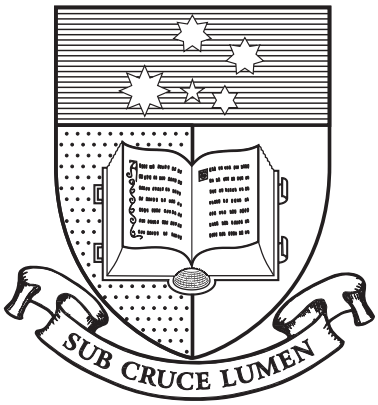

The University of Adelaide

School of Mechanical Engineering

Assessment of the Temporal Release of Atomic Sodium During a Burning Black Liquor Droplet Using Quantitative Planar Laser-Induced Fluorescence (PLIF)

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PhD Thesis

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Abstract

The release of sodium during the combustion of black liquor is a significant source of fume formation in a kraft recovery boiler, affecting efficiency in a pulp and paper mill. The fume is deposited on the surface of heat exchanger tubes in the upper furnace, causing fouling and corrosion, especially to the superheaters. This thesis reports on work done to develop improved understanding of fume formation.

The mechanisms of sodium release during each stage of black liquor combustion are influenced by the surface temperature. The addition of boron to the black liquor, which debottlenecks the recausticizing plant by a reduction in lime usage, also influences the characteristics of black liquor combustion, such as combustion time and swelling. Previously, no effective measurement technique has been available to quantify sodium concentration in the plume of a burning black liquor droplet with or without boron, or to record the distribution of surface temperature through the time history of a burning droplet. This thesis reports on the adaptation of two techniques for the measurement of the release of atomic sodium and the temperature history, and their application to investigate several aspects of the release of atomic sodium during combustion of black liquor in a flat flame environment.

The simultaneous employment of a planar laser-induced fluorescence (PLIF) technique with an absorption technique has been adapted to allow quantitative measurement of the release of atomic sodium. The absorption technique has been employed to correct for both fluorescence trapping due to absorption and attenuation by high concentration of the atomic sodium in the plume, and for collisional quenching by the other major gas components present in the flat flame. An independent assessment was performed using kinetic calculations, based on measured total sodium that is residual in a particle obtained at different stages in the combustion process. These independent assessments were used to provide greater insight in to the release process and to cross-check. The

influence of both the initial diameter of the droplet and addition of boron to the black liquor on the temporal release and the release rate of atomic sodium during the combustion have been performed using the present PLIF technique.

The second technique, two-dimensional two-colour optical pyrometry, has been adapted to measure the distribution of surface temperature and the swelling (change in surface area) of a burning black liquor droplet. The influence of surface temperature or the change in the external surface area of the droplet on the release of atomic sodium during the combustion of black liquor has been assessed through concurrent use of both adapted techniques.

The highest concentration of atomic sodium was measured in the final stage of combustion that of smelt coalescence, where it is an order of magnitude greater than in the other stages combined. While the extensive release of atomic sodium at high temperature in this final combustion stage occurs in only a relatively small percentage of droplets in a kraft recovery boiler, the effect could still be significant in fume formation. This is because the extensive release is expected to occur in the very small droplets, predominantly generated by splitting or physical ejection. Small droplets will have a very short combustion time and so could remain in suspension within hot gases for sufficient time for extensive release of sodium. These measurements outcomes can be used to support the future development of sub-models for computational fluid dynamics (CFD) models in order to better understand and optimise fume formation in a kraft recovery boiler.

Preface

"A journey of a thousand miles must begin with a single step."

Lao Tze

The work outlined in this thesis was performed in the Schools of Mechanical Engineering and Chemical Engineering at The University of Adelaide from September 2005 to May 2009. A section of the work was also carried out in the Process Chemistry Centre (PCC), Åbo Akademi in 2006 and 2007. This thesis by publication consists of eight chapters, preceded by short summary of each publication. The first chapter introduces the kraft pulping process and the importance of sodium in the pulping process. The second chapter covers the background for this thesis including black liquor, sodium emission, autocausticizing, laser diagnostic technique and surface temperature measurement technique. This chapter also describes the link between each of the publications. The next five chapters consist of five peer-reviewed journal articles, written jointly with other researchers from the PCC. These chapters present the key findings of the release of atomic sodium from black liquor using a laser diagnostic technique under various conditions, and equilibrium calculations of the composition distribution of sodium. The conclusions and implications are described in the last chapter of this thesis.

Thesis 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 myself, Woei Lean Saw, 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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Woei Lean Saw, 5th June 2009

List of Publications

Paper I W.L. Saw, G.J. Nathan, P.J. Ashman, Z.T. Alwahabi, Assessment of the release of atomic Na from a burning black liquor droplet using quantitative PLIF, Combustion Flame 156 (2009) 1471–1479.

Paper II W.L. Saw, G.J. Nathan, P.J. Ashman, Z.T. Alwahabi, M. Hupa, Simultaneous measurement of the surface temperature and the release of atomic sodium from a burning black liquor droplet, revised version submitted to Combustion and Flame on 10th November 2009.

Paper III W.L. Saw, G.J. Nathan, P.J. Ashman, M. Hupa, Influence of droplet size on the release of atomic sodium from a burning black liquor droplet in a flat flame, submitted to Fuel on 5th June 2009.

Paper IV W.L. Saw, M. Forssén, M. Hupa, G.J. Nathan, P.J. Ashman, The influence of boron on the emission of sodium during burning black liquor combustion under oxidative conditions, Appita J. 62 (3) (2009) 219–225.

Paper V W.L. Saw, G.J. Nathan, P.J. Ashman, M. Hupa, Influence of stoichiometry on the release of atomic sodium from a burning black liquor droplet in a flat flame with and without boron, Fuel, 10.1016/j.fuel.2009.11.023.

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"Gratitude is when memory is stored in the heart and not in the mind.

Lionel Hampton

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I would like express my gratitude to my principal supervisor, Professor Graham (Gus) Nathan, for providing me the opportunity to do research in such interesting areas of black liquor combustion incorporated with a laser diagnostic technique. I really appreciate his unwavering guidance, confidence and support throughout my PhD candidature. Thank you Gus. Dedicated support from my first co-supervisor, Dr. Peter Ashman, in constantly providing me with the insight into kinetics, and also his supervision is gratefully acknowledged. Dr. Zeyad Alwahabi, my second co-supervisor, has always provided valuable support in the area of laser diagnostic, and his supervision is also gratefully acknowledged.

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This work has been undertaken as part of a broader collaboration with Professor Mikko Hupa of ÅA-PCC. I would like to acknowledge him for giving me such valuable opportunities to visit PCC, as well as his supervision and support during the stay. Also, his valuable comments on joint publications are gratefully acknowledged. I want to thank Mr. Mikael Forssén, a previous member of ÅA-PCC, for his supervision, and also the friendly staff of ÅA-PCC for making my stay in Finland so enjoyable.

The editors and the anonymous journal reviewers are gratefully acknowledged for their insight comments on each of the papers listed in this thesis.

My Aussie family, the Yongs, especially Elizabeth, have always been available to give advice on English language and to share my ups and downs. This is greatly appreciated and unforgettable. Thank you.

Last but not least, I want to express my gratitude to my wife, Kai Lin and my family for their endless love and encouragement throughout the journey of completing this thesis. Thank you.

Woei Lean SAW

Summary of Each Paper

Paper I

This paper reports the development of the simultaneous measurements of planar laser-induced fluorescence (PLIF) and absorption technique to measure release of atomic sodium at high concentration during the combustion of black liquor. This technique was incorporated with an iterative correction to correct for fluorescence trapping and collisional quenching. The concentration of atomic sodium measured by the PLIF was compared with an independent first-order kinetic model. The values of the models were found to be higher than the values obtained from the PLIF, giving confidence that the correction, while high, is not excessive. The incorporation of the correction allows reliable measurement of the distribution of atomic sodium by PLIF at concentrations of 1 ppm, as can occur during black liquor combustion The concentration of atomic sodium during the stages of drying, devolatilisation and char combustion is an order of magnitude less than that in the smelt phase, of the order of 0.1 ppm in the present experiments.

Paper II

This paper reports the simultaneous measurements of the release of atomic sodium during the burning of a black liquor droplet, and its surface temperature, using PLIF and two-dimensional two-colour optical pyrometry techniques. A series of 10 mg black liquor droplets were burned in the flame provided by the flat flame burner at two flame conditions, fuel lean (Ø = 0.8), and fuel rich (Ø = 1.25). This study found that the surface temperature distribution is significantly non-isothermal. The study also found that the release of atomic sodium during the drying and devolatilisation stages was

correlated with the external surface area (or swelling). The paper also presents the first statistical analysis of surface temperature on a burning black liquor droplet.

Paper III

This paper reports the influence of initial droplet size on the temporal release and the release rate of atomic sodium during the burning of a black liquor droplet in a flat flame environment. Three different initial diameters of black liquor droplets, 1.3 mm (~2 mg), 1.7 mm (~5 mg) and 2.2 mm (~10 mg) were burned in a flat flame at equivalence ratios ($Ø_{bg}$) of 0.8, 0.9 and 1.25. A key finding of this study is that the relationship between the period of each of the combustion stages and the initial diameter is approximately parabolic. This demonstrates that the periods are dependent on the external surface area of the droplet. The total release of atomic sodium is greatest during the smelt coalescence stage and was found to be independent from initial droplet size compared with the stages of drying, devolatilisation and char combustion. In addition, the release rate of atomic sodium was found to be dependent upon initial diameter for all the black liquor combustion stages.

Paper IV

This paper reports the influence of boron on the emission of sodium during black liquor combustion under oxidative conditions within a single droplet furnace (SDF). A series 10 mg black liquor droplets were burned within the SDF at 900, 1000 or 1050ºC. The gaseous environment within the SDF was N_2 with oxygen added at a concentration of 2, 5 or 10 vol %. The loss of sodium was deduced by the difference between the initial sodium concentration and the sodium concentration left in the residue at specific exposure times. One of the key findings is that the difference between the sodium loss from the black liquor with and without boron increases at 900ºC, especially for higher oxygen concentrations. However, the difference between the sodium loss from the black liquor with and without boron decreases above 1000ºC. The addition of boron in black liquor also alters the characteristic combustion times.

Paper V

This paper reports the influence of boron on the temporal release of sodium during the burning of a black liquor droplet using the simultaneous measurements of PLIF and absorption techniques. A series of 10 mg black liquor droplets with or without boron were burned in the flame provided by the flat flame burner at three flame conditions, fuel lean ($Ø_{bg}$ = 0.8 and 0.9), and fuel rich ($Ø_{bg}$ = 1.25). One of the key findings was that the addition of boron to black liquor does not alter the trend of the release of atomic sodium. However, the trends are influenced by $Ø_{bg}$ (i.e. the excess oxygen) in the flame. The addition of boron to the liquor clearly reduced the total atomic sodium released, especially during the char consumption stage under oxidising conditions.