

Soot Measurement and Species Simulation in Laminar Premixed Flames

By

Kenneth J Ho

A thesis submitted for the degree of Masters in Engineering Science



Faculty of Engineering, Computer and Mathematical Science
School of Chemical Engineering
University of Adelaide, Australia

DECLARATION

This work contains no materials which has been accepted for the award of any other degree or diploma in any university or any tertiary institution 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.

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

Kenneth Ho

ACKNOWLEDGEMENT

I would like to express my gratitude to all those people around me who have contributed much to my research in gas combustion and laser diagnostics for the past 2 years. Furthermore, I would like to mention the outstanding supervision efforts of Dr Zeyad Alwahabi, Dr Peter Ashman and Professor Gus Nathan who have relentlessly guided me on the right track.

I would like to thank those people in the lab who have helped me much in the lab: Paul Medwell and Shaun Chan. Without their attention to details, I would never get see certain elements in a more prospective way. Not forgetting Wang Yu from Shanghai, China who has helped me much in terms of understanding the fundamentals of laser diagnostics and soot morphology.

Last but not least, I would like to acknowledge the efforts of the support staff: Jason Peak and Brian Mulcahy for their excellent craftsmanship and advice. Without them, my laboratory layout would have never come to fruit. Above all, I would like to thank my family for giving me the support and guidance that I needed throughout these 2 years.

SUMMARY

This thesis reports on the study of laminar premixed ethylene/air flat flames, in both rich and lean conditions (ϕ at 1.82 to 3.80) at atmospheric pressure. The work was divided into experimental measurements of soot particles and theoretical computations of chemical products. In the experimental part, both intrusive sampling probes and non-intrusive laser diagnostics techniques were applied. The experimental measurements cover soot volume fractions by laser extinction (LE) and laser-induced incandescence (LII), temperatures by thermocouple insertion and soot morphology by thermophoretic sampling/transmission electron microscopy (TEM). The theoretical computations were performed using a detailed reaction kinetic model consisting of 544 elementary reactions among 100 chemical species to describe the formation and growth of polycyclic aromatic hydrocarbons (PAHs) up to pyrene. Results arising from this research would create a potential database, combined with visualizations, to focus as an education tool for students and researchers alike.

Two-dimensional imaging by LII revealed relatively uniform soot distributions from ϕ at 1.82 to 2.22. However, annular distributions were observed for fuel-rich conditions (ϕ at 2.84 to 3.80) which were elucidated to ambient air mixing due to low nitrogen shroud. The calibrated soot volume fraction profiles were in close agreement with LE for slightly sooty flames but differ by a magnitude of three for much sootier circumstances. Variable changes to the refractive index of soot, m resulted in potential errors between 3 to 11 % for soot volume fractions. Thermophoretic sampling was employed to complement the above methods. From TEM images, it was evident that soot particles undergo coagulation and aggregation and is a function of fuel equivalence. No obvious trends were seen in the particle size distribution. The effect of a low premixed reactant velocity was found to influence the magnitude and shape of the temperature profiles due to burner plate heat transfer. Ceramic coating on thermocouple wires was demonstrated to affect estimated temperatures by 205 K. The kinetic model provided an insight into the concentration profiles of minor, intermediate and aromatic species as reported in literature. It also addressed the importance of propargyl recombination reaction ($C_3H_3 + C_3H_3 \rightarrow C_6H_6$) into benzene as a fundamental step towards PAHs growth. Finally, a sensitivity analysis was carried out to tackle the influence of temperatures on chemical species.

Table of Contents

| | |
|--|------------|
| DECLARATION | i |
| ACKNOWLEDGEMENT | ii |
| SUMMARY | iii |
| LIST OF FIGURES | vii |
| LIST OF TABLES | x |
| 1 INTRODUCTION | 1 |
| 2 LAMINAR PREMIXED FLAMES | 4 |
| 2.1 Introduction | 4 |
| 2.2 Use of Flat Flames..... | 5 |
| 2.3 Emissions from Premixed Combustion..... | 7 |
| 2.4 Gas Handling System | 8 |
| 2.5 Flowmeter Errors..... | 15 |
| 2.6 Visual Observations | 15 |
| 2.7 Summary | 16 |
| 3 LASER EXTINCTION | 18 |
| 3.1 Foundation of Laser Extinction..... | 18 |
| 3.2 Soot Volume Fraction by Laser Extinction..... | 18 |
| 3.3 Potential Errors Associated with Refractive Index of Soot..... | 20 |
| 3.4 Experimental Description..... | 22 |
| 3.5 Experimental Layout | 23 |
| 3.6 Source of Errors..... | 25 |
| 3.7 Results and Discussions | 27 |
| 3.8 Summary | 31 |
| 4 LASER-INDUCED INCANDESCENCE | 33 |
| 4.1 Theoretical Basis | 33 |
| 4.2 LII Considerations..... | 34 |
| 4.3 Laser Intensity Profile | 36 |
| 4.4 Time-Dependence Profile..... | 38 |
| 4.5 Calibration via Laser Extinction..... | 38 |
| 4.6 Experimental Description..... | 39 |
| 4.7 Experimental Layout | 41 |

| | | |
|-----------|--|------------|
| 4.8 | Sources of Error..... | 42 |
| 4.9 | Results and Discussions | 43 |
| 4.10 | Summary | 51 |
| 5 | FLAME TEMPERATURES | 53 |
| 5.1 | Choice of Measurement..... | 53 |
| 5.2 | Thermocouple Types | 54 |
| 5.3 | Thermocouple Properties and Their Advantages | 56 |
| 5.4 | Measurement of Gas Temperature | 57 |
| 5.5 | Factors Influencing Temperature | 59 |
| 5.6 | Experimental Description..... | 60 |
| 5.7 | Experimental Layout | 62 |
| 5.8 | Thermocouple Interruption..... | 63 |
| 5.9 | Results and Discussions | 64 |
| 5.10 | Summary | 67 |
| 6 | SOOT MORPHOLOGY | 69 |
| 6.1 | Development of Soot..... | 69 |
| 6.2 | Thermophoretic Sampling Particle Deposition | 73 |
| 6.3 | Sampling Layout | 74 |
| 6.4 | Results and Discussions | 76 |
| 6.5 | Summary | 81 |
| 7 | COMPUTATIONAL MODELLING | 83 |
| 7.1 | Chemical Kinetics | 83 |
| 7.2 | Flame Radicals | 85 |
| 7.3 | Computational Procedure | 90 |
| 7.4 | Results and Discussions | 97 |
| 7.5 | Sensitivity Analysis..... | 104 |
| 7.6 | Summary | 107 |
| 8 | CONCLUSION OVERVIEW | 108 |
| 9 | POTENTIAL WORK RECOMMENDATIONS | 110 |
| 10 | NOMENCLATURE..... | 111 |
| 10.1 | Symbols..... | 111 |
| 10.2 | Greek Symbols | 112 |
| 10.3 | Acronyms | 112 |
| 10.4 | Chemical Species Acronyms..... | 112 |
| 11 | BIBLIOGRAPHY | 113 |

APPENDICES

| | | |
|----------|---|------------|
| A | Premixed Flame Calculations..... | 128 |
| A.1 | Refractive Index of Soot..... | 128 |
| A.2 | Visual Determination of Laser Path..... | 128 |
| A.3 | Flame Extinction..... | 129 |
| A.4 | Soot Volume Fraction..... | 130 |
| A.5 | Treatment of LII Signals..... | 130 |
| A.6 | Radiation Heat Losses Correction..... | 131 |
| A.7 | Soot Microscopy Statistical Analysis..... | 132 |
| B | PREMIX Default Variables..... | 133 |
| B.1 | Solver Input Details..... | 133 |
| B.2 | Reaction Zone Dimensions..... | 134 |
| C | Tabulated Results..... | 135 |
| C.1 | Soot Volume Fraction (LE)..... | 135 |
| C.2 | Calibration of Soot Volume Fraction (LII)..... | 144 |
| C.3 | Temperatures after Correction..... | 150 |
| D | Mass Flow Controller Calibration Sheets..... | 157 |
| E | Publications..... | 159 |

LIST OF FIGURES

| | |
|---|----|
| Figure 1 Global carbon dioxide emissions from fossil fuel burning, 1950 – 2006 [31]..... | 4 |
| Figure 2 Schematic structure of the flat flame burner [34] against porous burner..... | 6 |
| Figure 3 Microstructure of soot particle from diesel combustion [48]..... | 8 |
| Figure 4 McKenna flat flame burner [34]..... | 9 |
| Figure 5 Front and side views of traverse and plate | 10 |
| Figure 6 Tube and Mass Flowmeters Calibration Setup..... | 11 |
| Figure 7 Calibration relationship between tube flowmeters and mass flow controller | 12 |
| Figure 8 Photographs of stabilised premixed ethylene flames at $\varnothing = 1.82$ to 3.80 | 15 |
| Figure 9 Helium-neon laser (Thorlabs, Inc) | 22 |
| Figure 10 Single beam procedure (Stanford Research Systems)..... | 23 |
| Figure 11 Laser extinction experimental layout | 23 |
| Figure 12 In-house built photodiode with sheath | 25 |
| Figure 13 Mean extinction measurements for He-Ne laser for the duration of 1 hour..... | 26 |
| Figure 14 Soot volume fraction profiles (Axial) by LE at $\varnothing = 1.82 - 3.80$; symbols: measurements; lines: third-order polynomial fit..... | 28 |
| Figure 15 Effect of different refractive index at $\varnothing = 2.22$ | 30 |
| Figure 16 Schematic diagram of the optical arrangements for 2-D LII measurements [81].... | 33 |
| Figure 17 TEM micrographs of laser-heated soot captured via thermophoretic sampling. Values of the laser fluence were a) 0.15, b) 0.3, c) 0.6 and d) 0.9 J/cm ² [87]..... | 36 |
| Figure 18 Fluence dependence of LII measured in steady laminar diffusion flames. Data were collected at $H = 20$ mm in the ethylene/air flame for detection gate durations of 19ns (+) and 85ns (\diamond), both gates opening coincident with the arrival of the ≈ 5 ns laser pulse. Data also shown for the methane/air flame at $H = 50$ mm with the 85ns gate (\bullet). Raw signals for each condition have been normalized to a value of 1.0 at a fluence of 0.6 J/cm ² . The solid line shown is the least-square power-law fit of the methane data for fluences greater 0.3 J/cm ² ; the fit follows the expression $\text{signal} \propto \text{fluence}^{0.34}$ [13]..... | 37 |
| Figure 19 Temporal profile of a LII signal obtained in the ethene-air laminar diffusion flame at heights of 10 and 30 mm above the fuel tube exit and at the radial locations corresponding to peak soot volume fraction for these heights [85]..... | 38 |
| Figure 20 Model Brilliant B Nd:YAG Twins [90] | 40 |
| Figure 21 High performance camera use fiber optic taper/face plate (B) to couple the intensifier (A) to the CCD (C) [91] | 40 |
| Figure 22 Interference filter of 410 nm \pm 10 nm | 41 |

| | |
|--|----|
| Figure 23 Laser induced-incandescence experimental layout | 41 |
| Figure 24 Comparison of LII beam profile at $\varnothing = 2.22$ at HAB 11 mm as function of radial position..... | 43 |
| Figure 25 LII signal (Arbitrary) as a function of laser fluence at $\varnothing = 2.22$ of HAB 11 mm; insert: burnt image at laser fluence of $6.85 \times 10^9 \text{ J/cm}^2$ | 44 |
| Figure 26 Time dependence of the LII signals as a function of HAB at $\varnothing = 2.22$; symbols: measurements; lines: second-phase exponential fit | 45 |
| Figure 27 Raw instantaneous LII images at $\varnothing = 1.82 - 3.80$ as a function of HAB 7 to 15 mm; excitation wavelength at 532 nm (Note RGB is based on colour map jet)..... | 46 |
| Figure 28 Normalized radial LII profiles, calibrated to the highest intensity at $\varnothing = 2.22$ | 48 |
| Figure 29 Soot volume fraction profiles (axial) as a function of HAB, calibrated to $\varnothing = 2.22$ | 49 |
| Figure 30 Comparison of radial soot volume fraction profiles between a) LE and b) LII at $\varnothing = 2.84$ | 51 |
| Figure 31 Basic thermocouple circuit [102] | 56 |
| Figure 32 Measured temperature profiles and their corresponding flowrates at $\varnothing = 2.07$ [114] | 59 |
| Figure 33 Effect of laminar burning velocities of ethane, ethylene and acetylene with air at atmospheric pressure as a function of equivalence ratio [94]..... | 60 |
| Figure 34 Cross-section of Type R thermocouple | 61 |
| Figure 35 Thermocouple placement layout | 62 |
| Figure 36 Flame disruption by thermocouple..... | 63 |
| Figure 37 Temperature profiles (axial) at $\varnothing = 1.82$ to 3.80 from HAB 3 to 19 mm at flame centreline; symbols: measurements; lines: third-order polynomial fit | 64 |
| Figure 38 Temperature profile (radial) at $\varnothing = 2.84$ at HAB 15 mm; line: second-order polynomial fit..... | 66 |
| Figure 39 Electron micrographs of soot particles chains. Mean diameter of particle ca. 200 \AA [1]..... | 69 |
| Figure 40 Schematic reaction path for soot formation in premixed flames [47] | 70 |
| Figure 41 H-abstraction- C_2H_2 -addition mechanism for PAH Growth [48] | 72 |
| Figure 42 TSPD experimental arrangement | 74 |
| Figure 43 TEM grid holder..... | 75 |
| Figure 44 TEM photographs (with a resolution of 64,000) of soot sampled at $\varnothing = 1.82, 2.22, 2.84$ & 3.80 as function of HAB at (a) 9mm, (b) 11mm, (c) 13mm, (d) 15mm, (e) 17mm | 78 |
| Figure 45 Mean particle size diameter as function of HAB as determined from TEM Photographs at..... | 79 |

| | |
|---|-----|
| Figure 46 Primary particle development at $\phi = 2.84$ for six HABs on flame centreline | 80 |
| Figure 47 Simple hydrocarbon fuels oxidation mechanism hierarchy [136]..... | 84 |
| Figure 48 Reaction mechanism for a stoichiometric C_2H_6 -air oxidation [137]..... | 85 |
| Figure 49 Schematic diagram of cyclopentadienyl radical reaction with methyl [140]..... | 87 |
| Figure 50 Resonantly-stabilized radicals with multiple electronic configurations [140]..... | 90 |
| Figure 51 Schematic diagram of propargyl recombination channels that form single-ring aromatic hydrocarbons [140]..... | 90 |
| Figure 52 Solution speed comparisons between different versions of CHEMKIN [®] (Linux 64-bit Platform)..... | 91 |
| Figure 53 Simulation pathway in PREMIX flame code | 92 |
| Figure 54 Relationship of PREMIX program to CHEMKIN and TRANSPORT pre-processors, and to the associated input and output files [154]..... | 93 |
| Figure 55 PREMIX procedural outlines | 95 |
| Figure 56 Starting estimate to the zone width and centre [154] | 96 |
| Figure 57 Minor species profiles at a) 1.95, b) 2.22, c) 3.10 & d) 3.80 | 98 |
| Figure 58 Intermediate species profiles at a) 1.95, b) 2.22, c) 3.10 & d) 3.80 | 99 |
| Figure 59 Aromatic species profiles at a) 1.95, b) 2.22, c) 3.10 & d) 3.80 | 102 |
| Figure 60 Effect of reduced temperature on minor species profiles at $\phi = 2.22$ as a function of HAB | 104 |
| Figure 61 Effect of reduced temperature on acetylene at $\phi = 2.22$ as a function of HAB..... | 105 |
| Figure 62 Effect of reduced temperature on aromatics growth at $\phi = 2.22$ as a function of HAB | 106 |
| Figure 63 Measurement of laser path at $\phi = 2.22$ | 128 |
| Figure 64 Solver default variables | 133 |
| Figure 65 Calibration Sheet for Ethylene Mass Flow Controller | 157 |
| Figure 66 Calibration Sheet for Air Mass Flow Controller | 158 |

LIST OF TABLES

| | |
|---|-----|
| Table 1 Actual flow conditions and equivalence ratios | 13 |
| Table 2 Summary of flame test conditions | 14 |
| Table 3 Summary of complex refractive index of soot | 20 |
| Table 4 Comparisons of methods used in flame temperature measurements [32] | 53 |
| Table 5 Summary of laser optical path through luminous part of flame | 129 |
| Table 6 Summary of reaction zone inputs used in CHEMKIN | 134 |
| Table 7 Summary of extinction measurements and soot volume fractions at $\varnothing = 1.82$ | 135 |
| Table 8 Summary of extinction measurements and soot volume fractions at $\varnothing = 1.95$ | 136 |
| Table 9 Summary of extinction measurements and soot volume fractions at $\varnothing = 2.08$ | 137 |
| Table 10 Summary of extinction measurements and soot volume fractions at $\varnothing = 2.22$ | 138 |
| Table 11 Summary of extinction measurements and soot volume fractions at $\varnothing = 2.84$ | 139 |
| Table 12 Summary of extinction measurements and soot volume fractions at $\varnothing = 3.10$ | 140 |
| Table 13 Summary of extinction measurements and soot volume fractions at $\varnothing = 3.80$ | 141 |
| Table 14 Summary of radial extinction measurements and soot volume fractions at $\varnothing = 2.84$ | 142 |
| Table 15 Calibration of LII signals into soot volume fraction at $\varnothing = 1.82$ | 144 |
| Table 16 Calibration of LII signals into soot volume fraction at $\varnothing = 1.95$ | 145 |
| Table 17 Calibration of LII signals into soot volume fraction at $\varnothing = 2.08$ | 145 |
| Table 18 Calibration of LII signals into soot volume fraction at $\varnothing = 2.22$ | 146 |
| Table 19 Calibration of LII signals into soot volume fraction at $\varnothing = 2.84$ | 146 |
| Table 20 Calibration of LII signals into soot volume fraction at $\varnothing = 3.10$ | 147 |
| Table 21 Calibration of LII signals into soot volume fraction at $\varnothing = 3.80$ | 147 |
| Table 22 Radial soot volume fractions from LII calibration at $\varnothing = 2.84$ | 148 |
| Table 23 Axial temperatures after radiation correction at $\varnothing = 1.82$ | 150 |
| Table 24 Axial temperatures after radiation correction at $\varnothing = 1.95$ | 151 |
| Table 25 Axial temperatures after radiation correction at $\varnothing = 2.08$ | 152 |
| Table 26 Axial temperatures after radiation correction at $\varnothing = 2.22$ | 153 |
| Table 27 Axial temperatures after radiation correction at $\varnothing = 2.84$ | 154 |
| Table 28 Axial temperatures after radiation correction at $\varnothing = 3.10$ | 155 |
| Table 29 Axial temperatures after radiation correction at $\varnothing = 3.80$ | 156 |
| Table 30 Radial temperatures after correction at $\varnothing = 2.84$ | 156 |