



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

Philip Joseph van Eyk

BE. (Chem) Hons., BSc

Thesis submitted for the degree of Doctor of Philosophy

School of Chemical Engineering
Faculty of Engineering, Computer & Mathematical Sciences
The University of Adelaide, Australia

May 2011

Table of Contents

ABSTRACT	v
DECLARATION	vii
ACKNOWLEDGMENTS	viii
PREFACE	x
CHAPTER 1 – INTRODUCTION	1
1.1 Background	2
1.2 Scope and structure of thesis.....	4
CHAPTER 2 – LITERATURE REVIEW	7
2.1 Introduction.....	8
2.2 Sodium occurrence in brown coal.....	8
2.3 Sodium transformations during combustion of brown coal.....	9
2.3.1 Physical transformations during coal combustion	9
2.3.2 Transformations of water-bound sodium within coal particle	10
2.3.3 Transformations of organic sodium within coal particle	11
2.4 Alkali catalysed gasification	11
2.5 Release of sodium and formation of deposits	13
2.6 Gas phase alkali chemistry	14
2.7 Measurement of sodium at high temperature	17
2.7.1 Overview	17
2.7.2 Direct sampling from process gas	17

2.7.3 Optical based techniques	18
2.7.4 Mass spectrometric methods	22
2.8 Implications for current study	22
2.9 Objectives of thesis	24

CHAPTER 3 – QUANTITATIVE MEASUREMENT OF ATOMIC SODIUM IN THE PLUME OF A SINGLE BURNING COAL PARTICLE26

CHAPTER 4 – SIMULTANEOUS MEASUREMENTS OF THE RELEASE OF ATOMIC SODIUM, PARTICLE DIAMETER AND PARTICLE TEMPERATURE FOR A SINGLE BURNING COAL PARTICLE.....37

CHAPTER 5 – THE RELEASE OF WATER-BOUND AND ORGANIC SODIUM FROM LOY YANG COAL DURING THE COMBUSTION OF SINGLE PARTICLES IN A FLAT FLAME47

CHAPTER 6 – MECHANISM AND KINETICS OF SODIUM RELEASE FROM BROWN COAL CHAR PARTICLES DURING COMBUSTION61

CHAPTER 7 – CONCLUSIONS..... 110

7.1 Conclusions.....	111
7.1.1 Quantitative measurement of atomic sodium in the plume of a single burning coal particle	112
7.1.2 Simultaneous measurements of the release of atomic sodium, particle diameter and particle temperature for a single burning coal particle	113
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	115
7.1.4 Mechanism and kinetics of sodium release from brown coal particles during combustion	116
7.2 Recommendations for future work	118

REFERENCES.....	121
APPENDIX A – STUDIES OF THE RELEASE OF SODIUM FROM PULVERISED COAL IN A FLAT FLAME BURNER	137
APPENDIX B – STUDY ON ATOMIC SODIUM RELEASE FROM PULVERISED COAL PARTICLES IN A PREMIXED NATURAL GAS FLAME	149
APPENDIX C – MEASUREMENT OF ATOMIC NA RELEASED FROM A COAL PARTICLE USING QUANTITATIVE PLANAR LASER INDUCED FLUORESCENCE.....	154
APPENDIX D – KINETICS OF SODIUM RELEASE FROM A SINGLE BROWN COAL PARTICLE BURNING IN A FLAT FLAME	159

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.

I give consent to this copy of my thesis when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968.

The author acknowledges that copyright of published works contained within this thesis (as listed within the Preface, page x) resides with the copyright holder(s) of those works.

I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library catalogue, the Australasian Digital Theses Program (ADTP) and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

11 November 2010

Philip Joseph van Eyk

Date

Acknowledgments

The completion of this thesis could not have been accomplished without the advice, guidance, support and contributions of many people.

I would firstly like to acknowledge the support given to me by my supervisors Associate Professor Peter Ashman, Professor Graham (Gus) Nathan and Dr. Zeyad Alwahabi. I thank Peter for all of the support he gave me through the up and down times of the PhD process, and the constant guidance in all things related to coal combustion and chemical kinetics. I thank Gus for contributing his knowledge and experience in the areas of fluid mechanics and combustion which were essential for my understanding of the underlying processes governing the results of this study. I thank Zeyad for the invaluable advice he has given over the years in relation to laser diagnostics and data analysis.

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.

I thank current and former Chemical Engineering Office staff members Terri Whitworth, Mary Barrow and Elaine Minerds for providing endless assistance relating to administrative matters for my PhD candidature. I would also like to thank the Chemical Engineering Workshop staff during the period of the experimental campaign of this work, especially Jason Peak and Brian Mulcahy, who constructed the flat flame burner utilised in this work.

I would like to thank fellow PhD candidates for their camaraderie during this gruelling process, including my office mates who shared room A305 with me during my PhD candidature; Dr. Nadar Qamar, Anne Philcox and Michael Roberts. I also thank Steven Amos and David Battye for being excellent sounding boards for ideas during the latter (and somewhat more difficult) stages. I thank Dr. Paul Medwell for informative discussions on laser diagnostic techniques. I would like to thank Dr. Woei Saw for the many discussions relating to sodium release from burning particles. I also acknowledge the valuable time I spent with Dr. Adam Kosminski; the discussions related (and unrelated) to sodium in brown coal helped me immensely while I tried to finish my thesis and work at the “Stalag” simultaneously.

I would like to thank my Mum, Dad, Grandmother and siblings, Andrew and Clare. The love and support you have given me throughout my life has led me to this definitive point, and I am extremely grateful.

Finally, I would like to thank Andrea for being the most loving, patient and understanding girlfriend, and now fiancée, for me over this long process. I know it has been a long time coming, and that we have put many things on hold to ensure I finish what I started, but because of your constant unwavering support, I have finally completed this arduous task. I am forever grateful. *Io vi amo mia principessa.*

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.