different sources (Sugarcane bagasse, olive residue, pine sawdust and torrefied pine sawdust) were utilized in this work to study the ignition and combustion characteristics of solid fuels in O2/N2 or O2/CO2 environments. The main objective is to study the effect of replacing background N2 with CO2, increasing O2 mole fraction and fuel type and rank on a number of qualitative and quantitative parameters such as ignition/combustion mode, ignition temperature, ignition delay time, combustion temperatures, burnout times and envelope flame soot volume fractions.

Regarding ignition, in the quiescent gas condition, bituminous and sub-bituminous coal particles experienced homogeneous ignition in both O2/N2 and O2/CO2 atmospheres, while in the
active gas flow condition, heterogeneous ignition was evident in O\textsubscript{2}/CO\textsubscript{2}. Anthracite, semi-
anthracite and lignites mostly experienced heterogeneous ignition in either O\textsubscript{2}/N\textsubscript{2} or O\textsubscript{2}/CO\textsubscript{2}
atmospheres in both flow conditions. Replacing the N\textsubscript{2} by CO\textsubscript{2} slightly increased the ignition
temperature (30-40K). Ignition temperatures increased with the enhancement of coal rank in
either air or oxy-fuel combustion conditions. However, increasing oxygen mole fraction
decreased the ignition temperature for all coals. The ignition delay of coal particles was
prolonged in the slow-heating O\textsubscript{2}/CO\textsubscript{2} atmospheres, relative to the faster-heating O\textsubscript{2}/N\textsubscript{2}
atmospheres, particularly at high-diluent mole fractions. At higher O\textsubscript{2} mole fractions, ignition
delays decreased in both environments. Higher rank fuels such as anthracite and semi-anthracite
experienced higher ignition delays while lower rank fuels such as lignite and biomasses
experienced lower ignition delay times.

In combustion, fuel particles were observed to burn in different modes, such as two-mode,
i.e., gas-phase or homogeneous mode (volatile matter envelope flames) followed by
heterogeneous mode (char surface oxidation), or in one-mode combustion (simultaneous volatile
and char), depending on their rank and the furnace conditions. Strong tendencies were observed
for all fuels to burn in one-mode when N\textsubscript{2} was replaced by CO\textsubscript{2}, and when O\textsubscript{2} mole fraction
increased in both environments. Moreover, increasing the coal rank, from lignite to bituminous,
enhanced the tendency of coal particles to exhibit a two-mode combustion behavior. Particle
luminosity, fragmentation and deduced temperatures were higher in O\textsubscript{2}/N\textsubscript{2} than in O\textsubscript{2}/CO\textsubscript{2}
atmospheres, and corresponding burnout times were shorter, at the same O\textsubscript{2} mole fractions.
Particle luminosity and temperatures increased with increasing O\textsubscript{2} mole fractions in both N\textsubscript{2} and
in CO\textsubscript{2} background gases, and corresponding burnout times decreased with increasing O\textsubscript{2} mole
fractions. Bituminous coal particles swelled, whereas sub-bituminous coal particles exhibited
limited fragmentation prior to and during the early stages of combustion. Lignite coal particles fragmented extensively and burned in one-mode regardless of the $O_2$ mole fraction and the background gas. The timing of fragmentation (prior or after ignition) and the number of fragments depended on the type of the lignite and on the particle shape. Temperatures and burnout times of particles were also affected by the combustion mode.

Higher rank coals required extra oxygen in CO$_2$ to match their temperature-time behavior in air. Sugarcane bagasse char needed the least amount of extra gas-phase oxygen in CO$_2$ to match its temperature-time behavior in air. In other words, the fuels which have more fuel-bound oxygen (i.e., lower rank coals and bagasse) required the least amount of gas-phase oxygen in CO$_2$ to match their temperature-time behavior in air.

In nearly all bituminous and biomass particles combustion, sooty envelope flames were formed around the particles. Replacement of background N$_2$ by CO$_2$ gas decreased the average soot volume fraction, $f_v$, whereas increasing $O_2$ from 20% to 30-40% increased the $f_v$ and then further increasing $O_2$ to 100% decreased the soot volume fraction drastically. bituminous coal particle flames generated lower soot volume fractions in the range $2 \times 10^{-5}$-$9 \times 10^{-5}$, depending on $O_2$ mole fraction. Moreover, biomass particle flames were optically thin and of equal-sized at all $O_2$ mole fractions.
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Electricity consumption, which grows faster than any other form of energy utilization, is increasing with the increasing global population (which increases by 80 million people per year\(^1\)). The world’s electricity consumption is predicted to increase by approximately 84% from 17,200 billion kWh to 31,700 billion kWh by 2035 [1]. According to this, 1 billion people will be living without electricity in 2030 (IEA). For yet others, power will remain seriously unaffordable [2]. Coal is used to generate 29.6% of the primary energy in the world and is the major source of electricity, delivering 40% of the worldwide electricity demand. In the US and some other countries this figure stands or exceeds 45% [3] (80% in Australia). Coal is expected to remain the most important source of electricity in the foreseeable future as it is more abundant and cheaper than other fossil fuels [1]. The usage of coal is projected to increase by over 40.3% from 2010 to 2035 [4, 5]. Especially, Non- Organization of Economic Cooperation and Development (OECD) Asian countries, i.e., China and India, will account for 87% of this increase to meet their electricity demand due to fast growing economic activity and population [5].

Coal has a high potential to pollute the environment from its production through consumption. Burning of the coal leads to CO\(_2\) emissions, which is confirmed to cause global warming as it contains carbon in its structure. Since coal is used as a primary power generation source around the world, all countries contribute to the emission of greenhouse gases. China, USA, and India are the top three countries that emit greenhouse gases via coal combustion in their power plants [6]. Greenhouse gas emissions from coal-burning power plants accounted for about 33% of the US emissions and for 43% of the global emissions in 2009 [7]. Other than that,
combustion of coal results in hazardous air pollutants such as sulfur dioxide (SO$_2$), nitrogen oxides (NO$_x$), and carbon monoxide (CO) gaseous emissions [8, 9].

Several strategies are being devised to either reduce the greenhouse gas emissions and/or to achieve its capture and sequestration. Such strategies include replacement of aging power plants with new higher efficiency plants, such as those employing supercritical steam technologies, and implementation of technologies that facilitate pre- or post-combustion capture of CO$_2$ [10]. One of these technologies is oxy-fuel combustion. Therein, by using an air-separation unit (ASU) to generate oxygen and nitrogen streams, firing pulverized coal with the oxygen stream, and drying the combustion effluent, this technique can generate a sequestration-ready high-CO$_2$-concentration gas effluent which may be subsequently stored in underground reservoirs. To moderate combustion temperatures in the furnace, the input oxygen stream is mixed with recycled dry flue gases (containing mostly CO$_2$); hence, combustion of coal takes place in O$_2$/CO$_2$ atmospheres. Another strategy to reduce greenhouse emissions is utilizing biomass as an energy source. In regards to its carbon dioxide emissions, biomass is considered nearly neutral since the carbon dioxide emissions released from converting biomass to energy are equivalent to the amount of carbon dioxide absorbed by the plants during their growing cycles [11-13]. The energy used in the growing, harvesting, and transportation processes results in CO$_2$ emissions that are detractors. As a result, when fired with primary fossil fuels, such as coal, the use of biomass can reduce the net production of carbon dioxide [12, 13].

The switch of combustion gas environment from air (or O$_2$/N$_2$) to O$_2$/CO$_2$ affects a variety of combustion related parameters such as ignition temperatures, delay times, combustion temperatures, burnout times and reactivities. Moreover, the particle ignition and combustion behavior as well as soot loading are also varied which will affect the simulation and design of
new generation of oxy-fuel burners and boilers in the future [14]. Since igniton and combustion characteristics of coal and biomass changes drastically in O₂/CO₂ environments, it is of scientific and technical interests to study the nature of combustion characteristics in oxy-combustion of both coal and biomass.

The dissertation is organized in nine chapters:

**Chapter 1** discusses temperature deduction methods of pulverized coal particles using Three-color Optical pyrometry burning in air environments. Temperature-time and luminous-area-time histories of burning coal particles are deduced from radiation intensity signals detected by a three-color optical pyrometer, using Planck’s theory. In this chapter, two different mathematical approaches are used to calculate such temperatures and areas, one based on the pyrometric signal ratio method, another based on the pyrometric signal least-square method and the transmissivities and responsivities of the light-path components of the pyrometer as a function of wavelength, are modeled mathematically. A sensitivity analysis is performed to investigate individual effects of parameters, such as the calibration method, the wavelength dependencies of filter transmissivities, and the photo-detector responsivities on the pyrometric signal ratio method temperature consistency.

**Chapter 2** describes combustion studies in air of pulverized fuel particles (three different coal ranks: a bituminous, a sub-bituminous coal and two lignite and sugarcane bagasse). Fuel particles, in the range of 75-90 μm, are injected in a bench-scale, transparent drop-tube furnace, electrically-heated to 1400 K. The combustion of individual particles in air is observed with three-color pyrometry and high-speed high-resolution cinematography to obtain temperature-time histories. Based on combined observations from these techniques, in conjunction to morphological examinations of particles, a comprehensive understanding of the combustion
behaviors of these fuels is developed. For all fuels, flame and char temperature profiles are deduced from pyrometric data and burnout times were measured. Combustion rates are calculated from luminous carbon disappearance measurements, and are compared with predictions based on published kinetic expressions.

**Chapter 3** assesses the ignition behavior (mode and delay times) of single-coal and single-char particles in O$_2$/N$_2$ and O$_2$/CO$_2$ atmospheres, with oxygen mole fractions in the range of 20-100%. Fuels include four pulverized coals from three different ranks (one high-volatile bituminous, one sub-bituminous and two lignites) as well as chars prepared from two of the coals. Particles of 75-90 μm are injected in a bench-scale, transparent drop-tube furnace (DTF), electrically-heated to 1400 K. Optical access of the furnace allows the ignition of individual particles to be observed with high-speed cinematography. A particle’s ignition delay is defined. The experiments are conducted at two different gas conditions inside the furnace: (a) quiescent gas condition (i.e., no flow or inactive flow) and, (b) an active gas flow condition in both the injector and furnace. The effects of background gas (N$_2$ or CO$_2$), fuel type (coal ranks and char) and increasing oxygen mole fraction in either N$_2$ or CO$_2$ on the ignition mode (homogeneous or heterogeneous) and ignition delay are discussed in either quiescent gas or active flow cases.

**Chapter 4** depicts the combustion behavior of single fuel particles (75-90 μm) in O$_2$/N$_2$ and O$_2$/CO$_2$ background gases, with oxygen mole fractions in the range of 20-100%. Fuels included four pulverized coals from different ranks of chapter 3 as well as a biomass residue. A bench-scale, transparent drop-tube furnace (DTF), electrically-heated to 1400 K is utilized to burn the fuels. The combustion of individual particles is observed with three-color optical pyrometry and high-speed high-resolution cinematography to obtain temperature and burnout time histories. Based on combined observations from these techniques, a comprehensive understanding of the
behaviors of these fuels is developed under a variety of conditions, including simulated oxy-fuel combustion. The effects of background gas (N$_2$ or CO$_2$), fuel type (coal ranks and char) and increasing oxygen mole fraction in either N$_2$ or CO$_2$ on the combustion mode (sequential or simultaneous volatile and char burning), combustion behavior (swelling, fragmentation, luminosity, etc.) ignition temperatures, volatile/char combustion temperatures and burnout times are discussed in the active flow cases and some quiescent gas conditions.

Chapter 5 describes the combustion behaviors of four different pulverized biomasses. Single particles of sugar cane bagasse, pine sawdust, torrefied pine sawdust and olive residue are burned in a drop-tube furnace, at 1400 K, in both air and O$_2$/CO$_2$ atmospheres containing 21, 30, 35, and 50% oxygen mole fractions. High-speed and high-resolution images of single particles are recorded cinematographically and temperature-time histories are obtained pyrometrically. The behavior of different biomasses is investigated and compared based on their origin, their type and their pre-treatment. Volatile flame of biomass fuels are compared with the coal volatile flames from different ranks (as appeared in chapters 4) from the perspective of ignition, luminosity, soot content, flame thickness and duration perspective. Moreover, the biomass char combustion was characterized in the case of temperature and burnout times.

Chapter 6 studies the combustion of higher rank coals (Anthracite, Semi-anthracite and two bituminous) from sources outside the United States. The same setup as chapters 4 and 5 are employed. The experimental conditions are similar to chapter 5 (drop-tube furnace at 1400 K, gas environment of air and O$_2$/CO$_2$ atmospheres containing 21, 30, 35, and 50% oxygen mole fractions, quiescent gas conditions, particle size 75-150 μm). On the basis of the observations made, a comprehensive examination of the ignition and combustion behavior of these fuels was achieved.
Chapter 7 investigates the soot loading of the coal particle flames. A new scheme is proposed to deduce the real-time soot volume fraction of burning solid fuel particles. Since particle temperatures, sizes and burnout times were investigated in the previous chapters, this chapter focuses on the soot volume fraction of the coal particle flames as a radiation related parameter in the flames. The experimental conditions are similar to chapter 3 and 4 (drop-tube furnace at 1400 K, gas environment of O$_2$/N$_2$ and O$_2$/CO$_2$ atmospheres containing 21-100%O$_2$, quiescent gas conditions, particle size 75-90 μm). The characteristics of bituminous coal flames are conferred and the effects of fuel type and source (Bituminous coals from different sources), background gases (N$_2$ or CO$_2$) and increasing oxygen mole fraction in either N$_2$ or CO$_2$ on the soot volume fraction are discussed.

Chapter 8 includes the conclusions of this work. Conclusions are presented in three categories; the effect of 8.1) replacing background N$_2$ gas with CO$_2$, 8.2) fuel types and coal ranks, and 8.3) oxygen mole fraction on ignition, combustion phenomena and quantitative parameters such as ignition temperatures, delay times, temperature and burnout time histories. 8.4) biomass combustion behaviors

Chapter 9 includes the suggestions for future work.

References


CHAPTER 1

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1. On the Deduction of Single Coal Particle Combustion Temperature from Three-Color Optical Pyrometry

Abstract

Temperature-time histories of burning single coal particles can be obtained with multi-color (multi-wavelength) optical pyrometry. With this method, a number of different temperatures can be deduced from the resulting number of two-color ratios. However, these two-color temperatures do not always agree, causing considerable uncertainty in the temperature measurement. This work used a three-color pyrometer and focused on identifying and minimizing the causes of disparity among the three deduced temperatures. Components of the pyrometer (such as dichroic filters, interference filters and photo-detectors) were modeled mathematically, taking into account their wavelength-dependent properties. The pyrometer was calibrated with both a high-temperature pre-calibrated tungsten lamp, and a moderately-high temperature blackbody cavity, to span the temperature range of interest in pulverized coal combustion. Temperatures were deduced based not only on a suitably-modified pyrometric signal ratio method but also, on a similarly modified pyrometric signal non-linear least-square method, to provide comparison. Results are exemplified by presenting radiation-signal-time and temperature-time profiles of single particles burning in air. The variation of the projected luminous area of burning particles was also computed using both methods, and area-time profiles are presented herein. The char particle emissivity was either treated as a quantity independent of the wavelength (i.e., assuming gray body behavior), or as a quantity assumed to depend linearly on the wavelength and using pertinent published emissivity data. Finally, a sensitivity analysis
was performed to investigate individual effects of parameters, such as the calibration method, the wavelength dependencies of filter transmissivities, and the photo-detector responsivities on the pyrometric signal ratio method temperature consistency.

1.1. Introduction

Temperature is a parameter of utmost importance in the analysis of combustion systems. Every part of a combustion event such as ignition, burnout and evolution of emissions, is related to temperature. Thus, the knowledge of true temperature is essential for combustion systems optimization.

Contact and non-contact techniques have been developed to measure temperature. Contact techniques mostly use thermocouples, which are immersed in a fluid or are in direct contact with a surface of a solid the temperature of which needs to be measured. However, measurement of temperature by contact is not possible in many laboratory and industrial applications because the target is not-accessible, too small, too hot, changing phase, or it is in motion. All of these restrictions apply to burning coal particles, rendering direct contact with thermocouples impossible. Non-contact methods have been developed to assess the temperatures of these types of targets, and optical pyrometry is one of them. One-color pyrometry and two-color pyrometry have been popular; the latter providing the advantage that the target emissivity may be canceled out when the ratio of signals at two different wavelengths is taken (gray-body assumption). These techniques calculate temperature, based on Planck’s radiation law. Hottel [1], among others [2-40], used such techniques and provided a perspective of radiometric temperature and emissivity measurement in furnaces. He reviewed the two-color ratio pyrometry method in
conjunction to luminous flame properties, and proposed both monochromatic and total emissivity expressions for soot-laden flames.

Whereas most researchers used two-color pyrometry in combustion studies, some constructed multi-color pyrometers, see for instance: [2,3,4,5]. Application of the ratio pyrometry method to the signals of these instruments yields multiple temperatures from the combination of wavelength pairs. For instance, three-color pyrometry yields three temperatures (two of which are independent, see Panagiotou, Levendis and Delichatsios [6]). However, a problem that is not encountered in either one- or two-color pyrometry (fortunately for those researchers) reveals itself in this technique, i.e., the three different temperatures do not necessarily agree. This can be the cause of great concern to a researcher in his/her quest for obtaining the true temperature of a target. In this case, the researcher may be left wondering whether the disagreement is caused by hardware issues, by the software algorithm, by the treatment of emissivities (coal is typically assumed as a gray-body, in which case the emissivities are independent of wavelength), or by the accuracy of the instrument calibration process. For instance, Bejarano and Levendis [7] used the three-wavelength instrument (640,810 and 998 nm) and the algorithm of Levendis, Estrada and Hottel [3] to deduce the temperature of burning single coal particles. However, they encountered disagreements of up to 200 K among the three-color temperatures ($T_{998/810}$, $T_{998/640}$, $T_{810/640}$) therein. The first of these temperatures, $T_{998/810}$, was typically the lowest and the last, $T_{810/640}$, was the highest, whereas $T_{998/640}$, was very close to the average value of all three temperatures. Thus, results were reported based on $T_{998/640}$, since not only it closely represented the average value of all $T$s but, also, involved the wavelengths that were the most spaced-apart in this instrument. It has been theoretically shown that the calculated error between the true and the measured temperatures is minimized by selecting wavelengths that
short and well spaced-apart (separated), see details in Jorgensen and Zuiderwyk [10], Spjut, Sarofim and Longwell [11] and Levendis, Estrada and Hottel [3]. Matsui et al. [12], using ratio pyrometry with a four-color instrument (centered at \( \lambda = 0.55, 0.75, 2.3 \) and 3.98 \( \mu \)m), also reported large discrepancies among different two-color temperatures. Discrepancy was also observed by Gat [14]. He utilized a least-square method to deduce snapshots (one instant in time) of coal particle temperatures, 63-75 \( \mu \)m in size, with a three-color pyrometer (0.8, 0.9 and 1.1 \( \mu \)m), using the gray-body assumption for emissivities. Whereas temperatures were calculated using the least-square method (which incorporated the signals from all three wavelengths in one equation and calculated one temperature), a limited number of calculations using two-color ratio pyrometry were also conducted. Therein, large differences among the pyrometric ratio temperatures (as much as 500 K) were observed.

The present work focuses on the causes of the aforementioned temperature discrepancies in three- (or multi-) color pyrometry, and aims at enhancing the confidence that one has on the temperature measurement. The three-color instrument of Levendis, Estrada and Hottel [3], described in the following section, was used herein. In that instrument the authors used a single fiber optic and dichroic filters (mirrors) to conduct and split the light to three photo-detectors, through interference filters. For analytical simplicity, they assumed that the wavelength dependences of the transmittances of the dichroic and the interference filters as well as the responsivities of the detectors were negligible, and treated them as wavelength-independent. Herein, the temperature-deduction algorithm was altered to include the wavelength dependencies of these components. This caused considerable mathematical complexity, but improved accuracy; the targeted outcome being to obtain better agreement among the resulting three temperatures. Moreover, the temperature output of the pyrometric signal ratio method was
compared to that from a pyrometric signal least-square method, and the existence and uniqueness of solutions for temperature were shown in the cases of both methods. Entire histories of both temperatures and luminous areas of burning single coal particles, simultaneously deduced from both ratio pyrometry and least square methods, have not been compared before. Finally, the calibration method was expanded to include more than one pre-calibrated device, and the gray-body assumption to describe the emissivity of the carbon particle was re-visited.

1.2. Experimental and Theoretical Considerations

1.2.1. Experimental setup

An electrically-heated laminar-flow drop-tube furnace was used, see Fig. 1, fitted with a transparent quartz tube with an inner diameter of 3 cm. The length of the radiation zone is 25 cm. The furnace is fitted at the top with a water-cooled injector. Pyrometric observations of single particles were conducted from the top of the furnace injector, viewing downwards along the central axis of the furnace, Fig. 1, which ideally is the particle's path-line. Thus, the luminous burnout histories of single coal particles - from ignition to extinction - were monitored. The travel distance of particles of coal in air, under the conditions of this study was in the order of a few to several centimeters. The dimensions of the particle injector are 61 cm length and 1.25 cm inner diameter, chosen based on design criteria outlined in Ref. [3]. Light from burning particles was focused by an inverted collimating lens (Oriel, 11 mm diameter, 19 mm focal length) on one end of an optical fiber. The distance between an igniting particle to the collimating lens is approx. 63 cm. To minimize reflected furnace radiation climbing the injector's inner walls (after multiple reflections therein) (a) the injector is black-passivated and (b) a pinhole is used between the lens and the fiber. The optical fiber, manufactured by General Fiber Optics, consists of a
high-transmittance (> 99.5%) fused silica core and doped fused silica cladding with an f-number of 2.2. This 1.6 m long, 1 mm diameter, single fiber optic has the advantage of maximizing light transmission efficiency since all of its cross-section is being utilized. Light from the furnace is transmitted through the optical fiber to the pyrometer assembly. The pyrometer uses two dichroic edge filters as spectrum splitters to direct the light to three photodetectors. Radiation is thus carried to the first spectrum splitter (Newport, 10QM20HL.9) mounted at 45° on a rotating stage (Melles Griot). At this angle the splitter has a reflecting window from 0.6 to 0.7 μm. A second dichroic splitter (Newport, 10QM20HL.11), with a reflecting window from 0.74 to 0.82 μm, is placed further along the light path, at an angle of 26.6°, to split the remaining portion of the spectrum (transmitted from the first splitter) between the two remaining channels. Three medium band-width interference filters (Oriel) with full width at half maximum (FWHM) of 70 nm are used to define the working wavelengths of 0.64, 0.81 and 0.998 μm. This arrangement avoids the absorption bands of water vapor and carbon dioxide, and has minimal interference from the elemental lines of sodium and potassium (589 nm and 766 nm, respectively), based on transmissivity curves supplied by the manufacturers for the particular dichroic splitters and interference filters used in this work. These interference bands are at the fringes of the bell-shape transmissivity curves of the filters. In conjunction with all these interference filters, aspheric lenses (19-mm focal length) are used to focus the light beams onto solid-state silicon photodetectors. The selection of the above three wavelengths was dictated by the expected particle temperatures and the effect of wavelength on photo-detector sensitivity. The silicon diode detectors (Oriel, model #71801) were selected to maximize the signal sensitivity. They also possess good stability and linearity. The high frequency response of these detectors is shown in Fig. 3 and their rise time is 75 ns; other details are provided in Ref. [3]. Data acquisition of the
photodetector-generated, upon amplification [3], was performed with the *LabView 8.0* software, at a sampling interval of 0.233 ms.
Figure 1. Schematic of the experimental setup showing features of the electrically-heated, drop-tube furnace used for pyrometric observations on the combustion of single coal particles. The three-color optical pyrometer and the associated calibration devices of (A) a pre-calibrated NIST lamp and (B) a blackbody cavity are also depicted.
1.2.2. Origin of Temperature Errors

Temperature errors in radiation pyrometry of in-furnace combustion events may be classified in the following major categories:

(a) **Errors caused by radiation interference with furnace gases.** These errors include the attenuation of radiation between the target and the optical fiber. The space between the burning particle and optical fiber is filled with gases, such as nitrogen, oxygen, carbon dioxide and water vapor. These gases absorb some of the radiation spectrum from the particle. To deal with this problem, the absorption bands of major gases inside the furnace were considered and wavelengths were chosen to avoid or, at the very least, minimize the absorption wavelength bands of such gases.

(b) **Errors caused by background radiation.** This kind of radiation stems from miscellaneous sources and includes direct radiation from the furnace walls, radiation from the furnace walls reflected on the inner surfaces of the particle injector, radiation from the furnace walls reflected on the particle surface, radiation from room lighting, etc. The former two components of radiation have been largely avoided by the design of the injector dimensions and the light collection system of the instrument, see Levendis et al. [3]. Radiation from the furnace walls reflected on the particle surface cannot be precluded, thus particle temperatures at or below the furnace wall temperature (herein 1400 K) are not considered herein. Room light was not a factor in this work, as verified with separate experiments with closed view-port shutters and/or without room lighting.

(c) **Errors caused by the target emissivity variations with \( \lambda \) and \( T \).** Errors may arise from the assumption that coal emissivities are independent of wavelength (gray emissivity assumption).
The emissivity of surfaces typically depends on material properties, shape, roughness, temperature and wavelength of observation. A number of papers focused on measuring spectral emissivity of different types of carbon at high-temperatures, including the work of Neuer [21] who investigated on the total and spectral emissivities of graphite at wavelengths between 0.5–8 μm, in the temperature range of 1300 - 2000 K. In the wavelength of interest to the work herein (0.5-1.1μm) they found the emissivity to decrease linearly with increasing wavelength (from 0.98 to 0.92). Not significant temperature dependence of the graphite emissivity was found in this range. Thorn and Simpson [19] determined the spectral emissivities of high-purity graphite and spectroscopic carbon electrodes at a single wavelength (0.653 μm), but varying temperature in the range of 1285-2035 K. They found weak dependences of emissivity in his temperature range: $10^{-5} \times T(K)$ for graphite and $10^{-7} \times T(K)$ for carbon. Fletcher and coworkers [20] reported on the spectral and total emissivities of different coal ranks from lignite to bituminous, in the temperature range of 400 to 473 K. They collected data at wavelengths between 2.2-17 μm and their particle size ranged from 40 to 120 μm. They reported that spectral emissivities of high-rank coals such as bituminous vary from 0.7 to 0.98. Lignites may have spectral emissivities as low as 0.5 in some part of the wavelength spectrum. As the wavelength of observation decreases and/or as particle size, coal rank and extent of burnout increases, the coals behave increasingly as gray-bodies. However, as burnout increases, the particle emissivity may either increase, decrease, or remain constant depending on the region of the wavelength spectrum. Such emissivity uncertainties may have a direct impact on the differing temperature measurements by multi-color pyrometry.

(d) Errors caused by optical fiber losses. The optical fiber used in this setup has a high transmittance (99.5%) [3], hence, the losses of radiation intensity therein are negligible.
(e) Errors caused by components of the pyrometer. These errors can be associated with the dichroic and interference filters, as well as with the focusing lenses and the photo-detectors. Dichroic filters are spectrum splitters and have the property of transmitting and reflecting part of the spectrum at pre-determined wavelengths. Dichroic filters can introduce errors in signals due to their efficiency and angle. Three interference filters are located after the beams are split and before the focusing lenses and photo-detectors. Focusing lenses and photo detectors are the last parts of error generators in the pyrometer, see Figures 1, 2. Herein, identical lenses and photo-detectors were used in all channels. All the dichroic and interference filters as well as the photo-detectors are wavelength-dependent components, hence their spectral response to incoming beams should be taken into account to reduce the error. This is the subject of an ensuing section of this manuscript.

(f) Errors caused by electronic noise. These types of errors may cause uncertainty in temperature, particularly in the case of weak signals, such as in the cases of low-temperatures and small luminous-areas, where the noise-to-signal ratios are high. In those cases, such electronic-noise-induced uncertainties may have a direct impact on the differing temperature measurements by multi-color pyrometry, as discussed in an ensuing section.

(g) Errors caused by computational procedures. These types of errors stem from numerical computations (such as numerical integrations) and statistical procedures (e.g. method of choosing baseline signals and linear or non-linear fittings). Such errors are addressed in an ensuing section.
1.2.3. Basic Pyrometric Principles

All bodies radiate thermal energy and their radiation is a function of the surface temperature and wavelength. Planck’s law describes the quantitative value of radiation intensity at a specified temperature and wavelength. The most efficient thermal radiator is called blackbody. A blackbody emits and absorbs all incident radiation.

The spectral radiation intensity for a blackbody surface obeys Planck’s law:

\[
I_{\lambda b} = \frac{c_1}{\lambda^5 \left( e^{\frac{c_2}{\lambda T}} - 1 \right)}
\]

(1)

For a non-blackbody surface:

\[
I_{\lambda} = \frac{\varepsilon_{\lambda,T} c_1}{\lambda^5 \left( e^{\frac{c_2}{\lambda T}} - 1 \right)}
\]

(2)

where \( \varepsilon_{\lambda,T} \) is the spectral (monochromatic) emissivity of the target. In many high-temperature applications, such as combustion of solids, the emissivity of a surface may not only be a function of wavelength, but also a function of temperature. However, based on Neuer’s findings [21], coal particle emissivity was herein taken to be only a function of wavelength, since it was shown to have only a weak functionality on temperature (in the range of 1300-2000 K). The spectral energy per unit time emitted by a non-blackbody surface with area A is:

\[
E_{\lambda} = \varepsilon_{\lambda} I_{\lambda b} A
\]

(3)

And the total energy per unit time emitted is:
\[ E(T) = \int_{0}^{\infty} \varepsilon_{\lambda} I_{ab} Ad\lambda \]  

(4)

Then the calculated voltage signal in channel \( n \) is:

\[ s_n = E(T) = A \int_{\lambda_{h_n}}^{\infty} \varepsilon_{\lambda} I_{ab} g_n(\lambda)d\lambda \]  

(5)

where \( n \) can be 1, 2 or 3 which represents 998, 810 and 640 nm channels, respectively, and \( g_n(\lambda) \) is the wavelength function of the combined transmittance of the associated dichroic filter \( (\tau_d) \), the associated interference filter \( (\tau_i) \) and the associated responsivity of photo-detectors \( (R_{pd}) \) for channel \( n \), as shown in relations (6), (7) and (8) as well as in Fig. 2. Thus, for each of the three channels of the instrument \( g_n(\lambda) \) is defined as follows:

Channel 1 (998nm): \[ g_1(\lambda) = \tau_{d_1}(\lambda)\tau_{d_2}(\lambda)\tau_{i_1}(\lambda)R_{pd}(\lambda) \]  

(6)

Channel 2 (810nm): \[ g_2(\lambda) = \tau_{d_1}(\lambda)[1 - \tau_{d_2}(\lambda)]\tau_{i_2}(\lambda)R_{pd}(\lambda) \]  

(7)

Channel 3 (640nm): \[ g_3(\lambda) = [1 - \tau_{d_1}(\lambda)]\tau_{i_3}(\lambda)R_{pd}(\lambda) \]  

(8)
1.2.4. Wavelength and filter bandwidth selection for the pyrometer

There are a number of factors that should be kept in mind when choosing wavelengths for a multi-color pyrometer for applications in the coal particle combustion: (a) To maximize the particle radiation intensity, and thus the intensity of the resulting pyrometric signals, the wavelengths should be selected in the vicinity of the peak of Planck’s spectral power curves. (b) Simple heat balance calculations showed that the coal particles are expected to burn in the broad neighborhood of 2000K, under furnace conditions used herein. Thus, to maximize transmission of radiation, pyrometric wavelengths were selected in the vicinity of the maximum in Planck’s radiation intensity profiles, $I_{\lambda, \text{max}}$, emanating from targets of such temperatures. $I_{\lambda, \text{max}}$ is given by one of the so-called displacement laws [3]. Using Wien’s displacement law $I_{\lambda, \text{max}}$ is obtained
from $\lambda T=2898 \, \mu m \, K$ and at $T=2000 \, K$, $\lambda=1.5 \, \mu m$. Using another displacement law [3] $I_{\lambda, \text{max}}$ is obtained from $\lambda T=3670 \, \mu m \, K$ and at $T=2000 \, K$, $\lambda=1.83 \, \mu m$. Furthermore, the slopes of the Planck’s radiation intensity, $I_{\lambda}$, curves at any given temperature, plotted versus wavelength, are steeper to the left side of the peaks, i.e., at wavelengths lower than the one corresponding to $I_{\lambda, \text{max}}$. Therefore, the wavelengths of the pyrometer were selected in this region (0.64, 0.81 and 0.998 µm) to maximize the instrument sensitivity to target temperature variations in the aforesaid broad temperature neighborhood of 2000 K. (c) The interference filter wavelength bandwidths should avoid the absorption bands of radiation by major combustion product molecules and free radicals, i.e. CO₂, H₂O, N₂, OH, CO, NO, etc. (d) The interference filter bandwidths should be sufficiently wide to generate strong signals from the small coal particles and, hence, minimize the noise level; however, they should be sufficiently narrow as to prevent interference with the other channel’s filter bandwidths in the spectrum range of interest.

The rate of change of the spectral intensity with respect to temperature is greater in both the visible range and in near-infrared range, than in the far-infrared range of the spectrum [27], resulting in a higher signal resolution. Hence, the wavelengths of the instrument were chosen to be in the near-visible/near-infrared range of spectrum centered at 0.64, 0.81 and 0.998 µm. Out of two available options for interference filters, filters with narrow bandwidth of 10 nm and filters with medium bandwidth of 70 nm, the latter were used in this application, based on their superior signal to noise ratios. It is relevant to note from the work of Gathers [22], that channel bandwidth is not a sensitive variable, as in his work filter bandwidths (in the range 20-150 nm) did not significantly affect the temperature error.

1.2.5. Wavelength-dependence modeling of the transmissivity of the dichroic and the interference filters and the responsivity of the photo-detectors
In this instrument, shown in Fig.1, a beam of combustion-generated radiation passes through the optical fiber and reaches the pyrometer. It subsequently goes through the collimating lens, dichroic filters, interference filters and focusing lenses before it is converted to electric currents in the photo-detectors. The resulting photo-currents are converted to voltage signals \( (S_n) \) and are amplified \( 10^8 \) times [3].

The voltage signal output of each channel of the pyrometer can be expressed as follows:

\[
S_n = C_n s_n = C_n A \int_{\Delta\lambda_n} \varepsilon_{\lambda_n} I_{\Delta\lambda_n}(\lambda) g_n(\lambda) d\lambda
\]  

(9)

where \( C_n \) is a calibration constant, as explained in the following. Interference and dichroic filters and silicone photo-detectors are the most important components of this pyrometer that exhibit spectral dependence behavior. This behavior was not taken into account in previous work in order to maintain computational simplicity i.e., to achieve a closed form solution for temperature [3]. That work treated the light transmission effectiveness of these filters and detectors as independent of the wavelength and, thus, included these terms in the calibration constants. This is not the case in the present work. Herein, the only factors that were treated as being independent of wavelength for all channels were geometric factors, based on the target size and shape, and light-transmission efficiencies of the optical fiber and lenses. These factors were included in the calibration constant \( (C_n \) of Eqn. 9), whereas the transmissivities of the filters and the responsivities of the detectors were accounted for in the radiation intensity integrals \( (g_n(\lambda) \) of Eqn. 9), as they experience variations throughout the wavelength bands. Moreover, there are overlaps among the filter spectra in some wavelength ranges, see Fig. 3.

1.2.5.1. Dichroic filters
A dichroic edge filter or beam splitter is a device that reflects a portion of an incident beam, depending on its wavelength, and transmits the rest of the beam. Transmittance responses of the two dichroic filters of this instrument are shown in Fig. 3. The transmittance of each dichroic filter was curve-fitted with a mathematical function. The best approximations for both dichroic filters were found to be the sum of $8$ sinusoidal functions. The statistics of fitted curves are shown in Table 1.

$$\tau_{d1}(\lambda) = \sum_{n=1}^{8} a_n \sin(b_n \lambda + c_n) \quad 0.5 \leq \lambda \leq 1.08(\mu m) \quad (10a)$$

$$\tau_{d2}(\lambda) = \sum_{n=1}^{8} d_n \sin(f_n \lambda + g_n) \quad 0.5 \leq \lambda \leq 1.08(\mu m) \quad (10b)$$

Where $a_n, b_n, c_n, d_n, f_n, g_n$ are constants resulting from the curve-fitting process.

1.2.5.2. Interference filters

Three medium-bandwidth (70nm) interference filters were used in this pyrometer, centered at 0.64, 0.81 and 0.998 $\mu m$. Interference filters were often assumed to be constant with wavelength in previous works [3, 7, 14] and consequently they were included in the calibration constants. In this work, the interference filters of each channel were fitted with appropriate functions. These functions were used to calculate $g_n(\lambda)$ in the radiation intensity integrals as in Eqns (6), (7) and (8) and Fig. 2. The fitted curves for each channel as Gaussian functions of wavelength are:

$$\tau_{int}(\lambda) = \sum_{k=1}^{2} a_k \exp\left[-(\frac{\lambda - b_k}{c_k})^2\right] \sim \begin{cases} j = 1 \rightarrow 0.88 \leq \lambda \leq 1.08(\mu m) \\ j = 2 \rightarrow 0.69 \leq \lambda \leq 0.96(\mu m) \\ j = 3 \rightarrow 0.5 \leq \lambda \leq 0.82(\mu m) \end{cases} \quad (11)$$
where \( j \) refers to interference filters 1, 2 and 3 (centered at 998 nm, 810 nm and 640 nm, respectively); \( a_k, b_k, c_k \) are constants resulting from curve-fitting.

1.2.5.3. Photo detectors

The photo detectors are the same for all three wavelength channels, shown in Fig. 2. However, as shown in Fig. 3, their spectral responsivities (i.e., the generated current (Amps) over the incident radiation (Watts)) are not constant with wavelength. Thus, the responsivity of photo-detectors was curve-fitted with a mathematical function. The best fitted curve was found to be the sum of 4 sinusoidal terms, as shown in Eqn. (12).

\[
R_{pd}(\lambda) = \sum_{n=1}^{4} a_n \sin(b_n \lambda + c_n) \quad 0.5 \leq \lambda \leq 1.08(\mu\text{m})
\]  

(12)

Where \( a_n, b_n, c_n, d_n, f_n, g_n \) are constants resulting from the curve-fitting process.

The superimposed manufacturer-supplied data (points) and fitted curves for the wavelength-dependent transmittances of the dichroic filters, the wavelength-dependent transmittances of the interference filters, and the wavelength-dependent responsivities of the photo-detectors are shown in Fig. 3. In a few places where the transmissivity values of the fitted curves were negative, those values were set equal to zero in the computational code.
Figure 3. Superimposed fitted curves and residuals for the wavelength-dependent transmissivities of two the dichroic filters (DF1, DF2), the three interference filters (998nm IF, 810nm IF, 640nm IF, FWHM=70 nm) as well as the responsivity of the silicone photo-detectors (A/W): $\tau_1(\lambda)$, $\tau_2(\lambda)$, $\tau_{i1}$ (998 nm), $\tau_{i2}$ (810 nm), $\tau_{i3}$ (640 nm) and $R_{pd}$. Transmittance and responsivity data were obtained from the manufacturer for the particular optical components used herein. The residuals (residual = data - fit) of each curve fitting are also shown at the bottom.

The goodness of curve-fitting of the component transmissivity and responsivity curves shown in Fig. 3 are listed in Table 1. The parameter SSE denotes the summed square error from the fitted curve to the data values; it is also called the summed square of residuals. A value near 0 indicates that the model has a small random error, and that the fit is more useful for prediction. The parameter R-square denotes how successful the fit is in representing the variation of the data. R-square is defined as the ratio of the variance of fitted values to the variance of the data values. R-square can take on any value between 0 and 1, with a value closer to 1 indicating that a greater proportion of the variance is accounted for by the model.

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<th>Goodness of fit</th>
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<th>R-square</th>
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</table>

Table 1. Sum Squared Errors (SSE) and R-square value of curves fitted to interference and dichroic filters as well as to silicone photo-detectors.

1.2.6. Temperature Calculation Methods

Two methods were developed and used to calculate temperature in this paper based on the three-color voltage signals of the optical pyrometer; results are compared for distinct coal particles from different ranks.

1.2.6.1. Modified Pyrometric Signal Ratio Method

This method improves on the simplified ratio pyrometry method of Levendis et al. [3]. For this three-wavelength instrument, Eqn. 9 is used to derive the following signal ratios, upon cancellations of the luminous area term, $A$, at each instant of time.

$$
\frac{S_i}{S_j} = \frac{C_i \int_{\Delta \lambda} \varepsilon_{\lambda} I_{\lambda b} g_{\lambda} (\lambda) d\lambda}{C_j \int_{\Delta \lambda} \varepsilon_{\lambda} I_{\lambda b} g_{\lambda} (\lambda) d\lambda} \quad i=1,2, \quad j=2,3, \quad i \neq j
$$

(13)

where $C_i$ and $C_j$ are calibration constants, $S_i$ and $S_j$ are measured voltage signals by the pyrometer at different channels.
Three different temperatures can be derived from the above signal ratio equations. First, three deviation functions, $e_{ij}$, are defined to solve these equations for $T$:

$$
e_{ij}(T) = \frac{S_i}{S_j} - \frac{C_i \int_{\Delta \lambda_j} \varepsilon_{ij} I_{i\lambda b} \rho_i(\lambda) d\lambda}{C_j \int_{\Delta \lambda_j} \varepsilon_{ij} I_{i\lambda b} \rho_j(\lambda) d\lambda} = 0 \quad i=1,2, \quad j=2,3, \quad i \neq j \tag{14}$$

The desired temperatures are the roots of $e_{12}$, $e_{13}$ and $e_{23}$. For every set of signal ratio $S_i/S_j$ with $\lambda_i > \lambda_j$, the deviation functions satisfy the following conditions:

$$\lim_{T \to -\infty} e_{ij}(T) = -\infty \quad \lambda_i > \lambda_j \tag{15}$$

$$\lim_{T \to 0} e_{ij}(T) = S_i/S_j > 0 \quad \lambda_i > \lambda_j \tag{16}$$

$$\frac{\partial e_{ij}}{\partial T} > 0 \quad \lambda_i > \lambda_j \tag{17}$$

Hence, based on the conditions (15), (16) and (17) above, each deviation function has a unique root. For the proof of these conditions, see Appendix part A.

Figure 4 shows typical behavior of deviation functions versus temperature for one set of signals at an instant of time in a particle’s combustion history.
Figure 4. Typical behavior of error functions of ratio pyrometric method for one set of signals at one instant of time in a particle’s combustion history. Roots are obtained where the deviation-functions equal to zero. The three deviation-functions above have different scales in order to be shown in one plot. (The trend and the sign of deviation-functions are of interest here, even if the absolute values are of different scales).

1.2.6.2. Non-linear Least-Square Method

Based on the measured voltage signals $S_1$, $S_2$ and $S_3$, this method finds the most probable distribution of Planck’s law that minimizes the sum of squared errors $\sum \Delta^2$ between the measured and calculated signals ($S$ and $s$, respectively).

$$\sum_{n=1}^{3} \Delta_n^2 = \sum_{n=1}^{3} (S_n - s_n)^2$$

(18)

$\sum_{n=1}^{3} \Delta_n^2$ is a function of both temperature and area, $\sum_{n=1}^{3} \Delta_n^2 = f(T, A)$. The first order partial derivatives of the function with respect to all independent variables, i.e. $T, A$, should equal to zero at the extremum points.

$$\frac{\partial}{\partial A} \sum_{n=1}^{3} \Delta_n^2 = \frac{\partial f}{\partial A} = 0$$

(19)

$$\frac{\partial}{\partial T} \sum_{n=1}^{3} \Delta_n^2 = \frac{\partial f}{\partial T} = 0$$

(20)

Substituting Eqn. 5 into the above:

$$\frac{\partial}{\partial A} \sum_{n=1}^{3} \Delta_n^2 = \frac{\partial f}{\partial A} = \sum_{n=1}^{3} \left[ (S_n - C_n A \int_{\Delta\lambda_n} \varepsilon_{\lambda_n} I_{\lambda_n} g_n (\lambda) d\lambda) (-2C_n \int_{\Delta\lambda_n} \varepsilon_{\lambda_n} I_{\lambda_n} g_n (\lambda) d\lambda) \right] = 0$$

(21)
\[
\frac{\partial}{\partial T} \sum_{n=1}^{3} \Delta_n \sum_{m=1}^{3} = \frac{\partial f}{\partial T} = \sum_{n=1}^{3} \left( S_n - C_n A \int_{\lambda_1}^{\lambda_2} \varepsilon_{\lambda_i} I_{\lambda b} g_n (\lambda) d\lambda \right) (-2C_n A \frac{\partial}{\partial T} \int_{\lambda_1}^{\lambda_2} \varepsilon_{\lambda_i} I_{\lambda b} g_n (\lambda) d\lambda) = 0
\] (22)

These are two equations with two unknowns \( T, A \). To obtain a solution for \( T \), each of the above equations is first solved for \( A \). Then \( A \) is eliminated between the two ensuing equations by equating them and, subsequently, a solution for \( T \) is obtained iteratively:

\[
A = \frac{\sum_{n=1}^{3} S_n C_n \int_{\lambda_1}^{\lambda_2} \varepsilon_{\lambda_i} I_{\lambda b} g_n (\lambda) d\lambda}{\sum_{n=1}^{3} C_n \int_{\lambda_1}^{\lambda_2} \varepsilon_{\lambda_i} I_{\lambda b} g_n (\lambda) d\lambda} = H(T)
\] (23)

\[
A = \frac{\sum_{n=1}^{3} S_n C_n \int_{\lambda_1}^{\lambda_2} \varepsilon_{\lambda_i} \frac{\partial I_{\lambda b} (\lambda, T)}{\partial T} g_n (\lambda) d\lambda}{\sum_{n=1}^{3} C_n \int_{\lambda_1}^{\lambda_2} \varepsilon_{\lambda_i} \int_{\lambda_1}^{\lambda_2} \varepsilon_{\lambda_i} \frac{\partial I_{\lambda b} (\lambda, T)}{\partial T} g_n (\lambda) d\lambda} = G(T)
\] (24)

\[A = H(T) = G(T)\] (25)

To obtain a convenient iterative process for deducing \( T \), we define a deviation function as follows:

\[\varepsilon(T) = H(T) - G(T) = 0\] (26)

The root of this equation is the desired temperature.

Fig. 5 shows a typical behavior of this deviation-function for one set of signals, at an instant of time in a particle’s combustion history.
Figure 5. Typical behavior of deviation-functions of the least-square pyrometric method for one set of signals, at an instant of time in a particle’s combustion history. A root is obtained where the deviation function equals to zero.

The root of the deviation function is $T_m$ and the related radiating area is $A_m$, i.e., $(T_m, A_m)$ is the extremum point of the function $\sum \Delta_n^2$. It will be shown in Appendix part B that this extremum point is the local minimum of this function.

A few assumptions were made:

a) The emissivity of the particles is assumed to be a function of wavelength only. There is evidence that this assumption is valid for carbon particles burning in air, as previously discussed.

b) The size of radiating area of a particle ($A$) and its temperature ($T$) are assumed to be independent parameters. Hence, $\sum_{n=1}^{3} \Delta_n^2$ can be assumed to be a function of two independent variables, $T$ and $A$. 
c) For simplicity, all of the other wavelength-dependent functions inside the integral of Eq. 5, i.e., the transmittances of dichroic and interference filters as well as the photo-detector responsivities are grouped together into one function of wavelength, $g_n(\lambda)$, for each channel $n$.

Using least square method, the mean radiating surface area of each particle can also be calculated besides temperature, using Eqn. 23 or Eqn. 24. The same parameter can also be calculated from a manipulation of the signal ratio pyrometric method, as outlined by Timothy et al. [23] and Levendis et al. [3].

### 1.2.7. Computational Considerations

A computer code has been written to calculate temperatures and generate temperature-time histories for burning particles using both of the aforementioned methods. Pyrometric signal files were acquired using the LabView 8.0 software. The sample collection card is of the Model PCI-6221 and output sampling rate is about 65 (samples/channel)/ms. Each signal file consists of four columns: one of them is time and the remaining three are voltages generated in each channel. Each file consists of approximately 2,000 to 10,000 time-dependent signal points. A mid-point iteration scheme, between an initial temperature (assumed to be the furnace wall temperature) and the resulting temperature from each iteration step, is performed to obtain the roots of the deviation-function at an instant of time.

A composite trapezoidal rule (the interpolating function is a first degree polynomial) with 200 $\Delta\lambda$ steps in the wavelength band of each interference filter ($0.88 \leq \lambda_1 \leq 1.08(\mu m)$, $0.69 \leq \lambda_2 \leq 0.96(\mu m)$, $0.5 \leq \lambda_3 \leq 0.82(\mu m)$), shown in Fig. 3, has been employed to perform numerical integrations. This is a sufficient number of steps as the outcome of the numerical integrations herein does not change with decreasing the step interval. The results of this scheme are also
compared with the results using other schemes, such as the composite Simpson’s rule (the interpolating function is a second degree polynomial), and the results are in good agreement (less than 0.2K for deduced temperature).

The voltage signals that are needed to calculate temperatures in a combustion event, are obtained by subtracting base-line signals (voltage outputs) from recorded signals (voltage outputs) at each channel of the pyrometer, i.e., \( S_{\text{event}} = V_{\text{event}} - V_{\text{baseline}} \). The baseline signals are established by averaging a sufficiently large number of data points (herein chosen as 200) prior to the onset of a combustion event. The signals were smoothed with a 15 points scheme, as follows:

\[
S_n(i) = \frac{\sum_{k=-7}^{7} S_n(i+k)}{15} \tag{27}
\]

The process of smoothing is limited to 15 points only, corresponding to 0.23 ms, so that no important combustion event gets masked on the temperature profiles. The same scheme is used for smoothing the temperature profiles, as shown below:

\[
T(i) = \frac{\sum_{k=-7}^{7} T(i+k)}{15} \tag{28}
\]

The first and last seven points \((i = 1,2,\ldots,7, i = n-7, n-6,\ldots n-1)\) of \( S_n \) and \( T \) are kept unchanged. They do not have significant effect on the profiles, as the number of points in each profile is more than 2000.
1.2.8. Coal particle emissivity

In general, the emissivity of coal particles may depend on both wavelength and temperature. However, Thorn and Simpson [19], and Neuer [21] showed that the emissivity of carbon (graphite) exhibits only a weak dependence on temperature in the wavelength range of this instrument (0.5 < \( \lambda \) < 1.1), at temperatures relevant to coal combustion in air (1300 K - 2000 K). Thus, the coal particle emissivity was taken herein to be a function of wavelength only. If the emissivity of the coals is approximated as a linear function of wavelength only, then:

\[
\varepsilon_\lambda = a + b\lambda
\]  \hspace{1cm} (29)

Such linear approximations are reasonable based on the data of Neuer [21], at least over the limited wavelength range of our interest herein (0.5 < \( \lambda \) < 1.1). Subsequently, based on the combined results of Refs.[19-21], the emissivity range of the two coals were assumed to be:

- Bituminous (PSOC-1451): 0.96-0.92 (for 0.5 < \( \lambda \) < 1.1),

then \( a =1.035 \), \( b =-0.125(1/\mu m) \)

- Lignite (PSOC-1507d): 0.98-0.95 (for 0.5 < \( \lambda \) < 1.1),

then \( a =0.725 \), \( b =-0.075(1/\mu m) \)

The difference between particle temperatures calculated with these linear emissivity approximations and those calculated from the customary gray-body assumption are discussed in the Section 3.3.
1.2.9. Calibration of the pyrometer

Calibration of the pyrometer was conducted with two different devices, a high-temperature tungsten lamp and a moderately-high temperature blackbody source, as shown in Fig. 1. The obtained data were used to derive a combined calibration curve. The advantage of combined calibration is that a wide range of temperatures were covered: 1273 to 2745 K. This range of temperature is of interest to single coal particles burning in air as well as in oxygen-enriched environments.

1.2.9.1. Use of a tungsten lamp pre-calibrated by NIST

A General Electric tungsten lamp was pre-calibrated by the US National Institute of Standards and Technology (NIST); apparent temperature values were provided at four specific wavelengths versus lamp current. Using Wien’s approximation and accounting for the emissivity of tungsten at the given wavelengths and apparent temperatures, true temperatures of the lamp can be computed [3,7].

$$\frac{c_1}{\lambda^5} \exp\left(-\frac{c_2}{\lambda T_a}\right) = \varepsilon \lambda \frac{c_1}{\lambda^5} \exp\left(-\frac{c_2}{\lambda T_l}\right)$$  \hspace{1cm} (30)

Calculated true lamp temperatures are in the range 1927-2745K.

1.2.9.2. Use of a blackbody furnace

For blackbody calibration of this pyrometer, a Pegasus-R high-temperature blackbody source Model 970 (from Isotech North America) was utilized. This is a compact, portable, high-temperature furnace for calibrating thermometers. This model has a 20mm cavity diameter with a 65mm depth. The temperature range is 473 K to 1473 K and the emissivity of the blackbody is
0.995. The entrance aperture diameter is 10mm and the stability of temperature is ±0.1K. The Pegasus-R blackbody source has been calibrated at the National Physical Laboratory (NPL) with an uncertainty of ±2 K.

In order to eliminate any background radiation, calibration tests were performed several times in a dark laboratory, even if no evidence was found that laboratory lights made any difference in the outcome.

The output calibration signals from the pyrometer were recorded at the three wavelengths (0.64, 0.81 and 0.998 μm) of this instrument. Typical signals generated from the NIST tungsten lamp were presented by Bejarano and Levendis [7], whereas typical signals generated by the blackbody cavity are illustrated in Figure 6a. The recorded signal ratios from both devices, at different wavelength pairs, are plotted as $S_i/S_2$ versus the integral ratios that appear in Eqn. 13 to determine $C_i/C_2$. The same procedure is applied to find $C_i/C_3$ from $S_i/S_3$ and to find $C_2/C_3$ from $S_2/S_3$ using the same Eqn. set.

For simplicity integral ratios are symbolized as $a_i/a_2$, $a_i/a_3$ and $a_2/a_3$, as shown below:

$$\frac{S_i}{S_j} = \frac{C_i}{C_j} \frac{\int_{\lambda} e_{i\lambda} I_{i\lambda b} g_i(\lambda) d\lambda}{\int_{\lambda} e_{j\lambda} I_{j\lambda b} g_j(\lambda) d\lambda} = \frac{C_i}{C_j} \frac{a_i}{a_j} \quad i=1,2, \quad j=2,3, \quad i\neq j$$  \quad (31)

Note that the signal ratio versus the integral ratio in each pair (e.g., $S_i/S_2$ versus $a_i/a_2$) is a straight line, where the slope is the calibration constant ratio ($C_i/C_2$) and the intercept should be zero. Wavelength-dependent parameters are excluded from calibration ratios; they are calculated inside the integrals shown above. In this procedure, the emissivity inside the integrals were either taken as those of tungsten at various temperatures and wavelengths (from Devos [24]) in the case
of the NIST lamp, or were assumed equal to 0.995, independently of temperature and wavelength, in the case of the blackbody cavity. Each integral can then be calculated from the known temperatures of the two sources, taking into account the wavelength-dependent transmissivities of all filters and responsivities of detectors, over the range of wavelengths, as shown in Eqns. 31. Figures 6 (b-d) show the combined calibration charts and calibration constants for each channel.

![Calibration charts](image)

**Figure 6.** (a) Typical blackbody furnace calibration signals captured by the pyrometer. (b-d) Pyrometer calibration charts combining data from two different sources: a NIST tungsten lamp and a blackbody furnace. The slopes of the linear fits are the ratios of calibration constants, \( \frac{C_1}{C_2} \), \( \frac{C_1}{C_3} \), \( \frac{C_2}{C_3} \).
The linear least-squares method is used to fit a linear polynomial to calibration data. A linear model is defined as an equation that is linear in the coefficients (here a first order polynomial). In this linear first order polynomial fit, the number of data is greater than the number of unknowns. Hence the system of equations is over-determined. The least-squares fitting process minimizes the summed square of the residuals between data and fitted curve (the first order polynomial herein).

Three kinds of errors are responsible for deviations from the expected zero intercepts in Fig.6: (i) errors in measured data (calibration points: \(T, S_i\)): these errors and their effects have been explained in Sections 2.2.a and 2.2.b. Some errors also arise from the precision of calibration procedures, particularly with the NIST lamp, where a small notched section of its tungsten filament has to be focused on. (ii) numerical integration errors to determine \(a_i/a_j\) in Figure 6: these errors and their quantitative effects were briefly described in Sections 2.2g and 2.7. (iii) curve-fitting errors: this error arises from the curve-fitting process.

1.3. Results and Discussion

1.3.1. Temperature-time histories of single coal particles

Representative pyrometric radiation intensity signals of individually-burning coal particles and associated temperature profiles, deduced from the above theoretical formulations and computer code, are shown in Fig. 7. These plots exemplify the agreement among the three temperatures calculated from the pyrometric signal ratio method and, also, the temperature calculated from the pyrometric signal least-square method. The temperature threshold value at the beginning and at the end of the temperature profiles of Fig. 7 was set to 1400 K, which was
the furnace wall temperature set-point of this study. The reason for this action is that temperature readings below the wall temperature were deemed unreliable, since in such cases the pyrometer may have detected wall radiation reflected on the particles. Therefore, temperatures calculated based on very weak signals encountered at the beginning and at the end of each radiation intensity profile, i.e., when the noise to signal ratios therein approached unity, the calculated temperatures were set to the threshold value of 1400 K.

![Pyrometric signal profiles and deduced temperature-time profiles of single particles from two different coal ranks (bituminous and lignite), using both ratio pyrometry and least-square pyrometry methods. The furnace wall temperature was set at 1400 K.](image)

**Figure 7.** Pyrometric signal profiles and deduced temperature-time profiles of single particles from two different coal ranks (bituminous and lignite), using both ratio pyrometry and least-square pyrometry methods. The furnace wall temperature was set at 1400 K.

In the case of strong pyrometric signals ($S$), the electronic noise caused very small uncertainties in temperature (<3 K) in the case of the $T_{998/810}$, which is the best case as the two signals ($S$) involved therein are the strongest pair, and within several degrees(<13 K) in the case of $T_{810/640}$, which is the worst case as the 640 nm signal is the weakest. Strong signals were encountered in most pyrometric profiles of burning coal particles, see Fig. 7. However, at the fringes of a profile, i.e., at its very beginning and particularly at its end, as the particle nears
extinction, weak signals are encountered because of low temperatures and small luminous areas. In these cases, the uncertainty in temperature increases drastically, especially in $T_{810/640}$, less so in $T_{998/640}$, but not much in the $T_{998/810}$ case. Therefore, with the exemption of the particle profile fringes, the temperature spreads among the three derived temperatures, $T_{998/810}$, $T_{998/640}$, $T_{810/640}$, are not affected by the uncertainty caused by the electronic noise. For instance, in the case of the particular bituminous coal profile shown in Fig. 7a, application of the method described by Bejarano and Levendis, in the time frame of 20-80 ms, resulted in electronic noise-induced uncertainty of up to several degrees ($<10$ K), meanwhile the spread between the highest and the lowest of the three temperatures was as much as 200 K. To the contrary, upon applying the methodology-improvements outlined in this manuscript, the corresponding spread was reduced to 24 K in the profile shown in Fig. 7a. Least-square method-based temperatures are in trend agreement with the $T_{998/810}$, but not necessarily identical in values.

The agreement among the three different temperatures, encountered in the case of the lignite coal particle shown in Fig. 7b, was less successful than that in the bituminous coal case. This may be attributed to observed fragmentation of the coal particles into a large number of pieces, see Ref. [25]. Mathematically speaking, in this case the area of the original particle does not change continuously as it burns. In fact, it changes abruptly at a moment in time by fragmentation. As a result, the mathematical formulation which is developed for continuity of the sum of squared errors $\sum \Delta^2$ versus $T$ and $A$ is compromised.

1.3.2. Luminous area-time histories of single coal particles

The variation of the luminous surface area of a burning bituminous coal particle is shown in Fig. 8. The area is calculated based on either the pyrometric signal least-square method or the
pyrometric signal ratio method, and results are shown superimposed in Fig. 8. In the former method, after establishing the particle temperature at each instant of burnout time, this temperature is applied to either Eqn. 23 or Eqn. 24 to determine the size of the luminous source. In the latter method, Eqn. 20 of Levendis Estrada and Hottel [3] was implemented using the 998 nm and 810 nm wavelengths, and the size of the luminous char particle at the early stages of char combustion as a chosen reference point. A shown in the photographic sequence of Fig. 8, the char particle size at 100 ms is equal to or just a little bigger than the original coal particle before ignition, i.e. at 10 ms; which is justifiable assuming a small degree of swelling. Thus, the particle size of the burning char at this stage was taken to be at the upper limit of the used size cut, i.e., 90 µm. The fact that the resulting area (or diameter) profiles, shown in Fig. 8, start from a zero value, is because the pyrometer detects the luminous area of each particle, instead of its geometric area, and the luminous area is indeed zero prior to ignition.

Coal particles are neither spherical nor homogeneous and, hence, their burning intensity is neither uniform in space nor constant in time. Nevertheless, it may be helpful and instructive to estimate an apparent effective diameter for coal particles during burning. This can then be verified by comparison with either initial average coal diameters (from nominal size-cuts based on sieving) or instantaneous particle diameters (from back-lit cinematographic observations). Subsequently, the history of particle diameter variation during combustion may be assessed with this method.

Based on the cinematographic observations of Levendis et al. [25], bituminous coal experiences sequential luminous volatile-matter flames and luminous char combustion. Cinematographically-determined initial back-lit coal particle sizes were between 70 to 100 µm (which is in agreement with the sieve size cut of 75-90 µm), volatile flame sizes were in the
range of 250-300 μm and initial char diameters were in the range of 80-100 μm. This is in very good agreement with the calculations shown herein, base on the pyrometric data alone.

Bituminous coal (Pittsburgh#8, Pennsylvania, PSOC-1451)

![Graph](image)

**Figure 8.** Variation of calculated diameters of a bituminous coal particle (from a 75-90 μm size cut) burning at a furnace wall temperature of 1400 K. Results from the pyrometric signal least square method and the pyrometric signal ratio method are shown superimposed. Also shown, at the bottom of the figure, is a time-resolved photographic sequence of events for such a particle, captured by high-speed back-lit cinematography.

1.3.3. Effect of particle emissivity on temperature

1.3.3.1. Pyrometric Signal Ratio Method

In this section, temperature–time histories of coal char particles were calculated based on two assumptions for char emissivity: (a) that particle emissivity varies linearly versus the wavelength, see Eqn. 29, and (b) that emissivity is independent of the wavelength (i.e., the gray-
body assumption based on [26,33]), in which case the emissivity ratio at two different wavelengths is unity. The former assumption, as applied herein, resulted in deviations of the emissivity ratios \((\varepsilon_{\lambda_1}/\varepsilon_{\lambda_2}, \varepsilon_{\lambda_1}/\varepsilon_{\lambda_3}, \varepsilon_{\lambda_2}/\varepsilon_{\lambda_3})\) from unity by at most 4-5%. The impact of these two different assumptions on temperature is exemplified in the temperature profiles of the two particles of Fig. 7. As shown in Fig. 9, the gray body assumption resulted in higher char temperatures, by approx. 40 K, in both cases. Thus, it is apparent that the deduced particle temperatures are sensitive to the values of the emissivity ratios used in the calculations. The gaps between the three ratio temperatures, however, remain approximately unchanged (in the order of ±30K) regardless of the emissivity assumption. It should be noted that in this calculation volatile matter flame emissivities were treated with the gray body emissivity assumption, based on the study of Panagiotou et al. [6]. The effect of sooty volatile matter on measurement of coal particle temperature has also been described in Refs. [1,8,28,29].

**Figure 9.** Effect of emissivity treatment (i.e., \(\varepsilon\) independent or linearly-dependent on \(\lambda\)) on the temperature-time history of single coal char particles using the pyrometric signal ratio method. The furnace wall temperature was set at 1400 K.

1.3.3.2. Pyrometric Signal Least-Square Method
Figure 10 shows the char particle temperature profiles obtained from the least-square method using either the gray-body or the linear emissivity assumptions. As in the case of the pyrometric signal ratio method discussed above, the gray body emissivity assumption resulted in calculated temperatures that were higher by 30-40K than those calculated based on the linear emissivity assumption for the same two coal particles.

![Figure 10](image)

**Figure 10.** Effect of emissivity treatment (i.e., $\varepsilon$ independent or linearly-dependent on $\lambda$) on the temperature-time history of single coal char particles using the pyrometric signal least-square method. The furnace wall temperature was set at 1400 K.

### 1.3.4. Effect of pyrometer calibration on temperature

In a previous section, we introduced two different methods to calibrate the pyrometer (tungsten lamp and blackbody cavity), the results of which were combined to derive the calibration constant ratios of Eqns. 31. The combined calibration was principally chosen to cover the widest possible temperature range pertinent to this study. The sensitivity analysis in this section compares the results of the combined calibration with the results of each calibration method, considered individually. Temperatures were calculated based on three different
calibrations (tungsten lamp, blackbody cavity, combined), for a number of particles from different coal ranks. The spreads among the three temperatures were recorded for the sections of each particle temperature profile where strong signals were encountered (i.e., high signal to noise ratio). Thus, temperatures at the very beginning and at the ending portions of each profile were not considered in this averaging process, as signals therein were generally noisy. Temperatures spreads were averaged for at least 50 points in different temperature-time profiles, and are shown in Table 2. Standard deviations (σ) for each set of temperature spreads are also shown in this table.

Table 2. Effect of calibration type on the agreement between pairs of temperatures in the pyrometric signal ratio method

<table>
<thead>
<tr>
<th>Calibration type</th>
<th>Tungsten Lamp</th>
<th>Blackbody</th>
<th>Combined</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average temperature spread between $T_{\text{max}}$ and $T_{\text{min}}$, where $T$ is any of $\lambda^{-1}<em>{640}$, $\lambda^{-1}</em>{810}$, $\lambda^{-1}<em>{998}$, $\lambda^{-1}</em>{1010}$</td>
<td>240 K (σ=38)</td>
<td>118 K (σ=32)</td>
<td>56 K (σ=15)</td>
</tr>
</tbody>
</table>

Table 2 illustrates that the worst agreement between the three temperatures is encountered when calibration was performed with the tungsten lamp only, whereas the best agreement is encountered when the combined calibration was implemented. The combined calibration encompasses 14 points, while the tungsten lamp and the blackbody calibrations include a lesser number of points, 9 and 5, respectively. Moreover, the combined calibration spans the temperature range of 1276 - 2745 K, which is a good match to coal temperatures encountered in this work. To the contrary, the individual tungsten lamp and blackbody calibrations span narrower temperature ranges, 1927 - 2745 K and 1276 - 1477 K, respectively. This finding suggests that it is appropriate to perform instrument calibrations with radiation sources that span...
the entire range of temperatures relevant to a given application. Increasing the number of calibration points may advance accuracy.

The following three sections examine the effects of the wavelength dependencies of the dichroic filters (Section 3.5), the interference filters (Section 3.6), and the photo-detectors (Section 3.7) on the spreads among the three temperatures of the pyrometric signal ratio method. In these sections, all calculations implemented the combined calibration and the linear emissivity assumption.

1.3.5. Effect of modeling the transmissivities of the dichroic filters on temperature

This section presents the effects of modeling the transmissivity of the dichroic filters either as a periodic function of wavelength, shown in Eqns. 10a and 10b, or as a constant with wavelength. In this calculation, the combined calibration was implemented, based on the results of the previous section. Also, the transmissivities of the interference filters and the responsivities of the detectors were assumed to be functions of wavelength, and every other parameter was kept the same as before. Pyrometric ratio temperatures were calculated for a number of 50 coal particles. As before, the spreads among the three temperatures were recorded for the sections of each particle temperature profile where strong signals were encountered. As shown in Table 3, the disagreement among the three pyrometric temperatures is reduced considerably by using the wavelength-dependent model for the dichroic filter transmissivities. Standard deviations (σ) for each set of temperature spreads are also shown in this table.

Table 3. Effect of mathematical treatment of the dichroic filter transmissivities on the agreement between pairs of temperatures in the pyrometric signal ratio method

<table>
<thead>
<tr>
<th>Dichroic filter model</th>
<th>Transmissivity assumed to be</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmissivity</td>
<td></td>
</tr>
</tbody>
</table>

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1.3.6. Effect of modeling the transmissivities of the interference filters on temperature

The effects of using a Gaussian function for modeling the wavelength-dependence of the transmissivity of the interference filters (Eqns. 11) are shown in Table 4. To arrive to these values, the same procedure was used as before, i.e., the combined calibration was implemented and, this time, the dichroic filter transmissivities and the detector responsivities were treated as functions of wavelength. As shown in Table 4, the disagreement among the three pyrometric temperatures is greatly reduced by using the wavelength-dependent model for the interference filter transmissivities. Standard deviations (σ) for each set of temperature spreads are also shown in this table.

Table 4. Effect of mathematical treatment of the interference filters transmissivity on the agreement between pairs of temperatures in the pyrometric signal ratio method.

<table>
<thead>
<tr>
<th>Interference filters model</th>
<th>Transmissivity assumed constant</th>
<th>Transmissivity assumed to be a function of wavelength (Eqns. 11 - 13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average temperature spread between ( T_{max} ) and ( T_{min} ), where ( T ) is any of ( T_{\lambda=998} ), ( T_{\lambda=988} ), ( T_{\lambda=910} ), ( T_{\lambda=810} ), ( T_{\lambda=410} ), ( T_{\lambda=498} )</td>
<td>116 K ( (\sigma=22) )</td>
<td>56 K ( (\sigma=15) )</td>
</tr>
</tbody>
</table>

1.3.7. Effect of modeling the responsivities of the silicon photo-detectors on temperature

The effects of using a periodic function to model the wavelength-dependence of the responsivities of the silicone photo-detectors (Eqn. 12) are shown in Table 5. To arrive to these
values, the same procedure was used as before, i.e., the combined calibration was implemented and, this time, both the dichroic and the interference filter transmissivities were treated as functions of wavelength. As shown in Table 5, the disagreement among the three pyrometric temperatures is reduced by using the wavelength-dependent model for the detector responsivities. However, the percentage of reduction in temperature is less than before. Standard deviations ($\sigma$) for each set of temperature spreads are also shown in this table.

**Table 5.** Effect of mathematical treatment of the photo-detectors responsivity on the agreement between pairs of temperatures in the pyrometric signal ratio method.

<table>
<thead>
<tr>
<th>Photo-detector model</th>
<th>Responsivity assumed constant</th>
<th>Responsivity assumed to be a function of wavelength (Eqn. 14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average temperature spread between $T_{\text{max}}$ and $T_{\text{min}}$, where $T$ is any of $T_{\lambda_{1}}$, $T_{\lambda_{2}}$, $T_{\lambda_{3}}$, $T_{\lambda_{4}}$</td>
<td>65 K ($\sigma=15$)</td>
<td>56 K ($\sigma=12$)</td>
</tr>
</tbody>
</table>

In summary, the combined effect of the wavelength dependencies of all pyrometric components examined above (dichroic filters (Section 3.5), interference filters (Section 3.6), and photo-detectors (Section 3.7)) was to reduce the average spread among the three temperatures of the pyrometric signal ratio method from 167 K to 56 K. In all of these calculations the combined calibration and the linear emissivity assumption were used.

**1.4. Conclusions**

Temperature-time and luminous-area-time histories of burning coal particles were deduced from radiation intensity signals detected by a three-color optical pyrometer, using Planck’s theory. Two different mathematical approaches were used to calculate such temperatures and
areas, one based on the pyrometric signal ratio method, another based on the pyrometric signal least-square method. In these calculations, the transmissivities and responsivities of the light-path components of the pyrometer (dichroic filters, interference filters and photo-detectors) that are functions of wavelength, were modeled mathematically. This action complicated the formulation and solution of governing equations, however it increased the rigor of the temperature deduction process. For each method, it was shown that a unique solution for temperature exists at any instant of time in the burnout histories of each single coal particle.

Use of this approach may enhance one’s confidence on the temperature calculation since the spread, which is typically encountered among the three derived temperatures in the case of the pyrometric signal ratio method was drastically narrowed. Further reductions in the aforesaid spread among the temperatures were encountered using multi-source calibrations and, by improving on the emissivity assumption for the surfaces of these particles. The resulting spread, $T_{min}$ to $T_{max}$ of the three temperatures in the pyrometric signal ratio method was reduced, on the average, to approx. 50 K. Also, it is worth noting that the temperature that involves the two strongest signals (herein 998 and 810 nm) provided the best resolution at the beginning and ending sections of each combustion event. Finally, temperatures deduced by the pyrometric signal least-square method were in between (or very near) the aforementioned $T_{min}$ to $T_{max}$ spread of the pyrometric signal ratio method, throughout the burnout history of particles, in all cases. This good agreement between the two methods adds to the credibility to the final temperature outcome of these calculations.

1.5. References


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[35] Solomon, P. R., Carangelo, R. M., Best, P.E., Markham, J. R., Hamblen, D. G., Fuel, 66,

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1.6. Appendix

A) Proofs of relations (15), (16) and (17)

Eq.15: \[ \lim_{T \to 0} e_{ij} \to -\infty \quad \lambda_i > \lambda_j \]

For \( \lambda_i > \lambda_j \),

\[
e_{ij} = \frac{S_i}{S_j} \left( \frac{C_i}{C_j} \int_{\lambda_{ij}}^{\infty} e_{ij} I_{ij}(\lambda) d\lambda \right) \tag{A1}
\]

\[
\lim e_{ij} = \lim_{T \to 0} \frac{S_i}{S_j} - \lim_{T \to 0} \frac{C_i}{C_j} \int_{\lambda_{ij}}^{\infty} f_j(\lambda) e^{-\frac{C_j}{\xi T} \lambda} d\lambda = \frac{S_i}{S_j} - \frac{C_i}{C_j} \lim_{T \to 0} f_j(\bar{\lambda}_j) e^{-\frac{C_j}{\xi T} \Delta \lambda_j} \tag{A2}
\]

\[
\begin{align*}
&= \frac{S_i}{S_j} - \frac{C_i}{C_j} f_j(\bar{\lambda}_j) \Delta \lambda_j \lim_{T \to 0} e^{-\frac{C_j}{\xi T} \Delta \lambda_j} \to -\infty, \quad \lambda_i > \lambda_j
\end{align*}
\]
Eq. 16: \[
\lim_{T \to 0} e_y \rightarrow \frac{S_i}{S_j} \quad \lambda_i > \lambda_j \quad T \to \infty \quad \lim_{T \to \infty} e_y = \lim_{T \to \infty} \frac{S_i}{S_j} - \lim_{T \to \infty} \frac{C_i \int_{\Delta \lambda_i} f_j(\lambda) e^{\frac{C_i}{\lambda^2} d\lambda}}{C_j \int_{\Delta \lambda_j} f_j(\lambda) e^{\frac{C_j}{\lambda^2} d\lambda}}
\]

\[
= \frac{S_i}{S_j} - \frac{C_i}{C_j} \lim_{T \to \infty} \frac{f_j(\lambda_i) e^{\frac{C_i}{\lambda_i^2} \Delta \lambda_i}}{f_j(\lambda_j) e^{\frac{C_j}{\lambda_j^2} \Delta \lambda_j}}, \quad \lambda_i > \lambda_j \quad (A3)
\]

The right hand term is indefinite as temperature tends to infinity. Hence, using L’hopital’s rule for n times:

\[
\lim_{T \to \infty} e_y = \frac{S_i}{S_j} - \frac{C_i}{C_j} \lim_{T \to \infty} \frac{f_j(\lambda_i) e^{\frac{C_i}{\lambda_i^2} \Delta \lambda_i}}{f_j(\lambda_j) e^{\frac{C_j}{\lambda_j^2} \Delta \lambda_j}} = \frac{S_i}{S_j} - \frac{C_i}{C_j} \frac{f_j(\lambda_i) \cdot \Delta \lambda_i}{f_j(\lambda_j) \cdot \Delta \lambda_j} \cdot \left(\frac{\lambda_j}{\lambda_i}\right)^n \cdot \lim_{T \to \infty} \frac{C_i}{C_j} \frac{\lambda_j^2}{\lambda_i^2} \quad (A4)
\]

Note that \( \lambda_i > \lambda_j \). Hence, \((\lambda_j/\lambda_i)^n \ll 1\) as n tends to infinity. Therefore, although the exponential term on the right-hand side tends to unity as temperature tends to infinity, \((\lambda_j/\lambda_i)^n\) tends to zero with applying L’hopital’s rule for several times.

(21) and (22) show that deviation functions cross zero at some value of T. Hence, roots of deviation functions exist. In order to prove the uniqueness of such roots, an approximate analysis was used to show that deviation functions \((e_y)\) are monotonic functions of temperature \((T)\) as follows (Eq. 23):
Proof of Eq.17:

\[
\frac{\partial e_{ij}}{\partial T} = 0 - \frac{\partial}{\partial T} \left( \frac{C_i \int_{\Delta \lambda_i} \varepsilon_{\lambda_i} I_{ib} g_i(\lambda) d\lambda}{C_j \int_{\Delta \lambda_j} \varepsilon_{\lambda_j} I_{ib} g_j(\lambda) d\lambda} \right)
\]

(A5)

For \( \exp(c_2 / \lambda T) \gg 1 \) which is the case herein (\( c_2 \) is Planck’s second constant=14,388 \( \mu \)m K),

\[
\frac{\partial e_{ij}}{\partial T} = - \frac{C_i c_2}{c_j T^2} \left\{ \left( \int_{\Delta \lambda_i} f_i(\lambda) \frac{e^{c_2}}{\lambda} d\lambda \right) \left( \int_{\Delta \lambda_j} f_j(\lambda) \frac{e^{c_2}}{\lambda} d\lambda \right) - \left( \int_{\Delta \lambda_j} f_j(\lambda) \frac{e^{c_2}}{\lambda} d\lambda \right) \right\} \left( \int_{\Delta \lambda_j} f_j(\lambda) \frac{e^{c_2}}{\lambda} d\lambda \right)^2
\]

\[
(A6)
\]

where \( f_i(\lambda) = g_i(\lambda) / \lambda^5 \) and \( f_j(\lambda) = g_j(\lambda) / \lambda^5 \) and both are positive. For a sufficiently narrow filter bandwidth (small \( \Delta \lambda_i \) and \( \Delta \lambda_j \)), as is the case herein,

\[
\frac{\partial e_{ij}}{\partial T} = - \frac{C_i c_2}{c_j T^2} \left\{ f_i(\lambda_i) f_j(\lambda_j) \frac{e^{c_2}}{\lambda_i} \frac{e^{c_2}}{\lambda_j} \Delta \lambda_i \Delta \lambda_j \left( \frac{1}{\lambda_i} - \frac{1}{\lambda_j} \right) \right\} \left( f_j(\lambda_j) \frac{e^{c_2}}{\lambda_j} \right)^2 > 0
\]

(A7)

Note that \( \lambda_i > \lambda_j \) and \( C_i, C_j \) and \( c_2 \) are positive constants.

From relations (A2), (A4) and (A7), it can be inferred that the deviation functions are monotonic with respect to temperature and their roots are unique.

B) Proof of the local minimum of the function \( \sum_{n=1}^{\lambda} \Delta_n^2 \)
For the extremum point derived in section 2.6.2, i.e., the root of \( e(T) \), to be the minimum, the determinant of the second order partial derivatives matrix, \( M \), of the sum of squared errors
\[
\sum_{n=1}^{3} \Delta_n^2 = f(T, A)
\]
should be nonzero. Furthermore, all of the eigenvalues of such a matrix should be positive at the respective extremum point.

\[
M = \begin{bmatrix}
\frac{\partial^2 f}{\partial A^2} & \frac{\partial^2 f}{\partial A \partial T} \\
\frac{\partial^2 f}{\partial A \partial T} & \frac{\partial^2 f}{\partial T^2}
\end{bmatrix}
\]

(B1)

Let the extremum point of \( \sum \Delta^2 \) be the pair of \( T_m \) and \( A_m \). If the determinant of \( M \) is nonzero and the eigenvalues of \( M \) are all positive, then \( \sum_{n=1}^{3} \Delta_n^2 \) will be minimized at this extremum point.

\[
\frac{\partial^2 f}{\partial A^2} = \frac{\partial^2}{\partial A^2} (\sum_{n=1}^{3} \Delta_n^2) = 2 \sum_{n=1}^{3} C_n^2 \left( \int_{\lambda_n} \epsilon_{\lambda_n} I_{\lambda b} g_n(\lambda) d\lambda \right)^2 > 0
\]

(B2)

In general, due to the continuity of \( \sum_{n=1}^{3} \Delta_n^2 \) with respect to \( T \) and \( A \):

\[
\frac{\partial^2 f}{\partial A \partial T} = \frac{\partial^2 f}{\partial T \partial A}
\]

(B3)

\[
\frac{\partial^2 f}{\partial A \partial T} = \frac{\partial^2 f}{\partial T \partial A} = \sum_{n=1}^{3} \left[ (-2S_n C_n \int_{\lambda_n} \epsilon_{\lambda_n} \frac{\partial I_{\lambda b}}{\partial T} g_n(\lambda) d\lambda) + 2C_n^2 A (\int_{\lambda_n} \epsilon_{\lambda_n} I_{\lambda b} g_n(\lambda) d\lambda) \right]
\]

(B4)

Substituting \( (T_m, A_m) \) resulting from Eqs. 29-32 into second order derivatives (B3) yields to:
\[ \frac{\partial^2 f}{\partial A \partial T} = \frac{\partial^2 f}{\partial T \partial A} = 0 \]

\[ \frac{\partial^2 f}{\partial T^2} = \sum_{n=1}^{3} -2C_n S_n A \int_{\Delta_n} \varepsilon_{\lambda_n} \frac{\partial^2 I_{ijb}}{\partial T^2} g_n(\lambda)d\lambda + 2C_n^2 A^2 \left[ \int_{\Delta_n} \varepsilon_{\lambda_n} \frac{\partial I_{ijb}}{\partial T} g_n(\lambda)d\lambda \right]^2 \]

\[ \frac{\partial^2 f}{\partial T^2} = \sum_{n=1}^{3} 2C_n A \left[ \int_{\Delta_n} \varepsilon_{\lambda_n} \frac{\partial I_{ijb}}{\partial T} g_n(\lambda)d\lambda \right] \left[ -S_n + C_n A \int_{\Delta_n} \varepsilon_{\lambda_n} I_{ijb} g_n(\lambda)d\lambda \right] + 2C_n^2 A^2 \left[ \int_{\Delta_n} \varepsilon_{\lambda_n} \frac{\partial I_{ijb}}{\partial T} g_n(\lambda)d\lambda \right]^2 \]

(B5)

For noise free signals, the first term in the right hand side at extremum point \((T_m, A_m)\) is approaching to zero. Hence, at \((T_m, A_m)\),

\[ \frac{\partial^2 f}{\partial T^2} \approx 2C_n^2 A^2 \left[ \int_{\Delta_n} \varepsilon_{\lambda_n} \frac{\partial I_{ijb}}{\partial T} g_n(\lambda)d\lambda \right]^2 > 0 \]

(B7)

at \((T_m, A_m)\)

(B8)

\[ \det M \bigg|_{T_m, A_m} = |M| = \left( \frac{\partial^2 f}{\partial A^2} \right) \left( \frac{\partial^2 f}{\partial T^2} \right) \bigg|_{T_m, A_m} > 0 \]

(B9)

Based on the symmetry of matrix \(M\) (because of \(\frac{\partial^2 f}{\partial A \partial T} = \frac{\partial^2 f}{\partial T \partial A}\)), the eigenvalues are always real at the extremum point. Subsequently, to show that the function \(\sum \Delta^2\) has a minimum at the extremum point, all eigenvalues, \(\zeta\), must be positive. To find the eigenvalues,
\[ |M - \mathcal{L}| = \begin{vmatrix} \frac{\partial^2 f}{\partial A^2} - \zeta & 0 \\ 0 & \frac{\partial^2 f}{\partial T^2} - \zeta \end{vmatrix} = 0 \] (B10)

\[ \zeta_1 = \frac{\partial^2 f}{\partial A^2} > 0, \quad \zeta_2 = \frac{\partial^2 f}{\partial T^2} > 0 \] (B11)

where I is the 2×2 unit matrix. \( \zeta_1, \zeta_2 \) are both positive, because \( \frac{\partial^2 f}{\partial A^2}, \frac{\partial^2 f}{\partial T^2} \) are both positive at \((T_m, A_m)\). So the extremum point of \( \sum_{n=1}^{3} \Delta_n^2 \) is a local minimum.
CHAPTER 2

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2. Combustion Behavior in Air of Single Particles from Three Different Coal Ranks and from Sugar Cane Bagasse

Abstract

Comparative combustion studies were performed on particles of pulverized coal samples from three different ranks: a high-volatile bituminous coal, a sub-bituminous coal, and two lignite coals. The study was augmented to include observations on burning pulverized woody biomass residues, in the form of sugarcane bagasse. Fuel particles, in the range of 75-90 μm, were injected in a bench-scale, transparent drop-tube furnace, electrically-heated to 1400 K, where they experienced high heating rates, ignited and burned. The combustion of individual particles in air was observed with three-color pyrometry and high-speed high-resolution cinematography to obtain temperature-time-size histories. Based on combined observations from these techniques, in conjunction to morphological examinations of particles, a comprehensive understanding of the combustion behaviors of these fuels was developed. Observed differences among the coals have been striking. Upon pyrolysis, the bituminous coal chars experienced the phenomena of softening, melting, swelling and formation of large blowholes through which volatile matter escaped. Combustion of the volatile matter was sooty and very luminous with large co-tails forming in the wake of the particle trajectories. Only after the volatile matter flames extinguished, the char combustion commenced and was also very luminous. In contrast, upon pyrolysis, lignite coals became fragile and experienced extensive fragmentation, immediately followed by ignition of the char fragments (numbering in the order of 10 to 100, depending on the origin of the lignite coal) spread apart into a relatively large volume. As no separate volatile matter combustion period was evident, it is likely that volatiles burned on the surface of the chars. The combustion of the sub-bituminous coal was also different. Most
particles experienced limited fragmentation, upon pyrolysis, to several char fragments, with or without the presence of brief and low-luminosity volatile flames; other particles did not fragment and directly proceeded to char combustion. Finally combustion of bagasse was once again very distinctive. Upon pyrolysis, long-lasting, low-luminosity, nearly-transparent spherical flames formed around slowly-settling devolatilizing particles. They were followed by bright, short-lived combustion of the chars. Both volatiles and chars experienced shrinking-core mode of burning. For all fuels, flame and char temperature profiles were deduced from pyrometric data and burnout times were measured. Combustion rates were calculated from luminous carbon disappearance measurements, and were compared with predictions based on published kinetic expressions.

2.1. Introduction

Coal is classified into four different types, lignite, sub-bituminous, bituminous and anthracite coals (the world-wide production of coal was ~7.3 billion short tons in 2008 [1]). These varieties all descended from the origin of formation of coal: the creation of peat or partially-decomposed plant materials [2]. Increased pressure and heat from overlaying strata caused peat to dry and harden into lignite. Lignite is a brown-black coal with high-moisture and high-ash contents. It is the lowest rank coal, as its heating value is low. Nevertheless, it is an important energy resource in some countries (~1.1 billion short tons produced in 2008 [1]). Under more pressure, peat formed a higher rank coal: sub-bituminous a dull-black coal. Higher pressure resulted in the formation of bituminous or soft coal, a high-heating value coal (~5.6 billion short tons produced in 2008 [1]). Even greater pressures, developed in folded rock strata during creation of mountain ranges, produced the anthracites or hard coals, possessing the
highest heating values and the lowest amounts of moisture and ash than other coal types (~0.6 billion short tons produced in 2008 [1]).

This study contrasts the combustion behavior of representative coals from the first three categories: bituminous, sub-bituminous and lignite. The coals were received from Penn State University Coal Sample Bank in sealed containers, and were ground and sieved; sizes in the range of 75-90 μm were burned in this work. The coals originated in different locations in the USA, listed below along with the associated Coal Sample Bank designations given in parentheses: a Wilcox seam lignite coal from Texas (PSOC-1443), a Beulah seam lignite coal from North Dakota (DECS-11), a Pittsburgh #8 bituminous coal from Pennsylvania (PSOC-1451), and a Wyodak seam River Basin sub-bituminous coal from Wyoming (DECS-26). All four coals were burned in air in a laboratory-scale, electrically-heated, laminar-flow drop-tube furnace fitted with a transparent quartz tube. Single particle combustion behavior was recorded with multi-color optical pyrometry and simultaneous high-speed cinematography. This work is part of a bigger investigation that examines the high-temperature, high-heating rate combustion of coal in a wide range of oxygen environments (O$_2$ mole fractions of 20-100%), with the balance gas being either nitrogen or carbon dioxide. Combustion of coal in such environments is pertinent to proposed clean coal technologies, most notably oxy-fuel combustion. This technology is currently of intense industrial interest, as it has the potential of generating power with low pollutant emissions and, at the same time, facilitating carbon dioxide sequestration. The goal of this particular work is to thoroughly examine and document the combustion behavior of representative coals from bituminous, sub-bituminous and lignite ranks burning in atmospheric-pressure air and, thus, generate a baseline against which ensuing oxy-fuel combustion experiments in the same laboratory setup will be evaluated. Sugar cane bagasse has also been
included in this study, to provide a comparative example of combustion of biomass. Bagasse is a byproduct of sugar production. It is the residual pulp left after the juice from sugar cane is extracted, hence, it can be considered as a waste fuel (the worldwide bagasse production in 2006 was in the order of 1 billion short tons [3]. A final goal of this work is to demonstrate that the combination of multiple diagnostic techniques is necessary to comprehensively assess the combustion behavior of these fuels.

2.1.1. Review of Relevant Previous Studies on Coal Combustion

As coal is the prominent fuel in power generation worldwide, a voluminous scientific literature has been assembled detailing its combustion characteristics and the emissions therefrom. The number of scientific investigations on coal combustion peaked in the early 1980’s and, thereafter, subsided as environmental concerns and economic considerations promoted the use of cleaner-burning fuels, such as natural gas. However, premium fuels may become costlier in the future, as their known reserves are projected to be consumed sooner than those of coal [4]. Hence, interest in coal has been “re-ignited”, with the caveat that its combustion must be conducted in an environmentally-benign manner. As a result of this historic progression of coal-related research a great deal of the relevant literature is decades-old and, accordingly, the diagnostic techniques used are dated to that era. Moreover, as a great number of different coals exist internationally, and have been tested in a multitude of different combinations of experimental furnaces and operating conditions, systematic efforts to contrast the combustion behavior of different coal ranks have been hampered. As a result, there are still un-answered questions regarding the modes of ignition, combustion and extinction of coal particles of different ranks. Whereas providing answers to all such questions can be an impossibly large task, this work endeavors to expand the scientific knowledge already provided by many existing
excellent publications. Some of these publications are mentioned in the following paragraphs, but the reader should keep in mind that the list is by all means not all-inclusive.

The physical and chemical processes that are involved in the pyrolysis and combustion of coal particles are complex. Depending on the rank of coal, the heating rate, the particle size, as well as the rates of decomposition and oxygen transfer, the volatile matter evolution and homogeneous combustion, and the heterogeneous combustion of the solid residue may occur separately or simultaneously [5]. In the early stages of coal combustion, the particle reaches sufficiently-high temperatures to release volatile matter, which surrounds the surface of the particle to form soot, tar, ash, or decompose to produce gas [6,7,8,9]. Such devolatilization continues to occur within the particle, releasing volatile gases which diffuse to the surface typically causing swelling in bituminous coals [9,10], or fragmentation in lignites [9,11]. Such phenomena are clear examples of how the devolatilization of coal types differs, mainly because of their specific coal rank [11-15]. Other relevant studies include those of Tidona et al. [16], Niksa et al. [8], Saito et al. [17], Monson et al. [18], Stanmore et al. [19], Wall et al. [20], and Roberts et al. [21].

Seeker et al. [22] and McLean et al. [23] showed that in the case of bituminous coal particles the volatiles issue in jets or trails, forming a condensed phase matter around the particle which is not always distributed in spherically-uniform clouds. Bituminous coals are typically swelling, forming cenospheric chars. In regions where there are no volatile jets, the possibility for heterogeneous surface reaction with oxygen has been suggested. No volatile trails were observed for anthracites and lignites and condensed phase matter was not formed. Such coals are non-swelling. The findings were attributed to the chemical composition of the coal particles; bituminous volatiles contain soot-producing heavy hydrocarbons, whereas lignite volatiles
contain mainly CO, CO$_2$, H$_2$, H$_2$O and light hydrocarbons. Thomas et al. [24] reported that ignition and combustion behavior varies; particles of an Australian lignite experienced heterogeneous combustion before the onset of volatile evolution. Leslie et al. [25] reported that, under certain conditions, the combustion of 60 µm particles of a Montana lignite coal occurred by direct oxygen attack with little separate evolution of volatiles. Annamalai and Durvetaki [26] examined the transition from homogeneous to heterogeneous ignition and noted that the latter is favored for small particle sizes. Midkiff et al. [27] examined the combustion of bituminous and sub-bituminous coals and concluded that heterogeneous reactions are favored by small particle size, high oxygen concentration and decreased material rank. Such observations were also in line with findings of Sweeny and Grow [28] and De Soete [29] on the same lignite coal (Beulah) who concluded that the higher the oxygen concentration, the higher the temperature and hence the surface reaction rate, and the smaller the particle size, the greater the likelihood of heterogeneous ignition prior to devolatilization.

Field [30], Mitchell [10], and Hurt and Mitchell [11] reported that the reactivity of chars increases several fold as the rank of a coal decreases from anthracite to lignite. This conclusion was also supported by Joustenoja et al. [9]. Moreover, Hurt and Mitchell [11] presented unified high-temperature char combustion kinetics for a suit of coals of various rank and illustrated that their apparent reactivity decreases with increasing rank of the parent coal; or in other words it correlates inversely with the carbon content of coals. On the other hand, Timothy et al. [31] reported longer devolatilization times and slower burning rates for a lignite coal as compared to a bituminous coal, and Sahu et al. [32,33] reported the apparent reaction rate for chars from a lignite coal (PSOC-1443) to be slower than that of chars from a bituminous coal (PSOC 1451); these two coals are also included in the present study.
Previous results on coal particle combustion have shown a lot of data scatter, depending on the furnace gas temperature used, on the coal types and their origins, on the coal particle size and, of course, on particle-to-particle variability. Nevertheless, to form a general opinion on the overall temperatures and conversion times of single pulverized coals burning in air, one may consider the results of a number of previous studies. Timothy et al. [31,34] observed the entire combustion history of individual coal particles and found that the average particle surface temperatures (at 50% burnout, i.e., presumably during char combustion) were 2000 K for a lignite coal, and 2300 K for a bituminous coal, both 90-105 μm at a furnace gas (air) temperature of 1700 K. Associate devolatilization durations were 6-12 ms, but volatile matter flame temperatures were not measured. They also reported overall particle burnout-times of 30 and 60 ms for the bituminous and lignite coals, respectively. Loewenberg and Levendis [35] as well as Bejarano & Levendis [36] reported on the entire combustion history in air of 45-53 μm single particles of pre-devolatilized chars of a bituminous coal (PSOC-176) and deduced both apparent and intrinsic reactivities. Average char surface temperatures varied from 1600-1800 K, at furnace air temperatures of 1300-1500 K, respectively. Atal and Levendis [37] and Levendis et al.[38] followed combustion along the trajectory of 75-90 μm single bituminous coal particles from Pittsburgh #8 (PSOC-1451) in 1450 K air. They reported volatile flame temperatures in the vicinity of 2200 K and burn times of 10 ms; residual char temperatures were in the vicinity of 1800 K and burn times in the order of 50 ms. Sahu et al. [33] reported on combustion observations, in 1450 K air, of smaller size (45-53 μm) pre-pyrolyzed chars of the same bituminous coal (PSOC-1451), as well as chars of lignite coal (PSOC-1443). They reported temperatures in the vicinity of 2000 K and burn times of 15-50 ms; they also derived apparent kinetic rates. Murphy and Shaddix [39] conducted observations at one instant in a particle’s
history, in 24%-oxygen containing gas, and reported that the average char particle temperatures of a sub-bituminous (Highvale) coal was 2100 K and that of an Eastern US bituminous coal was 2200 K. The furnace gas temperature was non-uniform experiencing a cooling trend of 1600-1400 K along the furnace axis. Joutsenoja et al. [9] also conducted observations at one instant in a particle’s history burning at gas temperatures in the vicinity of 1150 K. A French lignite coal (Gardanne) and two German high-volatile-b bituminous coals (Westerholt, Göttelborn), in the range of 75-180 µm, were burned in atmospheric pressure air. Average particle temperatures were reported to be rather similar, in the range of 2280-2300 K; standard deviations were in the range 52-67 K.

2.2. Physical and chemical properties of the fuels

Samples for the four coals were obtained from the Penn State Coal Sample Bank, and were ground, sieved to different sizes, and dried. The size cut of 75-90 µm was selected for these experiments. Two of the coals (PSOC-1451 and PSOC-1443) were extensively characterized in previous research, see Sahu et al. [32,33]. Bagasse was obtained from a sugar-cane plant in Brazil, it was dried, chopped in a household blender and sieved. Again, the size cut of 75-90 µm was selected for these experiments; the aspect ratio of these particles was much higher than those of the coals. The proximate and ultimate analysis of these fuels is shown on Table 1.

<table>
<thead>
<tr>
<th>Rank and Fuel Source</th>
<th>PSOC-1451</th>
<th>DECS-11</th>
<th>PSOC-1443</th>
<th>DECS-26</th>
<th>Bagasse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous High Volatile A Pittsburgh #8 Pennsylvania</td>
<td>Lignite A Beulah, North Dakota</td>
<td>Lignite A Titus, Texas</td>
<td>Sub-Bituminous B River Basin Wyodak, Wyoming</td>
<td>Sugarcane Residue Brazil</td>
<td></td>
</tr>
<tr>
<td>Proximate Analysis as received, and (upon re-evaluating moisture)</td>
<td>Moisture (%)</td>
<td>Volatile matter (%)</td>
<td>Fixed Carbon (%)</td>
<td>Ash (%)</td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
<td>--------------</td>
<td>---------------------</td>
<td>-----------------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>2.5</td>
<td>33.4 (13.2)</td>
<td>28.5 (18.6)</td>
<td>26.3 (13.1)</td>
<td></td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>33.6</td>
<td>37.4 (48.6)</td>
<td>44.2 (50.3)</td>
<td>33.1 (39.0)</td>
<td></td>
</tr>
<tr>
<td>Fixed Carbon (%)</td>
<td>50.6</td>
<td>22.9 (29.8)</td>
<td>12.0 (13.7)</td>
<td>35.1(41.4)</td>
<td></td>
</tr>
<tr>
<td>Ash (%)</td>
<td>13.3</td>
<td>6.4 (8.4)</td>
<td>15.3 (17.4)</td>
<td>5.6 (6.5)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate Analysis (on a dry basis)</th>
<th>Carbon (%)</th>
<th>Hydrogen (%)</th>
<th>Oxygen (%) (by diff.)</th>
<th>Nitrogen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (%)</td>
<td>71.9</td>
<td>66.2</td>
<td>56.8</td>
<td>69.8</td>
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<tr>
<td>Hydrogen (%)</td>
<td>4.7</td>
<td>4.0</td>
<td>4.1</td>
<td>5.7</td>
</tr>
<tr>
<td>Oxygen (%)</td>
<td>6.9</td>
<td>18.6</td>
<td>15.8</td>
<td>15.6</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>1.4</td>
<td>0.9</td>
<td>1.1</td>
<td>0.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate Analysis (on a dry basis)</th>
<th>Sulfur (%)</th>
<th>Sodium (%)</th>
<th>Ash (%)</th>
<th>Heating Value Dry Fuel (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur (%)</td>
<td>1.4</td>
<td>0.7</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Sodium (%)</td>
<td>0.06</td>
<td>0.66</td>
<td>0.04</td>
<td>0.09</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>13.7</td>
<td>9.6</td>
<td>21.4</td>
<td>7.6</td>
</tr>
</tbody>
</table>

For the four coals and their proximate and ultimate analysis data was obtained from the Penn State Coal Sample Bank; upon opening the sealed containers of the supplied coal samples, variations of moisture content with storage in the laboratory were observed for all, but the bituminous, coals. The measured moisture content values are listed (in parentheses) and the remaining proximate analysis values were re-calculated and are also shown (in parentheses). The specific bagasse sample was analyzed at the University of São Paulo laboratories, São Carlos Campos.

### 2.3. Experimental methodology

The combustion studies of free-falling coal and bagasse particles were carried out in an electrically heated, laminar flow, vertical drop tube furnace at a constant wall temperature of 1400K. Drop tube furnaces or entrained flow reactors are considered to be appropriate devices for such studies, as they reproduce conditions suitable to those in practical systems, while providing a relatively simple configuration [40,41]. The radiation cavity of this furnace (an ATS
unit) is 25 cm long and is heated by hanging molybdenum disilicide elements. A sealed 7 cm i.d. transparent quartz tube was fitted in this furnace. The gas temperature profile, as measured along the centerline of the quartz tube with suction thermometry, was fairly constant throughout the length of the radiation zone at \( \sim 70 \) K below the wall temperature. Particle heating rates were very high, calculated to be in the order of \( 10^5 \) K/s. Air was introduced to the radiation cavity of the furnace through a water-cooled stainless-steel injector and also through a flow straightener, coaxial to the furnace injector, Fig. 1. The fuel particles were introduced through a port at the top of the injector by first placing them on the tip of a beveled needle syringe. Gentle taps on the needle allowed single coal particles to enter the injector and, subsequently, the furnace. The air entering through the flow straightener was preheated in the annular space between the injector and the quartz tube before it reached the main radiation cavity. The combined flow at wall temperatures of 1400 K resulted in a gas velocity of 4.55 cm/s and a gas residence time of 5.5 s inside the furnace radiation cavity.

Optical access to the radiation zone of the furnace was achieved through three observation ports: one at the top and two diagonally situated at the sides of the furnace. Pyrometric observations of single particles were conducted from the top of the furnace injector, viewing downwards along the central axis of the furnace, Fig. 1, which ideally is the particle's path-line. Accordingly, the luminous burnout histories of single particles - from ignition to extinction – could be monitored. To minimize reflected furnace radiation climbing the injector's inner walls (upon multiple reflections) (a) a 61.0 cm long injector was used, 1.25 cm i.d., (b) the injector was black-passivated and (c) a pinhole is used between the lens and the fiber. An optical fiber made with of a high-transmittance (> 99.5%) fused silica core and doped fused silica cladding with an f-number of 2.2, transmitted light from the furnace to the pyrometer assembly. This pyrometer
used two dichroic edge filters as spectrum splitters to direct the light to the three interference filters. These filters have effective wavelengths of 640, 810 and 998 nm with bandwidths (FWHM) of 70 nm. The selection of these three wavelengths was based on the expected particle temperature range and on the effects of wavelength on photo-detector sensitivity. Furthermore, these wavelengths avoid interference by the absorption bands of carbon dioxide, and minimize interference from the line emissions of sodium (0.589 and 0.5896 μm) and potassium (0.7665 and 0.7699 μm). In conjunction with these interference filters, silicon diode detectors were selected to maximize the signal sensitivity. They also possess good stability and linearity. Details of the pyrometer optics, electronics, calibration and performance are given by Levendis, Estrada and Hottel [42]. The voltage signals generated by the three detectors were amplified and then processed by a microcomputer using the LabView software.

Temperature is deduced from the three output voltage signals of the pyrometer using a non-linear least square method, based on Planck’s law. Details of this method are given by Khatami and Levendis [43]. This method was chosen over the pyrometric signal ratio method, as it utilizes all three signals of the three-color pyrometer simultaneously and generates one temperature profile. Hence, the reader can focus on the coal combustion characteristics, instead of being distracted by the presentation of three, albeit often agreeing, temperature profiles. A detailed comparison of the two methods is provided in the aforementioned reference. Instead of assuming gray body behavior for the chars, i.e., \( \frac{ε_2}{ε_1} = 1 \), the coal char emissivity was calculated assuming that it changed linearly with the wavelength \( ε = a + bλ \), based on carbon emissivity measurements conducted elsewhere [44, 45]. Application of this method to a single solid particle, like the coal char particles of this work, yields surface temperatures. However, the case of sooty envelope diffusion flames surrounding a bituminous coal particle during the
volatile combustion stage is more complicated. A sufficiently-large flame-surrounded coal particle remains at a relatively low temperature as it devolatilizes, so that its intensity of emission in the near-infrared may be neglected [46, 47]. Therefore, most of the radiation intensity contributions stem from luminous soot in the envelope flame. Moreover, color pyrometry of a population of soot particles in the flame, spread over a range of temperatures, tends to be biased towards the hottest soot particles. It has been shown before theoretically [45] that the effective emissivity of the soot, although in isothermal flames follows an inversely proportional dependence on the wavelength, it exhibits a graybody-like characteristic, i.e., it is nearly independent of the wavelength, if a strong linear variation in temperature exists across the soot layer. As typical fuel particle envelope flames can be expected to be non-isothermal in the radial direction [47], the reported volatile flame temperatures in this work were calculated with the gray-body assumption. Hence, the volatile flame temperatures calculated with this assumption are heavily weighted towards the highest soot temperatures in these particle envelope flames. Whether the soot particles temperatures are equal to those of the surrounding gas in the flame can be debatable. Matsui et al. [48], have estimated that the difference between the gas and soot temperature inside the cylinder of a diesel engine is in the order of 1 K, because of the small size of soot particles. Because of the comparable combustion times and flame temperatures between the fuel in a diesel engine and the particles of the present experiments, it is likely that the gas and soot temperatures are also comparable herein. On the other hand, there could be some small differences arising from temperature-gradient induced thermo-phoretic effects on soot particles.
Figure 1. Schematic of the drop-tube furnace, a more detailed rendering has been shown in [49].

High-speed cinematography was conducted through slotted side quartz windows of this furnace, see Fig. 1, with or without backlight. A NAC HotShot 512SC Self-Contained Digital High-Speed video camera was used, at a speed of 1000 frames/s. The camera was fitted with an Olympus-Infinity Model K2 long-distance microscope lens to provide high-magnification and high-resolution images of the combustion events.

2.4. Experimental results

2.4.1. Pyrometric Traces
Combustion profiles of single fuel particles were observed during their entire burnout time in air, see Fig. 2. Each row of Figure 2 displays profiles of two different fuel particles, one in each column. At the top of every entry, the detected radiation intensity traces are displayed, expressed as experimental voltage signals $S_n$, for all three wavelengths of the pyrometer ($n = 1, 2, 3$). At the bottom of every entry, corresponding temperature profiles are shown.

### 2.4.2. High-Speed Cinematography stills

Selected images from high-speed and high-resolution cinematography of typical combustion events involving particles of all fuels examined herein are displayed in Fig. 3.

### 2.4.3. Scanning Electron Microscopy Images

SEM images are shown in Fig. 4. A different fuel is displayed in every row. In the left column representative untreated fuel particles are shown, in the right column pyrolyzed fuel particles are depicted, i.e., chars. To obtain these chars, fuel particles were first fluidized in nitrogen and then thin dispersions thereof were introduced to the drop-tube furnace, under steady-state, steady-flow conditions. They were pyrolyzed therein, at the same wall temperature as implemented in the combustion experiments, i.e., 1400 K. Examination of all these particles reveals differences in their original morphological characteristics and, most notably, in the transformations that take place upon pyrolysis. Structural evolution and morphological changes of the chars generated during the pyrolysis stage relate to char reactivity (Cetin et al. [50] and Refs 7-14 therein).

(a) BITUMINOUS COAL (Pittsburgh #8, Pennsylvania, PSOC-1451)
(b) SUB-BITUMINOUS COAL (Wyodak, Wyoming, DECS-26)

(c) LIGNITE COAL (Beulah, North Dakota, DECS-11)

(d) LIGNITE COAL (Wilcox, Texas, PSOC-1443)
Figure 2. Radiation intensity signals, measured by three-color optical pyrometry in voltage against time, for single particles of the five fuels of this study burning in air. Each trace is followed by temperature profiles deduced from all signals using a non-linear least square method. Particle size was 74-90 μm and furnace wall temperature was set to 1400K.

(a) BITUMINOUS COAL (Pittsburgh #8, Pennsylvania, PSOC-1451)
(b) SUB-BITUMINOUS COAL (Wyodak, Wyoming, DECS-26)

(c) LIGNITE COAL (Beulah, North Dakota, DECS-11)

(d) LIGNITE COAL (Wilcox, Texas, PSOC-1443)

(e) BAGASSE BIOMASS (Brazil)
**Figure 3.** Selected images from high-speed cinematography of typical combustion events involving particles of all five fuels used in this work (bituminous, sub-bituminous, two lignite coals and bagasse biomass). The diameter of the wire shown in sequence (a) is 250 μm. The displayed numbers in each frame are in milliseconds, where zero does not mark beginning of combustion it merely represents beginning of the depicted sequence. In the case of the sub-bituminous coal two sequences are included, one where volatile flame was present (top), and one where it was absent (bottom). In the depicted frames of the Beulah lignite two particles ignite and burn in similar fashion. Particle size was 74-90 μm and furnace wall temperature was set to 1400K.

(a) BITUMINOUS COAL (Pittsburgh #8, Pennsylvania, PSOC-1451)

(b) SUB-BITUMINOUS COAL (Wyodak, Wyoming, DECS-26)
Figure 4. SEM micrographs of particles of the five fuels used in this work (bituminous, sub-bituminous, lignite(2) coals and bagasse biomass). In the left column fuel particles are shown, in the right column the depicted fuel particles have been pyrolyzed in nitrogen, i.e., they arechars. Pyrolysis took place in the
2.5. Discussions

Combustion behavior observations

Simultaneous examination of the results of the three aforementioned diagnostic techniques (pyrometry, back-light cinematography and scanning electron microscopy) proved to be instrumental in unraveling the combustion behavior of these fuels. Such techniques revealed combustion characteristics that are highly-dependent on the rank of these fuels.

(a) Bituminous coal particles consistently exhibited two peaks in each profile, an exceedingly strong first peak followed by a significantly less pronounced second peak, see Fig. 2a. The first peak is attributed to volatile matter burning homogeneously with air in luminous envelope flames, which typically lasted for 10-20 ms. The second peak is attributed to heterogeneous combustion of char residues. This behavior of bituminous particles has been well-documented in the literature (see for instance Timothy et al. [34]; Levendis et al. [38]) and it is very evident in the cinematographic images of Fig. 3a. Upon particle heat up in the furnace, devolatilization commenced and the volatile matter ignited forming envelope diffusion flames. Such flames were sooty and very bright with diameters three times as large as those of the particles. As the particles fell by gravity in the drop-tube furnace sooty wakes or contrails formed behind them, giving the impression of meteors streaking in the sky. The effects of devolatilization are evident in the SEM photographs of Fig. 3a. During devolatilization, the initially very sharp-edged bituminous coal particles softened and morphed into bubbly cenospheric entities with blowholes, generated by hastily escaping volatile matter, punctuating their surfaces. The modulations in the
signal profiles may denote rotations of the flame and or evolution of burning volatile jets. The modulations in the temperature profile signify disturbances of the flame for instance by oxygenation when a wake or jets form, and most cinematographic observations show notable disturbances.

Upon extinction of the volatile flames, the char residues came in plain view certainly heated to some temperature, but not ignited yet. The temperature profiles dipped momentarily (for a few ms), and then rose again, as ignition of the residual chars occurred and heterogeneous combustion commenced. Combustion of the chars was lengthy and bright. Detected temperatures of most chars remained rather constant with time, whereas the radiation intensities plateaued for some time and, thereafter, declined slowly. This behavior could be taken as an indication of initial burning at decreasing density as the oxygen partially penetrates the cenosphere’s interior through blowholes. As the heterogeneous reactions intensify, oxygen penetration dwindles and the particle burns with decreasing external surface area or, rather, with decreasing radiating surface as ash coverage of the exterior surface spreads when the radius recedes. Cinematographic observations suggest that final diameters do not diminish to zero, but instead approach those of the ash residues. Extinction of the chars occurs while their diameters were still fairly significant (a fraction of the initial diameters) and ensuing sizable and low-weight ash particles were seen to linger in the back-lit furnace for a period of time, slowly settling by gravity.

(b) Sub-bituminous coal particles occasionally exhibited two peaks in each pyrometric profile. Most of the collected traces, however, contained only one peak. Examples are shown in Fig. 2 b, one for each case. Such behaviors were unraveled by resorting to cinematographic diagnostics, which revealed that in a limited number of cases a volatile flame occurred for a brief duration of time, i.e., a few milliseconds. Such flames were much smaller and less bright than those of the
bituminous coals, see Fig. 3b (top). Upon extinction of the flames, particles fragmented to several entities (in the range of 5-10), and the ensuing chars burned heterogeneously. The majority of the coal particles fragmented and then appeared to burn heterogeneously, without any evidence of initial volatile flames, see Fig. 3b (bottom). There was also a third behavioral category of sub-bituminous particles which experienced neither volatile matter flames nor fragmentation during devolatilization with the ensuing single chars burning heterogeneously. SEM micrographs revealed that the sub-bituminous particles were not as sharp-edged as the bituminous particles, their surfaces were less smooth or glassy, with much more flaky structure evident, see Fig. 4b. Upon pyrolysis some particles showed limited swelling, whereas others showed deep cracks which are likely to lead to fragmentation see Fig. 4b. The pyrometric and cinematographic profiles suggest that the chars burn as shrinking core spheres with decreasing temperatures. The strongest radiation intensities are associated with those chars that exhibit volatile flames and fragment, see Fig. 2a, the weakest are associated with those which neither exhibit volatile flames nor fragment, see Fig. 2b.

(c, d) Lignite coal particles generated only one pyrometric peak during combustion, see Figures 2c and 2d. Matching cinematographic observations also show no evidence of visibly-detached volatile flames for either of the two lignites. As mentioned in the Introduction Section, previous work by Anamalai and Durbetaki [26], Madkiff et al. [27] and Sweeny and Grow [28] as well as Lau and Niksa [51] have reported that small particles of low rank coals ignite heterogeneously. Specifically to the Beulah lignite (DECS-11) Sweeny and Grow [28] reported that it ignited heterogeneously and that volatile combustion was not observed to play a major role in the combustion process. Howard and Essenhigh [52] postulated that since the volatile flux decreases with decreasing particle size (as the volume to surface ratio decreases), the volatile flame
attaches to the particle surface and gas-phase combustion occurs simultaneously with heterogeneous combustion on the surface of the particle. Based on their experimental measurements, they derived a criterion of a particle diameter below which flames do not detach. For a Pittsburgh seam coal they reported that particles with diameters below 65 µm experienced concurrent heterogeneous and gas phase combustion on their solid surfaces. A consistent observation in the case of lignite particles was that particles fragmented during the process of devolatilization to a large number of pieces. It does not appear that the high moisture content of these lignite coals is the cause of the fragmentation, since dried coal samples experienced the same behavior. For the Beulah lignite (DECS-11) the phenomenon was more pronounced resulting in a larger number of fragments. For this coal fragmentation appeared to initiate upon ignition. This coal’s tendency for fragmentation is rather evident in the SEM micrographs displayed in Fig. 4c. The original coal particle surfaces were rough and flaky with many peaks and valleys; pyrolyzed particle surfaces were even rougher with many chasms or crevasses separating chunks of material, giving the impression of particles ready to crumble. Some of the fragmentation was evident before ignition, for a period of several milliseconds, and some happened after ignition. Upon ignition, 50 to 100 different fragments burned very brightly occupying a near-spherical volume of a few millimeters in diameter, and gave the impression of miniature fireworks, see Fig. 3c. Particles burned with decreasing size with not much evidence of ash left behind; most likely the small size of the ash makes it difficult to observe. The combustion behavior of the Texas lignite (PSOC-1443) was in line with that of the aforementioned Beulah lignite, but all events were more subdued, see Figs. 2d, 3d and 4d. Also, unlike the case of the Beulah lignite, for this coal fragmentation was seen to consistently commence prior to ignition. Visible volatile flames were again absent, combustion of
fragmenting chars was less pronounced, with a smaller number of fragments burning (in the range of 10-20). Based on the aforementioned criterion of Howard and Essenhigh [52] and on the calculated fragment sizes for the two lignite coals (20-30 μm in diameter), it is likely that these coals experienced concurrent heterogeneous and gas phase combustion on their solid surfaces. The burning of the volatiles at the particle surface provides an explanation for the observation that the lignite fragments particles burned very bright, see Fig. 3c and d. The fact that the Beulah lignite particles burned brighter than the Wilcox lignite particles in the cinematographic images, may be attributed to (a) the more intense fragmentation, which provides more total surface area for reaction, (b) their higher fixed carbon and oxygen content, and (c) their higher sodium content (by an order of magnitude more than all other fuels), which emits visible light. The latter is not detected by the pyrometer, but the former two phenomena result in pyrometric profiles for the Beulah lignite that typically have stronger and wider signal peaks as well as higher temperatures. Finally, unlike the Beulah lignite, the Wilcox lignite particles typically reached their maximum radiation intensities as well as their maximum temperatures early in the burnout histories, and thereafter they experienced monotonic decreasing in both parameters with time. The expedient increase in intensity may be attributed to their higher degree of pre-ignition fragmentation and to their higher content of minerals, such as calcium, which have been found to catalyze the combustion rate [53, 54]. The slow decrease in radiation intensity and temperature, after the peaks, may be attributed to the much higher ash content of this lignite coal that hinders the heterogenous combustion as it accumulates on the receding surface of the chars.

(e) Bagasse particles consistently exhibited only one peak in each pyrometric profile, typically wide and smooth of low signal intensity, see Fig. 2e. However photographic evidence, an example of which is displayed in Fig. 3e, consistently shows two-phase combustion. First
volatile matter burns homogeneously with air in luminous, but rather transparent and remarkably spherical envelope flames. The flames experience a shrinking core mode. Inside those flames bagasse particles are seen to rotate leisurely and shrink in size as they form chars. Upon extinction of the volatile flames the char particles experience a brief ignition delay period, appearing dark. Ignition commences at a corner of a char and then it propagates over the entire surface.Chars burn heterogeneously in a luminous shrinking core mode, leaving minuscule ash residues behind. The bagasse particles are displayed in Fig. 4e, where their high aspect ratio is apparent and their plant-origin and woody structure are evident. A pyrolyzed bagasse particle is also displayed in Fig. 4e, and has the visual appearance of plastically deformed lingo-cellulose with many little holes dotting its surface, as also documented in the microscopy results of Cetin et al. [50]. There is disagreement between the cinematographic data, which documents two-phase combustion, and the pyrometric data, which consistently records only one peak. This disagreement may be explained based on the argument that the volatile matter combustion could not be detected by the pyrometer, as it occurred in a CO/light-hydrocarbon-fueled flame which is typically non-sooty. This issue is currently under investigation in this laboratory by analyzing the pyrolysis and combustion products of bagasse. Preliminary results were presented in Bragato et al. [55].

**Pyrometric Temperature-Time Data**

Experimental particle temperature and burnout time information is presented in Table 2, based on a minimum of 20 single particle combustion profiles from each of the five fuels. As there are considerable particle-to-particle variations, in size, shape, structure and, presumably, composition there was large variability in the combustion behaviors. The temperature data
displayed in Table 2 represent the maximum temperatures reached in a particle’s profile, averaged over the number of particles whose combustion was monitored.

Volatile Matter Flame Temperatures and Durations

Maximum volatile matter flame temperatures for the bituminous coals were well-above 2000 K. Such flames were highly-luminous and their durations were in the range of 10-20 ms. In the few cases where sub-bituminous coals sustained feeble volatile combustion flames, such flames were of shorter duration, in the order of several ms. The bagasse volatile matter flames lasted for more than 20 ms, but their temperatures were not measured, as pyrometric recordings could not be obtained because the low-luminosity of such non-sooty flames.

Char Temperatures and Combustion Durations

Maximum char surface temperatures for all of the coals burned were typically under 2050 K and above 1700 K, see Table 2. There was little differentiation among the temperatures of the lignite and sub-bituminous coal chars (all being in the neighborhood of 2000 K), with the Beulah lignite chars exhibiting the highest temperatures, closely followed by those of the sub-bituminous chars and the Wilcox lignite chars. The temperatures of the bagasse chars were in the neighborhood of 1900 K and, finally, those of bituminous chars were in the neighborhood of 1800 K. The chars of the fragmenting coals (lignites and sub-bituminous) burned the fastest (16-40 ms), with the combustion of the highly-fragmenting Beulah lignite being the most expedient of all, see Table 2. The bagasse chars burned in 24-38 ms, as recorded by cinematography. In this case there has been a disagreement between the cinematographic and pyrometric recordings of time, with the latter technique consistently recording shorter burntimes (16 ms). The disagreement was attributed to the fact that only cinematography was successful in capturing the
last stages of bagasse char, as they shrunk to very small sizes. Finally, the combustion of the non-fragmenting, but swelling and cenosphere-forming bituminous chars lasted for 60-120 ms, which is much longer than those of the other fuels.

It should be mentioned that the results shown in Table 2 are in overall agreement with snippets of information from the number of studies reviewed in an earlier section of this manuscript. However, as such prior information was gathered under different fuel input and furnace operating conditions exact comparisons do not always hold.

<table>
<thead>
<tr>
<th>FUEL TYPE</th>
<th>MAXIMUM FLAME TEMPERATURE</th>
<th>MAXIMUM CHAR TEMPERATURE</th>
<th>VOLATILE MATTER BURN-TIME</th>
<th>CHAR BURN-TIME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous (PSOC-1451)</td>
<td>Flame present in all cases 2225 K (σ = 116)</td>
<td>1775 K (σ = 59 K)</td>
<td>10 ms (σ = 4 ms) cine10-25ms</td>
<td>60 ms (σ = 22 ms) cine 80-120 ms</td>
</tr>
<tr>
<td>Sub-bituminous (DECS-26)</td>
<td>Flame in some cases: 2228K (σ = 118 K)</td>
<td>2014 K (σ = 90 K)</td>
<td>6 ms (σ = 2 ms)</td>
<td>32 ms (σ = 8 ms)</td>
</tr>
<tr>
<td>Beulah Lignite (DECS-11)</td>
<td>No Flame</td>
<td>2047 K (σ = 58 K)</td>
<td>Burning concurrently with chars</td>
<td>25 ms Cluster σ = 8 ms</td>
</tr>
<tr>
<td>Wilcox Lignite (PSOC-1443)</td>
<td>No Flame</td>
<td>2000 K (σ = 93 K)</td>
<td>Burning concurrently with chars</td>
<td>41 ms Cluster σ=10 ms</td>
</tr>
<tr>
<td>Bagasse</td>
<td>Flame in all cases, but not detected by pyrometer</td>
<td>1890 K (σ =60 K) cine 20-30 ms</td>
<td></td>
<td>16 ms (σ = 5 ms) cine 24-38 ms</td>
</tr>
</tbody>
</table>

Table 2. Maximum temperatures and burnout times of fuel particles burning in air. Particle size was 74-90 μm and furnace wall temperature was set to 1400K.
2.6. Conclusions

In this work, five fuels were burned under controlled conditions in a laboratory laminar-flow electrically-heated drop-tube furnace, fitted with a transparent quartz tube. The list of fuels included coals of different ranks (a bituminous, a sub-bituminous and two lignites) and, also, bagasse, which is sugar cane residue. High-temperature, high-heating rate combustion of these fuels, pulverized and sieved in the size range of 75-90 µm, occurred in the single particle mode. Ratio pyrometry, in the visible and near-infrared, and simultaneous high-speed high-resolution cinematography, in conjunction with SEM observations of the fuels and their chars, were used to assess/contrast the combustion behavior of the fuels. This assessment occurred under conventional combustion conditions in air, and will be used as a baseline for future studies targeting alternative conditions, where the N₂ is replaced by CO₂ and the O₂ is varied. Results obtained included pre- and post-ignition characteristics as well as quantitative observations on complete temperature-time histories of single particles. Results showed that the combustion behavior of the fuels from the different geological ranks is very disparate. The swelling bituminous coal consistently experienced distinct volatile matter and residual char combustion phases. The sum of these phases lasted longer than burnout durations for the other types of fuels. Volatile matter flames were sooty, bright, non-transparent and elongated with contrails of soot. Inside those flames, the pyrolyzing coal particles swelled and increased in size. The non-swelling, but often fragmenting, sub-bituminous coal particles experienced variable behavior with few particles experiencing brief, small and round detached volatile-matter flames and fragmentation, whereas others did not experience flames and/or fragmentation. The consistently-fragmenting lignite coals did not experience detached volatile flames, instead it is likely that volatiles burned on char surfaces. One of the two lignites (Beulah) experienced more extensive
fragmentation than the other (Wilcox). The fragmentation of the former coal started upon ignition, whereas that of the latter coal started prior to ignition. Finally, bagasse experienced two-phase combustion; with large, spherical, transparent, low-luminosity and shrinking core flames. Inside those flames the pyrolyzing bagasse particles visibly shrank in size. Upon extinction of the flames, the char particles burned in shrinking core mode. The temperature-burntime data was used to calculate combustion rates from luminous carbon disappearance observations. They were found to be in line with results from calculations with published kinetic expressions in the literature. Results are shown below in the Appendix.

2.7. References


2.8. Appendix: On the apparent reaction rates of the coals

Apparent combustion rates were calculated based on luminous carbon disappearance observations, as obtained from pyrometry and cinematography. This exercise was done for two of the coals, the Pittsburgh bituminous and the Texas lignite, for which previous studies have
also deduced apparent rates. This gave the opportunity for comparisons. To do so several assumptions on the physical phenomena taking place during the combustion of these particles had to be made. Generally, construction of combustion models can help to constrain an observer’s subjective impressions to abide by the laws of physics, in conjunction with sets of data.

Sahu et al. [33] burned two of the fuels of the present study, the bituminous and one of the two lignite coals, and derived Arrhenius-type rate expressions \( R_a = A_a e^{E_a/RT} p_s^m \) using a limiting form (at high Thiele modulus) of Gavalas’ “random pore” model [56]:

\[
Pittsburgh\; Bituminous,\; PSOC-1451: \quad R_a = \left[ 107.1 e^{-1700/RT} \right] p_s^m \quad \text{(g cm}^{-2} \text{ s}^{-1}) \quad (1)
\]

\[
Texas\; Lignite,\; PSOC-1443: \quad R_a = \left[ 20.8 e^{-14000/RT} \right] p_s^m \quad \text{(g cm}^{-2} \text{ s}^{-1}) \quad (2)
\]

In these expressions, \( E_a \) is the apparent activation energy and \( A_a \) is the apparent pre-exponential factor, which accounts for particle-to-particle variations in reactivity and porosity [56, 57]. The reaction order \( m \) was assumed by Sahu et al. [33] to be unity. They characterized the properties of an \( i \)th particle by two random variables: its initial radius, \( r_0 \), assuming spherical shape, and \( A_a \). To use these expressions in this work, the external surface of non-fragmenting chars was calculated based on an average initial radius of the coal particles. Several additional simplifying assumptions were necessary. The possible swelling in size of bituminous chars was somewhat accounted for by assuming that the initial char diameter was at the upper limit of the coal size cut used herein, i.e., 90 μm. The fragmentation of the Texas lignite coal (PSOC-1443) was also taken into account; a nominal number of 20 fragments were assumed for this lignite based on the cinematographic observations. By assuming all the fragments to be of equal size
and spherical (which of course is not realistic), then the initial diameter of the Texas lignite fragments was calculated to be 30 μm.

Next, the partial pressure of oxygen at the surface of the chars, \( p_{\text{os}} \), had to be calculated, as it is required for solving Eqs. (1) and (2). To accomplish this, the analysis of Levendis et al. [54, 58] was followed. Therein, an oxygen conservation equation around a burning carbon particle was considered, and included both oxygen diffusion to its surface as well as convective flow away from its surface, i.e., Stefan flow (see Levendis et al. [58], Eq. 2). The sole product of char oxidation was assumed to be CO, based on the findings of Arthur [59], Mitchell and co-workers [60,61] and Tognoti [62] among others, as reviewed by Levendis et al. [38], given the high surface temperatures reached during oxidation of the chars herein (see Table 2). Accordingly, Levendis et al. [58] derived a simplified expression for the char burnout time for combustion of a carbon sphere under diffusion control, \( t_{\text{b,diffusion}} \):

\[
t_{\text{b,diffusion}} = \sigma_a \times (a_i^2 - a_f^2) / 56 \times RT_m / D_b \times (1/\ln[1 + 3/4y_\infty])
\]  

(3)

where \( \sigma_a \) is the apparent density of the char, \( a_i \) and \( a_f \) are the initial and final radii of the char particle, 56 is a constant that includes the density of oxygen, \( R \) is the ideal gas constant (conveniently taken as 82.06 atm cm³ / mole K), \( T_m \) is the mean temperature in the film, \( D_b \) is the binary diffusivity of oxygen in nitrogen and \( y_\infty \) is the oxygen mole fraction in the bulk, herein 0.21.

Furthermore, the initial oxygen mole fraction at the char surface, \( y_{\text{O2s}} \) was obtained by integrating Eqn. 6 of Levendis et al. [58] which, upon separation of variables, yielded:

\[
y_{\text{O2s}} = (4/3 + y_\infty) \times \exp - ((a_i^2 RT_m \sigma_a) / 56P_{\text{tot}}D_b t_{\text{b,observed}}) - 4/3
\]  

(4)
Given the properties of the Pittsburgh bituminous and the Texas lignite chars, as reported by Sahu et al. [33], Table 3 was constructed. The final radii of the burned chars were calculated based on the ash contents of the chars which are 19% and 36%, respectively for the two aforementioned coals, assuming shrinking core combustion and comparable char and ash residue densities. The density of the ash was assumed to be 3.5 g/cm$^3$ in both cases based on the work of Loewenberg and Levendis [35].

Table 3. Calculated and measured parameters for two of the coals of this study.

<table>
<thead>
<tr>
<th>Property ↓</th>
<th>FUEL →</th>
<th>Bituminous Coal (PSOC-1451)</th>
<th>Texas Lignite Coal (PSOC 1443)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial radius of char ($a_i$)</td>
<td></td>
<td>$45 \times 10^{-6}$ m</td>
<td>$15 \times 10^{-6}$ m</td>
</tr>
<tr>
<td>Final radius of char ($a_f$)</td>
<td></td>
<td>$11 \times 10^{-6}$ m</td>
<td>$9 \times 10^{-6}$ m</td>
</tr>
<tr>
<td>Apparent char density ($\sigma_a$)</td>
<td></td>
<td>$0.9$ - $0.5^*$ g/cm$^3$</td>
<td>$1.1$ g/cm$^3$</td>
</tr>
<tr>
<td>Bulk oxygen ($y_\infty$)</td>
<td></td>
<td>$21%$</td>
<td>$21%$</td>
</tr>
<tr>
<td>Surface oxygen ($y_{O2s}$)</td>
<td></td>
<td>$1$ - $4.6%$ (pyrometry) $3.3$ - $11%$ (cine)</td>
<td>$13%$</td>
</tr>
<tr>
<td>Film temperature</td>
<td></td>
<td>$1587$ K</td>
<td>$1700$ K</td>
</tr>
<tr>
<td>Diffusion-limited burntime ($t_{b, \text{diffusion}}$)</td>
<td></td>
<td>$75$ - $42$ ms</td>
<td>$6.7$ ms</td>
</tr>
<tr>
<td>Observed average burntime ($t_{b, \text{observed}}$)</td>
<td></td>
<td>$60$ ms (pyrometry) $100$ ms (cine.)</td>
<td>$31$ ms</td>
</tr>
</tbody>
</table>

*The apparent density for chars from this coal has been reported to be $0.5$ g/cm$^3$ by Sahu et al. [33] and $0.9^*$ g/cm$^3$ by Sahu et al. [32], based on different determinations, therefore both values were examined herein.

A few words of caution regarding the calculated parameters for the Texas lignite are warranted here. It was assumed that the Texas lignite particle fragments burned discretely, i.e., without particle-to-particle interactions. However, the lignite particles actually burned in the vicinity of each other, as illustrated in the cinematographic sequences of Fig. 3. In these spherical
clusters of particle fragments some volatile matter was possibly present and, also, there might have been competition for oxygen among neighboring char fragments for their surface reactions. Thus, the bulk oxygen mole fraction within the cluster of fragments \( y_c, \text{ in cluster} \) might have been lower than the value of \( y_c = 21\% \), that prevailed in the furnace. This would have resulted in lower combustion rates. Such an event could have affected not only the Texas lignite, but also the Beulah lignite even more severely so, as it disintegrated into a larger number of fragments (order of 100). The possibility of interactive combustion was examined based on results reported by Annamalai et al. [63], and using parameters as defined and symbolized therein. First the particle number density, \( n \), in the cluster was calculated; then a group number, \( G \), was calculated, defined as the transport rate between the particles in the cloud over the transport rate between the cloud and the ambiance. This was expressed as \( G = 4 \pi n a R_c^2 \), (see Annamalai et al. [63]). In this equation, \( a \) is the particle radius and \( R_c \) is the fragment dispersion radius, here taken from the photographs of Fig. 3d. The quantity \( l/a \) was also calculated, where \( l \) is the particle-to-particle distance. Finally, the fuel volume fraction, therein defined as \( \sigma_{\text{fuel}} \), was considered and compared with results reported by Annamalai et al. [63], Figure 154, page 591. Results are shown in Table 4.

**Table 4.** Calculated interactive combustion parameters for the two lignite coals herein

<table>
<thead>
<tr>
<th>Parameter ↓</th>
<th>Texas Lignite (PSOC 1443)</th>
<th>Beulah Lignite (DECS 11)</th>
<th>Criteria /Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>( 1.13 \times 10^{10} )</td>
<td>( 3.5 \times 10^{9} )</td>
<td>Since ( n &gt; 10^9 ) both cases may experience some interactive combustion</td>
</tr>
<tr>
<td>( G )</td>
<td>( 1.2 )</td>
<td>( 1.6 )</td>
<td>Since ( 0.3 &lt; G &lt; 9 ) then there may be interactive combustion for a single film model</td>
</tr>
</tbody>
</table>
Since $l/a > 20$ both cases should not experience interactive combustion.

<table>
<thead>
<tr>
<th>$l/a$</th>
<th>30</th>
<th>66</th>
<th>Since $l/a &gt; 20$ both cases should not experience interactive combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Figure 154 Annamalai et al. [63]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\sigma_{\text{fuel}} = 1.6 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$R_c/a = 50$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\sigma_{\text{fuel}} = 1.5 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$R_c/a = 190$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>both cases lie barely within the region of interactive combustion</td>
</tr>
</tbody>
</table>

Using the results shown in Table 4, it appears that some degree of interactive combustion is possible in the cases of both lignite coals. This possibility would reduce the values of $y_{\infty}$ and $y_{O_2s}$, whereas it would increase $t_{b, \text{diffusion}}$.

Using these values, the Regime of Combustion can be identified as number II, where both diffusion and reaction are present [5]. This would signify partial penetration of oxygen in a particle’s pores. With the additional understanding obtained with this analysis, it is likely that Regime II is still valid, but the Thiele modulus is high, the pore penetration is limited and reaction takes place in a thin outer shell. That is combustion is perhaps occurring under the upper end of Regime II conditions, but not quite under the diffusion-limited Regime III of combustion.

Next the apparent reaction rates for two of the coals were calculated using the parameters of Table 3. As the total pressure was atmospheric ($p_{\text{tot}} = 1 \text{ atm}$), the partial pressure at the char surface was set at the value of the mole fractions at the surface ($p_s = y_s \times p_{\text{tot}}$); hence,

Pittsburgh Bituminous, PSOC-1451: $R_a = \left[ 107.1 \ e^{-17,000/RT} \right] p_s^{m} = 0.01-0.09 \text{ (g cm}^{-2} \text{ s}^{-1})$, depending on the apparent density on Table 3, which influences the $p_s$ value, and
Texas Lignite, PSOC-1443:  

\[ R_a = \left[ 20.8 \ e^{\frac{14,000}{RT}} \right] p_s^m = 0.08 \ \text{(g cm}^{-2} \text{s}^{-1}) \]

In this expression the ideal gas constant, \( R \) is 1.978 cal/g-mol K to match the units of the activation energy which are cal/g-mol and the reaction rate order, \( m \), was taken as unity, as specified by Sahu et al. [33]. Calculation of the apparent rate of the Pittsburgh #8 coal, based on rate parameters deduced by Hurt and Mitchell [11] see Table 1, and using yields \( R_a = 0.003-0.01 \) (g cm\(^{-2} \) s\(^{-1} \)). Such rates are lower than those of Sahu et al. [33].

Based on data, collected in this study, on average initial char diameter, density, luminous burnout time, as shown in Table 3, the observed apparent burning rate for bituminous char particles was calculated to be \( R_a = 0.008-0.02 \) (g cm\(^{-2} \) s\(^{-1} \)), again depending on the apparent density range shown in Table 3, at a gas temperature of 1400 K; also assuming that all carbon was burned in the luminous combustion period. The reader should note that the accuracy of this calculation is commensurate to the accuracy of the several assumptions needed on average particle size, average burn-time, density, etc. Another method to calculate reaction rate involves an energy balance around a burning char particle, as outlined by Mitchell and McLean [7], assuming CO as the primary combustion product in the boundary layer. Input to this equation was the char particle temperature, herein taken as a representative time-averaged value from pyrometric profiles equal to 1750 K. Using this approach \( R_a = 0.011 \) (g cm\(^{-2} \) s\(^{-1} \)), which is well-within the aforementioned range of \( R_a = 0.008-0.02 \) (g cm\(^{-2} \) s\(^{-1} \)). This calculated rate range partially overlaps both the rate ranges deduced from the expressions of Sahu et al. (1989) and Hurt and Mitchell [11].

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Subsequently, turning attention to the Texas lignite coal (PSOC-1443) chars, apparent rates calculated by Hurt and Mitchell [11] were $R_a = 0.05 \text{ (g cm}^{-2} \text{s}^{-1})$. This is lower than the aforementioned rate of $0.08 \text{ (g cm}^{-2} \text{s}^{-1})$ calculated from the expression of Sahu et al. [32].

Again, based on the luminous carbon disappearance observations of this study (initial char diameter (80 µm), volume, external surface of the char, density and luminous burnout time of the cluster of all fragments) it was calculated that $R_a = 0.04 \text{ (g cm}^{-2} \text{s}^{-1})$ at a furnace temperature of 1400 K. However, had the rate herein been calculated based on the diameter of a single char fragment (30 µm), volume, external surface of the fragment, density and luminous burnout time of a single fragment, then $R_a = 0.02 \text{ (g cm}^{-2} \text{s}^{-1})$. Had the calculation of the combustion rate been performed based on an energy balance around a single char fragment, as outlined by Mitchell and McLean [7], using a char particle temperature of 1900 K, then $R_a = 0.03 \text{ (g cm}^{-2} \text{s}^{-1})$, which is between the aforementioned values. Such cluster and single fragment combustion rates are a little lower than the rates of 0.05 and 0.08 (g cm$^{-2}$ s$^{-1}$) calculated using the data of Hurt and Mitchell [11] and Sahu et al. [32], respectively.

**Table 5. Calculated apparent combustion rates for two of the coals of this study**

<table>
<thead>
<tr>
<th>Apparent combustion rate of char (g cm$^{-2}$ s$^{-1}$)</th>
<th>Bituminous Coal (PSOC-1451)</th>
<th>Lignite Coal (PSOC 1443)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Based on luminous carbon disappearance (i.e., average observed burntime)</td>
<td>0.008-0.02</td>
<td>0.02 for a fragment 0.04 for cluster</td>
</tr>
<tr>
<td>Based on an energy balance around burning chars and using average observed surface temperatures</td>
<td>0.011</td>
<td>0.03 for a fragment</td>
</tr>
<tr>
<td>Based on the expression of Sahu et al. [32]</td>
<td>0.01-0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>Based on the expression of Hurt and Mitchell [11]</td>
<td>0.003-0.01</td>
<td>0.05</td>
</tr>
</tbody>
</table>
CHAPTER 3

Appeared in Combustion and Flame 159, 3554-3568, 2012

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1 Mechanical Engineering Department, Northeastern University, Boston, MA, 02115, USA
3. Ignition characteristics of single-coal particles from three different ranks in $\text{O}_2/\text{N}_2$ and $\text{O}_2/\text{CO}_2$ atmospheres

Abstract

This work assessed the ignition behavior of single-coal and single-char particles in $\text{O}_2/\text{N}_2$ and $\text{O}_2/\text{CO}_2$ atmospheres, with oxygen mole fractions in the range of 20-100%. Fuels included four pulverized coals from three different ranks (one high-volatile bituminous, one sub-bituminous and two lignites) as well as chars prepared from two of the coals. Particles of 75-90 $\mu$m were injected in a bench-scale, transparent drop-tube furnace (DTF), electrically-heated to 1400 K. Optical access of the furnace allowed the ignition of individual particles to be observed with high-speed cinematography. A particle’s ignition delay was defined as the time lapsed from the instant when the particle exited the injector to the onset of its luminous combustion in the furnace. The experiments were conducted at two different gas conditions inside the furnace: (a) quiescent gas condition (i.e., no flow or inactive flow) and, (b) an active gas flow condition in both the injector and furnace. In the former case, the axial gas temperatures in the DTF were found to be similar in the $\text{N}_2$ and $\text{CO}_2$ background cases and, consequently, small differences were observed in the ignition delay and in the ignition behavior of coal particles in $\text{O}_2/\text{CO}_2$ and $\text{O}_2/\text{N}_2$ atmospheres. These small differences were easily accounted for by disparities in the physical properties of the background gases. Increasing the oxygen mole fraction in either $\text{N}_2$ or $\text{CO}_2$ reduced the ignition delay mildly. To the contrary, in the latter case, i.e., under the active gas flow condition the axial gas temperatures in the DTF were found to be disparate in the $\text{N}_2$ and $\text{CO}_2$ background cases. The ignition delay of coal particles was drastically prolonged in the slow-heating $\text{O}_2/\text{CO}_2$ atmospheres, relative to the faster-heating $\text{O}_2/\text{N}_2$ atmospheres, particularly
Photographic evidence showed that under active gas flow, which is relevant to practical applications in utility furnaces, ignition of volatiles in envelope flames was suppressed in the presence of CO₂. As a result, whereas in the quiescent gas condition, bituminous and sub-bituminous coal particles experienced homogeneous ignition in both O₂/N₂ and O₂/CO₂ atmospheres, in the active gas flow condition heterogeneous ignition was evident in O₂/CO₂. Lignite coal particles often fragmented before ignition; this increased the likelihood of heterogeneous ignition in both O₂/N₂ and O₂/CO₂, in either active or inactive gas flows.

3.1. Introduction

This manuscript reports on ignition of single coal particles from different ranks in various O₂/N₂ and O₂/CO₂ environments. This information may be valuable in predicting differences in conventional pulverized coal combustion and in the newly-proposed oxy-coal combustion. Such information may be instrumental for numerical modeling and prediction of the performance of oxy-coal burners. Conditions of interest to oxy-coal combustion (an advanced “clean-coal” technology that facilitates carbon dioxide capture and sequestration [1, 2]) were included in this investigation. Whereas, oxy-coal combustion technology is currently targeting overall oxygen mole fractions in the range of 20-40% [2, 3] in CO₂, herein oxygen mole fractions as high as 100% were explored. This was done to (i) obtain basic understanding of the combustion behavior of these solid fuels over the entire possible range of oxygen enhancement, above and beyond the oxygen content of air, and (ii) because oxy-combustion at high oxygen mole fractions (>40%), by local injection of neat O₂, is of industrial interest for a variety of reasons, including improvement of coal ignition, flame stabilization at a particular location in the furnace, compact flame generation, flame stability and, eventually, reduction of the boiler size and hence reduction.
of the cost of the powerplant [4, 5, 6]. High oxygen mole fractions in N₂ were used herein for
coloration with CO₂ background gases.

Previous studies on coal ignition reported on: (a) ignition mechanism and ignition
temperature, and (b) ignition delay mostly in air or in other O₂/N₂ environments. In the following
two sub-sections, brief reviews are conducted on the relevant literature. The first sub-section
outlines works relevant to identifying the mechanism of coal particle ignition, i.e., a gas mode
ignition (ignition of the volatile matter in an envelope flame surrounding a devolatilizing char
particle), heterogeneous mode ignition (which often signifies surface ignition) or a combination
of both. The ignition mode may change with particle size, coal type, heating rate, oxygen mole
fraction and temperature and type of background gas. The second sub-section outlines other
relevant works on ignition delay of coal particles, burning in either O₂/N₂ or O₂/CO₂ background
gases.

3.1.1. Review of previous studies on ignition mechanisms (mode) of single-coal particles
burning in O₂/N₂ and O₂/CO₂ atmospheres

The topic of ignition mechanisms of solid fuel particles in air and in other O₂/N₂
environments has been a controversial subject for the last half century. Howard and Essenhigh
[7, 8] proposed a model for the ignition and combustion of single bituminous coal particles in air,
exposed to high heating rates (~ 10⁴ K/s). When heated, coal generates volatiles that may ignite
before the solid residue ignites; this happens if the volatiles are produced in sufficient quantity to
generate a mixture strength above the low flammability limit and with temperature above the
auto-ignition temperature. However, Howard and Essenhigh [7] proposed that at high heating
rates, the finite time lag before volatiles are released becomes important, and if the particles
reach a sufficiently high temperature rapidly, it is possible that the particles ignite and burn by direct oxygen attack on the solid surface before devolatilization sets in. They argued that if ignition could start in the volatiles initially, a large amount of volatile loss at or before the flame front was expected to evolve and result in a low flammability limit mixture; however, the evolved volatile loss was not deemed sufficient to attain such a mixture. Moreover, since fixed carbon started to vanish fast at the moment of ignition, an effective envelope diffusion flame could not be established to screen the solid particle from attack. From gathered evidence, they inferred that ignition most probably commences on the particle surface for the particle size of their study ($d_p<200\mu$m).

Overall, the effect of particle diameter and heating rate on the ignition mode of coal particle is widely accepted. De soete [9] among others [10, 11] proposed that gas-phase ignition usually takes place when large particles are heated slowly (less than 100 K/s) while heterogeneous ignition typically happens when small particles (less than 100µm) are heated quickly. Other research groups illustrated that additional parameters such as oxygen mole fraction, coal type (volatile matter content) and ambient gas temperature also affect the ignition mechanism of coal particles. Annamalai and Durbetaki [12] developed a theory on the transition of ignition between gas-phase ignition (homogeneous ignition) and heterogeneous ignition phases. They determined ignition temperatures using either homogeneous or heterogeneous ignition assumptions for various coal types. They predicted that heterogeneous ignition is more likely to happen for particles of small size (less than 400µm), high oxygen mole fractions in the background gas (typically more than 0.15) and coals of low rank. Moreover, Du and Annamalai [13] predicted the effect of ambient temperature and coal volatile matter content on the transition of ignition modes and on the ignition temperature. Their model showed that heterogeneous ignition was the
prevalent mode for coals containing less than 70% volatile matter, at ambient temperature above 900 K.

Wall and coworkers [14, 15] used multiple experimental techniques to re-examine the view which was developed in previous years supporting the likelihood of heterogeneous ignition in the case of small particles (<100µm). They showed that apart from the effects of volatile matter content, oxygen concentration and particle size, experimental factors such as the injected sample mass, the particle heating rate, the surrounding gas conditions and the way in which the particles are heated influence the ignition mechanism and the associated ignition temperature. Most importantly, Wall and coworkers [14, 15] stated that the definition of ignition defines the ignition mode. For instance, whereas Howard and Essenhigh [7, 8] defined the ignition event based on the percentage loss of carbon and volatiles during the early moments of burning, Wall and coworkers [14, 15] relied on optical diagnostics (photomultiplier, photo-detector and video camera) to define the mode of particle ignition based on its luminosity and size during the early moments of burning.

The aforementioned works mainly examined the ignition mechanism of coal particles burning in air or in other O₂/N₂ atmospheres. The ignition mechanism of coal particles in O₂/CO₂ atmospheres, over a wide range of oxygen mole fractions, has not been investigated thoroughly before. Moreover, the comparison of ignition phenomena of coal particles in N₂ and CO₂ background gases has not been presented before.

3.1.2. Review of previous studies on ignition delay time of single-coal particles burning in O₂/N₂ and O₂/CO₂ atmospheres
Kimura et al. [16], Kiga et al. [17], and Liu et al. [18] have all observed lengthier ignition delays for coal particles when N\textsubscript{2} was replaced with CO\textsubscript{2}, keeping O\textsubscript{2} at 21%. Toftegaard et al. [2], placed emphasis on the heat capacity of the background gas, expressed on a volumetric basis, which they called the heat sink (the product of density and the mass-based heat capacity, $\rho c_{p,\text{gas}}$). This term is also prominent in the equation of the adiabatic thermal explosion theory [19], quoted by Shaddix and Molina [20] in relation to coal particles that ignite homogeneously, i.e., with gas-phase ignition of volatiles. At the aforementioned gas temperature of 1400 K, for instance, the volumetric heat capacity (heat sink) of CO\textsubscript{2} (0.504 kJ/m\textsuperscript{3}-K) is 1.67 times the volumetric heat capacity (heat sink) of N\textsubscript{2} (0.301 kJ/m\textsuperscript{3}-K). This increases the heat losses from the particle and delays ignition, i.e., it increases the ignition delay at comparative oxygen levels.

Besides the transport properties of the gas, the reactivity of the local fuel-oxidizer mixture and the associated heat release have been identified as parameters influencing the homogeneous ignition delay [20, 21]. It has been reported that increasing the mixture reactivity and the heat release should decrease the ignition delay time (Toftegaard et al.[2]). Thus, higher oxygen mole fractions are expected to increase the reactivity of the local mixture and, thereby decrease the ignition delay time [2, 20, 21]. All of the above studies assumed that the coal particles burn in the same mode (gas ignition mode, also called homogeneous mode) at similar oxygen levels in either N\textsubscript{2} or CO\textsubscript{2} environments. Rathnam et al. [22] reported that differences in reactivity of coal particles burning in O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2} environments are negligible.

Initial work in this laboratory, see Stivers and Levendis [23], used high-speed cinematography to observe the ignition of four coals of different ranks in a transparent DTF, under active laminar gas flow with various O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2} atmospheres. Ignition delays were found to be very different in the two cases, particularly at high background gas mole fractions.
Whereas, the ignition delay was found to vary little with oxygen concentration in N₂ background gas, it was found to increase drastically with decreasing oxygen mole fraction in CO₂ background gas. Such drastic differences in ignition delay were beyond what the differences of volumetric heat capacities (heat sinks) of O₂/N₂ and O₂/CO₂ gas combinations could account for. This investigation will show that differences in gas temperature, caused by the flow of the injector gas along the axis of the DTF, in conjunction with associated ignition mode changes, are responsible for the most observed differences in ignition delay.

In summary, this work aims at investigating the ignition mechanism of 75-90 µm coal particles from different ranks, under high temperatures in the DTF and high particle heating rates (~5×10³ and 8×10³ for active flow in pure CO₂ and pure N₂, respectively and 10⁴ K/s for quiescent gas conditions) in either O₂/N₂ or O₂/CO₂ atmospheres, with 20%<O₂<100%, and at quantifying the ignition delay periods of these coal particles. Ignition of pre-made chars of two of the coals was also investigated.

3.2. Physical and chemical properties of the fuels

Coals from three different ranks, listed in Table 1, were burned in this study. Samples for the four coals were obtained from the Pittsburgh Coal Bank, and were ground, sieved to the size cut of 75-90 µm, and dried. Two of the coals (PSOC-1451 and PSOC-1443) were extensively characterized in previous research, see Sahu et al. [24, 25] and Bejarano and Levendis [26]. The size cut of 75-90 µm was selected for these experiments to be in line with the works of Levendis et al. [27] for combustion in air and Khatami et al. [28] for combustion in O₂/N₂ and O₂/CO₂ environments. The results of proximate and ultimate analysis of the four coals of this work are shown in Table 1. In order to assess the effects of volatile matter on the ignition, the chars were
prepared by pyrolyzing two of the coals of this study (PSOC-1451 and DECS-11) in either neat N₂ or CO₂ gases. To prepare the chars, the coals were introduced to another DTF in the laboratory, of similar architecture. That furnace is equipped with a particle fluidizer/feeder, described elsewhere [29, 30]; its wall temperature was set at 1400K. The devolatilization time of coal particles was assumed to be equal to their residence time in the radiation zone of the DTF, which was calculated to be in the order of 1 s.

**Table 1. Chemical Composition of the Coals used in this study**

<table>
<thead>
<tr>
<th>Rank and Fuel Source</th>
<th>PSOC-1451</th>
<th>DECS-26</th>
<th>DECS-11</th>
<th>PSOC-1443</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bituminous High Volatile A Pittsburgh #8 Pennsylvania</td>
<td>Sub-Bituminous B River Basin Wyodak, Wyoming</td>
<td>Lignite A Beulah, North Dakota</td>
<td>Lignite A Titus, Texas</td>
</tr>
<tr>
<td>Proximate Analysis as received, and (upon re-evaluating moisture)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>2.5</td>
<td>26.3 (13.1)</td>
<td>33.4 (13.2)</td>
<td>28.5 (18.6)</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>33.6</td>
<td>33.1 (39.0)</td>
<td>37.4 (48.6)</td>
<td>44.2 (50.3)</td>
</tr>
<tr>
<td>Fixed Carbon (%)</td>
<td>50.6</td>
<td>35.1 (41.4)</td>
<td>22.9 (29.8)</td>
<td>12.0 (13.7)</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>13.3</td>
<td>5.6 (6.5)</td>
<td>6.4 (8.4)</td>
<td>15.3 (17.4)</td>
</tr>
<tr>
<td>Ultimate Analysis (on a dry basis)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>71.9</td>
<td>69.8</td>
<td>66.2</td>
<td>56.8</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>4.7</td>
<td>5.7</td>
<td>4.0</td>
<td>4.1</td>
</tr>
<tr>
<td>Oxygen (%) (by diff.)</td>
<td>6.9</td>
<td>15.6</td>
<td>18.6</td>
<td>15.8</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>1.4</td>
<td>0.9</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Sulfur (%)</td>
<td>1.4</td>
<td>0.4</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Sodium (%)</td>
<td>0.06</td>
<td>0.09</td>
<td>0.66</td>
<td>0.04</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>13.7</td>
<td>7.6</td>
<td>9.6</td>
<td>21.4</td>
</tr>
<tr>
<td>Heating Value Dry Fuel (MJ/kg)</td>
<td>31.5</td>
<td>28.2</td>
<td>25.7</td>
<td>23.0</td>
</tr>
</tbody>
</table>

The four coals and their proximate and ultimate analysis data was obtained from the Penn State Coal Sample Bank; however, upon opening the sealed containers of the supplied coal samples, variations of moisture content with storage in the laboratory were observed for all, but the bituminous, coals. The measured moisture content values are
listed (in parentheses) and the remaining proximate analysis values were re-calculated and are also shown (in parentheses).

3.3. Experimental

3.3.1. Drop tube furnace (DTF)

The combustion studies of free-falling coal particles were carried out in an electrically heated, laminar flow DTF at a constant wall temperature of 1400K. Drop tube furnaces or entrained flow reactors are considered to be appropriate devices for laboratory studies, as they reproduce conditions suitable to those in practical systems, while providing a relatively simple configuration. The radiation cavity of this furnace (an ATS unit) is 25 cm long and it is heated by hanging molybdenum disilicide elements. A sealed 7 cm i.d. transparent quartz tube was fitted in this furnace. Gas was introduced to the radiation cavity of the furnace through a water-cooled stainless-steel injector and, also, through a flow straightener, coaxially to the furnace injector, Fig. 1. During the active flow experiments each of these two flow streams was set to 0.5 lpm. Fuel particles were introduced through a port at the top of the injector by first placing them on the tip of a beveled-needle syringe. Gentle taps on the needle allowed single coal particles to enter the injector and, subsequently, the furnace. The gas entering through the flow straightener was preheated in the annular space between the injector and the quartz tube before it reached the main radiation cavity. The combined flow at wall temperatures of 1400 K resulted in an average calculated gas flow velocity of approximately 2 cm/s inside the furnace radiation cavity. Optical access to the radiation zone of the furnace was achieved through three observation ports: one at the top and two orthogonally situated at the sides of the furnace.
3.3.2. High-speed camera

A NAC HotShot 512SC Self-Contained Digital High-Speed video camera was used, at a speed of 1000 or 2000 frames/s. The camera was fitted with an Olympus-Infinity Model K2 long-distance microscope lens to provide high magnification images of the combustion events. Another macro focusing zoom lens, Vivitar Series 1 with 67mm diameter f2.8-f3.8, was
implemented to monitor the ignition delay distances at high CO₂-content environments (70%CO₂ and 60%CO₂). High-speed cinematography was conducted through slotted side quartz windows of this furnace at the presence of backlight.

### 3.3.3. Gas compositions

Gas compositions tested in the furnace included different mixtures of either O₂/N₂ or O₂/CO₂. Beginning with 20% O₂ and either 80% N₂ (≈ air) or 80% CO₂, the oxygen concentration was increased in increments of 10% up to a maximum of 70% O₂. Additionally, testing was performed in a 100% O₂ environment to determine how the particles burn in the absence of either supplemental gas. Flowmeters were calibrated with a bubble flowmeter (SUPELCO Analytical, Model: 20428-U). Oxygen partial pressures were controlled with pre-calibrated flowmeters, and were verified by an oxygen analyzer (Horiba, Model MPA-510).

### 3.3.4. Gas temperature

Coal ignition and combustion experiments were conducted under two different axial gas temperature profiles in the DTF: (i) one achieved under an active gas flow condition, and (ii) another achieved under a quiescent gas condition (inactive flow, i.e., no flow). Active flow was created by setting each of the injector and furnace flow streams to 0.5 lpm. Quiescent gas condition was created by turning off the gas flows 10 seconds prior to the particle injection. The selection of this time delay was supported by an experiment conducted with a bare thermocouple (OMEGA type K model KMQXL-020, 250 μm bead diameter, 50 μm wire diameter, 500 μm sheath diameter, 1 m long), which was already inserted in the furnace. This experiment showed that it took at most 2 seconds for the gas temperature at an axial location in the DTF below the tip of the injector to reach thermal equilibrium again, upon turning off the gas flows. Therefore,
the 10 seconds waiting time for attainment of quiescent conditions was deemed more than adequate.

For both flow conditions in the DTF (active flow and quiescent), the same bare thermocouple was used to measure the axial profile of the centerline gas temperature. The measured temperatures with this method were corrected for radiation effects as explained in Appendix A. The results are illustrated in Fig.2.

![Graph showing gas temperature profiles](image)

**Figure 2.** Centerline gas temperature inside the drop-tube furnace for pure N₂ and pure CO₂ in two different cases: quiescent gas condition and active gas flow. The temperatures were measured by a 250 μm bare thermocouple type K and they were corrected for radiation effects by the method discussed in Appendix A. The furnace wall set-point temperature (1400K) has been also shown in this plot.

Under the active gas flow condition, the gas temperature profiles were previously measured by Khatami et al.[28] with suction thermometry (an aspirated shielded thermocouple) along the centerline of the quartz tube. The current method was deemed to be necessary given the absence of flow in the quiescent condition, and it was also deemed to be more appropriate even in the active flow condition, given the low flowrates therein, as explained in Appendix B. It also
allowed temperature sampling closer to the injector tip. A comparison of the gas temperature profiles obtained by the two methods, in the section of the centerline length where measurements overlapped, is given in Appendix B. The agreement was deemed satisfactory.

As shown in Fig. 2, the there is a sizable temperature gap between the neat N$_2$ and the neat CO$_2$ gases under the active gas flow condition, whereas there is no significant gap under the quiescent gas condition (no flow). The highest temperature gap under active gas flow condition took place below the injector tip and amounted to 130 K. Thereafter, the gap diminished farther away from the injector tip, as the gas temperatures increased along the centerline of the furnace. Gas temperatures eventually stabilized in both environments at circa 1320 K. Under the quiescent gas condition (no flow), the gas temperature profiles were similar in either N$_2$ or CO$_2$ environments. Both temperatures increased along the centerline of the furnace and stabilized at an estimated 1340 K. The furnace wall set-point temperature ($T_w$) was 1400 K, as monitored by type-S thermocouples embedded in the wall.

3.3.5. Particle and gas velocity

The particle velocity in the furnace was determined by the summation of the particle terminal velocity and the gas velocity:

$$V_p = V_t + V_g$$

(1)

where $V_p$, $V_t$ and $V_g$ are particle velocity, terminal velocity and gas velocity, respectively. The particle terminal velocity was determined using the following relation:

$$V_t = \frac{(\rho_p D_p^2 g)}{18\mu}$$

(2)
Where \( \rho_p \) and \( D_p \) are particle density and diameter, respectively, and \( \mu \) is the dynamic viscosity of the fluid environment. It should be pointed out that this equation will not yield an accurate velocity for the cases where the volatiles around the particle are burning and creating a bubble of buoyant gas.

Particle terminal velocities, \( V_t \), in \( \text{O}_2/\text{N}_2 \) and \( \text{O}_2/\text{CO}_2 \) are nearly-identical because the dynamic viscosities of \( \text{N}_2 \) and \( \text{CO}_2 \) at the gas temperature range of this study (1200-1350K) are almost identical. They were in the neighborhood of 13 cm/s and 10 cm/s for coal particles and char particles, respectively, regardless of the background gas. In comparison, average gas velocities, \( V_g \), in the DTF were calculated to be 2 cm/sec. As a result, the coal and char particle velocities, \( V_p \), were calculated to be 15 cm/s and 12 cm/s, respectively.

3.4. Methodology

3.4.1. Cinematography

Optical access to the radiation zone of the furnace was achieved through sets of observation windows (view-ports), diagonally situated on the periphery of the cylindrical furnace. Particles were observed from the side of the DTF, as shown in Fig. 1, while a strong halogen light (300 W) shined through frosted glass from the opposite side to illuminate the silhouette of the particles (back-lighting). Fig.1 also illustrates the ignition delay distance inside the furnace. The particle history in the furnace was captured cinematographically from particle entry, upon exiting the tip of the injector tube, to the onset of visible combustion and beyond. For the majority of testing, captured events occurred in the first 6 cm of a particle’s travel path, after entering the furnace. Some follow-up testing was also performed with the camera observing through the
bottom view-port, to view coal particle combustion in active flow containing high CO₂ mole fractions, where combustion takes longer to initiate.

An ignition delay time was recorded for each sample, defined herein as the time between the initial entrance of a (backlit) particle from the injector’s tip into the furnace and the first appearance of luminous combustion (ignition by either the onset of a luminous volatile matter flame or luminous char surface oxidation). The ignition delay times were recorded in two different gas conditions: (1) A quiescent gas condition (no flow), which was created by turning off the gas flow a few seconds prior to the particle introduction (by gravity) to the furnace. (2) An active gas flow condition in the DTF, where 1 lpm was split between the injector and the furnace, as shown in Fig.1. Information about gas temperatures under these conditions is presented in Fig.2 and Appendix A. The ignition delay time was measured using the camera playback function of the software, which allowed the video to be viewed one frame at a time with each frame showing the time at which it was recorded. Additionally, the size of each particle was measured to ensure that the particles chosen for ignition length measurement were of both representative and comparable size, since particle size has a large effect on ignition delay [32]. Due to the nature of the video images, however, the particle sizes are estimates only and these values include an amount of inherent error; their inclusion is mainly to provide a confirmation of their relative size. Any clumps of particles were excluded from measurements; only particles which appeared to be single were counted to maintain consistent results.

A minimum of 15 samples of single coal particles were chosen for each testing case with up to 30 samples in several cases. The average and standard deviation for all cases were plotted as a function of the oxygen mole fraction for both N₂ and CO₂ atmospheres. It should be noted here that the physical and chemical properties of individual coal particles varied significantly
because, while they were nominally in the 75-90 µm range, they were actually irregular in shape, size and composition. Hence, particles that ignited either far above or far below the typical locations were not included in the statistical analysis. These outliers were eliminated from the data set.

3.5. Results and discussions

3.5.1. Experimental ignition observations

Selected images from high-speed and high-resolution cinematography of typical ignition events involving particles of all coals in various oxygen concentrations in N₂ and CO₂ environment examined herein are displayed in Figs. 3 and 4.

3.5.1.1. Quiescent gas condition (no flow) in the injector and in the furnace

Figs 3a and 3b illustrates the ignition events of bituminous and lignite coal particles, respectively, under the quiescent gas condition in the furnace. It should be mentioned again that the determination of ignition mode in this work was relied on luminous emissions.

*Bituminous coal (Pittsburgh #8):* Bituminous coal particles ignited in homogeneously (in the gas mode) in either N₂ or CO₂ background gases, see Fig. 3a. Apparently, evolved volatile matters from the particle reached sufficient volume fractions in the vicinity of the particle to exceed the lower flammability limit and, also, exceed the auto-ignition temperature of their mixture with oxygen in the bulk gas under the quiescent gas condition in the furnace (at Tₜ~1340K). Upon ignition, a diffusion flame forms around a particle. It appears that the diffusion flames built up slower in the O₂/CO₂ than in the O₂/N₂ environments, with the same O₂ mole fraction. Moreover, the flames appeared dimmer in CO₂-based atmospheres. At 21%O₂, flames also appeared wider
and longer in CO$_2$ than in N$_2$ background gases. At higher oxygen mole fractions, the flames appeared brighter in either O$_2$/N$_2$ or O$_2$/CO$_2$ atmospheres.

**Lignite coal (Beulah):** Fig.3b illustrates that the lignite coal particles fragmented in either O$_2$/N$_2$ or O$_2$/CO$_2$ atmospheres. Fragmentation reduces the particle size and increases the possibility of heterogeneous ignition. Indeed, most of the lignite coal particles appear to ignite heterogeneously in both environments. The number of fragments is comparable in O$_2$/N$_2$ and O$_2$/CO$_2$ atmospheres. However, the ignited fragments are brighter in O$_2$/N$_2$ than in O$_2$/CO$_2$.

(a) BITUMINOUS COAL (Pittsburgh #8, Pennsylvania, PSOC-1451)

(b) LIGNITE COAL (Beulah, North Dakota, DECS-11)
Figure 3. Quiescent gas conditions (no flow in the DTF): Selected images from high-speed cinematography of typical ignition events in various oxygen partial pressures (21-40%O₂) in N₂ and CO₂ environments involving particles of two coals used in this work (a bituminous and a lignite). The diameter of the wire shown in some photographs is 100 μm. The displayed numbers in each frame are in milliseconds, where zero does not mark the beginning of ignition. It merely represents the beginning of the depicted sequences. Nominal particle sizes were in the range of 75-90 μm, and the furnace wall temperature was set to 1400K.

3.5.1.2. Active flow of injector and furnace gases

*Bituminous coal (Pittsburgh #8):* In O₂/N₂, ignition of bituminous coal particles in air appeared to take place in the gas phase (homogeneously), see Fig.4a. This observation is in line with the findings of Shaddix and Molina [21] in nitrogen background gas, and with the predictions of the theoretical model of Annamalai and Durbetaki [12]. At high oxygen mole fractions (≥ 70% -) in N₂, however, it is unclear whether the bituminous coal particles ignited homogeneously or heterogeneously as the ensuing volatile flames burned close to the particle surfaces, see Fig.5a.

In O₂/CO₂ the likelihood of heterogeneous ignition mode of bituminous particles increased as the CO₂ content in the diluent gas increased, see Fig.4a. At O₂ mole fractions lower than or equal to 40% in CO₂, all of the particles ignited heterogeneously at hot spots on their surfaces. Hot spots may be constituted by sharp edges or other deformations, mineral inclusions, etc. (see
Levendis et al. [33]). This behavior is mainly attributed to the lower devolatilization rate of the volatile matter in the CO$_2$ atmosphere (as compared to N$_2$) upon particle injection in the DTF, due to the lower centerline gas temperatures encountered in the CO$_2$ background gas, see Fig.2. Therefore, the unburned volatile matter that accumulated around a particle may have found sufficient time to diffuse away and, by doing so, it could not attain the volumetric fractions that are necessary to reach the low flammability limit of the mixture. Zhang et al. [34] also noticed this phenomenon. At higher oxygen mole fractions in CO$_2$ ($O_2 \geq 70\%$), it is unclear whether the bituminous coal particles ignited homogeneously or heterogeneously as the ensuing volatile flames burned close to the particle surfaces, see Fig.4.

*Sub-bituminous coal (Wyodak):* Similar to the case of bituminous coal particles, homogeneous ignition was *mostly* observed for the cases of non-fragmenting sub-bituminous coal particles in N$_2$ at $20\% < O_2 < 40\%$. *Some* particles exhibited homogeneous ignition forming nearly-spherical envelope flames at $< 40\% O_2$. At oxygen mole fractions $\geq 40\%$ in N$_2$, some sub-bituminous coal particles exhibited limited fragmentation before and after ignition. This phenomenon increased the tendency of heterogeneous ignition of the fragments, see Fig.4b. At $O_2 \geq 70\%$ extensive fragmentation was observed and there was evidence of heterogeneous ignition of the fragments, see Fig.4b.

In CO$_2$ background gases, with O$_2$ mole fractions of 30% and 40%, all of the particles ignited heterogeneously at hot spots on the particle surface. This ignition behavior is similar to the ignition of bituminous coal particles burning at the same O$_2$ mole fractions, and was again attributed to the lower centerline gas temperature in CO$_2$ background gases at the tip of the injector in the case of active gas flow (Fig.2). Extensive fragmentation was also evident in cases analogous to similar oxygen mole fractions to N$_2$ atmospheres, see Fig.4b.
Lignite coals (Beulah and Wilcox): In N₂, the lignite coal particles of this study typically fragmented before or after the onset of ignition. The ignition mechanism of lignite particles usually depended on the timing of fragmentation. Whenever fragmentation took place during the particle heat up, heterogeneous ignition was more likely to happen due to the small size of the particle fragments [8, 11] and to the associated small fluxes of evolved volatile matters from each fragment, see for example Fig.5c for the air case. In contrast, when a particle did not fragment prior to the onset of ignition, there was evidence in some cases that homogeneous (gas phase) ignition occurred; see Fig.4c and 4d with 30% and 40% O₂ in N₂. The ensuing volatile flames in these cases were faint and brief and typically non-sooty and they may have contributed to subsequent extensive fragmentation.

In CO₂, with oxygen mole fractions of 30% and 40%, the cooler furnace centerline gas temperature of the background gas may have provided additional time for particle fragmentation to occur prior to ignition. Therefore, the observed heterogeneous ignition is most likely due to the extensive volatile loss as well as due to the resulting small sizes of the particle fragments [8, 11], Figs 4c and 4d.

(a)BITUMINOUS COAL (Pittsburgh #8, Pennsylvania, PSOC-1451)
(b) SUB-BITUMINOUS COAL (Wyodak, Wyoming, DECS-26)

AIR

21%O₂-79%CO₂

21%O₂-79%CO₂

(c) LIGNITE COAL (Beulah, North Dakota, DECS-11)

AIR

21%O₂-79%CO₂

21%O₂-79%CO₂
Figure 4. Active gas flow conditions: Selected images from high-speed cinematography of typical ignition events in various oxygen partial pressures (20-70%O₂) in N₂ and CO₂ environments involving particles of all four coals used in this work (bituminous, sub-bituminous and two lignite coals). The diameter of the wire shown in some sequences is 100 μm. The displayed numbers in each frame are in milliseconds, where the zero does not mark beginning of ignition. It merely represents the beginning of the depicted sequences. Nominal particle sizes were in the range of 75-90 μm, and the furnace wall temperature was set to 1400K.
3.5.2. Further investigation on the coal particle ignition mode

In general, ignition of single coal particles may occur in homogeneously (in the gas phase), heterogeneously or with a combination of both, based on prevailing parameters such as the particle size, heating rate and history, coal type, volatile matter content and devolatilization rate, background gas temperature and oxygen mole fraction, etc. It also depends on the definition of the ignition event [15]. Particle ignition temperatures have been reported by Khatami et al. [28] and Qiao et al. [35] to be fairly comparable (slightly higher) when N₂ was replaced by CO₂.

An analysis of the critical particle diameter for achieving either homogeneous or heterogeneous ignition and combustion, based on the work of Howard and Essenhigh [7] and Khatami et al. [28] is presented in Appendix C. The results are in agreement with the observed experimental trends and magnitudes. They confirm that under the conditions of this study, heterogeneous ignition is favored in CO₂ background gas and under the active flow conditions. To the contrary, under the N₂ background gas and quiescent gas condition, homogeneous ignition is favored. Ignition of the fragmenting lignite particles is predicted, and seen, to be likely heterogeneous under most conditions.

3.5.3. Coal particle ignition delay times

Experimental ignition delay times of coal particles were obtained at two different gas conditions: (a) quiescent (inactive) gas conditions in the furnace which provide a comparable gas temperature profile along the centerline of the DTF for both O₂/N₂ and O₂/CO₂ environments. (b) An active gas flow condition in the injector and furnace which results in lower gas temperatures in O₂/CO₂ than in O₂/N₂ environments downstream of the injector. Expressions, found in the literature [19, 36], for predicting of ignition delay times in either homogeneous or heterogeneous
ignition modes are shown in Appendix D. Theoretically predicted ignition delay times based on these expressions were calculated and were compared with the experimental ignition delays in the quiescent (inactive) gas condition, as listed in Fig. D2.

3.5.3.1. Ignition delay times in the presence of quiescent gas condition (no flow)

When quiescent gas conditions were achieved in the furnace, by turning off the gas flows, the furnace gases equilibrated to the spatial temperature distributions depicted in Fig. 2. When coal particles were gravity-fed to the furnace they heated up in similar gas temperatures in either N₂- or CO₂- containing gases, see Fig. 2. The ignition delays of these coal particles are plotted versus oxygen mole fractions in Figs. 5a and b, expanded versions of which are included in Figs. D1 and D2 of Appendix D. Fig.5a shows that the ignition delay times of bituminous coal particles in quiescent gas were longer in CO₂ than in N₂ (by a factor of 1.68 at 20%O₂). The ignition mode in this case was homogeneous, based on the cinematographic results (section 5.1.1, Fig.3a). The theoretical model that is pertinent to homogeneous ignition, given by Equation D.1 in Appendix D, indicates that the higher specific heat (\(c_v\)) of CO₂ (by 1.66 times higher than that of N₂) is responsible for the longer ignition delay time in the O₂/CO₂ atmospheres. As oxygen mole fraction increased, the ignition delays of bituminous coal particles in O₂/CO₂ decreased significantly, while the ignition delays in O₂/N₂ were not affected considerably.

Beulah lignite coal particles experienced longer ignition delays in CO₂ than in N₂ (by a factor of 1.32 at 20%O₂), see Fig. 5b and Fig.D2 of Appendix D. The lignite particles characteristically fragmented and they most likely ignited heterogeneously even under the quiescent gas conditions (Section 5.1.1, Fig.3b). The theoretical model that is pertinent to
heterogeneous ignition, given by Equations D.2-D.4 in Appendix D, indicates that the lower mass diffusivity ($D_0$) of O$_2$ in CO$_2$ is responsible for the longer ignition delay times in O$_2$/CO$_2$ background gases, as the thermal conductivities, $k_f$, of CO$_2$ and N$_2$ are nearly identical in this range of temperatures.

3.5.3.2. Ignition delay times in the presence of active gas flow

3.5.3.2.1 Coal particles

The results shown in Figures 5a, 5b, 5c and 5d suggest that in nitrogen environments, increased oxygen mole fractions have minimal effects on the ignition delay of the coal particles, under the conditions examined herein. This was also the case in quiescent gas environments and it may partially be attributed to the fact that the ignition modes in both gas conditions (flow and quiescent) are the same (homogeneous) and the volumetric heat capacities, $c_v$, of oxygen and nitrogen are very similar.
Figure 5. Coal and char particles (75-90 μm) ignition delay times versus oxygen mole fractions for various O₂/N₂ and O₂/CO₂ gas mixtures in the furnace. (a) and (b): Bituminous (PSOC-1451) and Beulah Lignite (DECS-11) in the two cases of quiescent gas and active flow inside the furnace. (c) and (d): Sub-bituminous (DECS-26) and Titus Lignite (PSOC-1443) in the case of active flow inside the furnace. (e) and (f): Bituminous coal (PSOC-1451) and char, Beulah Lignite coal (DECS-11) and char in the case of flow inside the furnace.

The ignition delay of the coal particles in O₂/CO₂ environments was much longer than in O₂/N₂ environments under active flow. In quiescent (inactive) gas condition, the different thermo-physical properties (\(c_v\) in homogeneous ignition and \(D_0\) in heterogeneous ignition) of the
background gases (O₂/N₂ and O₂/CO₂) were identified as the reason for the difference in ignition delay (by up to a factor of 1.68). However, the significantly larger ignition delays in O₂/CO₂ atmospheres under active gas flow conditions (up to a factor of 6.25 [23]) may be mostly attributed to the lower gas temperature. In fact, this can be shown by superimposing deduced coal particle ignition temperatures, as reported in Ref. [28], on the furnace centerline gas temperature profiles of Fig. 2. The case of the bituminous coal is exemplified in Fig. 6. The particle ignition temperature in air was deduced to be in the vicinity of 1200 K, under the common conditions of this study and of Ref. [28]. The particle ignition temperatures in CO₂-containing atmospheres were found to be approx. 25 K higher, say 1225 K [28]. Both of these temperatures are depicted as horizontal lines on Fig. 6 and then the corresponding distances from the injector tip are estimated to be 0.25 cm and 1.5 cm, respectively, for the N₂- and the CO₂-containing atmospheres. Given that the terminal velocities of coal particles were calculated in Section 3.5 to be similar in the two atmospheres, the elapsed times for the particles to travel the aforesaid distances in the furnace, from the injector tip to the locations where the gas temperature at-least equaled the corresponding observed particle ignition temperatures, is proportional to the traveled distances, x. Hence the ratio of the elapsed times is: \( t_{\text{CO}_2}/t_{\text{N}_2} = x_{\text{CO}_2}/x_{\text{N}_2} = 1.5/0.25 = 6 \). This compares favorably with the aforementioned factor of up to 6.25, by which the ignition delays in CO₂ are prolonged over those in N₂. Of course, there are additional contributions to the ignition delay discrepancy stemming from the different \( c_v \) of the two gases, from uncertainties regarding the ignition location of the particles, from uncertainties in radial deviations of the particle trajectories from the centerline of the furnace, where gas temperatures were measured, from uncertainties caused by switching from homogeneous to heterogeneous ignition in N₂ and CO₂, respectively, etc.
It should be noted here that as the intensity of the active flow in the DTF increased, the ignition delays of coals increased in both O$_2$/N$_2$ and O$_2$/CO$_2$ atmospheres. In fact, when in additional experiments the flowrates in the furnace increased from a combined injector and furnace flow of 1 lpm, as in the case above, to 2 lpm a similar trend was observed, albeit with particle ignition delays longer by 10-25%.

The fact that coal particle ignition delays (in both time and distance [23]) were observed to be drastically different (by up to a factor of 6.25 under this particular active flow), and were not as different (by up to a factor of 1.68) under quiescent gas in the DTF is likely to be an observation of importance to practical applications. In commercial furnaces the flow is, of course, active and the preheat of the injection gases is limited for practical considerations, such as to avoid premature ignition in the windbox. Hence, the cooler injection jets (relative to the furnace gases) penetrate some distance in the combustion chamber [37-42], perhaps in a pattern different than in the DTF because of turbulent mixing. Cool injection gases may significantly
delay ignition in the case of oxy-combustion, as compared to air, and push the flame to a
different location in the boiler. In fact a recent study by Smart et al. [38], using digital imaging to
observe an oxy coal flame, concluded that the flame temperature decreases with the recycle ratio
(i.e., the amount of CO₂). High levels of CO₂ resulted in delayed combustion and had a
detrimental effect on flame stability.

Two additional observations may be made from the results of Fig. 5: (a) The Beulah lignite
(DECS-11) coal particles consistently experienced longer ignition delays than the rest of the
coals only at the presence of N₂. This is likely related to the timing of fragmentation of this coal
in N₂, which (unlike the Wilcox Texas lignite - PSOC-1443) typically occurred after ignition [27,
28] or the absence of detected soot radiation as proposed by an anonymous reviewer. (b) The
bituminous coal (PSOC-1451) experienced much longer ignition delay times in CO₂ than
particles of the other coals. That was not the case under the quiescent condition, or in N₂ under
either the quiescent condition or the active flow condition. A possible explanation may be that all
coals under active flow in CO₂ background gases ignited heterogeneously (even the bituminous
coal !). The other three coals, however, fragmented to small pieces which are more effectively
carried with the injection gas to hotter regions of the furnace where they ignited and burned. To
the contrary, the bituminous coal forms char cenospheres, which are light and buoyant and, thus,
they stayed longer in the cooler region of the furnace, directly below the injector, which delayed
their ignition.

3.5.3.2.2. Coal Char particles

Coal char particles from the bituminous coal and from one of the lignite coals were burned
in this work to study the effect of volatile matter on the ignition delay times under active flow
conditions. As mentioned earlier, char particles were prepared from the coals (75-90 µm) in a similar DTF in either N₂ or CO₂, at \( T_f = 1400 \) K. Results are shown in Figs. 5e and 5f, superimposed with those of coal particles, under active flow conditions in both O₂/N₂ and O₂/CO₂ atmospheres.

**Bituminous coal (Pittsburgh #8):** For this coal results were rather varied. While char ignition delay times were longer than those of the parent coal in N₂ background gas, they were shorter in CO₂. Likely explanations are as follows: In O₂/N₂ atmospheres whose temperature increases rapidly along the centerline of the furnace, see Fig. 2, the bituminous coal particles ignited homogeneously, when the volatiles mole fraction in the boundary layer of the particle exceeded the lower flammability limit and their temperature exceeded the auto-ignition temperature of their constituents. Char particles were devoid of volatiles and, thus, their ignition was heterogeneous and was slower. Thus, in N₂ the presence of the volatiles appears to have accelerated the ignition process, as coals ignited faster than chars. To the contrary, in O₂/CO₂ atmospheres whose temperature increased slowly along the centerline of the furnace, see Fig. 2, bituminous coal particles ignited heterogeneously. Char particles also ignited heterogeneously, but faster. In CO₂ the presence of coal volatiles appears to have impeded the ignition process. It is likely that if their auto-ignition temperature is not readily reached, as they were released in the boundary layer, their accumulation therein impeded oxygen diffusion and mass transport to the particle surface and delayed heterogeneous ignition.

**Lignite coal (Beulah):** Lignite char particles consistently ignited faster than lignite coal particles in either O₂/N₂ or O₂/CO₂ atmospheres, heterogeneously so in both cases. This is most likely because the average char particle was smaller than the average coal particles. This is because these chars were made from the pyrolysis of fragmenting lignite coals during
preparation in N₂ or CO₂ in the DTF. The chars were not size re-classified after their preparation.

3.6. Conclusions

The goal of this study was to observe the ignition characteristics and assess the ignition delay of single coal particles (and of chars therefrom), when N₂ was replaced by CO₂. Pulverized coal particles from three different ranks (bituminous, sub-bituminous and lignite) were burned in this study. A drop-tube furnace was utilized under different gas atmospheres: O₂/N₂ or O₂/CO₂ with O₂ mole fractions ranging from 20% to 100%. Coal particles were in the size cut of 75-90 µm. The furnace wall temperature was set to 1400 K, whereas the centerline furnace gas temperature varied based on the gas flow intensity and composition in the furnace and injector. Two sets of coal ignition experiments were systematically conducted: (a) quiescent (inactive) gas conditions (b) Active gas flow conditions in the injector and in the furnace. Particle heating rates were in the order of 5×10³-10⁴ K/s. The most important conclusions of this work are as follows:

(a) In the case of quiescent (inactive) gas condition in the furnace:

1- Bituminous coal particles ignited homogeneously (gas mode) in either O₂/N₂ or O₂/CO₂ atmospheres. Lignite coal particles experienced extensive bulk fragmentation and heterogeneous ignition in both background gases.

2- Bituminous and lignite coal particles experienced longer ignition delay times in O₂/CO₂ than in O₂/N₂ environments. Increasing oxygen mole fractions decreased the ignition delay times in both the O₂/CO₂ and the O₂/N₂ atmospheres.
(b) In the case of active gas flow conditions in the injector and the furnace:

3- The ignition mode of coal particles in this case was altered when O\textsubscript{2}/N\textsubscript{2} were replaced by O\textsubscript{2}/CO\textsubscript{2} gases.

4- Higher rank coals (all bituminous particles and some sub-bituminous coal particles) ignited homogeneously in O\textsubscript{2}/N\textsubscript{2} atmospheres. Lignite coal particles fragmented before and/or after ignition. Those that fragmented before ignition were more likely to ignite heterogeneously, whereas those that fragmented after ignition experienced occasional homogeneous ignition in gas phase in O\textsubscript{2}/N\textsubscript{2} atmospheres. In O\textsubscript{2}/CO\textsubscript{2} atmospheres, particles from all different coal ranks appeared to ignite heterogeneously.

5- For all coals, the ignition delay time was much longer in O\textsubscript{2}/CO\textsubscript{2} than in O\textsubscript{2}/N\textsubscript{2} atmospheres. Increasing the oxygen mole fraction decreased the ignition delay time in O\textsubscript{2}/CO\textsubscript{2}, whereas the ignition delay times in O\textsubscript{2}/N\textsubscript{2} atmospheres were not significantly affected.

6- Char particles ignited heterogeneously. Observed discrepancies between their ignition delays and those of coal particles were influenced by the background gas (N\textsubscript{2} or CO\textsubscript{2}), coal type (rank) and combustion behavior (e.g. fragmentation).

7- A conclusion of relevance to industrial applications of oxy-coal combustion is that replacement of the flow of air by O\textsubscript{2}/CO\textsubscript{2} gases can affect the heating rate of pulverized coal injection jets and, thereby, may cause large differences in the ignition delay of coal particles. This may affect the flame location, length and stability to an extent depending on the velocity of the jet flow, its CO\textsubscript{2} content and its preheat temperature.
3.7. References


APPENDIX

3.8. Appendix A: Bare Thermocouple Temperature Correction for Radiation Effects

Gas temperature measurements conducted with bare thermocouples need to be corrected to exclude the furnace wall radiation effects (in both the N₂ the the CO₂ cases), and to exclude the gas radiation effects on the bead (in the CO₂ case only). The gas temperature correction is based on an energy balance on the thermocouple bead.

\[
\rho C_p V \frac{dT_b}{dt} = \dot{Q}_{\text{convection}} + \dot{Q}_{\text{radiation}} + \dot{Q}_{\text{cat}} + \dot{Q}_{\text{conduction}}
\]  

(A.1)

The thermocouple bead is assumed to be in thermal equilibrium with its surroundings (steady state) and the conduction along the bead wires is neglected based on the following considerations. The wire of the K-type OMEGA thermocouple used in this experiment was measured under an optical microscope to be approx. 50 μm, the bead was 250 μm, whereas the sheath (cladding) was 500 μm. The magnitude of the conduction term \( \dot{Q}_{\text{conduction}} = - k A_{\text{cross section of wire}} \frac{\Delta T}{\Delta x} \) was assessed based on the assumption that the quantity \( \Delta T/\Delta x \) is in the order of 300
K / 3 cm or 100 K/cm. Using this value, it was calculated that the conduction term is 215 times smaller than the radiation term and 20 times smaller than the convection term, thus, based on Grosshandler’s recommendation [43], the conduction term was neglected. Catalytic contributions are also neglected, since these experiments were in inert gases (N₂ or CO₂). Therefore, the energy balance A.1 simplifies to:

\[ \dot{Q}_{\text{convection}} + \dot{Q}_{\text{radiation}} = 0 \]  

(A.2)

The convection term, \( \dot{Q}_{\text{convection}} \) is determined from:

\[ \dot{Q}_{\text{convection}} = h \times A_b \times (T_{\text{gas}} - T_b) \]  

(A.3)

Where \( A_b \) is the thermocouple bead area and \( T_{\text{gas}} \) and \( T_b \) are the gas temperature and bead temperature, respectively. The convection heat transfer coefficient, \( h \), can be calculated using either of following the Nusselt number expressions for flow around a spherical object [44, 45]:

\[ \begin{align*} 
    Nu &= \frac{h \times D_b}{\mu(T_{\text{gas}})} = 2.0 + 0.6 \text{Re}_{D_b}^{0.3} \left( \frac{\mu(T_{\text{gas}})}{\mu(T_b)} \right)^{1/3} T_{\text{gas}} \quad 0 < \text{Re}_{D_b} < 200 \\
    Nu &= \frac{h \times D_b}{\mu(T_{\text{gas}})} = 2.0 + 0.4 \text{Re}_{D_b}^{0.6} \left( \frac{T_{\text{gas}}}{T_b} \right) + 0.06 \text{Re}_{D_b}^{0.3} \left( \frac{T_{\text{gas}}}{T_b} \right) \Pr^{1/3} \left( \frac{\mu(T_{\text{gas}})}{\mu(T_b)} \right)^{3/4} \quad 3.5 < \text{Re}_{D_b} < 76000 \text{ & } 0.71 < \Pr < 380 
\end{align*} \]  

(A.4)

A few words should be said about the selection of the Nusselt number for the thermocouple in these calculations. In this work the thermocouple was approximated as a sphere, which is the shape of its bead. The gas streamlines in the DTF were envisioned to flow around the bead and the wires were immersed in the wake of the flow. To clarify the geometry and orientation of the thermocouple a pertinent detail is shown in the apparatus schematic of Fig. 1. The aforementioned Nusselt number expressions (Eqn. A4) for flow around a single sphere were
selected for this calculation as the most appropriate representations of this setup. The authors are cognizant of the fact that in a comprehensive review put together by Shaddix on how to correct thermocouple measurements for radiation effects [46] a Nusselt number expression corresponding to a cylindrical geometry was recommended for thermocouple measurements, however such a geometry is appropriate for thermocouples with their leads stretched in diametrically opposite directions. Such thermocouple configurations are typically used in flame measurements to prevent sagging of the thermocouple wires. The recommended Nusselt number expressions for those thermocouples were in fact developed by Collis and Williams [47] and Andrews et al. [48] for “circular wires placed normal to a horizontal airstream”, i.e., cross flow over a cylinder, in the context of research relevant to hot wire anemometers. Therefore, whereas stretched thermocouples resemble cylinders in cross flow (see Fig. 1 in ref. [46] and Fig. 1 in ref. [47]), the thermocouple configuration used herein resembles a sphere.

The thermophysical properties in the aforementioned Nu numbers are evaluated at gas temperature, except for the viscosity $\mu(T_b)$, which is calculated at the bead temperature.

The radiation heat transfer ($\dot{Q}_{\text{radiation}}$) between wall and bead in the presence of an absorbing gas is:

$$\dot{Q}_{wb} = \sigma \varepsilon_b A_b (1 - \alpha_{\text{gas}}) (T_w^4 - T_b^4)$$

(A.5)

For the thermocouples (Type K) in this work, the bead emissivity ($\varepsilon_b$) was taken from Ref. [46] as 0.2-0.25 at 1500K. The CO$_2$ gas absorptivity ($\alpha_{\text{gas}}$) was determined by the following equation [49-51]:

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The correction factor for carbon dioxide gas, \( C(P) \), was obtained from Fig. 13.19 in Ref. [51]. The emissivity \( \varepsilon_{\text{gas}} \) was evaluated from partial pressure of the gas and the characteristic length [49-51]. The characteristic length was defined as [49-51]:

\[
Le = 3.66 \frac{V_{\text{chamber}}}{A_{\text{chamber}}}
\]  

(A.7)

The gas emissivity for carbon dioxide (CO\(_2\)) in a mixture with non-radiating gases at 1 atm total pressure can be determined from Refs. [49-51].

The energy balance then simplifies to:

\[
h \times A_b \times (T_{\text{gas}} - T_b) + \sigma \varepsilon_b A_b \left(1 - C(P) \left(\frac{T_{\text{gas}}}{T_b}\right)^{0.65} \varepsilon_{\text{gas}}\right) \left(T_w^4 - T_b^4\right) = 0
\]  

(A.8)

Finally, after some manipulation, the energy equation yields:

\[
h \left(\frac{T_{\text{gas}}}{T_b} - 1\right) + \sigma \varepsilon_b \left(1 - C(P) \left(\frac{T_{\text{gas}}}{T_b}\right)^{0.65} \varepsilon_{\text{gas}}\right) \left(T_w^4 - T_b^4\right) = 0
\]  

(A.9)

This is an implicit non-linear algebraic equation in terms of \( T_{\text{gas}} \). This equation was solved by trial and error for \( T_{\text{gas}} \) because some parameters in this equation such as \( \varepsilon_{\text{gas}} \) and \( h \) are gas-temperature (\( T_{\text{gas}} \)) dependent.

Figs. A1.a and A1.b display the measured (uncorrected) and the radiation-corrected centerline gas temperatures inside the DTF in the cases of active gas flow and quiescent gas conditions, respectively.
**Figure A1.** Corrected and uncorrected centerline gas temperatures inside the drop-tube furnace for neat N\textsubscript{2} and neat CO\textsubscript{2} in two different cases, (a) active gas flow and (b) quiescent gas condition. The temperatures were measured by a type-K bare thermocouple and they were then corrected for radiation effects by the aforementioned method.

3.9. Appendix B: Bare Thermocouple and Aspirated Thermocouple (Suction Thermometry) Temperature Comparison

In this manuscript a bare thermocouple (Type K, 250 μm bead diameter) was used to measure the centerline gas temperature profile in the furnace. This is in contrast to previous measurements [28] where an aspirated thermocouple (suction thermometer) was used. The switch to a bare thermocouple was dictated by the need to obtain temperature measurements in quiescent gas conditions, where suction thermometry could not be used, since it requires flow. Moreover, it provided additional benefits, as it allowed higher resolution in the upper part of the DTF, since the outlet of the injector could be more readily approached by the slender bare thermocouple rather than by the bulkier suction thermometry probe. Finally, uncertainties regarding the intensity of suction around the aspirated thermocouple were avoided. During the previous measurements the flowrate in the suction probe was regulated to provide isokinetic flow sampling conditions, in order to avoid sucking gas from the surroundings of the targeted
locations. Isokinetic sampling by the suction thermometer is needed from a flowfield perspective, however one has to be cognizant that a higher flowrate is most-likely desirable to render convection, and not radiation, the dominant heat transfer mode around the shielded thermocouple bead [52].

The centerline temperature profile in the furnace, as measured by the bare thermocouple, upon radiation corrections has been presented in Fig. 2. In the figure below (Fig. B1) the gas temperature profiles obtained with suction thermometry, as appeared in Ref. [28], have been superimposed with the gas temperature profiles obtained with the bare thermocouple (upon radiation corrections). It can be seen that in the range of axial distances in the DTF displayed in the plot of Ref. [28], i.e., $x > 0.5$ cm, the agreement between both methods is fairly good and in the ordinate scale used before it is hardly distinguishable.

![Figure B1](image)

**Figure B1.** Superimposed centerline gas temperature inside the DTF for pure N$_2$ and pure CO$_2$ in the case of active gas flow using two different methods: (I) naked thermocouple and (II) suction thermometry (Fig.1). (I) naked thermocouple: the temperatures were measured by a bare thermocouple type K and they were corrected for radiation effects by the method discussed in Appendix A. (II) suction thermometry: the temperature measurement was conducted by Khatami et al. [28] and presented here for comparison.
3.10. Appendix C: Prediction of ignition and combustion mode in quiescent gas condition

Howard and Essenhigh [8] defined a critical particle size, \( d_c \), for a given set of conditions such that for the particles smaller than that size \( (d < d_c) \), the flame does not lift away from the particle, hence volatiles and chars burn simultaneously on the surface of the particle.

\[
d_c = \sqrt{\frac{12DP((p_{O_2})_\infty - (p_{O_2})_s)}{d(\Delta V_v/V_0) \rho_c y_v f_v RT_i}}
\]

where \( D \) (cm\(^2\)/s) is the binary diffusion coefficient of O\(_2\) in either N\(_2\) or CO\(_2\) at the background gas temperature and pressure, \( P \) (atm) is the total pressure of the background gas (1 atm in the work herein), \( (p_{O_2})_\infty \) is the mole fraction of oxygen in the bulk gas and \( (p_{O_2})_s \) is the mole fraction of oxygen on the outer surface of the flame sheet surrounding a particle. \( \Delta V_v \) is the volatile matter evolved from solid fuel as pyrolysis products. \( V_0 \) is the initial volatile matter content listed in Table 1, \( \rho_c \) (g/cm\(^3\)) is the density of the coal, \( y_v \) is the mass fraction of volatile matter in the original coal, \( f_v \) (moles/g) are the moles of oxygen required to burn a unit mass of volatiles, \( R \) (cm\(^3\)atm / mole K) is the ideal gas constant, and \( T_i \) (K) is the ignition temperature of the fuel in a given background gas. Further details of the calculation are given by Khatami et al. [28].
Figure C1. Critical particle diameters determined for two flow conditions: quiescent gas condition (inactive) and gas flow (active). Particles with sizes smaller than the critical diameter burn in one-mode (simultaneous volatile and char combustion). (a) Critical particle diameter for bituminous coal particles of this study (PSOC-1451). The actual particle size range (75-90μm) is denoted by the two horizontal lines. (b) Critical particle diameter for the (DECS-11) lignite coal particles of this study. The typical fragment size of this coal (30μm) is also shown as a line.

Figs. C1-a and C1-b indicate that unlike the active flow condition in the furnace, the quiescent gas condition does not influence the ignition and combustion mode of coal particles significantly when N₂ is replaced by CO₂. Moreover, according to this model, bituminous coal particles burn with two distinct modes (volatile followed by heterogeneous char) in the case of quiescent gas conditions in either N₂ or CO₂ background gases, whereas lignite coal fragments burn in one-mode. The outcomes of this model are in agreement with the cinematographic results reported in Sections 5.1.1 and 5.1.2.
3.11. Appendix D: Prediction of ignition delay times

D.1. Homogeneous ignition delay

In a gas phase homogeneous one-step reaction, according to adiabatic thermal explosion theory, the ignition delay time is given by [19]:

\[ t_i = \frac{c_v(T_0^2/T_a^2)}{q_c Y_{F,0} A \exp(-T_a/T_0)} \]  

where \( c_v \) is the constant volume specific heat of the background gas, \( T_a \) is the activation temperature defined base on activation energy [19], \( T_0 \) is the initial temperature of the local fuel/oxidizer mixture, \( q_c \) is the combustion heat release per mass of fuel, \( Y_{F,0} \) is the initial mass fraction of fuel and \( A \exp(-T_a/T_0) \) is the reactivity of the fuel/oxidizer mixture.

Under the quiescent gas condition, the bituminous coal particles (PSOC-1451) ignited homogeneously in both N\(_2\) and CO\(_2\) background gases. Ignition delay times are plotted in Fig.D1 against oxygen mole fractions. The volumetric heat capacities (heat sinks) of the corresponding background gases were superimposed on the same figure. It can be seen that ignition delay times are analogous to volumetric heat capacities in both trend and span.
D.2. Heterogeneous ignition delay

The ignition delay time of a solid carbon particle in a drop tube furnace can be calculated by the following expression of Bandyopadhyay and Bhaduri [36], based on an energy balance:

$$t_i = \frac{d_p}{B} \int_{T_i}^{T_g} \frac{dT}{273} \begin{bmatrix} 0.01 O_2 \frac{1}{k_o e^{-E/RT}} + \frac{2k_f}{d_p} (T_g - T) + \sigma(T_w^4 - T^4) \end{bmatrix}$$

(D.2)

where $A = \rho_0 \beta \varphi$, $\rho_0$ is the density of $O_2$, $\beta$ is ratio of the weight of coal to the weight of oxygen (stoichiometric coefficient) and $\varphi$ is the calorific value of coal. $B = 6/\rho C_d$, $\rho$ is the density of the coal particle and $C_d$ is the specific heat of coal. $d_p$ is the particle diameter, $T_g$ is the gas temperature, $O_2$ is the oxygen concentration in the reacting gas, $D_0$ is the diffusion coefficient at
a reference temperature (293 K), $k_f$ is the thermal conductivity coefficient of the gas and $T_w$ is the wall temperature of the furnace (1400 K in this study). $E$ and $k_0$ are activation energy and pre-exponential factors in the Arrhenius form of the reactivity of each coal, respectively. $T_{p0}$ and $T_{pi}$ are the temperatures of the particle at the tip of the injector and at the ignition moment, respectively. The Nusselt number of the flow for small particles of this work (less than 100\(\mu\)m) is 2.

Equation (D.2) can be manipulated to obtain:

$$t_i = \int_{\tau_{m}}^{T_{f}} f(T) dT$$ (D.3)

where:

$$f(T) = \frac{d_p / B}{T_g} \left( A \left[ \frac{0.01O_2}{d_p} \right] + \frac{2k_f(T_g - T)}{d_p} + \frac{\sigma(T_w^4 - T^4)}{k_0 e^{-E/RT} + 2D_0(T_g/273)^2} \right)$$ (D.4)

$f(T)$ is a positive number because: $T < T_{pi} < T_g < T_w$. Eqn. D.3 illustrates that the ignition delay ($t_i$) is the area under the curve $f(T)$ in the $T$-$f(T)$ surface. Therefore, the parameters that increase the function $f(T)$ also increase the heterogeneous ignition delay times. Enhancement of oxygen mole fraction, gas conductivity and binary gas diffusivity, reactivity, density, specific heat and calorific value of coal reduce $f(T)$ and consequently decrease ignition delay times ($t_i$). However, if coal particle size is large, the ignition delay time is lengthier.

The heterogeneous ignition delay for Beulah lignite coal (DECS-11) was determined based on Eqn. D.2 and it is shown in Fig.D2.
Figure D2. Comparison of the linear fit trend of the experimental and theoretical ignition delay times for the Beulah Lignite coal (DECS-11) particles (75-90 μm) versus oxygen mole fractions for various O₂/N₂ and O₂/CO₂ gas mixtures in the furnace. The gas condition in the furnace is quiescent (inactive).
CHAPTER 4

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4. Combustion Behavior of Single Particles from Three Different Coal Ranks and from Sugar Cane Bagasse in $O_2/N_2$ and $O_2/CO_2$ Atmospheres

Abstract

The combustion behavior of single fuel particles was assessed in $O_2/N_2$ and $O_2/CO_2$ background gases, with oxygen mole fractions in the range of 20-100%. Fuels included four pulverized coals from different ranks (a high-volatile bituminous, a sub-bituminous and two lignites) as well as pulverized sugarcane-bagasse, a biomass residue. Particles of 75-90 μm were injected under laminar flow in a bench-scale, transparent drop-tube furnace (DTF), electrically-heated to 1400 K where, upon experiencing high heating rates, they ignited and burned. The combustion of individual particles was observed with three-color optical pyrometry and high-speed high-resolution cinematography to obtain temperature and burnout time histories. Based on combined observations from these techniques, a comprehensive understanding of the behaviors of these fuels was developed under a variety of conditions, including simulated oxy-fuel combustion. The fuels exhibited distinct combustion behaviors. In air, the bituminous coal particles burned in two distinctive modes; the volatiles burned in bright envelope flames surrounding the devolatilizing char particles followed by heterogeneous char combustion. The volatile matter of sub-bituminous coal particles burned either in subdued envelope flames, surrounding devolatilizing and occasionally fragmenting chars, or heterogeneously at the char surface. Lignite particles typically burned with extensive fragmentation, and their volatiles burned simultaneously with the char fragments. The volatiles of bagasse particles burned in spherical and transparent envelope flames. Increasing the oxygen mole fraction in $N_2$, increased
flame and char surface temperatures, and decreased burnout times; particles of all fuels burned more intensely with an increasing tendency of the volatiles to burn closer to the char surface. When the background gas N₂ was substituted with CO₂, the combustion of all fuels was distinctly less intense; at moderate O₂ mole fractions (<30%) most particles did not ignite under active flow conditions in the furnace (they did ignite under quiescent gas flow conditions in the DTF). Increasing the oxygen mole fraction in CO₂ increased the likelihood of combustion and its intensity. Combustion of volatiles in envelope flames was suppressed in the presence of CO₂, particularly under active gas flow in the DTF.

4.1. Introduction

Previous work in this laboratory contrasted the combustion behavior of pulverized bituminous, sub-bituminous and two lignite coals, as well as of sugarcane bagasse, under conventional air-fired conditions [1]. This work examines the combustion behavior of the same fuels burning in O₂/CO₂ and O₂/N₂ atmospheres. Conditions of interest to oxy-coal combustion (an advanced “clean-coal” technology that facilitates carbon dioxide capture [2, 3]) were included in this investigation. Whereas, oxy-coal combustion technology is currently targeting overall oxygen mole fractions in the range of 20-40% [3, 4] in CO₂, herein oxygen mole fractions as high as 100% were explored. This was done to (i) obtain basic understanding of the combustion behavior of these solid fuels over the entire possible range of oxygen enhancement, above and beyond the oxygen content of air, and (ii) because oxy-combustion at high oxygen mole fractions (>40%), by local injection of neat O₂, is of industrial interest for a variety of reasons, including improvement of coal ignition, flame stabilization at a particular location in the furnace, compact flame generation, flame stability and, eventually, reduction of the boiler size and hence reduction of the cost of the power plant [5, 6, 7]. High oxygen mole fractions in N₂
were used herein for comparison with CO₂ background gases. All four coals were burned in a laboratory-scale, electrically-heated, laminar-flow drop-tube furnace fitted with a transparent quartz tube. Single particle combustion behavior was observed with three-color optical pyrometry and simultaneous high-speed cinematography. This work is part of an extensive investigation on the ignition and combustion of coal in gases containing high volume fractions of CO₂, as well as on the gaseous and particulate emissions therefrom.

In the following two sub-sections, the relevant literature is briefly reviewed. The first sub-section outlines other works on combustion of coal particles at high oxygen concentrations in either nitrogen or carbon dioxide background gases. The second sub-section outlines works relevant to identifying the mode of particle combustion. In this work, the term two-mode combustion is used to signify events where has gas-phase (homogeneous) combustion of the volatile matter in an envelope flame, surrounding a devolatilizing char particle, is distinct from the ensuing heterogeneous solid char combustion. The term one-mode combustion is used to signify events where either (i) combustion of devolatilized chars takes place, or (ii) combustion of the volatile matter takes place in the proximity of the char surfaces with, presumably, simultaneous burning of the char. The combustion mode is influenced by particle size, coal type, oxygen mole fraction, type and temperature of background gas and heating rate.

4.1.1. Overview of relevant previous studies on oxy-coal combustion in O₂/N₂ and O₂/CO₂ atmospheres

Timothy et al. [8] performed one of the first investigations on the combustion characteristics of single coal particles at elevated oxygen concentrations in nitrogen. Three bituminous and two lignite coals, with particles sizes of 38-45 and 90-105 µm, were burned at furnace temperatures
of 1250 and 1700K, and at oxygen mole fractions ranging from 15% to 100%. They used a two-color pyrometer to record entire particle temperature histories, burnout times, devolatilization times and changes in luminous particle areas during combustion. They recorded pyrometric signals that included one or two peaks, depending on the coal type and on the oxygen mole fraction in the gas. They reported that the burning temperature (at 50% burnout) of single-coal particles increased with oxygen mole fraction, from 2200 (at 20% O2) to 3000K (at 100% O2) for a bituminous coal, and from 2000 (at 20% O2) to 2800K (at 100% O2) for a lignite. Particle devolatilization and char burnout times of all coal particles decreased as oxygen mole fraction increased.

Joutsenoja et al. [9] measured temperature snapshots of burning single coal particles in an entrained-flow reactor using a pyrometric method; the gas temperature ranged between 1150-1270K, and oxygen volume fractions between 3-30%. They burned lignite, bituminous and anthracite coals, in the size range of 75 to 180µm. They reported that enhancing the oxygen mole fraction increased the particle temperature of all coals in the range of 2200 K (20% O2) to 2700 K (30% O2) and reduced the burn-out time, as inferred by an ash tracing technique. For the lignite coal of their study, they reported that burning particles fragmented in O2 concentrations in the range of 21-30%. They also pointed out that swelling of high-volatile coal particles took place in the early stages of combustion.

Murphy and Shaddix [10] measured temperature snapshots of chars from a bituminous coal and a sub-bituminous coal, in O2/N2 with various oxygen mole fractions (6-36%), using an entrained flow reactor, operated at 1400-1800K, coupled to a pyrometer. They found that increasing the oxygen mole fraction in this range increased the char temperatures from 1800 to 2300 K. Despite the faster particle combustion rates in such conditions, the kinetic data,
interpreted with a single-film oxidation model, demonstrated increasing kinetic control in oxygen-enriched combustion. Shaddix and Molina [11] reported lower temperatures for the combustion of these coals when N₂ was replaced with CO₂.

Bejarano and Levendis [12] monitored entire combustion histories of single particles of a bituminous coal and a lignite coal, as well as of mono-disperse synthetic chars, at increasing O₂ mole fractions in either N₂ or CO₂ balance gases. Three-color pyrometry was used as the sole diagnostic method for deducing temperatures and burnout times of single coal particles. Their experiments revealed that coal particles burned at higher mean temperatures and shorter combustion times in O₂/N₂ than in O₂/CO₂ environments, at the same oxygen mole fractions. They inferred some burning characteristics of the bituminous and lignite coals such as volatile and char combustion modes. However, use of a single diagnostic technique prevented the assessment of the phenomena that manifested themselves throughout the combustion history of the coals, such as fragmentation, ignition delay, combustion mode, flame shape and location, etc.

Zhang et al. [13] burned a bituminous coal in air with two O₂/CO₂ mixtures (with O₂ in the range of 21-27%) in a DTF operated at 1073 K or 1273 K. They used in-situ photography, and monitored the CO emissions and char properties. Based on observations of delayed ignition in the presence of CO₂, they reasoned that the volatiles preferentially remained in the vicinity of a particle’s surface to form a thick protective sheath. These unburned volatiles mainly converted to CO in a weak detached flame, through partial oxidation. Partial oxidation and gasification of chars to CO were, also, favored under those conditions, due to insufficient O₂ in the vicinity of the char particles. These partial oxidation and gasification reactions lowered the heat-release rate and decreased the char temperature significantly. Zhang et al. [14] also investigated the experimental combustion of a brown coal in O₂/N₂ and O₂/CO₂ mixtures, with O₂ in the range of
21-36%. This time they employed two-color pyrometry and photography to measure the optical intensity of the flames and observe the combustion. They reported that substitution of CO₂ for N₂ enhanced the coal particle pyrolysis prior to ignition, as CO₂ reacted with the resulting chars to form additional combustible gases in the particle vicinity. On the other hand, Brix et al. [15] burned a bituminous coal in a DTF (operated between 1173K and 1673K) in both O₂/N₂ and O₂/CO₂ atmospheres (5< O₂<28%), and reported that coal devolatilization generated similar volatile yields and char morphologies in both background gases. Their work concluded that a shift from air to oxy-coal combustion did not influence the devolatilization process significantly.

A number of other investigators also reported on the oxy-fuel combustion of coal and chars from different origins and ranks ([16-27]). Smart et al. [16] implemented digital imaging techniques to monitor the flame generated by a high-volatile and a low-volatile coal (rank not specified) in both air and in O₂/CO₂ mixtures (25< O₂<38%). Flame temperatures reached 1600-1900K, increasing with increasing O₂, but decreasing in the presence of CO₂. Moreover, high CO₂ content in the gas delayed the combustion and impaired the flame stability. Kim et al. [18] also utilized digital imaging techniques to monitor the group flames of two sub-bituminous coals in O₂/N₂ and O₂/CO₂ atmospheres (5< O₂<50%). Their results illustrated that increasing O₂ mole fractions accelerated combustion and shortened the flame length. The flame lengths in CO₂ were shorter than the flame lengths in N₂ background gas. Liu et al. [19,20] examined the combustion of several high-volatile bituminous coals in a vertical combustor, with gas temperatures in the range of 1373 to 1650 K, in both air and O₂/CO₂ atmospheres (21< O₂<35%). They reported that replacement of N₂ by CO₂ decreased the gas temperature and the coal burnout fraction. They also reported that the O₂ mole fraction in CO₂ needs to be 30% or higher, to match the gas temperatures and burnout effectiveness of the coal-air flames. Huang et al. [21] burned
bituminous coal particles (11-33 µm) in a thermo-gravimetric analyzer (TGA) in O₂/CO₂ atmospheres (10< O₂<80%). They reported that as oxygen mole fractions increased, burnout times decreased. Li et al. [22] used a DTF as well as a TGA to monitor the combustion of low-rank coal particles (63-90 µm) at gas temperatures of 1073-1673 K in the former furnace, and 1273 K in the latter. They reported that the volatile matter yield was higher in CO₂ than in N₂ environment, and that the degree of burnout increased with increasing oxygen mole fraction (10< O₂<21%). In addition, burnout was higher in air than in 21%O₂-79%CO₂. Li et al. [23] investigated the combustion of anthracite and bituminous char particles (63-90 µm) in a DTF at 1200°C in either air or 21%O₂-79%CO₂. They reported that the burnout degree and the reaction rate were lower in the latter case. Different pore structures were detected in chars generated in O₂/CO₂ and O₂/N₂ environments, which influenced combustion behavior, such as fragmentation.

This literature survey suggests that the substitution of N₂ with CO₂, as the background combustion gas, decelerates the combustion reactions. Nevertheless, unraveling of the phenomena involved is complicated, as there is a lot of disparity in the literature regarding the selection of fuels and the implemented combustion conditions, i.e., coal origin and rank, particle size, furnace temperature and O₂/N₂ or O₂/CO₂ mixture composition. Furthermore, most of the previous works were limited to oxygen mole fractions well-below 50%, and did not monitor the entire combustion behavior history of individual burning particles in O₂/CO₂ environments. Moreover, in most of the previous studies, the combustion of coal particles was reported based on a single diagnostic technique. However, as recently shown in this laboratory [1], multiple diagnostic techniques are necessary to assess the combustion behavior of single fuel particles. This investigation burned coals from different ranks (and a biomass) in a DTF and used concurrent three-color pyrometry and high-speed, high-resolution cinematography to monitor the
entire burnout history of single particles and assess their time-dependent combustion behavior in both O₂/N₂ and O₂/CO₂, with O₂ mole fractions covering the entire (20-100%) range of oxygen enhancement.

The literature in the following sub-section was found instrumental in interpreting some of the combustion phenomena that were observed in this work.

4.1.2. Overview of previous studies on the mode of combustion of coal particles

Howard and Essenhigh [28] recognized the possibility of overlap of homogeneous (volatile matter) and heterogeneous (char) burning near the particle surface. They reported that particle size affected this behavior and they introduced the concept of a critical particle size, below which the volatile matter flame does not lift from the particle surface and, thus, volatiles and chars burn simultaneously on, or near, the particle surface. The critical particle size was found to depend on the physical and chemical properties of the fuel (rate of volatile evolution), burning environment (oxygen mole fraction and diluent gas) as well as on the ignition (or flame) temperature. For instance, when a Pittsburgh-seam bituminous coal particle was burned in air, the critical particle diameter was determined to be 65 µm [28]. Midkiff et al. [29] investigated the influence of bituminous and sub-bituminous coal ranks on the simultaneous devolatilization and char combustion, and implied that the occurrence of simultaneous hetero/homogeneous reactions was more likely for lower coal ranks. The background gas in their work was 23%O₂-77%Ar, and the coal particles were sieved to sizes less than 74µm. They determined that the maximum critical particle diameter was 78 µm for the bituminous coal, and 52 µm for the sub-bituminous coal of their study. Other researchers (among them Saastamoinen et al. [30], Saito et al. [31] and Veras et al. [32]) studied this subject further and concluded that simultaneous combustion of volatile
matter and char is increasingly favored by higher oxygen concentrations as well as by decreasing particle sizes. Although most of the above works pointed out the role of oxygen content on the overlap of volatile and char burning near the surface, they did not discuss the influence of elevated oxygen mole fractions (over 30% volume) or the effects of substituting the background N₂ gas with CO₂. Saito and coworkers [31] quantified the fraction of volatile matter released from coals of different particle sizes burning in air. They reported that although the combustion behavior of pulverized coal was basically a sequential two-staged process, consisting of homogeneous gas-phase followed by heterogeneous solid-phase combustion, these two stages were not completely distinct and residual carbon burning was affected by late evolution of volatile matter. The present work interprets the influence of fuel type/rank, O₂ mole fraction and substitution of N₂ by CO₂ on the critical particle diameter, in view of the experimental observations and the analytical model of Howard and Essenhigh [28], which is delineated in the Discussion Section.

### 4.2. Physical and Chemical properties of the fuels

Samples for the four coals were obtained from the Pittsburgh Coal Bank, and were ground, sieved to the size cut of 75-90 µm. Two of the coals (PSOC-1451 and PSOC-1443) were extensively characterized in previous research, see Sahu et al. [33, 34] and Bejarano and Levendis[12]. Sugarcane bagasse was obtained from a bio-ethanol production plant in Brazil; it is fibrous and woody in nature. It was dried, chopped in a household blender, and sieved; the size cut of 75-90 µm was again selected for these experiments to be in line with the work of Levendis et al. [1]. The results of proximate and ultimate analysis of four coals and bagasse of this work are shown in table 1.
### Table 1. Chemical Composition of the Coals and the Bagasse Biomass

<table>
<thead>
<tr>
<th>Rank and Fuel Source</th>
<th>PSOC-1451</th>
<th>DECS-11</th>
<th>PSOC-1443</th>
<th>DECS-26</th>
<th>Bagasse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous High Volatile A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pittsburgh #8 Pennsylvania</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lignite A Beulah, North Dakota</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lignite A Titus, Texas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sub-Bituminous B River Basin Wyodak, Wyoming</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sugarcane Residue Brazil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Proximate Analysis as received, and (upon re-evaluating moisture)</th>
<th>2.5</th>
<th>33.4 (13.2)</th>
<th>28.5 (18.6)</th>
<th>26.3 (13.1)</th>
<th>4.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (%)</td>
<td>33.6</td>
<td>37.4 (48.6)</td>
<td>44.2 (50.3)</td>
<td>33.1 (39.0)</td>
<td>83.9</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>50.6</td>
<td>22.9 (29.8)</td>
<td>12.0 (13.7)</td>
<td>35.1 (41.4)</td>
<td>7.7</td>
</tr>
<tr>
<td>Fixed Carbon (%)</td>
<td>13.3</td>
<td>6.4 (8.4)</td>
<td>15.3 (17.4)</td>
<td>5.6 (6.5)</td>
<td>4.0</td>
</tr>
<tr>
<td>Ash (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate Analysis (on a dry basis)</th>
<th>71.9</th>
<th>66.2</th>
<th>56.8</th>
<th>69.8</th>
<th>44.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (%)</td>
<td>4.7</td>
<td>4.0</td>
<td>4.1</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>6.9</td>
<td>18.6</td>
<td>15.8</td>
<td>15.6</td>
<td>45.5</td>
</tr>
<tr>
<td>Oxygen (%) (by diff.)</td>
<td>1.4</td>
<td>0.9</td>
<td>1.1</td>
<td>0.9</td>
<td>0.2</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>1.4</td>
<td>0.7</td>
<td>0.7</td>
<td>0.4</td>
<td>0.07</td>
</tr>
<tr>
<td>Sulfur (%)</td>
<td>0.06</td>
<td>0.66</td>
<td>0.04</td>
<td>0.09</td>
<td>-</td>
</tr>
<tr>
<td>Sodium (%)</td>
<td>13.7</td>
<td>9.6</td>
<td>21.4</td>
<td>7.6</td>
<td>4.2</td>
</tr>
<tr>
<td>Ash (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heating Value Dry Fuel (MJ/kg)</td>
<td>31.5</td>
<td>25.7</td>
<td>23.0</td>
<td>28.2</td>
<td>16.3</td>
</tr>
</tbody>
</table>

The four coals and their proximate and ultimate analysis data was obtained from the Penn State Coal Sample Bank; however, upon opening the sealed containers of the supplied coal samples, variations of moisture content with storage in the laboratory were observed for all, but the bituminous, coals. The measured moisture content values are listed (in parentheses) and the remaining proximate analysis values were re-calculated and are also shown (in parentheses). The specific bagasse sample was analyzed at the University of São Paulo laboratories, São Carlos Campos.
4.3. Experimental setup and methodology

Drop tube furnaces or entrained flow reactors were considered to be appropriate devices for such studies, as they reproduced conditions suitable to those in practical systems, while providing a relatively simple configuration ([35, 36]). The combustion studies of free-falling coal and bagasse particles were carried out in an electrically heated, laminar flow, vertical drop tube furnace (DTF) at a constant wall temperature of 1400K. The radiation cavity of this furnace (an ATS unit) was 25 cm long and was heated by hanging molybdenum disilicide elements. A sealed 7 cm i.d. transparent quartz tube was fitted in this furnace. Different gas mixtures (O₂/N₂ or O₂/CO₂) were introduced to the radiation cavity of the furnace through a water-cooled stainless-steel injector and also through a flow straightener, coaxially to the furnace injector, Fig. 1. The fuel particles were introduced through a port at the top of the injector by first placing them on the tip of a beveled needle syringe. Gentle taps on the needle allowed single coal particles to enter the injector and, subsequently, the furnace. The gas entering through the flow straightener was preheated in the annular space between the injector and the quartz tube before it reached the main radiation cavity. The combined flow at wall temperatures of 1400 K resulted in an average gas velocity of 4.55 cm/s and a gas residence time of 5.5 s inside the furnace radiation cavity.
Figure 1. Schematic of the drop-tube furnace; a detailed rendering has been shown in Bejarano and Levendis [12].

The gas temperature profiles, shown in Fig. 2, were measured along the centerline of the quartz tube with suction thermometry at several gas compositions. In all cases, centerline furnace gases heated up and asymptotically reached a temperature that is 50 K below the furnace wall set-point temperature of 1400 K. Neat CO$_2$ gas was the slowest to heat-up. The highest temperature gap between the neat N$_2$ and neat CO$_2$ gases took place below the injector tip and amounted to 150 K. Thereafter the gap diminished, and farther away from the injector tip the gas temperatures in all environments stabilized at a value circa 50 K below the wall temperature. The temperature gaps between the cases of O$_2$/N$_2$ and O$_2$/CO$_2$ gas blends were smaller than 150 K, as expected. Similar temperature gaps were reported by Shaddix and Molina [37, 38]. Particle heating rates were very high, calculated to be in the order of $10^5$ K/s. Particles ignited at axial
locations in the furnace where the gas temperatures were similar (ca. 1300 K), regardless of the gas composition, as documented in [39].

Optical access to the radiation zone of the furnace was achieved through three observation ports: one at the top and two orthogonally situated at the sides of the furnace. Pyrometric observations of single particles were conducted from the top of the furnace injector, viewing downwards along the central axis of the furnace, Fig. 1, which ideally was the particle's path-line. Accordingly, the luminous burnout histories of single particles - from ignition to extinction – could be monitored. To minimize reflected furnace radiation climbing the injector's inner walls (upon multiple reflections) (a) a 61.0 cm long injector was used, 1.25 cm i.d., (b) the injector was black-passivated and (c) a pinhole was used between the lens and the fiber. An optical fiber transmitted light from the furnace to the pyrometer assembly. This pyrometer used two dichroic edge filters as spectrum splitters to direct the light to the three interference filters. These filters had effective wavelengths of 0.640, 0.810 and 0.998 μm with bandwidths (FWHM) of 70 nm. Details of the pyrometer have been given by Levendis, Estrada and Hottel [40]. The voltage signals generated by the three detectors were amplified and then processed by a microcomputer using the LabView software.

![Graph showing gas temperature vs. distance from injector tip for different gas compositions.](image)
Temperature was deduced from the three output voltage signals of the pyrometer using a non-linear least square method, based on Planck’s law. Details of this method and of the instrument calibration were given by Khatami and Levendis [41]. For the char surfaces, gray-body behavior was assumed (canceling the emissivities \(\varepsilon_{12}/\varepsilon_{21}\)), during the char combustion mode. The case of sooty envelope diffusion flames surrounding a bituminous coal particle (and some sub-bituminous particles) during the volatile combustion stage was more complicated. As sufficiently-large flame-surrounded coal particles were pyrometrically-detected to remain at relatively low temperatures as they devolatilized, their intensity of emission in the near-infrared was neglected [42, 43]. Therefore, most of the radiation intensity contributions stemmed from luminous soot in the envelope flame. Moreover, color pyrometry of a population of soot particles in the flame, spread over a range of temperatures, tends to be biased towards the hottest soot particles. It has been shown before theoretically [43] that the effective emissivity of the soot, although in isothermal flames follows an inversely proportional dependence on the wavelength, it exhibits a graybody-like characteristic, i.e., it is nearly independent of the wavelength, if a strong linear variation in temperature exists across the soot layer. As typical fuel particle envelope flames can be expected to be non-isothermal in the radial direction [43], the reported volatile flame temperatures in this work were calculated with the gray-body assumption. Hence, the volatile flame temperatures calculated with this assumption are heavily weighted towards the highest soot temperatures in these particle envelope flames. Whether the soot particles temperatures are equal to those of the surrounding gas in the envelope flame can be debatable. Matsui et al. [44], estimated the difference between the gas and soot temperature inside the
cylinder of a diesel engine to be in the order of 1 K, because of the small size of soot particles. Because of the comparable combustion times and flame temperatures between the fuel in a diesel engine and the particles of the present experiments, it is likely that the gas and soot temperatures in the flame are also comparable herein. This assumption is also in agreement with the reports of Howard and Essenhigh [28].

High-speed cinematography was conducted through slotted side quartz windows of this furnace with or without backlight, see Fig. 1. A *NAC HotShot 512SC* Self-Contained Digital High-Speed broadband video camera was used, at speeds of 1000 or 2000 frames/s. The camera was fitted with an *Olympus-Infinity* Model K2 long-distance microscope lens to provide high-magnification images of the combustion events.

### 4.4. Experimental results

#### 4.4.1. Pyrometric Traces

Temperature profiles of single fuel particles were obtained during their entire burnout history at oxygen mole fractions of 20% to 100% O$_2$, in both N$_2$ and CO$_2$ background gases; examples are included in Fig. 3. In each case two profiles are superimposed, corresponding to particles burning in O$_2$/N$_2$ and O$_2$/CO$_2$, respectively.

(a) BITUMINOUS COAL (Pittsburgh #8, Pennsylvania, PSOC-1451)

(b) SUB-BITUMINOUS COAL (Wyodak, Wyoming, DECS-26)
Figure 3. Sample temperature-time profiles of single particles of the five fuels of this study burning under active furnace gas flow conditions (1 lpm in furnace, 1 lpm in injector) in different oxygen mole fractions (20-100% O₂) in O₂/N₂, O₂/CO₂, or O₂ atmospheres. Temperatures were deduced from three-color pyrometry, using a non-linear least square method. Fuel particle sizes were in the range of 75-90 μm, and furnace wall temperature was set to 1400K.
4.4.2. High-Speed Cinematography stills

Selected images from high-speed, high-resolution cinematography of particles of all five fuels burning at various oxygen mole fractions, in either N₂ or CO₂ atmospheres, are displayed in Fig.4.

(a) BITUMINOUS COAL (Pittsburgh #8, Pennsylvania, PSOC-1451)

<table>
<thead>
<tr>
<th>PSOC-1451: AIR</th>
<th>PSOC-1451: 27%O₂-73%CO₂</th>
<th>PSOC-1451: 27%O₂-73%N₂</th>
<th>PSOC-1451: 37%O₂-63%CO₂</th>
<th>PSOC-1451: 37%O₂-63%N₂</th>
<th>PSOC-1451: 68%O₂-32%CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2</td>
<td>6</td>
<td>12</td>
<td>20</td>
<td>75</td>
</tr>
<tr>
<td>0</td>
<td>30</td>
<td>40</td>
<td>48</td>
<td>58</td>
<td>68</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>3</td>
<td>7</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td>4</td>
<td>7</td>
<td>14</td>
<td>19</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>4</td>
<td>7</td>
<td>9</td>
<td>18</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>4</td>
<td>7</td>
<td>9</td>
<td>18</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>4</td>
<td>7</td>
<td>9</td>
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<td>0</td>
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<td>4</td>
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<td>9</td>
<td>18</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>4</td>
<td>7</td>
<td>9</td>
<td>18</td>
</tr>
</tbody>
</table>
PSOC-1451: 68%O₂-32%N₂

(b) SUB-BITUMINOUS COAL (Wyodak, Wyoming, DECS-26)

DECS-26: AIR

DECS-26: 27%O₂-73%CO₂

DECS-26: 27%O₂-73%N₂

DECS-26: 37%O₂-63%CO₂

DECS-26: 37%O₂-63%N₂

DECS-26: 68%O₂-32%CO₂
DECS-26: 68%O₂-32%N₂

(c)LIGNITE COAL (Beulah, North Dakota, DECS-11)

DECS-11: AIR

DECS-11: 27%O₂-73%CO₂

DECS-11: 27%O₂-73%N₂

DECS-11: 37%O₂-63%CO₂

DECS-11: 37%O₂-63%N₂

DECS-11: 68%O₂-32%CO₂
DECS-11: 68%O₂-32%N₂

(d)LIGNITE COAL (Wilcox, Texas, PSOC-1443)

PSOC-1443: AIR

PSOC-1443: 27%O₂-73%CO₂

PSOC-1443: 27%O₂-73%N₂

PSOC-1443: 37%O₂-63%CO₂

PSOC-1443: 37%O₂-63%N₂

PSOC-1443: 68%O₂-32%CO₂
PSOC-1443: 68%O₂-32%N₂

(e) BAGASSE BIOMASS (Brazil)

Bagasse: AIR

Bagasse: 37%O₂-63%CO₂

Bagasse: 37%O₂-63%N₂

Bagasse: 68%O₂-32%CO₂

Bagasse: 68%O₂-32%N₂
Figure 4. High-speed, high-magnification cinematography of typical combustion events of single particles of the five fuels of this study burning under active furnace gas flow conditions (1 lpm in furnace, 1 lpm in injector) in different O₂/N₂ or O₂/CO₂ atmospheres. The displayed numbers in each frame denote milliseconds, where zero does not mark the beginning of combustion, it merely represents the beginning of each depicted sequence. Nominal particle sizes were in the range of 75-90 μm, and furnace wall temperature was set to 1400K. Magnifications are not the same in all cases; for sizing purposes the diameter of the platinum wire shown in several photographs is 150μm. The camera aperture and exposure time were changed to enhance focusing and image clarity. The exposure time was either 0.5 ms (at 2000 frames/s) or 1ms (at 1000 frames/s).

4.4.3. Observations on combustion behavior based on pyrometry and cinematography

Based on pyrometric observations under active gas flow in the DTF, the bituminous coal particles consistently exhibited two-mode combustion (i.e., sequential volatile matter and char combustion) in 21 - 37% O₂ mole fractions in N₂. In cinematographic observations, the volatile flames could be identified easily for this bituminous coal since its volatiles contain tars, which pyrolyzed and formed soot, which burned with high luminosity, see Fig. 4. In some cases, the envelope flames formed a tail (wake or contrail) as the soot was swept by the relative velocity between particles and surrounding gas. Such tails sometimes could be seen to detach from the flame envelope and burn separately. Upon replacing N₂ with CO₂ in the active furnace and injector gas flow streams, no particles ignited at 20% O₂, some particles ignited at 27% O₂, whereas most particles ignited at 37% O₂. The particles that burned in 27-37%O₂ in CO₂ did so mostly in one-mode combustion (i.e., without evidence of detached volatile matter flames) and appeared dim and blurry. Such results are summarized in the schematic of Fig. 5. It should be
mentioned, however, that under quiescent flow conditions in the DTF (when the furnace gas and the injector gas flow streams were momentarily turned off) ignition of particles was evident, even at O₂ mole fractions as low as 20%; thereafter, particles burned in a subdued two-phase combustion mode [39]. Dim combustion was also inferred by Zhang et al. [13], who reported that the average intensity of coal particles burning in O₂/CO₂, with O₂ < 30%, was lower than that in air.

**Figure 5.** A summary of observed modes of combustion events (two-mode, one-mode or no event) of single particles of the four coals of this study, burning under active furnace gas flow conditions in
different O₂/N₂ or O₂/CO₂ atmospheres. Particle sizes were in the range of 75-90 μm, and furnace wall temperature was set to 1400K. Observations were made based on combined pyrometric and cinematographic techniques.

At O₂>37% in CO₂, one-mode combustion was still observed for the vast majority of cases under active gas flow in the DTF, while in N₂, both one and two modes of combustion were observed with equal frequency. Generally, the likelihood of distinct volatile matter combustion mode occurring in CO₂ (for the particle size range of this study) was much lower than in N₂. In all cases, particles burned brighter at increasing O₂ mole fractions in CO₂.

Some sub-bituminous coal particles at O₂ mole fractions ranging between 21%-48% in N₂, were consumed with distinct volatile and char combustion modes while others burned in one-mode, as summarized in Fig. 5. Above 48% O₂ in N₂, nearly-all particles burned in one mode, see Fig. 4. In CO₂ atmospheres, under active gas flow in the DTF, no particles ignited in 20% O₂, whereas only a few particles ignited at 27% O₂. With O₂ mole fractions in the range of 27%-37%, a few particles exhibited distinct volatile and char combustion behaviors; most particles burned in one-mode. Again, particle combustion in CO₂ was dim and blurry, as compared to that in N₂. At O₂>37% in CO₂, nearly-all particles burned with one-mode combustion. The volatile flames at O₂ ranging between 21-37% in N₂ were more spherical in shape than those of the bituminous coal particles and did not exhibit sooty contrails, see Fig.4b. This is probably because flames of sub-bituminous coal particles contained lower amounts of tars and particulates than those of bituminous coal and therefore formed less soot. At O₂>48%, in N₂, the two modes of combustion overlapped and the particles appeared to burn in one-mode. Fragmentation of particles was evident in some cases in either N₂ or CO₂ gases.
Combustion of Beulah lignite coal particles in various oxygen mole fractions in N\textsubscript{2} was characterized by extensive fragmentation. The fragmentation typically started upon ignition and the fragments spread in a nearly-spherical constellation, see Fig. 4. Fragmentation took place at all O\textsubscript{2} mole fractions implemented herein (20-100\%); in fact fragmentation was also observed at 10\% and 15\% O\textsubscript{2} in N\textsubscript{2}, which were explored in additional experiments. Fragmentation was also present when pre-dried coal was burned. In the very initial stages of combustion, there was occasional evidence of brief and faint burning of volatiles. The volatile flame was located at the core of the spherical constellation of burning fragments. The number of burning fragments in air was estimated by Levendis et al. [1] to be in the order of 100, and did not vary considerably with increasing O\textsubscript{2} mole fraction in N\textsubscript{2} environments. However, at increasing oxygen mole fractions, the particle fragments were brighter and burned faster. The size of the spherical constellation of fragments, did not change significantly with the increase of the oxygen mole fraction in the background gas. In CO\textsubscript{2} atmospheres, at O\textsubscript{2}<27\%, the coal particles appeared dim, indicative of slow oxidation. Some particles fragmented and the number of fragments was typically less than 10 under active gas flow. The tendency for reduced fragmentation in CO\textsubscript{2} environments was also observed by Li et al. [23], and it is likely due to the subdued devolatilization phenomena in the cooler injector jet, see Fig. 2. At very high O\textsubscript{2} levels (>68\%) in CO\textsubscript{2}, the combustion images resembled those in N\textsubscript{2}, i.e. the number of fragments increased, the particle fragments burned more luminously and the burning fragments dispersed in all directions forming again a spherical constellation, see Fig.4c. In general, besides the aforementioned initial brief volatile burning, all fragments burned in one mode under all conditions, as depicted in Fig. 5.

Most of the Wilcox lignite coal particles in air burned with occasional evidence of brief and faint initial burning of volatiles, see Fig. 4d. At O\textsubscript{2}<27\% a few particles displayed a distinct
volatile evolution and char burning behavior similar to the sub-bituminous coal. Cinematography images revealed fragmentation of burning coal particles in various oxygen mole fractions in N₂. Unlike Beulah lignite, fragmentation of the Wilcox lignite typically started prior to the onset of ignition. The number of fragments in air was estimated by Levendis et al. [1] to be about 20-30, and did not vary considerably with O₂ mole fractions in N₂. Again, the brightness and intensity of combustion drastically increased with O₂. In CO₂, at O₂<27%, the burning particles appeared dim and blurry. The number of fragmented particles prior to ignition was typically less than 10 and some particles also fragmented during combustion. When the oxygen mole fraction reached or exceeded 68% in CO₂, the number of fragments did not change significantly, but they burned very brightly, see Fig.4d. In general, besides the aforementioned initial brief volatile burning, all fragments burned in one mode under all conditions, see Fig. 5.

Pyrometric observations indicated that the bagasse particles burned in one-mode, in all of the O₂/N₂ and O₂/CO₂ atmospheres. However, cinematographic observations revealed distinct volatile-mode combustion and char-mode combustion in O₂/N₂ atmospheres. This clearly demonstrates that multiple diagnostic tools are necessary to assess the combustion behavior of fuel particles. Cinematography stills showed that in O₂/N₂ atmospheres (at least for the observed cases of air and 37% O₂ in N₂), the volatiles evolved and burned in non-sooty and spherical flames enveloping each particle. As these flames were transparent, the engulfed cellulosic particles could be seen to shrink during the volatile matter burning, as they lost mass. Upon extinction of the volatile flame, luminous burning of the char commenced. Then, the char itself also exhibited a shrinking core behavior. When the background gas was switched to CO₂, under active flow conditions in the DTF, the particles did not burn at 20%O₂. Even at 27%O₂ particles rarely burned and the few that did, burned in a single-mode. At 37% O₂, all particles burned in
one-mode combustion. At higher O\textsubscript{2} mole fractions (such as 68\%O\textsubscript{2}) in either N\textsubscript{2} or CO\textsubscript{2}, cinematographic observations revealed that particles ignited heterogeneously from one or more hot spots and burned with one mode combustion. Release of the volatile matter was evident throughout such combustion events. See Fig. 4e.

4.5. Discussion

4.5.1. Significance of combustion mode (one or two pyrometric peaks)

Combustion of solid fuel particles typically involves gas-phase (homogeneous) burning of volatile matter followed by heterogeneous combustion of chars. However, this sequential burning mode depends on combustion conditions and fuel characteristics. Howard and Essenhigh [28] studied the related phenomena and proposed a model to assess whether burning of the volatiles and chars occur sequentially (two-mode combustion) or overlapped (one-mode combustion). They postulated that for a particular set of combustion conditions and fuel properties, particles are subjected to simultaneous combustion of volatiles and chars (one-mode combustion). For char ignition and combustion to take place, oxygen needs to reach its surface. This implies that for one-mode combustion the volatiles ignite and burn at (or close to) the particle surface. Howard and Essenhigh [28] defined a critical particle size, \( d_c \), for a given set of conditions such that for the particles smaller than that size \( (d < d_c) \), the flame does not lift away from the particle, hence volatiles and chars burn simultaneously on the surface of the particle.

\[
d_c = \sqrt{\frac{12 D P ((p_{O_2})_s - (p_{O_2})_g)}{d \frac{dV}{dt} \frac{dY_{O_2}}{dt} p c Y_{O_2} R T_i}}
\]  

(1)
where $D$ ($\text{cm}^2/\text{s}$) is the binary diffusion coefficient of $\text{O}_2$ in either $\text{N}_2$ or $\text{CO}_2$ at the background gas temperature and pressure, $P$ (atm) is the total pressure of the background gas (1 atm in the work herein), $(p_{\text{O}_2})_\infty$ is the mole fraction of oxygen in the bulk gas and $(p_{\text{O}_2})_s$ is the mole fraction of oxygen on the outer surface of the flame sheet surrounding a particle. $\Delta V_v(g)$ is the volatile matter evolved from solid fuel as pyrolysis products. $V_0(g)$ is the initial volatile matter content listed in Table 1, $\rho_c$ ($\text{g/cm}^3$) is the density of the coal, $y_v$ is the mass fraction of volatile matter in the original coal, $f_v$ (moles/g) are the moles of oxygen required to burn a unit mass of volatiles, $R$ ($\text{cm}^3\text{atm} / \text{mole K}$) is the ideal gas constant, and $T_i$(K) is the ignition temperature of the fuel in a given background gas. The surface partial pressure of oxygen $(p_{\text{O}_2})_s$ in Eq. 1 depends on the prevailing oxygen concentration in the bulk gas, $(p_{\text{O}_2})_\infty$, and can be calculated based on one of two models [28]: (i) only gaseous reactants of combustion were assumed present at the outer surface of the flame sheet, and (ii) both reactants and products of gas combustion were present and in equilibrium at the outer surface of the flame sheet. Herein, model (ii) was implemented as it was deemed to be more realistic.

For each coal, the parameters of binary diffusivity, ignition temperature and fractional devolatilization rate, that appear in Eq. (1) differ depending on the $\text{N}_2$ and $\text{CO}_2$ background gases, as discussed below. They are listed in Table 2.

4.5.1.1. Binary diffusivity of oxygen, $D$

The binary diffusivity, $D$, of $\text{O}_2$ in $\text{N}_2$ is circa 30% higher than that of $\text{O}_2$ in $\text{CO}_2$ at the same gas temperature. In this work, the diffusivities were set as: $D_{\text{O}_2-\text{N}_2} = 2.778$ ($\text{cm}^2/\text{s}$) and $D_{\text{O}_2-\text{CO}_2} = 2.133$ ($\text{cm}^2/\text{s}$) at the gas temperature of 1300K, in the neighborhood of which particles appeared to auto-ignite under all conditions [39].
4.5.1.2. Particle ignition temperature, $T_i$

In this work, ignition temperatures, $T_i$, of single coal particles were obtained from the pyrometric temperature profiles, at the instant of time where their temperatures started rising drastically. This is exemplified in the coal particle combustion events shown in Fig. 6, whose initial stages are displayed with higher resolutions in the temperature and time domains than those shown in Fig. 3 or those previously reported in Ref. [1].

Figure 6. Temperature profiles of single coal particles at the time of their ignition. (a-d) bituminous coal particles (PSOC-1451) burning at various O$_2$/N$_2$ and O$_2$/CO$_2$ atmospheres. (e-h) lignite coal particles (PSOC-1443) burning at various O$_2$/N$_2$ and O$_2$/CO$_2$ atmospheres. Presumed ignition points are marked with arrows.

(a) Bituminous coal: For bituminous coal particles burning in air, observed ignition temperatures were in the vicinity of 1200 K. This is in line with the ignition temperature of 1000°C (1273 K) reported by Howard and Essenhigh [28], who burned the same coal (Pittsburgh #8), using analogous gas temperatures, heating rates and particle sizes. Since the particle ignition temperature should be less than or equal to the gas temperature at the location of ignition, this value is supported by the gas temperature measurements conducted herein with suction thermometry. The gas temperature in N$_2$-containing gases where the bituminous coal particles
were observed to ignite herein [39] was in the range of 1310-1330 K, therefore the aforementioned particle ignition temperature of ca. 1200 K at the ignition location is reasonable. Moreover, the theoretical model of Annamalai and Durbetaki [45] predicted ignition temperatures to be in the range of 1150-1200K, for either homogeneous or heterogeneous ignition of bituminous coal particles in air. As O₂ mole fractions in N₂ increased from 0.2 to 1, the ignition temperatures decreased by 100-150 K. This is again in agreement with results reported by Annamalai and Durbetaki [45, Fig.6a therein] and by Du and Annamalai [46 Fig.8 therein]. In O₂/CO₂ atmospheres, ignition temperatures of coal particles were observed to be a little higher than those in O₂/N₂. This is in agreement with the findings of Qiao et al. [47], who reported an increase of circa 20K at 21%O₂. Moreover, this result is in accord with gas temperatures at the location of ignition of bituminous particles in CO₂ environments which were in the range of 1325-1345K [39], a little higher than those in N₂.

(b) Lignite Coal: For lignite coal particles burning in air, pyrometricaly observed ignition temperatures were in the vicinity of 1050 K. Unlike bituminous coal, ignition temperatures of lignite coal particles in air have been rarely reported in the literature. Annamalai and Durbetaki [45] reported different theoretical predictions for ignition temperatures for homogeneous and heterogeneous ignition modes of lignites. They also reported predictions on the transition between the two ignition modes. Moreover, their predictions of ignition temperatures based on the homogeneous gas-phase ignition (Fig.3b of Ref. [45]) were fairly comparable to predictions of ignition temperatures based on heterogeneous ignition (Fig. 6a and 6b of Ref. [45]):

*Homogeneous ignition temperature for lignites:*
for the original particle sizes of this study (75-90 µm): 952-1000K
for the estimated fragment size of this study (30 µm): 1176 K

*Heterogeneous ignition temperature for lignites:*

for the original particle size of this study (75-90 µm): 950-970K
for the estimated fragment size of this study (30 µm): 1111 K

The temperature observed herein (1050 K) for lignite ignition in air is within the aforementioned ranges. Moreover, it is consistent with gas temperatures at the location where the lignite coal particles ignited in the furnace herein, in either N₂ or CO₂, which were in the range of 1300-1325K [39]; as such values place an upper limit on the particle ignition temperatures. For higher O₂ mole fractions in N₂ background gas of 21-100%, the ignition temperatures were decreased by 100-150 K, based on the results herein and on the predictions of Annamalai and Durbetaki [45, Fig. 6a therein] and Du and Annamalai [46, Figure 8 therein]. Others [48-51] reported similar trends. Ignition temperatures were a little higher in O₂/CO₂ atmospheres and a decreasing temperature trend with increasing O₂ was again observed.

4.5.1.3. Fractional devolatilization rates, \( \frac{d(\Delta V_v)}{V_0} \)

The amounts of volatile matter released in N₂ and CO₂ atmospheres during coal pyrolysis (\( \Delta V_v \)) have been estimated based on the mass loss in the furnace during preparation of chars, whereas the initial content of volatile matter, \( V_0 \), was taken from Table 1. Hence, for the bituminous coal, \( \frac{\Delta V_v}{V_0} = 0.71 \) in N₂ and 0.86 in CO₂, whereas for the Wilcox lignite coal \( \frac{\Delta V_v}{V_0} = 0.65 \) in N₂ and 0.87 in CO₂. Howard [28:Fig.5] also reported 0.71 for the same bituminous coal.
These values are also in accord with those reported by Duan and coworkers [52] for a Chinese bituminous coal: \( \frac{\Delta V_v}{V_0} = 0.66 \) in N\(_2\) and 0.72 in CO\(_2\). \( \frac{\Delta V_v}{V_0} \) values were assumed constant for each coal, regardless of the O\(_2\) mole fraction. Fractional devolatilization times were then estimated based on recorded ignition delay times of the coal particles, in tests conducted in this laboratory under the same flow rates (active flow condition) in the DTF [53, 39]. This step can be debatable since devolatilization happens not only before but, also, during the combustion of the volatiles; perhaps even more intensely during the latter period [28]. For instance, based on the ignition delay time observed herein, the bituminous coal fractional devolatilization rate in air was calculated to be 47(s\(^{-1}\)), whereas that calculated from Howard and Essenhigh’s results and methodology [28] was 23(s\(^{-1}\)), i.e., lower by a factor of 2. This discrepancy is likely caused by the injection jet gas temperatures experienced by the fuel particles [39] and was accounted for in a sensitivity analysis, presented below. Finally, it should be mentioned that devolatilization rates cannot be expected to be linear with time, thus the aforementioned values are average times at best.

**Table 2.** Physical and chemical properties of bituminous and lignite coals used in Eq. (1)

<table>
<thead>
<tr>
<th>Coal</th>
<th>( \rho_c ) (g/cm(^3))</th>
<th>( \gamma_v )</th>
<th>( f_v ) (moles/g)</th>
<th>( \frac{d \left( \frac{\Delta V_v}{V_0} \right)}{dt} ) in air</th>
<th>( \frac{d \left( \frac{\Delta V_v}{V_0} \right)}{dt} ) in 27%O(_2)-73%CO(_2)</th>
<th>( T_i ) (K) in 27%O(_2)-73%CO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous PSOC-1451</td>
<td>1.18</td>
<td>0.33</td>
<td>0.11</td>
<td>41</td>
<td>6</td>
<td>1240</td>
</tr>
<tr>
<td>Lignite PSOC-1443</td>
<td>1.1</td>
<td>0.45</td>
<td>0.1</td>
<td>63</td>
<td>9.65</td>
<td>1065</td>
</tr>
</tbody>
</table>

Based on the above, the calculated critical particle diameters versus oxygen mole fraction in either N\(_2\) or CO\(_2\) atmospheres are shown in Figs 7a and 7b, for the bituminous and Wilcox lignite coals, respectively. The actual particle diameters and/or fragment sizes are also shown in
Fig. 7. If the actual particle or fragment size is smaller than the critical particle diameter at a given oxygen mole fraction \( (d < d_c) \), then volatile matter and char are predicted to burn simultaneously on the particle surface. Otherwise, if \( (d > d_c) \), the volatile matter flame is expected to lift away from the particle surface and distinct volatile and char burning modes are expected to occur. Increasing the \( \text{O}_2 \) mole fraction typically increases the critical particle diameters. Moreover, at a specific oxygen mole fraction, higher critical particle sizes were calculated in \( \text{CO}_2 \), as compared to \( \text{N}_2 \) background gases. In other words, it becomes increasingly more likely for particles of a given size to burn in one-mode (simultaneous volatile and char combustion) at high \( \text{O}_2 \) mole fractions and in the presence of \( \text{CO}_2 \) instead of \( \text{N}_2 \).

Specifically, in the case of the 75-90µm bituminous coal particles burning in air and in other moderate oxygen mole fractions in \( \text{N}_2 \) background gas, combustion takes place in two distinct modes. However, at high \( \text{O}_2 \) mole fractions in \( \text{N}_2 \) and \( \text{CO}_2 \), combustion may take place simultaneously. This theoretical prediction is in line with the experimental results summarized in Fig. 5. However, while the model predicts that the critical value is reached at an \( \text{O}_2 \) mole fraction of 55% for bituminous coal particles, see Fig. 7a, experiments suggest that it was reached at an \( \text{O}_2 \) as low as 37%, see Fig. 5. The source of this small discrepancy might be due to the simplifications in the Howard and Essenhigh [28]’s model (spherical particle, Stefan flow is not accounted for, etc.), particle-to-particle variabilities in the physical and chemical properties of the coals as well as uncertainties in the involved parameters. In the case of lignite fragment sizes \( \approx 30\mu m \) [1]), the results shown in Fig. 7b indicate that the diameters of such fragments have always been well-below the critical diameters in the cases of all \( \text{O}_2 \) mole fractions in either \( \text{N}_2 \) or \( \text{CO}_2 \). Therefore, in all lignite coal cases examined, volatile matter and chars are predicted to burn
simultaneously at, or near, the particle surface. This model prediction is in line with the experimental observations herein. See Fig. 5 for lignite coals.

**Figure 7.** Critical particle diameter for one-mode (simultaneous volatile+char) burning vs. oxygen mole fractions in either O$_2$/N$_2$ or O$_2$/CO$_2$ atmospheres. Particles with sizes smaller than the critical diameter burn with one-mode simultaneous volatile and char combustion. Oxygen partial pressure at the flame front surface is modeled by assuming that both combustion reactants and products are present at their equilibrium concentrations. (a) Critical particle diameter for bituminous coal particles of this study (PSOC-1451). The actual particle size range (75-90 µm) is denoted by the two horizontal lines. (b) Critical particle diameter for the (PSOC-1443) lignite coal particles of this study. The typical fragment size of this coal (30 µm) is also shown as a line.

To assess the influence of the parameters of ignition temperature and fractional devolatilization rate, on the critical particle diameter, see Eqn. 1, sensitivity analyses were conducted. First, the aforementioned ignition temperatures of the bituminous and lignite coals, listed in Table 2, were perturbed by ±100 K (to span the ranges given in Refs. [45, 46]), and
results are shown in Fig 8. It is shown that the effect of ignition temperature on the critical particle diameter is too little to alter any of the aforesaid conclusions.

Subsequently, based on the prior discussion, a sensitivity analysis was conducted to assess the critical diameter when the fractional devolatilization rate was varied by a factor of 2. The results indicate that the effect of devolatilization rate on the critical particle diameters is important, see Fig. 9. However, this variation did not affect major conclusions of this analysis, such as the higher critical diameter calculated in CO₂ than in N₂, the mostly upward trend with increasing O₂, as well as the lack of intersection of the computed critical diameter curves with the observed lignite fragment sizes.

**Figure 8.** Sensitivity analysis to investigate the effects of ignition temperature (Tᵢ) on the critical particle diameter for one-mode burning vs. oxygen mole fractions in either O₂/N₂ or O₂/CO₂ atmospheres. Oxygen partial pressure at the flame front surface is modeled by assuming that both combustion reactants and products are present at their equilibrium concentrations. (a) For bituminous coal particles of this study (PSOC-1451), ignition temperature was spanned 200K (e.g. in the range 1100-1300K for burning in air). The actual particle size range (75-90µm) is denoted by the two horizontal lines. (b) For the (PSOC-1443) lignite coal particles of this study, ignition temperature was spanned 200K (e.g. in the range 950-1150K for burning in air). The typical fragment size of this coal (30µm) is also shown as a line.
Figure 9. Sensitivity analysis to investigate the effects of fractional devolatilization rate \( \frac{d\Delta V_p}{dt} \) on the critical particle diameter for one-mode burning vs. oxygen mole fractions in either O\(_2\)/N\(_2\) or O\(_2\)/CO\(_2\) atmospheres. Oxygen partial pressure at the flame front surface is modeled by assuming that both combustion reactants and products are present at their equilibrium concentrations. (a) For bituminous coal particles of this study (PSOC-1451), the devolatilization was spanned from 35% to 88% volatiles release in the original coal. The actual particle size range (75-90\( \mu \)m) is denoted by the two horizontal lines. (b) For the (PSOC-1443) lignite coal particles of this study, the devolatilization was spanned from 41% to 85% volatiles release in the original coal. The typical fragment size of this coal (30\( \mu \)m) is also shown as a line.

4.5.2. Effect of diluent gases (N\(_2\) and CO\(_2\)) and oxygen mole fraction on temperatures and burnout times

Temperature and burnout time data are shown in Fig. 10. The temperatures were maximum deduced temperatures in single particle combustion histories, as exemplified in Fig. 3. The particle burnout times displayed in Figs. 10 and 12 were deduced from pyrometry, based on the duration of the recorded highest-intensity signal (\( \lambda = 998 \) nm) of a particular event from its onset (particle ignition) to its termination (particle extinction), both defined when the signal exceeds its
baseline by a factor of at least one thousand, i.e., $S_{\text{signal}}/S_{\text{baseline}} > 1,000$. Burnout times recorded by cinematography (not shown) were typically a few milliseconds longer. This is because at the fringes of each signal-intensity versus time pyrometric profile (i.e., at the onset of ignition and extinction) the signals were often too weak to be reliably resolved from background noise. This was not a problem in cinematography as an observer is typically able to detect, in the recordings of the broadband camera, the particle luminosity in those domains. The discrepancy between pyrometric and cinematographic burnout times was more accentuated in O2/CO2 than in O2/N2 atmospheres, because of the faintness of the burning particles in the former environments.

Each data point represents mean values from at least 30 individual particle combustion events. Notable exceptions are the data in CO2 with O2 mole fractions $\leq 30\%$, where only very few particles ignited and burned under active flow conditions in the DTF, operated at 1400K. In those cases, data points were calculated based on the few events that were captured. Standard deviation bars (2σ) are shown on each datum point. Some fuels burned in two-modes (volatile matter and char combustion), some in one-mode and, yet some had particles that experienced either two-mode or one-mode, depending on the conditions or just on particle-to-particle physical and chemical variabilities. Separate plots were generated for two-mode and one-mode combustion temperatures.

Typically, temperatures of particles burning either with a two-mode combustion or with one-mode combustion were higher in O2/N2 than in analogous O2/CO2 environments, whereas corresponding burnout durations were briefer, see Fig. 10. The reduction of luminous particle temperatures when O2/N2 mixtures were replaced by O2/CO2 has been related to various factors and phenomena. The factor controlling the volatiles flame temperature is the volumetric heat capacity ($pc_{\rho,\text{gas}}$) of the background gas, which is higher for CO2 than for nitrogen, by a factor of
1.6. This leads to lower flame temperatures in CO₂ (and indeed to a lower tendency for soot formation from released volatiles). The factors influencing the char combustion temperature are the lower binary diffusivity of O₂ in CO₂ and, possibly, the endothermicity of CO₂ gasification reactions, as concluded by Shaddix and Molina, Molina and Shaddix and Hecht et al. [37, 38, 54]. The thermal properties of the background gases (ρ, cₚ,gas, k thermal conductivity, μ dynamic viscosity and α thermal diffusivity) influence the convective heat transfer coefficient, h. However, since the Reynolds number of these minuscule (75-90 µm) coal particles turns out to be small (Re<0.02), the resulting Nusselt number is ≈2; therefore, the large disparities of the density and heat capacity of the two gases are not expected to play a significant role in heat convection. Furthermore, heat conduction is similar in the two background gases, since the values of k do not differ much. Finally, the difference in gas radiation between O₂/CO₂ and O₂/N₂ atmospheres has a small effect on the total radiation, as the particle radiation dominates the gas radiation during combustion [55]. Substitution of N₂ with CO₂ in the background gas affects the temperatures of both the volatile matter flame and the chars considerably. In contrast, the recorded temperatures of particles burning in one-mode are less affected by the replacement of N₂ with CO₂ in the background gas. The corresponding longer burnout durations in O₂/CO₂ mixtures are related to the lower temperatures of the fuel particles in such environments.

**Bituminous Coal.** As O₂ increased, volatile flame and char temperatures increased and burnout times decreased, as also mentioned elsewhere [12], see Fig. 10a, 10b and 10j. For particles that burned in one-mode, the temperatures also increased (2100-2700K) with O₂ increasing from 50% to 100%, whereas the burn-time declined mildly, see Figs. 10c and 10j. The temperatures of these particles were comparable to those recorded for chars in two-mode combustion. For particles burning in one-mode, the temperature differences between O₂/N₂ and analogous O₂/CO₂
were narrower (<120 K) than the temperature gaps of coal chars, see Fig 10c. These lower temperature differences may be due to the likelihood of the volatiles oxidizing on or in the vicinity of the particle surface, throughout burnout, preventing the CO₂ molecules from reaching the particle surface and, consequently lessening the possibility of endothermic char gasification reactions. Burnout time differences in N₂ and CO₂ were considerable (40ms) for particles burning in two-mode, whereas they were not significant for particles exhibiting one-mode combustion (2-4ms), see Fig. 10j. The total burnout time difference decreased to a few milliseconds (5ms) and became insignificant as oxygen partial pressure increased to 80%. In summary, the background gas type had an extensive effect on the bituminous coal temperatures and burnout times when combustion occurred in two-modes, whereas it had a mild effect when combustion occurred in a single-mode.

Sub-Bituminous Coal. As oxygen increased from 20% to 100%, in either N₂ or CO₂, volatile flame and char temperatures increased drastically, see Figs 10d and e. On the other hand, burnout times decreased sharply until O₂ reached circa 50%. Thereafter, burnout times decreased mildly with increasing O₂. Similarly, for particles burning in one-mode combustion, temperatures increased dramatically (from 1700 to 3000K) as O₂ increased from 20% to 100%O₂, see Fig. 10f. The temperatures of particles burning with one-mode combustion were rather comparable to those recorded for the chars burning in two-modes. Burnout times for those particles decreased sharply (from 35ms to 20ms) as O₂ climbed from 20% to 50%, and then decreased mildly thereafter, see Fig. 10k. The temperature and burnout time differences in N₂ and CO₂ environments were in the range 200-400K and 3-30ms at various O₂ mole fractions, see Figs. 10f and 10k.
**Beulah and Wilcox Lignite.** Combined pyrometric and cinematographic results illustrated that lignite coal mostly burned with one-mode combustion at all oxygen mole fractions, in both background gases, see Figs 3 and 4. A very brief volatile flame appeared in some cases in the middle of the constellation of the fragments, typically when fragmentation occurred after ignition. Beulah and Wilcox lignite coal particles (75-90 µm) fragment to particles as small as 10µm and 30µm, respectively at all oxygen mole fractions. The small sizes of the fragments favor simultaneous volatile and char combustion, thus, one-mode temperature and burnout time were deduced for these coals. Figs 10g, 10h, 10m and 10n illustrate the maximum temperatures and burnout times, respectively, of lignite coal particles at various oxygen mole fractions in either N$_2$ or CO$_2$ environments. As oxygen mole fraction increases from 20-100%, the particles burn hotter and faster. The temperature gap between combustion in N$_2$ and CO$_2$ was generally small and was attributed to the one-mode combustion. The Wilcox lignite exhibited the smallest gaps in temperatures (>200K) and burnout times between combustion in N$_2$ and CO$_2$ background gases, at the same O$_2$, among all the fuels examined herein.
Figure 10. Maximum deduced temperatures (a-i) and recorded burnout times (j-n) for particles (75-90µm) from Pittsburgh # 8 bituminous coal (PSOC-1451), Wyodak sub-bituminous coal (DECS-26), Beulah lignite coal (DECS-11), Wilcox lignite coal (PSOC-1443) and sugarcane bagasse (biomass) burning in O$_2$/N$_2$ and O$_2$/CO$_2$ at T$_{\text{furnace}}$=1400K. Solid symbols denote that fuel particles burned with two-mode combustion, whereas open symbols denote that fuel particles burned with one-mode combustion.

Bagasse. Although bagasse particles burned with two distinct modes in O$_2$/N$_2$ (air and 37% O$_2$), the volatile flames could not be detected by the pyrometer, due to their non-sooty low-luminosity nature. Therefore, only char temperatures and burnout times are presented in this section. Results in Fig. 10i show that as oxygen mole fraction increased from 20% to 100%, char temperatures increased from 1900 to 2900K in N$_2$ and from 1550 to 2900K in CO$_2$. Corresponding char burnout times decreased from 17 to 8 ms, and from 35 to 13 ms, see Fig. 10l. The maximum observed char particle temperature gaps between N$_2$ and CO$_2$ were circa 500K at 27% O$_2$. Thereafter, the temperature gaps decreased with increasing O$_2$. Consequently, the corresponding differences in the char burnout times in N$_2$ and CO$_2$ atmospheres were 20 ms in 27% O$_2$ and they diminished at oxygen mole fractions higher than 37%.
4.5.3. Effects of fuel type on temperature and burnout times

Maximum deduced temperatures and recorded burnout times, averaged over many particle combustion events, for the five fuels of this investigation are shown in Figs. 11 and 12, respectively. All modes of combustion, as experienced by various fuel particles at all explored conditions are superimposed, i.e., two-mode separate homogeneous and heterogeneous combustion as well as one-mode, presumably simultaneous combustion. The two most prominent trends illustrated in Fig. 11 are the following, (a) large increase of temperature with increasing oxygen mole fractions and, (b) lower temperatures encountered in CO2 background gas, relative to those in N2. Corresponding trends in burnout times are illustrated in Fig. 12, where (a) large decreases with increasing oxygen mole fraction are noticeable, becoming milder at high O2 and, (b) longer burnout times are encountered in CO2 background gas, relative to those in N2.

Several additional trends are evident in Figs 11 and 12. Volatile combustion is the hottest and fastest, typically followed by one-mode combustion and then by heterogeneous char combustion. Higher coal ranks experienced a tendency to burn in two-modes, i.e., sequential volatile and char combustion. In such cases, it appears that the high intensity and the considerable duration of the volatile flames induced the evolution and consumption of most of the volatile matter content in the particles and, perhaps, left only small amounts of volatiles to burn concurrently with the char. This statement is based on the cinematographic evidences herein and on the findings of Howard and Essenhigh [28]. As a result of this behavior, the temperature difference between volatile matter flames and chars increased with the increase of coal rank. To the contrary, in the case of lignites, the volatile and char temperatures were not distinguishable and the volatile and char presumably burned simultaneously on or near the particle surface.
Moreover, low rank coal particles typically burned hotter than high rank coals in either O₂/N₂ or O₂/CO₂ atmospheres. For instance, regarding the particles which burned with one-mode combustion, Beulah lignite particles burned hotter than particles of other fuels in either O₂/N₂ or O₂/CO₂ atmospheres, see Fig. 11. This phenomenon is likely attributed to enhanced oxygen diffusion to the solid matrix because of the fragmentation of such coals, and because of enhanced chemical kinetics caused by the catalytic effects of the higher mineral matter contents of these coals.

Figure 11. Superimposed comparative homogeneous (volatile matter flames), heterogeneous (char) and one-mode maximum combustion temperatures for different fuel particles (75-90μm) burning at T_{\text{furnace}}=1400K. Left column: in N₂, and Right column: in CO₂ background gases. The volatile burnout times in Fig. 12 were determined from the span of the first peak of a two-peak signal. Volatile matter burnout times of bituminous coal particles were comparable to
those of sub-bituminous coal in O₂/N₂ atmosphere, whereas they were somewhat shorter in CO₂ (specifically for O₂<60%), see Fig. 12, lines a and b. Char burnout times of bituminous coal particles were longer than those of sub-bituminous coal and bagasse particles in either O₂/N₂ or O₂/CO₂ atmospheres, see Fig.12 lines c, d and e. In contrast to contrast the disparate char burnout times (Fig. 12 lines c-e), the burnout times of particles of different coals that were consumed in one-mode combustion were rather comparable (Fig. 12 lines f-i); Wilcox lignite coal particles burned a little slower than the rest, while bituminous coal particles burned a little faster, see Fig. 12 line f.

Bagasse char burnout times in either O₂/N₂ or O₂/CO₂ were exceptionally short (see Fig. 12 line e) due to their low fixed carbon content (7.7%), see Table 1. Based on photographic observations, as the low-luminosity nearly-transparent volatile matter flames of bagasse prevented pyrometric observations, such flames lasted longer than those of other fuels (bituminous and sub-bituminous). For instance, cinematographically-recorded times (not shown in Fig. 12) were 38 ms at 20% O₂ and 20 ms at 37% O₂, both in N₂. Likely explanations for such relatively long flame durations are based on (a) the large content of volatile matter (83.9%) of this fuel, see Table 1, and (b) on their typically larger particle size, as shown in Fig. 4. Bagasse particles often appear on cinematographic stills to be larger than the nominal 75-90 µm sieve size possibly because they are needle-like and, thus, make it through the sieves if only their diameters fit the mesh sizes. Such needle-like particles as they enter the furnace soften/melt and reshape themselves into spheroid particles (see Fig.4 of Ref. [1]) of dimensions larger than the nominal sieve size.
Figure 12. Superimposed comparative homogeneous (volatile matter flames), heterogeneous (char) and one-mode combustion times for different fuel particles (75-90µm) burning at $T_{\text{furnace}}=1400\text{K}$. Left column: in $\text{N}_2$, and Right column: in $\text{CO}_2$ background gases.

4.5.4. Identification of $\text{O}_2/\text{CO}_2$ compositions where fuel particles burned similarly to air

Different such $\text{O}_2/\text{CO}_2$ compositions in oxy-fuel combustion have been reported in the literature [2, 3]; in some cases they were based on wet flue-gas recycling, whereas in other cases on dry flue-gas recycling. In the latter case, higher oxygen mole fractions are required for matching temperatures. Searching for $\text{O}_2/\text{CO}_2$ atmospheres that can simulate combustion in air, one should keep in mind that there are several parameters which need to be taken into consideration such as temperature, burnout time, combustion mode, radiation intensity and
ignition delay. Focusing on just one parameter such as temperature is not sufficient for a comprehensive comparison. As ignition delay is part of an ongoing investigation in this laboratory [39, 53], a preliminary comparison may be based herein on temperatures and burnout times. Moreover, based on the results herein, there are different temperatures to be matched (volatile flame temperatures, char temperatures or one-mode temperatures). On this basis, the amounts of oxygen in carbon dioxide needed for each coal particle to burn similarly to air are shown in Table 3, where the given ranges are sufficiently wide to match not only the temperatures but, also, the observed burnout times for each coal. Higher rank coals show wider ranges in Table 3 and they need more oxygen in a CO\textsubscript{2} environment to behave as they do in air (21\% O\textsubscript{2}). On the other hand, the fuels which have more oxygen in their structure (lower rank coals and, particularly, bagasse) need less extra oxygen to bring their burning behavior in O\textsubscript{2}/CO\textsubscript{2} on par with that in air. The oxygen concentrations in CO\textsubscript{2} that yield the same combustion times as in air may be compared with values obtained from pilot plants, based on matching heat transfer rates [17, 19].

**Table 3.** O\textsubscript{2}/CO\textsubscript{2} compositions for different fuels to simulate combustion in air, based on volatile, char and one mode combustion temperatures and burnout times.

Dried flue gas recirculation was simulated.

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>O\textsubscript{2} mole fraction in CO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous (PSOC-1451)</td>
<td>32-40%</td>
</tr>
<tr>
<td>Sub-bituminous (DECS-26)</td>
<td>33-39%</td>
</tr>
<tr>
<td>Wilcox lignite (PSOC-1443)</td>
<td>31-36%</td>
</tr>
<tr>
<td>Beulah lignite (DECS-11)</td>
<td>30-32%</td>
</tr>
<tr>
<td>Bagasse char (sugarcane biomass)</td>
<td>28-30%</td>
</tr>
</tbody>
</table>
4.6. Conclusions

In this study, pulverized fuel particles from three different coal ranks and a biomass were burned in a drop-tube furnace under active gas flow composed of either O$_2$/N$_2$ or O$_2$/CO$_2$. The fuel particles were in the size cut of 75-90 µm. The furnace wall temperature was set to 1400 K, whereas the furnace gas temperature in either O$_2$/N$_2$ or O$_2$/CO$_2$ in the section where particle combustion took place was lower by ~50 K. The goal was to assess the combustion behavior of single fuel particles with combined pyrometric and cinematographic diagnostic tools, when N$_2$ was replaced by CO$_2$, with O$_2$ mole fractions ranging from 20% to 100%. Entire temperature-burnout time histories of individual fuel particles were recorded and quantitative results have been presented. The most important conclusions are as follows:

i. Fuel particles were observed to burn in different modes, such as two-mode, i.e., gas-phase or homogeneous mode (volatile matter envelope flames) followed by heterogeneous mode (char surface oxidation), or in one-mode combustion (simultaneous volatile and char), depending on their rank and the furnace conditions. Strong tendencies were observed for all fuels to burn in one-mode when N$_2$ was replaced by CO$_2$, and when O$_2$ mole fraction increased in both environments. Moreover, increasing the coal rank, from lignite to bituminous, enhanced the tendency of coal particles to exhibit a two-mode combustion behavior. The calculated critical particle size, $d_c$, under which simultaneous combustion is thought to take place, typically increased with increasing oxygen mole fraction in the gas, and it also increased when N$_2$ was replaced by CO$_2$.

ii. Temperatures and burnout times of particles were affected by the combustion mode. For each coal, the particle temperature and burnout time when one-mode combustion was experienced were usually between volatile and char (two-mode) temperatures and
burnout times of similar particles burning under the same conditions (O\textsubscript{2} mole fraction and diluents gas).

iii. Particle luminosity, fragmentation and deduced temperatures were higher in O\textsubscript{2}/N\textsubscript{2} than in O\textsubscript{2}/CO\textsubscript{2} atmospheres, and corresponding burnout times were shorter, at the same O\textsubscript{2} mole fractions. Particle luminosity and temperatures increased with increasing O\textsubscript{2} mole fractions in both N\textsubscript{2} and in CO\textsubscript{2} background gases, and corresponding burnout times decreased with increasing O\textsubscript{2} mole fractions. Bituminous coal particles swelled, whereas sub-bituminous coal particles exhibited limited fragmentation prior to and during the early stages of combustion. Lignite coal particles fragmented extensively and burned in one-mode regardless of the O\textsubscript{2} mole fraction and the background gas. The timing of fragmentation (prior or after ignition) and the number of fragments depended on the type of the lignite and on the particle shape.

iv. Higher rank coals required extra oxygen in CO\textsubscript{2} to match their temperature-time behavior in air. Sugarcane bagasse char needed the least amount of extra gas-phase oxygen in CO\textsubscript{2} to match its temperature-time behavior in air. In other words, the fuels which have more fuel-bound oxygen (i.e., lower rank coals and bagasse) required the least amount of gas-phase oxygen in CO\textsubscript{2} to match their temperature-time behavior in air.

4.7. References


CHAPTER 5

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5. Combustion of Single Biomass Particles in Air and in Oxy-Fuel Conditions

Abstract

The combustion behaviors of four different pulverized biomasses were evaluated in the laboratory. Single particles of sugar cane bagasse, pine sawdust, torrefied pine sawdust and olive residue were burned in a drop-tube furnace, set at 1400 K, in both air and O$_2$/CO$_2$ atmospheres containing 21, 30, 35, and 50% oxygen mole fractions. High-speed and high-resolution images of single particles were recorded cinematographically and temperature-time histories were obtained pyrometrically. Combustion of these particles took place in two phases. Initially, volatiles evolved and burned in spherical envelope flames of low luminosity; then, upon extinction of these flames, char residues ignited and burned in brief periods of time. This behavior was shared by all four biomasses of this study, and only small differences among them were evident based on their origin, type and pre-treatment. Volatile flames of biomass particles were much less sooty than those of previously burned coal particles of analogous size and char combustion durations were briefer. Replacing the background N$_2$ gas with CO$_2$, i.e., changing from air to an oxy-fuel atmosphere, at 21% O$_2$ impaired the intensity of combustion; reduced the combustion temperatures and lengthened the burnout times of the biomass particles. Increasing the oxygen mole fraction in CO$_2$ to 28-35% restored the combustion intensity of the single biomass particles to that in air.

5.1. Introduction

Biomass has higher volatile matter content than coal, but it has less carbon, more oxygen and a lower energy content (heating value). The use of biomass in existing pulverized coal power
plants requires only minor modifications as compared to the construction of new biomass-specific fired power plants, making the co-firing of biomass with coal an easier and less costly way for generating power. Co-firing is becoming more common in coal power plants because replacing part of the coal with biomass results in lower pollutant and greenhouse gas emissions, as compared to firing neat coal [1, 2]. Co-firing biomass and coal reduces the emissions of SO₂, NOₓ and CO₂. Altogether elimination of such emissions may be achieved in future power plants (termed zero emission power plants) by implementing carbon dioxide capture and storage (CCS) techniques. However, co-firing coal with biomass reduces the power output of a power-plant in proportion to the amount of the latter fuel [3, 4, 5].

Oxy-fuel combustion is a promising technology for facilitating CCS. It burns fuel in a mixture of oxygen and recycled flue gases (mainly CO₂) instead of air in conventional combustion. The exhaust flue gases consist mainly of CO₂, approx. 95% on a dry volume basis, and small amounts of excess oxygen, nitrogen and, to a lesser extent, pollutants, such as nitrogen oxides (NOₓ) and sulfur oxides (SOₓ) (approx. 0.1–0.2% dry volume basis) [6]. The combination of oxy-fuel combustion, as a CCS technology, with biomass [2] could effectively provide a method which would not only avoid further CO₂ emissions but, perhaps even help reduce the atmospheric CO₂. Simpson et al. [7] compared the efficiency of oxy-fuel combustion and post-combustion carbon dioxide separation cycles by thermodynamic analysis. They concluded that the air separation efficiency in oxy-fuel technology must increase sufficiently to offset the additional cost and inefficiency of requiring a CO₂ purification unit on the back end. They proposed that oxy-fuel combustion may be more attractive for systems operating with oxygenated fuels such as biomass. For such systems, the development of near-stoichiometric combustors would not need expensive CO₂ purification units. Moreover, a recent investigation
revealed that biomass/coal blend combustion may be a method for controlling the excess heat generated from oxy-combustion of coal, a proposed “clean” coal technology. They utilized a TGA-DSC technique at 1173 K to burn blends of a lignite coal and two biomasses, at high oxygen partial pressures. They reported that the heat flux from the combustion of lignite increased dramatically when the oxidizing medium was altered from dry air to neat oxygen. However, in the case of co-firing lignite with biomass under neat oxygen, the excess heat flux arising from the combustion of lignite was reduced and the temperature of the combustion chamber was thus controlled. Based on their results, they suggested that co-combustion of coal/biomass blends in enriched oxygen environments may be an alternative method to CO$_2$ recycling in future oxy-fuel combustion systems.

All biomasses are composed of three main components: cellulose, hemicellulose and lignin. For instance, the sugar-cane bagasse sample burned herein contained 41.3% cellulose, 34.3% hemicelluloses and 13.8% lignin. Whereas cellulose and hemicellulose are macromolecules constructed from different sugars, lignin is an aromatic polymer synthesized from phenylpropanoid precursors [9]. Hemicellulose is easily degraded, and its pyrolysis takes place at temperatures in the range of 493–588 K. The pyrolysis of cellulose occurs in the 588–673 K range, whereas that of lignin covers a wider temperature range (423–1176 K) [10].

Torrefaction is a useful pre-treatment for the biomass materials as they are sometimes difficult to fluidize and introduce into furnaces because of their fibrous shapes [11]. The management and milling of torrefied biomass is easier than that of the parent biomass. That is why the torrefaction process is being introduced to industrial practices [12, 13]. This process consists of heating the biomass in nitrogen, or in a low oxygen-containing atmosphere, to temperatures up to 573 K. In this process, the biomass dries, and as the temperature increases,
certain changes take place in the molecular structure. Light hydrocarbon molecules are released through the decomposition of the reactive hemicellulose fraction [14]. Torrefied fuels are easier to manage, and they contain more fragile particles as well as a higher energy density than the parent biomass particles [15, 16]. During the torrefaction process, the biomass loses typically 30% of its mass, but only 10% of its energy content [17]. The resulting higher energy density of the torrefied fuel reduces the transportation costs.

Biomass pyrolysis has been investigated in numerous studies. Results are highlighted in several reviews, including those in Refs. [3, 18, 19, 20, 21, 22]. The pyrolytic products are H₂, H₂O, CO, CO₂, CH₄, other light hydrocarbons, tar, ash and char. At temperatures below 773 K, biomass fuels decompose into primary volatiles. At these temperatures, tars are produced by depolymerisation reactions while pyrolytic water is produced by dehydration reactions. The main gaseous products of pyrolysis are CO₂ and CO. At temperatures above 773 K, the primary volatiles are subject to a secondary pyrolysis, during which tars are converted into a variety of gaseous species, especially CO, light hydrocarbons, hydrogen and CO₂. At high heating rates, biomass decomposes expediently generating mostly gas, vapors and char [23]. The char that remains upon termination of the pyrolysis reactions is enriched in carbon [24].

Implementation of optical pyrometry and high speed cinematography for the study of ignition and combustion of single coal particles and streams of coal particles has been well documented [25, 26, 27, 28, 29, 30, 31, 32, 33]. However, there is a scarcity of analogous studies on biomass particle ignition and combustion characteristics. On the other hand, Wornat et al. [34] studied the combustion rates of single particles of two biomass chars (southern pine and switch grass), with nominal sizes in the range of 75-106 µm, in a laminar flow reactor with 6% and 12% O₂ mole fraction (balance N₂) at 1600 K. In situ measurements using a two-color
optical pyrometer and a video camera revealed that biomass char particles burned over a wider temperature range (1500-1950K, $\Delta T \approx 450$ K) than high volatile bituminous and lignite coal particles (1800-1950K, i.e., $\Delta T \approx 150$ K versus 1900-2000 K, i.e., $\Delta T \approx 100$ K, respectively). Austin et al. [35] conducted an experimental study in a drop-tube furnace, burning 300-1500 µm corncob particles in air using a video camera (50-100 frames per second) and an infrared phototransistor. They determined that the burning times of the volatiles and the ignition delay times increased with the increase of the initial particle density and diameter. Meesri and Moghtaderi [36] burned pine sawdust particles at drop-tube furnace temperatures of 1473K in air and reported particle temperatures circa 1700K. They also reported that the char oxidation reactions occurred in Regime II, where chemical reactions and pore diffusion happen concurrently. Arias et al. [37] studied the ignition and combustion characteristics of coal/biomass blends under oxy-fuel conditions. They burned a bituminous coal and bituminous coal/eucalyptus biomass blends (90%-10% or 80%-20%, by weight) Their experiments were performed in an electrically-heated entrained flow reactor (EFR) set to 1273 K. Oxy-fuel combustion of pulverized fuels (75-150 µm) occurred with 21%, 30% and 35% $O_2$ mole fraction in $CO_2$, and was compared with results obtained in air. When coal was blended with the biomass, its ignition temperature in air was reduced. However, this effect was less pronounced in the case of oxy-fuel combustion, regardless of $O_2$ concentration. The effect of blending biomass and coal on burnout effectiveness was negligible. Riaza et al. [2] observed similar results. Borrego et al. [38] obtained chars from different biomasses by pyrolysis in air and in oxy-fuel environments, and reported no significant differences between the char characteristics, i.e., pore volume, morphology, surface area and reactivity.
In addition to the above studies, some other notable investigations reported on experiments and numerical modeling of single-particle biomass combustion [39, 40, 41, 42]; however, the number of experimental works on this topic is very limited [43]. Additional studies are warranted to document the entire combustion behavior of biomass fuels, especially the phase of the volatile matter combustion. Such studies may be instrumental in assessing the radiating behavior of biomass particles in furnaces. In particular, little (if anything) has been reported on the experimental combustion behavior of individual biomass particles in oxy-combustion conditions, and this is of special interest to co-firing coal and biomass in future oxy-fuel power plants. The present work reports on systematic \textit{in situ} combustion study of different biomasses (residual or torrefied) in a laboratory-scale drop-tube furnace, under both conventional (air) and oxy-fuel conditions by means of optical pyrometry and high-speed back-light cinematography. Comparisons with the combustion characteristics of coal particles studied in previous work in this laboratory are made.

5.2. Bio-Fuel Characteristics and Experimental Methods

5.2.1. Biomass samples

Four different residue biomasses were studied, olive residue (OR), which are residues from the olive oil production industry, pine sawdust (PI), torrefied pine sawdust (TOPI), and sugarcane bagasse (SCB), which is a residue of bio-ethanol and sugar production. Olive residue is the part of the olive that remains after the olive oil has been extracted. Nowadays olive residue biomass is used as a low cost renewable fuel for domestic and industrial heating. The olive residue sample used in this work was supplied by ELCOGAS, S.A., which is an IGCC power station located in Puertollano (Ciudad Real, Spain), that processes a 50:50 blend (based on weight) of coal and petcoke, and occasionally also includes biomass in the fuel blend. The pine
sawdust sample was obtained from a pellets industry, Pellets Asturias, S.L., situated in Tineo (Asturias, Spain), which has a yearly production of 30,000 tons of pellets. The torrefaction of pine sawdust was carried out at INCAR-CSIC. The torrefaction treatment conditions were selected according to the results obtained in previous studies [15]. Briefly, the torrefaction of pine sawdust was performed using a horizontal quartz reactor, where 10–15 g of biomass was heated at a rate of 10 K min\(^{-1}\) under a nitrogen flow rate of 50 mL min\(^{-1}\) up to 513 K. The samples were kept at the final temperature for 1 hour. The mass loss from the sample was measured and then the sample was sieved to 75-150 µm. Sugar cane bagasse was collected directly from a mill located in Brazil – São Paulo State. The bagasse was washed, dried at 90°C for 24 hours, chopped in a household blender and sieved. All biomass samples were less than a year old and were kept in closed glass bottles in the laboratory under standard temperature and pressure conditions.

Photographs and scanning electronic microscope images of the different biomasses samples are presented in Fig. 1. All of the samples were ground and sieved to 75-150 µm. The proximate and ultimate analyses and gross calorific values of the biomasses are given in Table 1.
Figure 1. Physical appearance of the biomasses residue; (a) original biomasses, as received, (b) ground and sieved, (c) SEM micrographs detailing individual particles.

Table 1. Biomass type, origin and chemical composition

<table>
<thead>
<tr>
<th>Sample</th>
<th>Origin</th>
<th>Proximate Analysis (wt%, db)</th>
<th>Ultimate Analysis (wt%, daf)</th>
<th>HHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ash</td>
<td>V.M.</td>
<td>F.C.*</td>
</tr>
<tr>
<td>OR</td>
<td>Olive residue</td>
<td>7.6</td>
<td>71.9</td>
<td>20.5</td>
</tr>
<tr>
<td>SCB</td>
<td>Sugarcane bagasse</td>
<td>4.2</td>
<td>87.8</td>
<td>8.0</td>
</tr>
<tr>
<td>PI</td>
<td>Pine sawdust</td>
<td>3.8</td>
<td>79.8</td>
<td>16.4</td>
</tr>
<tr>
<td>TOPI</td>
<td>Torrefied pine sawdust</td>
<td>4.2</td>
<td>75.5</td>
<td>20.3</td>
</tr>
</tbody>
</table>

* determined by difference

5.2.2. Experimental Approach

5.2.2.1. Drop-tube furnace (DTF)

An electrically-heated laminar-flow drop-tube furnace was used for the combustion experiments. The furnace (an ATS unit) was fitted with an alumina tube (Coors) with an inner diameter of 7 cm. It was heated with molybdenum disilicide heating elements, defining a radiation zone of 25 cm in length. The furnace was fitted at the top with a water-cooled injector.
(Fig. 2a). Details of the design of the furnace injector are provided elsewhere [30, 44]. To introduce single biomass particles into the furnace injector, the following technique was used. A few particles were placed inside the tip of a beveled syringe needle. The needle was inserted into a port at the top of the injector, which was rotated half a revolution back and forth and then gently tapped. Single particles could thus be dropped into the furnace injector. Upon exiting the injector, the particles reacted with the preheated furnace gases. The furnace wall temperatures \(T_i\) were continuously monitored by type-S thermocouples embedded in the wall. Particle heating rates were very high, calculated to be in the order of \(10^4\) K s\(^{-1}\). Optical access to the radiation zone of the furnace was achieved through three observation ports: one at the top (Pyrometer) and two orthogonally situated at the sides of the furnace. The pyrometer and the high speed cinematography camera were used as experimental devices to study the burning of single biomass particles.

5.2.2.2. Optical pyrometer

Pyrometric observations of burning single particles were conducted from the top of the furnace injector, viewing downward along the central axis of the furnace is typically a particle’s path-line. Thus, complete luminous burnout histories of single biomass particle - from ignition to extinction - were monitored. An optical fiber made up of a high- transmittance (> 99.5%) fused silica core and doped fused silica cladding with an \(f\)-number of 2.2, transmitted light from the furnace to the pyrometer assembly. The pyrometer used two dichroic edge filters as spectrum splitters to direct the light to the three interference filters (Fig.2b). These filters had effective wavelengths of 0.640, 0.810 and 0.998 μm with bandwidths (FWHM) of 70 nm. In conjunction with these interference filters, silicon diode detectors were employed to maximize the signal sensitivity. They also possessed good stability and linearity. Details of the pyrometer optics and
electronics were supplied by Levendis et al. [28, 30]. The voltage signals generated by the three detectors were amplified and then processed by a microcomputer using LabView software. The temperature was deduced from the three output voltage signals of the pyrometer using a non-linear least square method, based on Planck’s radiation law. Details of this method were supplied by Khatami and Levendis [44].

5.2.2.3. High-speed camera

High-speed cinematography was conducted through the slotted side quartz windows of the drop-tube furnace against backlight (Fig. 2a). A NAC HotShot 512SC self-contained digital high-speed video camera was used, at speeds of 1000 or 2000 frames/s. The camera was fitted with an Infinity model K2 long-distance microscope lens to provide high-magnification images of the combustion events (Fig.2c).

5.2.3. Gas temperatures and Furnace Gas Compositions

Combustion experiments of biomass particles were conducted under a quiescent gas condition (i.e., no gas flow). Quiescent gas condition was created by turning off the gas flows 10 seconds prior to the particle injection. The design of this experiment has been documented by Khatami et al. [33]. A slender bare thermocouple (Omega type K) was used to measure the axial profile of the centerline gas temperature. The measured temperatures with this method were corrected for radiation effects as outlined by Khatami et al. [33]; results are illustrated in Fig.3. Under the quiescent gas condition (no flow), the gas temperature profiles were similar in either N₂ or CO₂ environments. Both temperatures increased along the centerline of the furnace and stabilized at an estimated 1340 K. The furnace wall set-point temperature (T_w) was 1400 K, as monitored by type-S thermocouples embedded in the wall. The gas compositions in the furnace
included air as well as mixtures of oxygen (mole fractions of 21% O₂, 30% O₂, 35% O₂ and 50% O₂) in carbon dioxide to simulate oxy-combustion conditions. In this manuscript all gas compositions are given on a mole fraction basis, which is equivalent to a volume fraction basis, as percentages (%).

**Figure 2.** Schematic of the experimental setup and diagnostic facilities. (a) Laminar-flow, electrically-heated drop-tube furnace (DTF), (b) Three-color optical pyrometer, (c) High speed camera (NAC) fitted with a long-range microscope lens (Infinity K2).
Figure 3. The centerline furnace gas temperature under quiescent conditions (no gas flow)[47].

5.3. Results and Discussion

5.3.1. Cinematographic observations

Six snapshot photographic sequences for each biomass sample at different gas atmospheres during burnout history of the particle are shown in Fig. 4. The particles ignited very close to the injector tip at the top of the DTF, immediately upon entering the radiation zone. Upon ignition, the flames surrounding individual particles grew bigger and increasingly luminous. For all biomass fuels at all gas compositions, the envelope flames had strikingly spherical shapes with fairly uniform luminosity. Some other similar burning characteristics were also observed for all the biomasses. The similarities included the sequential particle devolatilization with ignition and burning of the volatiles around the particle, followed by the ignition, combustion and extinction of the char residues.

a) Sugar cane bagasse
Bagasse – AIR
c) Pine sawdust
PI - Air

OR - Oxy 30%

OR - Oxy 35%

OR - Oxy 50%

PI - Oxy 21%
d) Torrefied pine sawdust

TOPI - Air

TOPI - Oxy 21%

TOPI - Oxy 30%
Figure 4. High-speed, high magnification cinematography images of single particles of biomass residues in different atmospheres. Displayed numbers under each image represent frame times of combustion in milliseconds. Biomass samples are: a) sugarcane bagasse (SCB), b) olive residue (OR), c) pine sawdust (PI), and d) torrefied pine sawdust (TOPI).

The ignition of particles was determined visually as the onset of luminous combustion. However, the determination of the precise initial instant of ignition of the volatile matter proved to be difficult for several reasons. Firstly, as Grotkjaer et al. [45] have already pointed out, the ignition temperatures of biomass are fairly low and lie in the range of 500-600 K in air. In this study, the volatiles ignition took place at temperatures much lower than the furnace wall temperature (1400 K) and could not be categorically discerned by optical techniques. Secondly, the volatiles envelope flames had low luminosities and typically exhibited low contrast with the background furnace surfaces.
5.3.2. Pyrometric Signals

Figure 5 shows sample radiation intensity signals, corresponding to the 0.640, 0.810 and 0.998 μm pyrometric wavelengths, obtained from single particles of each type of biomass burning in air. As can be seen in this figure, the signals of the PI, TOPI and SCB particles exhibit two different zones: the first peak corresponds to volatiles combustion in envelope flames and the second peak corresponds to subsequent char combustion. The first peak (corresponding to volatiles combustion) of OR signals is much weaker than that of other biomass samples.

![Graphs showing pyrometric signals for different biomass types](image)

**Figure 5.** Three-color pyrometry– generated signals from single particles of biomass residues burning in air. Biomass samples are: pine sawdust (PI), torrefied pine sawdust (TOPI), sugarcane bagasse (SCB), and olive residue (OR).

5.3.3. Combustion temperatures and burnout times

To facilitate a quantitative comparison between the different biomass fuels burning in the diverse atmospheres of this study, burnout times of the volatiles and burnout times of chars were directly obtained from both pyrometric and cinematographic observations, whereas char combustion temperatures were deduced from pyrometric data. The particle burnout times, displayed in Figs. 6 and 7, were deduced from pyrometric signals for volatile matter and char
combustion phases, based on the duration of the recorded highest-intensity signal ($\lambda = 0.998 \mu m$) of a particular event from its onset (particle ignition) to its termination (particle extinction), both defined when the signal exceeded its baseline by a factor of at least one thousand, i.e., $S_{signal}/S_{baseline} > 1,000$. Each data point represents mean values from a minimum of 15 individual particle combustion events. Standard deviation bars (2σ) are shown on each datum point. Volatile burnout times recorded by cinematography (e.g., see Fig.4) were typically shorter (by 10%) than the pyrometric volatile burnout times (Fig. 6). The discrepancy between pyrometric and cinematographic volatile burnout times was attributed to the fact that low-luminosity, nearly-transparent flames are hard to identify visually in photographic records (visible bandwidth is 0.4-0.7 µm), whereas the pyrometer is able to record radiation emanating from non-sooty flames at the near-infrared wavelengths of 0.81 µm and 0.998 µm. In the case of the olive residue biomass (OR) which have lower volatile matter content than the other biomasses, the duration of the volatile matter combustion phase could not be reliably assessed because even the pyrometric signals were too weak. However, the volatiles combustion peaks were clearly distinguishable in the cases of SCB, PI and TOPI biomasses (see Fig. 5).

The volatile matter flame temperature deduction method is currently under development in this laboratory for such lowly-sooty flames, for which the gray-body emissivity assumption [44] may not be valid. Thus, the temperatures of the volatile matter flames are not reported herein. The presented char temperatures in Fig. 8 are peak temperatures recorded in individual particle burnout histories, averaged over at least 15 single particle cases. Char temperatures were deduced by the method of Khatami and Levendis [44].
**Figure 6.** Average burnout times for the volatiles of three of the biomass fuels of this work (sugarcane bagasse (SCB), pine sawdust (PI) and torrefied pine sawdust (TOPI)) burning in air and in different oxy-fuel atmospheres.

**Figure 7.** Average burnout times for the chars of all the biomass fuels of this work (sugarcane bagasse (SCB), pine sawdust (PI), torrefied pine sawdust (TOPI and olive residue (OR)) burning in air and in different oxy-fuel atmospheres.
Figure 8. Average deduced temperatures for the burning chars of all the biomass fuels of this work (pinesawdust (PI), torrefied pine sawdust (TOPI), sugarcane bagasse (SCB), and olive residue (OR)) burning in air and in different oxy-fuel atmospheres.

5.3.4. Effect of atmospheric composition (replacement of N$_2$ by CO$_2$) and O$_2$ mole fraction

5.3.4.1. Combustion Behavior

The weakest particle combustion intensities were obtained in the 21%O$_2$-79%CO$_2$ atmosphere for all biomass samples. The weaker particle combustion intensities in 21%O$_2$-79%CO$_2$ atmosphere than in air are due to the lower particle temperatures, which resulted from the lower diffusivity of oxygen in CO$_2$ than in N$_2$ [46, 47]. It has also been determined that the higher volumetric heat capacity of CO$_2$ (than N$_2$) contributes to the lower particle temperatures [47].

At 21% O$_2$, both in the N$_2$ and CO$_2$ environments, the ignition and combustion of the volatiles and the ignition of the char residues occurred sequentially in a particle’s time-history profile (Fig. 4). When the combustion of the volatiles was completed, the flame extinguished and, subsequently, char ignition took place. Some differences were observed in the time periods
between volatile extinction and char ignition in air and in the 21%O_2/79%CO_2 atmosphere; the former was in the neighborhood of 2 ms, whereas the latter was much lengthier, at 5-8 ms.

At higher oxygen mole fractions (>30%) in CO_2, the following behaviors were observed: (i) ignition of the volatiles started earlier, i.e., the ignition delay period was briefer; (ii) the volatile flames were less bright (e.g., see Fig. 4: bagasse at 35% and 50% O_2 mole fractions), most likely because under such conditions soot oxidation reactions were more prominent than soot formation reactions in the envelope flames; and finally, (iii) the incandescent residual char particles of all fuels emitted stronger radiation and they appeared brighter. In the 50%O_2-50%CO_2 atmosphere, chars ignited while the volatiles were still burning. At such an elevated oxygen mole fraction, the phases of the homogeneous volatiles combustion and heterogeneous residual char combustion became nearly indistinguishable. Moreover, char combustion was very fast.

5.3.4.2. Temperatures and burnout times

Devolatilization of particles occurs both pre- and post-ignition in the furnace. Pre-ignition devolatilization times are affected by the ignition delay period, which is in turn influenced by the volumetric heat capacity (heat sink) of the surrounding gas. Post-ignition devolatilization times are affected by the flame temperature, which is influenced by the composition, and thus, the properties of the surrounding gas. Hence, both times are affected by the substitution of N_2 with CO_2 gas in oxy-combustion. In this work, only the post-ignition devolatilization and simultaneous volatiles combustion phenomena could be monitored. In general, longer volatile and char burnout times were observed when N_2 was replaced by CO_2, at the same oxygen mole fraction (i.e., longer burnout times in 21%O_2/79%CO_2 than in 21%O_2/79%N_2), see Figs 6 and 7.
Moreover, the burnout time decreased as the oxygen mole fraction increased from 21% to 35%. These results are in agreement with previous studies which were carried out for coal particles of all ranks [2, 32, 48]. In the cases of both coal and biomass char particles it is likely that combustion occurred in Regime II, i.e., under both kinetic and diffusion control [44]. For biomass chars this was illustrated with calculations outlined in the Appendix, whereas for coal chars, burning under identical conditions, similar calculations have been performed in Refs. [32] and [48]. Figure 7 shows that increasing the O₂ mole fraction further, from 35% to 50%, had a less pronounced effect on the char burnout time. Peak char temperatures, averaged over particles, during combustion of biomass in both air and simulated oxy-fuel conditions, shown in Fig. 8, are heavily dependent on the oxygen mole fraction. The temperatures of all biomass particles burning in air were higher than those burning in 21%O₂ diluted with CO₂. At higher oxygen mole fractions (>21%) in CO₂, the char combustion temperatures increased while the durations of char combustion decreased. Increasing the oxygen mole fraction in CO₂ to 30-35% restored the combustion intensity of single fuel particles to the level found in conventional combustion in air, for all biomass fuels tested herein. This is in agreement with observations on coal particle combustion reported in Ref. [33].

5.3.5. Effect of biomass type

Biomass particles burned expediently under the conditions of this work. Biomass devolatilization commences at low temperatures (at around 473 K [19, 45]). As the particles heated up, devolatilization accelerated until most of the volatiles were released. The heating rate of the particles in the drop tube furnace was high (in the order of 10⁴ K s⁻¹ [34]). Biomass structures, and heavy hydrocarbons and tars, produced by the devolatilization step have been reported to expediently convert into smaller molecules by cracking reactions in the proximity of
the devolatilizing particles [49]. In fact, previous work in this laboratory [50, 51, 52, 53] pyrolyzed various biomasses under relevant high heating-rate conditions and elevated furnace temperatures and found that the pyrolytic products were mainly light hydrocarbon gases (such as methane, ethylene, ethane, acetylene, propylene, benzene, ethyl-benzene, etc.), as well as hydrogen, carbon monoxide and carbon dioxide.

The proximate and ultimate analyses of the different biomasses were similar, see Table 1, and so was their combustion behavior. The sugarcane bagasse, SCB, has the highest volatile matter content, therefore extra time was likely needed for devolatilization, and the combustion duration of the volatiles of this fuel was indeed observed to be lengthier (see Fig. 6). On the other hand, SCB has the least fixed carbon content and, thus, it exhibited the shortest char burnout duration (Fig. 7).

The envelope flames of olive residues, OR, were slightly less distinguishable cinematographically than those of the other biomass fuels. The corresponding pyrometric signals were also weaker than those of the rest of the samples. It is notable that OR had the lowest volatile matter content than the rest of the biomasses examined herein. Moreover, it was found that the OR char temperatures were the lowest among those of the other fuels, in all gas atmospheres in the DTF and the burnout times of the OR chars were less influenced by the oxygen mole fraction in the gas, as shown in Fig. 7. Regarding the combustion behavior of the chars, it is notable that OR had the highest ash, which may have increased the catalytic effect on the char burnout and have thus decreased the influence of oxygen content of the surrounding gas. High ash content and possible, yet unexplored, physical structure-related reasons (pore sizes, porosity, tortuosity) may have been responsible for the lower char temperatures.
The torrefied pine sawdust (TOPI) chars burned hotter than the other biomass chars under all oxy-fuel conditions. Differences in the combustion behavior of the pine sawdust (PI) and the torrefied pine sawdust (TOPI) were very small. However, a more luminous flame was observed in the case of TOPI (Fig. 4). This is perhaps because a lower amount of CO₂ was supposedly released with the TOPI volatiles as a consequence of the torrefaction pre-treatment while the hydrogen content of the torrefied sample and, therefore, the release of hydrocarbon gases (e.g. CH₄ and C₂H₆) remained unchanged [15]. The CO₂ dilutes the rest of the combustible gases and produces lower luminosity flames. The TOPI biomass released a greater amount of energy per unit mass during combustion due to the fact that its calorific value was higher than that of raw biomass (PI). This effect was confirmed by the typically hotter char temperatures of TOPI. Average volatile burnout times of the original PI were longer; however, the char combustion times were generally similar, perhaps a little shorter for the original PI in comparison with the torrefied TOPI under oxy-fuel atmospheres.

5.3.6. On the differences of single-biomass and single-coal particle combustion

Several recent studies in this laboratory have focused on the combustion behavior of coal particles of all ranks in conventional (air) and oxy-fuel conditions [30, 31, 32, 48]. In comparison to coal, biomass particles exhibit certain physical and chemical differences, the most prominent of which have as follows: (1) Raw biomasses have a highly fibrous nature. (2) The biomass particles are less dense than coal particles, therefore the total mass burnt for the same nominal particle size is lower. (3) Biomass has much lower heating value than coals [20], see also Tables 1 and Table A2 in Appendix 2. (4) Biomass has a different elemental composition with a high proportion of oxygen. See Tables 1 and Table A2 in Appendix 2. (5) The proximate composition of the biomass is different, i.e., biomass contains a higher proportion of volatile matter and a
smaller proportion of fixed carbon than coal. Biomasses contain 70-80% volatile matter while most of the volatile matter contents of coals studied in this laboratory did not exceed 45%, see Table 1 and Table A2 in Appendix 2. The aforementioned structural and chemical composition disparities resulted in the following combustion behavior differences between biomass studied herein and coal reported in Refs [32, 34, 48]:

(i) Pyrometric combustion intensities

The radiation intensity signals captured by the pyrometer during the combustion of biomass particles were weaker than those captured during combustion of coal particles under identical experimental conditions [48], especially during the phase of volatiles combustion. Moreover, the variability of the pyrometric signals of biomass particles was higher than those of coal, as there were more particle-to-particle size variations and shape irregularities in the biomass samples.

(ii) Volatile particle envelope flame combustion

The compounds released from biomass in the form of volatiles are different than those from coal. The cellulose and hemicellulose components of biomass decompose to small molecules in the form of volatile gases, tars and pyrolytic water [54]. These volatiles are generally lighter than those formed from coal [23]. The volatile flames of biomasses were observed to be typically transparent, and nearly non-sooty, similar to those of low rank coals [32], whereas those of the bituminous coals were sooty. The percentage of bonded oxygen in biomasses is much higher than that of coals (Table 1 and Table A2). Therefore, the volatiles contain high quantities of CO and CO₂ as well as hydrogen and light hydrocarbons [24, 50, 51]. They also contain smaller amounts of tars and other condensables than the volatiles of coal particles. To the contrary, bituminous coal volatiles contain mostly heavy hydrocarbons, tars, condensables and light
hydrocarbons [53]. In previous studies [31, 32, 33, 48], bituminous coal particles released a high amount of volatiles, with long soot-containing contrails forming in the wake of each settling particle whereas lignite coal particles released light hydrocarbons and CO, resulting in occasional, faint and brief volatile flames with a large extent of char fragmentation. Anthracite coals released very small amount of volatiles and did not establish an envelope flames. Biomass particles burned with distinctive volatiles flames without contrails. Unlike the combustion behavior of coals, which differs widely with rank, type and seam, the combustion behavior of biomasses from the four different sources of this study appears to be more unified. The ignition of biomass volatiles started earlier (shorter ignition delays) and their ensuing combustion occurred in envelope flames that were spherical and peripherally-uniform, even in the cases of elongated or otherwise irregularly-shaped particles. Furthermore, as biomass has a lower apparent density than coal (representative values for which have been reported as 1.32 g cm\(^{-3}\) for bituminous, 1.30 g cm\(^{-3}\) for subbituminous and 1.29 g cm\(^{-3}\) for lignite [56], whereas for biomasses is typically in the range of 0.4 - 0.5 g cm\(^{-3}\) [57], the burning biomass particles were very buoyant and settled very slowly in the furnace. The observed volatile flame burnout times (Fig. 8) of the biomasses were generally much lengthier than those of the coal flames; for instance, they were lengthier than those of bituminous coal particles of comparable nominal size by a factor of eight [30, 32], which is much higher than the ratio of their volatile contents. This is likely due to the fact that because of their elongated shapes and, thus, their higher aspect ratios, biomass particles tend to be overall bigger than coal of the same size cut.

(iii) Char combustion

Whereas coal chars typically exhibited a rather uniform temperature profile during their combustion before experiencing a slow decrease towards burnout [30, 31, 32, 48], the
temperature profile of biomass chars increased throughout their combustion history. Examples of biomass (bagasse) char and coal (bituminous) particle temperature-time profiles are illustrated in Figure 9 (the temperature of the volatile envelope flames of the biomass particles is not included in this plot, as it is currently under investigation). In general, biomass chars burned at a somewhat higher average temperature than bituminous char particles (by 50-100 K), as can be attested by comparing the results shown in Fig.8 and those in Refs. [30, 31, 32, 48]. Biomass char particles burned with lower average temperatures (by 100-200 K) than lignite char particles in similar gas environments. Moreover, the biomass char burnout times were much briefer than the coal particle chars burnout times due to lower fixed carbon content of the biomass. Biomass chars have higher reactivity than coal chars, as reported by Matsumoto et al. [58] and Ollero et al. [59]. Matsumoto et al. [58] showed that a woody biomass char had five times higher reactivity than a sub-bituminous coal char at high heating rates encountered in an entrained flow reactor and gas temperatures in the range of 1200-1450 K. The higher reactivity of biomass char was partly attributed to faster char gasification reactions, such as $\text{C(s) + CO}_2 \rightarrow 2\text{CO}$. This was also related to the higher concentration of alkali metals, which act as a catalyst and to the higher oxygen to carbon ratio in biomass char [58, 59].

![Figure 9](image_url)

**Figure 9.** Deduced temperature-time profiles of single particles of biomass (sugar cane bagasse) and coal (bituminous) burning in air. The original particle sizes are 75-90µm for both fuels. The biomass char size is 25-30µm. The temperature of biomass char increases during the combustion history of the particle whereas that of the coal char remains mostly constant.
5.4. Conclusions

Biomass particles were burned in a laboratory-scale drop-tube furnace at 1400 K in air and in different oxy-fuel atmospheres, simulated by dry O₂/CO₂ gases. Experiments were performed under quiescent gas conditions. Striking differences were observed between the combustion behavior of the biomass particles burned herein and those of coal particles of all ranks investigated in previous studies in this laboratory. The biomass particles released large amounts of volatiles that burned in the form of spherical envelope flames. Ensuing biomass char combustion produced stronger pyrometric signals than the combustion of the volatile matter. Increasing the oxygen mole fraction in CO₂ reduced the luminosity of the flames. The combustion intensity of the biomass was stronger in air (21% O₂-79% N₂) than in an oxy-fuel atmosphere with the same oxygen mole fraction (21% O₂-79% CO₂). Increasing the oxygen mole fraction in the CO₂ background gas enhanced the combustion intensity of biomass. It decreased the burnout times of volatiles and of the char residues, whereas it increased the temperature of the burning char particles. Similar trends were observed for all tested biomass samples from disparate sources, including the raw and torrefied pine sawdust. Thus, unlike the combustion behavior of coals, which differs widely with rank, type and seam, the combustion behavior of biomasses from the four different sources of this study appears more unified. Olive residue chars (OR) burned at lower temperatures than the other biomass fuels, whereas bagasse chars (SCB) burned at higher temperatures than the other biomass fuels. The volatile flames of biomass particles are less sooty than those of bituminous coal particles.
5.5. References


5.6. Appendix 1

Calculation of the oxygen mole fraction at the biomass char particle surface and of the diffusion-limited burnout time

Based on a derivation by Levendis et al.[26], the average oxygen mole fraction on the char particle surface can be estimated by the following formula:

\[
y_{O_2s} = (4/3 + y_{O_2\infty}) e^{-\frac{a^2 R T m \rho c}{56 R T m D s, obs}} - 4/3
\]  

(A.1)

In this relation, \(y_{O_2\infty}\) is assumed to be an average value. \(a_i, \rho_c, T_m, D, t_B, R\) and \(P_{tot}\) are initial burning particle radius, initial particle density, film temperature between the char particle and flow, bulk diffusion coefficient of \(O_2\) in the diluents gas, observed particle burnout time, gas universal constant and total pressure of the system, respectively.

If \(y_{O_2s}\) is zero or close to zero, the combustion takes place at diffusion limited conditions (Regime III), whereas if \(y_{O_2s}\) is close to \(y_{O_2\infty}\), the combustion happens at kinetically limited condition (Regime I). Any \(y_{O_2s}\) in-between the above values results in kinetic-diffusion limited condition (Regime II).

The time \(t_B\) required for combustion under diffusion control (Regime III) becomes [26]:

\[
t_B = \frac{\rho_c (a_i^2 - a_f^2) RT_m}{56 D} \frac{1}{\ln(1 + \frac{3}{4} y_{O_2\infty})}
\]  

(A.2)
In Eq. A.2, \( a_f \) is the final particle radius after extinction, which herein is estimated based on the ash content in the parent biomass composition.

For instance, for sugarcane bagasse burning in air with the observed parameters of this study \( a_0=15 \mu m \), \( a_f=2.5 \mu m \), \( \rho_c=0.2 \text{ g/cm}^3 \), \( T_m=1600 \text{ K} \), \( P_{\text{tot}}=1 \text{ atm} \), \( D_{O_2-N_2}=3.49 \text{ cm}^2/\text{s} \), \( t_{B-\text{obs}}=18 \text{ (ms)} \), \( R=82 \text{ (atm cm}^3/\text{mol.K)} \), oxygen mole fraction on the particle surface from A.1, \( y_{O_2} \), was calculated to be 0.08 and the diffusion limited burnout time from A.2, \( t_B \), was calculated to be 10 (ms). On the other hand, for sugarcane bagasse burning in 21%O\(_2\)-79%CO\(_2\), \( T_m=1500 \text{ K} \), \( D_{O_2-CO_2}=2.73 \text{ cm}^2/\text{s} \), \( t_{B-\text{obs}}=23 \text{ (ms)} \) and the rest of parameters are similar to those of combustion in air. In this case, oxygen mole fraction on the particle surface from A.1, \( y_{O_2} \), was 0.09 and the diffusion limited burnout time from A.2, \( t_B \), was 12 (ms). Therefore, under the experimental conditions of this study, combustion of bagasse in either air or oxy-fuel condition (21%O\(_2\)-79%CO\(_2\)) took place in Regime II which is a combination of kinetic and diffusion limited cases. From Eq. A.2 for diffusion limited case, the burnout time is inversely proportional to the mass diffusivity of oxygen in the diluents gas and this seems to be the case in the current work, because:

\[
\frac{t_{B-\text{obs}-\text{Air}}}{t_{B-\text{obs}-21\%O_2/79\%CO_2}} = \frac{18}{23} = 0.78 \approx \frac{D_{O_2-CO_2}}{D_{O_2-N_2}} = \frac{2.73}{3.49} = 0.77
\]

The resulted observed burnout times and calculated diffusion limited burnout times versus oxygen concentration for sugarcane bagasse in different oxy-fuel condition is shown in Fig. A.1.
Figure A.1. Comparison of experimentally-observed and calculated diffusion-limited burnout times of sugarcane bagasse char particles, plotted against bulk oxygen mole fraction.

Appendix 2

Characterization of coals used for comparison with the biomasses [32, 48]

Table A2. Coals used for purposes of comparison with biomasses: rank/type and chemical composition [34, 53]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rank/Type</th>
<th>Proximate Analysis (wt%, db)</th>
<th>Ultimate Analysis (wt%, daf)</th>
<th>HHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ash</td>
<td>V.M.</td>
<td>F.C.*</td>
</tr>
<tr>
<td>AC [53]</td>
<td>Anthracite</td>
<td>14.2</td>
<td>3.6</td>
<td>82.2</td>
</tr>
<tr>
<td>PSOC-1451[34]</td>
<td>Bituminous</td>
<td>13.3</td>
<td>33.6</td>
<td>50.6</td>
</tr>
<tr>
<td>DECS-26 [34]</td>
<td>Sub-bituminous</td>
<td>5.6</td>
<td>33.1</td>
<td>35.1</td>
</tr>
<tr>
<td>PSOC-1443 [34]</td>
<td>Lignite</td>
<td>15.3</td>
<td>44.2</td>
<td>12.0</td>
</tr>
</tbody>
</table>

* determined by difference
CHAPTER 6

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6. Single Particle Ignition and Combustion of Anthracite, Semi-Anthracite and Bituminous Coals in Air and Simulated Oxy-Fuel Conditions

Abstract

A fundamental investigation has been conducted on the combustion behavior of single particles (75-150 μm) of four coals of different ranks: anthracite, semi-anthracite, medium-volatile bituminous and high-volatile bituminous. A laboratory-scale transparent laminar-flow drop-tube furnace was used to burn the coals, electrically-heated to 1400 K. The experiments were performed in different combustion atmospheres: air (21%O₂/79%N₂) and four simulated dry oxy-fuel conditions: 21%O₂/79%CO₂, 30%O₂/70%CO₂, 35%O₂/65%CO₂ and 50%O₂/50%CO₂. The ignition and combustion of single particles was observed by means of three-color pyrometry and high-speed high-resolution cinematography to obtain temperature-time histories and record combustion behavior. On the basis of the observations made with these techniques, a comprehensive examination of the ignition and combustion behavior of these fuels was achieved. Higher rank coals (anthracite and semi-anthracite) ignited heterogeneously on the particle surface, whereas the bituminous coal particles ignited homogeneously at the gas phase. Moreover, deduced ignition temperatures increased with increasing coal rank and decreased with increasing oxygen concentrations. Strikingly disparate combustion behaviors were observed depending on the coal rank. The combustion of bituminous coal particles took place in two phases. First, volatiles evolved, ignited and burned in luminous enveloping flames. Upon extinction of these flames, the char residues ignited and burned. In contrast, the higher rank coal
particles ignited and burned heterogeneously. The replacement of the background N₂ gas of air with CO₂ (i.e., changing from air to an oxy-fuel atmosphere) at the same oxygen mole fraction impaired the intensity of combustion. It reduced the combustion temperatures and lengthened the burnout times of the particles. Increasing the oxygen mole fraction in CO₂ to 30-35% restored the intensity of combustion to that of air for all the coals studied. Volatile flame burnout times increased linearly with the volatile matter content in the coal in both air and all oxygen mole fractions in CO₂. On the other hand, char burnout times increased linearly or quadratically versus carbon content in the coal, depending on the oxygen mole fraction in the background gas.

6.1. Introduction

Coal has been, and will continue to be, one of the major energy resources in the long term because of its abundant reserves and competitively low price, especially for use in power generation. The share of coal in world energy consumption was 30.3% in 2011, as opposed to 33.1% for oil and 23.7% for natural gas [1]. A diverse power generation portfolio including Carbon Capture and Storage (CCS) technologies and renewable energies is needed to reduce atmospheric CO₂ to below 1990 levels [2]. The deployment of oxy-fuel combustion in coal-fired utility boilers is seen as one of the major options for CO₂ capture. In this technology instead of using air as oxidizer, a mixture of oxygen and recycled flue gas (mainly CO₂ if dried) is employed to yield an effluent stream, rich in CO₂. However, the successful implementation of oxy-fuel combustion technology depends on fully understanding the difficulties that can arise from replacing nitrogen (inert) by CO₂ (reactive) in the oxidizer stream. Several factors such as char and volatile combustion or flame ignition and stability may be affected [3].
Previous work in this laboratory contrasted the combustion behaviors of single solid fuel particles of a bituminous high-volatile type-A coal, three low rank coals (low carbon content and low heating value coals): a sub-bituminous and two different lignites, as well as biomass (sugarcane bagasse) under air and under simulated dry oxy-firing conditions [4, 5]. This work aims at examining the combustion behavior of additional bituminous coals (high- and medium-volatile types-B) as well high rank coals (high carbon content and high heating value coals), i.e., anthracite and semi-anthracite. The combustion and emission studies of bituminous coals has been well-documented in the aforementioned studies of Khatami et al. and Kazanc et al. in this laboratory [4, 5, 6] as well as in other studies including those of [7-10]. However, studies on anthracite and semi-anthracite coal particle ignition and combustion are scarce.

There are several possible oxy-fuel combustion zones which are a function of the preheat temperature and oxygen mole fraction of the oxidant stream [11]. Air-like oxy-fuel combustion systems have been viewed not only as an appropriate technology for new units but also as a retrofit strategy for existing coal-fired power plants. Oxygen concentrations that are similar to, or higher than, those of air combustion systems are used in these oxy-fuel regimes (with a flue gas recycle rate of 60-80% vol, the oxygen mole fraction is about 30% in the oxidizer stream) However, oxygen-enriched combustion (where the oxygen mole fraction is significantly higher than 21%) and full oxy-fuel combustion with neat oxygen are of industrial interest for several reasons (e.g., improved coal ignition, higher flame temperature, greater flame stability, reduction in boiler size and consequently lower plant costs).

The aim of the present work is to evaluate the effect of oxygen mole fraction on the ignition and combustion characteristics of bituminous and higher rank coals. The coals selected were burned in different O₂/CO₂ environments (21-50% O₂) in a laboratory-scale, electrically-heated,
laminar-flow drop-tube furnace fitted with a transparent quartz tube. An air combustion atmosphere (i.e., 21%O₂/79%N₂) was used as a baseline for comparison with O₂/CO₂ background gases. The ignition and combustion behavior of single particles was observed by means of three-color optical pyrometry and simultaneous high-speed high-resolution cinematography. The data obtained contributes to the understanding of coal combustion phenomena, in both air and in oxy-firing conditions.

6.2. Materials and methods

6.2.1. Coal samples

Four coals of different ranks were burned: an anthracite from Asturias, Spain (AC), a semi-anthracite from the Hullera Vasco Leonesa in León, Spain (HVN), a South African high-volatile bituminous coal supplied by the Aboño power plant in Asturias (SAB), and a medium-volatile bituminous coal from Mexico (UM). The semi-anthracite coal (HVN) is a physical blend of approximately 90% anthracitic and 10% low volatile bituminous coal from the same mine. The coals were ground and sieved to a particle size cut of 75-150 μm. The fuels were dried prior to the experiments. Proximate analyses were obtained using a LECO TGA-601 in accordance with ASTM D7582-10 [12]. Ultimate analyses was determined using a LECO CHNS-932 instrument in accordance with ASTM D3176-89 [13]. Results of the analyses of the coals are presented in Table 1.

Table 2. Proximate and ultimate analyses of the coals

<table>
<thead>
<tr>
<th>Coal</th>
<th>AC</th>
<th>HVN</th>
<th>UM</th>
<th>SAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Spain</td>
<td>Spain</td>
<td>Mexico</td>
<td>S. Africa</td>
</tr>
<tr>
<td>Rank</td>
<td>an</td>
<td>sa</td>
<td>mvb</td>
<td>hvb</td>
</tr>
<tr>
<td>Proximate Analysis (wt.%, db)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>14.2</td>
<td>10.7</td>
<td>21.1</td>
<td>15.0</td>
</tr>
<tr>
<td>V.M.</td>
<td>3.6</td>
<td>9.2</td>
<td>23.7</td>
<td>29.9</td>
</tr>
</tbody>
</table>
6.2.2. Experimental apparatus and procedure

The combustion studies of free-falling coal particles were performed in an electrically-heated laminar-flow drop-tube furnace, a detailed description of which has been provided elsewhere [14]. Here only a brief description of the reactor is given. The radiation cavity of the furnace (an ATS unit) is 25 cm long and is heated with molybdenum disilicide heating elements. A sealed transparent quartz tube with a 7-cm inner diameter was fitted in this furnace. A water-cooled injector was used to introduce single fuel particles at the top of the furnace (Fig. 1a). The furnace wall temperatures \( T_f \) were continuously monitored by means of type-S thermocouples embedded in the wall. The particle heating rates were high, calculated to be of the order of \( 10^4 \) K/s. Optical access to the radiation zone of the furnace was achieved through three observation ports: one at the top (used for pyrometry) and two orthogonally situated at the sides of the furnace (used for cinematography).
Figure 1. Schematic of the experimental setup and diagnostic facilities. (a) Drop tube furnace (DTF), (b) three-color optical pyrometer and (c) high speed camera.

Pyrometric observations of the burning single particles were conducted from the top of the furnace injector, viewing downwards along the central axis of the furnace, as this ideally would be the particle’s trajectory. In this way, complete luminous burnout histories of the single coal particles - from ignition to extinction - were recorded. Details of the pyrometer optics, electronics, calibration hardware and performance have been reported elsewhere [15], so here only a brief description is provided. An optical fiber made up of a high-transmittance (> 99.5%) fused silica core and doped fused silica cladding with an f-number of 2.2, transmitted light from the furnace to the pyrometer assembly. The pyrometer used two dichroic edge filters as spectrum splitters to direct the light to the three interference filters (see Fig. 1b) having effective wavelengths of 0.640, 0.810 and 0.998 μm and bandwidths (FWHM) of 70 nm. In conjunction with the interference filters, silicon diode detectors were employed, the voltage outputs of which represented spectral radiation intensities of burning particles. These signals were used to deduce particle temperatures [16].

High-speed cinematography was conducted through the slotted side quartz windows of the drop-tube furnace against backlight (Fig. 1a). A NAC HotShot 512SC self-contained digital high-speed video camera was used, set to speeds of 1000 or 2000 frames/s. The camera was fitted with an Olympus-Infinity Model K2 long-distance microscope lens to provide high-magnification images of the combustion events (see Fig. 1c).

The morphology of the coal chars was examined by means of scanning electron microscopy (SEM). Secondary electron images of the samples were obtained with a field emission scanning electron microscope (Quanta FEG-650-FEI) operated at 30 kV.
6.2.3. **Furnace gas temperature and composition**

Coal particle combustion experiments were conducted under quiescent gas conditions (i.e., no gas flow in the drop-tube furnace) in order to equalize the axial temperature profiles of N$_2$- and CO$_2$-containing furnace gases, as documented by Khatami et al. [5]. As shown in Fig. 2, under quiescent gas conditions (no flow), the axial gas temperature profiles in the furnace increased along its centerline and in a short distance from the particle injector tip they reached asymptotically 1340 K. The gas compositions inside the furnace included air as well as the following four binary mixtures of O$_2$/CO$_2$ (21%O$_2$/79%CO$_2$, 30%O$_2$/70%CO$_2$, 35%O$_2$/65%CO$_2$ and 50%O$_2$/50%CO$_2$).

![Figure 2](image)

**Figure 2.** Centerline gas temperature inside the drop-tube furnace filled with either neat N$_2$ or neat CO$_2$. The furnace wall temperature was set at 1400 K.

6.3. **Results**

6.3.1. **Temperature-time history of coal particles**
Typical examples of radiation intensity-time and temperature-time profiles of single coal particles during their entire burnout history in air-firing conditions are displayed in Fig. 3. The radiation intensity traces were represented by the output voltage signals $S_n$ of all three wavelength channels of the pyrometer. The temperature deduction method has been described in Ref. [16].

![Figure 3. Examples of pyrometric profiles of (a) anthracite (AC), (b) semi-anthracite (HVN), (c) hvb bituminous (SAB), (d) mvb bituminous (UM) particles (75-150 μm) during their combustion in air, at a wall temperature of 1400 K and their deduced particle temperatures. Volatile flame and char combustion phases are denoted. The three pyrometric signals were centered at 998, 810 and 640 nm. I stands for the onset of ignition.](image)

In the case of the bituminous coal two separate combustion phases were distinguished by three-color pyrometry (see Figs. 3c and 3d). In contrast, the anthracitic and most of the semi-anthracite coal particles experienced only one combustion phase (see Figs. 3a and 3b).
6.3.2. High-speed cinematography stills

Selected images from high-speed, high-resolution cinematography of particles of the four coals burning in air (21%O₂/79%N₂) and in three of the simulated oxy-fuel atmospheres studied (21%O₂/79%CO₂, 30%O₂/70%CO₂ and 50%O₂/50%CO₂), are shown in Figs. 4-7.

**Anthracite (AC) at 21%O₂/79%N₂**

![Images of particles at 21%O₂/79%N₂](image)

**Anthracite (AC) at 21%O₂/79%CO₂**

![Images of particles at 21%O₂/79%CO₂](image)

**Anthracite (AC) at 30%O₂/70%CO₂**

![Images of particles at 30%O₂/70%CO₂](image)

**Anthracite (AC) at 50%O₂/50%CO₂**

![Images of particles at 50%O₂/50%CO₂](image)

**Figure 4.** High-speed, high magnification cinematography images of single particles (75-150 μm) of anthracite coal (AC) in air and different O₂/CO₂ atmospheres. The displayed numbers in each frame denote milliseconds. A thermocouple wire (100 μm) is shown in the 21%O₂/79%CO₂ case to facilitate assessment of the particle/flame size.
Figure 5. High-speed, high magnification cinematography images of single particles (75-150 μm) of semi-anthracite coal (HVN) in air and different O₂/CO₂ atmospheres. The displayed numbers in each frame denote milliseconds.
Figure 6. High-speed, high magnification cinematography images of single particles (75-150 μm) of medium volatile bituminous coal (UM) in air and different O₂/CO₂ atmospheres. The displayed numbers in each frame denote milliseconds. A thermocouple wire (100 μm) is shown in the 21%O₂/79%N₂ case to facilitate assessment of the particle/flame size.
Figure 7. High-speed, high magnification cinematography images of single particles (75-150 μm) of high volatile bituminous coal (SAB) in air and different O₂/CO₂ atmospheres. The displayed numbers in each frame denote milliseconds.

Most of the AC coal particles in air burned with no evidence volatile matter flames (see Fig. 4). These coal particles ignited and burned heterogeneously by direct attack of oxygen on their surfaces. Due to the known low reactivity of the anthracite AC particles [17], their ignition was delayed. The color of the particles changed from dark (black) to bright (nearly-white) as their surfaces became incandescent; this change occurred gradually over a few milliseconds.
As the HVN coal is a physical blend of approx. 90% anthracitic and 10% low volatile bituminous coal from the same mine, most HVN coal particles burned in the same way as the AC anthracite coal particles. A few particles, however, experienced small enveloping flames attributed to combustion of volatiles (see Fig. 5, second frames in first and fourth cases). Once the flames were extinguished, the resulting chars proceeded to burn heterogeneously.

The two bituminous coals of this study, UM and SAB, experienced similar combustion trends, as exemplified in Figs. 6 and 7, including homogeneous ignition and combustion of volatiles in envelope flames, followed by heterogeneous ignition, combustion and extinction of the resulting chars. The volatiles produced large sooty flames that ignited in the gas phase and completely surrounded individual particles. The different relative velocities between the free-falling particles and surrounding furnace gas led to the formation of contrails that burned in the wake of the particles; sometimes the gas flames expanded backwards from the particles. Since the volatiles contain tars, in some cases drops of burning tars can be distinguished inside the flame as sources of high luminosity. Tars need more time to burn up, hence occasionally some of these drops continued to burn while the flame burned out. In atmospheres containing 21% O₂ the drops were sometimes quenched before completely burning out resulting in the formation of soot ligaments. This phenomenon was especially noticeable in the 21%O₂/79%CO₂ atmosphere. Upon extinction of a volatile flame, the luminous combustion of the char commenced. The recorded cinematographic images suggest the final diameters of the chars approached those of the estimated size of ash residues, as discussed in the Appendix.

For the four coals studied, when N₂ was replaced with CO₂, keeping the oxygen mole fraction constant, the burning particles appeared dimmer. This is indicative of slower oxidation, which causes lower flame/particle temperatures. Dim combustion was also observed by Zhang et
al. [18], who reported that the average intensity of coal particles burning in O₂/CO₂ with oxygen concentrations below 30%, was much lower than that in air. Moreover, in our study the brightness and intensity of combustion increased drastically with O₂ in the O₂/CO₂ environments, which is indicative of rapid oxidation. In fact, particle combustion images of the 30%O₂/70%CO₂ atmosphere resembled those in air.

### 6.3.3. Morphology of coal chars

The chars obtained from coal devolatilization under N₂ and CO₂ background gases in an entrained reactor were examined by SEM; sample images are shown in Fig. 8. These photographs were obtained in prior experiments, described in Ref. [19], at an average reactor gas temperature of 1273 K. This temperature is in the range of gas temperatures encountered in the experiments herein in the region of the furnace wherein particle devolatilization has been observed to take place prior to ignition, i.e., in the first centimeter of the furnace, see temperature profile shown in Fig. 2. As shown in Fig. 8, the anthracite (AC) and the semi-anthracite (HVN) coal chars consist of angular solid particles with sharp edges. The AC chars have sharper edges (see Fig. 8a,b,e,f) than the HVN chars. The medium volatile bituminous UM chars have striking bubble-like network-type structures (Fig. 8c, g). The particles must have exhibited intense swelling and bubbling during devolatilization to form cenospheric char particles with almost transparent walls. Large blow-holes often appear on the surfaces, particularly in CO₂ (Fig. 8g). Cenospheric char formation with associated swelling was also observed in the case of the high-volatile bituminous SAB particles (Figs. 8d, h). However, the walls of the SAB cenospheres appear to be much thicker and much more opaque than those of the UM cenospheres.
Fig. 8. SEM images of the anthracite (AC), semi-anthracite (HVN) and medium- and high-volatile bituminous (UM, SAB) coal char particles obtained under N₂ (a–d) and CO₂ (e–h) in an entrained flow reactor (EFR) at 1273 K and a particle residence time of 2.5 s [19].

6.4. Discussion

The ignition and combustion behavior of anthracite, semianthracite and bituminous coal particles were determined based on the combined diagnostic techniques of pyrometry and backlight cinematography, in conjunction of scanning electron microscopy.

6.4.1. Ignition phenomena and ignition temperatures

(a) Ignition mode

Ignition-related events of anthracite, semi anthracite and bituminous coal particles, are illustrated in the initial stills of the photographic sequences depicted in Figs 4-7. The determination of ignition mode in this work relied on luminous emissions. Anthracite and semi-anthracite coal particles ignited heterogeneously on the particle surfaces. Such ignition mode is attributed to the low volatile matter content and high fixed carbon content of these coals. In the case of a few semi-anthracite particles, gas-phase (homogeneous) ignition took place due to their
higher volatile matter content as discussed earlier. The nature of the heterogeneous ignition of anthracite and semi-anthracite particles is however different to that of lignite coals, previously studied in this laboratory [5]. Although the lignite coal particles contained sufficient amounts of volatile matters for gas-phase ignition, their extensive fragmentation and the small fragment sizes were the main reasons for their heterogeneous ignition [5]. The much higher volatile content bituminous coal particles of this study ignited in the gas phase (homogeneously). The homogeneous ignition mode of bituminous coal in the current study is in line with previous observations in this laboratory for the Pittsburgh #8 high-volatile bituminous coal [5].

(b) Ignition Temperatures

In this study, ignition temperature was defined as the first point where the maximum particle temperature gradient (dT_p/dt) was recorded, see Fig. 9a. Fig. 9b shows the ignition temperatures in air as well as in different O_2/CO_2 atmospheres for various fuels, under the conditions of this study. Each data point in this figure represents average ignition temperatures from at least 8 randomly-selected particles. Ignition temperature data for lignite coal particles from a previous study in this laboratory [4] are also displayed in this figure for comparison.
Figure 9. (a) Typical ignition temperature criterion for a pyrometric profile which is defined as the point where the maximum particle temperature gradient was recorded (b) Average deduced ignition temperatures for the four coals of the current study in air and different oxy-fuel environments. Ignition temperatures of lignite, a low rank coal, were also inserted herein from a previous study in this laboratory [4].

Fig.9 illustrates that higher rank coals ignited at higher temperatures. Moreover, replacing $N_2$ with $CO_2$ increased the ignition temperature, but only negligibly. Increasing oxygen mole fraction in $CO_2$ consistently decreased the ignition temperature for all coal ranks.

6.4.2. Combustion mode

Single particle combustion modes were discussed comprehensively in previous studies [4, 5, 20]. In summary, Howard and Essenhigh [20] studied the combustion phenomena of coal particles and proposed a model to assess whether the burning of the volatiles and char takes place sequentially or simultaneously. Khatami et al. [4, 5] employed that model to a number of coals from different ranks in a variety of oxygen-nitrogen and oxygen-carbon dioxide environments.
The terms *two-mode* and *one-mode* combustion were used to respectively signify events where gas-phase combustion of the volatiles takes place in an enveloping flame, prior to heterogeneous char particle combustion, and where volatile and solid char combustion take place simultaneously.

(a) *Anthracitic* and the majority of semi-*Anthracite coal* particles exhibited only one wide peak in each pyrometric profile, which is attributed to heterogeneous combustion of the char (see Figs. 3a and 3b) with possible simultaneous burning of volatiles. This observation is consistent with the cinematographic behavior, where there is no evidence of an enveloping flame corresponding to volatiles combustion, but only that of the incandescent burning char. Such anthracitic coals produced no incandescent trails of volatiles (see Figs. 4 and 5). Moreover, most of the anthracite particles and some semi-anthracite particles exhibited striking undulation patterns (wave patterns) in their radiation intensity pyrometric signals. As the deduced temperature profiles do not show such undulations, but deduced luminous cross sectional areas do (with a method outlined in Ref. [16]), such conspicuous undulation patterns were attributed to particle rotations during combustion. Such patterns can indeed be detected in cinematographic sequences as the one shown in Fig.10. Somehow the anthracite char particles, which as documented earlier (see Section 3.3) retain their planar and angular shapes upon devolatilization and supposedly throughout char combustion, experienced rotation (tumbling) as they fell in the drop tube furnace. These coals are non swelling and they release much fewer volatiles than the bituminous coals, as also reported by Seeker et al. [21].
Figure 10. An example of a pyrometric profile of an anthracite coal particle (75-150 µm) burning in air, at a wall temperature of 1400 K and its deduced particle temperature profile.

(b) The \textit{bituminous coal} particles exhibited two peaks in each profile, an exceedingly strong first peak followed by a less pronounced second peak (see Figs. 3c and 3d). The first peak is attributed to volatiles burning homogeneously in luminous enveloping flames, whereas the second peak is attributed to the heterogeneous combustion of char. The combustion of the chars was lengthy and bright. The bituminous coals are rich in volatile hydrocarbons and tars, some of which are soot precursors [22]. Bituminous coals typically swell up and form cenospheric spheroid chars, as illustrated in section 3.3. In doing so, they expel volatiles in jets or trails (e.g.
Fig. 6, 30%O₂/70%CO₂, 8 ms, Fig. 7, 21%O₂/79%N₂, 23 ms), forming condensed matter around a particle. In the regions where there are no jets of volatiles, there is a possibility of heterogeneous surface reaction with oxygen. The temperatures of most bituminous chars experienced small variations with time, whereas the radiation intensity and particle diameter plateaued for a time and then, slowly decreased. This behavior of the bituminous particles is clearly illustrated in the cinematographic images (see Figs. 6 and 7), and has been well documented in the literature [4, 14, 21, 23, 24].

6.4.3. Effect of fuel type on temperature and burnout time

The burnout time data and temperatures are shown in Figs. 11 and 12, respectively. The pyrometric burnout times are based on the duration of the pyrometer signal from its onset (particle ignition) to its termination (particle extinction), both defined herein when the highest-intensity signal (λ = 998 nm) of a particular event exceeds the baseline by a factor of at least ten, i.e., $S_{signal}/S_{baseline} > 10$. The temperatures displayed were the maximum temperatures deduced from the single particle combustion histories (as exemplified in Fig. 3). Each data point represents the mean values from at least 15-20 individual particle combustion events.
Figure 11. Average burnout times for the four coals (a-d) studied in air and different oxy-fuel environments. The error bars represent standard deviations of the data (2σ).
In this sub-section only the examples in the air atmosphere are described for a clearer comparison between the coals. The burnout times of the bituminous particles were much shorter than the burnout times of the anthracitic particles. This may be due to the higher volatile matter content of the bituminous coals (which enhances subsequent char combustion), and to their higher reactivity. As high rank coals release few volatiles, there were very small differences between the chars and the original coal particles. On the other hand, in the case of the bituminous coals, their chars showed significant signs of swelling after devolatilization [19]. This created more specific surface area, and therefore enhanced particle reactivity. As can be seen from Fig. 11, the burnout times in air for the anthracitic coals were the longest, 294 ms and 215 ms for AC.
and HVN, respectively; whereas for bituminous coals UM and SAB the burnout times were 114 ms and 86 ms, respectively.

As can be seen in the cinematographic records, bituminous coals displayed a tendency to burn in two-mode combustion. Volatiles often contain a large amount of stored energy (heating value) and, as can be seen in Fig. 12, the combustion of volatiles was the hottest and the fastest (typically lasting 10-15 ms in air). Lower temperatures were reached during char combustion. The high-volatile bituminous SAB coal contained the highest amount of volatile matter. The average temperatures reached during its combustion in air were also the highest, 2079 K and 1795 K for volatiles and char, respectively, whereas in the combustion of the medium volatile bituminous UM coal in air, which has a lower volatile matter content, average temperatures of 1967 K and 1686 K were reached for volatiles and char, respectively. On the other hand, anthracitic coals burned in one-mode combustion by direct attack of oxygen on the char surface. During the combustion of AC and HVN in air, the average char temperatures reached were 1825 K and 1811 K, respectively.

6.4.4. Effect of the diluent background gases (N₂ and CO₂) and oxygen mole fraction on temperatures and burnout times

As can be seen in Fig. 12 the particle temperatures (in the case of bituminous coals for both volatiles and chars) were higher during their combustion in 21%O₂/79%N₂ than in 21%O₂/79%CO₂, whereas their corresponding burnout times were shorter (see Fig. 11). A factor controlling the particle temperatures is the volumetric heat capacity of the surrounding gas mixture, which is higher in O₂/CO₂ than in O₂/N₂, atmospheres causing both the volatile matter flame temperatures and the char temperatures to drop [4, 8, 25]. Other important factors which
influence char combustion temperature are the lower binary diffusion of O$_2$ in CO$_2$ and the endothermicity of the char-CO$_2$ reactions [25, 26, 27]. Larger CO concentrations, formed partly due to incomplete combustion of the volatiles, and partly driven from char CO$_2$ gasification reactions, would also contribute to the worsening of the burning properties of the coal, by forming a persistent cloud around the particle, thereby preventing the access of oxygen to the surface of the particle [17].

The particle temperature (in the case of the bituminous coals for both the char and the volatiles) increased and the burnout times decreased with the enhancement of the oxygen content in the CO$_2$ mixture. However, the shortening in the burnout times and the enhancement of temperatures was not the same for all the coals studied. It was more marked in the case of the anthracitic coals since the bituminous coals reached a high burnout value in atmospheres with lower oxygen content (i.e., 21%O$_2$/79%N$_2$ and 21%O$_2$/79%CO$_2$) [28]. Increasing the O$_2$ percentage in the CO$_2$ mixture up to 50% was still insufficient to match the heat capacity of air (Heat capacity of pure gases (at 1400K) are N$_2$ 34.18kJ/kmol-K; O$_2$ 36.08 kJ/kmol-K and CO$_2$ 57.83kJ/kmol-K). Therefore, heat capacity of the air and some of the O$_2$/CO$_2$ environments in this study are: Air=34.6 kJ/kmol-K, 21%O$_2$/79%CO$_2$=53.3 kJ/kmol-K, 50%O$_2$/50%CO$_2$= 47 kJ/kmol-K). However, the rise in the mass flux rate increased the reactivity characteristic of the local mixture [27]. Bejarano et al. [8] found that the higher the oxygen mole fraction, the higher the char surface temperature and the shorter the burnout time. In addition, if there is sufficient oxygen, the homogeneous combustion of the gasification-derived CO to CO$_2$ could provide extra heat. Joutsenoja et al. [29] measured temperature snapshots of burning single particles in an entrained flow reactor using a pyrometric method, when the oxygen mole fraction ranged
between 3 and 30% and they also reported that the particle temperature increased with oxygen mole fraction.

In summary, coals burned hotter and faster in N₂ than in CO₂ background gases at comparable oxygen mole fractions. To attain the same volatiles flame and char temperatures as in air (21%O₂), the oxygen content in CO₂ mixtures had to be increased to ~35% for these bituminous coals, and to ~30% for these anthracitic coals. The values of oxygen needed to achieve the same particle char and volatiles temperatures in oxy-fuel conditions as in air-firing, are shown in Table 2. Increasing the oxygen concentration to such values also led to shortened burnout times and temperature hikes, although they are less remarkable. These results are in agreement with previous studies carried out for other fuels with different experimental devices [10, 30, 31]. These observations have practical ramifications in the operation of future furnaces operating under oxy-coal combustion conditions. The successful implementation of O₂/CO₂ technology in conventional pulverized coal boilers requires a full understanding of the changes that occur when N₂ is replaced by CO₂ in a combustion atmosphere; this is essential for designing and modeling oxy-fuel combustion at an industrial scale. One should keep in mind however, that had combustion occurred in active flow conditions in the furnace and not under the quiescent conditions of this study (which resulted in the gas temperature profiles depicted in Fig.2) the O₂/CO₂ gas temperatures would have been lower than the O₂/N₂ gas temperatures, since CO₂ heats up slower [5]. This would have resulted in lower coal particle temperatures in CO₂ background gases than those reported herein. Hence, somewhat higher oxygen mole fractions in CO₂ would have been needed than those shown in Table 2 to match the particle temperatures in conventional air combustion. Alternatively, preheating of the O₂/CO₂ gases
could have been implemented to compensate for their slower heating in the furnace. In this case the mole fractions listed in Table 2 may still be valid, depending on the degree of preheating.

**Table 2.** Oxygen content in the O\textsubscript{2}/CO\textsubscript{2} required to achieve the same char and volatile temperature as in air-firing conditions.

<table>
<thead>
<tr>
<th>Equivalent T\textsubscript{volatile}</th>
<th>AC</th>
<th>HVN</th>
<th>UM</th>
<th>SAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent T\textsubscript{char}</td>
<td>32.8</td>
<td>31.5</td>
<td>29.4</td>
<td>34.1</td>
</tr>
</tbody>
</table>

6.4.5. Effect of volatile matter (VM) content on the volatile flame burnout times

Figure 13 shows the volatile flame burnout times of the different coals in this study versus volatile matter content of the fuels burning in air and in various O\textsubscript{2}/CO\textsubscript{2} atmospheres. The volatile burnout times increased linearly with increasing volatile matter content (VM) of the coals in all gas environments. The linear dependency equations of volatile burnout times (t\textsubscript{volatiles}) and volatile matter content in the coal (VM) are shown in Fig 13. It should be mentioned that the linear equations in Fig.13 were derived for the experimental conditions of this study (i.e., T\textsubscript{f}=1400 K and particle sizes 75-150µm) and may not be necessarily valid for different experimental/operating conditions.
Figure 13. Average observed volatile burnout times versus volatile matter content (VM) of the coals. The experiment was performed at 1400 K furnace temperature with particle diameters in the range 75 µm to 150 µm.

6.4.6. Effect of carbon content (C) on the char burnout times

Figure 14 shows the char burnout times of different coals versus carbon content of the fuels burning in air and in various O₂/CO₂ atmospheres. The char burnout times increased with increasing carbon content (C) of the coals in all gas environments. However, the dependency of char burnout times versus carbon content (C) was quadratic for air and lower oxygen mole fractions in CO₂ (21%O₂), whereas this dependency became linear at higher O₂ mole fractions (35%O₂, 50%O₂). The quadratic and linear equations of char burnout times (t_char) versus carbon content of the coal (C) are also displayed in Fig. 14. It should be again mentioned that the equations shown in Fig. 14 were derived for the experimental conditions of this study (T_f=1400 K and particle sizes 75-150µm) and, again, may not be necessarily valid for different experimental/operating conditions.
Figure 14. Average char burnout times versus carbon content (C) of the coals. The experiment was performed at 1400 K furnace temperature with particle diameters in the range 75 µm to 150 µm.

6.5. Conclusions

Pulverized fuel particles (75-150 µm) from four high and medium rank coals were burned in a drop-tube furnace, set at 1400 K under air and simulated dry oxy-firing conditions. The goal was to assess the ignition and combustion behaviors of single coal particles in different combustion atmospheres with combined cinematographic and pyrometric diagnostic tools. The most important conclusions are as follows:

(a) High rank coals (anthracite and semi-anthracite) ignited heterogeneously from the particle surface, whereas bituminous coals ignited in the gas phase (homogeneously).
(b) Ignition temperatures increased with the enhancement of coal rank in either air or oxy-fuel combustion conditions. However, increasing oxygen mole fraction from 21% to 50% in CO₂ decreased the ignition temperature for all coals.
(c) Replacing the N₂ in air by CO₂ slightly increased the ignition temperature (30-40K).
(d) The two bituminous coal particles tested burned with distinct volatile matter and char combustion phases (i.e., two-mode combustion), whereas the anthracitic and most semi-anthracite coal particles burned in a single combustion phase, which was mostly attributed to char. The temperatures of the bituminous coal char particles were lower than those of the anthracitic coals, and their combustion durations were much shorter.

(e) For the four coals studied, particle luminosity and the deduced temperatures were higher in the 21%O₂/79%N₂ atmosphere than in 21%O₂/79%CO₂. The replacement of N₂ by CO₂ reduced the bituminous volatiles flame temperatures by as much as 210 K, and coal char surface temperatures by as much as 140 K, at comparable oxygen mole fractions. The corresponding drop for anthracitic coals was around 125 K. The combustion times increased by as much as 60 ms in the case of the anthracitic coals, and 30 ms in the case of bituminous coals.

(f) As the oxygen concentration in the CO₂ mixtures increased from 21% to 50%, the temperature of the char particles increased up to 320 K for the anthracitic coals and 310 K for the bituminous coals. The temperature of the volatiles increased by as much as 400 K for the bituminous coals. Also an important reduction in burnout time was observed, especially in the case of anthracitic coals.

(g) Equivalent bituminous coal volatiles and char temperatures as well as burnout times to those measured in air were attained when the oxygen content in the CO₂ mixtures was ~30-35%. This observation has practical ramifications in the operation of practical systems.

(h) The volatile burnout times increased linearly with increasing volatile matter content (VM) of the coals in all gas environments.
(i) The dependency of char burnout times versus carbon content (C) was quadratic for air and lower oxygen mole fractions in CO\textsubscript{2} (21%O\textsubscript{2}) while this dependency was linear at higher O\textsubscript{2} mole fractions (35%O\textsubscript{2}, 50%O\textsubscript{2}).

6.6. References


6.7. Appendix

Calculation of diffusion-limited burnout times

The average oxygen mole fraction on the char particle surface can be estimated by the following formula [32]:

\[
y_{O_2,s} = (4/3 + y_{O_2,\infty}) e^{-\left(\frac{2RT_\infty p_c}{56R_T D_{mol,\infty}}\right)} - \frac{4}{3}
\]  

(A.1)

In this relation, \( y_{O_2} \) is assumed to be an average value. \( a_i, \rho_c, T_m, D, t_B, R \) and \( P_{tot} \) are initial burning particle radius, initial particle density, film temperature between the char particle and flow, bulk diffusion coefficient of \( O_2 \) in the diluents gas, observed particle burnout time, gas universal constant and total pressure of the system, respectively.

If \( y_{O_2,s} \) is zero or close to zero, the combustion takes place at diffusion limited conditions (Regime III), whereas if \( y_{O_2,s} \) is close to \( y_{O_2,\infty} \), the combustion occurs at kinetically limited conditions (Regime I). Any \( y_{O_2,s} \) in-between the above values results in kinetic-diffusion limited condition (Regime II).

The time \( t_B \) required for combustion under diffusion control (Regime III) becomes [32]:
In Eq. A.2, \(a_f\) is the final particle radius after extinction, which herein is calculated based on the ash content in the parent coal composition and assuming shrinking core combustion and comparable char and ash residue densities [14].

For instance, for anthracite (AC) burning in air with the observed parameters of this study
\[a_0=56.25 (\mu m), a_f=19 (\mu m), \rho_c=1 (g/cm^3)\] [33], \(T_m=1612 K, P_{tot}=1\) (atm), \(D_{O2,N2}=3.37\) (cm²/s), \(t_{B-obs}=294\) (ms), \(R=82\) (atm.cm³/mol.K), oxygen mole fraction on the particle surface from A.1, \(y_{O_2,s}\), was calculated to be 0.09 and the diffusion limited burnout time from A.2, \(t_B\), was calculated to be 134 (ms). On the other hand, for anthracite (AC) burning in 21%O₂-79%CO₂, \(T_m=1550 K, D_{O2-CO2}=2.63\) (cm²/s), \(t_{B-obs}=358\) (ms) and the rest of parameters are similar to those of combustion in air. In this case, oxygen mole fraction on the particle surface from A.1, \(y_{O_2,s}\), was 0.09 and the diffusion limited burnout time from A.2, \(t_B\), was 165 (ms). Therefore, under the experimental conditions of this study, combustion of anthracite in either air or oxy-fuel condition (21%O₂/79%CO₂) took place in Regime II which is a combination of kinetic and diffusion limited cases.

The resulted observed burnout times and calculated diffusion limited burnout times versus oxygen concentration for anthracite (AC), semi-anthracite (HV) and one of the bituminous coals (SAB) in different oxy-fuel condition is shown in Fig. A.1.
Figure A.1. Comparison of experimentally-observed and calculated diffusion-limited burnout times of anthracite, semi-anthracite and bituminous char particles, plotted against bulk oxygen mole fraction.
7. Soot loading, temperature and size of envelope flames of coal particles in conventional- and oxy- combustion conditions (O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2})

Abstract

This work assesses instantaneous spatially-average soot loading of volatile matter envelope flames forming around burning single coal particles. Flame temperature and size were also calculated simultaneously. Three different bituminous coals were monitored in both conventional air combustion and simulated oxy-fuel combustion; O\textsubscript{2} varied between 20-100\% in either N\textsubscript{2} or CO\textsubscript{2}. Single particles, 75-90 \textmu m, were injected and burned in a transparent drop-tube furnace (DTF), set at a wall temperature of 1400K, and were monitored by optical pyrometry and high-speed cinematography. The free falling bituminous coal particles formed bright volatile matter envelope flames with soot contrails. Since particle temperatures and burnout times were investigated in past research in this laboratory, this work focuses on the soot loading of the coal particle flames. Different models were used for calculating soot volume fractions and results were all within a factor of 1.5. Under similar conditions, all bituminous coal flames had similar soot volume fractions, in the range of 20-90 ppm. At similar furnace gas temperatures and comparable O\textsubscript{2} mole fractions, when the background N\textsubscript{2} gas was replaced with CO\textsubscript{2} the particle envelope flames of all fuels were characterized by lower soot volume fractions, lower temperatures and bigger luminous areas. When the O\textsubscript{2} mole fraction increased in either N\textsubscript{2} or CO\textsubscript{2} background gases, particle envelope flames of the fuels were characterized by initially increasing–then decreasing soot volume fractions, monotonically-increasing temperatures and decreasing sizes.
7.1. Introduction

Soot consists of submicron carbonaceous particles which form in the pyrolysis of hydrocarbon fuels. During combustion of solid fuels, such as coal, soot is generated when volatile matter undergoes secondary reactions at high temperatures in an oxygen deficient environment [1]. Soot is important to combustion systems because of its radiative heat transfer effects and its pollution potential if not burned in the flame envelope [1, 2].

Observations on the volatile flames of single coal particles have been made by a number of research groups, including [2, 3, 4, 5, 6, 7]. McLean et al. [3] observed that during combustion of bituminous coal particles a condensed soot-like phase formed by released volatile matter, which was then either consumed under oxidizing conditions or persisted throughout the reactor under reduced oxygen conditions. Seeker et al. [4] observed trails of soot during volatile combustion of large bituminous particles (>80 µm); however, they didn’t observe trails of soot for either small bituminous particles or lignite or anthracite particles.

In furnaces, contributions to radiation heat transfer stem from soot in volatile flames, burning chars and gas. Evidence of the dominant role of soot luminosity in radiation heat transfer of furnace flames has been long standing [8]. Soot volume fraction has been identified as the geometric feature of soot that affects radiation rather than particle sizes and shapes [9]. The soot volume fraction of a coal flame, \( f_v \), along with its temperature, is a key parameter in determining the radiative heat transfer in a furnace [10], as illustrated by the following equation: 
\[
E_{\text{total}} = \varepsilon_{\text{total}} A \sigma T^4 \Delta t, \quad \text{where:} \quad \varepsilon_{\text{total}} = 1 - \left[1 + k f_v L T / c_2\right]^{-4} \]
[8].

The formation of soot during combustion of bituminous coals was studied by Timothy et al. [2] in various \( O_2/N_2 \) environments, using optical pyrometry and high-speed photography. They
proposed a nearly-spherical soot shell model to quantify the soot concentration. Panagiotou et al. [11] applied Timothy’s model [2] to estimate $f_v$ in the volatile flames of spherical and monodisperse particles of polystyrene, burning in air, based on pyrometric measurements. They reported $f_v$ in the range of 4 - 40 ppm.

Recently, oxy-fuel combustion is considered an emerging and viable technology to reduce emissions of pollutants and facilitate capture and sequestration of CO$_2$, a greenhouse gas [12]. Although many aspects of this technology have been studied [12], only few investigations have reported on soot emissions relevant to oxy-fuel combustion [13, 14, 15]. Morris et al. [13, 14] reported that burning a bituminous coal under both simulated oxy-fired and actual recycled flue gas conditions produced a lesser amount of soot than under conventional air conditions, whereas Stimpson et al. [15] concluded that the air-fired flames produced less unburned soot than the oxy-fired flames.

Although the aforementioned investigations have been performed on clouds of coal particles burning under oxy-combustion conditions [13-15], fundamental work on the soot volume fraction, $f_v$, in volatile matter flames of single particles under such conditions is scarce. Information on soot volume fractions is essential for heat transfer and CFD modeling of new generation burners and boilers operating at oxy-fuel combustion conditions. Herein, an emission-based method is introduced to calculate $f_v$ in volatile envelope flames of single coal particles. This method is based on pyrometric combustion data in conjunction with different models for assessing soot volume fractions. This investigation expands on relevant preliminary previous work in this laboratory [16]. It (a) develops models for calculating soot volume fractions in particle envelope flames, (b) reports on absolute values of instantaneous and temporally-average soot volume fractions in such flames in conventional air combustion, to complement information
in the literature, (c) provides new information on instantaneous and temporally-average soot volume fractions in such flames in simulated oxy-coal combustion, and (d) demonstrates the similarity of soot loading values for three bituminous coals of disparate origins.

7.2. Experimental approach

The proximate and ultimate analyses of the fuels are shown in Table 1. Data for the coals were obtained from the Penn State Coal Sample Bank in the US (for PSOC-1451) and from the Institute National del Carbon (INCAR-CSIC) in Spain (for SAB and UM). All fuels were dried, ground and sieved to 75-90 μm, to be consistent with previous experiments [5-7,17,18].

**Table 1. Chemical Composition of the Bituminous Coals from different sources [24]**

<table>
<thead>
<tr>
<th>Rank and Fuel Source</th>
<th>Bituminous High Volatile A Pittsburgh #8 Pennsylvania</th>
<th>Bituminous High Volatile (hvb) S. Africa</th>
<th>Bituminous Medium Volatile (mvb) Mexico</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel name</td>
<td>PSOC-1451</td>
<td>SAB</td>
<td>UM</td>
</tr>
<tr>
<td>Proximate Analysis (as received)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>33.6</td>
<td>29.9</td>
<td>23.7</td>
</tr>
<tr>
<td>Fixed Carbon (%)</td>
<td>50.6</td>
<td>55.1</td>
<td>55.2</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>13.3</td>
<td>15.0</td>
<td>21.1</td>
</tr>
<tr>
<td>Ultimate Analysis (on a dry basis)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>71.9</td>
<td>81.5</td>
<td>86.2</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>4.7</td>
<td>5.0</td>
<td>5.5</td>
</tr>
<tr>
<td>Oxygen (%) (by diff.)</td>
<td>6.9</td>
<td>10.5</td>
<td>5.9</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>1.4</td>
<td>2.1</td>
<td>1.6</td>
</tr>
<tr>
<td>Sulfur (%)</td>
<td>1.4</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Sodium (%)</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash (%)</td>
<td>13.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heating Value Dry Fuel (MJ/kg)</td>
<td>31.5</td>
<td>27.8</td>
<td>27.8</td>
</tr>
</tbody>
</table>

Combustion of free-falling coal particles was carried out in an electrically heated, laminar flow drop tube furnace (DTF) at a wall temperature, $T_w$, of 1400K [5-7,17,18]. Gas was introduced to the radiation cavity of the furnace through a water-cooled stainless-steel injector (1
cm I.D.) as well as coaxially through a flow straightener. Optical pyrometric access to the radiation zone of the furnace was achieved from the top, through the particle injector, whereas simultaneous high-speed cinematography was performed from the sides [6, 7]. Entire luminous burnout histories of single particles were monitored. Pyrometer filters with effective wavelengths of 640, 810 and 998 nm, and bandwidths (FWHM) of 70 nm were used; other details are given in Refs. [19] and [20]. The baseline gas condition was air, and O2 mole fraction increased from 21% to 100% in either N2 or CO2 background gases. Coal particle combustion experiments were conducted under a quiescent gas condition to equalize gas temperatures in N2 and CO2 cases [5]. At $T_w=1400$ K, axial gas temperature profiles in either N2 or CO2 environments increased along the centerline of the furnace and stabilized at 1340 K [5].

7.3. Theoretical models for deduction of soot volume fraction

Herein, three different models are presented for calculating the soot volume fraction in flames, based on pyrometric measurements of emitted radiation intensity signals from burning single particles of coal. The first two models use the linear least square pyrometric method of Khatami and Levendis [20] in conjunction with two different soot emissivity functions: (a) one proposed by Hottel and Broughton [8, 21] based on soot particles whose sizes satisfies ($\pi D_{soot} > 5\lambda$), and (b) one attributed to Rayleigh [22, 23] based on soot particles whose sizes satisfies ($\pi D_{soot} < 0.6\lambda/n$). Using the aforementioned linear least square pyrometric method, flame temperatures and sizes can also be calculated along with emissivity, based on these functions. The third model (formulated Timothy et al. [2]), is a method which was specifically developed for ratio pyrometry. This method does not calculate flame temperatures, thus temperatures were separately calculated by the aforementioned linear least square pyrometric method using the gray
body assumption [11], as previously outlined [20] and documented [24], and were then input to this model.

7.3.1. The non-linear least square pyrometric method in conjunction with emissivity functions

The non-linear least square method for calculating temperatures, formulated by Khatami and Levendis [20], was modified for simultaneous measurement of flame temperature, soot volume fraction and size:

\[ \sum_{i=1}^{N} \Delta T_i^2 = \sum_{i=1}^{N} (S_i - s_i)^2 \]  

\[ s_i = C_i A \int_{\lambda_1}^{\lambda_2} \varepsilon_{\lambda i} \frac{I_{\lambda b}(\lambda) g_i(\lambda)}{\lambda} d\lambda \]  

\( S_i \) is the experimental pyrometric wavelength at channel i, \( I_{\lambda b} \) is Planck’s spectral radiation intensity of a blackbody surface, \( A \) is the radiative area, \( g_i(\lambda) \) is the geometric factor of the setup [20], and \( \varepsilon_{\lambda i} \) is the emissivity. As mentioned before two different functions were used for emissivity: Hottel and Broughton’s (for \( \pi D > 5\lambda \)), and Rayleigh’s (for \( \pi D < 0.6\lambda/n \)):

(i) Hottel and Broughton [21] proposed Eq. (3) to estimate the spectral emissivity of sooty flames:

\[ \varepsilon_{\lambda i} = 1 - \exp\left(-\frac{0.526SL}{A^{1/3}}\right) \]  

They mentioned that the monochromatic emissivity of a gas due to its soot content does depends on temperature \( T \), soot path length, \( L \), and soot mole fraction (moles of carbon per mole of gas), \( S \), in the gas. \( L \) was estimated according to Hottel [8, 21], as \( L = 3.6 V/A \sim A^{1/2} \) where \( V \) is the volume of the flame, detected cinematographically. They also measured \( \alpha \) to
be 1.39 for visible and 0.95 for infrared wavelengths. Upon substitution of Eq. (3) into Eq. (2) for each wavelength, $T$, $SL$ and $A$ are the unknowns. Assuming that the volatile flame gases are ideal, the soot mole fraction, $S$, is related to the volumetric soot concentration, $f_v$, by:

$$S = f_v \left( \frac{\rho_{\text{soot}}RT}{MW_{\text{soot}}P_{\text{total}}} \right)$$

(4)

Therefore, the aforementioned least square method becomes:

$$\sum^3_{i=1} \lambda^2 \sum^3_{i=1} (c_i - c_i A \int_{\lambda_i} (1 - \exp(-\frac{0.526 f_{\text{soot}}RT}{MW_{\text{soot}}P_{\text{total}}}) \frac{\phi}{\lambda^2} \frac{\lambda^4}{x^5 (\phi^{x/2} - 1) - 1} c_i)^2)$$

(5)

Eq. (5) is a function of $T, f_v$ and $A$.

(ii) Rayleigh’s emissivity function is [22]:

$$\varepsilon_{\lambda} = 1 - \exp(-\frac{F_{\lambda}}{2}) f_v L$$

(6)

$$F_{\lambda} = \frac{36\pi nk}{(n^2 - k^2 + 2)^2 + 4(nk)^2}$$

(7)

The most important assumption in the Rayleigh approach is that the soot particles are sufficiently small [23]. $F_{\lambda}$ is the absorption coefficient of soot; $f_v$ is the soot volume fraction; $n$ and $k$ are real and imaginary parts of the soot refractive index, respectively [25-30]. $F_{\lambda}, n$ and $k$ are wavelength dependent parameters. Therefore:

$$\sum^3_{i=1} \lambda^2 \sum^3_{i=1} (c_i - c_i A \int_{\lambda_i} (1 - \exp(-\frac{36\pi nk}{(n^2 - k^2 + 2)^2 + 4(nk)^2}) \frac{\phi}{\lambda^2} \frac{\lambda^4}{x^5 (\phi^{x/2} - 1) - 1} c_i)^2)$$

(8)

Eq. (8) is a function of $T, f_v$ and $A$. 

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The following three equations were solved simultaneously to minimize the error function

\[ \sum \Delta_i^2 \] in Eqs. 5 or 8 and deduce \( T, f_v \) and \( A \):

\[
\frac{\partial}{\partial T} \sum_{i=1}^{3} \Delta_i^2 = 0, \quad \frac{\partial}{\partial f_v} \sum_{i=1}^{3} \Delta_i^2 = 0, \quad \frac{\partial}{\partial A} \sum_{i=1}^{3} \Delta_i^2 = 0 \tag{9}
\]

The solution of Eqs. (9) is subject to the inequality constraints of 1000 < \( T < 3000 \) K, 0 < \( d < 1000 \) \( \mu m \) and \( 10^{-3} < f_v < 10^{-9} \). The optimization scheme will be discussed briefly in Section 3.3.

7.3.2. The model of Timothy, Sarofim, Froelich and Beer

Based on experimental observations, Timothy et al. [2] formulated a semi-empirical model to determine the radiation intensity of a coal particle in a furnace surrounded by an optically thin spherical shell of isothermal soot (see Ref. [2]-Fig. 3). Moreover, particle temperatures need to be obtained prior to \( f_v \) deduction. In this case they were obtained with the pyrometric non-linear least square method [20] with the gray emissivity assumption. Panagiotou et al. [11] manipulated Timothy’s model [2] according to parameters of this experimental setup (\( \gamma_p = D_{pp}/D_f \), \( \gamma_r = D_r/D_f \)):

\[
\frac{s_{p,i}}{s_{r,i}} = \frac{(\pi a^2/12 \times d_r^3) \times (F_{\lambda} / D_{pp}) \times \left[0 - (1 - \gamma_p)^2 + (1 - \gamma_r)^2 - (\gamma_r - \gamma_p)^2\right]}{\varepsilon_{r,i} \frac{\pi D_{pp}^3}{4 d_r^2} \times \frac{1}{\varepsilon_{r,i} \gamma_p - 1}} \tag{10}
\]

Subscripts \( p, f, ins \) and \( r \) refer to particle, flame, instantaneous inside flame and reference source characteristics, respectively. \( D_p \) and \( d \) stand for particle and flame diameters. The reference data in the denominator of Eq. (10) is obtained from calibration sources with known signal, temperature, emissivity and pinhole diameter [17, 19, 20]. \( F_{\lambda} \) is the absorption coefficient of
soot (Eq. 8). Using the experimental pyrometric signals for the coal particle and reference source
\( S_{p,\lambda} \) and \( S_{r,\lambda} \), the \( f_v \) history of the flame was determined, as illustrated in Ref. [16].

7.3.3. Refractive indices

According to the aforementioned models, refractive indices of soot particles are extremely important parameters in \( f_v \) deduction. Since non-agglomerated soot particles are typically very small (5-80 nm), they are assumed to be at the temperature of the ambient gas [31] and, they strongly emit thermal radiation in the visible and infrared wavelength regions. Six published expressions of refractive indices [25-30] were employed to investigate the effect of refractive index models on particle soot volume fractions. In the wavelength range of 0.65 \( \mu \)m - 1 \( \mu \)m refractive indices variations are in the ranges of 1.65 \( < n < 1.95 \) and 0.5 \( < k < 1 \) [25-30].

7.3.4. Computational considerations

Pyrometric signal files were acquired using the LabView 8.6 software using the Model PCI-6221 sample collection card, at an output sampling rate of 65 (samples/channel)/ms. A computer code has been written in MATLAB to calculate flame temperatures-time, soot volume fractions-time and average flame diameters-time histories for burning particles using least square method with either Rayleigh or Hottel approximations. An optimization method with the interior-point approach for constrained minimization (MATLAB help v.12) is implemented to solve inequality constraint problems as formulated in Eqs. (5) and (6) and Eqs. (9) and (10). In Timothy’s model, Eq. (11) was explicitly solved to attain real time \( f_v \) profiles.
7.4. Results and Discussion

7.4.1. Cinematographic observations

Snapshot images from high-speed, high-resolution cinematography of fuel particles burning in air and in selected simulated oxy-fuel conditions are displayed in Fig.1. As this work focuses on the volatile flame, only that phase of the particle combustion history is displayed. Coal particles travelled fast under gravity in the quiescent conditions of the DTF, forming soot contrails.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Bituminous Coals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size bar: 100 μm</td>
<td>PSOC-1451 SAB UM</td>
</tr>
<tr>
<td>Air</td>
<td>![Image]</td>
</tr>
<tr>
<td>21%O₂-79%CO₂</td>
<td>![Image]</td>
</tr>
<tr>
<td>30%O₂-70%CO₂</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

Figure 1: Snapshot images from high-speed cinematography of typical volatile flames enveloping 75-90 μm particles, in O₂/N₂ and O₂/CO₂ environments. The diameter of the wire shown in some photographs is 70 μm.

7.4.2. Pyrometric results

Representative pyrometric radiation intensity signals of single fuel particles and associated temperature, mean diameter and soot volume fraction profiles, deduced from Eqs.(5-6) and Eqs. (9-10) and aforementioned computer codes, are shown in Fig.2. These plots show the histories of the radiation-relevant parameters of the flame including temperature, soot volume fraction and flame size throughout entire volatile combustion durations of individual particles. The
aforementioned models were employed for the soot volume fraction determinations. As the model that uses the Rayleigh emissivity function was deemed to be most appropriate for the small soot particles in the envelope flames, it was given more prominent status ($\pi D_{\text{soot}} < 0.6\lambda/n$, hence as $\lambda \approx 1 \, \mu m$, and the refractive index $n \approx 1.8$ then $D_{\text{soot}} < 330 \, \text{nm}$). However the Hottel and Broughton ($\pi D_{\text{soot}} > 5\lambda$, hence as $\lambda \approx 1 \, \mu m$, $D_{\text{soot}} > 1.6 \, \mu m$) that uses an emissivity function appropriate for bigger size particles may be relevant to agglomerated soot, which is present in soot contrails as documented by Panagiotou et al. [11, Fig. 7]. Such contrails are in the pyrometer’s line of view, as observations are conducted from the top of the furnace where particles were allowed to free-fall. Finally the model of Timothy et al. is also meritorious, but since the soot temperature herein was calculated separately with a gray body emissivity it was mostly used for comparison in this work. The soot volume fractions and temperatures from the different models are compared in a subsequent section (sensitivity analysis) to show the consistency of the results.

Figure 2: Typical three color (998, 810 and 640nm) pyrometric time-profiles of signal intensities, flame temperatures, flame diameter and soot volume fractions of (a) bituminous (PSOC-1451) and (b)
bituminous (SAB), (c) bituminous (UM) particles burning in air. Calculations were performed using the using the non-linear least-square pyrometric method in conjunction with the Rayleigh emissivity function.

7.4.3. Effects of fuel type

Average of peak $f_v$ values encountered in $f_v$-time profiles of the three bituminous coals of this study are shown in Fig.3. Although the same rank coals were chosen from three different sources and locations, the soot volume fractions of the three bituminous coals are comparable in all O$_2$ mole fractions. SAB flames had slightly lower soot volume fractions, perhaps since this coal contains more oxygen in its structure. UM is a medium volatile bituminous coal and contains less volatile matter than the other two coals, hence UM may be expected to contain less soot. However, UM contained less oxygen in its structure than the other two coals thus, as a result, its soot volume fractions were similar to those of PSOC-1451.

![Figure 3](image)

**Figure 3:** Effect of fuel type: peak soot volume fractions, averaged over many particles, in envelope flames of bituminous coal particles (PSOC-1451, SAB and UM) burning in N$_2$ background gas.

7.4.4. Effect of replacement of background N$_2$ by CO$_2$

Replacement of N$_2$ by CO$_2$ decreased the average $f_v$, as seen in Figs 3 and 4. At 21% O$_2$ in CO$_2$, the luminosity of flames was low and the $f_v$ was also considerably low (in the case of
PSOC-1451 coal by a factor of 4 lower than in air). At higher O₂ mole fractions in CO₂, \( f_v \) was lower (by a factor of 2 for the aforesaid coal) than the corresponding values in N₂. Lower soot/flame temperatures and soot gasification in CO₂ environments are likely responsible for this behavior.

### 7.4.5. Effect of O₂ mole fraction

As shown in Figs 3 and 4, increasing O₂ mole fraction in either N₂ or CO₂ environments enhanced the average \( f_v \) to peak values around 30-40% O₂. This may be attributed to competition of soot formation and oxidation mechanisms, as both the flame temperature and the availability of O₂ in the flame zone increases [32]. Thereafter, average \( f_v \) decreases with increasing O₂ due to the combination of elevated temperatures, abundant oxygen and oxidizing radicals (OH, O) which brink the coal particle envelope flames closer to the char surface, suppress soot formation and promote its oxidation. Soot volume fractions of bituminous coal particle flames in air and in higher O₂ concentrations in N₂ are in the range 20-90 ppm (2×10⁻⁵ - 9×10⁻⁵), in line with calculations based on findings in Ref.[2].

**Figure 4:** Effect of O₂ mole fraction and N₂/CO₂: peak soot volume fractions, averaged over many particles, in envelope flames of bituminous coal particles (PSOC-1451) burning in N₂ and CO₂ background gases.
Figure 5: Flame size contraction: peak soot volume fractions, averaged over many particles, in envelope flames of bituminous coal particles (PSOC-1451) burning in N\textsubscript{2} and CO\textsubscript{2} background gases.

7.4.6. Sensitivity analysis

7.4.6.1. Effect of model on flame temperature and soot volume fraction

Soot volume fractions, \( f_v \), and flame temperatures, \( T \), based on the three aforementioned models are shown in Fig. 6. Although \( f_v \) and \( T \) trends are similar for all three models, the values of \( f_v \) differ by up to 35%, whereas the values of \( T \) differ by up to 5-10% (60-180 K). Timothy’s method results in the lowest values \( f_v \) and \( T \), Rayleigh’s approximation in the highest and Hottel’s method lies in between. Other researchers [23] also reported higher pyrometric soot temperatures by Rayleigh’s than by Hottel’s model. The lower \( f_v \) from Timothy’s model may be due to the soot shell approximation in that method, which does not account for the entire flame volume and contrail. The higher \( f_v \) predictions of Rayleigh may be related to the assumption of small soot particle size which results in a higher particle density in a specific flame volume.
Figure 6: Comparison of results from the Rayleigh, Hottel and Timothy models. On the left: peak soot volume fractions, averaged over many particles, in envelope flames of bituminous coal particles (PSOC-1451) burning in N₂ and CO₂ background gases. On the right deduced flame temperatures; the temperature corresponding to the Timothy model was deduced based on the gray body radiation assumption and corresponds to values reported in [32].

Although the soot path length, \( L \), was treated as a function of flame diameter as mentioned above, it was also perturbed in all Hottel and Rayleigh models in the range of 1/2-1/8 flame diameter; differences in the results were not significant.

7.4.6.2. Effect of refractive indices \((n, k)\)

The chemical composition and structure of soot particles depend on fuel type and combustion conditions [26]. Therefore, the optical constants of soot may differ from those of pure graphite. Optical constants (refractive indices) from six different studies [25-30] were tested in Fig.7 to investigate the sensitivity of the \( f_v \) on these parameters; disparities in values reported therein are due to different measurement methods and different fuel feedstocks. Optical constants from Dalzell and Sarofim[26], Lee and Tien[27] and Chang et al.[29] produced similar \( f_v \), whereas those from Stull [25], Blokh[28] and Krishnan[30] resulted in 50% lower \( f_v \) values in 20-40% O₂. At higher O₂, differences in \( f_v \) values became less pronounced.
Figure 7: Effect of optical constants (different refractive indices): peak soot volume fractions, averaged over many particles, in envelope flames of bituminous coal particles (PSOC-1451) burning in air. Refractive indices from six different investigations were used.

7.5. Conclusions

This study deduced time-histories of soot volume fractions in volatile envelope flames of bituminous coal particles burning O$_2$/N$_2$ and O$_2$/CO$_2$ environments. Three different, based on optical diagnostics, were implemented to simultaneously deduce flame soot volume fractions, $f_v$, temperatures, $T$, and sizes, $D_f$, during the volatile combustion phase of 75-90µm coal particles in a drop tube furnace. Replacement of background N$_2$ by CO$_2$ gas decreased the average $f_v$, whereas increasing O$_2$ from 20% to 30-40% increased the $f_v$, but further increasing O$_2$ to 100% decreased the soot volume fraction drastically. Bituminous coal particle flames generated soot volume fractions in the range of 20-90 ppm, depending on the O$_2$ mole fraction. A sensitivity analysis - performed to assess the effects of different methods and of uncertain radiative parameters (such as refractive indices) - showed a combined variation of up to 50% in calculated values of soot volume fractions.
7.6. References


CHAPTER 8
8. Conclusions

The ignition and combustion of various coals and biomass particles in a drop-tube furnace (DTF) were investigated in various O₂/N₂ and O₂/CO₂ environments in this study. An electrically-heated laminar-flow drop-tube furnace was used for the combustion experiments. It was heated with heating elements, defining a radiation zone. The furnace was fitted at the top with a water-cooled injector. The single fuel particles introduced into the furnace injector using a beveled syringe needle. Single particles could thus be dropped into the furnace injector. Upon exiting the injector, the particles reacted with the preheated furnace gases. Particle heating rates were very high, calculated to be in the order of 10⁴ K s⁻¹. Two different combustion optical diagnostic facilities were implemented to characterize the ignition and combustion behaviors of the fuels independently: Three-wavelength optical pyrometer and high speed camera. Optical access to the radiation zone of the furnace was achieved through three observation ports: one at the top (Pyrometer) and two orthogonally situated window at the sides of the furnace.

Optical pyrometer was implemented to monitor the burning history of the fuel particle from the top of the furnace injector, viewing downward along the central axis of the furnace is typically a particle’s path-line. Thus, complete luminous burnout histories of single biomass particle - from ignition to extinction - were monitored. An optical fiber transmitted light from the furnace to the pyrometer assembly. The pyrometer conducted the light to the three interference filters. These filters had effective wavelengths of 0.640, 0.810 and 0.998 μm with bandwidths (FWHM) of 70 nm. Silicon diode detectors were employed to maximize the signal sensitivity. The voltage signals generated by the three detectors were amplified and then processed by a computer using LabView software. The temperature was deduced from the three output voltage signals of the pyrometer using a non-linear least square method, based on Planck’s law. Several
computer codes were written with MATLAB to deduce several parameters of particle flame and char such as temperature, area, soot volume fraction, etc. throughout the burning period. High-speed cinematography was conducted through the slotted side quartz windows of the drop-tube furnace against backlight. A NAC HotShot 512SC self-contained digital high-speed video camera was used, at speeds of 1000 or 2000 frames/s. The camera was fitted with an Infinity model K2 long-distance microscope lens to provide high-magnification images of the combustion events.

The optical pyrometer was calibrated for the desired High temperature range, using Tungsten lamp and blackbody devices. The details of the calibration were presented in chapter 1 and Appendix 1.

Combustion experiments of fuel particles were conducted under a quiescent gas (i.e., no flow) or an active flow conditions. Quiescent gas condition was created by turning off the gas flows 10 seconds prior to the particle injection. A slender bare thermocouple (Omega type K) was used to measure the axial profile of the centerline gas temperature. The measured temperatures with this method were corrected for radiation effects. Under the quiescent gas condition (no flow), the gas temperature profiles were similar in either N₂ or CO₂ environments. Both temperatures increased along the centerline of the furnace and stabilized at an estimated 1340 K. The furnace wall set-point temperature (\(T_w\)) was 1400 K, as monitored by type-S thermocouples embedded in the wall. The gas compositions in the furnace included O₂/N₂ or O₂/CO₂ mixtures (O₂ mole fractions of 21-100 %) to simulate oxy-combustion conditions. The gas flowrates for active flow conditions were controlled by Matteson Flowmeters and they were calibrated and pre-checked by bubble flowmeters.

Conclusions are presented in three categories; the effect of 8.1) replacing background N₂ gas with CO₂, 8.2) fuel types and coal ranks, and 8.3) oxygen mole fraction on ignition, combustion
8.1. The effect of replacing background N$_2$ gas with CO$_2$

In the case of quiescent (inactive) gas condition in the furnace, bituminous coal and biomass particles ignited homogeneously (gas mode) in either O$_2$/N$_2$ or O$_2$/CO$_2$ atmospheres. Lignite coal particles experienced extensive bulk fragmentation and heterogeneous ignition in both background gases. Anthracite also experienced heterogeneous ignition in both background gases. Ignition temperatures increased slightly (<40K) for all fuels when N$_2$ was replaced by CO$_2$. All coal ranks including Anthracite, semi-anthracite, bituminous and lignite coal particles experienced longer ignition delay times in O$_2$/CO$_2$ than in O$_2$/N$_2$ environments. In quiescent gas condition, mode of combustion did not change considerably for all fuels when N$_2$ was replaced by CO$_2$.

In the case of active gas flow conditions in the injector and the furnace, the ignition mode of coal particles in this case was altered when O$_2$/N$_2$ were replaced by O$_2$/CO$_2$ gases. Higher rank coals (all bituminous particles and some sub-bituminous coal particles) ignited homogeneously in O$_2$/N$_2$ atmospheres. Lignite coal particles fragmented before and/or after ignition. Those that fragmented before ignition were more likely to ignite heterogeneously, whereas those that fragmented after ignition experienced occasional homogeneous ignition in gas phase in O$_2$/N$_2$ atmospheres. In O$_2$/CO$_2$ atmospheres, particles from all different coal ranks appeared to ignite heterogeneously. Fuel particles were observed to burn in different modes, such as two-mode, i.e., gas-phase or homogeneous mode (volatile matter envelope flames) followed by heterogeneous mode (char surface oxidation), or in one-mode combustion (simultaneous volatile...
and char), depending on their rank and the furnace conditions. In active gas flow, strong
tendencies were observed for all fuels to burn in one-mode when N₂ was replaced by CO₂. This
observation was supported by the findings of Howard and Essenhigh [1].
Particle luminosity, fragmentation and deduced volatile and char temperatures were higher in
O₂/N₂ than in O₂/CO₂ atmospheres, and corresponding burnout times were shorter, at the same
O₂ mole fractions for all fuels.

Replacement of background N₂ by CO₂ gas decreased the average of peak soot volume
fractions in bituminous coal combustion.

8.2. The effects of fuel ranks, types, and elemental composition

The ignition mode varied with coal ranks. Anthracite coal particles ignited
heterogeneously. Semi anthracite mostly ignited heterogeneously while bituminous coal particles
consistently ignited in gas phase or homogeneously. Lignite coals fragmented extensively and
they mostly ignited heterogeneously from particle surface with some limited gas phase ignition.
Ignition temperatures increased as the coal rank enhanced from lignite to anthracite for either N₂
or CO₂ atmospheres and for all O₂ mole fraction of this study. Furthermore, higher rank coals
experienced higher ignition delay times than low rank coals.

Increasing the coal rank, from lignite to bituminous, enhanced the tendency of coal particles
to exhibit a two-mode combustion behavior. However, further increasing the coal rank to semi-
anthracite and anthracite decreased the tendency of two-mode burning and enhanced the one-
mode heterogeneous combustion. Anthracite coal particles experienced an andulation pattern
during the burnout history. Bituminous coal particles swelled, whereas sub-bituminous coal
particles exhibited limited fragmentation prior to and during the early stages of combustion. Lignite coal particles fragmented extensively and burned in one-mode regardless of the O₂ mole fraction and the background gas. The timing of fragmentation (prior or after ignition) and the number of fragments depended on the type of the lignite and on the particle shape.

Char temperatures rose with the coal rank decrease perhaps due to the higher impurities. Lignite coals had higher char temperatures than bituminous and bituminous experienced higher char temperatures than anthracite. Corresponding burnout times were augmented for higher rank coals (such as anthracite) due to higher carbon content than lower rank coals (such as lignite).

Higher rank coals required extra oxygen in CO₂ to match their temperature-time behavior in air. Sugarcane bagasse needed the least amount of extra gas-phase oxygen in CO₂ to match its temperature-time behavior in air. In other words, the fuels which have more fuel-bound oxygen (i.e., lower rank coals and bagasse) required the least amount of gas-phase oxygen in CO₂ to match their temperature-time behavior in air.

8.3 The effects of oxygen mole fraction

Increasing O₂ mole fraction decreased the ignition temperatures for all coal ranks from anthracite to lignite. Ignition mode was not affected by increasing O₂ in quiescent gas in the experimental conditions or this study. Increasing oxygen mole fractions from 20% to 50% decreased the ignition delay times in both the O₂/CO₂ and the O₂/N₂ atmospheres for all fuels.

Increasing O₂ mole fraction did not change the combustion mode of fuels in quiescent gas condition. However, in active gas flow condition, strong tendencies were observed for all fuels to burn in one-mode when O₂ mole fractions increased in both environments. Coal particle
luminosity and temperatures increased drastically with increasing \( \text{O}_2 \) mole fractions in both \( \text{N}_2 \) and in \( \text{CO}_2 \) background gases, and corresponding burnout times decreased with increasing \( \text{O}_2 \) mole fractions.

About particle soot loading, increasing \( \text{O}_2 \) from 20% to 30-40% increased the soot volume fraction, but further increasing \( \text{O}_2 \) to 100% decreased the soot volume fraction drastically. Bituminous coal particle flames generated soot volume fractions in the range of 20-90 ppm, depending on the \( \text{O}_2 \) mole fraction.

8.4 On the biomass combustion behaviors

Striking differences were observed between the combustion behavior of the biomass particles burned herein and those of coal particles of all ranks investigated in other studies in this laboratory. The biomass particles released large amounts of volatiles that burned in the form of spherical envelope flames. Therefore, unlike coal combustion, biomass volatile flame burnout times were significantly longer than char burnout times. Ensuing biomass char combustion produced stronger signals than the combustion of the volatile matter. Increasing the oxygen mole fraction in \( \text{CO}_2 \) surprisingly reduced the luminosity of the flames. The combustion intensity of the biomass was stronger in air (21% \( \text{O}_2 \)-79% \( \text{N}_2 \)) than in an oxy-fuel atmosphere with the same oxygen mole fraction (21% \( \text{O}_2 \)-79% \( \text{CO}_2 \)). Increasing the oxygen mole fraction in the \( \text{CO}_2 \) background gas decreased the burnout times of volatiles and of the char residues, whereas it increased the temperature of the burning char particles. Similar trends were observed for all tested biomass samples from disparate sources, including the raw and torrefied pine sawdust. Thus, unlike the combustion behavior of coals, which differs widely with rank, type and seam, the combustion behavior of biomasses from the four different sources of this study appears more unified. The volatile flames of biomass particles were less sooty than those of coal particles.
8.4. References

CHAPTER 9
9. Suggestions for Future Work

9.1. Determining instantaneous temperature of burning biomass and coal particles and flames without wavelength independent emissivity assumption

Temperature is the most basic and important parameter in combustion; nonetheless, its accurate determination in combustion is often in doubt. This is particularly true for the miniscule particles of pulverized solid fuels that are injected and burned in power-plants. Accurate determination of particle combustion temperatures is paramount for successful development of new technologies, since the ash vaporization rate, the slagging and fouling propensity in boilers, the reactivity of fuel, the convective and radiating properties, as well as its gaseous and particulate emissions are strongly temperature-dependent phenomena. Knowledge of true temperature of coal and biomass particles is essential for designing a boiler (e.g., identification of the location and arrangement of burners, determination of boiler dimensions, positioning of heat exchangers, etc.), for selecting fuels (or fuel blends) and operating conditions as well as for minimizing the emissions of pollutants.

Coal particle temperatures are customarily deduced by remote optical pyrometry based on Planck’s law of radiation. Optical pyrometry is not only preferred but also necessary for observing the miniscule fast-burning pulverized coal particles injected in a furnace, since it is not intrusive and can be conducted from afar. Most often, a two-color ratio pyrometry technique is used, since it conveniently allows cancellation of the spectral (i.e., mono-chromatic) emissivities of a carbon particle at two different wavelengths of observation. The underlying assumption, that the spectral emissivity is independent of the wavelength, is called the gray-body radiation assumption and has been also implemented in this study (chapter 1).
Temperature measurements on single-coal particles or particle clouds were conducted employing two-color or multi-color pyrometry and assuming *gray body radiation*. More specifically, the *gray body radiation* assumption has found widespread use in the temperature deduction of burning coal chars. It should be noted here that, under typical conditions, the combustion of the popular mid-rank coals (bituminous and sub-bituminous) takes place in two sequential stages: homogeneous volatile matter combustion in envelope flames followed by heterogeneous oxidation of the char residues (see Chapters 2-6). To the best of our knowledge, little if any has been reported in the literature on the temperature of the volatile matter particle envelope-flames which typically precede char combustion, with the exception of previous publications in this laboratory [1-3]. In those works the emissivity of the sooty and luminous, volatile matter particle envelope flames was also assumed to be gray, based on theory developed by Panagiotou et al. [4] for spatially-non-isothermal flames. Therefore, the assumption that the spectral emissivity of burning coal particles is independent of the wavelength (*gray body*) has been used by his group for determining the temperatures of both the volatile envelope flame and the char combustions phases. Nevertheless, this assumption, even if convenient in simplifying the deduction of temperature from Planck’s law, is not certain. In fact, while Ayling and Smith [5] also made such an assumption early on in the pertinent literature, they expressed reservations by stating that data collected elsewhere suggests that carbon is *non-gray*. The accuracy of the gray body emissivity assumption has also been questioned by other researchers [6-9]. In fact, Solomon et al. [6, 7] suggested that the spectral emittance of individual coal particles is time-varying and, thus, it changes throughout the particle burnout times.

Furthermore, as various directives to increase the usage of biomass and bio-fuels in combustion are being legislated and materialized around the world (e.g., European Directive
pulverized coals may be blended with all kinds of pulverized biomasses and, thus, the spectral emissivity of such biomass particles is also needed for temperature determinations.

Figure 1 exemplifies the magnitude of the temperature uncertainty based on data collected in our laboratory. It shows the temperature profile of a 75-90 μm bituminous coal particle (PSOC-1451) burning in air when the gray body radiation assumption is perturbed. The entire intensity-time profile of the particle, including the initial volatile flame and the ensuing char combustion phase, was monitored by the three-color pyrometer in this laboratory and temperatures were deduced as outlined in Chapter 1, based on the pyrometric ratio method with $\lambda_1=998\text{nm}$ and $\lambda_2=810\text{nm}$. The temperature profile was deduced using the *gray body radiation* assumption ($\varepsilon_{\lambda_1}/\varepsilon_{\lambda_2} = 1$) and, also, using hypothetical emissivity ratios differing from the *gray body emissivity* assumption by ±10% ($0.9 \leq \varepsilon_{\lambda_1}/\varepsilon_{\lambda_2} \leq 1.1$), and assuming that such ratios stayed constant throughout burnout. The results show that such variations in the emissivity ratio caused more than 200 K difference in temperature, which is a large uncertainty, indeed. Similar temperature differences were reported by Ref. [9]. Such temperature uncertainties can cause an error of 60% in the calculation of the apparent reaction rate [10], an error of more than one order of magnitude in the calculation of the fractional ash vaporization rate [11] and will, also, be very misleading in the prediction of slagging and fouling tendencies in a boiler. Published data [7-9] also shows that the spectral emissivities of coals vary from particle to particle, depending on physico/chemical properties.
Figure 1: (a) Radiation intensity profiles emitted from a 75-90 μm bituminous coal particle burning in air, as monitored by narrow-bandwidth wavelengths windows centered at $\lambda_1=998\text{nm}$ and $\lambda_2=810\text{nm}$ $\lambda_3=640\text{nm}$. (b) Temperature profiles determined with the pyrometric ratio method using the pair of $\lambda_1=998\text{nm}$ and $\lambda_2=810\text{nm}$ and assuming spectral emissivity ratios in the range of $0.9 \leq \varepsilon_{\lambda_1}/\varepsilon_{\lambda_2} \leq 1$.

Figure 2. High-speed, high magnification cinematography images of a single particle of a biomass residue.

Based on our work so far, we encountered the biggest uncertainty in the temperature determination in the volatile matter flames of biomass particles which are remarkably spherical and barely luminous, see Fig. 2.

Pyrometric temperatures of biomasses using the gray radiation assumption are much lower (by several hundred degrees) than those of the volatile flames of bituminous coal particles, even
if equilibrium adiabatic flame temperatures, calculated with the code \textit{STANJAN} with input measured pyrolyzate compositions in both cases, were not far apart. Moreover the, gray body radiation assumption, unlike in the case of char combustion of biomass and coal and even volatile flame combustion of coal, produces poor results in the case of biomass particles. This is judged by large disagreement of the three two-color temperatures of the three color pyrometer, see Fig. 3. Clearly, if temperature (and other radiative properties) of biomass are to be assessed and compared to those of coal, which biomass is to partially replace in boilers, a reliable temperature deduction method is necessary. It is already known that co-firing biomass with coal in a boiler, if the overall fuel mass flowrate is kept constant, reduces the primary furnace temperatures and consequentially decreases the thermal efficiency; the question is by how much and how can a new boiler be designed to minimize this loss.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Temperature profiles using the pyrometric ratio method of 75-90 µm (a) biomass and (b) bituminous coal particles burning in air, as monitored by narrow-bandwidth wavelength windows centered at $\lambda_1=998\text{nm}$ and $\lambda_2=810\text{nm}$ $\lambda_3=640\text{nm}$ using the gray body emissivity assumption ($\varepsilon_{\lambda_1}/\varepsilon_{\lambda_2} = \varepsilon_{\lambda_2}/\varepsilon_{\lambda_3} = \varepsilon_{\lambda_3}/\varepsilon_{\lambda_1} = 1$).}
\end{figure}

The future work will be defined as formulation and validation of a real-time determination of the instantaneous temperature (as well as emissivity and size) of individual fuel particles, both coals and biomasses, throughout their burnout history, without making the simplifying
assumptions on their spectral emissivity. Thereafter, the radiative power intensity of the fuels will be assessed and compared.

9.2. Soot loading of biomass particles in conventional and oxy-fuel combustion

Soot loading was discussed for coal particle flames in chapter 7. Soot loading is a very temperature dependent phenomenon as it was discussed. For burning biomass particle flames, since the temperature measurements are not still reliable with the current method (discussed in sec. 9.1 above), the relevant soot volume fractions are uncertain. There are other uncertainties such as Rayleigh and Hottel emissivities for small and large particle [12] which needs to be revisited for biomass flames. These empirical relations were mostly developed for coal and other sooty liquid fuel flames. One proposal is to reexamine the Eq. 3 and Eq. 6 in chapter 7 for optically thin vbiomass flames in the cases of small and large soot particles (Hottel and Broughton’s for $\pi D_{\text{soot}} > 5\lambda_x$ and Rayleigh’s for $\pi D_{\text{soot}} < 0.6\lambda/n$). Moreover, the hydrodynamic of biomass particles in our system is such that the terminal velocity of the particles is nearly zero and the particles look floating. Therefore, the fluid flow conditions of biomass particles are different than that of coal particles which prevents to draw any comparison on soot loading for biomass and coal flames.

9.3. Group of particles combustion

The combustion diagnostics of single-particle combustion of coal and biomass in conventional (air) and oxy-fuel environments was studied in this study. The combustion behaviors of particle groups are extremely important for real combustion systems. While several research works and reviews have been done on group particle combustion in air [13, 14], the
Experimental study of group particles combustion in oxy-fuel environment is absent in the literature. More importantly, the blending of several fuels (such as coal-biomass and recently coal-coal) is now being widely investigated due to its lower pollutions and synergetic effects [15-17]. Experimental combustion diagnostics of group particles from blended fuels would be a good area for the future studies.

9.4. References


APPENDIX 1
1. NIST tungsten lamp method

Calibration curves for the pyrometer were created using a NIST tungsten lamp method. The set-ups were placed centrally below the furnace as its vertical geometry made it feasible. Such configurations allowed the free movement and handling of the calibration equipment and direct exposure to the light signal, reducing unwanted radiation capture from the furnace wall reflection.

The National Institute for Standards & Technology (NIST) provided pre-calibrated data for the gas-filled tungsten lamp consisting of apparent temperature values \( T_a \) of 1800 K and 2000 K vs. specific wavelengths (0.65, 0.8, 0.975, and 1.20 µm) as seen in Table 1, columns 1-4. By applying Wien’s law from Eq. (1) and Eq. (2) to these tabulated temperatures, the true temperature of the lamp was computed with the emissivity of tungsten at any given wavelength and listed in Table 1, column 5.

\[
\frac{c_1}{\lambda_5} \exp\left(\frac{-c_2}{\lambda T_a}\right) = \varepsilon_\lambda \frac{c_1}{\lambda^5} \exp\left(\frac{-c_2}{\lambda T_t}\right)
\]

\[
T_t = \left(\frac{\lambda}{c_2} \ln \varepsilon_\lambda + \frac{1}{T_a}\right)^{-1}
\]

**Table 1.** NIST-supplied data (columns 1-4)

<table>
<thead>
<tr>
<th>( T_a ) (K)</th>
<th>( \lambda ) (µm)</th>
<th>( \varepsilon_{T_t} )</th>
<th>Lamp Current (A dc)</th>
<th>( T_t ) (K)</th>
<th>( 1/T \times 10^4 ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>0.650</td>
<td>0.444</td>
<td>23.343</td>
<td>1927</td>
<td>5.189</td>
</tr>
<tr>
<td>1800</td>
<td>0.800</td>
<td>0.421</td>
<td>24.382</td>
<td>1971</td>
<td>5.074</td>
</tr>
</tbody>
</table>
The lamp was mounted at the bottom of the furnace on its upright position held by a metallic frame. The structure had a single black wall on which a customized pinhole device sat flat for viewing of the tungsten light bulb. The device consisted of two pinholes of the same sizes, 1.2 mm, specifically aligned and spaced apart (1.5 cm) to allow through only a defined width of the view field. The desired area of viewing in the lamp filament had already being pre-marked by NIST, where the temperature was the hottest during lit-up. The lamp and the pinhole device were attached to the metallic frame so there was a certain freedom of rotation and translation along the centerline of the lamp. A long black hollow cylinder emulated the vertical injector and the furnace silica tube with dimensions of 62 cm in length and 1.1 cm i.d. This one was positioned horizontally, perpendicular to the lamp filament so the light could travel from the pinhole directly to the inside of the beam and reach the opposite end where a lens connected to the pyrometer fiber optic. The sample signals captured by the three-color pyrometer at the three different wavelengths are illustrated in Fig. 1.
True Lamp Temperature = 1927 K

True Lamp Temperature = 1971 K

True Lamp Temperature = 2392 K
True Lamp Temperature = 2479 K

**Figure 1.** Sample NIST lamp calibration signals as recorded by the three-color pyrometer with their respective true lamp temperature.

**Figure 2.** NIST lamp, mirror, pinhole, power supply and current meter

Amp meter (FLUKE 375)
The lamp was powered by a Kikusui regulated power supply controlled by a Keithley 230 programmable voltage source. The Keithley settings were adjusted to:

Program mode: Continuous

Voltage (source): 0.9995 (V)

Current (I-limit): 2×10⁻³ or 20×10⁻³ (A)

Output: Operate

The Kikusui power supply control the voltage by the voltage knob to obtain the desired DC current in the circuit. The DC current in the lamp circuit was measured and recorded by a new Amp meter (Fluke 375). During experimentation the output calibration signals of the pyrometer for every wavelength (998 nm, 810 nm and 640 nm) were recorded. Tabulated NIST current values were attained by controlling the voltage source (using KIKUSUI voltage knob), increasing the light intensity emitted by the tungsten lamp into the pinhole device.

The non-linear least square method was formulated by Khatami and Levendis [1] and is simplified and calibrated as:

\[
\sum_{n=1}^{3} \Delta_n^2 = \sum_{n=1}^{3} (S_n - s_n)^2
\]  

(1)

\[
s_n = C_n A \int_{\Delta \lambda} e_{\lambda n} I_{\lambda b}(\lambda) d\lambda
\]  

(2)

where \(S_n\) is the experimental pyrometric wavelength at channel n and \(I_{\lambda b}\) is the Planck’s law for spectral radiation intensity of a blackbody surface:
\[ I_{\lambda b} = \frac{c_1}{\lambda^5 \left( e^{\frac{c_2}{\lambda T}} - 1 \right)} \]  

Eq. (3) can be simplified further more by applying Wien’s Law to the denominator in such way that for each channel:

\[ S_n = C_n \varepsilon_n AC_1 \Delta \lambda \lambda_0^{-5} e^{-\frac{C_2}{\lambda T}} \]  

\[ \ln(S_n) = \ln(C_n) + \ln(\varepsilon_n) + \ln(k) - \frac{C_2}{\lambda_0 T} \]  

\[ \ln\left(\frac{S_n}{\varepsilon_n}\right) = \ln(C_n) + \ln(k) - \frac{C_2}{\lambda_0 T} \]  

Therefore the recorded signals were plotted in logarithmic form as the ratio of signal to emissivity for each of three wavelength channels as a function of the inverse temperature. \( K \) is the multiplication of constants for each channel. By using the expression \( \ln(S_n / \varepsilon_n) \) the wavelength-dependence of the emissivity of tungsten was taken into account. The best-fit line analysis was done for each channel (998, 810 and 640). \( \ln(C_n) + \ln(k) \) is the intercept of the line and \( \ln(k) \) is constant for each channel. \( C_n \) is the calibration constant for each channel.

The calibration procedure was performed about four times. The calibration of the pyrometer with the tungsten lamp yielded satisfactory repeatability. The complete data is listed in Tables 2-4 and plotted in Fig 2.
Table 2. Experimental recorded signals and tungsten spectral emissivities [2] for NIST supplied temperatures

<table>
<thead>
<tr>
<th>( \lambda ) (( \mu \text{m} ))</th>
<th>( T_t ) (K)</th>
<th>( 1/T_x \times 10^{-4} ) (A dc)</th>
<th>Lamp Current</th>
<th>( V_1 ) (V)</th>
<th>( V_2 ) (V)</th>
<th>( V_3 ) (V)</th>
<th>( \varepsilon_{998} )</th>
<th>( \varepsilon_{810} )</th>
<th>( \varepsilon_{640} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>1927</td>
<td>5.189</td>
<td>23.3</td>
<td>0.722</td>
<td>0.197</td>
<td>0.029</td>
<td>0.384</td>
<td>0.421</td>
<td>0.443</td>
</tr>
<tr>
<td>0.8</td>
<td>1971</td>
<td>5.074</td>
<td>24.4</td>
<td>0.8875</td>
<td>0.2529</td>
<td>0.0396</td>
<td>0.383</td>
<td>0.42</td>
<td>0.441</td>
</tr>
<tr>
<td>0.975</td>
<td>2034</td>
<td>4.916</td>
<td>25.95</td>
<td>1.155</td>
<td>0.3505</td>
<td>0.0606</td>
<td>0.381</td>
<td>0.419</td>
<td>0.44</td>
</tr>
<tr>
<td>1.2</td>
<td>2152</td>
<td>4.647</td>
<td>28.6</td>
<td>1.746</td>
<td>0.584</td>
<td>0.1164</td>
<td>0.378</td>
<td>0.414</td>
<td>0.439</td>
</tr>
<tr>
<td>0.65</td>
<td>2392</td>
<td>4.181</td>
<td>33.3</td>
<td>3.12</td>
<td>1.195</td>
<td>0.2885</td>
<td>0.375</td>
<td>0.408</td>
<td>0.435</td>
</tr>
<tr>
<td>0.8</td>
<td>2479</td>
<td>4.034</td>
<td>35.2</td>
<td>3.834</td>
<td>1.5412</td>
<td>0.3989</td>
<td>0.373</td>
<td>0.405</td>
<td>0.432</td>
</tr>
<tr>
<td>0.975</td>
<td>2577</td>
<td>3.88</td>
<td>38.12</td>
<td></td>
<td></td>
<td></td>
<td>0.372</td>
<td>0.404</td>
<td>0.431</td>
</tr>
</tbody>
</table>

Table 3. Calculation sheet

<table>
<thead>
<tr>
<th>( \lambda_{998} ) (( \mu \text{m} ))</th>
<th>( \lambda_{810} ) (( \mu \text{m} ))</th>
<th>( \lambda_{640} ) (( \mu \text{m} ))</th>
<th>( A ) (( \mu \text{m}^2 ))</th>
<th>( \Delta \lambda ) (( \mu \text{m} ))</th>
<th>( C_1 ) (W. ( \mu \text{m}^2 \text{sr} ))</th>
<th>( C_2 ) (( \mu \text{m} \cdot \text{K} ))</th>
<th>( 1/T ) (1/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.998</td>
<td>0.81</td>
<td>0.64</td>
<td>1130400</td>
<td>0.07</td>
<td>0.000059552</td>
<td>14388</td>
<td>0.000518941</td>
</tr>
<tr>
<td>0.998</td>
<td>0.81</td>
<td>0.64</td>
<td>1130400</td>
<td>0.07</td>
<td>0.000059552</td>
<td>14388</td>
<td>0.000507357</td>
</tr>
<tr>
<td>0.998</td>
<td>0.81</td>
<td>0.64</td>
<td>1130400</td>
<td>0.07</td>
<td>0.000059552</td>
<td>14388</td>
<td>0.000491642</td>
</tr>
<tr>
<td>0.998</td>
<td>0.81</td>
<td>0.64</td>
<td>1130400</td>
<td>0.07</td>
<td>0.000059552</td>
<td>14388</td>
<td>0.000464684</td>
</tr>
<tr>
<td>0.998</td>
<td>0.81</td>
<td>0.64</td>
<td>1130400</td>
<td>0.07</td>
<td>0.000059552</td>
<td>14388</td>
<td>0.00041806</td>
</tr>
</tbody>
</table>
### Table 4. 998 nm channel constant (C998) calculation for different NIST temperatures (signals)

<table>
<thead>
<tr>
<th>ln (V1/ε998)</th>
<th>ln(K998)(const.)</th>
<th>ln(C998)</th>
<th>C998</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.631382586</td>
<td>1.560171409</td>
<td>6.616629</td>
<td>747.421</td>
</tr>
<tr>
<td>0.840373532</td>
<td>1.560171409</td>
<td>6.616629</td>
<td>747.421</td>
</tr>
<tr>
<td>1.109056248</td>
<td>1.560171409</td>
<td>6.616629</td>
<td>747.421</td>
</tr>
<tr>
<td>1.530188541</td>
<td>1.560171409</td>
<td>6.616629</td>
<td>747.421</td>
</tr>
<tr>
<td>2.118662255</td>
<td>1.560171409</td>
<td>6.616629</td>
<td>747.421</td>
</tr>
<tr>
<td>2.330085504</td>
<td>1.560171409</td>
<td>6.616629</td>
<td>747.421</td>
</tr>
<tr>
<td>#NUM!</td>
<td>1.560171409</td>
<td>6.616629</td>
<td>747.421</td>
</tr>
</tbody>
</table>

### Table 5. 810 nm channel constant (C810) calculation for different NIST temperatures (signals)

<table>
<thead>
<tr>
<th>ln (V2/ε810)</th>
<th>ln(K810)(const.)</th>
<th>ln(C810)</th>
<th>C810</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.7594291</td>
<td>2.603766552</td>
<td>5.958233</td>
<td>386.926</td>
</tr>
<tr>
<td>-0.50726056</td>
<td>2.603766552</td>
<td>5.958233</td>
<td>386.926</td>
</tr>
<tr>
<td>-0.17851021</td>
<td>2.603766552</td>
<td>5.958233</td>
<td>386.926</td>
</tr>
<tr>
<td>0.344035009</td>
<td>2.603766552</td>
<td>5.958233</td>
<td>386.926</td>
</tr>
<tr>
<td>1.07463429</td>
<td>2.603766552</td>
<td>5.958233</td>
<td>386.926</td>
</tr>
<tr>
<td>1.336429546</td>
<td>2.603766552</td>
<td>5.958233</td>
<td>386.926</td>
</tr>
<tr>
<td>#NUM!</td>
<td>2.603766552</td>
<td>5.958233</td>
<td>386.926</td>
</tr>
<tr>
<td>ln (V3/ε640)</td>
<td>ln(K640)(const.)</td>
<td>ln(C640)</td>
<td>C640</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------</td>
<td>----------</td>
<td>--------</td>
</tr>
<tr>
<td>-2.72627394</td>
<td>3.781596909</td>
<td>5.2585031</td>
<td>192.1936</td>
</tr>
<tr>
<td>2.410215757</td>
<td>3.781596909</td>
<td>5.2585031</td>
<td>192.1936</td>
</tr>
<tr>
<td>1.982479834</td>
<td>3.781596909</td>
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<td>192.1936</td>
</tr>
<tr>
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<td>192.1936</td>
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<tr>
<td>0.410650945</td>
<td>3.781596909</td>
<td>5.2585031</td>
<td>192.1936</td>
</tr>
<tr>
<td>0.079714829</td>
<td>3.781596909</td>
<td>5.2585031</td>
<td>192.1936</td>
</tr>
<tr>
<td>#NUM!</td>
<td>3.781596909</td>
<td>5.2585031</td>
<td>192.1936</td>
</tr>
</tbody>
</table>
\[ \ln \left( \frac{V_{998}}{\varepsilon_{998}} \right) = -14444 \left( \frac{1}{T} \right) + 8.1768 \]

\[ \ln \left( \frac{V_{810}}{\varepsilon_{810}} \right) = -17853 \left( \frac{1}{T} \right) + 8.562 \]
Figure 3. Semi-logarithmic calibration plots at the different color of the three-color pyrometer. The NIST lamp calibration results were plotted for a least square method calibration to obtain calibration constants $C_998$, $C_810$ and $C_640$. 

A comparison was then performed between the experimental and the theoretical slopes to prove the validity of the calibration, as discussed further below.

In principle, to further prove the validity of the tungsten lamp calibration, the experimental slope equation was compared to the theoretical values given in Levendis et al. 1992 and also shown in Table 5. The slope of the best-fit straight line is given by Eq. (6) where $c_2$ is 14388 \( \mu \text{m} \) by definition and $\lambda_n$ represents the channel wavelengths. This experimental slope equation has been included in Fig. 3 for all three pyrometer channels.

\[
\frac{-c_2}{\lambda_n} = \ln(V_{640}/\varepsilon_{640}) = -22531 \frac{1}{T} + 9.0401
\]

Rearranging Eq. 6 to its equation of the line form yields Eq. (8). It is noted that the right hand side of Eq. (6) represents the best-fit line expression in Fig. 3.
\[ \ln \left( \frac{S_n}{\varepsilon_n} \right) = \left( -\frac{C_n}{\lambda_n} \right) \frac{1}{T} + \ln(C_n) + \ln(k) \] (8)

Table 5 includes the theoretical slope, computed using Eq. (7), (8), for every wavelength as well as the experimental slope, which in this case was determined, as mentioned before, by the best-fit line test for the tungsten lamp data points.

Table 7. Theoretical and Experimental Slopes

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>998</td>
</tr>
<tr>
<td>Theory</td>
<td>-14416</td>
</tr>
<tr>
<td>Experiment</td>
<td>-14444</td>
</tr>
</tbody>
</table>

Maximum error between experimental and theoretical slopes are about 0.4%.

Factors that significantly influenced the success of the calibration lamp procedure involved the thickness of the cables and the robustness of the mogul-type socket used with the high current lamp (40 amp). The slight overheating of the cables and connections can cause filament temperature drifts and erroneous readings.

2. References


Temperature deduction codes with MATLAB

1. Simplified ratio method using grey-body assumption

```matlab
function WienApproximation
clf
clc
%================================ Load File =================================
fileName = 'SCB-AIR-6_006.lvm';

%================================ Toggle Temp Ratios ON/OFF =================
if(1) %Switch between (1)/(0) to turn on/off Temp calculation
    for 998/640 ratio
        colorRatio = 'RoverB';
        %title('998/640')
        colorspec = 'b';
        CalculateTemperature(fileName,colorRatio,colorspec)
    end

    if(1) %Switch between (1)/(0) to turn on/off Temp calculation
        for 998/810 ratio
            colorRatio = 'RoverG';
            %title('998/810')
            colorspec = 'g';
            CalculateTemperature(fileName,colorRatio,colorspec)
        end

    if(1) %Switch between (1)/(0) to turn on/off Temp calculation
        for 810/640 ratio
            colorRatio = 'GoverB';
            %title('810/640')
            colorspec = 'm';
            CalculateTemperature(fileName,colorRatio,colorspec)
        end

%================================ Establish Baseline ========================
function CalculateTemperature(fileName,colorRatio,colorspec)
    u = units;

dataMatrix = load(fileName);
    t = dataMatrix(:,1);
    t = t - min(t);    %This makes all time on the graph relative (always starts
                        %at 0)

    blue = dataMatrix(:,2); %blue = 640nm wavelength
    OffsetBlue = dataMatrix(1:4,2); %This Offset brings the temperature
                                    %baseline to 0
    blue = blue - mean(OffsetBlue);

    % ===== Smoothing V3 =======
    for i=8:size(t)-7
```
blue(i)=(blue(i-7)+blue(i-6)+blue(i-5)+blue(i-4)+blue(i-3)+blue(i-2)+blue(i-1)+blue(i)+blue(i+1)+blue(i+2)+blue(i+3)+blue(i+4)+blue(i+5)+blue(i+6)+blue(i+7))./15;
end

green = dataMatrix(:,3);  %green = 810nm wavelength
OffsetGreen = dataMatrix(1:4,3);
green = green - mean(OffsetGreen);

% ===== Smoothing V2 ======
for i=8:size(t)-7
    green(i)=(green(i-7)+green(i-6)+green(i-5)+green(i-4)+green(i-3)+green(i-2)+green(i-1)+green(i)+green(i+1)+green(i+2)+green(i+3)+green(i+4)+green(i+5)+green(i+6)+green(i+7))./15;
end

red = dataMatrix(:,4);  %red = 998nm wavelength
OffsetRed = dataMatrix(1:4,4);
red = red - mean(OffsetRed);

% ===== Smoothing V1 ======
for i=8:size(t)-7
    red(i)=(red(i-7)+red(i-6)+red(i-5)+red(i-4)+red(i-3)+red(i-2)+red(i-1)+red(i)+red(i+1)+red(i+2)+red(i+3)+red(i+4)+red(i+5)+red(i+6)+red(i+7))./15;
end

%============================= Zero Iterations =============================
%Assume term in parentheses (in Wien Appx.) is =1 to find an initial value for T to use for Wien Appx.
switch(colorRatio)
case('RoverB')      %998/640
    beta = 8090;       %beta = slope of calibration line =
    alpha = -0.8647;   %alpha = intercept of calibration line = -ln(1/C)
    numerator = beta;
    e1=0.998;
    e2=0.81;
    e3=0.64;
    denominator = log(red./blue) - alpha;
    T = numerator./denominator;

case('RoverG')      %998/810
    beta = 3411;
    alpha = -0.3857;
    numerator = beta;
    e1=0.998;
    e2=0.81;
    e3=0.64;
end
\[
denominator = \log(\text{red./green}) - \alpha;
T = \frac{\text{numerator}}{\text{denominator}};
\]

```matlab
% case('GoverB') 810/640
beta = 4679;
alpha = -0.479;
numerator = beta;
e1=0.998;
e2=0.81;
e3=0.64;
denominator = \log(\text{green./blue}) - \alpha;
T = \frac{\text{numerator}}{\text{denominator}};
end
```

%============================= Wien's Approximation =====================

\[
\lambda_{\text{Red}} = 0.998 \text{u.um};
\lambda_{\text{Green}} = 0.810 \text{u.um};
\lambda_{\text{Blue}} = 0.640 \text{u.um};
c_2 = 14388 \text{u.um.u.K};
\]

```matlab
for i=0:1:4
switch(colorRatio)
  case('RoverB') 998/640
    numerator = beta;
e1=0.998;
e2=0.81;
e3=0.64;
wien = (1-exp(-c2./\lambda_{\text{Red}}*T))/(1-exp(-c2/\lambda_{\text{Blue}}*T));
denominator = \log(\text{red./blue})+\log(\text{e3./e1}) - \alpha + \log(wien);
    Temp = \frac{\text{numerator}}{\text{denominator}};
  case('RoverG') 998/810
    numerator = beta;
e1=0.998;
e2=0.81;
e3=0.64;
wien = (1-exp(-c2./\lambda_{\text{Red}}*T))/(1-exp(-c2/\lambda_{\text{Green}}*T));
denominator = \log(\text{red./green})+\log(\text{e2./e1}) - \alpha + \log(wien);
    Temp = \frac{\text{numerator}}{\text{denominator}};
  case('GoverB') 810/640
    numerator = beta;
e1=0.998;
e2=0.81;
e3=0.64;
wien = (1-exp(-c2./\lambda_{\text{Green}}*T))/(1-exp(-c2/\lambda_{\text{Blue}}*T));
denominator = \log(\text{green./blue})+\log(\text{e3./e2}) - \alpha + \log(wien);
    Temp = \frac{\text{numerator}}{\text{denominator}};
end
end
```

%---------Explanation of alpha, beta---------%

%beta = slope of calibration curve = (c2*[1/lambda2-1/lambda1])
%alpha = \ln(1/Instrument Constant); It is the negative of the y-intercept of the
%calibration curve (the y-intercept is actually equal to: -ln(1/Instrument Constant))

%============== Plot Signal ================================
subplot(2,1,1)
plot(t/u.ms,red,'r',t/u.ms,green,'g',t/u.ms,blue,'b');
%Axis Formats: Time Axis goes from min to max time (exactly same as temp
%plot); Signal Axis has 20% gap above peak and below 0
axis([min(t)/u.ms max(t)/u.ms (0-0.2*max(red)) (1.2*max(red))])
xlabel('time [ms]')
ylabel('Signal [V]')
legend('998','810','640')
title(fileName)
hold on

%================================ Eliminate Noise =============================
%Smoothing function: eliminates noise under a given signal strength and
%makes the temperature equal to 1400K
sizeTemp = size(Temp);
for i = 1:sizeTemp
    if red(i)<0.003 || green(i)<0.003 %|| blue(i)<0.005
        Temp(i)=1000;
    end
end

%============== Plot Temperature ================================
subplot(2,1,2)
%Temp_smooth=smooth(t/u.ms,abs(Temp),0.1,'rloess');
%plot(t/u.ms,abs(Temp),colorspec,t/u.ms,Temp_smooth,'r-')
plot(t/u.ms,abs(Temp),colorspec)
axis([min(t)/u.ms max(t)/u.ms 1000 2600])
%axis([min(t)/u.ms max(t)/u.ms 300 5500])
xlabel('time [ms]')
ylabel('Temperature [K]')
legend('998/640','998/810','810/640')
grid on
hold on

%================================ Plot Color ================================
%Particle_color =Temp_smooth/max(Temp_smooth);
%length=size(Temp_smooth);
%for i=1:length
%    colorMat = [1,Particle_color,0];
%end
%figure(2)
%plot(t/u.ms,Particle_color)
2. Ratio method with modeled filters and detectors using grey-body assumption

clear
clf
clc
fileName = 'PSOC-1451_75-90_1127C_40%O2_60%N2_004c.lvm';
dataMatrix = load(fileName);
%======================== Establish Baseline ============================%
t1 = dataMatrix(:,1);
t1 = t1 - min(t1);    %This makes all time on the graph relative (always
starts at 0)
t=1000*t1;
V3 = dataMatrix(:,2);             %blue = 640nm wavelength
OffsetV3 = dataMatrix(1:100,2);   %This Offset brings the temperature
baseline to 0
V3 =V3 - mean(OffsetV3);

V2 = dataMatrix(:,3);            %green = 810nm wavelength
OffsetV2 = dataMatrix(1:100,3);
V2 =V2 - mean(OffsetV2);

V1 = dataMatrix(:,4);              %red = 998nm wavelength
OffsetV1 = dataMatrix(1:100,4);
V1 =V1 - mean(OffsetV1);
%================================Constants===============================%
C1=0.59552*10^(-4);    % W.(micro m)^2/sr %
C2=14388;              % micro m.K %
C=9*10^(2);              % V/W %
%===============================Wavelengths Generation===================%
la1=linspace(0.90,1.05,200);
la2=linspace(0.68,0.96,200);
la3=linspace(0.52,0.82,200);

%================================(Interference filters)-Transmissivity ==============
IF1=(0.5822*exp(-((la1-0.9741)./0.01827).^2)+0.5893*exp(-((la1-1.006)./0.02504).^2));
IF2=(0.2277*exp(-((la2-0.7896)./0.02343).^2)+0.5536*exp(-((la2-0.8151)./0.05286).^2));
IF3=(1.926*exp(-((la3-0.6655)./0.04706).^2)-1.467*exp(-((la3-0.6749)./0.04176).^2));

%================================(Dichroic filters)-Transmittance =======================
T11=(0.9066*sin(5.099.*la1+3.207)+0.2149*sin(21.38.*la1+3.194)+0.203*sin(12.75.*la1+1.523)+0.05797*sin(43.3.*la1-0.9239)+0.05437*sin(34.57.*la1-0.6235)+0.02909*sin(64.7.*la1+1.626)+0.03346*sin(52.36.*la1-1.184)+0.01113*sin(118.5.*la1-1.066));

T12=(0.9066*sin(5.099.*la2+3.207)+0.2149*sin(21.38.*la2+3.194)+0.203*sin(12.75.*la2+1.523)+0.05797*sin(43.3.*la2-0.9239)+0.05437*sin(34.57.*la2-
\[ T_{13} = (0.9066 \sin(5.099 \cdot la3 + 3.207) + 0.2149 \sin(21.38 \cdot la3 + 3.194) + 0.203 \sin(12.75 \cdot la3 + 1.523) + 0.05797 \sin(43.3 \cdot la3 - 0.9239) + 0.05437 \sin(34.57 \cdot la3 - 0.6235) + 0.02909 \sin(64.7 \cdot la3 + 1.626) + 0.03346 \sin(52.36 \cdot la3 - 1.184) + 0.01113 \sin(118.5 \cdot la3 - 1.066)); \]

\[ T_{21} = (0.6822 \sin(5.395 \cdot la1 + 2.851) + 0.4538 \sin(10.86 \cdot la1 + 2.576) + 0.09207 \sin(32.5 \cdot la1 + 3.094) + 0.08945 \sin(21.67 \cdot la1 - 0.2405) + 0.06195 \sin(43.33 \cdot la1 - 0.5456) + 0.02536 \sin(65 \cdot la1 + 0.02227) + 0.02217 \sin(54.16 \cdot la1 + 2.599) + 0.02566 \sin(75.83 \cdot la1 + 2.804)); \]

\[ T_{22} = (0.6822 \sin(5.395 \cdot la2 + 2.851) + 0.4538 \sin(10.86 \cdot la2 + 2.576) + 0.09207 \sin(32.5 \cdot la2 + 3.094) + 0.08945 \sin(21.67 \cdot la2 - 0.2405) + 0.06195 \sin(43.33 \cdot la2 - 0.5456) + 0.02536 \sin(65 \cdot la2 + 0.02227) + 0.02217 \sin(54.16 \cdot la2 + 2.599) + 0.02566 \sin(75.83 \cdot la2 + 2.804)); \]

\[ T_{23} = (0.6822 \sin(5.395 \cdot la3 + 2.851) + 0.4538 \sin(10.86 \cdot la3 + 2.576) + 0.09207 \sin(32.5 \cdot la3 + 3.094) + 0.08945 \sin(21.67 \cdot la3 - 0.2405) + 0.06195 \sin(43.33 \cdot la3 - 0.5456) + 0.02536 \sin(65 \cdot la3 + 0.02227) + 0.02217 \sin(54.16 \cdot la3 + 2.599) + 0.02566 \sin(75.83 \cdot la3 + 2.804)); \]

\[ \%====================(Photo-detectors)-Responsivity ====================% \]

\[ R_1 = (0.6584 \sin(5.178 \cdot la1 - 2.449) + 0.1963 \sin(10.35 \cdot la1 + 3.252) + 0.01612 \sin(22.67 \cdot la1 - 2.383) + 0.003888 \sin(42.32 \cdot la1 - 1.085) + 0.002487 \sin(31.7 \cdot la1 - 2.227) + 0.001835 \sin(53.65 \cdot la1 + 0.1776) + 0.006553 \sin(76.63 \cdot la1 + 0.9638)); \]

\[ R_2 = (0.6584 \sin(5.178 \cdot la2 - 2.449) + 0.1963 \sin(10.35 \cdot la2 + 3.252) + 0.01612 \sin(22.67 \cdot la2 - 2.383) + 0.003888 \sin(42.32 \cdot la2 - 1.085) + 0.002487 \sin(31.7 \cdot la2 - 2.227) + 0.001835 \sin(53.65 \cdot la2 + 0.1776) + 0.006553 \sin(76.63 \cdot la2 + 0.9638)); \]

\[ R_3 = (0.6584 \sin(5.178 \cdot la3 - 2.449) + 0.1963 \sin(10.35 \cdot la3 + 3.252) + 0.01612 \sin(22.67 \cdot la3 - 2.383) + 0.003888 \sin(42.32 \cdot la3 - 1.085) + 0.002487 \sin(31.7 \cdot la3 - 2.227) + 0.001835 \sin(53.65 \cdot la3 + 0.1776) + 0.006553 \sin(76.63 \cdot la3 + 0.9638)); \]

\[ \%======================================================================\]

\[ \text{for } i = 1: \text{size}(t) \]

\[ \%======================================================================\]

\[ \text{if } V1(i) < 0.01 | | V2(i) < 0.01 \% V3(i) < 0.00001 \]
T98(i) = 1400;
%T96(i) = 1400;
%T86(i) = 1400;
Tls(i) = 1400;
%A(i) = 0;
cls(i) = 0;
dr(i) = 0;
else
    e12 = @(T2) V1(i) ./ V2(i) - (0.9737 * 2.1498 * trapz(la1, (la1.^-5)).*(exp(C2./(T2*la1))).^-1).*IF1.*T11.*T21.*R1)./(trapz(la2, (la2.^-5)).*(exp(C2./(T2*la2))).^-1).*IF2.*T12.*(0.92-T22).*R2));
    T2 = fzero(e12, [400, 5000]);
    T98(i) = T2;
end

% A = 2.5593*(V1(i).*exp((14417./T98(i))).^0.5);
% dr(i) = d2;
%================================ T(998/640) =============================
%================================ T(998/640) =============================
e13 = @(T3) V1(i) ./ V3(i) - (0.9496 * 7.8118 * trapz(la1, (la1.^-5)).*(exp(C2./(T3*la1))).^-1).*IF1.*T11.*T21.*R1)/trapz(la3, (la3.^-5)).*(exp(C2./(T3*la3))).^-1).*IF3.*(0.90-T13).*R3));
    T3 = fzero(e13, [400, 5000]);
    T96(i) = T3;
%================================ T(810/640) =============================
e23 = @(T4) V2(i) ./ V3(i) - (0.9746 * 3.5425 * trapz(la2, (la2.^-5)).*(exp(C2./(T4*la2))).^-1).*IF2.*T12.*(0.92-T22).*R2)/trapz(la3, (la3.^-5)).*(exp(C2./(T4*la3))).^-1).*IF3.*(0.90-T13).*R3));
    T4 = fzero(e23, [400, 5000]);
    T86(i) = T4;
%================================ T(least sqr.) =============================
% y1 = (la1.^-5).*((exp(C2./(T1*la1))).^-1).*0.5506*exp((-((la1-0.9738)./0.01734).^2)+0.5974*exp(-((la1-1.005)./0.02647).^2)).*T11.*T21;
% a1 = trapz(la1, y1);
% y2 = (la2.^-5).*((exp(C2./(T1*la2))).^-1).*0.2182*exp((-((la2-0.7879)./0.02179).^2)+0.5687*exp(-((la2-0.8148)./0.05184).^2)).*T12.*(1-T22);
% a2 = trapz(la2, y2);
% y3 = (la3.^-5).*((exp(C2./(T1*la3))).^-1).*0.6862*exp((-((la3-0.6439)./0.04651).^2)).*T13;
% a3 = trapz(la3, y3);
% z1 = exp(C2./(T1*la1)).*((la1.^-6).*((exp(C2./(T1*la1))).^-2).*0.5506*exp(-((la1-0.9738)./0.01734).^2)+0.5974*exp(-((la1-1.005)./0.02647).^2));
% b1 = trapz(la1, z1);
% z2 = exp(C2./(T1*la2)).*((la2.^-6).*((exp(C2./(T1*la2))).^-2).*0.2182*exp(-((la2-0.7879)./0.02179).^2)+0.5687*exp(-((la2-0.8148)./0.05184).^2));
% b2 = trapz(la2, z2);
% z3 = exp(C2./(T1*la3)).*((la3.^-6).*((exp(C2./(T1*la3))).^-2).*0.6862*exp(-((la3-0.6439)./0.04651).^2));
% b3 = trapz(la3, z3);
\% A1 = \left( \frac{1}{2 \pi C_1 C} \right) \left( 0.94 \times 10.039 \times a_1 \times V_1(i) + 0.965 \times 4.5288 \times a_2 \times V_2(i) + 0.99 \times a_3 \times V_3(i) \right) / \left( 0.883 \times 100.781 \times a_1 \times 2 + 0.9312 \times 20.51 \times a_2 \times 2 + 0.98 \times a_3 \times 2 \right) ; \\

\% A2 = \left( \frac{1}{2 \pi C_1 C} \right) \left( 0.94 \times 10.039 \times b_1 \times V_1(i) + 0.965 \times 4.5288 \times b_2 \times V_2(i) + 0.99 \times b_3 \times V_3(i) \right) / \left( 0.883 \times 100.781 \times a_1 \times b_1 + 0.9312 \times 20.51 \times a_2 \times b_2 + 0.98 \times a_3 \times b_3 \right) ; \\

e(\text{T1}) = \text{A1} - \text{A2} ; \\
T1 = \text{fzero(e, [400, 5000])} ; \\
Tl(i) = T1 ; \\

\% e(\text{T1}) = (1/(2*pi*C1*C)) \left( 0.94 \times 7.8118 \times \text{trapz(la1, (la1.^-5).*(exp(C2./(T1*la1))-1)).^2} \right) / \left( 0.883 \times 61.0242 \times \text{trapz(la1, (la1.^-5).*(exp(C2./(T1*la1))-1)).^2} \right) ; \\

\% T1 = fzero(e, [400, 5000]) ; \\
Tls(i) = T1 ; \\
A1 = \left( \frac{1}{2 \pi C_1 C} \right) \left( 0.94 \times 7.8118 \times \text{trapz(la1, (la1.^-5).*(exp(C2./(T1*la1))-1)).^2} \right) / \left( 0.883 \times 61.0242 \times \text{trapz(la1, (la1.^-5).*(exp(C2./(T1*la1))-1)).^2} \right) ; \\
A(i) = A1 ; \\
dls(i) = (A1/pi)^0.5 ; \\
end

end
%================================== Plot Signal ===================================
 subplot(2,1,1)
 plot(t,V1,'r-',t,V2,'g',t,V3,'b');
 % Axis Formats: Time Axis goes from min to max time (exactly same as temp
 % plot); Signal Axis has 20% gap above peak and below 0
 % axis([min(t) max(t) (0-0.2*max(V1)) (1.2*max(V1))])
 % xlabel('time [s]')
 % ylabel('Signal [V]')
 % legend('998','810','640')
 % title(fileName)
 % hold on

%================================== Plot Temperature ===================================

 plot(t,T98,'g');
 % axis([min(t) max(t) 1300 2400])

 % hold on
 % grid on
 % plot(t,T96,'b');
 % hold on
 % plot(t,T86,'m');
 % hold on
 % plot(t,Tls,'black')
 % legend('998/810','998/640','810/640','Least Sqr')
 % plot(t,A,'r')
 % hold on

plot(t,dls,'g')
 hold on
 plot(t,dr,'g:')
xlabel('time [ms]')
ylabel('Particle Diameter [micro meter]')
legend('Least square method','Ratio method')
 % ylabel('Particle Area [micro meter]^2')
3. Non-linear least square method using grey-body assumption

clear
clf
clc
fileName = 'Nickel-4%Rhodium thermocouple-test_004_the best.lvm';
dataMatrix = load(fileName);
%================================ Establish Baseline =========================%
t1 = dataMatrix(:,1);
t1 = t1 - min(t1);    %This makes all time on the graph relative (always starts at 0)
t=1000*t1;
V3 = dataMatrix(:,2);             %blue = 640nm wavelength
OffsetV3 = dataMatrix(1:50,2);   %This Offset brings the temperature baseline to 0
V3 =V3 - mean(OffsetV3);
V2 = dataMatrix(:,3);            %green = 810nm wavelength
OffsetV2 = dataMatrix(1:50,3);
V2 =V2 - mean(OffsetV2);
V1 = dataMatrix(:,4);              %red = 998nm wavelength
OffsetV1 = dataMatrix(1:50,4);
V1 =V1 - mean(OffsetV1);
%================================ Constants================================% 
C1=0.59552*10^(-4);    % W.(micro m)^2/sr %
C2=14388;              % micro m.K %
C=3*10^(2);              % V/W %
%================================ Wavelengths Generation================%%% 
la1=linspace(0.90,1.05,200);
la2=linspace(0.68,0.96,200);
la3=linspace(0.52,0.82,200);
%================================ Transmittance curves================%%% 
T11=(0.8937*sin(5.598.*la1+2.988)+0.2867*sin(11.21.*la1+2.932)+0.1834*sin(22.84.*la1+2.08)+0.06848*sin(45.57.*la1-2.492)+0.05299*sin(34.88.*la1-0.9589)+0.02384*sin(68.68.*la1-1.319)+0.02741*sin(57.08.*la1+1.331)+0.01324*sin(102.7.*la1-0.1004));

T12=(0.8937*sin(5.598.*la2+2.988)+0.2867*sin(11.21.*la2+2.932)+0.1834*sin(22.84.*la2+2.08)+0.06848*sin(45.57.*la2-2.492)+0.05299*sin(34.88.*la2-0.9589)+0.02384*sin(68.68.*la2-1.319)+0.02741*sin(57.08.*la2+1.331)+0.01324*sin(102.7.*la2-0.1004));

T13=(0.8937*sin(5.598.*la3+2.988)+0.2867*sin(11.21.*la3+2.932)+0.1834*sin(22.84.*la3+2.08)+0.06848*sin(45.57.*la3-2.492)+0.05299*sin(34.88.*la3-0.9589)+0.02384*sin(68.68.*la3-1.319)+0.02741*sin(57.08.*la3+1.331)+0.01324*sin(102.7.*la3-0.1004));
T21=(0.7645*\sin(5.434.*la1+3.003)+0.5377*\sin(9.86.*la1+3.32)+0.08677*\sin(38.69.*la1-1.895)+1.781*\sin(62.53.*la1+4.367)+0.1936*\sin(25.32.*la1-3.557)+1.744*\sin(62.12.*la1-4.74)+0.04144*\sin(102.1.*la1-1.684)+0.1619*\sin(69.07.*la1+8.78));

T22=(0.7645*\sin(5.434.*la2+3.003)+0.5377*\sin(9.86.*la2+3.32)+0.08677*\sin(38.69.*la2-1.895)+1.781*\sin(62.53.*la2+4.367)+0.1936*\sin(25.32.*la2-3.557)+1.744*\sin(62.12.*la2-4.74)+0.04144*\sin(102.1.*la2-1.684)+0.1619*\sin(69.07.*la2+8.78));

T23=(0.7645*\sin(5.434.*la3+3.003)+0.5377*\sin(9.86.*la3+3.32)+0.08677*\sin(38.69.*la3-1.895)+1.781*\sin(62.53.*la3+4.367)+0.1936*\sin(25.32.*la3-3.557)+1.744*\sin(62.12.*la3-4.74)+0.04144*\sin(102.1.*la3-1.684)+0.1619*\sin(69.07.*la3+8.78));

%================================T(Ratio Pyrometry)=================================%
for i=1:size(t)
    %================================T(998/810)=================================%
    if V1(i)<0.01|| V2(i)<0.01 %V3(i)<0.00001
        %T98(i)=1400;
        %T96(i)=1400;
        %T86(i)=1400;
        Tls(i)=1000;
    else
        e12=@(T2)V1(i)./V2(i)- (0.9737*2.1529*trapz(la1,(la1.^-5).*(((exp(C2./(T2*la1))-1)).^-1).*\(0.5506*exp(-((la1-0.9738)/0.01734).^2)+0.5974*exp(-((la1-1.005)/0.02647).^2)).^T11.*(1-T21)))./(\(0.5506*exp(-((la1-0.7879)/0.02179).^2)+0.5974*exp(-((la1-0.8148)/0.05184).^2)).*T12.*\(1-T22)));
        % T2=fzero(e12,[400,5000]);
        % T98(i)=T2;
    end
    %================================T(998/640)=================================%
    if V1(i)<0.1
        e13=@(T3)V1(i)./V3(i)- (0.9496*10.039*trapz(la1,(la1.^-5).*(((exp(C2./(T3*la1))-1)).^-1).*\(0.5506*exp(-((la1-0.9738)/0.01734).^2)+0.5974*exp(-((la1-1.005)/0.02647).^2)).^T11.*(1-T21)))./(\(0.6862*exp(-((la3-0.6439)/0.04651).^2)).*T13);
        % T3=fzero(e13,[400,5000]);
        % T96(i)=T3;
    else
        e23=@(T4)V2(i)./V3(i)- (0.9746*4.5288*trapz(la2,(la2.^-5).*(((exp(C2./(T4*la2))-1)).^-1).*\(0.2182*exp(-((la2-0.7879)/0.02179).^2)+0.5687*exp(-((la2-0.8148)/0.05184).^2)).*T12.*\(1-T22)));
T22))./trapz(la3, (la3.^-5).*(((exp(C2./(T4*la3))-1)).^-1).*0.6862*exp(-(la3-0.6439)./0.04651).^2).*1-T13));

T4=fzero(e23, [400, 5000]);
T86(1)=T4;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

T(least sqr.)%%%%%%%%%%%%%%%%%%

y1=(la1.^-5).*(((exp(C2./(T1*la1))-1)).^-1).*0.5506*exp(-(la1-0.9738)./0.01734).^2+0.5974*exp(-(la1-1.005)./0.02647).^2).*T11.*T21;
% y1=trapz(la1,y1);
% z1=exp(C2./(T1*la1)).*((la1.^-6).*((exp(C2./(T1*la1))-1)).^-2).*0.5506*exp(-(la1-0.9738)./0.01734).^2)/V1(i);
% b1=trapz(la1,z1);
% z2=exp(C2./(T1*la2)).*((la2.^-6).*((exp(C2./(T1*la2))-1)).^-2).*0.2182*exp(-(la2-0.7879)./0.02179).^2)/V2(i);
% b2=trapz(la2,z2);
% z3=exp(C2./(T1*la3)).*((la3.^-6).*((exp(C2./(T1*la3))-1)).^-2).*0.6862*exp(-(la3-0.6439)./0.04651).^2)/V3(i);
% b3=trapz(la3,z3);

A1=(1/(2*pi*C1*C))*(0.94*10.039*a1.*V1(i)+0.965*4.5288*a2.*V2(i)+0.99*a3.*V3(i))./(0.883*100.781*la1.*^2+0.9312*20.51*la1.*^2+0.98*la1.*^2);

A2=(1/(2*pi*C1*C))*(0.94*10.039*b1.*V1(i)+0.965*4.5288*b2.*V2(i)+0.99*b3.*V3(i))./(0.883*100.781*la1.*b1+0.9312*20.51*la1.*b1+0.98*la1.*b1);

e=@(T1)A1-A2;
T1=fzero(e, [400, 5000]);
T1s(i)=T1:

e=@(T1) (1/(2*pi*C1*C))*(10.039*trapz(la1, (la1.^-5).*(((exp(C2./(T1*la1))-1)).^-1).*0.5506*exp(-(la1-0.9738)./0.01734).^2+0.5974*exp(-(la1-1.005)./0.02647).^2).*T11.*T21).*V1(i)+4.5288*trapz(la2, (la2.^-5).*((exp(C2./(T1*la2))-1)).^-1).*0.2182*exp(-(la2-0.7879)./0.02179).^2)/V2(i)+trapz(la3, (la3.^-5).*((exp(C2./(T1*la3))-1)).^-1).*0.6862*exp(-(la3-0.6439)./0.04651).^2)/V3(i).

1/(2*pi*C1*C))*(10.039*trapz(la1, exp(C2./(T1*la1))).*((la1.^-6).*((exp(C2./(T1*la1))-1)).^-2).*0.5506*exp(-(la1-0.9738)./0.01734).^2+0.5974*exp(-(la1-1.005)./0.02647).^2).*T11.*T21).^2+20.51*trapz(la2, (la2.^-5).*((exp(C2./(T1*la2))-1)).^-1).*0.2182*exp(-(la2-0.7879)./0.02179).^2+trapz(la3, (la3.^-5).*((exp(C2./(T1*la3))-1)).^-1).*0.6862*exp(-(la3-0.6439)./0.04651).^2).

1/(2*pi*C1*C))*10.039*trapz(la1, exp(C2./(T1*la1))).*((la1.^-6).*((exp(C2./(T1*la1))-1)).^-2).*0.5506*exp(-(la1-0.9738)./0.01734).^2+0.5974*exp(-(la1-1.005)./0.02647).^2).*V1(i)+4.5288*trapz(la2, exp(C2./(T1*la2))).*(la2.^-5).*((exp(C2./(T1*la2))-1)).^-2).*0.2182*exp(-(la2-0.7879)./0.02179).^2+trapz(la3, (la3.^-5).*((exp(C2./(T1*la3))-1)).^-1).*0.6862*exp(-(la3-0.6439)./0.04651).^2).

1/(2*pi*C1*C))*10.039*trapz(la1, exp(C2./(T1*la1))).*((la1.^-6).*((exp(C2./(T1*la1))-1)).^-2).*0.5506*exp(-(la1-0.9738)./0.01734).^2+0.5974*exp(-(la1-1.005)./0.02647).^2).*V1(i)+4.5288*trapz(la2, exp(C2./(T1*la2))).*(la2.^-5).*((exp(C2./(T1*la2))-1)).^-2).*0.2182*exp(-(la2-0.7879)./0.02179).^2+trapz(la3, (la3.^-5).*((exp(C2./(T1*la3))-1)).^-1).*0.6862*exp(-(la3-0.6439)./0.04651).^2).

1/(2*pi*C1*C))*10.039*trapz(la1, exp(C2./(T1*la1))).*((la1.^-6).*((exp(C2./(T1*la1))-1)).^-2).*0.5506*exp(-(la1-0.9738)./0.01734).^2+0.5974*exp(-(la1-1.005)./0.02647).^2).*V1(i)+4.5288*trapz(la2, exp(C2./(T1*la2))).*(la2.^-5).*((exp(C2./(T1*la2))-1)).^-2).*0.2182*exp(-(la2-0.7879)./0.02179).^2+trapz(la3, (la3.^-5).*((exp(C2./(T1*la3))-1)).^-1).*0.6862*exp(-(la3-0.6439)./0.04651).^2).

1/(2*pi*C1*C))*10.039*trapz(la1, exp(C2./(T1*la1))).*((la1.^-6).*((exp(C2./(T1*la1))-1)).^-2).*0.5506*exp(-(la1-0.9738)./0.01734).^2+0.5974*exp(-(la1-1.005)./0.02647).^2).*V1(i)+4.5288*trapz(la2, exp(C2./(T1*la2))).*(la2.^-5).*((exp(C2./(T1*la2))-1)).^-2).*0.2182*exp(-(la2-0.7879)./0.02179).^2+trapz(la3, (la3.^-5).*((exp(C2./(T1*la3))-1)).^-1).*0.6862*exp(-(la3-0.6439)./0.04651).^2).
6)*(exp(C2/(T1*la2))^-1)).^-2).*(0.2182*exp(-(la2-0.7879)/0.01734).^-2)*V2(i)+trapz(la3,exp(C2/(T1*la3)).*(la3.^-6).*((exp(C2/(T1*la3))-1)).^-2)*0.5506*exp(-(la3-0.9738)/0.02179).^-2)*0.5687*exp(-(la3-0.8148)/0.05184).^-2)).*T11.*T21.*trapz(la1,exp(C2/(T1*la1)).*(la1.^-5).*((exp(C2/(T1*la1))-1)).^-1).*(0.5506*exp(-(la1-0.9738)/0.01734).^-2)+0.5974*exp(-(la1-0.8148)/0.05184).^-2))*V3(i)./(100.781*trapz(la1,la1.^-6).*(exp(C2/(T1*la1))-1)).^-1).*(0.5506*exp(-(la1-0.9738)/0.01734).^-2)+0.5974*exp(-(la1-0.8148)/0.05184).^-2)).^2))+20.51*trapz(la2,la2.^-5).*(((exp(C2/(T1*la2))-1)).^-1).*(0.2182*exp(-(la2-0.7879)/0.01734).^-2)*0.5506*exp(-(la2-0.9738)/0.02179).^-2)*0.5687*exp(-(la2-0.8148)/0.05184).^-2).*T12.*(1-T22)).*trapz(la2,exp(C2/(T1*la2)).*(la2.^-6).*(exp(C2/(T1*la2))-1)).^-2)*0.2182*exp(-(la2-0.7879)/0.01734).^-2)*0.5506*exp(-(la2-0.9738)/0.02179).^-2)*0.5687*exp(-(la2-0.8148)/0.05184).^-2)))+0.883*100.781*trapz(la3,la3.^-5).*(((exp(C2/(T1*la3))-1)).^-1).*(0.5506*exp(-(la3-0.9738)/0.01734).^-2)+0.5974*exp(-(la3-0.8148)/0.05184).^-2)).*V3(i)+0.99*trapz(la3,la3.^-5).*(((exp(C2/(T1*la3))-1)).^-1).*(0.6862*exp(-(la3-0.6439)/0.04651).^-2)).*V3(i)+(0.94*10.039*trapz(la1,la1.^-5).)*(exp(C2/(T1*la1))-1)).^-1).*0.965*4.5288*trapz(la2,la2.^-5).*(exp(C2/(T1*la2))-1)).^-1).*0.99*trapz(la3,la3.^-5).*(exp(C2/(T1*la3))-1)).^-1).*0.6862*exp(-(la3-0.6439)/0.04651).^-2)).

% T1=fzero(e,[400,5000]);
% T1s(i)=T1;
% A(i)=(1/(2*pi*C1*C))*(0.94*10.039*trapz(la1,la1.^-5).*)(exp(C2/(T1*la1))-1)).^-1).*0.5506*exp(-(la1-0.9738)/0.01734).^-2)*0.5974*exp(-(la1-0.8148)/0.05184).^-2).*T11.*T21.*V1(i)+0.965*4.5288*trapz(la2,la2.^-5).*(exp(C2/(T1*la2))-1)).^-1).*0.2182*exp(-(la2-0.7879)/0.01734).^-2)*0.5974*exp(-(la2-0.8148)/0.05184).^-2).*T12.*(1-T22)).*V2(i)+0.99*trapz(la3,la3.^-5).*(exp(C2/(T1*la3))-1)).^-1).*0.6862*exp(-(la3-0.6439)/0.04651).^-2)).

% for i=8:size(t)-7
% if T96(i)~=1400
% T96(i)=(T96(i-7)+T96(i-6)+T96(i-5)+T96(i-4)+T96(i-3)+T96(i-2)+T96(i-1)+T96(i+1)+T96(i+2)+T96(i+3)+T96(i+4)+T96(i+5)+T96(i+6)+T96(i+7))./15
% end
% if T86(i)~=1400
% T86(i)=(T86(i-7)+T86(i-6)+T86(i-5)+T86(i-4)+T86(i-3)+T86(i-2)+T86(i-1)+T86(i+1)+T86(i+2)+T86(i+3)+T86(i+4)+T86(i+5)+T86(i+6)+T86(i+7))./15
% end

%========================== Smoothing T96,T86 =========================
% end
%================================= Plot Signal ================================
subplot(2,1,1)
plot(t,V1,'r-',t,V2,'g--',t,V3,'b :');
%Axis Formats: Time Axis goes from min to max time (exactly same as temp
%plot); Signal Axis has 20% gap above peak and below 0
axis([min(t) max(t) (0-0.2*max(V1)) (1.2*max(V1))])
%xlabel('time [ms]')
ylabel('Signal [V]')
legend('998','810','640')
%title(fileName)
hold on

%================================= Plot Temperature ==============================
subplot(2,1,2)
%plot(t,T98,'black','linewidth',1.5);
%hold on
%plot(t,T96,'c--');
%hold on
%plot(t,T86,'m :');
%hold on
plot(t,Tls,'g', 'linewidth',1.5)
axis([min(t) max(t) 1000 2400])
xlabel('time [ms]')
ylabel('Temperature [K]')
grid on
%legend('Least Sqr')
Non-linear least square method using 1st order polynomial emissivity vs. wavelength

```matlab
clear
clf
clc

C1=747.421;         % calibration const. for 998 nm %
C2=386.926;         % calibration const. for 810 nm %
C3=192.1936;        % calibration const. for 640 nm %
C1=0.59552*10^-4;    % W.(micro m)^2/sr %
C2=14388;            % micro m.K %
C=3*10^2;            % V/W %
del_la=0.07;          %filter band width, unit: micro m%
la1=0.998;           %filter 1 wavelength, unit: micro m%
la2=0.81;            %filter 2 wavelength, unit: micro m%
la3=0.64;            %filter 3 wavelength, unit: micro m%

fileName = 'Platinum TC test2_004.lvm';
dataMatrix = load(fileName);
%======================== Establish Baseline ============================%
t1 = dataMatrix(:,1);
t1 = t1 - min(t1);    %This makes all time on the graph relative (always
starts at 0)
t=1000*t1;
V3 = dataMatrix(:,2);             %blue = 640nm wavelength
OffsetV3 = dataMatrix(1:100,2);   %This Offset brings the temperature
baseline to 0
V3 =V3 - mean(OffsetV3);
V2 = dataMatrix(:,3);            %green = 810nm wavelength
OffsetV2 = dataMatrix(1:100,3);
V2 =V2 - mean(OffsetV2);
V1 = dataMatrix(:,4);              %red = 998nm wavelength
OffsetV1 = dataMatrix(1:100,4);
V1 =V1 - mean(OffsetV1);

% ===== Smoothing V3 ======
for n=8:size(t)-7
    V3(n)=(V3(n-7)+V3(n-6)+V3(n-5)+V3(n-4)+V3(n-3)+V3(n-2)+V3(n-1)+V3(n)+V3(n+1)+V3(n+2)+V3(n+3)+V3(n+4)+V3(n+5)+V3(n+6)+V3(n+7))./15;
end
% ===== Smoothing V2 ======
for n=8:size(t)-7
    V2(n)=(V2(n-7)+V2(n-6)+V2(n-5)+V2(n-4)+V2(n-3)+V2(n-2)+V2(n-1)+V2(n)+V2(n+1)+V2(n+2)+V2(n+3)+V2(n+4)+V2(n+5)+V2(n+6)+V2(n+7))./15;
end
% ===== Smoothing V1 ======
for n=8:size(t)-7
```

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V1(n) = (V1(n-7) + V1(n-6) + V1(n-5) + V1(n-4) + V1(n-3) + V1(n-2) + V1(n-1) + V1(n) + V1(n+1) + V1(n+2) + V1(n+3) + V1(n+4) + V1(n+5) + V1(n+6) + V1(n+7)) / 15;

for n = 1:size(t)
    if V1(n) < 0.002 || V2(n) < 0.002 || V3(i) < 0.00001

%========================Wavelengths Generation=========================%

lan1 = linspace(0.90, 1.05, 200);
lan2 = linspace(0.68, 0.96, 200);
lan3 = linspace(0.52, 0.82, 200);

%=========================Transmittance curves==========================%

T11 = (0.8937*sin(5.598.*lan1+2.988)+0.2867*sin(11.21.*lan1+2.988)+0.1834*sin(2.84.*lan1+2.08)+0.06848*sin(45.57.*lan1-2.492)+0.05299*sin(34.88.*lan1-0.9589)+0.02384*sin(68.68.*lan1-1.319)+0.02741*sin(57.08.*lan1+1.331)+0.01324*sin(102.7.*lan1-0.1004));

T12 = (0.8937*sin(5.598.*lan2+2.988)+0.2867*sin(11.21.*lan2+2.988)+0.1834*sin(2.84.*lan2+2.08)+0.06848*sin(45.57.*lan2-2.492)+0.05299*sin(34.88.*lan2-0.9589)+0.02384*sin(68.68.*lan2-1.319)+0.02741*sin(57.08.*lan2+1.331)+0.01324*sin(102.7.*lan2-0.1004));

T13 = (0.8937*sin(5.598.*lan3+2.988)+0.2867*sin(11.21.*lan3+2.988)+0.1834*sin(2.84.*lan3+2.08)+0.06848*sin(45.57.*lan3-2.492)+0.05299*sin(34.88.*lan3-0.9589)+0.02384*sin(68.68.*lan3-1.319)+0.02741*sin(57.08.*lan3+1.331)+0.01324*sin(102.7.*lan3-0.1004));

T21 = (0.7645*sin(5.434.*lan1+3.003)+0.5377*sin(9.86.*lan1+3.32)+0.08677*sin(38.69.*lan1-1.895)+1.781*sin(62.53.*lan1+4.367)+0.1936*sin(25.32.*lan1-3.557)+1.744*sin(62.12.*lan1-4.74)+0.04144*sin(102.1.*lan1-1.684)+0.1619*sin(69.07.*lan1+8.78));

T22 = (0.7645*sin(5.434.*lan2+3.003)+0.5377*sin(9.86.*lan2+3.32)+0.08677*sin(38.69.*lan2-1.895)+1.781*sin(62.53.*lan2+4.367)+0.1936*sin(25.32.*lan2-3.557)+1.744*sin(62.12.*lan2-4.74)+0.04144*sin(102.1.*lan2-1.684)+0.1619*sin(69.07.*lan2+8.78));

T23 = (0.7645*sin(5.434.*lan3+3.003)+0.5377*sin(9.86.*lan3+3.32)+0.08677*sin(38.69.*lan3-1.895)+1.781*sin(62.53.*lan3+4.367)+0.1936*sin(25.32.*lan3-3.557)+1.744*sin(62.12.*lan3-4.74)+0.04144*sin(102.1.*lan3-1.684)+0.1619*sin(69.07.*lan3+8.78));
Tl(n) = 1000;
Area(n) = 0;
d(n) = 0;
else

e = @(T1) (1/(2*pi*C1*C)) * (10.039 * trapz(lan1, (lan1.^-5).*(((exp(C2./(T1*lan1))-1)).^-1).*((0.5506*exp(-((lan1-0.9738)./0.01734).^2)+0.5974*exp(-((lan1-1.005)./0.02647).^2)).*V1(n)+4.5288*trapz(lan2, (lan2.^-5).*(((exp(C2./(T1*lan2))-1)).^-1).*((0.2182*exp(-((lan2-0.7879)./0.02179).^2)+0.5687*exp(-((lan2-0.8148)./0.05184).^2))).*V2(n)+trapz(lan3, (lan3.^-5).*(((exp(C2./(T1*lan3))-1)).^-1).*((0.6862*exp(-((lan3-0.6439)./0.04651).^2))/V3(n))./(100.781*trapz(lan1, (lan1.^-5).*(((exp(C2./(T1*lan1))-1)).^-1).*((0.5506*exp(-((lan1-0.9738)./0.01734).^2)+0.5974*exp(-((lan1-1.005)./0.02647).^2)).*V1(n)+4.5288*trapz(lan2, (lan2.^-5).*(((exp(C2./(T1*lan2))-1)).^-1).*((0.2182*exp(-((lan2-0.7879)./0.02179).^2)+0.5687*exp(-((lan2-0.8148)./0.05184).^2))).*V2(n)+trapz(lan3, (lan3.^-5).*(((exp(C2./(T1*lan3))-1)).^-1).*((0.6862*exp(-((lan3-0.6439)./0.04651).^2))))).

T1 = fzero(e, [1000, 4000]);
Tls(n) = T1;
A1 = (1/(2*pi*C1*C)) * (10.039 * trapz(lan1, (lan1.^-5).*(((exp(C2./(T1*lan1))-1)).^-1).*((0.5506*exp(-((lan1-0.9738)./0.01734).^2)+0.5974*exp(-((lan1-1.005)./0.02647).^2)).*V1(n)+4.5288*trapz(lan2, (lan2.^-5).*(((exp(C2./(T1*lan2))-1)).^-1).*((0.2182*exp(-((lan2-0.7879)./0.02179).^2)+0.5687*exp(-((lan2-0.8148)./0.05184).^2))).*V2(n)+trapz(lan3, (lan3.^-5).*(((exp(C2./(T1*lan3))-1)).^-1).*((0.6862*exp(-((lan3-0.6439)./0.04651).^2)))))
1) * (0.5506 * exp(-(lan1 - 0.9738) / 0.01734) ^ 2) + 0.5974 * exp(-(lan1 - 1.005) / 0.02647) ^ 2) * T11 * T21. ^ 2 + 20.51 * trapz(lan2, (lan2.^-5) .* exp((C2./(T1*lan2)) - 1)). ^ -1) * (0.2182 * exp(-(lan2 - 0.7879) / 0.02179) ^ 2) + 0.5687 * exp(-(lan2 - 0.8148) / 0.05184) ^ 2) * T12 * (1 - T22). ^ 2 + trapz(lan3, (lan3.^-5) .* ((exp(C2./(T1*lan3)) - 1)). ^ -1) * (0.6862 * exp(-(lan3 - 0.6439) / 0.04651) ^ 2) .* (1 - T13). ^ 2); 

Area(n) = A1; 

d(n) = (A1/pi)^0.5; 
end 
end 

for n = 1:size(t) 

if V1(n) < 0.002 || V2(n) < 0.002 % V3(i) < 0.00001 

T(n) = 1000; 

d(n) = 0; 
eps1(n) = 0; 
eps2(n) = 0; 
eps3(n) = 0; 
else 

A = [0 -1 -0.998; 0 1 0.998; 0 -1 -0.81; 0 1 0.81; 0 -1 -0.64; 0 1 0.64]; 
b = [0; 1; 0; 1; 0; 1]; 
lb = [1000; []; []]; 
ub = [3500; []; []]; 
x0 = [1000; 0.1; 0.1]; % Starting guess at the solution 
OPTIONS = optimset('Algorithm', 'interior-point'); 
func = @(x) (V1(n) - C1 * C1 * (pi/4) * d(n)^2 * del_la * (x(2) + la1 * x(3)) * la1^(-5) * exp(- C2/(la1 * x(1))) )^2 - (V2(n) - C1 * C1 * (pi/4) * d(n)^2 * del_la * (x(2) + la2 * x(3)) * la2^(-5) * exp(- C2/(la2 * x(1))) )^2 + (V3(n) - C1 * C1 * (pi/4) * d(n)^2 * del_la * (x(2) + la3 * x(3)) * la3^(-5) * exp(- C2/(la3 * x(1))) )^2; 
[x, fval] = fmincon(func, x0, A, b, [], [], lb, ub, [], OPTIONS); 
T(n) = x(1); 
eps1(n) = x(2) + x(3) * 0.998; 
eps2(n) = x(2) + x(3) * 0.810; 
eps3(n) = x(2) + x(3) * 0.640; 
end 
end 

subplot(2,3,1) 
plot(t, V1, 'r-', t, V2, 'g', t, V3, 'b'); 
axis([min(t) max(t) (0-0.2*max(V1)) (1.2*max(V1))]) 
xlabel('time [s]') 
ylabel('Signal [V]') 
legend('998', '810', '640') 
%title(fileName) 
hold on
```matlab
subplot(2,3,2)
plot(t,T)
xlabel('time [ms]')
ylabel('T [K]')
hold on
subplot(2,3,3)
plot(t,Area)
xlabel('time [ms]')
ylabel('d [um^2]')
hold on
subplot(2,3,4)
plot(t,eps1)
xlabel('time [ms]')
ylabel('e1')
hold on
subplot(2,3,5)
plot(t,eps2)
xlabel('time [ms]')
ylabel('e2')
hold on
subplot(2,3,6)
plot(t,eps3)
xlabel('time [ms]')
ylabel('e3')
hold on
```
5. Non-linear least square method using 2st order polynomial emissivity vs. wavelength

clear
clf
clc

Ci1=747.421; % calibration const. for 998 nm %
Ci2=386.926; % calibration const. for 810 nm %
Ci3=192.1936; % calibration const. for 640 nm %
C1=0.59552*10^(-4); % W.(micro m)^2/sr %
C2=14388; % micro m.K %
C=3*10^(2); % V/W %
del_la=0.07; %filter band width, unit: micro m%
la1=0.998; %filter 1 wavelength, unit: micro m%
la2=0.81; %filter 2 wavelength, unit: micro m%
la3=0.64; %filter 3 wavelength, unit: micro m%

fileName = 'Platinum TC test2_004.lvm';
dataMatrix = load(fileName);

%======================== Establish Baseline ============================%
t1 = dataMatrix(:,1);
t1 = t1 - min(t1); %This makes all time on the graph relative (always
starts at 0)
t=1000*t1;
V3 = dataMatrix(:,2); %blue = 640nm wavelength
OffsetV3 = dataMatrix(1:100,2); %This Offset brings the temperature
baseline to 0
V3 =V3 - mean(OffsetV3);

V2 = dataMatrix(:,3); %green = 810nm wavelength
OffsetV2 = dataMatrix(1:100,3);
V2 =V2 - mean(OffsetV2);

V1 = dataMatrix(:,4); %red = 998nm wavelength
OffsetV1 = dataMatrix(1:100,4);
V1 =V1 - mean(OffsetV1);

% ===== Smoothing V3 ======
for n=8:size(t)-7
    V3(n)=(V3(n-7)+V3(n-6)+V3(n-5)+V3(n-4)+V3(n-3)+V3(n-2)+V3(n-1)+V3(n)+V3(n+1)+V3(n+2)+V3(n+3)+V3(n+4)+V3(n+5)+V3(n+6)+V3(n+7))./15;
end
% ===== Smoothing V2 ======
for n=8:size(t)-7
    V2(n)=(V2(n-7)+V2(n-6)+V2(n-5)+V2(n-4)+V2(n-3)+V2(n-2)+V2(n-1)+V2(n)+V2(n+1)+V2(n+2)+V2(n+3)+V2(n+4)+V2(n+5)+V2(n+6)+V2(n+7))./15;
end
% ===== Smoothing V1 ======
for n=8:size(t)-7
\[
V1(n) = \frac{(V1(n-7) + V1(n-6) + V1(n-5) + V1(n-4) + V1(n-3) + V1(n-2) + V1(n-1) + V1(n) + V1(n+1) + V1(n+2) + V1(n+3) + V1(n+4) + V1(n+5) + V1(n+6) + V1(n+7))}{15};
\]

end

%==================================Wavelengths Generation=================================

\[
\text{lan1} = \text{linspace}(0.90, 1.05, 200);
\]

\[
\text{lan2} = \text{linspace}(0.68, 0.96, 200);
\]

\[
\text{lan3} = \text{linspace}(0.52, 0.82, 200);
\]

%==================================Transmittance curves======================================

\[
T11 = (0.8937 \times \sin(5.598 \times \text{lan1} + 2.988) + 0.2867 \times \sin(11.21 \times \text{lan1} + 2.932) + 0.1834 \times \sin(22.84 \times \text{lan1} + 2.08) + 0.06848 \times \sin(45.57 \times \text{lan1} - 2.492) + 0.05299 \times \sin(34.88 \times \text{lan1} - 0.9589) + 0.02384 \times \sin(68.68 \times \text{lan1} - 1.319) + 0.02741 \times \sin(57.08 \times \text{lan1} + 1.331) + 0.01324 \times \sin(102.7 \times \text{lan1} - 0.1004));
\]

\[
T12 = (0.8937 \times \sin(5.598 \times \text{lan2} + 2.988) + 0.2867 \times \sin(11.21 \times \text{lan2} + 2.932) + 0.1834 \times \sin(22.84 \times \text{lan2} + 2.08) + 0.06848 \times \sin(45.57 \times \text{lan2} - 2.492) + 0.05299 \times \sin(34.88 \times \text{lan2} - 0.9589) + 0.02384 \times \sin(68.68 \times \text{lan2} - 1.319) + 0.02741 \times \sin(57.08 \times \text{lan2} + 1.331) + 0.01324 \times \sin(102.7 \times \text{lan2} - 0.1004));
\]

\[
T13 = (0.8937 \times \sin(5.598 \times \text{lan3} + 2.988) + 0.2867 \times \sin(11.21 \times \text{lan3} + 2.932) + 0.1834 \times \sin(22.84 \times \text{lan3} + 2.08) + 0.06848 \times \sin(45.57 \times \text{lan3} - 2.492) + 0.05299 \times \sin(34.88 \times \text{lan3} - 0.9589) + 0.02384 \times \sin(68.68 \times \text{lan3} - 1.319) + 0.02741 \times \sin(57.08 \times \text{lan3} + 1.331) + 0.01324 \times \sin(102.7 \times \text{lan3} - 0.1004));
\]

\[
T21 = (0.7645 \times \sin(5.434 \times \text{lan1} + 3.003) + 0.5377 \times \sin(9.86 \times \text{lan1} + 3.32) + 0.08677 \times \sin(38.69 \times \text{lan1} - 1.895) + 1.781 \times \sin(62.53 \times \text{lan1} + 4.367) + 0.1936 \times \sin(25.32 \times \text{lan1} - 3.557) + 1.744 \times \sin(62.12 \times \text{lan1} - 4.74) + 0.04144 \times \sin(102.1 \times \text{lan1} - 1.684) + 0.1619 \times \sin(69.07 \times \text{lan1} + 8.78));
\]

\[
T22 = (0.7645 \times \sin(5.434 \times \text{lan2} + 3.003) + 0.5377 \times \sin(9.86 \times \text{lan2} + 3.32) + 0.08677 \times \sin(38.69 \times \text{lan2} - 1.895) + 1.781 \times \sin(62.53 \times \text{lan2} + 4.367) + 0.1936 \times \sin(25.32 \times \text{lan2} - 3.557) + 1.744 \times \sin(62.12 \times \text{lan2} - 4.74) + 0.04144 \times \sin(102.1 \times \text{lan2} - 1.684) + 0.1619 \times \sin(69.07 \times \text{lan2} + 8.78));
\]

\[
T23 = (0.7645 \times \sin(5.434 \times \text{lan3} + 3.003) + 0.5377 \times \sin(9.86 \times \text{lan3} + 3.32) + 0.08677 \times \sin(38.69 \times \text{lan3} - 1.895) + 1.781 \times \sin(62.53 \times \text{lan3} + 4.367) + 0.1936 \times \sin(25.32 \times \text{lan3} - 3.557) + 1.744 \times \sin(62.12 \times \text{lan3} - 4.74) + 0.04144 \times \sin(102.1 \times \text{lan3} - 1.684) + 0.1619 \times \sin(69.07 \times \text{lan3} + 8.78));
\]

\[
\text{for } n = 1 : \text{size(t)}
\]

\[
\text{if } V1(n) < 0.003 \text{ || V2(n) < 0.003 } \% V3(i) < 0.0001
\]
Tls(n)=1000;
Area(n)=0;
d(n)=0;
else

e=@(T1)(1/(2*pi*C1*C))*(10.039*trapz(lan1,(lan1.^-5).*(((exp(C2./(T1*lan1))-1)).^-1).*V1(n)+4.5288*trapz(lan2,(lan2.^-5).*(((exp(C2./(T1*lan2))-1)).^-1).*V2(n)+trapz(lan3,(lan3.^-5).*(((exp(C2./(T1*lan3))-1)).^-1).*V3(n)))/(100.781*trapz(lan1,(lan1.^-5).*(((exp(C2./(T1*lan1))-1)).^-1).*V1(n)+4.5288*trapz(lan2,(lan2.^-5).*(((exp(C2./(T1*lan2))-1)).^-1).*V2(n)+trapz(lan3,(lan3.^-5).*(((exp(C2./(T1*lan3))-1)).^-1).*V3(n))).
T1=fzero(e,[1000,4000]);
Tls(n)=T1;
A1=(1/(2*pi*C1*C))*(10.039*trapz(lan1,(lan1.^-5).*(((exp(C2./(T1*lan1))-1)).^-1).*V1(n)+4.5288*trapz(lan2,(lan2.^-5).*(((exp(C2./(T1*lan2))-1)).^-1).*V2(n)+trapz(lan3,(lan3.^-5).*(((exp(C2./(T1*lan3))-1)).^-1).*V3(n))).
\[
1. \times (0.5506 \times \exp(-((\text{lan1}-0.9738)/0.01734)^2)) + 0.5974 \times \exp(-((\text{lan1}-1.005)/0.02647)^2)) \times \text{T11} \times \text{T21}) \times 20.51 \times \text{trapz(\text{lan2}, (\text{lan2}^2))} + 20.51 \times \text{trapz(\text{lan2}, (\text{lan2}^2) \times \exp(-((\text{lan2}-0.7879)/0.02179)^2)) \times \text{T12} \times (1- \text{T22})) \times 2 \times \text{trapz(\text{lan3}, (\text{lan3}^2))} \times (\exp(C2/\text{T1} \times \text{lan3})) - 1)^{-1} \times (0.6862 \times \exp(-((\text{lan3}-0.6439)/0.04651)^2)) \times (1- \text{T13})) \times 2); \\
\text{Area(n)=A1; d(n)=(A1/\pi)^0.5; end end} \\
\text{for n=1:size(t)}  \\
\text{if V1(n)<0.003 || V2(n)<0.003 && V3(n)<0.0001} \\
\text{T(n)=1000; d(n)=0; eps1(n)=0; eps2(n)=0; eps3(n)=0; else}  \\
\text{A=[0 -1 -0.998 -0.996; 0 1 0.998 0.996; 0 -1 -0.81 -0.6561; 0 1 0.81 0.6561; 0 -1 -0.64 -0.409; 0 1 0.64 0.409]; b=[0; 1; 0; 1; 0; 1]; lb=[1000; []; []; []]; ub=[3500; []; []; []]; x0 = [1000; 0.1; 0.1; 0.1]; % Starting guess at the solution OPTIONS = optimset('Algorithm','interior-point'); func=@(x)(V1(n)-C11*C1*(\pi/4)*d(n)^2*del_la*(x(2)+la1*x(3)+x(4)*la1^2)*la1^(-5)*exp(-C2/(la1*x(1))))^2+(V2(n)-C12*C1*(\pi/4)*d(n)^2*del_la*(x(2)+la2*x(3)+x(4)*la2^2)*la2^(-5)*exp(-C2/(la2*x(1))))^2+(V3(n)-C13*C1*(\pi/4)*d(n)^2*del_la*(x(2)+la3*x(3)+x(4)*la3^2)*la3^(-5)*exp(-C2/(la3*x(1))))^2; [x,fval] = fmincon(func,x0,A,b,[],[],lb,ub,[],OPTIONS); \\
\text{T(n)=x(1); eps1(n)=x(2)+x(3)*0.998+x(4)*0.998^2; eps2(n)=x(2)+x(3)*0.810+x(4)*0.81^2; eps3(n)=x(2)+x(3)*0.640+x(4)*0.64^2; end end} \\
\text{subplot(2,3,1)} \\
\text{plot(t,V1,'r-',t,V2,'g',t,V3,'b'); axis([min(t) max(t) (0-0.2*max(V1)) (1.2*max(V1))]) xlabel('time [s]')}

ylabel('Signal [V]')
legend('998','810','640')
$title(fileName)
hold on

subplot(2,3,2)
plot(t,T)
xlabel('time [ms]')
ylabel('T [K]')
hold on
subplot(2,3,3)
plot(t,Area)
xlabel('time [ms]')
ylabel('d [um]')
hold on
subplot(2,3,4)
plot(t,eps1)
xlabel('time [ms]')
ylabel('e1')
hold on
subplot(2,3,5)
plot(t,eps2)
xlabel('time [ms]')
ylabel('e2')
hold on
subplot(2,3,6)
plot(t,eps3)
xlabel('time [ms]')
ylabel('e3')
hold on
APPENDIX 3

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A3. Experimental and modeling study of Single Coal Particle Combustion in O₂/N₂ and Oxy-fuel (O₂/CO₂) Atmospheres

Abstract

Coal particle combustion experiments were performed in a drop tube furnace (DTF) with oxygen concentration from 21 to 100%, in N₂ and CO₂ mixtures, under quiescent flow conditions. Small particles (75-90µm) of a high-volatile bituminous coal (PSOC-1451) and a lignite coal (DECS-11) are analyzed with particular attention to the particle burnout times and the particle surface temperatures. These experimental measurements are compared with the predictions of a comprehensive model of coal combustion. Combustion of coal particles is a multi-scale process where both chemical and physical phenomena are involved, thus it requires a coupled and accurate description of the kinetics as well as of the heat and mass transport phenomena. Important features of the model are a multistep kinetic scheme of coal volatilization and detailed kinetics of the successive gas-phase reactions and of the heterogeneous reactions of both char oxidation and gasification. The achieved overall agreement between the experimental data and the numerical predictions, in terms of particle temperature and burnout times, highlights the capability of the model to simulate the effect of different operating conditions in the coal combustion processes.

1. Introduction

Due to growing energy demand of developing countries the use of fossil fuels is expected to increase, along with the use of alternative energy sources [1]. The larger availability and lower cost of coal, with respect to other fossil fuels, makes it a leading energy resource for the production of electricity in the world [2]. Unfortunately, coal is a source of environmental
concern not only because of its strong greenhouse impact but also because of emission of nitrogen and sulfur oxides [3-5] and the formation of aerosol particles [6]. For these reasons “clean coal” technologies are of intense technological interest nowadays. In addition to experimental investigations and hardware development, reliable numerical models are needed to support the design and optimization of coal combustors and gasifiers.

Different strategies can be used for reducing the CO₂ emission from coal-fired power plants: pre- and post-combustion capture, oxy-fuel combustion and chemical looping [7]. Among these different technologies, the oxy-fuel combustion is the most likely technology for retrofitting existing coal-fired power plants [8]. In oxy-fuel combustion, air is substituted with an O₂/CO₂ mixture and thus numerous gas properties such as density, heat capacity, diffusivity and gas emissivity change with consequences on the coal reactivity.

Coal combustion is a multi-phase, multi-scale and multi-components process which involves several species, different kinetics (devolatilization reactions, char heterogeneous reactions, secondary gas phase reactions) as well as transport processes at both the particle and the reactor scale.

Coal pyrolysis or devolatilization is the first step in coal combustion and influences ensuing phenomena. It is generally agreed that the combustion rate does not depend only on the rank and type of the different coals, but also depends on the operating conditions (heating rate, pyrolysis temperature, residence time) [9-11]. Models of coal devolatilisation were developed from simple empirical expressions of total mass release, with either one or two rate expressions [12] or with multi-step kinetic mechanisms [13] or finally with the description of the evolution of the lattice structures of the coal, such as those found in the FLASHCHAIN [14], FG-DVC [15] and CPD [16] models. A predictive mechanism of coal pyrolysis, recently proposed by the authors [17],
characterizes the released species with lumped components and allows a direct coupling with a detailed kinetic mechanism of secondary gas phase reactions [18].

The effects of the N$_2$ and the CO$_2$ background gases on coal pyrolysis are not well defined in the literature. From one side, several experimental studies suggest that coal devolatilization increases in CO$_2$ atmospheres [19, 20], due to the effect of the heterogeneous reactions between char and CO$_2$. Rathnam et al. [19] reported that the devolatilization rate of a bituminous coal, pyrolyzed in low heating rate conditions (25 K/min), was similar in either N$_2$ or CO$_2$ at temperatures lower than $\sim$1000 K, whereas at temperatures higher than 1000 K, the coal devolatilization rate was higher in CO$_2$ than in N$_2$. They also reported similar results in CO$_2$ and in N$_2$ in a drop tube furnace with four different coals at 1673 K [19]. These results were confirmed by Al-Makhadmeh et al. [20]. They observed the combustion of a lignite coal and of a bituminous coal in a drop tube reactor in N$_2$ and CO$_2$ atmosphere. The released volatiles were similar for both atmospheres at temperatures lower than 1173 K, while a larger amount was observed in CO$_2$, at higher temperatures.

From the other side, different studies show a minor or even a negative effect of CO$_2$ atmosphere on coal reactivity [21, 22]. Brix et al. [21] analyzed the pyrolysis of a bituminous coal in a drop tube furnace in N$_2$ and CO$_2$ atmospheres, and they found a similar morphology of the residual char and a similar volatile release, in both cases. Borrego and Alvarez [22] analysed the pyrolysis of a high and a low volatile bituminous coal in a drop tube furnace at 1573 K in N$_2$ and CO$_2$ environments and they found a negative effect of CO$_2$ on the coal volatilization.

The heterogeneous reactions of the char are anyhow the rate determining step in the coal combustion process. The char residue accounts for 30 to 70% of the initial weight, depending on the rank and origin of the coal and on the furnace operating conditions. The
oxidation/gasification time dictates the dimension of the furnace [23]. Over the years, several models have been developed for the char oxidation and gasification reactions [23-32]. These kinetic models address different aspects of the char oxidation, including detailed kinetic mechanism [24, 31], annealing mechanism [25, 26, 28], char morphology and particle distribution [23, 25, 32], and ash inhibition or catalytic effects [25, 27].

Experimental measurements have been conducted to assess the effect of physical aspects of coal particles (rank, origin and particle size) and operating parameters (temperature, heating rate, and the surrounding gas composition) on particle ignition, burnout times, and char combustion temperatures [33-38].

Both homogeneous and heterogeneous ignitions of the coal have been observed [33, 34, 36]. Khatami et al. [36] analysed the effects of the coal rank and surrounding gas composition on the ignition delay. They observed strong tendencies of homogeneous ignition for a bituminous coal and heterogeneous ignition for two lignites at O$_2$ concentrations lower than 40% in either N$_2$ or CO$_2$ background gases. Moreover, they also observed longer ignition delay times in CO$_2$ atmospheres. This behavior was mostly attributed to the higher heat capacity of O$_2$/CO$_2$ mixtures compared to the O$_2$/N$_2$ mixtures for homogeneous ignition and lower mass diffusivity of O$_2$ in CO$_2$ than in N$_2$, in heterogeneous ignition. Additionally, the experimental results highlighted a linear correlation between the ignition delay time and the O$_2$ concentration, in either the CO$_2$ or the N$_2$ mixtures. Similar results have been obtained by Shaddix and Molina [37], who concluded that the higher heat capacity of CO$_2$ is the main reason for the longer ignition delays in CO$_2$ mixtures in homogeneous ignition.

Levendis and co-wokers [35, 39-42] studied the single-particle combustion of different coals by varying the temperature conditions and the oxygen concentration. Bejarano and
Levendis [35] and Khatami et al. [42] investigated char surface temperatures and burnout times of several coal of different rank, at O\(_2\) concentrations from 21% up to 100% in N\(_2\) and CO\(_2\) background gases. They reported maximum char temperatures of 2100-2300 K for 75-90 \(\mu\)m lignite and 1800-2000 K for bituminous coal particles, in air at a drop tube furnace temperature of 1400 K. Accordingly, the burnout times of the bituminous coal were longer than those of the lignite coal (~50 ms versus ~40 ms, respectively). Temperature and burnout differences decrease with increasing O\(_2\) concentration. At furnace temperatures of 1400-1600 K, Murphy and Shaddix [43] measured a char surface temperature of 2200 K for a sub-bituminous coal and of 2000-2100 K for a bituminous coal at 24% O\(_2\). Shaddix et al. [44] found that the maximum mean temperatures for Pittsburgh bituminous chars were in the range of 1800-2000 K when furnace temperatures were in the range of 1130-1650 K at 24% O\(_2\) in N\(_2\). Corresponding temperatures for Beulah lignite char particles were in the range of 2000-2100 K.

In this work, two different coals are analysed in a drop tube furnace with a wide range of oxygen concentration (from 21% O\(_2\) to 100% O\(_2\)) both in O\(_2)/N\(_2\) atmosphere and O\(_2)/CO\(_2\) atmosphere. The drop tube furnace was operated with quiescent gas conditions, in order to minimize the differences in the axial profiles of gas temperatures caused by the different heat capacity of the two gas environments [35, 36]. The combustion of the same two coals in active flow environments in the drop tube furnace has been reported previously [42]. The experimental measurements obtained herein are then compared with the predictions of a comprehensive multi-scale, multi-phase and multi-component model able to describe combustion and gasification of coal particles.
2. Experimental Method

2.1. Fuels

A bituminous coal (PSOC-1451) and a lignite coal (DECS-11), obtained from the Pittsburgh Coal Bank, are analyzed in this study. Their proximate and ultimate analyses are shown in Table 2.

<table>
<thead>
<tr>
<th>Table 2. Proximate and Ultimate analysis of the Coals used in this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rank and Fuel Source</td>
</tr>
<tr>
<td>Bituminous High Volatile A</td>
</tr>
<tr>
<td>Pittsburgh #8 Pennsylvania, USA</td>
</tr>
<tr>
<td>Lignite A Beulah, North Dakota, USA</td>
</tr>
<tr>
<td>Proximate Analysis as received, and (upon re-evaluating moisture)</td>
</tr>
<tr>
<td>Moisture (%)</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
</tr>
<tr>
<td>Fixed Carbon (%)</td>
</tr>
<tr>
<td>Ash (%)</td>
</tr>
<tr>
<td>Ultimate Analysis (on a dry basis)</td>
</tr>
<tr>
<td>Carbon (%)</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
</tr>
<tr>
<td>Oxygen (%) (by diff.)</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
</tr>
<tr>
<td>Sulfur (%)</td>
</tr>
<tr>
<td>Sodium (%)</td>
</tr>
<tr>
<td>Calcium (%)</td>
</tr>
<tr>
<td>Ash (%)</td>
</tr>
<tr>
<td>Heating Value Dry [MJ/kg]</td>
</tr>
</tbody>
</table>

The two coals and their proximate and ultimate analysis data are obtained from the Penn-State Coal Sample Bank; however, upon opening the sealed containers of the supplied coals, variations of moisture content with storage in the laboratory were observed for the lignite. The measured moisture content values are listed (in parentheses) and the remaining proximate analysis values were re-calculated and are also shown (in parentheses).
The two coals were dried, ground and sieved to the size cut of 75-90 µm. This size cut was selected to be consistent with previous experiments [5, 35, 36].

2.2. Drop tube furnace (DTF)

The combustion of free-falling coal particles was carried out in an electrically heated, laminar flow drop tube furnace at a constant nominal wall temperature of 1400 K. The radiation cavity of this furnace is 25 cm long and it is heated by hanging molybdenum disilicide elements. A sealed 7 cm I.D. transparent quartz tube was fitted in the furnace. Gas was introduced to the radiation cavity of the furnace through a water-cooled stainless-steel injector (1 cm I.D.) as well as coaxially through a flow straightener to the furnace injector (Figure 12). Optical access to the radiation zone of the furnace for the pyrometer was achieved from the top of the furnace, through the particle injector. Additional observations were performed through observation ports located at the sides of the furnace using a high-speed cinematographic camera, as outlined by Levendis et al. [39].

![Figure 12. Schematic of the drop-tube furnace (DTF) and gas temperature measurement setup. More detailed figures can be found in [5, 35, 39, 45].](image-url)
2.3. Gas compositions

Gas compositions tested in the furnace included different mixtures of either O₂/N₂ or O₂/CO₂. The first conditions were air (~20%O₂ in N₂) and (20%O₂ in CO₂). Then, the oxygen concentration was increased in increments of 10% or 20% up to pure oxygen. Additionally, testing was performed in a 100% O₂ environment to determine how the particles burned in the absence of either supplemental gas. Oxygen partial pressures were controlled with pre-calibrated flowmeters, and were verified by an oxygen analyzer (Horiba, Model MPA-510).

2.4. Gas temperature

The coal particle combustion experiments were conducted under a quiescent gas condition (inactive flow, i.e., no injector flow and no furnace flow), to avoid the influence of the unheated flow gas condition. Quiescent gas condition was created by turning off the gas flows a few seconds prior to the particle injection. Therefore when the particles were introduced in the furnace, the centerline gas temperature was maintained at elevated levels, asymptotically approaching the wall temperature of the furnace, comparably fast in nitrogen and carbon-dioxide gases, as illustrated in Figure 2. Thus, the quiescent gas condition was implemented in this laboratory to provide the most experimentally-attainable uniformity in axial and radial temperature distribution in the furnace, and to equalize the furnace gas temperature profiles in the cases of N₂ or CO₂ background gases. More details on quiescent gas condition versus active flow in DTF are given in Khatami et al. [36]. It also allowed temperature sampling closer to the injector tip. A slender bare thermocouple (OMEGA type K model KMQXL-020, 250 μm bead diameter, 50 μm wire diameter, 500 μm sheath diameter, 1 m long) was used to measure the centerline gas temperature. The measured temperatures with this method were corrected for radiation effects as explained in Khatami et al [36]. The results are illustrated in Figure 13.
Figure 13. Centerline gas temperature inside the drop-tube furnace for pure N\textsubscript{2} and pure CO\textsubscript{2} in quiescent gas condition. This plot also shows the furnace wall set-point temperature (1400 K).

As shown in Figure 13, the neat N\textsubscript{2} and CO\textsubscript{2} gases under quiescent condition behave in the same way and the gas temperature profiles are similar. At the furnace wall set-point temperature ($T_w$) of 1400 K, as monitored by type-S thermocouples embedded in the wall, both axial gas temperature profiles along the centerline of the furnace are stabilized at about 1350 K.

2.5. Three-color optical pyrometer measurements and cinematography measurements

Pyrometric observations of single particles were conducted from the top of the furnace injector, viewing downwards along the central axis of the furnace (see Figure 12), which ideally was the particle's path-line. Accordingly, the luminous burnout histories of single particles - from ignition to extinction - could be monitored. An optical fiber transmitted light from the furnace to the pyrometer assembly. This pyrometer used two dichroic edge filters as spectrum splitters to direct the light to three interference filters. These filters had effective wavelengths of 0.640, 0.810 and 0.998 μm with bandwidths (FWHM) of 70 nm. Details of the pyrometer can be found in Levendis et al. [46]. The voltage signals generated by the three detectors were amplified and then processed by a microcomputer using the LabView 8.6 software. Temperature was deduced
from the three output voltage signals of the pyrometer using a non-linear least square method, based on Planck’s law and gray-body assumption [45, 46].

Cinematographic measurements have been carried out in order to compare the particle life times obtained with the optical pyrometer. At low O₂ concentrations, there is a discrepancy between the two methods. This fact is due to the very low luminosity of the coal particle as it approaches its extinction point. The radiation intensity emitted from the particle falls below the detection limit of the optical pyrometer, whereas it is still visible in the cinematographic records. Figure 14 shows several photographs of the burning of bituminous coal particles in different atmospheres.

(a) Bituminous coal particle (PSOC-1451), 75-90 µm, burning in 21%O₂-79%N₂

(b) Bituminous coal particle (PSOC-1451), 75-90 µm, burning in 21%O₂-79%CO₂

(c) Bituminous coal particle (PSOC-1451), 75-90 µm, burning in 40%O₂-60%CO₂
The bituminous coal particle shows the formation of a flame envelope around the particle because of the combustion of the volatile matter released during the pyrolysis. As oxygen concentration increases, the volatile flame becomes more intense, brief and bright, which is also the case for the ensuing char oxidation. The flame is brighter and the reactivity of the char is higher in the $\text{N}_2$ mixtures when compared with the corresponding flame and reactivity in the $\text{CO}_2$ mixtures. The higher heat capacity of $\text{CO}_2$ and the higher diffusivity of $\text{O}_2$ in $\text{N}_2$ mixtures explain these behaviors, as explained in an ensuing section.

3. Comprehensive mathematical model of coal particle combustion

A comprehensive mathematical model, which attempts to tackle the complex, multi-scale, multi-phase problem of coal combustion in the drop tube reactor, needs to analyze the chemistry of the process coupled with the intra and inter-phase heat and mass resistances.

3.1. Kinetic Model

The following mechanism describe the chemistry of the whole process:

- Pyrolysis or volatilization reactions of the coal particles
- Secondary gas-phase reactions of the released gases
- Heterogeneous reactions of the residual char

3.1.1 Pyrolysis or volatilization reactions of the coal particles
The main characteristic of the multi-step kinetic model of coal pyrolysis lies in its predictive capability: the only information required is the elemental composition of the coal and the operating conditions. The model is relatively simple but at the same time flexible and reliable and able to predict not only the devolatilization of the different coals in a wide range of operating conditions, but also the distribution of gas and tar species. In agreement with the work of Zhao et al [47], three reference coals are used to characterize the devolatilization process. The pyrolysis of any coal is obtained as a weighted sum of the pyrolysis of each reference coal. In this way, the coal rank is considered through the elemental composition and this affects the coal conversion and the properties of the residual chars. Table 2 reports the distribution of the reference coals of the lignite and bituminous one.

Table 2. Reference Coal Distribution of the lignite and bituminous coal

<table>
<thead>
<tr>
<th>Coal</th>
<th>Reference Coals Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>COAL₁</td>
</tr>
<tr>
<td>DECS 11 PSOC 1451</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>0.22</td>
</tr>
</tbody>
</table>

The devolatilization of each reference coal is described with competitive and successive reactions of thermal decomposition at low and high temperatures, cross-linking and reticulation reactions, and release of chemi-adsorbed species. Stoichiometric coefficients, product distribution and kinetic parameters of each reference coal depend on their composition and reference structure. The kinetic mechanism of coal pyrolysis consists of ~30 species involved in ~30 reactions [17]. The coal pyrolysis model was validated with several experimental data obtained from different coal in different conditions and reactors [48-52]. The comparisons refer
to the solid residue and the release of gas and tar species. Further details on the kinetic model and comparisons with experimental data have been reported in Sommariva et al. [17].

3.1.2 Secondary gas-phase reactions of the released gases

The volatile species released during the coal pyrolysis are a complex mixture of different products ranging from light gases up to heavy tar components. These products, once released in the surrounding gas phase, can undergo secondary gas phase reactions. In order to simplify the description of the complex mixture of heavy species, a careful selection of reference tar species has been done [17]. All these species were already considered inside a detailed pyrolysis and combustion mechanism of hydrocarbon fuels up to gasoline and diesel oil [18]. This kinetic model, consisting of more than 10000 reactions and 350 species, was developed and validated over several years [53] on the basis of a hierarchical modularity and is available on the web in CHEMKIN format, with thermo properties (http://creckmodeling.chem.polimi.it).

3.1.3 Heterogeneous reactions of the residual char

Herein the attention is mainly devoted to the following competitive three different classes of char heterogeneous reactions:

1- Annealing reactions

2- Char combustion reactions

3- Char gasification reactions

The thermal treatment of char particles at high temperatures causes an ordering of the turbostratic structure of the residual char with an increase of the graphitic domains and a parallel decrease of the intrinsic reactivity. This process is known as thermal annealing. It is well known [54, 55] that long heat treatment and high pyrolysis temperatures favor the formation of
Increasingly crystalline structures and several pertinent mechanisms are discussed in the literature [25, 26, 28]. Accordingly, the coal pyrolysis model of Sommariva et al. [17] was slightly modified and three different char pseudo-components are considered in the residual charcoal matrix. Together with a hydrogenated species CHAR$_H$ (C$_2$H) with a C/H ratio equal to coronene (C$_{24}$H$_{12}$), a distinction is made between an amorphous and disordered structure (CHAR$_C$) and an ordered graphitic one (CHAR$_G$).

Competitive reactions between char oxidation and annealing are considered in the model. During the coal devolatilization process the formation of both CHAR$_H$ and CHAR$_C$ takes place. Their relative amount depends on the rank of the original coal. Successive transformations involve firstly a dehydrogenation step from CHAR$_H$ to CHAR$_C$, and secondly the formation of CHAR$_G$ with the progressive ordering and inertization of the char structure at higher temperatures. The devolatilization phase takes usually place at moderate temperatures, too low for a significant annealing reaction transforming CHAR$_C$ into CHAR$_G$. While the first transformation involves the char dehydrogenation [56], the formation of CHAR$_G$ from CHAR$_C$ represents the transformation of young char to annealed char [28]. Table 3 reports the rate constant parameters of the thermal annealing mechanism. The annealing mechanism was developed on the basis of a comparison with experimental data of char elemental composition and char reactivity loss [57].

**Table 3. Simplified mechanism of the thermal annealing process**

<table>
<thead>
<tr>
<th>Annealing Reactions</th>
<th>Kinetic Expression$^*$</th>
<th>$\Delta H^0_r$ $^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$ CHAR$_H$ $\rightarrow$ 2CHAR$_C$ + 0.5H$_2$</td>
<td>1.0 x 10$^{11}$ exp(-3.35 x 10$^5$/RT)[CHAR$_H$]</td>
<td>0</td>
</tr>
<tr>
<td>$R_2$ CHAR$_C$ $\rightarrow$ CHAR$_G$</td>
<td>3.0 x 10$^3$ exp(-2.10 x 10$^5$/RT)[CHAR$_C$]</td>
<td>0</td>
</tr>
<tr>
<td>$R_3$ CHAR$_C$ $\rightarrow$ CHAR$_G$</td>
<td>1.0 x 10$^{11}$ exp(-4.6 x 10$^5$/RT)[CHAR$_C$]</td>
<td>0</td>
</tr>
</tbody>
</table>
\* Units are \( m^3, s, kJ, \text{kmol}. \)

The residual char can then undergo oxidation and gasification reactions. The char reactivity is the result of the coal structure and composition, as well as of the pyrolysis conditions. The kinetic mechanisms of char oxidation and gasification are based on char structure and were developed using experimental information. The heterogeneous reactions reported in Table 4 and in Table 5 refer to the particle volume and thus the reaction rates are expressed as \( \text{kmol/m}^3/\text{s} \). The heats of heterogeneous reactions were determined considering only the enthalpy of formation of the gas species \( \text{CO}, \text{CO}_2, \text{H}_2\text{O} \).

Table 4 shows the proposed char oxidation model. The kinetic parameters (activation energy and pre-exponential factor) of the char heterogeneous reactions are of the same order of magnitude of those reported in references [58-62].

**Table 4. Simplified mechanism of the oxidation process**

<table>
<thead>
<tr>
<th>Oxidation Heterogeneous Reactions</th>
<th>Kinetic Expression*</th>
<th>( \Delta H^0_{r,*} )</th>
</tr>
</thead>
</table>
| \( R_4 \) \( \text{CHAR}_H + 0.75\text{O}_2 \rightarrow 0.5\text{H}_2\text{O} \)  
+CO+\( \text{CHAR}_C \) | \( 5.5 \times 10^7 \exp(-1.20 \times 10^5/\text{RT}) \)  
[\( \text{CHAR}_H \)] \( [\text{O}_2]^{0.78} \) | -231000 |
| \( R_5 \) \( \text{CHAR}_C + \text{O}_2 \rightarrow \text{CO}_2 \) | \( 7.3 \times 10^7 \exp(-1.35 \times 10^5/\text{RT}) \)  
[\( \text{CHAR}_C \)] \( [\text{O}_2] \) | -393700 |
| \( R_6 \) \( \text{CHAR}_C + 0.5\text{O}_2 \rightarrow \text{CO} \) | \( 1.5 \times 10^9 \exp(-1.60 \times 10^5/\text{RT}) \)  
[\( \text{CHAR}_C \)] \( [\text{O}_2]^{0.78} \) | -110500 |
| \( R_7 \) \( \text{CHAR}_G + \text{O}_2 \rightarrow \text{CO}_2 \) | \( 2.3 \times 10^7 \exp(-1.55 \times 10^5/\text{RT}) \)  
[\( \text{CHAR}_G \)] \( [\text{O}_2] \) | -393700 |
| \( R_8 \) \( \text{CHAR}_G + 0.5\text{O}_2 \rightarrow 2\text{CO} \) | \( 6.1 \times 10^7 \exp(-1.80 \times 10^5/\text{RT}) \)  
[\( \text{CHAR}_G \)] \( [\text{O}_2]^{0.78} \) | -110500 |

* Units are: \( m^3, s, kJ, \text{kmol}. \)

Experimental measurements show a positive effect of the hydrogen content on the char reactivity [56]. Thus, \( \text{CHAR}_H \) is the most reactive pseudo-component, followed by \( \text{CHAR}_C \), and \( \text{CHAR}_G \) is the least reactive. The relative reactivity of the three char components \( \text{CHAR}_H: \text{CHAR}_C: \text{CHAR}_G \) is \( \approx 40:20:1 \) at 1173 K. This ratio is only a guess of the relative
reactivity. While the lowest reactivity of CHAR\textsubscript{G} is due to the annealing process, the different reactivity of CHAR\textsubscript{H} and CHAR\textsubscript{C} is not affecting in a significant way the particle burning time, in the current experimental conditions.

The first reaction in Table 3 (R\textsubscript{4}) is a partial oxidation of CHAR\textsubscript{H} with the formation of CHAR\textsubscript{C}, H\textsubscript{2}O and CO. Under low temperature conditions the main product of oxidation reaction is CO\textsubscript{2} while under high temperature conditions CO is the dominant product [24, 63]. The two oxidation reactions for CHAR\textsubscript{C} and for CHAR\textsubscript{G}, respectively, account for this behavior. The prediction of CO/CO\textsubscript{2} ratio for the three char components are close to the correlation of Tognotti et al. [63] and that of Campbell and Mitchell [24].

Finally, Table 5 lists the kinetic parameters of the char gasification mechanism with H\textsubscript{2}O and CO\textsubscript{2}.

**Table 5.** Simplified mechanism of the gasification process.

<table>
<thead>
<tr>
<th>Gasification Heterogeneous Reactions</th>
<th>Kinetic Expression*</th>
<th>$\Delta H^0 _r ,*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R\textsubscript{9} CHAR\textsubscript{H} + 0.5H\textsubscript{2}O $\rightarrow$ H\textsubscript{2} + 0.5CO + 1.5CHAR\textsubscript{C}</td>
<td>4.6x10\textsuperscript{8} exp(-1.94x10\textsuperscript{5}/RT) $[\text{CHAR}\textsubscript{H}]$ $[\text{H}_2\text{O}]$</td>
<td>65600</td>
</tr>
<tr>
<td>R\textsubscript{10} CHAR\textsubscript{C} + H\textsubscript{2}O $\rightarrow$ H\textsubscript{2} + CO</td>
<td>1.5x10\textsuperscript{9} exp(-2.22x10\textsuperscript{5}/RT) $[\text{CHAR}\textsubscript{C}]$ $[\text{H}_2\text{O}]$</td>
<td>131300</td>
</tr>
<tr>
<td>R\textsubscript{11} CHAR\textsubscript{G} + H\textsubscript{2}O $\rightarrow$ H\textsubscript{2} + CO</td>
<td>2.9x10\textsuperscript{8} exp(-2.26x10\textsuperscript{5}/RT) $[\text{CHAR}\textsubscript{G}]$ $[\text{H}_2\text{O}]$</td>
<td>131300</td>
</tr>
<tr>
<td>R\textsubscript{12} CHAR\textsubscript{H} +0.5CO\textsubscript{2} $\rightarrow$0.5H\textsubscript{2}O +0.5CO+2CHAR\textsubscript{C}</td>
<td>3.0 x10\textsuperscript{9} exp(-2.31x10\textsuperscript{5}/RT) $[\text{CHAR}\textsubscript{H}]$ $[\text{CO}_2]$</td>
<td>20500</td>
</tr>
<tr>
<td>R\textsubscript{13} CHAR\textsubscript{C} + CO\textsubscript{2} $\rightarrow$2CO</td>
<td>4.0x10\textsuperscript{9} exp(-2.51x10\textsuperscript{5}/RT) $[\text{CHAR}\textsubscript{C}]$ $[\text{CO}_2]$</td>
<td>173000</td>
</tr>
<tr>
<td>R\textsubscript{14} CHAR\textsubscript{G} + CO\textsubscript{2} $\rightarrow$2CO</td>
<td>1.0x10\textsuperscript{9} exp(-2.57x10\textsuperscript{5}/RT) $[\text{CHAR}\textsubscript{G}]$ $[\text{CO}_2]$</td>
<td>173000</td>
</tr>
</tbody>
</table>

* Units are: m\textsuperscript{3}, s, kJ, kmol.

The relative reactivity of the three charry components are similar to the previous ones. Gasification reactions with H\textsubscript{2}O are about thousand times slower than the corresponding
oxidation reactions. Gasification reactions with CO$_2$ are about 4-5 times slower than the ones with H$_2$O at 1200 K.

The whole set of heterogeneous reactions was extensively validated [57] by using a large set of experimental data coming from different sources and experimental devices, such as thermogravimetric balances and entrained flow reactors. Several comparison are reported in the Supplemental Material. The whole kinetic scheme results in a good compromise between accuracy and computational efforts maintaining a wide applicability and remaining completely predictive, as it does not require ‘ad hoc’ experiments.

3.2. Mathematical Model

The comprehensive model solves energy and mass balance equations for gas and solid phases, together with empirical submodels used for the closure of the balance equations. Pyrolysis is a primary process by which the coal produces residual char, heavy volatile species (tar) and permanent gaseous products. The released volatiles mix with the surrounding gas in the drop tube reactor. The model considers gas and solid temperature and species profiles not only in the gas phase but also inside the coal particle. Thus, the mathematical model consists of two submodels: the first one at the particle scale and the latter at the reactor scale. This approach is a further extension of previous models discussed, applied, and validated elsewhere [64].

3.2.1 The Particle Mass and Heat Balances

The particle model provides the internal description to account for intraparticle heat and mass-transfer resistances, assuming isotropic particles. The accuracy depends on the number of discretization sectors N (see Figure 4).
Figure 15. Particle sketch: the particle is divided into N spherical sectors (j = 1 to N) of equal volume.

Assuming N sectors inside the particle, the model governing equations regarding the mass (solid and gas phase) and energy balances around each particle sectors are:

\[
\frac{dm_{ji}^S}{dt} = V_j R_{ji} \quad (1)
\]

\[
\frac{dm_{ji}^G}{dt} = [J_{j-1}^j S_{j-1}^j - J_j S_j^j] + V_j R_{ji} \quad (2)
\]

\[
\sum_{i=1}^{NCP} m_{ji}^S \rho_{ji} S_j^j \frac{dT_j}{dt} = [Q_{j-1}^j S_{j-1}^j - Q_{j}^j S_j^j] + \left[ S_j^j \sum_{i=1}^{NCP} J_{j-1}^j h_{j-1}^j - S_j^j \sum_{i=1}^{NCP} J_j^j h_j^j \right] + V_j HR_j \quad (3)
\]

where \( m_{ji}^S \) is the mass of the i-th component in the j-th particle sector of the solid phase, \( m_{ji}^G \) is the mass of the i-th volatile component in j-th particle sector, \( t \) is the time variable, \( V_j \) and \( S_j \) are the volume and the external surface of the j-th particle sector. \( J_{j-1} \) and \( J_j \) are the mass fluxes of j-1th sector and j-th sector, respectively. \( R_{ji} \) is the net formation rate of the i-th component resulting from the multi-step devolatilization model and from the heterogeneous gas-solid reactions. The energy balance determines the particle temperature and accounts for the heat conduction \( (Q_j) \), the enthalpy flux relating to the mass diffusion \( (J_j h_j) \) and the heat of reactions \( (HR) \). The heat of pyrolysis is less than 1% of the combustion heat, thus it was neglected in our simulations.

Mass and heat flux terms inside the particle follow the constitutive Fick, Darcy and Fourier laws:
\begin{align}
J_{j,i} &= -D_{j,i}^{\text{eff}} MW_i \frac{dC_{j,i}}{dr} - y_{j,i} Da_j \rho_j c_j \frac{d\rho_j}{dr} \\
Q_j &= -k_j \frac{dT_j}{dr} \end{align}

where \( D_{j,i}^{\text{eff}} \), \( Da_j \) and \( k_j \) are the effective diffusion, Darcy and conduction coefficients inside the j-th particle sector, respectively. \( MW_i \) is the molecular weight of i-th gas species, \( y_{j,i} \) is the mass fraction of i-th gas species in j-th sector of particle, \( \mu_j \) is the viscosity in j-th sector, \( \rho_j \) is the gas density in j-th sector, \( \varepsilon_j \) is the porosity of j-th particle sector and \( C_{j,i}, P_j \) and \( T_j \) are the concentration of i-th gas species, pressure and temperature of j-th sector, respectively.

Inside the drop tube furnace, the coal particle moves in a quiescent environment with a velocity \( v_r \) derived from the momentum equation:

\[
m_p \frac{dv_r}{dt} = -(\rho_p - \rho_s) g V_p - 0.5 f \rho_s v_r \left| v_r \right|
\]

where \( m_p \) is the mass of the particle, \( g \) is the gravity constant and \( f \) is the friction factor, evaluated as \( f = \frac{24}{Re} \left( 1 + 0.14 Re^{0.7} \right) \) [65].

At the external particle surface, the flux contributions inside the particle are replaced by the flux exchanged with the bulk phase:

\[
J_{N,i} = Sh \frac{D^n}{d_p} MW \left[ C_{N,i} - C_{\text{bulk}}^{\text{i}} \right]
\]

\[
Q_N = Nu \frac{\lambda_p}{d_p} \left[ \frac{\kappa^{'}/2}{e^{\kappa^{'}/2} - 1} \right] \left[ T_N - T_{\text{bulk}} \right] + \sigma \varepsilon_{\text{surf}} \left[ T_N^4 - T_{\text{wall}}^4 \right]
\]
where Sh and Nu are Sherwood and Nusselt numbers, respectively, which were evaluated from Ranz and Marshall correlations [66], \( \kappa = - \frac{\sum_{i=1}^{NCg} J_{N,i} d_p}{\lambda_g} C P_g \) is a modified version of the Peclet number [43] in order to take into account the effect of the Stefan flow; \( \sigma \) is the Stefan-Boltzmann constant, \( T_{wall} \) is the wall temperature and \( \varepsilon_{rad} \) is the emissivity of carbonaceous particle, here assumed as 0.85 [67, 68].

3.2.2 Thermophysical and Effective Properties

As already discussed by Lautenberger and Fernandez-Pello [69] in the mathematical formulation of their Gpyro model for the simulation of combustion and gasification of solid fuels, it is necessary to give a proper emphasis to the property estimations as well as to their modifications during the combustion process. As the coal particle is heated and pyrolyzed, different gaseous and condensed species are formed with relevant morphological modifications. The model does not consider the initial swelling and size increase during devolatilization, but it accounts for diffusivity variations with conversion. Effective properties of the residual char particle are calculated by proper weighting of the local compositions. The size and porosity of the individual particles change, not only because of drying and devolatilization but mainly because of char gasification and combustion. Accordingly to Satterfield [70], the effective pore diffusion coefficient, \( D_{eff}^{ij} \), is evaluated on the basis of the equation

\[
D_{eff}^{ij} = \left[ \frac{1}{D_{m}^{ij}} + \frac{1}{D_{K}^{ij}} \right]^{-1} \frac{\varepsilon_j}{v_j},
\]

where \( D_{m}^{ij}, D_{K}^{ij} \) are the molecular and Knudsen diffusion of i-th species into j-th sector, respectively.
τₗ is the tortuosity of j-th particle sector. An initial mean pore diameter of ~0.3 µm for the bituminous coal and ~0.6 µm for the lignite have been chosen in this work [23, 60, 71, 72].

Porosity is a property of each condensed phase species and is again calculated as weighted porosity with the local composition. Char porosity significantly varies with the fuel conversion and is estimated on the basis of empirical correlations. These variations are considered and the model accounts for particle shrinkage during char conversion. According to Gil et al. [73], a linear relation between the porosity (εⱼ) and particle sector conversion χⱼ is applied to each particle sector:

\[ εⱼ = ε₀ + χⱼ (1 - ε₀) \]  \[ (9) \]

A coal initial porosity of ~25% has been chosen for both coals, following literature information [41, 73, 74]. The initial tortuosity was assumed to be \( \sqrt{2} \) [75]. In agreement with the porosity evolution, the tortuosity decreases linearly with the particle sector conversion χⱼ:

\[ τⱼ = τ₀ - χⱼ (τ₀ - 1) \]  \[ (10) \]

3.2.3 The Gas Mass and Heat Balances

Species and energy balances of the gas phase can be expressed as:

\[ \frac{d g_i}{dt} = J_{N,i} + R_{g,i} \]  \[ (11) \]

\[ \frac{d}{dt} \sum_{i=1}^{NCP} g_i \cdot C_r T^r = \sum_{i=1}^{NCP} J_{N,i} h_{N,i} + Q_N + HR_g \]  \[ (12) \]

where gᵢ is the mass of component i in the gas phase, Jᵢ is the total mass and heat exchanged between the gas phase and the particles, respectively. Rₑᵢ is the formation/disappearance of i-th species due to gas phase reactions, HRₑᵢ is the total heat of
reactions due to gas phase reactions. More detailed information about ancillary equations was reported in Pierucci and Ranzi [65].

The model is constituted by a system of \( (NCP_p+1)N+ NCP_g+2 \) ODE equations to describe the particle system, where \( NCP_p \) is the number of species involved in the solid kinetic model, \( N \) the number of particle sectors and \( NCP_g \) the number of species considered in the gas kinetic model. The large ODE system has been solved by using BzzMath library, which is available in [76].

4. Comparison between experimental data and model predictions

Particle surface temperatures and burnout times were experimentally measured and at least 20 replicate tests were analyzed in each condition.

The bituminous and the lignite coal particles have different burning behaviors. The bituminous coal shows both a homogeneous combustion with an envelope flame of the volatile matter and a heterogeneous combustion of the solid residue (Figure 14). The lignite coal mostly burns with the simultaneous combustion of the volatiles and the char residue, and it often undergoes significant fragmentation. The combustion behavior of the lignite coal in question was postulated based on experimental observations, described in detail in [36, 42] and confirmed with the ignition and combustion model of Howard and Essenhigh [34], also described in those references. This behavior also depends on the devolatilization products: lignite releases a larger amount of light gases. Moreover, the combustion characteristics largely depend also on the \( O_2 \) concentration in the \( N_2 \) or \( CO_2 \) mixtures [36]. Some particular aspects of the observed combustion behavior of lignite, such as the postulated simultaneous volatile and char burning as well as the observed fragmentation could not be comprehensively modeled herein.
Figure 16 shows an overall view of the experimental results in terms of the particle life time and the surface temperature versus the oxygen concentration, for both coals and gas mixtures. The life time of the coal particle was estimated as the sum of the ignition delay [36] and the particle burnout time.

The particle burnout times were deduced from pyrometry, based on the duration of the recorded highest-intensity signal ($\lambda = 998$ nm) of a particular event from its onset (particle ignition) to its termination (particle extinction), both defined when the signal exceeds its baseline by a factor of at least one thousand, i.e., $S_{\text{signal}}/S_{\text{baseline}} > 1,000$. Burnout times recorded by cinematography (not shown) were typically a few milliseconds longer, with the exemption of the case of moderate oxygen mole fractions. The most notable case recorded herein was that of 20%O$_2$/80%CO$_2$, where combustion was generally very dim, as shown in Fig. 3b, to be reliably captured by the pyrometer. In these cases the pyrometric signals during the particle char extinction period were weak and were marred with electronic noise, as the last pockets of carbon were burned in the forming residual ash particles. In such cases the burnout time discrepancy as recorded by the two methods was in the tens of milliseconds.

Each data point represents mean values from at least 20 individual particle combustion events. Standard deviation bars ($2\sigma$) are shown on each datum point.
Figure 16. Recorded particle life times (a,c) and maximum deduced temperatures (b,d) for particles (75-90µm) from pulverized USA coals (Pittsburgh # 8 bituminous HVA (PSOC-1451) and Beulah lignite (DECS-11) burning in O₂/N₂ and O₂/CO₂ atmospheres at T_{furnace}=1400 K.

The bituminous coal shows the longer particle life times until 40%-50% O₂ in both gas mixtures. At higher O₂ concentrations, and associated high surface temperatures, the particle life times of the two coals become very similar. In these conditions, the life time of about 25-30 ms is mostly related to the heating of the particle. The maximum char temperatures reached by the lignite are always 100-200 K higher than those of the bituminous coal.

The higher temperatures of lignite chars than those of bituminous char particles may most likely be attributed to the typically reported in the literature higher reactivities of the lignite chars. Field [77] reported that the reactivity of chars increases, by a factor of ~8, as the rank of
coals decreases from anthracite to lignite. Mitchell [78] confirmed that the reaction rates of a lignite coal were faster than the rates of two bituminous coals. The higher reactivity of the lignite coal char particles than those of the bituminous coal can be partly attributed to a lower mass transport limitation [79]. In the case of lignite coal, the predicted higher internal burning rate is due to the higher effective oxygen diffusivity (i.e. higher char porosity). Furthermore, the higher reactivity of the lignite coal can also be partly attributed to the effects of various minerals contents. For instance, the calcium content in the bituminous coal amounts to only 0.28% of its mass whereas in the lignite coal it amounts to 1.8% (see Table 1), i.e., 6.6 times more. It has been shown before in controlled combustion experiments by Levendis et al. [80] that impregnating carbonaceous synthetic chars with calcium increased their observed mean combustion temperatures by 200-300 K, and reduced their burnout times by 10-20%.

At high $O_2$ concentrations excellent agreement was observed between pyrometric and cinematographic measurements of the burnout times. To the contrary at low $O_2$ concentrations, the cinematographic measurements are more reliable, due to the mentioned low luminosity of the bituminous char particles during the near-extinction phase.

4.1. Combustion in the $O_2/N_2$ mixture

Figure 17 shows the comparisons between experimental and predicted life times of bituminous and lignite particles in the $N_2$ mixtures.
Figure 17. Life time of coal particles (80µm) in the furnace versus O₂ mole fraction in N₂ mixture (a) bituminous (PSOC 1451) and (b) lignite coal (DECS-11). Experimental data (symbols) and model predictions at 95% conversion (solid line) and 90% (dashed line).

Two different predicted life times are reported. In agreement with the work of Senior [81], the predicted profiles assume the life time as those corresponding to both 90% and 95% conversion of coal, on dry ash free (daf) basis. The overall agreement is satisfactory, even if the life time of the lignite coal is slightly underestimated.

In order to better analyze the difference between the two predicted life times, Figure 7 shows the time evolution of the coal conversion, at different O₂ concentrations.

Figure 18. Time evolution of 80µm coal particle conversion at different O₂ mole fraction in N₂ mixtures (a) bituminous (PSOC 1451) and (b) lignite coal (DECS-11).
From Figure 18 it is possible to observe that the initial heating of the particle and the first devolatilization phase are independent of the $O_2$ concentration. During this phase, the initial release of volatiles species from bituminous and lignite coals accounts for ~25% and ~40% conversion by mass, respectively. A second release of volatile species (~15% and ~10% respectively) occurs during the initial char oxidation phases. This is due to the slower decomposition of the reference species COAL$_1$ and the slow release of chemi-adsorbed species from the metaplast. When char starts to react heterogeneously, the corresponding particle porosity is about 0.45-0.5 in the case of the bituminous coal and 0.6-0.65 in the case of lignite. The assumption of 90% and 95% conversion as corresponding to the life time differently affect the results of the two coals. Bituminous coal, because of its lower reactivity, shows a larger sensitivity than lignite coal.

Figure 19 shows the core and surface temperature evolution at different $O_2$ concentration. Due to the small particle diameter, only five discretization shells are sufficient to describe the internal resistances with a good accuracy. Results obtained from more numerous shells showed negligible differences in the final results. The combustion in pure $O_2$ is obviously much faster, and homogeneous and heterogeneous combustion occur almost simultaneously. The peak temperature is thus high and very sharp. On the contrary, the combustion in air is slower with different times for the gas phase combustion and the char oxidation, well highlighted by the plateau of the temperature at ~60 ms.
Figure 19. Time evolution of the surface (solid line) and core (dashed line) temperature of a coal particle (80µm) at different O₂ concentrations in N₂; (a) bituminous (PSOC 1451) and (b) lignite coal (DECS-11).

Figure 20 shows the comparison between the maximum measured and the predicted core and surface temperatures versus the O₂ mole fraction, for both coals.

Figure 20. Particle temperature versus O₂ mole fraction in N₂. Comparison between experimental data for maximum surface temperature (symbols) and predictions of surface and core temperatures (lines) in the cases of (a) bituminous (PSOC 1451) and (b) a lignite coal (DECS-11). The experimental particle sizes were in the range of 75-90 µm, the modeled size was 80µm.
The same thermal conductivity value was applied for both coals. The difference between the particle core and surface is due to the different porosity, which corresponds to a different diffusivity and reactivity. The temperature difference between the surface and the core of the particle increases with increasing oxygen mole fractions, because of the increase of the transport resistances. The general agreement is satisfactory. A slight over-prediction of bituminous coal temperatures can be observed at the intermediate oxygen concentration.

On the contrary, the model under-predicts the temperatures of the lignite coal mainly at low O2 mole fractions. Two main factors may explain this deviation. First, the model considers only a single and completely mixed gas phase surrounding the particle, without the proper gas phase discretization. This simplification can become more stringent in the lignite case, where a larger amount of volatile products is released. Second, the model does not account for the observed lignite particle fragmentations, emphasizing in this way the role of diffusion phenomena within the particle.
Figure 21. Molar fraction evolution of the major gaseous combustion products in different particle shells in the case of a bituminous coal (PSOC-1451) particle (80µm) burning in air.

In order to illustrate the model performance, Figure 21 displays the profiles of major species inside the bituminous coal particle in 21% O$_2$-79% N$_2$ atmosphere. In the first 10 ms, i.e. during the pyrolysis process with the fast release of gas and tar products, there is sharp reduction of O$_2$ with corresponding peaks of CO, CO$_2$, and H$_2$O. The next peaks, at about 20 ms, correspond to a further release of CO, CO$_2$ and H$_2$O, derived from the metaplastic phase. Once the devolatilization phase is almost completed, O$_2$ penetrates inside the particle and reacts with the residual char. Figure 21a shows that the reaction time is partially controlled by effective O$_2$ diffusion inside the particle. Due to the diffusion limitations, O$_2$ can reach the core of the particle after ~65 ms after the complete conversion of the external sectors. CO is the main gaseous
product from the heterogeneous reactions. The CO, CO$_2$ and H$_2$O peaks observed at $\sim$45 ms are the products of the combustion reaction of CHAR$_{HI}$. The successive peaks are mainly due to combustion reactions of the CHAR$_C$.

4.2. Combustion in the O$_2$/CO$_2$ mixture

In comparison with the combustion in the N$_2$ mixtures, longer particle burnout times and lower surface temperatures are obtained when burning coal particles in CO$_2$ mixtures, as already shown in Figure 5.

Figure 22. Life times and temperatures of coal particles in the furnace burning in O$_2$/CO$_2$ atmospheres. Experimental maximum surface temperatures and times (symbols) were compared with predictions of
surface and core temperatures (lines) in the cases of (a) bituminous (PSOC 1451) and (b) a lignite coal (DECS-11). Predictions for conversions of 90 and 95% are shown. The experimental particle sizes were in the range of 75-90 µm, the modelled size was 80µm.

These facts are mainly due to the higher heat capacity of CO₂ and to the lower oxygen diffusivity in CO₂ than in N₂ mixtures. Figure 22 shows a satisfactory agreement between experimental data and model predictions and the observed deviations are consistent with the previous ones. It is worth to underline that the overestimation and/or underestimation of the particle life time is also affected by the assumption of the particle conversion level.

The sensitivity analysis shows that the contribution of the char gasification reactions is limited and accounts for ~2-8% of the particle life time in the current experiments, in line with the observations of Reference [8]. To the contrary, the effect of the endothermic char gasification reactions is to reduce the maximum particle temperature of ~50-100 K.

4.3. Sensitivity analysis

The effect of several parameter on the coal reactivity, such as the heat capacity, diffusivity, char gasification reaction, particle diameter, porosity, pore diameter and tortuosity was investigated through sensitivity analyses.

CO₂ atmosphere increases the particle life time. As already discussed, the CO₂ heat capacity and the binary molecular diffusion coefficient are responsible of this behavior. In order to investigate the contribution of these two phenomena, a few simulations artificially modifying N₂ properties were carried out.

The dashed lines of Figure 12 show the predicted particle life time, when the N₂ heat capacity was assumed equal to that of CO₂ (black line) and when the same diffusivity of O₂ in
CO₂ was applied to the O₂/N₂ mixture (grey line). The higher CO₂ heat capacity is more significant at moderate oxygen mole fractions (<30%), reducing the increase of the gas phase temperature induced by the exothermic oxidation of both gas products and char, even though oxygen diffusivity plays a significant role.

**Figure 12.** Effect of the heat capacity and the binary molecular diffusivity on the particle life time for (a) bituminous coal and (b) for the lignite coal. Legend: black and grey solid line represent the simulations in O₂/CO₂ and in O₂/N₂, respectively; black dash line represents the simulation with binary molecular diffusivity Dₐ₂/N₂ and with N₂ heat capacity equal to that of CO₂; gray dash line is the simulation with Dₐ₂/N₂ equal to that of Dₐ₂/CO₂ in O₂/N₂ mixture.

Figure 13 shows the sensitivity analysis of the particle life time to particle diameter, porosity, pore diameter and tortuosity, respectively.
Figure 13. Sensitivity analysis of (a) particle diameter, (b) porosity, (c) pore diameter and (d) tortuosity on the particle life time for bituminous and lignite coal in $O_2/N_2$ mixture. The parameter variations was ± 25% in respect to the relative reference value.

The particle diameter affects the particle life time with a power of 1.0-1.4. During oxidation the coal particle passes through all the typical regimes: Regime I (kinetic control), Regime II (internal diffusion control) and Regime III (external mass transfer control). During the pyrolysis, Regime I prevails and in these conditions characteristic time of reaction is proportional to the particle diameter. When char oxidation commences, Regimes II and III increase in importance. At low temperatures (moderate oxygen concentration) the internal diffusion becomes the controlling step (as clearly shown in Figure 10) and thus a linear ‘$d$ law’ is followed. Finally, at high temperatures (in oxygen-rich mixtures), Regime III, increases becomes prominent and the
burning time varies according to the ‘d^2 law’, typical of pure external mass transfer resistances. The porosity and pore diameter weakly affect the particle life time. These effects are less important than the choice of the final conversion (90% or 95%) corresponding to the predicted particle life time. Tortuosity shows a higher sensitivity, mainly at low oxygen concentrations. The effect of these parameters on surface temperatures, less important at low O_2 concentrations, becomes ~ 20-40 K at the highest O_2 concentration.

Figure 14 shows the effect of the Stefan flow on the particle life time and the particle temperature. The Stefan flow caused an unimportant effect on the particle life time, under the current experimental conditions. To the contrary, the reduction of the heat transfer coefficient increased the maximum particle temperature significantly, by as much as 100 K at 100% O_2.

Figure 14. Effect of the Stefan flow on the particle life time and particle temperature for DECS-11 coal. Dashed line without the Stefan flow correction; solid line including Stefan flow correction

The physical description of the gas phase is very simplified and we assumed a 0D model with a volume gas phase ~40^3 times greater than the particle one. This simplified model cannot predict well the volatile combustion time, due to the diffusion effects of volatile combustion, as shown by Vascellari et al. [82]. Figure 15 shows the effect of the gas volume on the combustion time of the lignite coal in the O_2/N_2 environment. The increase of the gas volume makes the
particle life time higher. On the contrary, halving the gas volume the particle life time decreases. Further reductions do not significantly modify the results. Of course, gas phase and surface temperatures increase with volume reductions. Only a 1D model could give a more correct description of the system.

Figure 15. Effect of the gas volume on the combustion of the lignite coal in O\textsubscript{2}/N\textsubscript{2} environment. Symbol: black line correspondence at a volume of 200% of the reference volume; (b) black dash line correspondence at the reference volume; (c) dash grey line correspondence at a volume of 50% of the reference volume (d) solid grey line correspondence at a volume of 25 % of the reference volume.

5. Conclusions

Experimental measurements of coal particle life times and surface temperatures of a high-volatile bituminous coal (PSOC-1451) and a lignite coal (DECS-11) were performed in a drop tube furnace, under quiescent gas conditions. Different reactive gaseous mixtures, both O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2} with oxygen mole fractions ranging from 21 to100%, were considered. The furnace wall temperature was set at 1400 K.

The experimental results show longer particle life times and lower surface temperatures for the bituminous coal, when compared with the corresponding lignite data. Moreover, at moderate
oxygen mole fractions, longer particle life times and lower temperatures are observed in the cases of both coals burning in the O₂/CO₂ mixtures. Increasing the oxygen concentration, the differences between the two coals (bituminous and lignite) and the two background gases (N₂ and CO₂) become less important.

These experimental data are then compared with the predictions of a comprehensive multi-scale, multi-phase and multi-component model of coal pyrolysis and combustion. The main characteristics of the model lie in a detailed description both of the kinetic mechanisms involved in coal combustion processes and of the heat and mass transport resistances. The model predictions show an overall good agreement with experiment data both in terms of particle life time and surface temperature. As expected, the lignite coal is more reactive and consequently its particle life time is shorter. The chars resulting from lignite volatilization are also more reactive, partly because the larger release of gas products increases the particle porosity favoring the oxygen diffusion.

The presence of CO₂ in the atmosphere reduces the overall reactivity of both coals. Two are the main factors responsible of such a behavior. The higher CO₂ heat capacity reduces the surrounding gas temperature. The lower oxygen binary molecular diffusion in CO₂, in respect of that in N₂, reduces the O₂ flux to and inside the particle with a resulting decrease of reactivity. While the overall agreement between experimental measurements and model predictions suggests that the model may already be used as a predictive tool, the sensitivity analysis also shows that an extension towards a simplified 1D model of the gas phase could be very useful to improve the reliability of model predictions.
6. References


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APPENDIX 4

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A4. Emissions of NO\textsubscript{x} and SO\textsubscript{2} from Coals of Various Ranks, Bagasse and Coal-Bagasse Blends Burning in O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2} Environments

Abstract

Oxy-coal combustion is a viable technology, for new and existing coal-fired power plants, as it facilitates carbon capture and, thereby, can mitigate climate change. Pulverized coals of various ranks, biomass, and their blends were burned in order to assess the evolution of combustion effluent gases, such as NO\textsubscript{x}, SO\textsubscript{2} and CO\textsubscript{2} under a variety of background gas compositions. The fuels were burned in an electrically-heated laboratory drop-tube furnace in O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2} environments with oxygen mole fractions of 20%, 40%, 60%, 80%, and 100%, at a furnace temperature of 1400 K. The fuel mass flow rate was kept constant in most cases, and combustion was fuel-lean. Results showed that in the case of for four coals studied, NO\textsubscript{x} emissions in O\textsubscript{2}/CO\textsubscript{2} environments were lower than those in O\textsubscript{2}/N\textsubscript{2} environments by amounts that ranged from 19-43% at the same oxygen concentration. In the case of bagasse and coal/bagasse blends, the corresponding NO\textsubscript{x} reductions ranged from 22-39%. NO\textsubscript{x} emissions were found to increase with increasing oxygen mole fraction till \textapprox 50% O\textsubscript{2} was reached; thereafter, they monotonically decreased with increasing oxygen concentration. NO\textsubscript{x} emissions from the various fuels burned did not clearly reflect their nitrogen content (0.2-1.4%), except when large content differences were present. SO\textsubscript{2} emissions from all fuels remained largely unaffected by the replacement of the N\textsubscript{2} diluent gas with CO\textsubscript{2}; whereas they typically increased with increasing sulfur content of the fuels (0.07-1.4%), and decreased with increasing calcium content of the fuels (0.28-2.7%). Under the conditions of this work, 20-50% of the fuel-nitrogen was converted to NO\textsubscript{x}. The amount of fuel sulfur converted to SO\textsubscript{2} varied wildly, depending on the fuel and, in the case of the
bituminous coal, also depending on the O₂ mole fraction. Blending the sub-bituminous coal with bagasse reduced its SO₂ yields, whereas blending the bituminous coal with bagasse reduced both its SO₂ and NOₓ yields. CO emissions were generally very low in all cases. The emission trends were interpreted based on separate combustion observations.

1. Introduction

Half of the electricity in the US (40% globally) is generated by electric utilities burning coal. Electric utilities are responsible for 73% of the total US emissions of SO₂ as well as 22% of the total US emissions NOₓ emissions [1]. Nearly all of the utility-generated SO₂ emissions and most of the utility-generated NOₓ (NO, NO₂) emissions arise from coal-burning power-plants, as coal contains sulfur and nitrogen in its matrix. NOₓ and SO₂ are regulated atmospheric pollutants [1]. Such power-plants are also among the largest point source emitters of the major greenhouse gas: carbon dioxide (CO₂). Thus, regulatory pressure is expected in the future to reduce and/or capture and sequester CO₂ emissions. Whereas, power generation from CO₂-neutral renewable fuels is being promoted, coal utilization is expected to continue in the future, as the reserves of coal are abundant [2]. Thus, methods for achieving “clean”-coal combustion are of technological interest.

Following coal, petroleum and natural gas, biomass is the next abundant carbon-based energy resource [3]. Co-combustion of biomass and coal has generated widespread interest, because of the reduced emissions of gases such as CO₂, SO₂ and NOₓ compared to those emitted by the combustion of neat coal. Biomass alone may not be used as a fuel in existing coal-fired furnaces due to its low bulk density, high moisture content and low energy content [4, 5]. However, its co-firing with coal is advantageous, based on its higher volatile matter content and
its lower pyrolysis temperature which can aid the ignition and combustion characteristics of the blend [6]. Each percentage point of coal replaced by biomass results in about 60 Mt of CO\textsubscript{2} avoided per year globally [7]. Co-utilization of biomass, also provides an economical and sustainable method for electric power generation [8]. Moreover, using waste biomass as a fuel curtails its prolonged storage which can generate methane (CH\textsubscript{4}), a potent greenhouse gas. Therefore, based on recognized environmental and economic benefits of using biomass as a fuel [9-13], it has been projected that the biomass share in electricity production may increase from the current 1.3% to some 3%-5% by 2050 [7].

For the reasons discussed above this study incorporated bagasse, which is a waste residue after sugar and/or ethanol have been produced from sugar cane. The largest producers of bagasse are India and Brazil. The sugar cane harvest in Brazil was 570 million tons in 2009. This process generated 190 million tons of bagasse residue, which supplied 3% of the Brazilian energy matrix that year. It is projected that by 2020 this figure will increase to 14% [14].

Given the documented increasing concentration of carbon dioxide in the atmosphere, and its likely relation to global warming, several technologies are being developed to facilitate carbon capture and storage (CCS) from fossil-fuel-fired power plants. Among them, oxy-fuel combustion is of technological interest, as it requires the least design and operational departures from currently practiced combustion techniques. The popularity of oxy-fuel combustion, initially proposed by Horn and Steinber [15] and Abraham [16], has increased dramatically in recent years. This technology is capable of providing a CO\textsubscript{2} volume fraction in the flue gas of 95% or higher, which is desirable for subsequent sequestration purposes [17].
In oxy-combustion, a fuel is burned in an O$_2$-CO$_2$ environment, as opposed to an O$_2$-N$_2$ environment in the case of conventional combustion in air. The differences between air and oxy-fuel combustion are mainly in the properties of CO$_2$ and N$_2$ diluent gases such as density, heat capacity, thermal and molecular diffusivities and gas emissivity. These properties influence the heat transfer, flammability limits, ignition behavior and the combustion kinetics of burning pulverized coal [18, 19]. Oxygen is supplied to the furnace by an air separation unit, and a portion of the flue gas is recycled to moderate the boiler temperature. Upon condensation of H$_2$O, the resulting combustion effluent is mostly CO$_2$, which may be subsequently pressurized, piped to a suitable underground reservoir, in which it is stored. As an additional benefit of this technology, sizeable reductions of NO$_x$ emissions have been reported [20-22].

This work is part of a broader basic investigation to assess the fundamentals of combustion behavior and evolution of gaseous and condensed phase emissions from coal and biomass, burning in different O$_2$/N$_2$ and O$_2$/CO$_2$ environments. This particular research addresses the evolution of the gas phase emissions of NO$_x$, SO$_2$ and CO$_2$. While there is not a standard background gas composition for oxy-coal combustion, the most accepted compositions, based on research undertakings and pilot studies, consist of 25%-42% O$_2$ mixed with typically dried recycled gases which, in turn, are mostly composed of CO$_2$ [23-32]. In contrast conventional fired combustion uses air, which is composed of 21% O$_2$-79%N$_2$. In oxy-coal combustion, the nitrogen is replaced by recycled CO$_2$. The oxygen range that was chosen for this study includes the conventional air-fired boiler setting (21% O$_2$), as well as the typical oxy-fuel combustion oxygen range (25%-42% O$_2$). The range was then expanded to include even higher oxygen mole fractions (up to 100%), as lowering the flue gas recirculation (if that were feasible given materials considerations) can decrease the size of boilers and reduce the electricity demands of
the flue-gas recirculation fans. Four coals of different ranks (bituminous, sub-bituminous and lignite) were burned. Moreover, sugarcane bagasse (a biomass residue from sugar or bioethanol production) was also burned under similar conditions, either as a neat fuel or blended with coal. In this study, the fuels were burned in an externally-heated drop-tube furnace in atmospheres of O₂/N₂/CO₂ gases. Flue gas recycling was simulated by the presence of CO₂. Therefore, since actual flue gas recycling was not implemented herein, combustion-generated NOₓ or SO₂ were not returned to the furnace. Thus, the impact of replacing N₂ with CO₂ was examined without (a) the interfering effects of NO “re-burning” on the final NOₓ emissions and (b) the effects of extended the residence time of SO₂ in the furnace and inhibited decomposition of any formed CaSO₄ in the ash because of enhanced SO₂ concentration in the furnace [33].

2. Literature review

2.1. Emissions of Nitrogen Oxides (NOₓ)

NOₓ emissions from burning coal are mostly comprised of “thermal-NOₓ” and “fuel-NOₓ”. The former stems from oxidation of atmospheric-nitrogen in the flame, whereas the latter originates from oxidation of the fuel-nitrogen. Pershing and Wendt [34] reported that the “fuel-NOₓ” constitutes over 75% of the total NOₓ emissions; a finding in good agreement with the results of Courtemanche and Levendis [35], who reported that fuel-NOₓ contributed 80% of the total NOₓ for experiments at various furnace temperatures and equivalence ratios. Fuel-nitrogen in coal is contained predominantly in pyrrolic-type groups (50-60%); pyridinic and quaternary forms have also been detected. Nitrogen contained in pyridinic groups has been reported to be more stable than that in pyrrolic groups [36]. In the combustion process, fuel-nitrogen evolves during both the devolatilization and the char oxidation phases; the distribution depending on the
fuel type, the temperature and the residence time. In the case of bituminous coals the volatile matter nitrogen is released in tarry compounds, which at high temperatures decay mostly to hydrogen cyanide (HCN) and soot-nitrogen [37]. In the case of low rank coals and biomass, light nitrogen species may be directly released from the solid matrix as HCN, ammonia (NH₃) and cyanuric acid (HNCO) [37]. A survey of the many possible reaction paths by which HCN is converted to NO and other products, through an amine radical pool, shows the complexity of the gas-phase chemistry [37, 38]. Flagan and Seinfeld [39] summarized the overall chemistry scheme as follows: fuel-N in tars converts expeditiously to HCN, proceeding to NH₄ intermediates, which then either oxidize to NO by reactions with oxidants such as OH or reduce to N₂ by reactions with NO. The majority of char-bound nitrogen may leave the surface as NO, which is formed as char nitrogen is oxidized to NO. This is then partially reduced by reactions with CO or char as it traverses the particle pores; un-reacted NO escapes from the boundary layer and mixes into the bulk gas. The char nitrogen conversion is complicated, as formation of CN or NH is also possible [39, 40].

Conversion of the mass of fuel-nitrogen to NOₓ in experimental systems varies from relatively low levels up to nearly 100% [41]. Levy [42] reported that the range of conversion of coal-bound nitrogen to NOₓ is wide (15-40%), and called this variability in fuel nitrogen conversion, and the lack of its clear understanding, a major unresolved issue in fuel NOₓ combustion control. This was echoed at a later time by Visona and Stanmore [43] and then, again, by Glarborg et al. [37], who remarked that in spite of progress over the last three decades, the basic mechanisms for fuel nitrogen conversion, are still being clarified, and unresolved issues may limit the potential for effective NOₓ control. The aforementioned variability also
underscores the opportunity for significant reductions in NO\textsubscript{x} emissions by appropriately controlling the combustion environment. This is especially of interest to combustion staging and, most recently, to oxy-combustion. Laboratory experiments in pulverized coal combustion have shown that the stoichiometry exerts a strong effect on NO\textsubscript{x} levels and on the distribution of fuel nitrogen among gaseous products. Pohl and Sarofim [44] burned bituminous and lignite coals in air over a wide range of bulk equivalence ratios (\(\phi = 0.1-5.5\)), at a furnace temperature of 1500 K. They reported that the conversion of the fuel-nitrogen to NO decreased with increasing \(\phi\), from 60\% at \(\phi=0.2\) to 10\% at \(\phi>1.5\). They mentioned that at high \(\phi\)s, nitrogen remained in the un-reacted chars. In agreement with the above, Courtemanche and Levendis [35] reported that, over a range of bulk equivalence ratios (\(\phi=0.5-1.5\)) and over a range of furnace temperatures (1300-1600K), the conversion of the nitrogen in a bituminous coal to NO\textsubscript{x} decreased with increasing \(\phi\) from 40\% at \(\phi=0.5\) to below 10\% at \(\phi=1.5\). The effect of furnace gas temperature, in the aforementioned range, on NO\textsubscript{x} was found to be significant. However, Kremer and Schulz [45] reported the NO emissions from combustion of high volatile bituminous coal to be rather independent of furnace temperature, as also did Spinti and Pershing\textsuperscript{46} for combustion of bituminous coal chars.

During pulverized coal combustion, fuel nitrogen is either released with the volatiles or remains within the char, roughly in proportion to the char yield [39]. This is supported by Haussmann and Kruger [41], who found that char nitrogen represents the majority of the original fuel nitrogen, in the gas temperature range of 1200-1700 K. Upon devolatilization, De Soete [47], and Chen and Niksa [48] reported that the fraction of char nitrogen converted into NO during char oxidation is roughly proportional to the degree of char burnout. No evidence was found by Nelson et al. [36] that the total fuel nitrogen released depends on coal rank or coal
nitrogen content, although the fraction of the coal-nitrogen released with the volatiles increases with decreasing rank, i.e., increasing oxygen content in the fuel [49]. Spinti and Pershing [46], detected some influences of the coal rank in the char combustion phase, and reported that when chars burned in nitrogen-free oxidant the char-N to NOx conversion was higher for lignites (50-60%) than for bituminous coals (40-50%). In addition to burning bituminous and lignite coals, Pohl and Sarofim [44] also burned lignite coal chars over a wide range of bulk equivalence ratios (\(\phi=0.1-5.5\)), at a furnace temperature of 1500K. They reported that the conversion of the fuel nitrogen in the lignite coal chars to NO decreased with increasing \(\phi\), from 25% at \(\phi=0.2\) to 4% at \(\phi>1.5\). Thus, by comparison with the aforementioned coal combustion experiments, they concluded that 60-80% of the NOx was contributed by the oxidation of nitrogen released with the volatiles, i.e., the remaining 20-40% NOx was released during char combustion. Pershing and Wendt [50] burned both bituminous and lignite coals and their chars at \(\phi=1.15\) and also concluded that less than half of the original coal nitrogen is converted to NOx during the char combustion phase. Levendis [51] reported on the roles of volatile matter combustion and char combustion phases of the Pittsburgh #8 bituminous coal on NOx formation at fuel-lean conditions (\(\phi=0.4\)). This coal released 60 wt% of its fuel nitrogen during devolatilization, 35 wt% during char combustion, with the remainder (5 wt%) staying with carbon in the ash. However, not all of the released ‘fuel-nitrogen’ formed NOx. Roughly 42-47% of the coal-nitrogen was converted to NOx, out of which approx. 15% was converted during the volatile and 30% during the char combustion phases. The above is in agreement with the findings of Pohl and Sarofim [44], who also reported \(\approx40\%\) for coal-nitrogen conversion to NOx for the same coal (Pittsburgh #8) burning under similar fuel-lean combustion conditions (\(\phi=0.5\)). Increasing the
gas temperature, in the limited range of 1400-1600 K, mildly increased the total amount of fuel nitrogen converted to NO\textsubscript{x} [51].

The effects of parameters such as nitrogen content in coal, particle size, surface area of the chars, total pressure, O\textsubscript{2} partial pressure in the gas, NO partial pressure in the gas, etc., are briefly discussed in this paragraph. Spinti and Pershing [46] reported that the apparent conversion of char-N to NO\textsubscript{x} decreased as the level of the initial NO\textsubscript{x} mole fraction in the surrounding gas increased. To the limit, in their study, the char-N to NO\textsubscript{x} conversion dropped to nearly 0% at a level of 900 ppm NO\textsubscript{x} in the flame. Chaikalangmuang et al. [52] reported that in un-staged burners, the formation of NO\textsubscript{x} increased with a coal’s volatile matter content, but in staged burners the formation of NO\textsubscript{x} decreased with increasing volatile matter content. Seeker et al. [53] reported that small particles produce more fuel-NO than large particles. Aho et al.[54] reported that NO formation decreased sharply with reactor pressure, and mildly increased with reactor temperature and oxygen mole fraction; they also provided an empirical formula to estimate the NO mole fraction based on those parameters ($y_{\text{NO}} \% = -11.63 + 0.04557 \times T (\degree \text{C}) - 2.33 \times p (\text{bar}) + 15.992 \times p_{\text{O}_2} (\text{bar})$). Visona and Stanmore [43] reported that increasing the inlet oxygen mole fraction (in the range of $y_{\text{O}_2}= 5$-25%) generated more NO. This was corroborated by Spinti and Pershing [46] (in the range of $y_{\text{O}_2}= 21$-28%) and by Hu et al.[55] (in the range of $y_{\text{O}_2}= 20$-50%). At higher oxygen mole fractions ($y_{\text{O}_2}> 50\%$) NO\textsubscript{x} emission decreased, and in pure oxygen it even went back to the same level as that in air. Lazaro et al. [56] reported that the lower the surface area of the char the higher the fraction of the char-nitrogen that is released as NO (the NO/N ratio).
Finally, there has been some research related to the evolution of NO\textsubscript{x} in CO\textsubscript{2}-rich atmospheres, as is the case in oxy-fuel combustion [17, 23-25, 27, 55, 57-60]. Comprehensive reviews on oxy-fuel combustion have been published in recent years [21, 22, 61], and have reported on emissions of NO\textsubscript{x}. In pilot-scale demonstrations on pulverized oxy-coal combustion, reductions in NO\textsubscript{x} emissions of as much as 65% have been observed [20, 22]. These drastic NO\textsubscript{x} reductions may be caused by factors, such as the absence of atmospheric nitrogen, changes in the combustion characteristics of coal, re-burning of the recycled exhaust gas, reactions with char, etc. [37, 42, 62].

2. Emissions of sulfur dioxide (SO\textsubscript{2})

Sulfur exists in coal in inorganic forms, predominantly pyrite (FeS\textsubscript{2}), or in organic forms, such as thiophene, sulfides and thiols. The sulfur content of coals varies from less than one percent to over 12wt% [63]. In fuel-lean combustion, the majority of this sulfur is typically oxidized to form SO\textsubscript{2} [29]. Courtemanche and Levendis [35] examined the emissions from combustion of a pulverized bituminous coal over a range of bulk equivalence ratios (\(\phi=0.5-1.5\)) and furnace temperatures (1300-1600 K). They reported that the conversion of the sulfur in the coal to SO\textsubscript{2} decreased with increasing \(\phi\), from nearly 100% at \(\phi=0.5\) to as low as 40% at \(\phi=1.5\). Moreover, a decrease in conversion with increasing furnace gas temperature was noticed. By examining the sulfur content in the parent coal and its char derivatives upon pyrolysis [45, 64, 65] it was determined that the sulfur that remained in the char was proportional to its mass yield. A few coals, however, were reported to exhibit preferential enriching of the char with sulfur [65]. Atal et al. [66] and Levendis [51] studied the sulfur release during volatile matter combustion and char combustion phases of the Pittsburgh #8 bituminous coal, under fuel-lean conditions. Nearly all the released sulfur (90-95%) was converted to SO\textsubscript{2}. Small amounts of sulfur remained
in the collected ash of this low-calcium content coal. Approx. 57 wt% of the sulfur content of this coal was released as \( \text{SO}_2 \) during the combustion of volatiles, whereas 33% of the parent coal sulfur was released during the combustion of char. This is contrary to the observation of Wells et al. [65] who found that the char was preferentially enriched in sulfur. The difference could possibly be due to the experimental temperatures, heating rates and oxidative conditions.

\( \text{SO}_2 \) emissions generally correlate with the sulfur content of the fuels. Thus, the addition of biomass has been shown to reduce \( \text{SO}_2 \) emissions, mainly due to its low sulfur content in most cases [67, 68] and due to biomass ash composition [61]. \( \text{SO}_2 \) emissions have also been correlated with the organic and inorganic sulfur content of fuels; it has been reported that bituminous coals have inorganic sulfur with a loosely bound portion that can be released at a faster rate than the inorganic sulfur [69]. Finally, \( \text{SO}_2 \) emissions have also been reported to inversely correlate with the calcium content of the fuels, as well as to that of other alkaline-earth metals (sodium, potassium and magnesium). High sulfur retention in the ash has been reported during combustion of sub-bituminous and lignite coals having calcium content in the ash sufficiently high to result in near-stoichiometric calcium and sulfur amounts [70]. Spliethoff & Hein [68] showed that the higher the alkaline-earth content in the ash, the more the sulfur retention therein. Raask [71] proposed an empirical formula for predicting the sulfate retention, \( S_r \), in the ash: 

\[
S_r = \left( \left(0.7 \text{ Na}\% + 0.41 \text{ K}\% + 0.8 \text{ Ca}\% + 1.32 \text{ Mg}\% \right) / \text{ S}\% \right) \times (1 - 0.09 \text{ (ash}\%)^{2/3}).
\]

**3. Experimental setup and procedure**

Coals from four different ranks were burned in this study, as listed in Table 1. Samples for the four coals were obtained from the Penn State Coal Bank, and were ground and sieved. A size cut
of 53-90 µm was used herein. Two of the coals (the PSOC-1451 bituminous and the PSOC-1443 lignite) were extensively characterized in previous research [72]. Sugar cane bagasse was collected directly from a mill located in Brazil – São Paulo State. The bagasse was washed, dried at 90°C for 24 hours, chopped in a household blender and sieved. Pictures of the raw bagasse before and after preparation are shown in Figure 1. Bagasse particles were needle-like in shape and proved difficult to fluidize and feed to the furnace through the capillary tubing used to feed the furnace injector, see Fig. 2. An exception was the case of particle sizes <53 µm that were selected for the experiments. These bagasse particles were fed to the furnace at a flowrate slower than that used for the coals. Properties of bagasse are also listed in Table 1. Blends of 25 wt% of biomass with two of the coals (the PSOC-1451 bituminous and the DEC-26 sub-bituminous) were also prepared and burned.

![Sample of Raw sugar cane bagasse (a) as received (b) after preparation](image)

**Figure 1.** Sample of Raw sugar cane bagasse (a) as received (b) after preparation

**Table 1.** Chemical Composition of the Coals and the Bagasse Biomass

<table>
<thead>
<tr>
<th></th>
<th>PSOC-1451</th>
<th>DECS-11</th>
<th>PSOC-1443</th>
<th>DECS-26</th>
<th>Bagasse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rank and Fuel Source</td>
<td>Bituminous High Volatile A</td>
<td>Lignite A</td>
<td>Lignite A</td>
<td>Sub-Bituminous B</td>
<td>Sugarcane Residue</td>
</tr>
<tr>
<td></td>
<td>Pittsburgh #8,</td>
<td>Beulah,</td>
<td>Titus, Texas</td>
<td>River Basin</td>
<td>Brazil</td>
</tr>
<tr>
<td></td>
<td>Pennsylvania</td>
<td>North Dakota</td>
<td></td>
<td>Wyodak, Wyoming</td>
<td></td>
</tr>
<tr>
<td>Proximate Analysis as received, and (upon re-</td>
<td></td>
<td></td>
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</tbody>
</table>
For the four coals and their proximate and ultimate analysis data was obtained from the Penn State Coal Sample Bank; upon opening the sealed containers of the supplied coal samples, variations of moisture content with storage in the laboratory were observed for all, but the bituminous, coals. The measured moisture content values are listed (in parentheses) and the remaining proximate analysis values were re-calculated and are also shown (in parentheses). The specific bagasse sample was analyzed at the University of São Paulo laboratories, São Carlos Campus.

Combustion experiments were conducted in an electrically-heated, drop-tube laboratory furnace (manufactured by ATS) (4.8 kW max), shown in Fig. 2. The furnace has been fitted with a high-density alumina tube (Coors), with an inner diameter of 3.5 cm. The radiation zone of the alumina tube, defined by aluminum silicate heating elements, is 20 cm long. To introduce the fuel powders into the furnace, a bed of particles was placed in a vibrated glass vial (test-tube), which was advanced by a constant-velocity syringe-pump (Harvard Apparatus). Fuel particles were entrained in a metered stream of oxidant gases, and entered a long capillary tubing (with 1.14 mm inner diameter) from MicroGroup. The tubing was vibrated to its natural frequency, by two vibrators (Vibro-Graver by Alltech), to ensure an unimpeded flow of particles to the water-cooled stainless steel furnace injector. Therefrom, the fuel particles entered the furnace.
Figure 2. Schematic of the electrically-heated laminar-flow drop-tube furnace

A background mixture of gases was introduced to the furnace in an annular space between the water-cooled sorbent injector and the inner walls of the alumina tube in the furnace. The gas mixture was preheated therein. The combined input flow rate of the particle fluidizing gas and the furnace gas was 4 lpm in all tests, thus, the gas residence time in the furnace, at the temperature of 1127 °C (1400 K) used in this study, was 1-2 s. Combustion occurred under laminar-flow conditions in the 20 cm hot zone of the furnace. Furnace wall temperatures ($T_w$) were continuously monitored by type-S thermocouples embedded in the wall. Gas temperatures ($T_g$) inside the furnace were measured at various axial and radial positions by an aspirated shielded thermocouple (suction pyrometer [66, 73]). The gas temperature profile, at various
compositions of O$_2$-N$_2$-CO$_2$ gases, along the centerline of the furnace is shown in Fig. 3. The radiation zone of the furnace spans the 0-25 cm range shown in this figure. For most of the axial profile of the furnace the gas temperature was measured to be fairly constant and close to the furnace wall set-point of 1400 K.

![Centerline Gas Temperature Profile](image)

**Figure 3.** Gas temperature profile along the centerline of the drop-tube furnace for different gas compositions.

The gaseous effluent of the furnace passed through a glass-microfiber filter to remove the ash, then through an ice-bath condenser to remove moisture. Thereafter, the effluent was channeled to continuous-flow analyzers to measure emissions of SO$_2$ (Rosemount Analytical UV SO$_2$ analyzer), NO$_x$ (Thermo Electron Model 10 Chemiluminescent NO-NO$_2$-NO$_x$ analyzer), CO (Horiba VIA-510 analyzer), and CO$_2$ (Horiba VIA-510 analyzer). Furthermore, the oxygen in the effluent was monitored throughout the experiments (Horiba MPA-510 analyzer). The outputs of the analyzers were recorded by a *Data Translation* card (PCI-6221) in a microcomputer, using *Lab View* software.
Tests were conducted in gas atmospheres of either O\textsubscript{2}/N\textsubscript{2} mixtures or O\textsubscript{2}/CO\textsubscript{2} mixtures. Five oxygen mole fractions were implemented (20%, 40%, 60%, 80%, and 100%). Gas flowrates were metered by \textit{Matheson} rotameters and mixture strengths were confirmed by using the oxygen analyzer. The injection rate of the coal powders was in the neighborhood of 0.4 g/min, whereas for the bagasse the injection rate was reduced to 0.06 g/min, to avoid plugging of the powder feeding system. Conditions were selected to be fuel-lean (\(\phi<1\)) in the baseline case, i.e., combustion in air. The bulk equivalence ratio was defined as \(\phi = \frac{(m_{\text{dry fuel}}/m_{\text{oxygen}})_{\text{actual}}}{(m_{\text{dry fuel}}/m_{\text{oxygen}})_{\text{stoichiometric}}}\), where the stoichiometric fuel-to-air ratios of the fuels were calculated from the ultimate analysis, shown in Table 1. The actual fuel-to-air ratios were calculated based on the monitored mass flow rates of the fuels and of the inlet gases. The amount of pulverized fuel fed during each experiment was calculated by measuring the weights of the powder contained in the vial at the beginning and at the end of each run. As both the gas and the fuel flow rates were kept constant in all cases, exceedingly fuel-lean combustion conditions were implemented at oxygen concentrations higher than those in air. A limited number of experiments were also conducted where the mass flow rate of the fuel increased with increasing oxygen mole fraction to keep the equivalence ratio constant at \(\phi=0.8\). Emissions of NO\textsubscript{x}, SO\textsubscript{2}, CO and CO\textsubscript{2} were recorded as mole fractions, expressed in ppm or percentages. Yields of pollutants were computed, based on the amount of fuel introduced to the furnace. Fuel-N to NO\textsubscript{x} conversion percentages were finally calculated based on measured NO\textsubscript{x} emissions during combustion in CO\textsubscript{2}. As this environment is devoid of atmospheric nitrogen, the only source of NO\textsubscript{x} emission was thought to be fuel-bound nitrogen, the amounts of which have been listed in Table 1. Every experiment lasted for 7-10 minutes after steady-state and steady-flow conditions were reached. Since samples have different
physical properties, the consumed masses were different for the neat fuels and their blends. Triplicate experiments were conducted.

4. Experimental results and observations

This section documents the effects of several parameters on the major gaseous emissions, such as (a) the fuel type (bituminous, sub-bituminous, two lignites and bagasse, as well as blends of bagasse with both bituminous and sub-bituminous coals), (b) the replacement of N\(_2\) by CO\(_2\), as the diluent gas, and (c) the variation of oxygen mole fraction in the furnace.

The calculated bulk equivalence ratios, together with integrated average emissions of NO\(_x\) and SO\(_2\) from combustion of the four coals of this work, are shown in Fig. 4. Bagasse and bagasse/coal blends were not included in this plot since their feeding rates were lower than those of coal and, thus, mole fractions of emitted pollutants therefrom cannot be directly compared. Instead, a comparison of the emission yields (mass of emissions/mass of fuel fed) of all fuels was made in Fig. 5, upon normalization with the amount of fuel introduced to and burned in the furnace. The total gas flow rates and the fuel mass flow rates were kept constant in the entire series of experiments for each fuel, thus the average bulk equivalence ratios, \(\phi\), varied as shown in the first rows of Figs. 4 and 5. It monotonically decreased with increasing oxygen mole fraction. The equivalence ratios, \(\phi_{bulk}\), of different coals were expected to be similar since they were all introduced at the same nominal feeding rates; however, as this calculation was based on the dry mass of the fuels, the low-moisture bituminous coal exhibited the highest \(\phi_{bulk}\) among all coals. The low values of \(\phi_{bulk}\) in the case of bagasse are due to the implemented reduced feeding
rates for this low density fuel. Moreover, equivalence ratios of blends fall between those of their neat fuels constituents as expected, see Fig. 5.

![Graph](image)

**Figure 4.** Average bulk equivalence ratios and mole fractions of NO\(_x\), SO\(_2\) and O\(_2\) in the combustion effluents of four pulverized coals. Combustion took place in various O\(_2\)/N\(_2\) (left column) and O\(_2\)/CO\(_2\) (right column) environments. Furnace temperature was kept at 1400 K.
Figure 5. Average bulk equivalence ratios, and mass yields of NO\textsubscript{x} and SO\textsubscript{2} emissions from burning two different pulverized coals, pulverized bagasse and mixtures thereof. Combustion took place in various O\textsubscript{2}/N\textsubscript{2} (left column) and O\textsubscript{2}/CO\textsubscript{2} (right column) environments. Furnace temperature was kept at 1400 K.

A) Effect of Fuel Rank and Fuel Type on the NO\textsubscript{x} and SO\textsubscript{2} emissions

(i) NO\textsubscript{x}: The NOx emissions from the bituminous coal were not too different from those of the lignite coals, even if the lignites had lower fuel-nitrogen content (1.4% for the former vs. 0.9% and 1% for the latter two). The NO\textsubscript{x} emissions from the sub-bituminous coal (0.9% nitrogen content) were distinctly lower than those of the other coals in most cases, as shown in Fig. 4
(mole fractions) and in Fig. 5 (yields). The lowest yields, by far, were those from burning bagasse, in accordance with its very low fuel-N content (0.2%), see Fig. 5. The NO$_x$ emission yields from the bituminous/bagasse blends, also shown in Fig. 5, fell between those of the neat fuel constituents, in both N$_2$ and CO$_2$ environments. More importantly, at most of these points (with the exception of 20% O$_2$) they were lower than the weighted-average emission yields ($0.25 \text{NO}_x\text{-bagasse} + 0.75 \text{NO}_x\text{-coal}$) of the neat bagasse and neat bituminous coal. This may be considered as an indication of possible synergistic interactions. On the other hand, the NO$_x$ emission yields from the sub-bituminous/bagasse blends, also shown in Fig. 5, exhibited a rather complex trend with some points in between and others higher than the emission yields from both the neat fuel constituents of the blend, in either N$_2$ or CO$_2$ environments. It should be mentioned, that the absolute NO$_x$ emissions (ppm) from the sub-bituminous/bagasse blends (not shown here) were in-between those of from the two neat fuel constituents.

(ii) SO$_2$: The sulfur content of the fuels had a more direct effect on SO$_2$ yields, see Fig. 4. Bituminous coal had the highest sulfur content of all four coal types (1.4%); therefore emission of SO$_2$ was by far the highest from this coal, followed by the Titus lignite (0.7%), the Beulah lignite (again, 0.7%) and the the sub-bituminous coal (0.4%). Based on the SO$_2$ yields, shown in Fig. 5, bagasse (0.07%) was a distant last. The SO$_2$ emission yields from both blends, shown in Fig. 5, fell in between those of their neat fuel constituents, in both N$_2$ and CO$_2$ environments. In most cases, they were significantly lower than the weighted-average emission yields of the neat constituent fuels ($0.25 \text{SO}_2\text{-bagasse} + 0.75 \text{SO}_2\text{-coal}$). For the bagasse-bituminous blend, SO$_2$ yields were lower by 52-77% than those from its neat coal constituent; whereas for the bagasse-sub-bituminous blend, SO$_2$ yields were lower by 74-94% than those from its neat coal in either N$_2$ or
CO\textsubscript{2} environments. This result showed that SO\textsubscript{2} emission is dependent on coal type. Once again, this may be considered as an indication of some form of synergistic behavior.

B) Effect of background gas on the NO\textsubscript{x} and SO\textsubscript{2} emissions

(i) **NO\textsubscript{x}**: NO\textsubscript{x} emissions from the different coals, compared at the same O\textsubscript{2} mole fraction, were lower in the CO\textsubscript{2} environments than in the N\textsubscript{2} environment. Average differences for the four coals were in the range of 19 to 43%, depending on the O\textsubscript{2} mole fraction. The corresponding range for bagasse and coal/bagasse blends was 22-39%.

As expected, at low oxygen mole fractions, the effect of the background gas on the NO\textsubscript{x} emissions from all fuels was more pronounced. For all coals, the NO\textsubscript{x} emissions at 20%O\textsubscript{2} in CO\textsubscript{2} were on the average 43% lower than those recorded at 20%O\textsubscript{2} in N\textsubscript{2}. Such difference decreased to 19% at 80% O\textsubscript{2}. For bagasse and coal/bagasse blends, the NO\textsubscript{x} emissions at 20%O\textsubscript{2} in CO\textsubscript{2} were on the average 34% lower than those recorded at 20%O\textsubscript{2} in N\textsubscript{2}. Such difference decreased to 22% at 80% O\textsubscript{2}.

(ii) **SO\textsubscript{2}**: SO\textsubscript{2} emissions from burning all fuels were largely unaffected by the substitution of CO\textsubscript{2} with N\textsubscript{2} see Figs. 4 and 5.

C) Effect of oxygen mole fraction on the NO\textsubscript{x} and SO\textsubscript{2} emissions

(i) **NO\textsubscript{x}**: The NO\textsubscript{x} emissions from coal increased with increasing oxygen partial pressure; they reached maxima in the broad neighborhood of 40-60% O\textsubscript{2}, and they decreased thereafter, see Fig 4. This trend was consistently observed for all coals, in either N\textsubscript{2} or CO\textsubscript{2} environments, but was not observed for bagasse, see Fig. 5. Also, this trend is valid regardless of the equivalence ratio. This was confirmed with supplementary experiments where the equivalence ratio was kept
constant ($\phi_{\text{bulk}} = 0.8$), by increasing the fuel feeding rates at increasing oxygen mole fractions, in the range of 20-100%. In all cases, NO$_x$ emissions at 20% oxygen mole fraction were comparable with those at 100% O$_2$, regardless of whether the $\phi_{\text{bulk}}$ or the fuel feeding rate was kept constant. Similar, although less pronounced, trends were observed in the case of the coal/bagasse blends.

(ii) SO$_2$: In the case of the bituminous coal and, to a lesser extent of its blend, the SO$_2$ emissions decreased with increasing oxygen mole fraction. In the case of the other fuels, a rather steady trend was followed with increasing oxygen mole fraction, see Figs. 4 and 5.

D) Conversion of fuel-nitrogen and sulfur to NO$_x$ and SO$_2$ emissions

The calculated conversions of the fuel nitrogen and sulfur elements to NO$_x$ and SO$_2$ emissions are shown in Fig. 6. Moreover, NOx emissions normalized with the fuel-N content are represented in this figure. For sulfur, this calculation was performed in the cases of both N$_2$/O$_2$ and CO$_2$/O$_2$, whereas for nitrogen this calculation was performed only in the case of CO$_2$/O$_2$ to exclude the contributions of the atmospheric nitrogen. The sulfur conversions are shown on the top row of Fig. 6. Based on these results, it appears that the bituminous coal realized the highest conversions of sulfur to SO$_2$ (40-100%), whereas the remaining fuels realized conversions lower than 50%. Sulfur conversions were largely independent of the background gas. For most fuels, they were not affected by the oxygen mole fraction either, with the notable exception of the bituminous coal, and to a lesser extent its blend, where decreasing trends with increasing oxygen mole fraction were observed.

The fuel-nitrogen conversions are shown on the second row of Fig. 6. Based on these results, it appears that all coals realized conversions of fuel-nitrogen to NO$_x$ in the range of 20-50%. This is
in agreement with the aforementioned results of Pohl and Sarofim [44] and Courtemanche and Levendis [35]. Nitrogen conversions were affected by the oxygen mole fraction in a fashion similar to that seen in the NO\textsubscript{x} emission plot of Fig. 4; i.e., in most cases there has been an increase with increasing oxygen mole fraction, followed by a decrease. The third row of the Fig. 6 provides an indication of the thermal NO\textsubscript{x} contribution of the fuels in N\textsubscript{2} environment. As the emissions are normalized with their fuel-nitrogen content, the difference between NO\textsubscript{x} emissions in different environments can be inferred from this plot.
**Figure 6.** Fuel-sulfur and fuel-nitrogen conversion to SO$_2$ and NO during combustion of the four pulverized coals, pulverized sugar-cane bagasse and two blends thereof. Combustion took place in various O$_2$/CO$_2$ (left column) and O$_2$/N$_2$ (right column) environments.

E) CO$_2$, CO and O$_2$ in the effluent gases

A few words should be said about the CO$_2$, CO and O$_2$ mole fractions in the effluent gases. CO$_2$ was monitored only in the presence of the N$_2$ diluent gas, since the CO$_2$ analyzer in this laboratory has a detection range limited to 0-20%. Results showed a correlation between the carbon content of the neat fuels and their CO$_2$ emissions. The highest CO$_2$ emissions (15-18%, depending on the O$_2$ mole fraction) were observed from the bituminous coal, which has the highest carbon content (71.9%). The lowest CO$_2$ emissions were observed (0.6-1.4%) from neat bagasse (after accounting for its different feeding rate), which are in line with its lower carbon content (44.3%). The trends of CO$_2$ emissions of the four coals with increasing oxygen mole fraction showed an initially mild increase until 40% O$_2$ and, thereafter, they remained nearly constant with further increases in O$_2$ mole fraction. This behavior was attributed to incomplete combustion of the fuels in air, as evidenced by some black carbon residue in the ashes. The explanation for this mild increase is that, in spite of the calculated fuel-lean equivalence ratios, the laminar flow nature of the drop-tube furnace impairs the mixing of coal and oxidizer gases. The highest slope of this increase was exhibited by the bituminous coal, which has the highest content of fixed carbon and the lowest content of oxygen in its structure; whilst the lowest slope was exhibited by bagasse which has the lowest amount of fixed carbon and the highest amount of oxygen in its structure, see Table 1.

CO emissions were not detected at oxygen concentrations higher than 40% for all fuel types in either N$_2$ or CO$_2$ environments. At 20% oxygen partial pressure, CO emissions were still low but
detectable. Moreover, CO emissions in the CO₂ environment were higher than those in the N₂ environment; perhaps by direct reactions of CO₂ with carbon in the char (gasification) [74]. CO emissions from bagasse were not-detected at any oxygen concentration.

The mole fractions of un-reacted oxygen in the combustion effluents are also shown in Fig. 4. The bituminous coal has the lowest oxygen content on a dry basis (6.9%); therefore, atmospheric oxygen consumption during combustion of this coal was expected (and seen) to be the highest, whereas that from the other three oxygen-richer coals was lower.

5. Discussion

A) Effect of Fuel Rank and Fuel Type on the NOₓ and SO₂ emissions

(i) NOₓ: Results shown in Figs. 4 and 5 reveal that the effects of either coal rank or coal nitrogen content on NOₓ emissions were not discernible. Coals that have the same nitrogen contents have different NOₓ emissions, as in the case of the Beulah lignite and Wyodak sub-bituminous coals (both have 0.9% fuel-N). Perhaps they contain different proportions of coal moieties where nitrogen resides (i.e., pyroles vs. pyridines); however, Glarborg [37] stated that for fuel-N oxidation the O/N ratio is more important than the nitrogen functionalities in the coals; and reported that as O/N increases, NO release also increases. This argument has also been supported by Hu et al.[55]. Herein, the Beulah lignite has an O/N ratio that is higher by ~20% than that of the Wyodak sub-bituminous coal. This is in-line with the fact that the average NOₓ emission of Beulah lignite is higher by ~40% than that of the Wyodak sub-bituminous coal. Furthermore, according to Spinti and Pershing [46] the ash content is also an important factor in the emissions of NOₓ. Ash in the pore matrix prevents reduction reactions of NOₓ. Indeed, this is in line with the higher NOₓ emissions from the Beulah lignite than from the Wyodak sub-bituminous coal,
since the ash content of the former coal is higher. Finally, the NOx emissions from bagasse are the lowest than those from the other fuels tested herein since it has the lowest fuel-N content by far (0.2%).

Moreover, there are additional factors that contribute to the disparities, or similarities, in NOx emissions from the types of fuels burned herein. These factors include differences in the predominant NOx precursors and formation pathways (HCN, NH3, HNCO, tar and soot nitrogen, etc.), differences in the partition between volatile and char nitrogen, as well as in predominant mode of combustion i.e., volatile matter flame vs. heterogeneous char combustion. The fact that the characteristics of the fuels and their modes of combustion vary dramatically, as documented in Ref. Levendis et al.[75], makes the explanation of the NOx release even more complicated. Equally-complicated is the explanation of the role of bagasse in the combustion of the blends, as discussed by Dong et al.[3], Vuthaluru [76], Arias et al.[77].

(ii) \( \text{SO}_2 \): The sulfur emissions from the different fuel types of this work correlate with the overall sulfur content in the fuels, as mentioned in the Results section. What merits discussion, however, is the fact that both the fuel sulfur emissions (Fig. 4) and the conversion of the fuel sulfur to \( \text{SO}_2 \) (Fig. 6) were much higher in the case of the bituminous coal, and to a lesser extent its blend, than in the cases of all other fuels. One explanation offered for this behavior is the fact that the bituminous coal has the lowest (by far) Ca/S ratio, see Table 1. Hence, retaining of significant amounts of sulfur in the ash [69, 78], as calcium sulfate \((\text{CaO} + \text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{CaSO}_4)\), would not be an effective mechanism for this fuel that has sub-stoichiometric Ca/S ratio. To the contrary, this may be an effective mechanism for the other fuels of this study that have super-stoichiometric Ca/S ratios. In fact, the \( \text{SO}_2 \) emissions from all the fuels of this work (shown in Fig. 4) correlate well (both in ordering and in magnitude) with the S/Ca mass ratios of the fuels,
derived from the data of Table 1. Moreover, the empirical equation of Raask [71] predicts that 9% of the sulfur may be retained in the ashes of the bituminous coal, 80% in the ashes of the Texas lignite, and that the entire fuel-S may be retained in the ashes of the remaining two coals. To experimentally investigate the above, the ashes of two of the coals were analyzed by Electron Microprobe Analysis (EMA), and results were tabulated in Table 2.

<table>
<thead>
<tr>
<th>Table 2. Fuel-S accounting for two of the coals in this study</th>
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<td><strong>Combustion condition</strong></td>
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<tr>
<td>S% in ash</td>
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<tr>
<td>S% in SO2</td>
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<tr>
<td>S% unaccounted for</td>
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In agreement with the above arguments, the results indicate that the majority of the sulfur in the fuel appears as SO₂ in the case of the bituminous coal, whereas it is retained in the ash in the case of the lignite coal. Considerable amounts of sulfur remained unaccounted for in this limited analysis, and it is possible that sulfur was converted to SO₃ or was absorbed by furnace alumina components. The reader should be cautioned that the particular furnace gas temperature (which is a bit lower than 1400 K) and the gas residence time (2 s herein) are very important parameters [79] and may have favored the calcination reaction and the thermodynamic stability of the sulfate product. Finally, the release of fuel sulfur to the gas phase may have been also influenced by the distributions of pyritic and organic sulfur in these coals, both listed in Table 1, as discussed by Zaugg, et al. [69]. However, no clear trend could be obtained with these parameters.

B) Effect of background gas on the NOₓ and SO₂ emissions
(i) NO$_x$: As mentioned before, total NO$_x$ emissions from the different coals, compared at the same O$_2$ mole fraction, were lower by 19-43% in CO$_2$ than in N$_2$. Part of this difference may be attributed to the contributions of atmospheric nitrogen ("thermal"-NO$_x$, formed by the Zeldovich mechanism [80]). In fact, Courtemanche and Levendis [35] reported that for the combustion of this specific bituminous coal in air, the atmospheric nitrogen contributes 20-25% of the total NO$_x$. To derive that value, results of experiments conducted in air were compared to those conducted in an argon-oxygen gas of equal specific heats. By contrasting the 20% O$_2$ cases herein in either N$_2$ or CO$_2$, the difference in total NO$_x$ emissions from the bituminous coal is much higher; it is nearly 50%, see Fig. 4. In these two cases, however, neither the volumetric specific heats of the gas are equal (they actually differ by ~59%), nor the combustion behaviors, as work in progress in this laboratory shows. Moreover, this discrepancy may be a consequence of ambient CO concentration during combustion. According to Liu et al.[27], initial CO formation is higher in CO$_2$ than in N$_2$ background gases at the same oxygen mole fraction. This was confirmed herein at the 20% O$_2$ case. As CO favors the reduction of NO$_x$ [27, 37], lower NO$_x$ yields were observed in CO$_2$ than in N$_2$ background gases.

It should be clarified here, that the aforementioned average NO$_x$ reduction range of 19-43% obtained when the N$_2$ background gas is replaced by CO$_2$ was obtained by comparing reductions at the same O$_2$ partial pressures. However, when a comparison is made between combustion in air and combustion at different O$_2$/CO$_2$ combinations, NO$_x$ reductions (averaged among all four coals) were calculated to be in the range of 9-43%. However, as NO$_x$ reductions during reburning of coal have been reported to be as high as 65% [20, 22], the difference may be attributed to the mechanism of “reburning” of NO$_x$, since actual flue gas recirculation (FGR) was present therein, i.e., a gas containing CO$_2$, NOx, etc. To the contrary, herein FGR was simulated
by introducing neat CO₂ to the furnace, i.e., without any NOₓ content. This merits further investigation.

(ii) SO₂: As mentioned before, there were no discernible effects of the background gas on SO₂ emissions.

C) Effect of oxygen mole fraction on the NOₓ and SO₂ emissions

(i) NOₓ: An important observation herein concerns the trend of NOₓ emissions with oxygen mole fraction, which exhibited a peak in the 40-60% O₂ range. This behavior has also been reported by Hu et al. [55], who noticed peak NOₓ emissions around 50% O₂. It should be mentioned here that current work in this laboratory shows that the combustion behavior of the fuel particles varies as the oxygen mole fraction increases, and as the N₂ background gas is replaced by CO₂. Hence, several compounded, and often competing, factors may be the cause of this peculiar trend, including the following four: (a) Changes in the amine radical pool chemical kinetics, as the volatile flames get hotter at increasing oxygen mole fractions. (b) Changes in the effectiveness of the oxygen transport and diffusion phenomena at the burning char surfaces, (c) NOₓ reduction reactions with carbon on char surfaces, (d) NOₓ reduction reactions with carbon monoxide in the pores of chars.

Glarborg [37] stated that different nitrogen species may evolve from unlike coal/biomass types burning under diverse conditions, however, all these species feed to an amine radical pool (see Fig. 8 of Ref. [37]). Subsequent reactions of NH and N depend only on the flame conditions (stoichiometry, temperature, total fixed nitrogen level, etc.). In the experiments herein, envelope flame temperatures increased with increasing oxygen partial pressure, as documented in ongoing pyrometric studies (see also Bejarano and Levendis [81], Fig. 5). This temperature rise is
expected to have enhanced the generation of NO from the amine radical pool, as exemplified with modeling predictions described in Fig. 9 of Ref. [37]. Indeed, as shown in Fig. 4; NO$_x$ increased as the oxygen mole fraction increased from 20% to 40-50%. The fact that this trend did not continue with further increases of O$_2$ and, thus temperature, indicates that other factors dominated at higher oxygen mole fractions. High-resolution high-speed cinematographic observations showed that in the case of the bituminous coal, combustion in air took place in two distinct phases: volatile matter burning in detached flames, followed by heterogeneous char oxidation [75]. However as the oxygen concentration increased beyond 40-50%, the flames retracted to the particle surfaces and, in many cases (particles), only one combustion phase was observed, i.e., volatiles and char burned simultaneously. This complete change in combustion mode may have imposed severe oxygen diffusion limitations to the char surface (over the entire particle burn-time), as the burning volatiles therein minimized the oxygen penetration in the pores, and thereby reduced the contributions of the char-N to the total fuel-NO formation. As mentioned in the Introduction, the char-N contributions are very important during combustion in air, perhaps more important than those of volatile nitrogen [44, 51]. Thus, the hypothesized minimization of the char-N contributions to the NO formation mechanism, at high O$_2$ mole fractions, can have significant consequences to the total amounts of NO released.

Moreover, as the char temperature increases with increasing O$_2$ mole fraction (see Fig. 4 of Ref. [81]) the atmospheric oxygen diffusion in the char pore network becomes progressively more restricted. Then as reported before [37, 55], at high temperatures the char+O$_2$ reaction becomes diffusion limited. Further increases in temperature promote mainly the char+NO reaction and/or, according to Thomas [62], the CO+NO reaction in the pores. These reactions reduce the
emissions of NO\textsubscript{x}. The latter reaction is expected to be more dominant in the case of the high-oxygen content low-rank coals and of the biomass.

(ii) \textbf{SO\textsubscript{2}}: The increasing deficit in the sulfur balance with increasing oxygen partial pressure may be due to the reactions involved in the Lead Chamber process [82] in which sulfuric acid production is controlled by the combination of the following reactions:

\begin{align*}
2 \text{NO} + \text{O}_2 &= 2 \text{NO}_2 \\
\text{SO}_2 + \text{NO}_2 &= \text{SO}_3
\end{align*}

The amount of NO\textsubscript{2} increases with O\textsubscript{2} concentration which would lead to larger amounts of SO\textsubscript{3} which would dissolve in the ice-bath. A recent study has also shown that the sampling of combustion products containing SO\textsubscript{2} resulted in oxidation reactions involving SO\textsubscript{2} in solution [83]. Although plausible further research is needed to show that these reactions are responsible for the deficiency in the sulfur balance in this study.

\textbf{6. CONCLUSIONS}

This study burned five pulverized solid fuels in a laboratory drop-tube furnace (a bituminous, a sub-bituminous and two lignite coals, as well as sugar-cane bagasse and its blends with two of the coals). Combustion took place under fuel-lean conditions in various O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2} environments. Emissions of hazardous gases were monitored with on-line analyzers. Results showed that:

- NO\textsubscript{x} emissions in O\textsubscript{2}/CO\textsubscript{2} environments were lower by 19-43% than those in O\textsubscript{2}/N\textsubscript{2} environments, at the same O\textsubscript{2} mole fractions (22-39% for bagasse and blends). However, when combustion in air was compared to combustion at different O\textsubscript{2}/CO\textsubscript{2} combinations, NO\textsubscript{x}
reductions (averaged among all four coals) were calculated to be in the range of 9-43% (9-33% for bagasse and blends).

- NO\textsubscript{x} emissions increased with increasing oxygen mole fraction until ~50% O\textsubscript{2} was reached; thereafter, they monotonically decreased with increasing O\textsubscript{2}. At 100% O\textsubscript{2}, NO\textsubscript{x} emissions became comparable to those in air. This trend was observed regardless whether the fuel mass flow rate or the equivalence ratio was kept constant.

- NO\textsubscript{x} emissions from the various fuels burned did not clearly reflect their nitrogen content (0.2-1.4%), except when large differences were present.

- Conversion of the fuel-nitrogen to NO\textsubscript{x} was in the range of 20-50% in all cases.

- SO\textsubscript{2} emissions remained largely unaffected by the replacement of the N\textsubscript{2} diluent gas with CO\textsubscript{2}. Only in the case of the bituminous coal, the SO\textsubscript{2} emissions depended on the O\textsubscript{2} mole fraction.

- The SO\textsubscript{2} emissions were found to be dependent on the sulfur and calcium contents of the fuels.

- Conversion of the sulfur in the fuel to SO\textsubscript{2} spanned the entire possible range, from a few percent to 100% in the cases examined herein.

- The CO emissions of the fuels were negligible in all cases, except in 20% O\textsubscript{2}, where they were measurable; they were higher in the CO\textsubscript{2} environment than in the N\textsubscript{2} environment.

7. References


[77] Arias B.; Pevida C.; Rubiera F.; and Pis J.J. Fuel 2008, 87(12), 2753-2759.


