Quantitative *in-situ* Measurements of Sodium Release during the Combustion of Single Coal Particles using Planar Laser Induced Fluorescence

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Abstract

The release of sodium from low rank coal during combustion is known to be an important factor in the phenomena of fouling and corrosion in industrial boilers. Although much is known about the gas phase chemistry of sodium compounds, and the likely sequence of events that lead to fouling and corrosion, very little fundamental work has been undertaken on the release of sodium from the coal particle as it is combusted. The principal objective of this study was to perform detailed quantitative measurements and mathematical modelling of sodium release during combustion of single brown coal particles.

Planar Laser Induced Fluorescence (PLIF) was applied for the *in-situ* measurement of the atomic sodium concentration field in the plume of single Loy Yang brown coal particles. Laser absorption measurements at the sodium D1 line (589.59 nm) were utilised to calibrate PLIF measurements of atomic sodium in a purpose designed flat flame environment. Detailed measurements of atomic sodium in the plume of single combusting brown coal particles of varying amounts and forms of sodium and of varying particle sizes were then undertaken. A run-of-mine Loy Yang brown coal sample and two samples that were processed using Mechanical/Thermal Expression (MTE), which removed a fraction of the inherent moisture and concomitant dissolved salts, were investigated. An experiment was also performed to simultaneously measure the particle temperature, particle size, and the atomic sodium concentration in the plume of a single burning Loy Yang brown coal particle.

From the experimental results, the proportions of sodium released during the stages of coal devolatilisation, char combustion and from the remaining ash after combustion were determined for the three coals used at various particle sizes. The relative differences between the sodium release behaviour of water-bound and organically bound sodium were also inferred. During char combustion, the release of sodium was determined to be dependent on both the particle temperature and particle size. In order to decouple these parameters and determine the true controlling parameter(s) for sodium release, a model was established for the release of sodium, the char burnout behaviour of the particles, and the particle surface temperature. By combining the modelling with further analysis of the experimental data, the temperature dependent kinetics of sodium release during brown coal char combustion were established. A full mechanism was also proposed for sodium release during the various stages of coal combustion, which suggested that the rate determining step for sodium release during char combustion is the formation of a reduced form of sodium in the char, which subsequently leads to the rapid loss of sodium from the particle.

The results of this study advance the knowledge of the release of sodium from brown coal combustion. Two major contributions are the development of a methodology that enables the direct *in-situ* measurements of the concentration of atomic sodium in the plume of individual burning coal particles, and the establishment of the kinetics and mechanism for the release of sodium during Loy Yang brown coal combustion. These results provide, for the first time, essential data for the development of sodium release sub-models within large scale brown coal boiler Computational Fluid Dynamic (CFD) models. Such models will help in the development of improved measures to mitigate fouling and corrosion problems in brown coal fired combustion and gasification systems.

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution to Philip Joseph van Eyk and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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11 November 2010

Philip Joseph van Eyk

Date

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I would like to acknowledge the financial and other support received for this research from the Cooperative Research Centre (CRC) for Clean Power from Lignite which was established under the Australian Government's Cooperative Research Centre's program. The project also received partial support from the Australian Research Council Discovery scheme, which is gratefully acknowledged. I would like to acknowledge the help and support given to me from former CRC staff, especially Dr. Peter Jackson who gave me expert advice on coal combustion and oversaw the project from Melbourne. Peter passed away in 2007 and is sadly missed.

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Preface

This thesis is submitted as a portfolio of publications according to the "Specifications for Thesis 2010" of the University of Adelaide. The journals in which the papers were published or submitted are two of the most highly ranked journals in the research field of Chemical Engineering. Data on the impact factors of the journals are listed below:

Journal Title	2009 Impact Factor	2009 Chemical Engineering Ranking +
Combustion and Flame	2.923	10/128
Proceedings of the Combustion Institute	3.256	6/128

+ Journal ranking in terms of 2009 Impact Factor in the field of Chemical Engineering

The main body of work contained in this thesis is within the following four journal papers:

1) **P. J. van Eyk**, P. J. Ashman, Z. T. Alwahabi, G. J. Nathan, "Quantitative measurement of atomic sodium in the plume of a single burning coal particle", *Combustion and Flame*, 155 (2008) 529-537. Copyright of this paper belongs to The Combustion Institute.

2) **P. J. van Eyk**, P. J. Ashman, Z. T. Alwahabi, G. J. Nathan, "Simultaneous measurements of the release of atomic sodium, particle diameter and particle temperature for a single burning coal particle", *Proceedings of the Combustion Institute*, 32 (2009) 2099-2106. Copyright of this paper belongs to The Combustion Institute.

3) **P. J. van Eyk**, P. J. Ashman, Z. T. Alwahabi, G. J. Nathan, "The release of water-bound and organic sodium from Loy Yang coal during the combustion of single particles in a flat flame", *Combustion and Flame*, 158 (2011) 1181-1192. Copyright of this paper belongs to The Combustion Institute.

4) **P. J. van Eyk**, P. J. Ashman, G. J. Nathan, "Mechanism and Kinetics of sodium release from brown coal char particles during combustion", *Combustion and Flame*, In Press. Copyright of this paper belongs to The Combustion Institute.

Some additional aspects of this work were published in peer-reviewed conference papers. These are included as appendices for completeness.

A) N. Syred, **P. J. van Eyk**, C. Y. Wong, Z. T. Alwahabi, G. J. Nathan, “Studies of the release of sodium from pulverised coal in a flat flame”, Proceedings of the 12th International Symposium on Applications of Laser Techniques to Fluid Mechanics, Lisbon, Portugal, 2004.

B) **P. J. van Eyk**, N. Syred, C. Y. Wong, C. P. Ung, P. J. Ashman, G. J. Nathan, Z. T. Alwahabi, "Study on atomic sodium release from pulverised coal particles in a pre-mixed natural gas flame." Proceedings of the 4th Australian Conference on Laser Diagnostics in Fluid Mechanics and Combustion, McLaren Vale, SA, 2005, 133-136.

C) **P. J. van Eyk**, P. J. Ashman, Z. T. Alwahabi, G. J. Nathan, “Measurement of atomic Na released from a coal particle using quantitative planar laser induced fluorescence”, Proceedings of the Australian Symposium on Combustion, University of Sydney, NSW, Australia, 2007, 114-117.

D) **P. J. van Eyk**, P. J. Ashman, Z. T. Alwahabi, G. J. Nathan, “Kinetics of sodium release from a brown coal particle burning in a flat flame”, Proceedings of the Australian Symposium on Combustion, University of Queensland, Brisbane, Australia, 2009, 215-218.

Chapter 1

INTRODUCTION

1.1 Background

The vast reserves of low-rank coal worldwide offer a long term supply of fuel for power generation. Low-rank coals are an important source of fuel for electricity generation for South Eastern Australia as well as in Germany, the United States and China. However, the relatively high sodium content of these coals is well known to be associated with many operational problems when the coals are combusted in boilers. Due to the drive to reduce coal consumption and CO_2 emissions worldwide, higher efficiency supercritical and ultra-supercritical boilers are now being deployed. Because these newer technologies result in higher temperatures both in the combustion and post-combustion zones, the problems associated with sodium in low rank coals are exacerbated compared to traditional coal fired boilers.

Fouling and corrosion of the boiler tubes caused by sodium compounds in an industrial low-rank coal-fired furnace is a common problem, and leads to losses of heat transfer efficiency and costly outages (Neville and Sarofim, 1985; Raask, 1985; Schobert, 1987; Schobert, 1995; Bryers, 1996). In fluidised bed combustion systems, agglomeration and defluidisation of the bed material can also be a significant problem, and is known to be caused by reactions of sodium compounds (Bartels *et al.*, 2008). Because of these problems, significant work has been undertaken to understand the processes involved, especially in regard to combustion based power generation. Although much is known about the gas phase chemistry of sodium compounds, and the likely sequence of events that lead to fouling and corrosion, very little fundamental work has been undertaken on the release of sodium from the coal particle as it is combusted.

The principal objective of this thesis is to improve the understanding of the release of sodium during the combustion of Victorian brown coal. This is achieved by performing detailed measurements and mathematical modelling on the release of sodium from single Victorian brown coal particles under combustion conditions. The results of this study will provide, for the first time, essential data for the development of sodium release sub-models within Victorian brown coal combustion Computational Fluid Dynamic (CFD) models. Such models will help in the development of improved measures to mitigate sodium related problems in industrial Victorian brown coal combustion systems.

1.2 Scope and structure of thesis

Chapter 2 provides a brief and critical review of the literature relating to sodium behaviour during the combustion brown coal. The emphasis of the chapter is on the forms of sodium in brown coals, and the transformations that occur to sodium during coal combustion that lead to the formation of deposits. Additionally, methods for the measurement of sodium species from high temperature gaseous environments are reviewed.

Chapter 3 is the first of four journal publications, which form the basis for this thesis, and presents a method for measuring the 2-dimensional concentration field of atomic sodium in the plume of a single coal particle with a temporal resolution that is fast compared to the combustion time of the particle. The work also assesses the accuracy of these measurements, and provides new insight by comparison of the measured sodium concentration field with a simple kinetic model.

Chapter 4 is the second of four journal publications, and provides spatially- and temporally-resolved simultaneous measurements of three important combustion parameters for a single coal particle, namely the quantitative concentration of atomic sodium in the plume of the particle, the surface temperature of the coal particle and the coal particle size.

Chapter 5 is the third of four journal publications, and provides new insight into the effect of the nature of sodium in the coal (either organically-bound or water-soluble) on the release of sodium during combustion. A run-of-mine Loy Yang brown coal (LY-ROM) and two Loy Yang brown coals (MTE1 and MTE2) that were processed using Mechanical/Thermal Expression (MTE), which removed a fraction of the inherent moisture and concomitant dissolved salts, are investigated. By utilising equilibrium calculations and the measured atomic sodium concentration field, the proportion of total sodium that is released during the various stages of coal combustion is determined for these three coals.

Chapter 6 is the final journal publication for this thesis, and uses a model for the release of sodium during the combustion of single brown coal char particles combined with further analysis on the data from Chapter 5 to determine the variation of the rate constant for sodium release with time for each of the experimental data sets. A char combustion and heat transfer model is also used to predict the char burnout behaviour and surface temperature of the particle as a function of time during combustion for each of the experiments. Thus, the temperature dependent kinetics of sodium release during brown coal char combustion are established. A full mechanism is also proposed for sodium release during the various stages of coal combustion.

Chapter 7 presents conclusions from the body of work along with recommendations for future work in this area of research.

Finally, a list of the references cited in Chapters 1, 2 and 7 is given. All other references cited in the individual journal papers (Chapters 3-6) are provided within the relevant papers.

The Appendices provide peer-reviewed conference papers that are relevant to this study. Appendices A and B are precursors to the main body of work included in this thesis; the qualitative measurement of Planar Laser Induced Fluorescence (PLIF) of atomic sodium in a natural gas flame seeded with pulverised coal particles. Appendices C and D present further work directly related to the quantitative measurement of atomic sodium using PLIF. Appendix C presents a short summary of the PLIF technique, and Appendix D presents new data not presented elsewhere on the release of sodium from Loy Yang coal in a natural gas flame as a function of stoichiometry.

Chapter 2

LITERATURE REVIEW

2.1 Introduction

The purpose of this chapter is to provide a brief and critical review of the established literature with regard to the behaviour of sodium during the combustion of brown coals and the formation of deposits in coal-fired boilers. The emphasis is on the forms of sodium in brown coal, the known transformations of sodium that occur during coal combustion, the physical mechanisms of deposit formation on boiler tubes, and the established gas phase reactions of sodium species that lead to the formation of deposits. Additionally, established methods for the direct measurement of sodium species in high temperature gaseous environments are reviewed.

2.2 Sodium occurrence in brown coal

Elemental sodium in coal may occur in several forms, and varies widely for different types of coal (Brockway *et al.*, 1991; Schobert, 1995). Clays of the form of aluminosilicates, montmorillonites and zeolites have been identified to contain sodium within coals (Kemezys and Taylor, 1964; Brown and Swaine, 1964; Sondreal *et al.*, 1977; Hale *et al.*, 1980). However, the proportion of this form of sodium is low in brown coals. Rather, a substantial amount of the sodium is in the form of salts dissolved in the inherent moisture in brown coals, principally as sodium chloride (Edgecombe, 1956; Hodges *et al.*, 1983), and is related to the salinity of the aquifers associated with the coal seam (Edger and Kaiser, 1984; Brockway and Borsaru, 1985). This type of sodium is henceforth termed "water-bound" sodium. Sodium is also present in large quantities in the form of exchangeable cations bound to carboxyl groups in the coal matrix (Durie, 1961; Durie and Swaine, 1971; Higgins *et al.*, 1980; Kiss, 1981; Kiss, 1982; Perry *et al.*, 1984). This type of sodium is henceforth termed "organic" sodium.

2.3 Sodium transformations during combustion of brown coal

2.3.1 Physical transformations during coal combustion

Combustion of brown coal in a boiler (either pulverised coal or fluidised bed combustion) occurs as a series of physical transformations to the individual coal particles. The first of these processes is the evaporation of moisture which occurs as the coal particle enters the hot environment of the boiler. After evaporation has occurred, the volatiles within the coal particle are released and burnt relatively quickly (Wall *et al.*, 1979). The char particle then ignites and is burnt over a substantially longer time scale than the combustion of the volatiles (Smith, 1982). During all of these stages, the various forms of sodium within the particle, including both water-bound and organic sodium, undergo physical and chemical transformations.

2.3.2 Transformations of water-bound sodium within coal particle

As discussed above, the initial process that occurs when a brown coal particle enters a boiler is the evaporation of the moisture remaining in the coal particle. This evaporation leads to a residue of dissolved salts within the coal particle, and it is likely that sodium salts form crystals of sodium chloride within the coal structure. As the temperature rises, the sodium chloride crystals melt; the melting point of NaCl is 801 °C (Dean, 1985). As a result, the molten sodium salt spreads evenly throughout the coal particle.

The next process, the release and combustion of volatiles from the coal, also coincides with a transformation of sodium within the coal particle. It has been reported by many authors that the release of chlorine from the coal is disproportionate to that of sodium during pyrolysis experiments (Kosminski and Manzoori, 1990; Shao *et al*., 1994; Quyn *et al*., 2002a; Kosminski *et al*., 2006). An explanation for this phenomenon is that the sodium chloride either dissociates or reacts inside the particle thereby preferentially releasing chlorine and retaining much of the sodium within the coal particle. It is also thought that part of the sodium is released by direct vaporisation of NaCl for temperatures above 750 °C (Kosminski and Manzoori, 1990). The sodium that is retained in the subsequent char particle is released during the high temperatures of char combustion, but the exact mechanism for this release is still not fully understood.

2.3.3 Transformations of organic sodium within coal particle

Organically bound sodium, however, has a set of different transformations. During devolatilisation, the decomposition of many functional groups occurs within the coal structure. It has been established from carbonisation experiments that, for Victorian brown coals, the carboxyl groups containing inorganic constituents begin to decompose from 400-600 °C to release CO_2 in direct proportion to the rate of decomposition of these groups (Murray, 1973; Schafer, 1979). Murray and Ledger (1972) found that the decomposition product of sodium carboxylates in brown coal pyrolysis was sodium carbonate. However, in that study determination of sodium carbonate was conducted ex-situ, and hence the exact form of sodium within the char particle after this decomposition is not clear. Sodium species that are originally attached to the organic coal structure have proven to be less volatile than NaCl during pyrolysis (Quyn *et al.*, 2002b; Kosminski *et al.*, 2006). Hence, it is likely that the majority of the organic sodium is retained in the char and is released during the high temperatures of char combustion. Again, the exact mechanism for the release is still not fully understood.

2.4 Alkali catalysed gasification

Some information in relation to the transformations of sodium within the char particle has been obtained from work in the area of alkali catalysed char gasification. For many decades, alkali catalysed char gasification has been studied due to the fact that small concentrations of alkali metals can increase the rate of the reactions of carbon with oxygen, carbon dioxide and water vapour. The mechanism of this catalytic behaviour is generally postulated to consist of an oxidation-reduction cycle in which oxygen is transferred to the carbon active sites through the catalytically active alkali species (Chen and Yang, 1997).

The exact nature of the alkali catalyst has been widely debated. Proposed active intermediates for an alkali species M (where M denotes either a sodium or potassium atom) include metallic M (McKee and Chatterji, 1975), M_2O (Veraa and Bell, 1978; McKee and Chatterji, 1982), M_2O_2 (McKee and Chatterji, 1975; Saber *et al.*, 1986), M_2CO_3 (McKee and Chatterji, 1975; Veraa and Bell, 1978), M-O-C compounds within the char particle (Freriks *et al.*, 1981; Yuh and Wolf, 1982; Mims and Pabst, 1982; Delannay *et al.*, 1984), and non-stoichiometric catalyst clusters on the char surface (Wood and Sancier, 1984; Saber *et al.*, 1988). Whichever the nature of the true active intermediate, it is clear that alkali compounds are retained in the char particle as active catalysts. The loss of catalyst from the char particle during gasification has also been studied (Sams *et al.*, 1985; Saber *et al.*, 1986; Shadman *et al.*, 1987; Meijer *et al.*, 1991). In those studies, it was found that the formation of a reduced form of the catalyst inside the particle was the prerequisite for a rapid loss of catalyst at high temperatures (Sams *et al.*, 1985; Shadman *et al.*, 1987).

The established mechanisms for alkali catalysed carbon gasification and catalyst loss provide valuable insight into the behaviour of alkali species within a char particle leading to sodium release during combustion of a char particle. However, for a full understanding of sodium release during brown coal combustion, it is necessary to have kinetic data available for sodium release during brown coal char combustion, and to establish a mechanism for sodium release during all stages of brown coal combustion.

2.5 Release of sodium and formation of deposits

There is considerable evidence that, at the high temperatures that prevail during char combustion (from 800 °C to as high as 1700 °C, depending on the combustion conditions), a significant amount of sodium is vaporised. Various studies have been conducted to determine the principle initiators of heat transfer surface deposits in industrial coal-fired boilers. The size distribution of the ash particles formed during pulverised coal combustion has been determined to be bimodal (Markowski *et al.*, 1980; Quann *et al.*, 1982); a sub-micron aerosol of less than 0.1 μm, and a larger (> 1 μm) size range. There have been many studies with the sole purpose of establishing the sodium partitioning in the ash from pulverised coal combustion (Neville and Sarofim, 1985; Gallagher *et al.*, 1990). The concentration of sodium has been shown to be enriched in the sub-micron fly ash (Ounsted and Schoen, 1960; Raask, 1981), with sodium sulphate being enriched on the surface of the fly ash particles for high sulphur coal (Gallagher *et al.*, 1996). Sodium sulphates (Bryers, 1996; Gallagher *et al.*, 1996) and sodium calcium sulfates (Sondreal *et al.*, 1977; Rindt *et al*. 1983; Conn and Jones, 1984) have also been observed in the inner layers of boiler convection deposits. For coals with high silicon content in the ash, sodium silicates can form, thus reducing the amount of sodium in the finer fly ash (Wibberley and Wall, 1989b; Lindner and Wall, 1990). However for low-ash coals, all the sodium may be vaporised to form a sub-micron fume (Lindner and Wall, 1990; Gallagher *et al.*, 1996). The proportion of sodium released during each of the stages of coal combustion remains unclear, and new measurements under well defined conditions are required to for a full understanding of the release of sodium during coal combustion to be obtained.

2.6 Gas phase alkali chemistry

Kinetic modelling of alkali metal vapours have been undertaken for many years in order to understand the transformations of alkali species in combustion and gasification, the formation of deposits and corrosion, and the mechanism of alkali induced flame inhibition. The reactions of sodium atoms with oxygen and nitrous oxide have been studied in detail (Husain and Plane, 1982; Husain *et al.*, 1984; Husain *et al.*, 1987; Plane, 1987; Plane and Rajasekhar, 1988a, 1988b, 1989; Rajasekhar *et al.*, 1989; Marshall *et al.*, 1990). Reactions of sodium with sulphur dioxide have been investigated by Shi and Marshall (1991). Reactions of sodium with water vapour are reported by Cox and Plane (1999), whereas reactions of sodium with nitric oxide are reported by Goumri *et al.* (1999). Kinetic studies of alkali species in flames are reported by many authors (Hynes *et al.*, 1984; Slack *et al.*, 1989;

Srinivasachar *et al*., 1990; Steinberg and Schoefield, 1990, 2002). Specifically, Hynes *et al*. (1984) have described the chemistry of sodium in hydrogen flames, Srinivasachar *et al*. (1990) have described the chemistry of sodium and chlorine in flames, and Steinberg and Schoefield (1990, 2002) have described the flame chemistry of sodium with sulphur in flames.

The mechanism of alkali species' behaviour in combustion of coal or biomass combustion was examined in detail by Glarborg (2007) and Glarborg and Marshall (2005). Investigations relating to combustion of coal include Wibberley and Wall (1982a), Wall (1992) and Niksa *et al*. (2001). Schobert (1995) reviewed the investigations undertaken on North American coals. By conducting thermodynamic modelling, Wibberley and Wall (1982a) calculated that sodium sulphate is stable only below 1300-1400 K in a pulverised coal-fired furnace atmosphere. At higher temperatures, the formation of sodium silicates is dominant. In the gas phase, the main species are chlorides and hydroxides, with the chlorine content in the fuel being the main factor determining the relative quantities (Srinivasachar *et al*., 1990). For temperatures below 1450 °C and high chlorine content, the NaCl is the dominant species, whereas for low chlorine content coals the NaOH is dominant above 1200 °C. Additionally, Srinivasachar *et al*. (1990) showed that equilibration of these two species was reached within only 5 ms.

The mechanism for the formation of alkali sulphate deposits is an issue that has been studied by many authors (Boll and Patel, 1960; Halstead and Raask, 1969; Steinberg and Schoefield, 1990, 2002, Iisa *et al.*, 1999; Glarborg and Marshall, 2005; Hindiyarti *et al.*, 2008). The original studies concluded that the sulfation of sodium chloride proceeds by the reaction of NaCl with SO_2 and ambient oxygen and water vapour in the flue gases (Boll and Patel, 1960; Halstead and Raask, 1969). It has also been suggested that the sulphation of NaCl is kinetically limited by the formation and availability of SO_3 (Steinberg and Schoefield, 1990, 2002; Iisa *et al.*, 1999). Work by Glarborg and Marshall (2005) suggested that sodium hydroxide and sodium chloride form sodium hydrogen sulphate and sodium oxysulphur chloride, which are precursors for sodium sulphate. More recent work (Hindiyarti *et al.*, 2008) suggests that the rate-limiting step may be the oxidation of alkali sulfite to sulphate in the gas phase, rather than the oxidation of SO_2 to SO_3 proposed by Steinberg and Schoefield (1990, 2002). Hence, sodium sulphate should exist at equilibrium in the gas phase.

Considerable research into equilibrium concentrations and kinetic modelling of alkali species in the gas phase has been undertaken. However, the building of these models requires the use of reliable data, and in many cases the current models have assigned estimated values for important parameters. Further research using direct *in-situ* measurements of alkali species in the gas phase is needed to understand the kinetics and mechanisms of alkali release from solid fuel combustion. Specifically, measurements of the direct release from fuel particles are needed as this provides the models with a source term that can lead to accurate prediction of behaviour in the gas and condensed phases.

2.7 Measurement of sodium at high temperature

2.7.1 Overview

In section 2.5 it was shown that there is considerable evidence that a significant amount of sodium is vaporised in the high temperatures that occur in coal combustion. Hence, there has been considerable research in recent decades to directly measure sodium concentrations in the flue gas of coal combustion. The techniques include direct sampling from process gas streams, optical techniques and mass spectrometric techniques. Techniques for measuring metal species in industrial processes are reviewed extensively by Monkhouse (2002, 2010). A short review of the methods that have been used for sodium is presented here. The emphasis of this section is on establishing which techniques are most appropriate for the measurement of the direct release of sodium from coal particles, both spatially and temporally.

2.7.2 Direct sampling from process gas

Direct sampling from process gas involves passing a small amount of the flue gases to a measuring system through short sampling lines. Condensation in the sampling tube is minimised by retaining the actual process pressure during measurements and by heating the entire tube to above the dew point. The quantity of Na can be determined by Inductively Coupled Plasma (ICP) combined with atomic emission spectrometry (AES) (eg. Seltzer and Meyer, 1997). Another technique is to absorb the Na onto one of many materials (Lee and Johnson, 1980). The absorbed sodium can then be determined by washing the material with water, and dissolving it in concentrated $HF+HClO_4$, and analysing for sodium content by Atomic Absorption Spectroscopy (AAS). The third method is to condense the sodium in a quenching spray of water and then use ICP AES to measure the quantity of sodium in the quench water. An example of this method is given by Ludwig *et al*. (2007). All of these methods have a relatively slow temporal response due to the fact that the measurement is not *in-situ* within the flue gas stream. Hence, direct sampling techniques are inadequate for the direct measurement of sodium release from combusting coal particles. In contrast, many optical methods allow *in-situ* measurements.

2.7.3 Optical based techniques

2.7.3.1 Absorption

The fundamentals of absorption spectroscopy have been reported extensively (Eckbreth, 1996; Monkhouse 2002, 2010, Demtröder, 2008). Due to the lack of availability of diode lasers at ~589 nm (the wavelength associated with the sodium D-lines), the measurement of sodium using tuneable diode laser absorption spectroscopy (TDLAS) have so far not been undertaken (Monkhouse, 2010). The only absorption technique that has been successfully used for sodium measurements is Differential Absorption Spectoscopy (DOAS). Borström *et al.* (2007) and Forsberg *et al*. (2009) report a technique for the quantitative measurement of alkali chloride vapours in an industrial process by DOAS. The path length used was 5 m, which is difficult to obtain in a laboratory scale experimental set-up for the determination of sodium release from coal combustion.

2.7.3.2 Atomic Fluorescence

Atomic fluorescence is spontaneous emission from atoms or molecules that have been excited by a light source at a specific wavelength (Daily, 1997). Laser Induced Fluorescence (LIF), which is defined by the use of a laser as the source of radiation, has been used for many decades to measure concentrations of atomic and molecular species (Eckbreth, 1996; Kohse-Höinghaus and Jeffries, 2002). The technique can be used as a point measurement to determine the concentration of an atomic or molecular species within a small measurement volume. The fluoresced light can be collected by using a monochromator, a photo-diode or an Intensified Charge Coupled Device (ICCD) camera. Additionally, the planar LIF (PLIF) method can be used whereby a 2D-section in the measurement volume is excited using a two cylindrical lenses to establish a laser sheet and the species of interest imaged onto an ICCD camera. This last point is what differentiates LIF from the other laser-based techniques for sodium measurements – the possibility of 2D concentration profiles of atomic sodium concentration.

Atomic sodium has been studied extensively with LIF, for development of the LIF method (Daily and Chan, 1978; Daily, 1978), and studies of the chemical kinetics of sodium in flames (Hynes *et al.*, 1984; Steinberg and Schoefield, 1990). Measuring concentrations of sodium with LIF in a small flame with pulverised coal has also been undertaken (Sweeny *et al.*, 1987), although in that work North Dakota lignite was studied which has significantly different properties compared to Victorian brown coals studied in this work. More recently, Nathan *et al.* (2003) used qualitative PLIF to analyse the temporal trends of atomic sodium release from single particles burning in a Bunsen burner. A series of studies thus followed in our laboratory (Syred *et al.*, 2004; van Eyk *et al.*, 2005), where the authors performed experiments on qualitative PLIF of atomic sodium in a flat flame burner fed with pulverised coal particles. The 2D nature of the PLIF measurements allows for a determination of spatial variations in the measurement volume to be observed. Also, PLIF images can be recorded at a high rate (depending on the ICCD), and hence variations of sodium concentrations with time are able to be determined. However, quantification of PLIF was not undertaken in these previous studies (Nathan *et al.*, 2003; Syred *et al.*, 2004; van Eyk *et al.*, 2005), and hence this is a major objective of the current work.

2.7.3.3 Photofragment Fluorescence

Photofragment Fluorescence techniques have been utilised extensively to measure alkali chloride and alkali hydroxide concentrations in a variety of systems (Oldenburg and Baugham, 1986; Chadwick *et al.*, 1995; Chadwick and Morrison, 1995; Chadwick *et al.*, 1997; Hartinger *et al.*, 1997; Gottwald and Monkhouse, 1999; Hidalgo-Núñez and Omenetto, 2001; Monkhouse *et al.*, 2003). The technique involves the excitation of NaCl and NaOH molecules by a UV-laser. Often a UV-laser such as a tripled or quadrupled Nd:YAG or an excimer laser is used (Monkhouse, 2010). Different types of molecules are discriminated using different excitation and/or detection wavelengths, since different molecules have different bond energies (Chadwick *et al*., 1995). However, the technique results in a point measurement, thereby not allowing for easy determination of the concentration field of sodium in a given environment.

2.7.3.4 Plasma Spectroscopy

All of the various forms of plasma spectroscopy use different methods of plasma generation to atomise and excite the species of interest (Monkhouse, 2010). Of these forms, Plasma Excited Atomic Resonance Line Spectroscopy (PEARLS) and Laser Induced Breakdown Spectroscopy (LIBS) have been used for measurements of sodium species in combustion systems. In PEARLS, a sample flow is taken along a sampling line and mixed in a nitrogen plasma jet, which heats the gas to 2100-2500 °C (Monkhouse, 2010). An example of this method is given by Häyrinen *et al*. (2004). Because PEARLS involves taking a sample for analysis it is not strictly *in-situ*. LIBS, on the other hand, is an *in-situ* method whereby a focussed beam of laser light produces a micro-plasma that causes all molecules, and even the smaller particles, to completely atomise. Atomic transitions are thus monitored using similar methods as described in section 2.7.3.2. An example of sodium measurement using LIBS is given by Molina *et al*. (2006).

2.7.4 Mass spectrometric methods

An in depth review of mass spectrometric methods is given by Suess and Prather (1999) and Monkhouse (2002). Techniques that have been applied to sodium measurements are High Pressure Mass Spectrometry (Wolf *et al*., 2004; Escobar *et al*., 2008) and Molecular Beam Mass Spectrometry (Oleschko *et al*., 2007; Blassing and Muller, 2010a, 2010b). The techniques give useful information on the final (equilibrium) form of sodium in the gas phase, but the techniques are not *in-situ*, and hence are inadequate for the direct measurement of sodium release from combusting coal particles.

2.8 Implications for current study

From the above review of literature, it is clear that previous investigators have made substantial contributions to the study of the behaviour of sodium in the combustion of brown coals and the formation of deposits in coal-fired boilers. Although part of the "water bound" sodium is thought to be released by direct vaporisation of NaCl, much of the sodium is retained in the subsequent char particle. The "organic" sodium is predominantly retained in the char particle. It is understood that both forms are subsequently released during the high temperatures of char combustion. However, the proportion of sodium released during each of the stages of coal combustion remains unclear, and new measurements under well defined conditions are required for a full understanding of sodium release during coal combustion.

The established mechanisms for alkali catalysed carbon gasification and catalyst loss provide valuable insight into the behaviour of alkali species within a char particle leading to sodium release during combustion of a char particle. However, for a full understanding of sodium release during brown coal combustion, it is necessary to have kinetic data available for sodium release during all stages of coal combustion. Specifically, measurements of the direct release from fuel particles is needed as this can provide the existing gas phase kinetic models with the source terms needed for accurate prediction of behaviour in the gas and condensed phases.

Of the techniques for measuring sodium species in high temperature environments, only the optical techniques reviewed in section 2.7.3 are truly *in-situ* and hence most appropriate for the measurement of the direct release of sodium from coal particles. Techniques including DOAS, LIF, Photofragment Fluorescence and LIBS are all *in-situ* techniques, however, only LIF can be performed using a laser sheet, thereby providing 2D spatial information as well as temporal information. Hence, the technique chosen for this thesis was planar laser induced fluorescence (PLIF).

2.9 Objectives of thesis

The primary objective of this thesis is to provide a thorough understanding of the release of sodium from the combustion of Victorian brown coal particles by performing detailed measurements using quantitative PLIF.

The detailed objectives of this study are:

1. To develop a technique for the quantitative measurement of the 2-dimensional distribution of atomic sodium as a function of time in the plume from a single burning coal particle using PLIF.
2. To provide, for the first time, spatially- and temporally-resolved simultaneous measurements of three important combustion parameters for a single coal particle. These are the quantitative concentration of atomic sodium, the surface temperature of the coal particle and the coal particle size.
3. To provide new insight into the release of sodium from brown coal during combustion by performing measurements of atomic sodium release, obtained using planar LIF, for Victorian brown coals of varying amounts and forms of sodium in the coal and varying particle sizes.
4. To analyse the data collected in objective 3 by modelling the release of sodium from single combusting brown coal particles and using a char combustion and heat transfer model with a view to obtaining a better

understanding of the kinetics of sodium release during char combustion.

5. To propose a full mechanism for the release of sodium during the various stages of coal combustion.

Chapter 3

QUANTITATIVE MEASUREMENT OF ATOMIC SODIUM IN THE PLUME OF A SINGLE BURNING COAL PARTICLE

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Chapter 4

SIMULTANEOUS MEASUREMENTS OF THE RELEASE OF ATOMIC SODIUM, PARTICLE DIAMETER AND PARTICLE TEMPERATURE FOR A SINGLE BURNING COAL PARTICLE

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Chapter 5

THE RELEASE OF WATER-BOUND AND ORGANIC SODIUM FROM LOY YANG COAL DURING THE COMBUSTION OF SINGLE PARTICLES IN A FLAT FLAME

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CHAPTER 5 – RELEASE OF WATER-BOUND AND ORGANIC SODIUM FROM LOY YANG COAL DURING COMBUSTION

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Chapter 6

MECHANISM AND KINETICS OF SODIUM RELEASE FROM BROWN COAL CHAR PARTICLES DURING COMBUSTION

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Abstract

A model for the release of sodium during the combustion of single Loy Yang brown coal char particles is presented. The model is combined with further analysis of recently published measurements of the release of sodium from single brown coal particles burning in a flat flame to estimate the rate constant for sodium release as a function of burnout time for these experiments. A char combustion and heat transfer model is also used to predict the char burnout behaviour and surface temperature of the particle as a function of time during combustion for each of the experiments. By combining the predicted time-temperature history of the particles with the estimated rate constant for sodium release, an Arrhenius expression for the release of sodium during char combustion is determined as:

$$k_{Na} = 10^{5.2\pm0.4}\exp\left(-214\,\mathrm{kJ/mol}/RT_c\right)$$

A full mechanism for sodium release during the various stages of coal combustion is also proposed. Utilising the proposed mechanism, the rate-determining step for sodium release during char combustion is proposed to be the formation of a reduced form of sodium in the char which subsequently leads to the rapid loss of sodium from the particle.

KEY WORDS: Sodium; char; model; kinetics

Nomenclature

Uppercase Symbols

A_{Na}	Pre-exponential factor for sodium release during char combustion (s^{-1})
A_R	Pre-exponential factor for char combustion (m/s)
Bi	Biot Number
C_c	Oxygen concentration at the char surface (g/m^3)
C_o	Oxygen concentration in the flat flame gases (g/m^3)
C_s	Oxygen concentration at the outer surface of the particle (g/m^3)
D_A	Molecular Diffusivity of oxygen through the flame (m^2/s)
D_e'	Effective Diffusivity of oxygen in the ash layer (m^2/s)
D_{Na}	Effective Diffusivity of vaporised sodium in the char particle (m^2/s)
E_{Na}	Activation energy for sodium release during char combustion (kJ/mol)
E_R	Activation energy for char combustion (kJ/mol)
H_c	Heat of combustion of carbon (J/g)
K_D	Rate coefficient of char combustion due to boundary layer diffusion of oxygen from the flame (m/s)
K_O	Overall rate coefficient of char combustion (m/s)
K_R	Intrinsic reactivity of char to oxygen (m/s)
$N_{Na,r}$	Flux of vaporised sodium within char particle at radial distance r from the particle centre ($mol/m^2.s$)
$N_{Na,r+\Delta r}$	Flux of vaporised sodium within char particle at radial distance $r+\Delta r$ from the particle centre ($mol/m^2.s$)
$N_{Na,s}$	Flux of vaporised sodium through particle surface ($mol/m^2.s$)
R	Universal gas constant (8.314 J/mol.K)
R_{Na}	Rate of reaction of char sodium leading to the release of vaporised sodium ($mol/m^3.s$)
Re	Reynolds Number
Sc	Schmidt Number
Sh	Sherwood Number
T_c	Temperature of inner char particle (K)
T_o	Temperature of surrounding room (K)

T_p	Temperature of outer layer of particle (K)
T_f	Temperature of flame (K)
$W_{Na,at}$	Flow of atomic sodium passing through a given height in the plume (mol/s)
$W_{Na,s}$	Flow of vaporised sodium passing through the particle surface (mol/s)
$X_{c,i}$	Conversion carbon in the char to carbon monoxide
$X_{a,i}$	Conversion inorganic matter in the char to ash

Lowercase Symbols

a_1	Integration Constant
a_2	Integration Constant
c_{Na}	Molar concentration of vaporised sodium within the char particle at radial distance *r* (mol/m^3)
$c_{Na,f}$	Molar concentration of vaporised sodium in the flame (mol/m^3)
$c_{Na,s}$	Molar concentration of vaporised sodium at the particle surface, $r = r_p$ (mol/m^3)
$c_{char-Na}$	Molar concentration of char-sodium within the particle (mol/m^3)
d_p	Diameter of particle (mm)
h_f	Convection heat transfer coefficient of flame (W/m^2.K)
h_D	Mass transfer coefficient for oxygen to particle (m/s)
$h_{D,Na}$	Mass transfer coefficient for vaporised sodium from particle (m/s)
i	Index for numerical calculation
k_c	Conduction heat transfer coefficient of char (W/m.K)
k_{Na}	Rate of sodium release from particle (s^{-1})
m_a	Initial mass of ash in particle (g)
$\dot{m}_c$	Rate of mass loss of carbon from char particle during combustion (g/s)
m_p	Initial mass of char particle (g)
$n_{char-Na}$	Total Number of moles of sodium remaining in particle at time *t* (mol)
n_{Na}	Total Number of moles of sodium released from particle at time *t* (mol)
$\dot{q}_{comb}$	Heat of combustion (W)
$\dot{q}_{cond}$	Heat of conduction (W)
$\dot{q}_{conv}$	Heat of convection (W)

$\dot{q}_{rad}$	Heat of radiation (W)
r	Radial distance from particle centre (mm)
r_c	Radius of char inside burning particle (mm)
r_p	Outer radius of burning particle (mm)
t	Time (s)
u_f	Velocity of flat flame gases (m/s)
x	Fraction of total sodium in atomic form

Greek Symbols

ε	Emissivity of particle
Λ	Gravimetric stoichiometric coefficient
μ_f	Viscosity of flat flame gases (kg/m.s)
ρ_a	Bulk density of ash (kg/m^3)
ρ_c	Bulk density of char (kg/m^3)
ρ_f	Density of flat flame gases (kg/m^3)
σ	Stefan-Boltzmann constant (5.669×10^{-8} W/m^2.K^4)

1. Introduction

The release of sodium within brown coal-fired boilers is known to cause fouling and corrosion of heat transfer surfaces [1, 2]. Sodium in brown coals may occur in two main forms; dissolved in the moisture in the coal (eg. sodium chloride [3, 4]), or organically bound to the coal matrix (eg. as cations attached to carboxylate groups [5]). The behaviour of sodium species during the combustion of coal has been studied experimentally by many authors, predominantly by analysing the deposits formed during coal combustion [2, 6 – 10], but more recently by on-line diagnostic techniques [11 – 13] and mass spectrometric methods [14, 15]. The final forms of sodium in post flame can now be modelled using well established reaction mechanisms [16 – 18]. However, the rate of sodium release directly from the coal particle during the various stages of coal combustion is not well known and further study is required in order for the phenomena of fouling and corrosion to be better understood. Specifically, kinetic data for sodium release during coal combustion is needed to provide a full understanding of the effect of the combustion process on the release of sodium.

In the past decade there have been several studies with the principal aim of understanding the release of alkali metals during the combustion and gasification of brown coals (eg. [14, 19 – 20]) and biomass fuels (eg. [21, 22]). It has been determined that alkali chlorides within the fuel release chlorine almost completely at temperatures well below 800 °C during devolatilisation, but a disproportionately lower amount of alkali metal is released during the same period [20, 22]. Alkali species that are originally attached to the organic coal structure have proven to be less volatile than alkali chlorides [20, 23]. The combination of these findings suggests that a significant quantity of sodium is expected to be retained in the char particle after the devolatilisation stage in brown coal combustion, and is subsequently released during the later stages of coal combustion. However, the kinetics of the release of sodium during the char combustion stage has not been established, and the mechanism is unknown.

It is well known that the gasification of chars with oxygen, carbon dioxide and steam is catalysed by small concentrations of alkali metals [24 – 33]. The mechanism of this catalytic behaviour is generally postulated to consist of an oxidation-reduction cycle in which oxygen is transferred to the carbon active sites via the catalytically active alkali and alkaline earth species. This mechanism has been shown to accurately describe the catalytic behaviour for a wide range of gasification temperatures up to at least 1350K [24 – 33]. The exact nature of the alkali catalyst has been widely debated. Proposed active intermediates for an alkali species M (where M denotes either a sodium or potassium atom) include metallic M [24], M_2O [24 – 26], M_2O_2 [27], M_2CO_3 [24, 26], M-O-C compounds within the char particle [28 – 31], and non-stoichiometric catalyst clusters on the char surface [32, 33]. Whatever the nature of the true active intermediate it is clear that alkali compounds, retained in the char particle, act as active catalysts. The loss of catalyst from the char particle during gasification has also been studied at temperatures up to 1300 K [27, 34 – 36]. The established mechanisms for alkali-catalysed char gasification provide valuable insight into the behaviour of alkali species within a char particle leading to sodium release during its combustion. However, for a full understanding of sodium release during brown coal combustion, it is pivotal that kinetic data are available for sodium release during this process, and that a full mechanism for sodium release during char combustion is established.

To meet this need, work within our laboratory [37 – 39] has focused on the direct measurement of atomic sodium from single coal particles burning in a flat flame using quantitative planar laser induced fluorescence (PLIF). In the most recent study [39], the concentration of atomic sodium, [Na], was measured in the plume above single coal particles burning in a flat flame, utilising the quantitative PLIF method that was established previously in our laboratory [37]. The coals used were run-of-mine Loy Yang brown coal and two samples of Loy Yang brown coal that had been processed by Mechanical Thermal Expression (MTE) – the combined application of pressure and temperature that can significantly lower the moisture content of brown coal, and consequently reduce the concentration of water-soluble sodium present in the coal. The dependence of atomic sodium concentration in the plume on particle size and particle temperature has also been studied by the simultaneous measurement of these three important parameters [38]. However, due to the complicated nature of the experiment, the data was only taken for one particle, and hence it is necessary to determine whether the results presented are general. Thus, this work utilises previously collected particle temperature data [38] to validate a char combustion and heat transfer model. Consequently, by utilising previously collected sodium release data [39] in combination with the char combustion and heat transfer model, the temperature dependence of sodium release during char combustion is able to be determined.

Combustion of char particles can occur in three main regimes. In the Zone I burning regime the rate of mass loss of char is limited by chemical reaction rates due to low temperatures. In this regime, the particle burns uniformly throughout its volume and hence particle diameter remains unchanged during combustion while the apparent density is reduced. In the Zone III burning regime, which occurs at high temperatures, the mass loss of char is limited by the diffusion of oxygen to the particle's external surface. In this regime, the particle apparent density remains constant and particle diameter reduces during combustion. It is well known that under realistic pulverized coal combustion conditions, the char particles burn under Zone II conditions where both chemical reaction rates and diffusion of oxygen are important [40 – 45]. However, for the large particles (2-5mm) and high particle temperatures (1200-1500K) used in our previous work [39], the Zone III burning regime is appropriate. The shrinking core model for char combustion is well known to be the best simple model to accurately describe char burnout behaviour of large particles [40]. The assumption that the carbon oxygen reaction only occurs at the outer surface of the char particle is implicit in the model. The shrinking core model has been used extensively to model the combustion of single char particles [eg. 46 – 48]. The model has been shown to accurately predict the burn-out behaviour of large char particles

[40]. Hence, by combining our recently published data [39] with a char combustion and heat transfer model which predicts the char burnout behaviour and surface temperature of the particle as a function of time during combustion, the kinetics of sodium release during char combustion can be determined.

The first aim of this paper is to analyse our previously published data [39] by modelling the sodium release during char combustion using a char-combustion and heat transfer model with a view to obtaining a better understanding of the kinetics of sodium release during char combustion. The second aim of this paper is to propose a full mechanism of sodium release during the various stages of coal combustion.

2. Model Development

2.1 Particle and reaction conditions

The flat flame burner that was utilised [39] to measure the release of atomic sodium from single combusting coal particles has been documented previously [37]. The burner was operated with natural gas and air to provide an equivalence ratio of 0.93 (excluding the contribution of the coal particle) for all the experiments performed by van Eyk *et al*. [39]. Individual coal particles, of various weights of 10 – 50 mg, were suspended 10mm above the burner surface on a loop made from 0.5-mm diameter platinum wire. The individual particles burned with the excess air in the natural gas flat flame. The temperature of the flame above the coal particles at 15mm above the wire was determined to be ~1200 ºC using corrected thermocouple measurements. Particle temperature, however, was previously measured [38] to be initially much lower than this (~900 ^{o}C under conditions typical of this work) as a result of the high rate of radiant heat exchange between the particle and the much cooler ambient surroundings that occurs with an open (i.e. unconfined) flat flame burner. A further consequence of this high rate of radiant heat exchange is that the net rate of heat transfer to the char particle (due to convection and radiation) is reduced and therefore the particle Biot number is substantially lower than it would be in a confined burner (as discussed in section 2.2) and so the temperature is expected to be approximately uniform throughout the particle.

The coals used for these tests were run-of-mine Loy Yang brown coal and two Loy Yang brown coals processed by Mechanical Thermal Expression. The MTE coals were obtained from the same laboratory as the previous work by Hulston *et al.* [49]. A chemical analysis of the run of mine Loy Yang coal (LY-ROM) is given in Table I. Table II shows the variations in some inorganic components between the three coals used. Subsequently, the coal samples used in these experiments were air-dried in an oven at 50 °C overnight, and crushed to produce particles of the size used for the present experiments (10-50 mg).

Table I – Loy Yang brown coal analysis

% Dry basis	
C	67.8
H	5.20
N	0.57
S	0.24
Cl	0.06
Ash	0.80
O (By difference)	25.3

% in ash	
SiO_2	12.9
Al_2O_3	31.4
Fe_2O_3	6.70
TiO_2	0.70
K_2O	0.77
MgO	12.2
Na_2O	11.3
CaO	5.60
SO_3	16.9

Table II – Total and water soluble concentrations of inorganic elements within coals used in this study [49]

		wt%, dry basis (± 0.01%)				
Coal		Na	Mg	Ca	Al	Fe
LY-ROM	Total	0.09	0.08	0.04	0.02	0.07
	Water Soluble	0.05	0.01	0.01	0.00	0.00
MTE1	Total	0.07	0.08	0.05	0.01	0.07
	Water Soluble	0.03	0.01	0.00	0.00	0.00
MTE2	Total	0.05	0.08	0.05	0.00	0.07
	Water Soluble	0.01	0.01	0.01	0.00	0.00

2.2 Model Assumptions

To model the release of sodium during char combustion, some assumptions about the coal particle and the combustion system must be made. These assumptions are:

1. Sodium that is bound in the char particle undergoes a chemical reaction that results in the formation of a gaseous sodium compound.

2. This sodium vapour then diffuses through the pore structure until it reaches the external surface of the char particle.

3. The loss of sodium from the external surface of the char is controlled by boundary layer diffusion to the flat flame gases.

4. The temperature of the char particle is uniform. To test this assumption, values of the Biot number were calculated. Equation (1) describes the Biot number with regard to heat transfer to the particle surface (radiative and convective) and conduction of heat within the particle.

$$\mathrm{Bi} = \frac{d_p}{k_c}\left(h_f - \sigma\varepsilon\left(T_c + T_o\right)\left(T_c^2 + T_o^2\right)\right) \tag{1}$$

   The char conductivity, k_c, was estimated to be ~1.5 W/m.K based on data presented by Kantorovich and Bar-Ziv [50]. By assessing all of the data produced from the char combustion and heat transfer model, it was determined that the maximum value of Bi within the entire data set is 0.07. It is well known that for Bi<<1, the rate of heat transfer via conduction within the particle is much faster than the rate of heat transfer to the particle surface. Hence, under the experimental conditions of this work, the char particle can be considered isothermal. It is worth noting that the large radiative losses from the particle to the ambient surroundings are significant in this analysis. Neglecting radiative losses in Eq. (1) leads to values of the Biot number in excess of 1, indicating the particle would experience significant internal temperature gradients.

5. All of the ash was assumed to form as a uniform layer around the char particle. To test this assumption, particles were removed and fractured to observe the cross section at various times during combustion. It was observed that a thin layer of ash existed around the inner char particle, as is assumed in the model.

6. All of the sodium initially present within the coal is eventually fully released if the particle is kept in the flame for an infinite amount of time. From previous work undertaken on combustion of Loy Yang brown coal [8, 9], it is understood that 100% of the initial sodium present in the coal is fully released under combustion conditions. Gallagher *et al.* [8] determined that essentially all the sodium reports to the submicron size range of ash after combustion, indicating that all of the sodium has vaporised and recondensed as fine particles. Gallagher *et al.* [8] hence concluded that all of the sodium in Loy

Yang coal is released and not captured by silicate formation. Lindner and Wall [9] also showed that at gas temperatures above 1200 ºC, all of the Na from Loy Yang coal particles is fully released before significant silicate reactions occurred. This was explained on the basis that silicate formation does not occur within the initial particle, but rather by volatilisation of Na and subsequent reaction with silicon in other coal particles [9]. Hence in the present conditions the absence of other coal particles, as well as the low silicon content in the fuel, limits the silicate formation. Thus, all of the sodium initially present with the coal is assumed to be eventually released at the temperatures utilised in our experiments.

2.3 Model for the release of sodium during char combustion

Within the char particle, the flow of gaseous sodium within the char particle passing through a spherical shell of thickness Δr within the char particle between r and r+Δr is given by equation (2):

$$N_{Na,r} \cdot 4\pi r^2 - N_{Na,r+\Delta r} \cdot 4\pi (r+\Delta r)^2 + R_{Na} \cdot 4\pi r^2 \Delta r = 0 \tag{2}$$

where R_{Na} is the rate of the rate of reaction of sodium within the char particle that leads to the formation of a gaseous sodium compound. By dividing by Δr and taking the limit as $\Delta r \to 0$, eq. (2) can be reduced to:

$$\frac{d}{dr}\left(r^2 N_{Na,r}\right) = r^2 R_{Na} \tag{3}$$

$N_{Na,r}$ can be determined from Fick's Law:

$$N_{Na,r} = -D_{Na}\frac{dc_{Na}}{dr} \tag{4}$$

where D_{Na} is the effective diffusivity of the gaseous sodium compound through the pores of the char particle. R_{Na} is assumed to be first order with respect to the char-sodium concentration, $c_{char\text{-}Na}$, and hence is given by:

$$R_{Na} = k_{Na}c_{char-Na} \tag{5}$$

Assumption 4 implies that the temperature within the particle is uniform. Since the rate constant for sodium release is only dependent on the particle temperature at the time when the sodium is released, k_{Na} is independent on the radial position within the char particle, r. Hence $c_{char\text{-}Na}$ at any given time is independent of r. Thus, combining equations (3), (4) and (5) and integrating, we obtain equation (6):

$$c_{Na} = -\frac{r^2}{6D_{Na}}k_{Na}c_{char-Na} - \frac{1}{2}\frac{a_1}{r} + a_2 \tag{6}$$

To solve for constants a_1 and a_2, two boundary conditions are needed. The first of these is that for $r = 0$, c_{Na} must be finite. Hence a_1 must equal zero. The second boundary condition is given by assumption 3; the loss of sodium from the external surface of the char is controlled by boundary layer diffusion to the flat flame gases. This is described by equation (7):

$$N_{Na,s} = h_{D,Na}(c_{Na,s} - c_{Na,f}) \tag{7}$$

where $N_{Na,s}$ is the flux of gaseous sodium passing through the particle surface. It is also assumed that the concentration of sodium in the flame, $c_{Na,f}$, is negligible compared to the concentration of sodium at the particle surface, $c_{Na,s}$. From equations (3) and (6), the flux of sodium at the char surface is given by:

$$N_{Na,s} = \frac{k_{Na} c_{char-Na} r_p}{3} \tag{8}$$

Therefore, by using equations (7) and (8), the concentration of released sodium at the particle surface was determined:

$$c_{Na,s} = \frac{k_{Na} c_{char-Na} r_p^2}{3h_{D,Na}} \tag{9}$$

Therefore, the constant a_2 is determined:

$$a_2 = \frac{k_{Na} c_{char-Na} r_p}{3h_{D,Na}} + \frac{r_p^2}{6D_{Na}} k_{Na} c_{char-Na} \tag{10}$$

The complete model is thus given by:

$$c_{Na} = \frac{r_p^2 - r^2}{6D_{Na}} k_{Na} c_{char-Na} + \frac{k_{Na} c_{char-Na} r_p}{3h_{D,Na}} \tag{11}$$

Hence, the distribution of vaporised sodium within the char particle is dependent on the reaction of char-sodium inside the pores, diffusion of vaporised sodium through the pores, and diffusion of vaporised sodium through the particle boundary layer. However, the molar flow of vaporised sodium at the particle surface $r = r_p$ is given by equation (12):

$$W_{Na,s} = 4\pi r_p^2 N_{Na,s} \tag{12}$$

Utilising equation (8), equation (12) becomes:

$$W_{Na,s} = -\frac{4}{3}\pi r_p^3 k_{Na} c_{char-Na} = -k_{Na} n_{char-Na} \tag{13}$$

Hence, the rate constant, k_{Na}, for the reaction of char-sodium that leads to the release of sodium can be determined from equation (14):

$$k_{Na} = -\frac{W_{Na,s}}{n_{char-Na}} \tag{14}$$

2.4 Determination of rate constant of reaction, k_{Na}

The total flow of atomic sodium, $W_{Na,at}$, through a given height in the plume was determined using previously published experimental data of [Na] in the plume [39], by equation (15):

$$W_{Na,at}(t) = \int_0^{2\pi}\int_0^{\infty} u_f.[Na](r,z,t).r.dr.d\theta \tag{15}$$

By assuming axisymmetry and numerically integrating eq. (15) at z = 15mm, the flux of atomic sodium at this height was determined at each time. The height of 15mm was used because atomic sodium was determined to be at chemical equilibrium with the other forms of sodium in previous analysis of the data [39]. The integration in the radial direction was undertaken for 0mm $\leq r \leq$ 20mm to account for all of the sodium within the plume. The velocity of the post-flame gases, u_f, was calculated based on the measured gas flow rates and the corrected thermocouple measurement of gas temperature (1200 ^{o}C) above the wire. Figure 1 shows an example of this variation for three typical tests.

At any time, t, the amount of atomic sodium as a fraction, x, of the total sodium within the plume depends mainly on the temperature and the composition of the post-flame gases. However, because the flame conditions remain the same for an entire experiment, and the plume temperature is mainly controlled by the gas flame conditions, x remains essentially constant for a given experiment. The total molar flow of vaporised sodium from the particle surface, $W_{Na,s}$, can hence be determined from the atomic sodium flow in the plume, and is given by eq. (16).

$$W_{Na,at} = -xW_{Na,s} \tag{16}$$

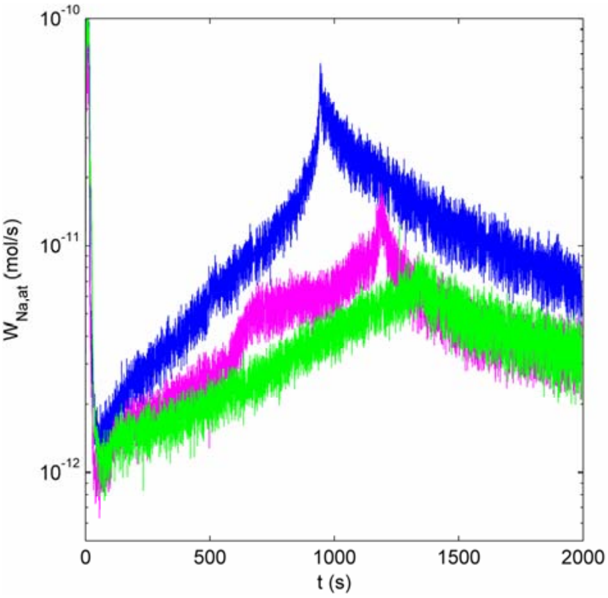

Figure 1: Examples of the dependence of the flow of atomic sodium, $W_{Na,at}$, on time, *t,* where measurements for — LY-ROM, — MTE1 and — MTE2 are taken at a point 15mm directly above the wire, for ~50mg particles.

Assumption 6 provides a means to determine the initial quantity of sodium in the char particle that remains within the particle following devolatilisation, $n_{char\text{-}Na}(0)$. By extrapolating $W_{Na,at}$ to infinity and integrating using equation (17), we obtain $n_{char\text{-}Na}(0)$:

$$n_{char-Na}(0) = \frac{1}{x}\int_0^{\infty} W_{Na,at} \cdot dt \qquad (17)$$

Thus at time *t*, the number of moles of char sodium within the char particle is given by equation (18):

$$n_{char-Na}(t) = \frac{1}{x}\left[\int_0^{\infty} W_{Na,at}(t)\cdot dt - \int_0^{t} W_{Na,at}(t)\cdot dt\right] \qquad (18)$$

Hence, using equation (14), the rate constant for the reaction leading to Na release at time *t* is given by equation (19).

$$k_{Na}(t) = \frac{W_{Na,at}(t)}{\left[\int_0^{\infty} W_{Na,at}(t)\cdot dt - \int_0^{t} W_{Na,at}(t)\cdot dt\right]} \tag{19}$$

Hence, the measurement of the concentration of atomic sodium in the plume was utilised to calculate the rate constant of sodium release at time *t*, by use of equation (19). Figure 2 shows an example of the variation of k_{Na} with time for three typical tests.

2.5 Char Combustion and Heat Transfer Model

To determine the temperature of the char particle as it burns, a char combustion and heat transfer model was developed. The first part of this model is a single particle char combustion model to determine the char burnout behaviour, and the second part is a heat transfer model to determine the particle surface temperature at various times during char combustion. Figure 3 shows the definitions of the important radial positions, oxygen concentrations and temperatures utilised in the char combustion and heat transfer model.

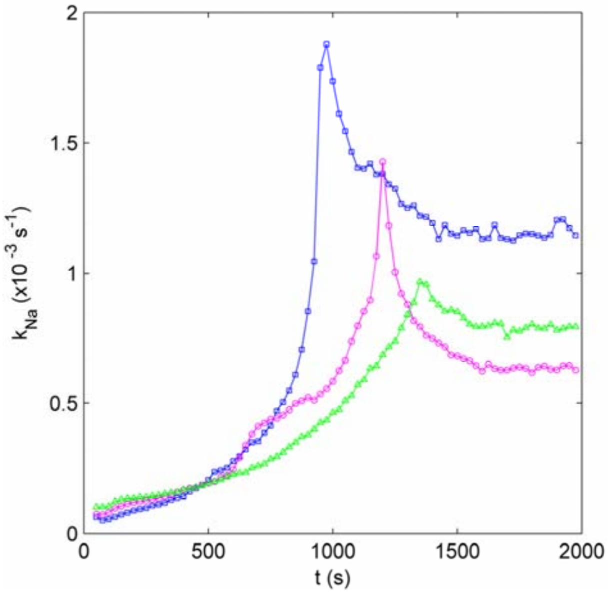

Figure 2: Example of the rate of sodium release, k_{Na}, versus time, *t*, determined from three individual experiments, for cases -□- LY-ROM; -○- MTE1; and -△- MTE2.

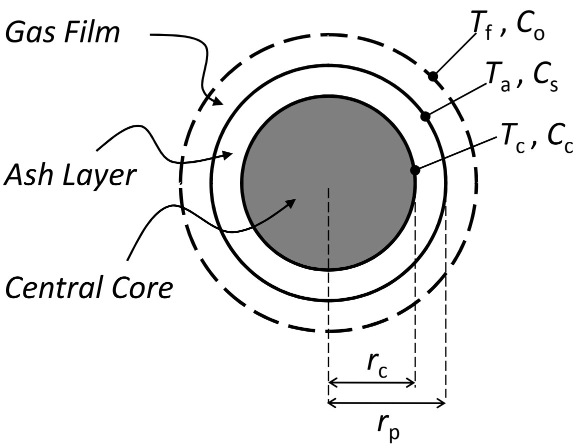

Figure 3: Schematic diagram showing the definitions of the important radial positions, oxygen concentrations and temperatures used in the model.

To model the combustion of a single char particle burning in a flat flame, an unreacted shrinking core model was used. The shrinking core model treats a burning char particle as the sequential operation of two basic processes: gas film diffusion, and chemical reaction on the outer surface of the char particle [40].

Gas film diffusion is modelled by equation (20):

$$\dot{m}_c = 4\pi r_p^2 K_D (C_o - C_s) \tag{20}$$

K_D is by definition the diffusional rate constant, and is determined from equation (21):

$$K_D = \Lambda h_D \tag{21}$$

The mass transfer coefficient h_D can be obtained from Sherwood Number correlations [51]. For a sphere:

$$\mathrm{Sh} \equiv \frac{h_D d_p}{D_A} = 2 + 0.6\mathrm{Re}^{1/2}\mathrm{Sc}^{1/3}, \tag{22}$$

where $$\mathrm{Re} \equiv \frac{\rho_f d_p u_f}{\mu_f} \tag{23}$$

and $$\mathrm{Sc} \equiv \frac{\rho_f}{\mu_f D_A} \tag{24}$$

For combustion, carbon monoxide is usually assumed the primary product at high temperatures. Hence, the stoichiometric gravimetric coefficient is assumed to be Λ=3/4 [40]. Once K_D is determined via equations (21) – (24), a correction is applied due to the phenomenon of Stefan flow, which leads to a reduction of mass transfer of oxygen to the surface of the char particle. This correction is applied using the methodology of Förtsch *et al.* [52]. The correction used in this work accounted for a change in K_D of only 3%, due to the nature of the gaseous species within the flat flame.

For a simple first order reaction of char in an oxygen-containing gas, the normalised rate of char combustion at the reaction front is given by equation (25):

$$\dot{m}_c = 4\pi r_p^2 K_R C_s \,, \tag{25}$$

where $K_R = A_R \exp\left(-E_R/RT_c\right)$ (26)

The particle reactivity has been expressed on an external surface area basis. Combining equations (20) and (25) to eliminate C_s, the complete model is given by:

$$\dot{m}_c = 4\pi r_p^2 K_O C_o \,, \tag{27}$$

where $K_O = \left(\frac{1}{K_D} + \frac{1}{K_R}\right)^{-1}$ (28)

The model was adapted for the system used in our experiments by ignoring the ash layer diffusion resistance term in the model. This adaptation is reasonable for particles with low ash content (such as Loy Yang brown coal) because the size of the ash layer is insignificant compared with the size of the char particle for the bulk of the combustion time. The particles used in the experiments were approximately spherical. Using equations (27) and (28), the radius of the char particle was determined numerically using equation (29):

$$r_{c,i+1} = r_{c,i} + \Delta t \frac{1}{\rho_c} K_{O,i} C_o \tag{29}$$

The radius of the particle including ash is determined assuming the conversion of carbon in the char to carbon monoxide, $X_{c,i}$, and the conversion of inorganic matter in the char to ash, $X_{a,i}$, are equal at a given time. All of the ash was assumed to form as a uniform layer around the char particle (assumption 5). Hence the outside radius of the particle was determined from:

$$r_{p,i} = \left(\frac{3}{4} \frac{X_i m_a}{\rho_a \pi} + r_{c,i}^3 \right)^{1/3} \tag{30}$$

where $X_i = \frac{4}{3} \frac{\pi \rho_c r_{c,i}^3}{m_p}$ (31)

By estimating the volume (from the radius measured at different locations using callipers) and measuring the mass of individual char particles, the average bulk density, ρ_c, for the LY-ROM, MTE1 and MTE2 char samples was determined to be 400, 800 and 1100 kg/m^3, respectively. The value of D_A was determined based on oxygen diffusing through the laminar flame environment. The reaction rate constant was determined based on the intrinsic reactivity data for Loy Yang brown coal char provided by Young and Smith [53].

A heat transfer model was used to determine the particle surface temperature at various times during char combustion. The model assumes that the energy inputs into the particle are convective heat transfer from the flame and heat of combustion generated from the burning carbon in the char particle.

$$\dot{q}_{conv} = 4\pi r_p^2 h_c (T_f - T_p) \tag{32}$$

$$\dot{q}_{comb} = \dot{m}_c H_c \tag{33}$$

The energy transfer from the particle is predominantly radiative. The model also assumed that the char particle was isothermal. Since the ash content of Loy Yang brown coal is very low (0.8% dry basis), conductive heat transfer through the ash layer is neglected in this model.

$$\dot{q}_{rad} = 4\pi r_p^2 \varepsilon\sigma(T_p^4 - T_o^4) \tag{34}$$

The particle heat balance is hence given by:

$$\dot{q}_{comb} + \dot{q}_{conv} - \dot{q}_{rad} = 0 \tag{33}$$

Thus, the particle temperature was calculated from equation (34):

$$\dot{m}_c H_c + r_{p,i}^2 h_c (T_f - T_{p,i}) - r_{p,i}^2 \varepsilon\sigma(T_{p,i}^4 - T_o^4) = 0 \tag{34}$$

The complete model required an iterative technique due to the fact that the temperature of the char particle affects the intrinsic reactivity of the char, which in turn affects the size of the char particle at a given time, which then changes the heat balance of the system. To determine the particle emissivity of the burning particle, the particle temperature data from van Eyk *et al.* [38] was used. By varying the emissivity of the particle in the model, the closest fit between the experimental and model data for particle temperature was determined for an emissivity of 0.75. This is further discussed in section 3.1.

3. Results and Discussion

3.1 Comparison of model results to experimental data

Figure 4 shows a comparison of the predicted temperatures and the experimental data of van Eyk *et al.* [38]. It is noted that the model does not agree well at the time associated with the end of char combustion (t > 850s). This is presumably due to the fact that the model neglects the effects of the ash layer on diffusion and heat transfer which will be more important as the char particle approaches complete burn-out. However, the experimental data and model agree well for the majority of char combustion time, especially considering the scatter in the experimental data. The model can thus be used as an approximate representation of the changes to particle temperature that occur during char particle combustion.

In previous work [38] we have shown that the peak sodium emission coincides with both the peak temperature and the instant when the coal particle stops shrinking. The maximum rate of release of sodium thus corresponds to the instant of complete char burnout. Hence, this provides a convenient parameter with which to compare the model prediction to the previously presented experimental data [39]. Figure 5 shows the model predictions of char burnout time, t_c, for the three coals and the experimental data from van Eyk *et al.* [39]. As seen in the figure, the model predictions of burnout time are in excellent agreement with the experimental data. The combination of Figures 4 and 5 shows that the model is able to accurately predict the char burnout behaviour and char temperature of the coals used in this work.

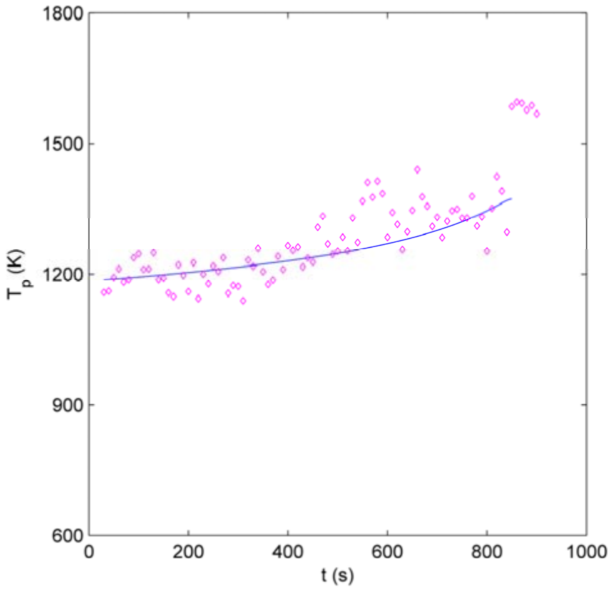

Figure 4: The dependence of particle surface temperature, T_p, on the initial particle mass, m_p, calculated for the char combustion and heat transfer model —,

and taken from experimental data [38] ◇.

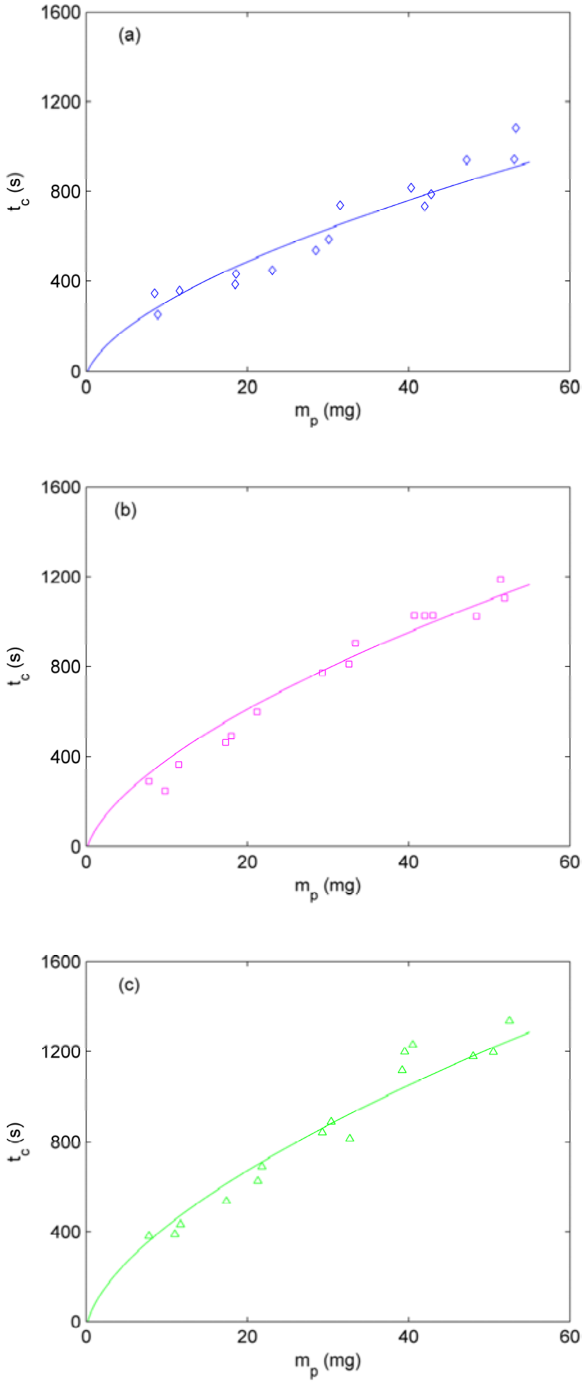

Figure 5: The dependence of char burn-out time, t_c, on the initial particle mass, m_p, calculated using the char combustion and heat transfer model (lines), and taken from experimental data [39] (points) for (a) LY-ROM; (b) MTE1; (c) MTE2.

3.2 Effect of temperature on sodium release during char combustion

van Eyk *et al*. [38] established that an increase in the temperature of a Loy Yang char particle leads to an increasing rate of sodium release during combustion. By utilising the char combustion and heat transfer model, it is possible to examine this result more extensively.

Figure 6 shows the variations of k_{Na} and char temperature with combustion time for various coals and particle sizes. The data presented is taken for the whole period of char combustion only. Both the rate of sodium release and the char particle temperature increase monotonically with combustion time. This confirms that the rate of sodium release is directly dependent on char temperature, as observed by van Eyk *et al*. [38].

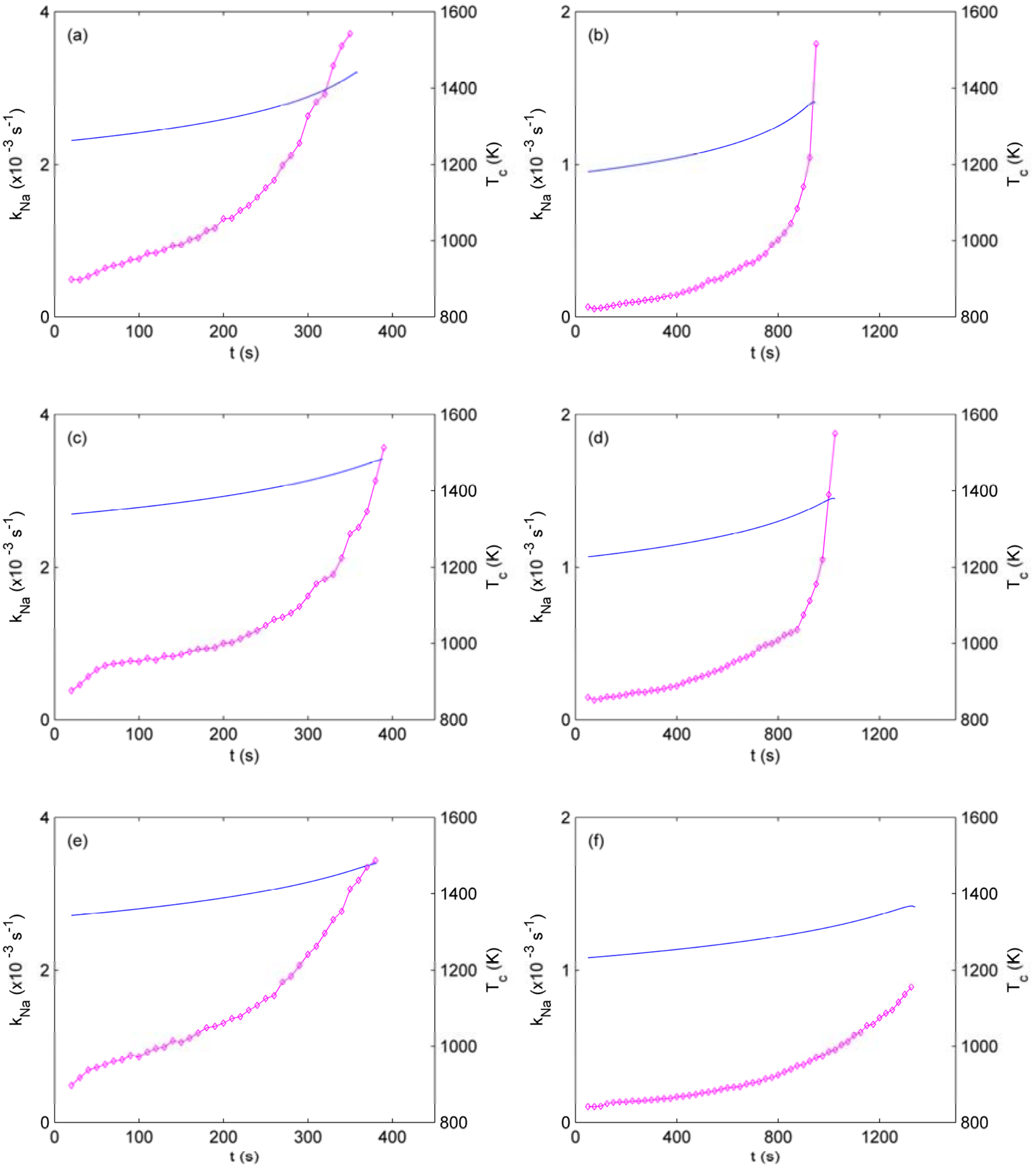

Figure 6: Typical measurements of k_{Na} (points) and T_c (lines), as a function of time, *t*, for (a) LY-ROM, 10±2 mg; (b) LY-ROM, 50±2 mg; (c) MTE1, 10±2 mg; (d) MTE1, 50±2 mg; (e) MTE2, 10±2 mg; (f) MTE2, 50±2 mg.

3.3 Kinetics of sodium release during char combustion

From the combination of experimental data and the output of the model a relationship between the rate of sodium release and char temperature can be determined. We define the temperature dependence of the rate of sodium release during the char combustion stage, k_{Na}, as:

$$k_{Na} = A_{Na}\exp(-E_{Na} / RT_c) \tag{35}$$

Hence by plotting $\ln k_{Na}$ versus $1/T_c$ it is possible to determine the activation energy, E_{Na}, and pre-exponential factor, A_{Na}, for sodium release during char combustion. By plotting the slope of each $\ln k_{Na}$ versus $1/T_c$ curve versus m_p for each set of data for all three coal types, it is possible to determine the average activation energy for sodium release during char combustion, E_{Na}, from equation (35). As shown in Figure 7, the average value for E_{Na} is 214 kJ/mol for all particle sizes and coal types. There are considerable variations in E_{Na} most likely caused by variations in individual particle properties that are not accounted for by the char combustion model. Similarly, by plotting the intercept of each $\ln k_{Na}$ versus $1/T_c$ curve versus m_p for all three coal types, it is possible to determine the pre-exponential factor for sodium release during char combustion, A_{Na}, from equation (35). As shown in Figure 8, the average value for A_{Na} is $10^{5.2}$ s^{-1} for all particle sizes and coal types. Again, the variations in A_{Na} are caused by variations in individual particle properties that are not accounted for by the char combustion model.

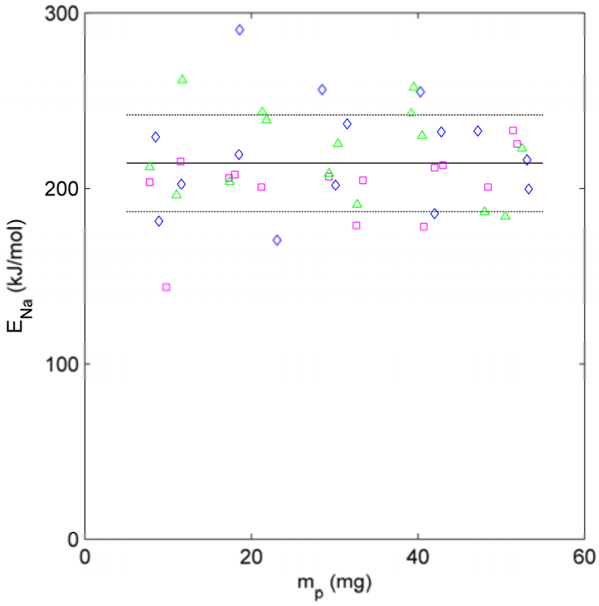

Figure 7: Activation Energy, E_{Na}, plotted against initial particle mass, m_p, for cases ◇ LY-ROM; □ MTE1; and △ MTE2. The solid line shows the mean activation energy and the dotted lines show one standard deviation from the mean.

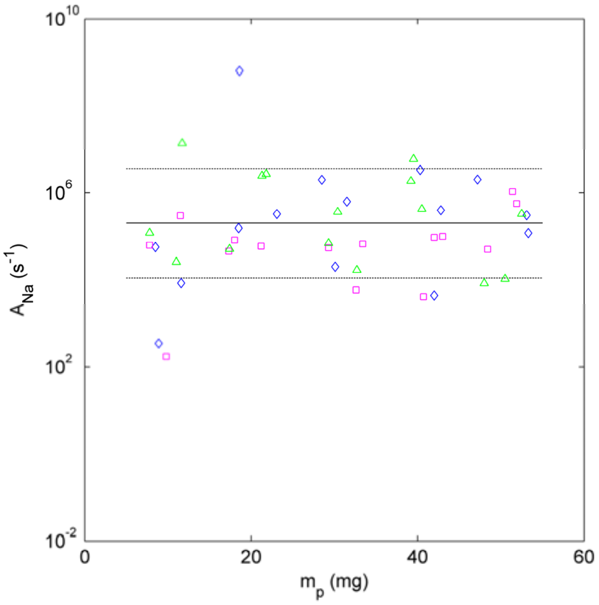

Figure 8: Pre-exponential factor, A_{Na}, plotted against initial particle mass, m_p, for cases ◇ LY-ROM; □ MTE1; and △ MTE2. The solid line shows the mean activation energy and the dotted lines show one standard deviation from the mean.

From Figures 7 and 8 it is observed that the values of E_{Na} and A_{Na} are closely relating to each other for the individual experiments. Hence, by choosing a constant E_{Na} equal to the average value from Fig.6 we seek to find the variation of A_{Na} that accounts for the range of data presented in this work. Equation (36) was used to determine the value of $\log A_{Na}$ for every point in the k_{Na} versus T_c data-set based on the average E_{Na} taken from Fig. 6.

$$\ln A_{Na} = \ln k_{Na} + \frac{E_{Na}}{RT_c} \tag{36}$$

In this way a distribution of values for A_{Na} were produced. Figure 9 shows the cumulative distribution of A_{Na} values collected in this study. It is seen that all of values for A_{Na} occur in the range of $10^{4.5}$ $s^{-1} < A_{Na} < 10^{5.8}$ s^{-1}. Also plotted in Figure 9 is a cumulative normal distribution with mean and standard deviations of $10^{5.2}$ and $10^{0.19}$ respectively. The cumulative normal distribution fits the data from this work quite closely, implying that the A_{Na} data is normally distributed around a mean of $10^{5.2}$ s^{-1}. It is also observed that 95% of the data has pre-exponential factors in the range of $10^{5.2\pm0.4}$ s^{-1}. Equation (37) was thus established that describes 95% of the data:

$$k_{Na} = 10^{5.2\pm0.4} \exp\left(\frac{-214\ \mathrm{kJ/mol}}{RT_c}\right) \tag{37}$$

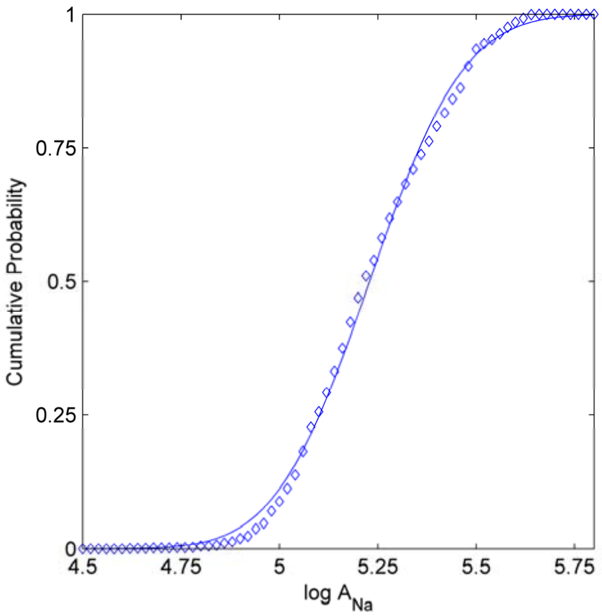

Figure 9: log A_{Na} versus Cumulative Probability for the complete data-set (points) and a normal distribution with mean = $10^{5.2}$ s^{-1} and standard deviation = $10^{0.19}$ s^{-1} (line).

It should be noted that Fig. 7 shows large uncertainties in the determination of characteristic activation energy for sodium release, E_{Na}. Hence, there is significant uncertainty in the mean activation energy used in equation (37). However, equation (37) provides a good description of 95% of the data collected for sodium release from the combustion of Loy Yang coal.

Figure 10 shows examples of $\ln k_{Na}$ as a function of $1/T_c$ for the three coals used in this study. It can be observed in Figure 10 that although there is some departure from a linear relationship for all cases, on average a single linear relationship exists between lnk_{Na} versus $1/T_c$, given by equation (37). It is also apparent that there is no dependence of initial particle mass, m_p, on the temperature dependence of k_{Na}. This implies that k_{Na} does not depend on diffusive processes within the particle, but rather is an intrinsic reaction rate of char-sodium during combustion. This also implies that the temperature dependent kinetics will be valid for both pulverised coal and fluidised bed combustion within the range of 1200-1500K calculated from our char combustion and heat transfer model.

3.4 Mechanism of sodium release during coal combustion

By utilising findings from previous work [39] along with the kinetics of sodium release during char combustion determined in this paper, it is possible to propose a mechanism for sodium release during coal combustion. Figure 11 shows a summary of the proposed mechanism for sodium release during the combustion of Victorian brown coal.

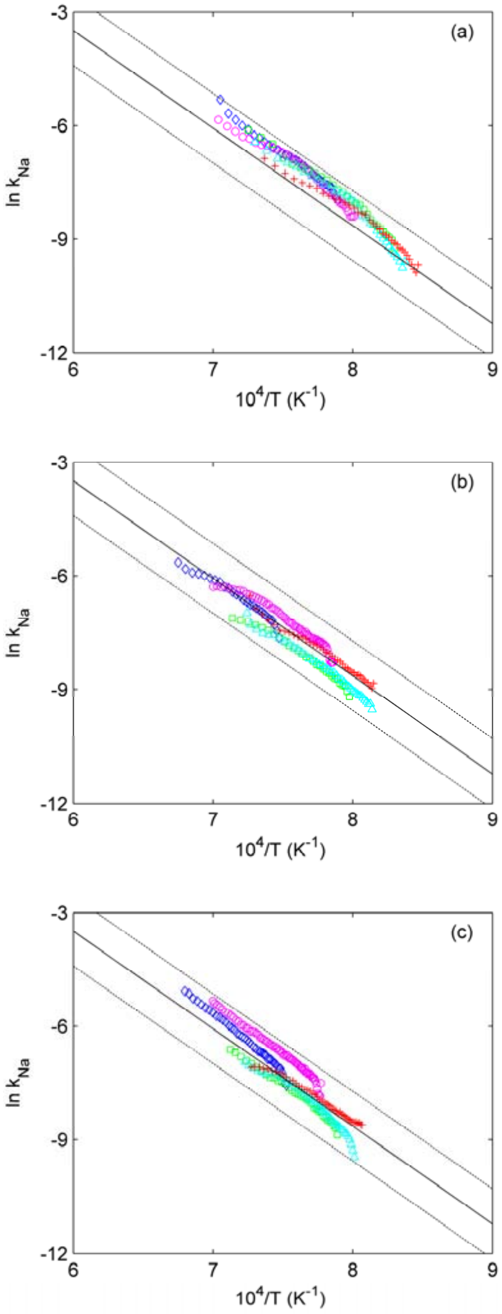

Figure 10: Typical Arrhenius plots of the rate of sodium release during char combustion for cases ◇ 10±2 mg; ○ 20±2 mg; □ 30±2 mg; △ 40±2 mg; and + 50±2 mg. (a) LY-ROM, (b) MTE1, (c) MTE2. The solid line is the average temperature dependence of reaction rate and the dotted lines show the range of pre-exponential factors that encompass 95% of the data.

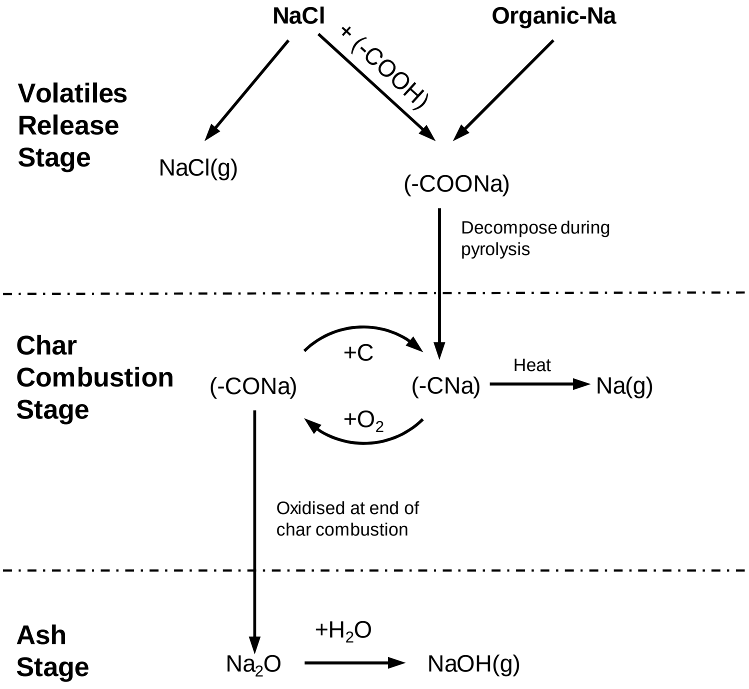

Figure 11: Proposed mechanism for sodium release during combustion of a brown coal particle.

In previous work [39], it was determined that approximately 33% of water-bound sodium was released from the particle during the devolatilisation stage. Additionally, negligible organically-bound sodium was released from the particle during the same period. Although the experimental conditions given in that study differ somewhat from those in a boiler, some mechanistic information can be obtained. Firstly, a possible mechanism for the significant release of water-bound sodium during the devolatilisation stage is direct vaporisation of NaCl from the coal particle. The fact that 67% of the water-bound sodium remains in the char after volatiles release implies that the water-bound sodium is interacting with the char to form a relatively stable sodium species. One possible mechanism suggested by both Kosminski *et al*. [20] for sodium chloride in brown coal gasification and van Lith *et al*. [22] for potassium chloride in biomass combustion, is that the alkali chloride reacts with the coal/biomass structure. In those studies it is suggested that the carboxylic acid groups within the coal/biomass structure react with MCl, thus retaining M and releasing HCl as follows:

$$(\text{-COOH}) + \text{MCl} \rightarrow (\text{-COOM}) + \text{HCl} \qquad \text{(R1)}$$

where M is the alkali metal species (either Na or K). It is clear that the higher the temperature of the devolatilisation process, the higher the proportion of NaCl that is released immediately from the coal particle via direct evaporation, rather than reacting according to reaction (R1). Additionally, this mechanism also implies that NaCl is transformed into a form of sodium that is bound to the coal material by carboxyl groups, (–COONa), in brown coals.

Unlike water-bound sodium, organic sodium has been shown to be almost completely retained in the char particle after devolatilisation [20, 39]. It has been shown [54] that (-COONa) groups decompose during devolatilisation leading to the release of CO_2 during pyrolysis. A possible reaction to describe this process is:

$$(-\text{COONa}) + \text{C} \rightarrow (-\text{CNa}) + \text{CO}_2 \qquad \text{(R2)}$$

where (–COONa) and (–CNa) are groups attached to the coal matter. Reaction (R2) implies that organic sodium is retained within the char particle during the devolatilisation stage, which is in agreement with recent findings [39].

During the char combustion stage, the (–CNa) groups will be oxidised by the O_2 in the flowing gases to form an oxidised surface species. Many studies [eg. 28 – 31] have concluded that sodium phenolate groups (–CONa) are present in sodium catalysed char gasification experiments. Hence it is assumed that (–CONa) forms according to reaction (R3). The sodium phenolate groups (–CONa) are known to act as catalysts for char gasification. The process is understood to be an oxidation/reduction process of the alkali catalyst species. Under the conditions of this study, reaction (R3) gives the oxidation process, and reaction (R4) gives the reduction process:

$$(-\mathrm{CNa}) + 1/2\mathrm{O_2} \rightarrow (-\mathrm{CONa}) \tag{R3}$$

$$(-\mathrm{CONa}) + \mathrm{C} \rightarrow (-\mathrm{CNa}) + \mathrm{CO} \tag{R4}$$

The loss of catalyst from the char particle during gasification has also been the subject of several studies [27, 34 – 36]. All of those studies suggested that the potassium catalyst took part in an oxidation-reduction cycle for catalytic gasification of carbon similar to reactions (R3) and (R4). It was found that regardless of the exact form of the active catalyst, the formation of a reduced form of the catalyst was the prerequisite for a rapid loss of catalyst at high temperatures [34, 35]. Shadman *et al*. [35] suggested that the loss of catalyst was due to evaporation of the reduced catalyst species according to reaction (R5):

$$(-\mathrm{CNa}) \rightarrow \mathrm{Na(g)} \tag{R5}$$

Saber *et al*. [33] showed that the activation energy of the rate limiting step for sodium catalysed gasification, reaction (R4), was approximately 180 kJ/mol, compared to the activation energy for sodium release determined in this study, 214 kJ/mol. Hence it appears likely that reaction (R4) is the rate determining step for both catalysed gasification and sodium release during char combustion, with the rate of this reaction having a pre-exponential factor and activation energy of $10^{5.2\pm0.4}$ s^{-1} and 214 kJ/mol, respectively, based on the present work.

It also appears that a significant amount of sodium is retained in the particle after the char has finished burning [39]. This is probably due to the presence of O_2 in the flame and reaction (R3) preventing the complete loss of sodium via reaction (R4) and (R6). During the stage where the ash particle remains in the flat flame environment (the "ash stage") a significant amount of sodium continues to be released [39]. It appears likely that at the end of char combustion, the remaining (–CONa) is oxidised to Na_2O. A possible mechanism for the sodium release during the "ash stage" was previously postulated involving the high-temperature reaction of Na_2O with water vapour from the flame to release NaOH, as suggested by van Eyk *et al*. [39].

$$\mathrm{Na_2O + H_2O \rightarrow 2NaOH} \qquad \text{(R6)}$$

Although the experimental system is simplified compared to realistic coal combustion systems, the mechanism for sodium release that is proposed is expected to be valid for all types of coal combustion. For pulverised coal combustion, the higher temperature for devolatilisation than was used in our experiments [38] will lead to additional release of water-bound sodium during the devolatilisation stage. For fluidised bed combustion, the temperature of devolatilisation is in the range of 1100-1200K, which is similar to our experiments, implying that the experimental data and mechanism should be directly applicable. The range of particle temperatures during char combustion that have been calculated from the model (1200-1500K) span a range of realistic conditions of both fluidised bed combustion and pulverised coal combustion. The mechanism of sodium release during char combustion should thus be applicable for all types of combustion of Victorian brown coals. During the period that the ash particle remains in the flat flame, the temperature is expected to be in the region of 1500-1600K, based on previous measurements [38]. This is probably somewhat higher than the conditions experienced by the ash particles in both pulverised coal and fluidised bed combustion. However, the reaction of sodium in the ash with ambient water vapour via reaction R6 is expected to occur even at lower temperatures, and may be an important source of vaporised sodium under pulverised coal combustion conditions. It is expected that this mechanism will have relevance to gasification systems.

It should be noted that this work was performed using very low ash Victorian brown coal. It was noted earlier (section 2.2) that for these coals, the combination of the low ash content and the specific reaction conditions used in our previous experiments, has led to a negligible formation of sodium silicates in the ash. However, for high ash coals the sodium release will also depend on the ash composition, as elements such as silicon are known to react with sodium in the coal particle, thereby reducing the release of volatile sodium [eg. 9, 10]. The currently proposed mechanism could possibly be extended to include sodium release from other types of brown coal by the inclusion of reactions accounting for the capture of sodium by silicates into the mechanism, and the determination of the kinetics for these reactions. Thus, further work investigating the kinetics of reactions of sodium with silicates and alumina-silicates for higher ash brown coals is warranted. The mechanism proposed in this study could also be extended to include reactions of sodium with other inorganic elements which are also present in higher ash coals.

4. Conclusions

From the results of this study, the following conclusions may be made with respect to the release of sodium from low rank coal chars during combustion.

1. The temperature dependent kinetics of the release of sodium during char combustion was found to obey an Arrhenius expression with pre-exponential and activation energies having average values of $10^{5.2\pm0.4}$ s^{-1} and 214 kJ/mol respectively.

2. A full mechanism for sodium release during coal combustion was proposed. During the char combustion stage, the sodium undergoes an oxidation/reduction process that leads to both catalysis of the char oxidation and the release of sodium from the char particle.

3. The rate determining step for sodium release was proposed to be the formation of a reduced form of sodium in the char which subsequently led to the rapid loss of sodium from the particle.

4. The mechanism of sodium release during volatiles release, char combustion and while the ash particle remains in the flame should have relevance to all types of combustion of Victorian brown coals.

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Chapter 7

CONCLUSIONS

7.1 Conclusions

The thesis advances the knowledge of the release of sodium from brown coal combustion. Its first major contribution is the development of a method that enables the planar, in-situ and time-resolved measurement of the concentration of atomic sodium in the plume of individual burning coal particles. This has been used to report the first measurements of the release of sodium during the various stages of coal combustion for single particles under well-defined conditions. While these data are limited to Loy Yang coal, the methodology is applicable to coal combustion more generally. The second major contribution is the proposal of a mechanism for the release of sodium during Loy Yang brown coal combustion based on an analysis of the kinetics of this process as determined from the detailed experimental data presented herein supported by a mathematical model of single particle char combustion which is also presented in this thesis. The mechanism is general enough to have relevance to the combustion of other brown coals with the incorporation of additional influences of other ash components, which are more significant in coals with higher ash than that of Loy Yang. The following sections outline the specific conclusions drawn from the various parts of this study.

7.1.1 Quantitative measurement of atomic sodium in the plume of a single burning coal particle

An experimental method for the quantitative measurement of sodium atoms in the plume of a single coal particle was established. From this study, the following conclusions were drawn:

1. The concentration of atomic sodium had a maximum at the base of the measurement plane, closest to the particle, and decreased with axial distance from the particle and radial distance from the axis, within the 30 mm measurement plane.

2. The temporal variation of the distribution of atomic sodium in the plume with particle combustion time was also measured. During char combustion, the sodium concentration increased to a peak that corresponded closely to the end of char combustion. Following this peak, the Na concentration was observed to decay.

3. A significant proportion of sodium was observed to be released during the ash phase, showing that significant quantities of sodium will continue to be released if a coal particle remains within the flame zone after combustion is completed.

4. The overall accuracy was assessed by comparison of the scatter obtained by normalising the data from five concentrations and four laser fluences using a single calibration constant, and was determined to be ±5.7%.

5. Independent verification was also obtained by comparison with a simple kinetic model.

6. By estimating fluxes of total Na at a location in the plume where equilibrium conditions can be inferred to occur, the calculated flux was found to be 90% of the total sodium in the coal particle, giving further confidence in the method.

7.1.2 Simultaneous measurements of the release of atomic sodium, particle diameter and particle temperature for a single burning coal particle

In this study, the measurement of three important parameters was performed simultaneously for a combusting ~50 mg Loy Yang brown coal particle. These were: the concentration of atomic sodium in the plume of the burning particle, the particle surface temperature and the particle diameter. From this study, the following conclusions were drawn:

1. The release rate of Na was not constant through the phases of devolatilisation, char combustion, and while the ash particle remains in the flame (“the ash phase”), but depends both on the surface temperature and the rate of combustion of the particle.

2. During the char phase, the atomic sodium concentration in the plume was found to be inversely dependent on particle diameter, but was also clearly dependent on the particle surface temperature.

3. For this particle, the sodium release continued for at least 500 s after char combustion was complete. During the ash phase the atomic sodium concentration was found to depend exponentially on the particle surface temperature. This implies that the residence time of coal particles in a flame after the end of char combustion has a dramatic influence on the quantity of sodium released from a coal flame.

4. It was apparent that the centreline decay of the atomic sodium concentration in the plume above this burning particle could be characterised by two regimes. In the region closest to the particle, the decay was characterised by first order chemical reaction, and beyond this by diffusion.

5. The transition height between the regions depends on the peak sodium concentration in the plume, but the extent of the reaction controlled region was at least 20 mm above the particle throughout the experiment, corresponding to about six times the initial particle diameter.

7.1.3 The release of water-bound and organic sodium from Loy Yang coal during the combustion of single particles in a flat flame

The results of this study provide for the first time quantitative data on the proportions of sodium released during each of the stages of devolatilisation, char combustion and ash in the combustion of brown coal. From the experimental results of this study, the following conclusions have been drawn on the release of sodium from low rank coals during combustion.

1. The release of sodium was found to be slower for the (de-watered) MTE samples than LY-ROM, and the peak sodium release occurred at later times for MTE coals.

2. The percentage of total Na released, compared to the initial sodium in the coals, during the combined char and ash stages was determined to be 80.9 ± 19.5 %, 87.9 ± 19.0 % and 93.0 ± 28.0 % respectively for LY-ROM, MTE1 and MTE2 respectively.

3. It was inferred by extrapolation that ~33% of the water-bound sodium is released in the volatiles stage, whereas only a negligible amount of organically-bound sodium is released during devolatilisation.

4. A possible mechanism was proposed for the incomplete release of water-bound sodium during the volatiles stage; the reaction of NaCl within the coal structure whereby the char retains Na, and HCl is released to the gas phase.

5. Up to 60% of the sodium was found to be released during the ash stage, following char combustion, under these experimental conditions. A possible mechanism is postulated involving the high-temperature reaction of Na_2O with water vapour to release NaOH, which equilibrates to produce atomic Na.

7.1.4 Mechanism and kinetics of sodium release from brown coal particles during combustion

In this study, a model for the release of sodium during the combustion of single Loy Yang brown coal char particles was presented. By combining the model with further analysis of the data presented in Chapter 5, the variation of a rate constant for sodium release with time for each of the experimental data set was determined. A char combustion and heat transfer model was also developed to predict the time-temperature history of the particles in the individual experiments. From the results of this study, the following conclusions have been drawn:

1. The overall model was found to accurately describe both the burnout behaviour of the coals used in the experiments (Chapter 5) and also the temperature changes that occur at the surface of the particle (Chapter 4).

2. By combining the modelled time-temperature history of the particles with the sodium release rate constant data, the temperature dependent kinetics of sodium release during char combustion were determined to obey an Arrhenius expression with pre-exponential and activation energies having average values of $10^{5.2\pm0.4}$ s^{-1} and 214 kJ/mol respectively.

3. A full mechanism for sodium release during coal combustion was also proposed. During the char combustion stage, the sodium undergoes an oxidation/reduction process that leads to both catalysis of the char oxidation and the release of sodium from the char particle.

4. The rate determining step for sodium release during char combustion was thus proposed to be the formation of a reduced form of sodium in the char which subsequently led to the rapid loss of sodium from the particle.

7.2 Recommendations for future work

The results of this thesis advance the knowledge on the phenomenon of sodium release during brown coal combustion. However, further studies are necessary to increase our knowledge of this important phenomenon of relevance to solid fuel fired boilers. These are presented here:

1. The coal studied in this thesis, Loy Yang brown coal, is a low ash brown coal. However, it is well known that the ash composition has an effect on the release of sodium by interacting with the sodium before it is released (eg. Wibberley and Wall, 1982b; Lindner and Wall, 1990). Hence, experiments utilising high ash coals could determine what additions to the mechanism presented in Chapter 6 will be needed to account for this effect.

2. Loy Yang brown coal has a relatively low content of sodium. However, some brown coals from other areas of the world (eg. South Australia) have a significantly higher sodium content. Hence, further experiments on high sodium coals are proposed to help elucidate if the kinetics of sodium release presented in this thesis are accurate for high sodium coals.

3. The experiments performed in this thesis were predominantly undertaken at one specific flame stoichiometry. Hence, further studies on what effect oxygen concentration has on sodium release should be performed. Specifically, experiments under gasification conditions are proposed to establish whether the mechanism and kinetics of sodium release presented in this thesis are accurate for a coal gasifier.

4. The kinetics and mechanism of sodium release are also sufficiently simple to be added directly to computational fluid mechanics codes for brown coal boilers. Hence, a modelling study on how the sodium release interacts with the time-temperature history of a boiler flame could provide guidance to the design of new boilers for brown coals.

5. It is well established that various sorbents, especially kaolinite rich clays (eg. Vuthularu, 1999), can be used to reduce the formation of submicron sodium fume in boilers. Hence, a systematic study on sodium capture in the sorbents using the laser diagnostic technique presented in this thesis are expected to help elucidate the kinetics of this sodium capture.

6. Currently, there is a lot of interest in Oxy-Fuel fired boilers to produce a pure stream of CO_2 for sequestration. It is unknown what impact the high CO_2 levels in flue gases will have on the release of sodium in brown coal fired boilers. Hence, studies in this area are called for.

7. Finally, other volatile metallic species can be directly measured using the technique utilised in this study: quantitative planar laser induced fluorescence. Thus, studies of the release of potassium (for biomass combustion), and heavy metals (eg. lead, mercury and arsenic release from municipal waste combustion) would enable the work to be extended to establish the mechanisms and kinetics of release during combustion and gasification.

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Appendix A

STUDIES OF THE RELEASE OF SODIUM FROM PULVERISED COAL IN A FLAT FLAME BURNER

Syred, N [a], van Eyk, P. [b], Chong, W. [c], Alwahabi Z. [b] , Nathan G [c].

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Appendix B

STUDY ON ATOMIC SODIUM RELEASE FROM PULVERISED COAL PARTICLES IN A PRE-MIXED NATURAL GAS FLAME

P.J. van Eyk [a,c], C.Y. Wong [b], N. Syred [d], E.P. Ung [b],
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van Eyk, P.J., Syred, N., Wong, C.Y., Ung, C.P., Ashman, P.J., Nathan, G.J. & Alwahabi, Z.T. (2005) Study on atomic sodium release from pulverised coal particles in a pre-mixed natural gas flame,
Proceedings of the 4th Australian Conference on Laser Diagnostics in Fluid Mechanics and Combustion, McLaren Vale, SA, 2005, pp. 133-136

NOTE:
This publication is included on pages 150-153 in the print copy of the thesis held in the University of Adelaide Library.

Appendix C

MEASUREMENT OF ATOMIC NA RELEASED FROM A COAL PARTICLE USING QUANTITATIVE PLANAR LASER INDUCED FLUORESCENCE

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Proceedings of the Australian Symposium on Combustion,
University of Sydney, NSW Australia, 2007, 114-117.

APPENDIX C

van Eyk, P. J., Ashman, P.J., Alwahabi, Z.T. & Nathan, G.J. (2007)
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Appendix D

KINETICS OF SODIUM RELEASE FROM A SINGLE BROWN COAL PARTICLE BURNING IN A FLAT FLAME

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Proceedings of the Australian Symposium on Combustion,
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APPENDIX D

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NOTE:
This publication is included on pages 160-163 in the print copy of the thesis held in the University of Adelaide Library.