Combustion Products from Ventilation Controlled Fires: Toxicity Assessment and Modelling

By

Omar Abdulaziz O. Aljumaiah

Submitted in accordance with the requirements for the degree of
Doctor of Philosophy

The University of Leeds

Energy and Resources Research Institute

School of Process, Environmental, and Materials Engineering

January 2012

STATEMENT

The candidate confirms that the work submitted is his own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

LIST OF PUBLICATIONS

Peer reviewed articles in scientific journals and conferences' proceedings:

1. Aljumaiah, O., G. E. Andrews, B. G. Mustafa, H. Al-qattan, V. Shah and H. N. Phylaktou,(*2011a)*, Air Starved Wood Crib Compartment Fire Heat Release and Toxic Gas Yields, In *Proceedings of the 10th International Symposium on Fire Safety Science, Maryland, USA,* edited by Spearpoint, 2011, International Association for Fire Safety Science.

2. Aljumaiah, O., G. E. Andrews, A. Abdullahi, B. Mustafa and H. N. Phylaktou,(*2010a)*, Wood Crib Fires under High Temperature Low Oxygen Conditions, In *Proceedings of the Sixth International Seminar on Fire and Explosion Hazards, Leeds,* edited by D. Bradley, G. Makhviladze and V. Molkov, 2011, Research Publishing Services, ISBN: 978-981-08-7724-8, DOI: 10.3850/978-981-08-7724-8_15-05

3. Aljumaiah, O., J. Jordan, G. E. Andrews and H. N. Phylaktou,(*2008)*, The Development of a Technique for the Combustion of Wood in a High Temperature Low Oxygen Compartment, In *Proceedings of the Saudi International Innovation Confrence, Leeds, U.K.,* ISBN: 978-0-9559241-2-5.

4. Aljumaiah, O., G. E. Andrews, Alshammari, Burell, Cox and H. N. Phylaktou,(*2010c)*, Toxic Emissions from Folded Cotton Towel Fires in a Low Ventilation Compartment, In *Proceedings of the Proceedings of the Sixth International Seminar on Fire and Explosion Hazards, Leeds,* edited by D. Bradley, G. Makhviladze and V. Molkov, 2011, Research Publishing Services, ISBN: 978-981-08-7724-8, DOI: 10.3850/978-981-08-7724-8_11-07

5. Aljumaiah, O., G. E. Andrews, Alqahtani, B. Husain, P. Singh and H. N. Phylaktou,(*2010b)*, Air Starved Acrylic Curtain Fire Toxic Gases using an FTIR, In *Proceedings of the Sixth International Seminar on Fire and Explosion Hazards, Leeds,* edited by D. Bradley, G. Makhviladze and V. Molkov, 2011, Research Publishing Services, ISBN: 978-981-08-7724-8, DOI: 10.3850/978-981-08-7724-8_11-08.

6. Aljumaiah, O., H. N. Phylaktou, G. E. Andrews, I. Heath and J. Ledger,(*2010d)*, Ghosting Flames in a Low Ventilation Compartment with Kerosene Pool Fires, In *Proceedings of the International Congress Combustion and Fire Dynamics, Santander, Spain,* edited by J. Capote and D. Alvear, 2010, University De Cantabria, ISBN: 978-84-86116-23-1.

7. Aljumaiah, O., G. E. Andrews, H. N. Phylaktou and A. Jimenez (2011b). "Low Ventilation Pool Fires." Journal of Hazardous Materials. *In press.*

Conference presentations and poster presentation:

1. Aljumaiah, O., G. E. Andrews, H. N. Phylaktou (2009) Co-Firing of Biomass Wood Pellets with Natural Gas, Energy Options for the Future, Society of Chemical Industry, Huddersfield.
   (1st Prize for the best potential commercial award for the presentation & Young Researcher of the Year from the Society of Chemical Industry)
2. Aljumaiah, O., G.E. Andrews, H. N. Phylaktou (2010) Electrical Cable Fires using the Cone Calorimeter for Toxic Gas Investigations, RE10, Fire Service College, Morton-in-marsh.

All the experimental work for the tests presented in the papers listed was carried by Omar Aljumaiah. In addition, the first draft, the final draft, the results calculations and analysis were all carried out by the candidate. The submission was also done by Omar, along with the approval of the final amendments pre-publication. The supervision of Professor Andrews and Dr. Phylaktou is gratefully acknowledged. Their contribution through the discussion meetings and proof readings is also acknowledged. The other authors listed in the publication were undergraduate or graduate (MSc) students who typically attended one test conducted by Omar Aljumaiah and wrote a project on the subject. They have not directly contributed to the published work done.

Paper 1, forms major part of chapter 4 of this thesis. Papers, 2 & 3 form major parts of chapter 5. Paper 4 form a major part of chapter 6. Paper 5 form a major part of chapter 7. And finally papers 6 and 7 form a major part of chapter 8.

ACKNOWLEDGMENTS

The author would like to thank several people, whom this work would not have been possible without their support.

My first appreciations and gratitude goes to my advisors Professor Gordon Andrews, and Doctor Roth Phylaktou, for their mentoring, support, and knowledge transfer through the years. They taught me as an undergraduate, and continued to provide valuable advice and discussion during my research in my postgraduate years. My appreciation is beyond written script, and I will be grateful to my experience in Leeds for the rest of my life.

A special thanks to Bob Boreham, the lab technician who has provided valuable help and expertise in the lab work, his presence in the lab throughout most of this work, was great help. Thank you Bob.

The valuable advice on the FTIR data processing and handling by Dr. Hu Li from the Engine research group at the University of Leeds, and Mr. Dominic Duggan of Quantitech, is also acknowledged. Thank you for your valuable advice, help, and time.

ABSTRACT

Toxic smoke from fires is regularly identified as the leading cause of death in fire casualties. In most countries statistics suggest more than 70% of fire deaths are caused by either toxic smoke inhalation, or heat burns and toxic smoke inhalation. In most cases, fire victims are impaired from escape due to smoke irritation and poor visibility. The fire community is now recognising the need for further research into the sub-lethal toxicity, as in most cases fire victims are impaired by these sub-lethal effects from making a safe escape. However, despite the recognition of the importance of the fire toxicity problem, limited work is done on quantifying the different fire smoke products. The available information is incomplete, and in many cases misleading.

This work, attempts to address the fire toxicity problem in depth. By using state of the art experimental techniques, a thorough investigation into toxic components of fire effluent is conducted. Using a specially designed reduced scale enclosure, and an FTIR sampling system, a series of experiments were conducted examining the toxic products of low ventilation compartment fires.

As a first objective, a review was conducted into the current practice of fire toxicity assessment; it was found out, that in most cases, the previously developed models, overlook the irritancy and sub-lethal quantification by adopting the lethal end-point for assessment. A review on the work exposure limits, and its relation to fire was provided.

In addition, this research included experimentally examining different types of fire fuels, relevant to residential and industrial fires. The fuels studied included wood cribs, cotton towels, acrylic curtains, and hydrocarbon pool fires. The fires were burnt at ventilation rates corresponding to 5, 11, 21, 37 ACH, which simulated conditions of a limited ventilation enclosures in modern buildings.

Quantified yields of irritant species, such as Acrolein, Formaldehyde, Benzene, Acetic Acid, and Acetaldehyde, are reported on a scale never accomplished before. In addition, detailed assessment of the measured species in terms of lethality and irritancy was reported. The amount of information gained from the experimental work, expanded our current understanding on toxic fire effluent, and was published in a series of publications. Finally, the gained knowledge from the experimental work was then used in an attempt to propose a new methodology for toxic fire prediction in fire models.

TABLE OF CONTENT

STATEMENT 1

LIST OF PUBLICATIONS 1

ACKNOWLEDGMENTS 4

ABSTRACT 5

TABLE OF CONTENT 6

LIST OF FIGURES 10

LIST OF TABLES 15

ABBREVIATIONS & SYMBOLS 17

1. CHAPTER ONE INTRODUCTION: 1

1.1 GENERAL INTRODUCTION 1
1.2 FIRE SMOKE HAZARD & STATISTICS 3
1.3 LETHAL & SUB LETHAL TOXICITY 6
1.4 FIRE AS A COMBUSTION SYSTEM 7
1.5 DEVELOPMENT & GROWTH OF COMPARTMENT FIRES 9
1.6 FIRE TERMINOLOGY 11
1.7 PROBLEM DESCRIPTION 13
1.8 AIMS & OBJECTIVES 15
1.9 THESIS STRUCTURE 16

2. CHAPTER 2: BACKGROUND & LITERATURE REVIEW 18

2.1 INTRODUCTION 18
2.1.1 Development of fire safety engineering *19*
2.1.2 Development of fire computational codes *21*
2.2 COMPARTMENT FIRES THEORETICAL BACKGROUND 23
2.2.1 Growth stage *23*
2.2.2 Flashover *27*
2.2.3 Heat release rate calculation *29*
2.2.4 Fully developed fire *30*
2.2.6 Combustion stoichiometry & species yields *33*
2.2.7 Characterization of compartment fires *43*
2.3 COMPARTMENT FIRE SMOKE & TOXIC EFFLUENT 48
2.3.1 Asphyxiant gases *48*
2.3.2 Irritant gases *51*

2.4 FIRE TOXIC SMOKE GENERATION STUDIES 59

2.4.1 Hood experiments 59

2.4.3 Reduced Scale Enclosure Studies (RSE) 63

2.4.3 Full Scale Studies 77

2.4.4 Bench Scale Studies 86

2.5 QUANTIFICATION OF TOXIC HAZARDS FROM FIRE EFFLUENT 89

2.5.1 Toxic Potency Based on Animal Exposure Studies 89

2.5.2 Toxic Potency Based on Chemical Analysis 91

2.6 COMPUTER SIMULATION OF FIRE HAZARD AND TOXIC PRODUCTS 105

2.7 CONCLUSIONS 106

3. CHAPTER 3: METHODOLOGY 108

3.1 EXPERIMENTAL: 109

3.1.1 Experimental compartments: 109

BACK 116

3.1.2 Gas analysis equipment: 119

3.1.3 Soot sampling equipment: 129

3.1.4 General experimental procedures in brief: 130

3.2 GAS ANALYSIS TECHNIQUES: 131

3.2.1 Cross analysers checking 131

3.2.2 Carbon balance for calculating AFR and Ø 132

3.2.3 Species yields calculation 133

3.2.4 Heat release rate from gas analysis 133

3.2.5 Combustion efficiency 134

3.3 FIRE TOXICITY ASSESSMENT: 134

3.3.1 N gas model used in this work 134

3.4 FIRE TESTS VARIABLES: 137

4. CHAPTER 4: WOOD CRIB COMPARTMENT FIRES 138

ABSTRACT 138

4.1 INTRODUCTION 139

4.2 EXPERIMENTAL SET UP 141

4.3 FIRE LOAD PINE WOOD CRIBS 143

4.4 RESULTS 145

4.4.1 Typical 4.8 kg Pine Wood Crib Compartment Fire Results for 11 ACH 145

4.4.2 Compartment Weight Loss and Rate of Mass Consumption 146

4.4.3 Compartment Average Ceiling Temperature 147

4.4.4 Compartment Oxygen and Oxygen Based Heat Release Rate (HRR) 148

4.4.5 Carbon Monoxide and Total Unburned Hydrocarbon Yields 149

4.4.6 Combustion Efficiency, Fire Equivalence Ratio and Mass Loss Based HRR 150

4.4.7 Acidic and Irritant Gas Yields 152

4.4.8 Toxic Yields as a Function of Equivalence Ratio 153

4.4.9 Peak Fire Properties as a Function of Ventilation Rate in ACH 153

4.4.10 Total Toxicity N on a LC_{50} and $COSHH_{15min}$ Basis 155

4.5 CONCLUSIONS 161

5. CHAPTER 5: WOOD CRIBS IN FURNACE 162

ABSTRACT 162

5.1 INTRODUCTION 163

5.1.1 FLAMMABILITY IN HIGH TEMPERATURES 164

5.2 THE DEVELOPMENT OF A TECHNIQUE HIGH TEMPERATURE LOW OXYGEN ENVIRONMENT 167

5.2.1 Equipments 167

5.2.2 Primarily testing and development 169

5.2.3 Conclusions 178

5.3 EXPERIMENTAL SETUP 178

5.4 RESULTS 181

5.4.1 Flame Observations, Oxygen and HRR. 181

5.4.2 Global Equivalence Ratio during the Constant HRR Period. 182

5.4.3 Compartment Temperatures 183

5.4.4 CO and Total Hydrocarbon (HC) Emissions and Combustion Efficiency 183

5.4.5 Toxic Emissions 186

5.4 CONCLUSION 189

6. CHAPTER 6: FOLDED COTTON TOWELS...190

ABSTRACT 190

6.1 INTRODUCTION 191

6.1.1 Toxicity Assessments for Fire Gases 192

6.1.2 Previous Work on Folded Cotton Towel Fires.. 194

6.2 EXPERIMENTAL TECHNIQUES 195

6.3 RESULTS 197

6.3.1 Mass Loss, Heat Release Rates (HRR) and Temperatures 197

6.3.2 CO, Hydrocarbon, Fire Equivalence Ratio and Combustion Efficiency 199

6.3.3 Toxic Yields of Acrolein and Formaldehyde... 199

6.3.5 Total Toxicity N Ratio for $COSHH_{15min}$ and LC_{50} 200

6.1.1 Major Contributing Gases to the Total Toxicity N 202

6.4 CONCLUSIONS 205

7. CHAPTER 7: ACRYLIC CURTAINS 206

ABSTRACT 206
7.1 INTRODUCTION 207
7.2 EXPERIMENTAL TECHNIQUE 208
7.3 RESULTS 211
7.3.1 Fire Temperature 211
7.3.2 Oxygen Depletion and Heat Release Rate (HRR) 213
7.3.3 Equivalence Ratio Variation with Time 214
7.3.4 CO and UHC Yields and the Combustion Inefficiency 215
7.3.5 Toxic Gas Yields and their Variation with Equivalence Ratio 217
7.3.6 Total Toxicity N and the Main Toxic Gases 221
7.4 CONCLUSIONS 224

8. CHAPTER 8: HYDROCARBON POOL FIRES 225

ABSTRACT 225
8.1 INTRODUCTION 226
8.2 EXPERIMENTAL TECHNIQUES 228
8.3 RESULTS 231
8.3.1 Heat Release Rate (HRR) and Mass Loss Rates (MLR) 231
8.3.2 Mean Ceiling Temperatures and Evidence for Ghosting Flames 232
8.3.3 Equivalence Ratio and Combustion Inefficiency 235
8.3.4 CO and HC Yields 235
8.3.5 Particulate Yields and Composition 237
8.4 CONCLUSIONS 239

9. CHAPTER 9: CONCLUSIONS AND FUTURE WORK: 240

9.1 MAIN FINDINGS AND CONCLUSIONS: 240
9.2 RECOMMENDATIONS AND FUTURE WORK: 243

REFERENCES 245

BIBLIOGRAPHY 267

APPENDIX A 291

APPENDIX B 296

APPENDIX C 299

APPENDIX D 300

LIST OF FIGURES

Figure 1-1: Pie chart analysis of the cause of death in fire casualties in the U.K. during the years 2005, 2006, 2007, & 2008 (National Statistics, 2007; National Statistics, 2008; National Statistics, 2009; National Statistics, 2010). 4

Figure 1-2: Leading cause of fire death in residential fires in the USA (USFA, 2011).... 5

Figure 1-3: Schematic of the heat fluxes and mass fluxes occurring in an enclosure fire (Karlsson and Quintiere, 1999b). 8

Figure 1-4: Idealised time history of temperature or heat release rate in an enclosure fire (Karlsson and Quintiere, 1999c) 10

Figure 2-1 Design fire heat release rate, (PD-7974-1, 2002). 26

Figure 2-2 Air and product flows encountered during the growth (a, b & c) and fully-developed (d) phases of a compartment fire. 31

Figure 2-3: Direct conversion between mixture fraction and equivalence ratio adopted from (Bundy et al., 2007). 36

Figure 2-4: Effect of under-ventilation on yields of Oxygen, CO2, and CO for many materials, adopted from (Tewarson, 2002). 39

Figure 2-5: Beyler’s experimental set up adopted from (Beyler, 1986a) 60

Figure 2-6: CO yields as a function of equivalence ratio from Beyler’s experiments. Adopted from (Beyler, 1983). 61

Figure 2-7: Morehart and Toner data from their hood experiments adapted from (Morehart et al., 1992). 62

Figure 2-8: Gottuk experimental configuration adapted from (Gottuk, 2002) 67

Figure 2-9: Gottuk and Beyler hexane results, along with Gottuk proposed correlation (Gottuk, 2002). 68

Figure 2-10: Experimental set up used by Lattimer 1996 adopted from (Gottuk, 2002). 69

Figure 2-11: CO yield as a function of none dimensional heat release rate (Wieczorek, 2003). 71

Figure 2-12: Compartment fuel mass loss rate versus ventilation parameter(Utiskul et al., 2005) 72

Figure 2-13: Sketch showing the dimensions and sampling locations of the RSE used by NIST (Bundy et al., 2007). 74

Figure 2-14CO yields vs equivalence ratio from the NIST study (Bundy et al., 2007).. 75

Figure 2-15: Averaged quasi-steady state mass fraction measurements as a function of the mixture fraction for Heptane (a), Toluene (b), and Polystyrene (c) without inclusion of soot (Left) and with the inclusion of soot (Right) (Ko, 2009). 76
Figure 2-16: HCN and CO yields as a function of the fire equivalence ratio in Nylon tests (Blomqvist and Lönnermark, 2001). 80
Figure 2-17: THC and HCN yields as a function of the fire equivalence ratio in TM/TM tests (Blomqvist and Lönnermark, 2001). 81
Figure 2-18: room corridor configuration in (Gann, 2010) study. 82
Figure 2-19: Purser furnace, now recognised as ISO19700, BS7990. 87
Figure 3-1: A sketch of the reduced scale enclosure. 110
Figure 3-2 A Picture of the reduced scale compartment sealed door, forced ventilation port, and extraction hood. 111
Figure 3-3: Suspended ceiling details (not to scale). 114
Figure 3-4: Rear thermocouple tree. 115
Figure 3-5: Central thermocouples tree. 116
Figure 3-6: Upper layer thermocouples distribution. 117
Figure 3-7: Gas fired 1.6 m^3 furnace. 118
Figure 3-8: Picture of the X-hole sample probe. 119
Figure 3-9: A schematic sketch of the analysers used. 122
Figure 3-10: A sketch of the basic FTIR components. 124
Figure 3-11: Michelson interferometer. 124
Figure 3-12: A typical interferogram. 125
Figure 3-13: An example of spectra for multi-component analysis. 126
Figure 3-14: Metered and gas analysis based AFR in a 37 ACH wood crib test. 132
Figure 3-15: HRR over time in a wood crib test. 134
Figure 4-1: (a) Crib construction; (b) partially burned crib at 5 ACH. 144
Figure 4-2: characteristics for 4.8 kg pine wood crib with 11ACH ventilation. 146
Figure 4-3: Pine wood crib: (a) mass loss; (b) rate of mass loss for 5, 11, 21, and 37 ACH ventilation. 147
Figure 4-4: Compartment mean ceiling temperature as a function of: (a) time; (b) equivalence ratio. 148
Figure 4-5: (a) Compartment oxygen (b) oxygen consumption based HRR as a function of time. 148

Figure 4-6: (a) Carbon monoxide and (b) total unburned hydrocarbons yields (g/kg) as a function of time. 149
Figure 4-7: (a) Combustion efficiency and (b) fire equivalence ratio as a function of time.......... 150
Figure 4-8: . (a) Combustion efficiency (CO + HC energy loss) as a function of time and (b) mass loss based HRR. 151
Figure 4-9: Yields of : (a) acrolein; (b) formaldehyde; (c), benzene; (d) acetic acid. .. 151
Figure 4-10: Toxic yields as a fucntion of the fire equivalence ratio. 152
Figure 4-11: Peak fire properties as a function of the air ventilation of the fire in ACH. 154
Figure 4-12: Normalised total toxicity N as a function of: (a) time; (b) equivalence ratio for 5–37 ACH.......... 155
Figure 4-13: Total normalised COSHH15min toxicity as a function of: (a) time; (b) equivalence ratio. 156
4-14: Contribution of the major toxic species to the overall toxicity at 5 ACH for: (a) LC50; (b) COSHH15min. 157
4-15: Contribution of the major toxic species to the overall toxicity at 11 ACH for (a) LC50; (b) COSHH15min. 158
Figure 4-16: Contribution of the major toxic species to the overall toxicity at 21 ACH for: (a) LC50; (b) COSHH15min. 159
Figure 4-17: Contribution of the major toxic species to the overall toxicity at 21 ACH for: (a) LC50; (b) COSHH15min. 160
Figure 5-1: FDS Burn or No Burn zones in the flame extension model adapted from (McGrattan et al., 2008b). 165
Figure 5-2: limits of flame temperature prediction of the influence of fire temperature on limiting oxygen for a critical temperature 1225 ^{O}C. 166
5-3: Initial furnace calibration main gases and average temperature. 169
5-4: Initial furnace calibration NO_x, UHC and average temperature. 170
Figure 5-5: Combustion of wood at the Test 1 furnace calibration conditions in Fig. 5-3. 171
Figure 5-6: The fire gas composition and temperature profiles for Test 2 at 300 ^{O}C and 12% initial oxygen.. 173
Figure 5-7: Fire gases composition and temperature for Test 3 with 400oC and 7% oxygen at the ignition time.......... 174

Figure 5-8: Test 4 fire gas composition and temperature at crib ignition conditions of about 6% oxygen and 300 ^{O}C with an ignition delay of about 1500s. 175
Figure 5-9: Fire gas composition and temperature for a temperature at main ignition of 550 ^{O}C and oxygen of 8%. 176
Figure 5-10: UHC levels and NO_X levels in Test 5. 177
Figure 5-11: Oxygen (a) and heat release rate (b) over time. 181
Figure 5-12: HRR at 500°C for pine cribs (a) and the mass burning rate of the cribs (b). 182
Figure 5-13: fire global equivalence ratio by carbon balance. 182
Figure 5-14: mean compartment temperature. 183
Figure 5-15: . CO ppm (a) and yield g/kg (b) emissions as a function of the time from autoignition of the pine crib for 3 and 9 kg cribs. 184
Figure 5-16: Total HC by FTIR ppm (a) and yield g/kg (b) emissions as a function of time from autoignition of the pine crib for 3 and 9 kg cribs.. 184
Figure 5-17: Combustion efficiency as a function of time from auto ignition of the wood for the 3 (LH scale) and 9 kg (RH scale) pine wood cribs. 185
Figure 5-18: Acrolein emissions for 3 and 9 kg crib fires (a) ppm (b) yield g/kg. 186
Figure 5-19: Formaldehyde emissions for the 3 and 9 kg fires (a) ppm (b) yield g/kg. 186
Figure 5-20: Total normalised toxicity N for LC50 and COSHH15min 187
Figure 5-21: Toxicity contributions for 3 kg wood crib fire (a) LC50 (b) COSHH15min. 187
Figure 5-22: Toxicity contribution for 9 kg wood crib fire (a) LC50 (b) COSHH15min. 188
Figure 6-1: Cotton towel fire weight loss (a) and rate of weight loss (b). 198
Figure 6-2: Oxygen concentrations (a) and oxygen consumption derived HRR (b). 198
Figure 6-3: HRR derived from the mass loss rate and Calorific Value (a), compared to that derived from oxygen consumption and corrected for combustion inefficiency (b). 198
Figure 6-4: mean upper layer temperature (a) and peak temperature above the fire (b). 198
Figure 6-5: CO (a) and total hydrocarbon, UHC, (b) yields in g/kg. 199
Figure 6-6: Combustion efficiency from CO and UHC (a) and equivalence ratio (b). 199
Figure 6-7: Toxic yields g/kg Vs time for acrolein (a) and formaldehyde (b). 200

Figure 6-8: Comparison of the total toxicity N for COSHH15min and LC50 for 11 ACH (a) and 21 ACH (b) for 20g of ethanol as the fire initiator. 201
Figure 6-9: Toxicity N for COSHH15min and LC50 for 11ACH with 0.2 kg of kerosene as an accelerant. 201
Figure 6-10: Percentage contribution to total N for 11ACH with 20g ethanol accelerant for COSHH15min (a) and LC50 (b). 202
6-11 : Percentage contribution to total N for 11ACH with Kerosene accelerant for COSHH15min (a) and LC50 (b). 203
6-12 Percentage contribution to total N for 11ACH with 20g ethanol accelerant for COSHH15min (a) and LC50 (b). 204
Figure 7-1: Pictures of the curtain set up, ignition, debris after the four fires. 210
Figure 7-2average upper layer tempera rue as a function of the fire duration. 212
Figure 7-3: The temperature directly above the fire load as a function of time. 212
Figure 7-4: Oxygen concentration as a function of time in the four tests. 213
Figure 7-5: Heat release rate as a function of time in the four tests. 213
Figure 7-6 mean ceiling layer equivalence ratio as function of time. 214
Figure 7-7: mean ceiling layer fire temperature as a function of equivalence ratio. 214
Figure 7-8: CO yield against time. 216
Figure 7-9: CO yields against fire equivalence ratio. 216
Figure 7-10: UHC yields against time. 216
Figure 7-11: UHC yield v. equivalence ratio. 216
Figure 7-12: Combustion efficiency v. time 217
Figure 7-13: Combustion efficiency v. equivalence ratio. 217
Figure 7-14: HCN yield v time from start of fire. 218
Figure 7-15: HCN yield v. equivalence ratio. 218
Figure 7-16: Acrolein yield v. time from start of fire. 218
Figure 7-17: Acrolein v. equivalence ratio. 219
Figure 7-18: Formaldehyde yield v. time. 219
Figure 7-19: Formaldehyde yield vs equivalence ratio. 219
Figure 7-20: LC50 relative toxicity for 11 ACH 222
Figure 7-21: LC50 relative toxicity for 21 ACH 222
Figure 7-22: COSHH15min relative toxicity for 11 ACH. 223
Figure 7-23: COSHH15min relative toxicity for 21 ACH. 223
Figure 8-1: Heat release rate as a function of time (a) and equivalence ratio (b). 232

Figure 8-2: Mass Loss Rate g/s as a function of time for the four fuels. 232
Figure 8-3: Average upper layer temperatures as a function of time (a) and global equivalence ratio (b). 233
Figure 8-4: Temperatures above the pool surface and at the rear vent of the compartment for Heptane and Diesel Tests.. 234
Figure 8-5: Equivalence ratio as a function of time in the four tests. 234
Figure 8-6: Combustion inefficiency as function of time in the four tests. 235
Figure 8-7: Oxygen concentration as a function of time (a) and equivalence ratio (b).236
Figure 8-8: Particulates yields as a function of time (a) and carbon yield as a function of equivalence ratio (b) 237

LIST OF TABLES

Table 1-1: Energy release intensities of selected combustion systems (Bradley, 1992; Cox, 1995) 9
Table 1-2: Fire Terms & Definitions extracted from (ISO-13943, 2008)......................11
Table 2-1: Fire growth rate coefficients and time to reach heat release rate of 1000 (PD-7974-1, 2002). 25
Table 2-2: Maximum theoretical yields and experimentally determined yields for well ventilated and under ventilated fires adopted from (Tewarson, 2002). 42
Table 2-3: ISO19706 classification of fire types in relation to fire toxicity. 47
Table 2-4: Summarised effect of CO inhalation on humans adapted from (Purser, 2010). 49
Table 2-5: Incapacitation due to HCN inhalation adapted from (Purser, 2010a). 51
Table 2-6: Effect tresholds in human volunteers exposed to acrolein adapted from (AEGL, 2010). 56
Table 2-7: Effect of duration of exposure to 0.3 ppm level of acrolein in human volunteers from (AEGL, 2010b). 56
Table 2-8: Major species yields from the NIST 1991 full scale study (Babruskas et al., 1991a)...78
Table 2-9: Average yields for pre flashover, and post flashover in the NIST full scale study (Gann et al., 2010). 84

Table 2-10: Major toxic species volume fraction and yields for the closed door tests (Gann et al., 2010).........85
Table 2-11: A summarised list of the currently used fire toxicity appartus, summarised from (Hull, 2008).........88
Table 2-12: a typical sample of animal based toxicity tests results obtained using different methods expressed as LC50 and IC50 in gm-3.........90
Table 2-13: Constants and LC50 concentrations for use in the Levin N-gas model.........92
Table 2-14: LC50 concentration for use in the Purser LC50 FED model.........94
Table 2-15: ISO13571 Incapacitation limits for different gases.........100
Table 2-16: Impairment of escape due to irritation effect, proposed by (Purser, 2010).........101
Table 2-17: a summary and comparison of potential toxicity assessment limits for fire gases.........104
Table 3-1: FTIR calibrated range for the 51 species.........128
Table 4-1: Toxicity assessment methods and their ratios (all concentrations are ppm).........140
Table 5-1: Summary of the primarily testing results.........177
Table 6-1: Critical toxic gas concentration ppm for three assessment methods.........193
Table 6-2: The major toxic species as a percentage of the overall toxicity N for COSHH 15 min. (HSE, 2005) toxic limits.........194
Table 6-3: The major toxic species as a percentage of the overall toxicity N for 30 minutes LC50 toxic limits (HSE, 2005).........194
Table 6-4: Cotton towel elemental composition and stoichiometric A/F.........197
Table 7-1: Summarised toxicity assesment limits related to acrylic curtains tests.........208
Table 7-2: Elemental analysis of the acrylic curtains.........209
Table 7-3: Comparison of published HCN yields in fires.........220
Table 8-1: Properties of the four fuels used in the pool fires.........229
Table 8-2: Summary of the conditions and time for the onset of ghosting combustion.........234
Table 8-3: Thermal Gravimetric Analysis of some of the Particle Filters.........238

ABBREVIATIONS & SYMBOLS

Abbreviations:

AEGL	Acute Exposure Guideline Levels of Hazardous Substances.
ASET	Available safe escape time
ACH	Air Changes per Hour
BSI	British Standards Institution
CFAST	Consolidated Model for Fire And Smoke Transport (Zone model produced by NIST)
CFD	Computational Fluids Dynamics
COHb	Carboxyhemoglobin
DNS	Direct numerical solution
EPA	Environmental Protection Agency (USA)
EVAC	Evacuation Model Developed for FDS
FDS	Fire Dynamics Simulator (Field (CFD) Model produced by NIST
FEC	Fractional Effective Concentration
FED	Fractional Effective Dose
FIC	Fractional Irritant Concentration
FID	Flame Ionisation Detector
FLD	Fractional Lethal Dose
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
GC-MS	Gas Chromatography combined with Mass Spectrometry
GER	Global Equivalence Ratio
IDLH	Immediately Dangerous to Life or Health
ISO	International Standardisation Organisation
LC_{50}	Lethal Concentration affecting 50% of the population
LER	Local Equivalence Ratio
NIOSH	National Institute of Occupational Safety and Health (USA)
NIST	National Institute for Standards and Technology (USA)
OD	Optical Density
OEL	Occupational Exposure Limit
PMMA	Polymethylmethacrylate
PVC	Polyvinyl chloride
RD	Respiratory rate depression
RD_{50}	The concentration causing 50% decrease in respiration rate

RSET	Required Safe Escape Time
TGA	Thermo-Gravimetrical Analysis
THC	Total amount of hydrocarbons
VOC	Volatile Organic Compound

Symbols:

A	area	m^2
A_f	Fuel Area	m^2
h	height	m
D	Diameter	m
V	volume	m^3
$\dot{V}$	Volume Flow Rate	m^3/s
P	Pressure	atm
R	Universal Gas Constant	J/(mol K)
U	Velocity	m/s
C_d	discharge coefficient	
$\dot{m}$	mass loss rate (mass flow rate)	kg/s
$\dot{m}_{fuel}$	mass loss rate of fuel	kg/s
$\dot{m}_{Air}$	mass supply rate of air	kg/s
AFR	air to fuel ratio ($\frac{\dot{m}_{Air}}{\dot{m}_{fuel}}$)	
MW_i	molecular weight of species i	kg/kmol
$MW_{mixture}$	molecular weight of mixture	kg/kmol
T	temperature	°C
t	time	s
Y_i	yield of species i	kg/kg
y_i	mass fraction of species i	
f_i	normalised yield	
$\dot{Q}$	heat release rate	kW

Greek Symbols:

$\emptyset$	Equivalence ratio	
χ	combustion efficiency	
$1-\eta_c$	combustion inefficiency	
ρ	Density	kg/m^3
ΔH	change in elthapy	kJ/mol
ΔH_c	Heat of combustion	kJ/kg
$\Delta H_{c.o2}$	heat of combustion per gram of oxygen consumed	kJ/kg_{o2}

Subscripts:

f	Fuel
CO	Carbon monoxide
CO_2	carbon dioxide
O_2	oxygen
HCN	Hydrogen Cyanide
HCL	Hydrogen Chloride
HBr	Hydrogen Bromide
HF	Hydrogen Fluoride
NOx	Nitrogen Oxides (No and NO_2)
UHC	unburnt hydrocarbons
For	Formaldehyde
Acro	Acrolein
Benz	Benzene
avg	average
air	ambient air
stoich	Stoichiometric composition.
max	maximum value
UL	Upper layer

Superscripts:

$\dot{}$	Indicates rate of change as in $\dot{m}$
`	Single prime (per unit width)
``	Double prime (per unit area)
``	Three prime (per unit volume)

1. CHAPTER ONE

INTRODUCTION:

1.1 GENERAL INTRODUCTION

Fire is one of the earliest technological discoveries by humankind, its controlled presence allowed extraordinary improvements to early civilisations. Once controlled, fire provided warmth, light, and numerous advantages to our ancestors. Nonetheless, once fire became out of control, it posed, and still poses, one of the most devastating experiences threatening permanent damage and destruction to our lives, civilisation, and environment. In modern times, the branch of science termed combustion embraces both controlled (wanted), and un-controlled (unwanted) fire processes (Cox, 1995). Nonetheless, more recent research on unwanted fires has emerged under the title fire safety science. This relatively newer discipline expanded the fundamental combustion studies on the fire process to include other phenomena associated with the subject such as: fire toxicity, fire safety engineering, psychological behaviour in fire, fire modelling, fire statistics, etc. The interest shown in the subject from all the mentioned groups indicates how challenging and complex a problem this is to our current scientific community, and to the larger society as a whole. As well as, establishes the need for multidisciplinary approach towards studying most topics in the field of fire safety science. Of the most crucial topics in fire science is the area of fire toxicity, in which, this work attempts to expand the current limits of knowledge and understanding.

One way to highlight the importance of fire related studies is to look at the financial cost related to the fire problem itself. In the U.K. the latest official estimates published in 2006 by the office of the deputy minister put the total cost of the fire problem in England and Wales at an estimated £ 7.03 billion for 2004. This include £ 2.77 billion incurred in anticipation of fire, £ 1.74 billion as the cost of the fire and rescue service, and the remaining £ 2.52 billion were for the consequences of fires which include: property damage or loss, business loss, economic cost of injuries and fatalities, and costs related to criminal justice services (ODPM, 2006). The huge economical cost of fire is not limited to the UK. In the USA the national fire data centre of the home land security puts the overall cost of fire to the USA at an estimate of $ 182 billion per year for 2007 (USFA, 2009). This estimate is considered conservative, as it does not include the volunteering fire-fighters time and other costs. Once the fire-fighters costs are included, as in the NFPA statistics, the estimate raises to $ 347 billion for the same year which represents 2.5% of the U.S. gross domestic product in 2007 (Hall, 2010).

The general public is usually unaware of the magnitude of these financial costs. Nonetheless, these estimates provide a clear indicator on how serious the fire problem is to the economy, environment, and society in general. In fact, governmental bodies, and universities in the industrialised countries, recognised the need for significant scientific research in order to make the best use of cost spent in anticipation of fire, and to minimise the cost incurred as a result of fire. Thus, fire research gathered an increasing attention and funding in the past few decades. Section 2.1 in Chapter 2 provides an overview of the development of fire studies and more specifically fire toxicity studies and how it affected our approach and understanding to the problem thus far.

Despite increasing efforts over the recent decades, and significant contributions from scientific studies on the fire problem, there remain major gaps in our full understanding of the fire phenomena; its behaviour, its products, and its effect are all areas of active research. One of the main areas that lack in understanding and data availability is the topic of incomplete combustion products and the resulting toxic effect in ventilation controlled fires. The importance of the fire toxicity studies as an emerging topic in fire science can be attributed to several aspects, most important of which is the high percentage of deaths reported from toxic smoke inhalation. This is evident from annual governmental reports of fire casualties. The following section will provide the reader with some of the most recent statistics from the UK and the USA which are representative of other parts of the industrialised world.

1.2 FIRE SMOKE HAZARD & STATISTICS

Compartment fires are normally accompanied by the release of huge amount of toxicants, mainly due to the restricted ventilation of the fire causing high in-efficiency burning conditions. As a result, it is commonly reported that most fire victims die from smoke inhalation, or smoke inhalation and subsequent burns (National Statistics, 2007). The latest governmental reports in the U.K. show the annual count of fire fatalities is ranging from 443 to 491 between 2005 and 2008. Figure 1-1 shows pie chart percentage analysis of the fire casualties' cause of death for the latest published reports. The shown statistics illustrate that smoke inhalation is the dominant cause of death, directly causing death without burns (≈42%), or jointly causing death with burns (≈21%), accumulating to a total of around 63% for the same period reported (National Statistics, 2007). Nonetheless, there is reason to believe that there is more toxic smoke casualties in the regions classified as others and burns. This is due to the fact that not all toxic components of the fire smoke are easily measured in fire victims, and that it is a common practice to limit the toxicology investigation to the level of Carboxyhemoglobin in the blood (COHb) which excludes toxicants other than CO from being taken into account (Purser, 2002).

The UK national statistics are based on the total fire incidents in the country with no details on differences between dwelling, industrial, or commercial fires. Nevertheless, an earlier analysis of the fire deaths in London during the period 1996-2000 suggests more than 85% of the fire deaths occurred in dwelling fires (Holborn et al., 2003). In addition, the same study presents an important categorisation of fire victims according to age groups, the analysis show that the age group, 60-79 had the highest percentage of fire casualties 32%, followed by the age group 80+ which consisted of 25% (Holborn et al., 2003). This suggests that significant proportions of the fire victims are of old age, and had difficulties in mobility. In fact, the authors in their conclusion state "The results would suggest that it is the weakest members of society—the old, the sick and disabled and those suffering from mental illness or an alcohol problem—that are most at risk of unintentional death due to fires in dwellings"(Holborn et al., 2003). This supports the argument, that in order to make significant progress in fire toxicity lethal problem, careful consideration should be given to the hazard of impairment of escape due to toxic smoke in fire studies.

,

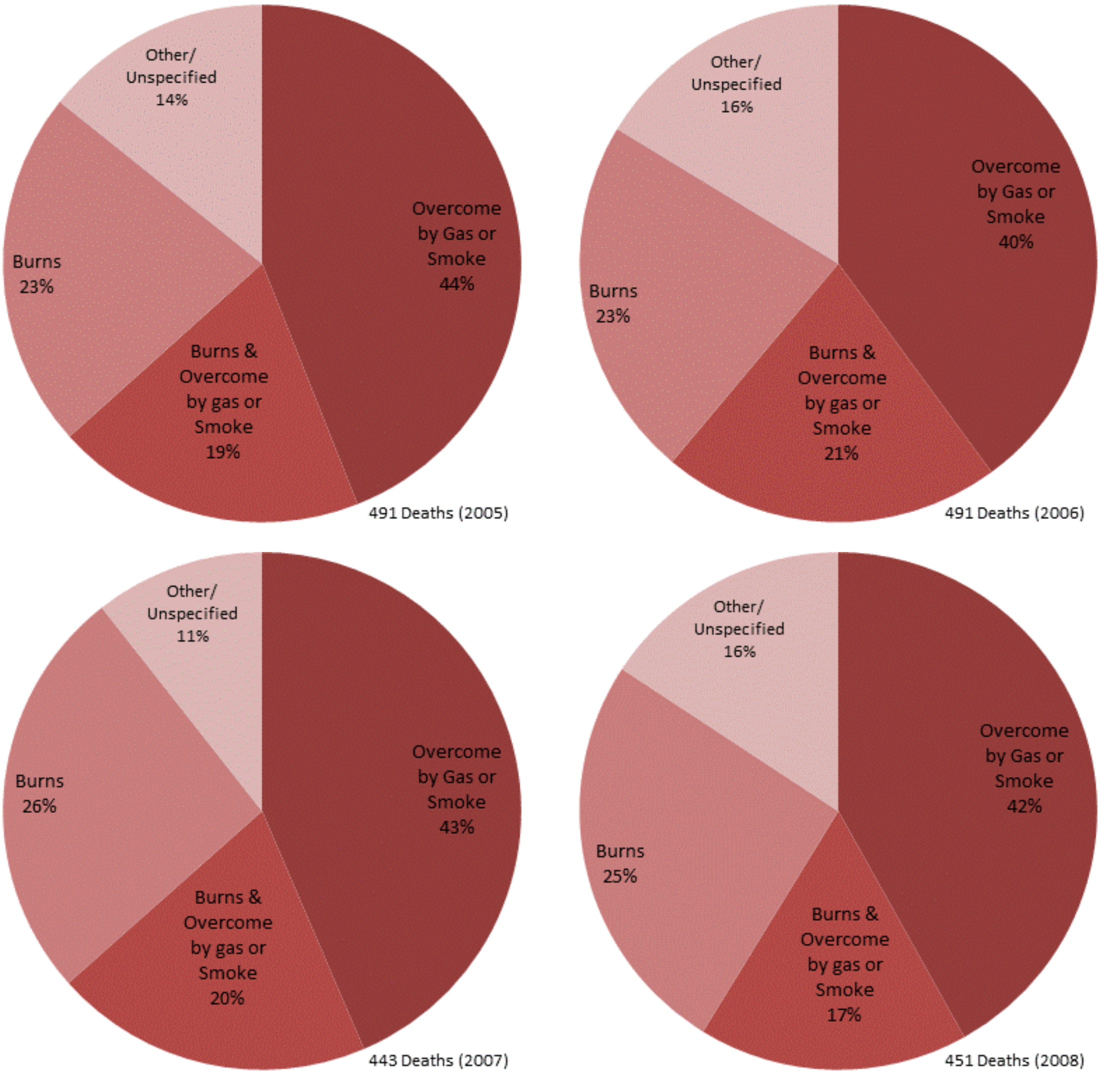


Figure 1-1: Pie chart analysis of the cause of death in fire casualties in the U.K. during the years 2005, 2006, 2007, & 2008 (National Statistics, 2007; National Statistics, 2008; National Statistics, 2009; National Statistics, 2010).

In addition, statistical analysis of the fire reports during 2002 in the USA, suggest that although 40% of the reported fires were outdoor fires, outdoor fatal fires form less than 3% of the total fatal fires. The data reported also suggest that 69.3 % of the fatal fires occurred in residential structures, 4.3% in non-residential structures, and around 20 % in vehicle fires (USFA, 2005). These findings, lead to another more in depth analysis of residential fires fatalities during the period 2007 through 2009. The analysis report was published in (USFA, 2011), and concluded the following:

1) 91 % of all civilian fatalities in residential building fires involve thermal burns and smoke inhalation or smoke inhalation alone, as shown in figure 1.2.
2) Bedrooms (55 %) are the leading location where civilian fire fatalities occur in residential buildings.
3) Smoking was the leading cause of fatal residential building fires.
4) The dominant factors contributing to civilian fire fatalities in residential buildings were Fire Pattern 60.7 %, Egress Problems 18.9 %, and Escape Problems 18.0%.

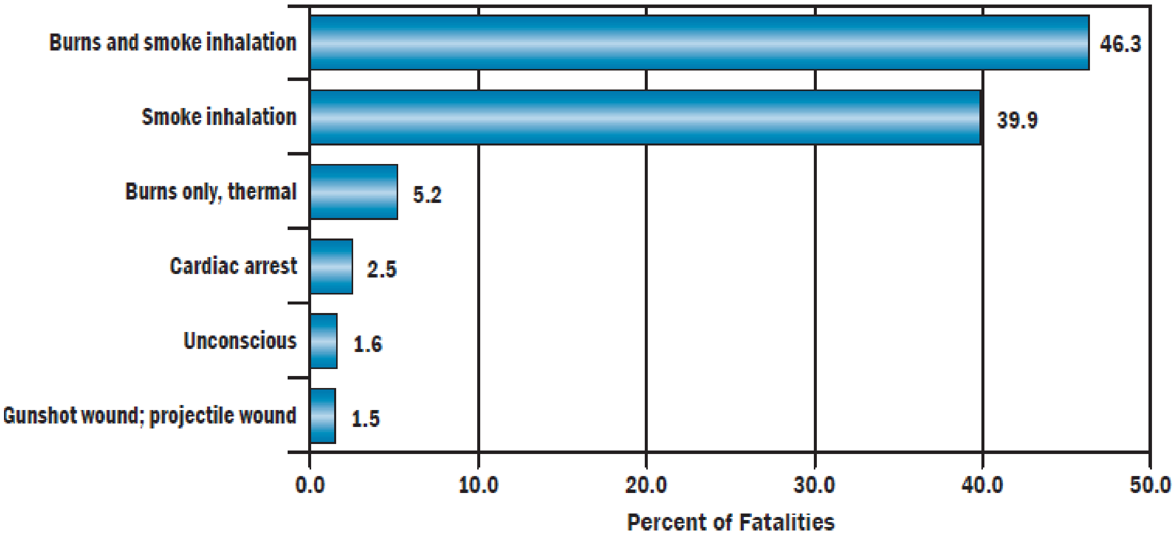


Figure 1-2: Leading cause of fire death in residential fires in the USA (USFA, 2011).

The reported statistics highlight the importance of compartment fire research, and the problem of fire toxicity as the leading cause of death. It can be argued that studies on open fires are of limited value to fire toxicity as it does not correspond to the conditions of confined, ventilation controlled, fires. In fact, it will be shown later in this thesis, in Chapter 2, that most of the available literature correspond to highly ventilated fires which does not represent the problematic conditions present in real limited ventilation compartment fires which cause the majority of deaths.

1.3 LETHAL & SUB LETHAL TOXICITY

Traditionally scientific research on the topic of fire toxicity adopted death as the endpoint of the toxic potency (Babrauskas et al., 1992; Hirschler, 1987; Levin, 1996; Purser, 1992). This remains as the dominant potency measure in fire studies represented by the additive summation of Lethal Concentration at which 50% of the populations is expected to die (LC_{50}) of the gases produced by a fire. Nevertheless, its implementation in the different fire toxicity assessment models is a developing research area (Purser, 2002; Purser, 2010c). However, although lethal potency may be sound for fire casualties' investigatory purposes, or materials regulatory research, it is often argued that a lower endpoint should be considered for fire safe engineering design and safe egress purposes. (Andrews et al., 2007; Andrews et al., 2005b; Andrews et al., 2005a; Purser, 2010b; Purser, 2010c) Nevertheless, the lower end point is a subject of active research and no clear agreed on limits are currently established (Gann, 2004a; Gann, 2004b).

In fact, as fire studies developed, more awareness of the toxicity problem emerged; resulting in an increased interest in a lower end point that is often described as the incapacitation point. This incapacitation concept falls in what is sometimes called fire sub lethal toxicity research which has gained an increasing interest, but limited knowledge in the last decade (Gann, 2004b). Indeed, it is now established, that for effective consideration of the fire toxicity problem, the fire smoke effect causing impairment of escape and incapacitation shall be a fundamental part of fire toxicity studies; although no full set of data is available for the complete species assessment. An original description and classification of the incapacitating effects of exposure to toxic smoke and heat in fires is provided by (Purser, 2002) as follows:

1. Impaired vision resulting from smoke obscuration and the painful effect of irritant smoke products and heat on the eyes.
2. Respiratory tract pain and breathing difficulties resulting from the inhalation of irritant smoke products that may be very hot. Lung inflammation may also occur leading to respiratory distress.
3. Narcosis from the inhalation of toxic gases, resulting in confusion and loss of consciousness.

4. Pain to exposed skin and the upper respiratory tract, followed by burns or hyperthermia, due to the effects of heat preventing escape. These effects may lead to collapse.

From a toxicological viewpoint, effects 2 and 3 are the most significant, with these products broadly described as irritants and narcotics. The topic of fire smoke toxic potency and the related toxicity assessment models are further discussed in details in Chapter 2.

(Hall, 2004a; Hall, 2004b) analysed fire casualties reports for a period of 5 years in the United States. He argues more than half of fire casualties and fire injuries incurred due to smoke inhalation can be saved if sub lethal toxicity effect is considered as a future protocol in fire design. He explains improved available time of escape and smoke detection systems could result in significant reduction in fire casualties > 50%, while considering sub lethal toxicity by providing extended escape time alone, without smoke detection, could result in a reduction of 25% of fire smoke injuries and casualties. It is hoped that this work will contribute to the limited knowledge in the area of sub lethal toxicity from compartment fires and ultimately result in better standards of fire smoke risk analysis.

.

1.4 FIRE AS A COMBUSTION SYSTEM

In this section, fire is presented and described as a combustion system to provide the reader with a comparative background to other combustion studies. According to the International Standardisation Organisation 2008, the general definition of a fire can be stated as the "process of combustion characterized by the emission of heat and fire effluent and usually accompanied by smoke, flame, glowing or a combination thereof" (ISO-13943, 2008). This is a specific description of what is known as fire. However, further precision leads into reclassifying the fire process into controlled and un-controlled fires. The same ISO states the following definition of un-controlled fire: "A self-supporting combustion that has not been deliberately arranged to provide useful effects and is not limited in its extent in time and space". Both definitions provide a sensible description to the fire process; nonetheless, they come short of providing the full details of the process. The general fire description is obviously too wide for the purpose of this study, as the un-controlled fire term can potentially include the process of deflagration or detonation which are not what is genuinely meant by fire in this work.

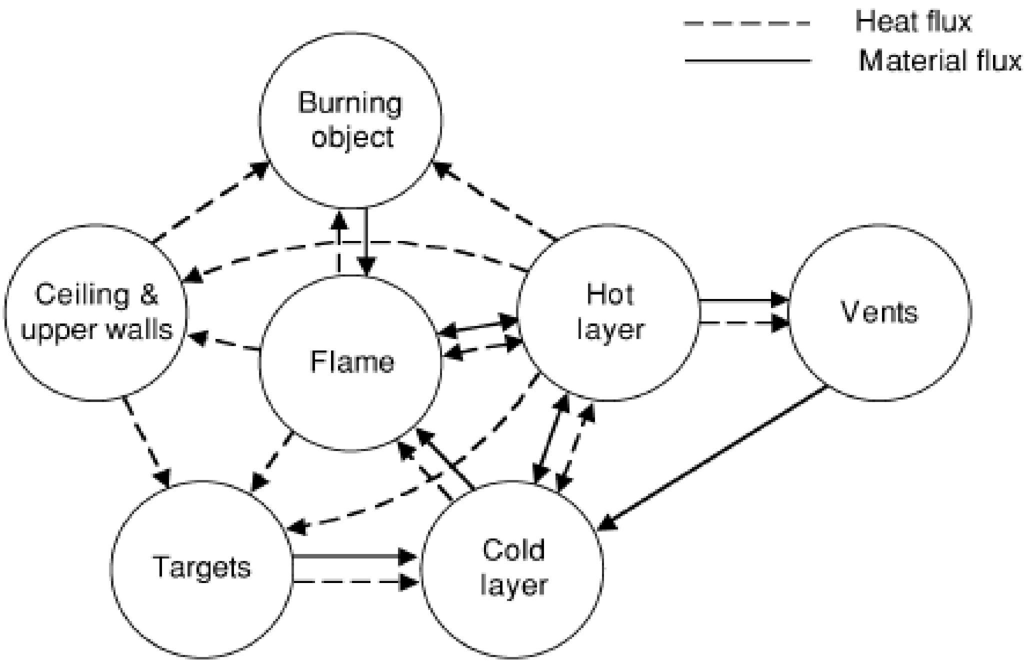


Figure 1-3: Schematic of the heat fluxes and mass fluxes occurring in an enclosure fire (Karlsson and Quintiere, 1999b).

From a process point of view, the most crucial feature that distinguishes fires, including un-controlled or un-wanted fires, from other combustion processes, is the positive feedback mechanism which controls the rate of fuel supply. In theory, as the fire products are produced, heat feedback from the products derives further volatilisation of the fuel source. This is even more crucial in the case of a compartment fire where the combustion products are trapped at the upper layer of the compartment forming a hot layer zone. Once this hot layer becomes hot enough it leads to what is called a flash over, a point after which any combustibles in the compartment are ignited. The feedback process is generally dominated by thermal radiation. Figure 1-3 shows a sketch of heat fluxes and mass fluxes in an enclosure fire.

Another crucial feature of compartment fires is the limitation of the fire by the amount of oxygen available to oxidise the fuel. In cases where a restricted ventilation occurs, the positive feedback derives the fire to a point after which there is not enough oxygen to oxidise vaporised fuel; and the generation of heat process is thus limited, limiting further growth of the fire. This later scenario is of particular important because, as it represents what most modern residential fires go throw resulting in significantly in-efficient combustion and great amounts of toxicants. This in-efficiency is regarded a major factor why un-controlled compartment fires are such a hazardous event.

That being said, the huge in-efficiencies, and the complexities in replicating the important parameters to represent a realistic compartment fire burning conditions, have made scientific investigation into the area of combustion products from fires more challenging. A useful comparison of the combustion energy intensities is presented by (Cox, 1995) with some data adapted from (Bradley, 1992) show the scale at which fire combustion is in-efficient.

Table 1-1: Energy release intensities of selected combustion systems (Bradley, 1992; Cox, 1995)

Combustion System	**Energy Release Intensity (MW.m^3)**
Aero gas turbine (take-off)	1500
Gas central heating boiler	200
Gasoline engine	100
Gas-fired fluidised bed	40
Pulverized coal combustor	10
Fire	0.5

1.5 DEVELOPMENT & GROWTH OF COMPARTMENT FIRES

In compartment fires, once ignition occurs, the fire may develop in various ways, depending on the ventilation available, type of fuel in the compartment, fuel orientation, and several other factors. These factors affect the fire growth, fire intensity, and the duration of the fire. (Karlsson and Quintiere, 1999a) provides a logical development description of few of the most common scenarios in an enclosure fire. It can be seen in Figure 1-4, once the ignition occurs; the initial growth phase develops at constantly increasing rate mostly dependant on the fuel type. During this period hot gases will accumulate at the top half of the compartment leading to change in fire growth rate commonly called flashover. Once the fire will reach this change in the growth rate (point A), what can be described as the beginning of the flashover period occurs. At this stage the fire growth is significantly altered by other factors in the enclosure most notably the available ventilation to the compartment. Lack of ventilation will result in oxygen depletion and the fire will start decaying significantly and possibly go off.

However, if enough ventilation is provided by the enclosure vents the fire will go through higher intensity and huge growth through the flashover period until the fire reaches point B. At point B the fire has reached the highest amount of possible ventilation to the enclosure and the fire is then restricted to this size. Post point B curve shows what is usually called fully developed enclosure fire. During which, the compartment is burning at the highest possible intensity. Another scenario may develop if the ventilation condition is altered as in point C, where a ventilation restricted fire received an un-expected event (such as opening a door) from which the fire growth resumed rather than stopped (Karlsson and Quintiere, 1999a).

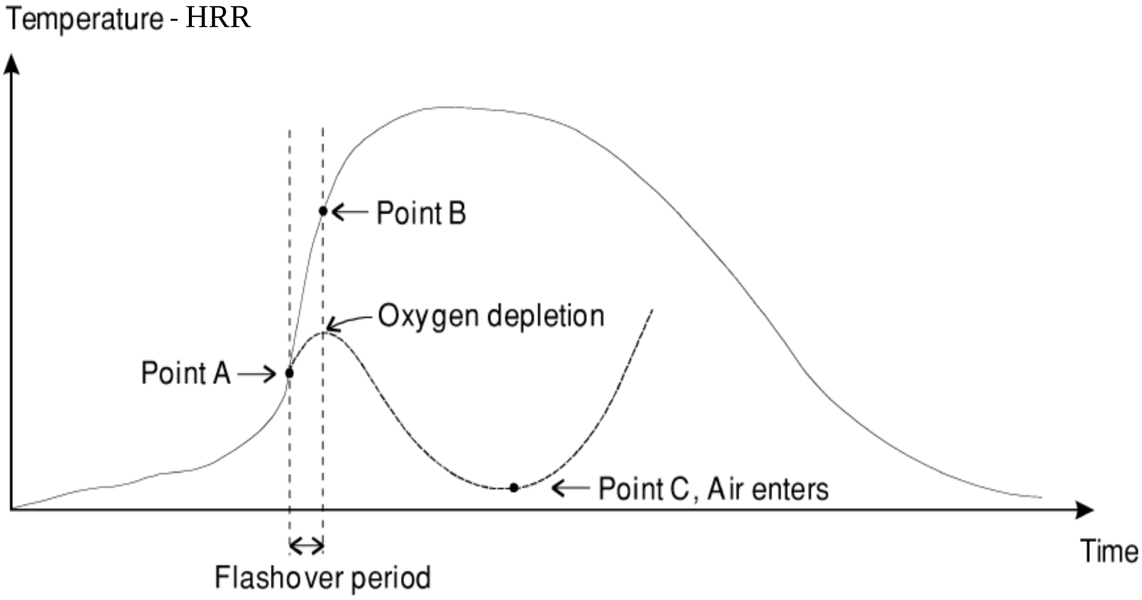


Figure 1-4: Idealised time history of temperature or heat release rate in an enclosure fire (Karlsson and Quintiere, 1999c)

From the earlier discussion it can be argued that in terms of fire intensity the fire flashover period is the most critical in the compartment fire history. In fact, it is commonly accepted that no survivors are expected to be found alive in post flashover fires (Drysdale, 1998). However, the hazard resulting from the onset of flashover is not limited to the compartment. In fact, post flashover fires commonly run at a very rich mixture and produce greater quantities of toxic species (Gottuk, 2002; Purser, 2002). These toxic products are then transported in adjacent means of escape and remote parts of the main building.

Flashover has been extensively studied due to its importance from fire development point of view. Studies done by (Graham et al., 1995; Holborn et al., 1993; Martin and Wiersma, 1979; Thomas, 1974; Thomas, 1980), and several others have yielded many definitions of the phenomena of flashover. (Drysdale, 1998) provides a list of the most important definitions of flashover accepted in the fire science community. They are stated as follows:

a) The transition from a localized fire to the general conflagration within the compartment when all fuel surfaces are burning;
b) the transition from a fuel controlled fire to a ventilation controlled fire; and
c) the sudden propagation of flame through the unburnt gases and vapours collected under the ceiling.

1.6 FIRE TERMINOLOGY

The terminology of fire science is developing, and it is often the case research studies assume different terms or description of a similar concept or phenomenon. An example of the inconsistency in the field is the different assumptions on the flashover definition, fire equivalence ratio and combustion efficiencies. The International Standardisation Organisation produced an approved document on the fire safety vocabulary. This document is reviewed and updated regularly. The latest edition of which is used in this work. In this section some of the important terms are defined for clarity (ISO-13943, 2008)

Table 1-2: Fire Terms & Definitions extracted from (ISO-13943, 2008)

Fire (General)	“process of **combustion** characterized by the emission of heat and **fire effluent** and usually accompanied by **smoke**, **flame**, **glowing** or a combination thereof”
Fire Uncontrolled	“self-supporting **combustion** that has not been deliberately arranged to provide useful effects and is not limited in its extent in time and space”
Combustion	“exothermic reaction of a substance with an **oxidizing agent**”
Equivalence ratio	**“fuel**/air ratio divided by the fuel/air ratio required for a **stoichiometric mixture”**
Pyrolysis	“chemical decomposition of a substance by the action of heat”
Stoichiometric mixture	“mixture of chemical reactants having proportions in accordance with the equation for a specified chemical reaction”
Stoichiometric combustion	“**combustion** in which the **equivalence ratio** is equal to unity”
Flame	“rapid, self-sustaining, sub-sonic propagation of **combustion** in a **-**

	gaseous medium, usually with emission of light”
Fire effluent	“totality of gases and aerosols, including suspended particles, created by **combustion** or **pyrolysis** in a **fire.**”
Smoke	“visible part of **fire effluent**”
Yield	“mass of a **combustion product** generated during **combustion** divided by the mass loss of the **test specimen.**”
Toxic hazard	“potential for harm resulting from exposure to **toxic combustion products**”
Toxic potency	“measure of the amount of **toxicant** required to elicit a specific **toxic** effect”
Fractional effective concentration (FEC)	“ratio of the **concentration** of an **irritant** to that concentration expected to produce a specified effect on an exposed subject of average susceptibility”
Fractional effective dose (FED)	“ratio of the **exposure dose** for an **asphyxiant** to that exposure dose of the asphyxiant expected to produce a specified effect on an exposed subject of average susceptibility”
Impaired escape capability	“effects on willingness and efficiency of **escape** actions, which may delay, slow or prevent evacuation”
Incapacitation	“state of physical inability to accomplish a specific task”
Lethal concentration 50	**“concentration** of a **toxic gas** or **fire effluent**, statistically calculated from concentration-response data, that causes death of 50% of a population of a given species within a specified **exposure time** and **post-exposure time**”
Lethal exposure dose 50	“product of LC50 and the **exposure time** over which it is determined”
Irritant	“(sensory/upper respiratory) gas or aerosol that stimulates nerve receptors in the eyes, nose, mouth, throat and respiratory tract, causing varying degrees of discomfort and pain with the initiation of numerous physiological defence responses”
Fire-safety engineering	“application of engineering methods based on scientific principles to the development or assessment of designs in the **built environment** through the analysis of specific **fire scenarios** or through the quantification of risk for a group of fire scenarios”
Fire model **or** Fire simulation	“calculation method that describes a system or process related to **fire** development, including fire dynamics and the effects of fire ex. **deterministic model**, **numerical fire model**, **physical fire model** and **probabilistic model.**”
Numerical fire model	“mathematical representation of one or more of different interconnected phenomena governing the development of a **fire**”
Means of escape	“structural means whereby routes intended to be safe are provided for persons to travel from any point in a **built environment** to a **place of safety.**”
Travel distance	“(escape from fire) distance that is necessary for a person to travel from any point within a **built environment** to the nearest exit, taking into account the layout of walls, partitions and fittings”
Flashover	“stage of fire transition to a state of total surface involvement in a **fire** of **combustible** materials within an **enclosure**”

1.7 PROBLEM DESCRIPTION

Modern fire engineering design relies heavily on computational modelling for the analysis of fire smoke hazard produced in compartment fires. The models are used for the purpose of establishing satisfactory fire strategy in buildings under development. Existing fire models, for example FDS5 (McGrattan et al., 2008a), are incapable of predicting incomplete combustion products relevant to fire smoke hazard in terms of acute lethal toxicity and/or severe irritation. The area of fire toxicity modelling is in its infancy, and model developers are restricted by the lack of information on toxic products from under-ventilated compartment fires.

The lack of information on fire smoke toxic species, not only affects the fire modelling development, but also affects the fire safety engineering current practice in general. For example, the British Standards Institution (PD-7974-1, 2002) suggests, in its latest guidance on initiating a fire within the enclosure of origin for fire safety engineering analysis, the use of 0.013 kg/kg as the CO production yield from the design fire. It also reports a range of CO yields for different fuels ranging from 0.006 to 0.063 based on (Tewarson, 2002) data for well ventilated fires. The provided numbers are not representative of the toxicity problem in ventilation controlled compartment fires. Although the standard provides a note explaining these values may be not be justified for smouldering or supressed fires, it comes short in providing information on the correct approach (PD-7974-1, 2002). Similarly, the Chartered Institution of Building Services Engineers (CIBSE) provides the same sets of data related to highly ventilated fires for the purpose of developing a design fire for hazard assessment. However, the (CIBSE, 2003) guide, notes that for ventilation restricted fires, CO production levels could reach 0.25 kg/kg.

More experienced engineers, who deploy CFD techniques, adopt what may be a better industry practice, starting with specifying a burner fire with a **fixed** heat release rate typically ranging from 1-5MW, depending on the building occupancy, and assume a **fixed** production yield of Carbon monoxide appropriate to ventilation controlled fires 0.2 kg/kg (Babrauskas et al., 1992; Grewolls, 2010; McGrattan et al., 2008a). Based on that, engineers more often than not restrict smoke hazard analysis to visibility and carbon monoxide levels. They use the output information for establishing the effectiveness of the mechanical extraction system proposed to provide clear means of escape and/or validate the building compartmentation. All, the mentioned methods of, the specified design fires, in (PD-7974-1, 2002), (CIBSE, 2003), and CFD fires, are underestimating the toxic hazard from compartment fires which is frequently reported by surviving fire victims as irritant and impairing escape.

Advancements in fire toxicity modelling, is impeded by the limited available information on fire smoke gases produced in ventilation restricted fires. There is an urgent need for precise experimental quantification of toxic yields from ventilation restricted fires, and especially irritant species (McGrattan, 2008). No complete set of data is available prior to this work.

In addition to the lack of available data on the toxic species, the toxic species assessment modelling is another area needing urgent update. This is because, although toxicity assessment models do exist, such as [N-Gas, FED, and FEC], they are often developed for different purposes, such as predicting lethality associated with materials research and development, or predicting human incapacitation. None of the models is developed to predict impairment of escape due to irritation. In addition, to make use of any existing toxicity assessment models, in hazard calculation, the assessment model requires input on all the toxic products of a fire, which is not feasible in the existing computational fire models.

Finally, the current computational capabilities restrict fire field models to track a limited number of variables. Bearing in mind, the limitation of the computational expense in fire field models, a novel approach is needed to represent the experimental data on toxic species produced in restricted ventilation fires in a summarized format useful for modelling purposes.

1.8 AIMS & OBJECTIVES

The principle aim of this work is to investigate and measure the toxic gas production in ventilation controlled fires using state-of-the-art experimental techniques. In addition, means of implementing the data in current industry fire models will be addressed. The specific objectives can be summarized as follows:

- Review available data on fire toxicity as well as the established toxicity assessment models in fire science. And their current application in computational fire models.
- Experimental investigation of the combustion products in limited ventilation fires including asphyxiant and irritant fire products, for a range of fire ventilation conditions (10-70 ACH), a range of fire burning conditions (localized burning, fast vertical propagation, smouldering, & post flashover), as well as a range of domestic and industrial fire fuels (Wood, Cotton, Acrylic, PVC Cables, Kerosene, Diesel, Toluene, and Heptane)
- Provide a quantified set of toxic gases yields produced in those fire conditions followed by toxicity assessment and toxic species ranking in terms of lethality and irritancy.
- Investigate possible correlations of toxic species production to fire equivalence ratio and temperature conditions, and provide a computationally inexpensive modelling approach to be implemented in future computational fire codes.

1.9 THESIS STRUCTURE

This thesis is divided into ten chapters. **Chapter 1** provides a short introduction to the fire toxicity problem including statistical overview and basic concepts of compartment fires followed by the aims and objectives of this work.

Chapter 2 provides the reader with more insight into the current status of published knowledge on the area of fire toxicity. It provides a literature review on topics related to this work; including previous studies on compartment fires, toxic effluent measurement methods, and toxicity evaluation and modelling. **Chapter 3** covers the methodology and experimental set up used in this work. Instrumentation and methodology used in the research conducted in this lab has been discussed in detail. In addition, CO equivalent toxicity methodology is presented in this chapter.

Chapter 4 provides an intensive study on toxic effluents from wood crib fire loads. It consist of an investigation on the effect of factors such as ventilation, fuel orientation, and fuel load density on the produced fire toxicity both in pre flashover and post flashover fires. The fire effluent is analysed and presented in terms of species yields, as well as lethal and sub lethal concentrations. The species produced are further analysed and ranked based on the toxic potency measure used.

Chapter 5 is an investigating on the burning behaviour of wood loads in the later stages of a fire. Wood, cribs are burnt in a gas fire furnace, to provide a quantification of the toxic yields, in conditions corresponding to post flashover fires.

Chapter 6 comprises a study on folded cotton towels fuel loads. Slow smouldering burning smouldering folded towels. In both sections, a range of ventilations is studied, and the toxic effluent is analysed in terms of lethality and sub lethality measures, based on which further analysis and ranking of toxic species is provided.

Chapter 7 provides a study on hanging acrylic curtains as a fast burning fire load. The fires represent a nitrogen containing fuel, where a different set of toxic species are expected. Similar to chapters 4 and 5 the toxic smoke results are analysed and reported in details.

Chapter 8 provides a study on hydrocarbon pool fires burning in low ventilation conditions. It starts with an investigation on the effect of ventilation on kerosene pool fires burning behaviour and toxic species production. This is followed by further investigation on the burning of different hydrocarbon fuels including Heptane, Toluene, and Diesel at low ventilation rates burning conditions.

Chapter 9 provides a summary of the main findings of this work, the conclusions, and recommendations for future work.

2. CHAPTER 2:

BACKGROUND & LITERATURE REVIEW

2.1 INTRODUCTION

The aim of this chapter is to provide the reader with the relevant background to this project. It starts with a short overview of the historical development of fire science and the emergence of fire toxicity as a fundamental part of the field. This is followed by, a theoretical background on compartment fires, including the different fire stages, fire development, and compartment fire characteristics. An in depth investigation to the fire toxic components, is then presented in section 2.3. A literature review of the relevant previous studies categorized into full scale studies, reduced scale enclosures studies, and bench scale studies is provided in section 2.4 and its subsections. The arguments around the advantages and disadvantages of the methods used in those studies are covered in detail. Quantification of the toxic hazard is also discussed in detail, and the final sections cover the existing fire models, and the limitations associated with toxic hazard modelling. It is expected that this chapter will set the scene for the experimental and theoretical methodology of this work, presented in chapter 3 and, provide basis for comparison, extrapolation and analysis in the subsequent chapters of this thesis.

2.1.1 DEVELOPMENT OF FIRE SAFETY ENGINEERING

Fire safety engineering (FSE) is considered a relatively new engineering discipline in terms of formal university education and research. The recognition of FSE as a distinctive scientific subject has only existed for few decades. This is relatively shorter than many engineering disciplines which have been taught in university across Europe for more than 200 years (Drysdale, 2010).

Nevertheless, as in many other areas, FSE derived from empiricism has existed for centuries. One example, of the progress through experience, is the developments of building regulations that included the use of non-combustible building structures, and spacing between buildings after the great fire of London in 1666. Other examples include the great theatre royal fire in 1887 and the empire palace theatre fire in 1911, which resulted in the use of fire proof curtains, and the adoption of 2.5 minutes as the standard evacuation time (Drysdale, 2010).

However, the most significant advances came in post the Second World War, during the second half of the previous century, when governmentally funded fire research bodies were established. The Fire Research Station in the United Kingdom, currently under the Building Research Establishment (BRE), the Fire Research Institute in Japan, and the Center for Fire Research at NBS now part of the National Institute for Standards and Technology (NIST) in the USA, were all working on the fundamentals of fire phenomena and the emerging field of fire dynamics (Drysdale, 2010). Technical reports produced from the mentioned establishments, along with the fundamentals of combustion and chemistry formed the early foundations of the FSE. Before long, the field was boosted by the emergence of university programs on the subject in the 1980's and 1990's, resulting in noticeable progress of scientific research in the field.

In the UK, over the past few decades building regulations have moved away from prescriptive regulations to functional regulations supported by detailed technical guidance. This resulted in a direct need for specialist and highly qualified fire safety engineers to accommodate the needs of the industry and its regulators. Subsequently, fire safety engineering programs have been developed based on the available knowledge drawn from the early technical reports, and demand was even higher for better understanding of the fire phenomena. From then on, the standards for scientific research in the field noticed a considerable improvement (Hull and Stec, 2010).

As the fire safety engineering advanced, several interconnected research areas grew within, the scope of fire engineering. Topics such as fire dynamics, fire chemistry, fire risk analysis, fire toxicity, fire modelling, came into existence. Furthermore, within these main topics more specific topics develop based on different views towards the problem investigated.

In fire toxicity studies, the most relevant area to this work, a large amount of the previous work was conducted based on two main views on the fire toxicity problem. Purser explains, one view on the reason behind the increase in fire smoke casualties, is that modern synthetic materials could have super toxic products (Purser, 2002). This view gained wide acceptance after super toxicants were detected in laboratory burning conditions from fire retarded materials. In theory, the supporters of this approach promote the use of small scale tests for burning new materials, and ranking its combustion products in terms of lethal dose produced (LC_{50}). Based on these tests, engineers are advised on which materials are available for use. Thus having control on the amount of possible toxic combustion products. This can be called materials based approach to toxicity (Purser, 2002).

The other view however, favours the hypothesis that incomplete combustion fire products were more or less the same over the years, but the increase in fire toxicity threat is due to the fact that modern living standards promote more confined fires with high growth rate resulting in fire conditions with higher toxic effluent. Thus, the focus of the research was on how to prevent or suppress factors leading to the toxic hazard conditions in terms of combustion product conditions. Factors such as ignition, flame spread, and rate of smoke production, were the focus of the research rather than attempting to quantify the toxic products in details. As a result, the experimental work focused on replicating fire conditions to obtain toxic yields relevant to realistic fire conditions. The favoured approach was conducting full scale tests with typical room loading such as a hotel room load to obtain major toxicants yields. Another approach was the use of smaller scale apparatus to replicate different fire conditions and obtain the toxic products yields. These yields are then used by engineers to construct different fire scenarios and estimate the time to incapacitation or death. The main weakness in this approach is that it is based on simplistic and erroneous assumptions regarding the amounts, effects, and interaction of toxic products. (Purser, 2002)

In addition to the research venues reported earlier, more work was put into attempts for developing suitable models to evaluate the toxic hazard from fire effluent. Starting with the rather simplistic 6 gas N model introduced by Levin and Babrasukas, and progressing to the improved versions of Fractional Effective Dose (FED), Fractional Effective Concentration (FEC), and Fractional Irritant Concentration (FIC) developed by Purser and others in the ISO standards. These models will be discussed in detail in the later sections of this chapter.

For significant development in the use of fire toxicity in engineering practices, including computational fire modelling, there exists a need for all of the above research areas. Small scale testing provides quantified yields of toxic species distinguishing the different materials, as well as medium scale and full scale for combustion conditions profile modelling. The information gained on toxic yields can then be implemented in conjunction with the toxicity assessment models in the computational code.

It is widely recognized that the current information on fire toxicity yields from compartment fires is insufficient and inadequate for use in computational codes and other engineering application. Available information is usually incomplete in details, and in many cases misleading. (McGrattan, 2008; Purser, 2002; Purser, 2010c) this raises the need for better standards of research and testing to avoid the weakness in previous studies highlighted in the following sections.

2.1.2 DEVELOPMENT OF FIRE COMPUTATIONAL CODES

Alongside the fundamental studies on compartment fires phenomena, a great interest in developing computational fire models developed. Early work include developing probabilistic models which investigate the chances of fire development from one stage to another based on mathematical rules obtained from historical and experimental data. However, the surge in computational power, in the past three decades, has shifted the interest into more deterministic computational modelling approach, which attempt to calculate the fire conditions in the enclosure based on interrelated conversation of mass and energy mathematical equations. These models can be classified into zone models and field models.

Current zone models typically capitalize on the critical fact that hot smoke tends to collect at the upper layer of the compartment due to buoyancy, and that the near floor region usually consist of relatively clean colder air. Consequently, in zone models the fire enclosure is divided into upper layer (Zone) and lower layer (Zone), with the temperature of each layer calculated from conversation of energy, the smoke from conservation of chemical species, and the height from conservation of mass. In addition, the losses to the opening and vents are usually taken into account. The most widely used zone model is CFAST by (Jones et al., 2000) from NIST, but several others are available such as: ASET-B by (Walton, 1985), BRANZFIRE by (Wade, 2004) and several others.

The other main stream of fire models adopted by engineers and scientists is called Field Models, which are based on Computational Fluid Dynamics (CFD) principles. In a CFD model each compartment is broken down to hundreds of thousands or millions of cells. Mathematical descriptions of mass, energy, species, and momentum conservation are enforced at each cell. The computational code, attempts to solve all these coupled equations to give a detailed description of the fire development. The most accredited code of this type is the Fire Dynamics Simulator FDS developed at NIST, parts of which are discussed in details in later sections. Nonetheless, several other codes are available including the general-purpose CFD codes such as PHONEICS, STAR-CD, ANSYS-CFX, and ANSYS-FLUENT, which may be used for fire modelling to a limited extent, and the more specific fire purpose models such as: JASMINE (developed by Fire Research Station, UK), KAMELON (developed by SINTEF/NTH, Norway), SMARTFIRE (developed by University of Greenwich, UK), SOFIE (developed by Cranfield University/Fire Research Station, UK), and FireFOAM an open source code maintained by OpenCFD Ltd.

CFD models provide a more detailed analysis than Zone models; they provide detailed information in each cell of the investigated domain, which can then be incorporated into visualizations software such as SomkeVIEW an animated video effective for presentations and analysis. However limitations, arise from the limited computational power available for the developers and users of the code. The complexity of fire process makes it one of the most challenging areas for CFD development as typical computational fire code consists of multiple sub codes solving a transient problem.

Therefore, any advancement is typically weighed in terms of gained accuracy against increase in computational cost.

2.2 COMPARTMENT FIRES THEORETICAL BACKGROUND

In this section, an elaboration on the initial description of compartment fires provided in the introduction is first reported; this is followed by basic principles of combustion process, along with their applicability to compartment fires research. The final part is a discussion on the compartment fire types, characterisation, and ISO fire classification of compartment fires for the purpose of toxicity studies.

2.2.1 GROWTH STAGE

The growth of an isolated fire in a compartment, to that where there is full room involvement has been briefly introduced in the previous chapter. The pre-flashover or growth stage is directly relevant to life safety, with flashover representing an ultimate limiting point for survival for the occupants of the fire compartment. In (Marchant, 1976) (Drysdale, 1998) expressed this with an inequality:

$$t_p + t_a + t_{rs} \leq t_u \tag{2.1}$$

where, t_p = the time to detection from ignition.

t_a = the time between detection and the beginning of escape activity.

t_{rs} = the time for the occupants to move to a place of relative safety.

t_u = the time from ignition for the fire to reach untenable conditions.

Before the development of oxygen consumption calorimetry, the only means of determining the HRR was by multiplying the fuel burning rate by the effective heat of combustion (ΔH_{eff}). The latter is the product of the heat of combustion (ΔH_c) and an efficiency factor (χ or η_{comb}) which reflects the unreleased heat release due to incomplete combustion (values between 0.4 – 0.7 (Tewarson, 1980). For this reason, the burning rate has been one of the most investigated parameters in the area of compartment fire research.

The burning rate of a fuel in the earliest stages of a compartment fire may be compared with an isolated fuel burning in the open, where the mass flux may be written as:

$$\dot{m}''_b = \frac{\dot{Q}''_F - \dot{Q}''_L}{L_v} \quad (\text{kg.m}^{-2}.\text{s}^{-1}) \tag{2.2}$$

where, $\dot{Q}''_F$ is the heat flux from the flame to the fuel bed (which is predominantly by radiation for fuel beds greater than 0.2m - 0.3m in diameter ((Babrauskas, 1995),

$\dot{Q}''_L$ is the heat lost to the environment through the fuel surface and;

L_v is the latent heat of vaporisation of the fuel,

with the large majority of the heat liberated during combustion being lost to the environment. However, in compartment fires, some of the heat otherwise lost is trapped under the ceiling. With time (particularly if there is flame impingement on the ceiling), this heated layer is able to exert an influence, namely a radiative heat flux back to the fuel bed, and thus Eq. 2.2 becomes:

$$\dot{m}''_b = \frac{\dot{Q}''_F + \dot{Q}''_E - \dot{Q}''_L}{L_v} \quad (\text{kg.m}^{-2}.\text{s}^{-1}) \tag{2.3}$$

where, $\dot{Q}''_E$ is the external heat flux acting on the fuel surface.

The effect of this heat flux is to increase the mass flux of the fuel. While this serves to increase the burning rate, more significantly, as the fuel area is a function of the mass flux, it will also serve to promote flame spread to adjacent combustible materials.

The effect of incident heat flux from the upper-layer, while not significant in wooden crib fires in enhancing the mass burning rate (because of shielding effect to material underneath provided by the crib’s structure and the low thermal conductivity of the surface char (Harmathy, 1978), it has a significant effect on liquid fuels (including thermo-plastics). (Bullen and Thomas, 1979)), in addition to (Takeda and Akita, 1981) and (Fleischmann and Parkes, 1997)), recorded enhanced burning rates of as high as 6 to 8 times the open burning rate for a number of liquid and thermoplastic fuels in small-scale tests

The early stages of a fire nearly always show acceleration in growth. Although a number of mathematical descriptions of fire growth can be employed, including exponential (e^t) and parabolic (t^n) functions; experimental studies (Heskstad, 1982; Schifiliti, 2002), have shown that a t^2 parabolic function (known a t^2 fire) gives a reasonable approximation of the accelerating fire growth. This relationship (Eq. 2.4) has proven to be a valuable tool to fire engineers in the initial appraisal of the risks and consequences that a particular fire scenario may pose to a building. Such an evaluation (known as a *design-fire*) can therefore allow a more enlightened investigation of the performance of prescriptive fire-safety measures, to ensure building codes are adequately and economically met.

$$\dot{Q}_g = \alpha(t - t_0)^2 \quad \text{(kW)} \tag{2.4}$$

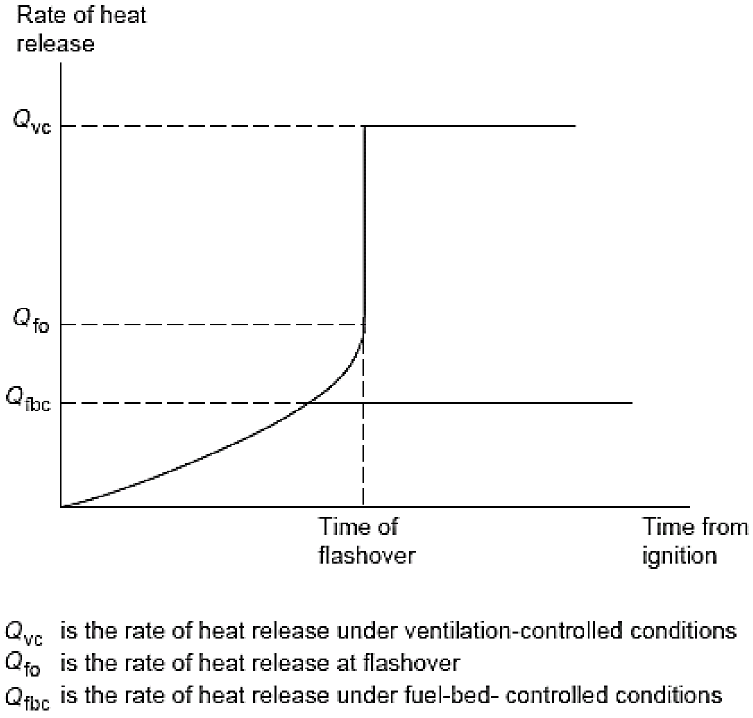
where, $\dot{Q}_g$ is the HRR of the fire during the period of growth, α is the growth rate coefficient or factor (kW.s^{-2}) and t_0 is the length of the incubation period (s).

In order to give a reasonable estimate of the rate of fire growth for a specific building, an understanding of its likely use (thus, the combustible materials present) is required. To account for this, there are four generic growth rate coefficients available, corresponding to ultra-fast, fast, medium and slow growth rates (PD-7974-1, 2002). For more precise determinations, (Schifiliti, 2002) published experimentally derived values of α, for a wide variety of individual items of furniture.

Table 2-1: Fire growth rate coefficients and time to reach heat release rate of 1000 (PD-7974-1, 2002).

Fire growth rate	Fire growth rate coefficient (kW.s-2)	Time for $\dot{Q}_g$ = 1000 kW (s)
Slow	0.0029	600
Medium	0.012	300
Fast	0.047	150
Ultra-fast	0.188	75

When determining the complete HRR history of a fire using these methods, the HRR during the fully-developed phase is nearly always taken as a constant. Providing there is sufficient fuel and ventilation to allow the fire to flash over, the HRR may be considered to grow as a t^2 fire up until this time. As equations are available to determine the HRR required for flashover as in (PD-7974-1, 2002), the time to flashover may be determined from compartment characteristics. Integration techniques will further allow the total heat released by the fire during the growth phase to be determined, which may be usefully employed to gauge the quantity of fuel remaining in the compartment.



Q_{vc} is the rate of heat release under ventilation-controlled conditions
Q_{fo} is the rate of heat release at flashover
Q_{fbc} is the rate of heat release under fuel-bed- controlled conditions

Figure 2-1 Design fire heat release rate, (PD-7974-1, 2002).

Presuming fuel quantity, ventilation and compartment characteristics allow flashover to occur, the fire HRR is usually assumed to jump immediately from the HRR for flashover ($\dot{Q}_{FO}$ in Figure 2-1) to that dictated by the ventilation ($\dot{Q}_{VC}$). Thereafter, the HRR is assumed to remain constant for the fully-developed phase. As the fully-developed phase may be considered to end once 80% of the fuel has been consumed, knowledge of the total fuel-load present for a specific compartment will allow the duration of the fully-developed phase to be determined. If ventilation-controlled burning is not established the maximum (constant) HRR must be determined from the amount, type and presentation of the combustible contents (calculation methodologies for both scenarios are published in (PD-7974-1, 2002). Thus, the fire safety engineer will have a reasonable estimate of the complete fire HRR history, accounting for known factors such as the fuel-load and compartment construction.

2.2.2 FLASHOVER

Flashover has been investigated by a number of workers, although the work and data of (Waterman, 1968) and that of (Hagglund et al., 1974) are amongst the most widely accepted. (Hagglund et al., 1974) defined the onset of flashover in a full-scale compartment, as the point at which paper targets situated at floor level were ignited by the incident radiant heat flux. He concluded that a heat flux of 20 kW.m^{-2} (at floor level) was required for flashover to occur, postulating that this heat flux came solely from the upper-layer and not from the flames above the fuel. While it has been argued that a heat flux of 20 kW.m^{-2} would be too low for spontaneous ignition of 'thick' pieces of wood or other combustible items (Martin and Wiersma, 1979), it would be sufficient to allow pilot ignition and rapid flame spread on such items. Waterman also found that flashover was not recorded until the burning rate exceeded 40g.s^{-1}.

(Hagglund et al., 1974) also investigated the conditions necessary for flashover to occur. Based on a different definition of the onset of flashover, (Hagglund et al., 1974) burnt wooden cribs of various sizes in a full-scale compartment, measuring parameters such as the compartment temperature, airflow and burning rates for a number of inlet openings. They found that for flashover to occur, the following criteria had to be met:

- Compartment temperatures of >600^{o}C.
- Burning rates of >80g.s^{-1}.
- Ventilation factors ($A_v H_v^{1/2}$) of >0.8m$^{5/2}$.

From their results, (Hagglund et al., 1974)developed an expression (Eq.2.5) for the limiting burning rate for flashover to occur (i.e. mass burning rate must be greater than this value for the fire to flash over).

$$\dot{m}_{\text{limit}} = 50 + 33.3 A_v H_v^{1/2} \quad (\text{g.s}^{-1}) \tag{2.5}$$

As this work was carried out in a full-scale compartment (ceiling height of 2.7m), if flashover involves heat being radiated to the lower-layer by the upper-layer, it should therefore be related to the compartment height - it would be anticipated that small-scale compartments would experience flashover at lower upper-layer temperatures, due to the fact that the heat feedback mechanism would be greater. This was confirmed by (Heselden and Melinek, 1975), who recorded upper-layer temperatures of 450^{o}C at flashover for their small-scale experiments.

(Babrauskas, 1980) expressed the point at which flashover occurred in terms of the fire's HRR, by employing a simple heat balance based about the assumption that flashover occurred at an average upper-layer temperature of 600^{o}C and that heat losses were to the floor and walls below the hot-layer only. He was able to deduce that the HRR necessary for flashover ($\dot{Q}_{FO}$) was:

$$\dot{Q}_{FO} = 600 A_v H_v^{1/2} \quad (\text{kW}) \tag{2.6}$$

Based upon a slightly more complex model by (Quintiere et al., 1978) in which a simple heat balance was applied to the upper-layer, McCaffrey *et al*. (Drysdale, 1998), using (Rockett, 1976) expression for the gas flow from an opening, derived a term for $\Delta T / T_a$ in terms of two dimensionless groups. By analysing the data from more than 100 experiments where steady burning rates were achieved (but the upper-layer temperature did not reach 600^{o}C), and deriving a suitable expression for h_k (the effective heat coefficient – kW.m^{-2}), McCaffrey *et al.* were able to derive an expression for the HRR required for flashover, using linear regression techniques.

$$\dot{Q}_{FO} = 610\left(h_k A_T A_v H_v^{1/2}\right)^{1/2} \quad (\text{kW}) \tag{2.7}$$

where A_T is the internal area (m^2) of the compartment less the area of any opening.

This expression particularly highlights the importance of the lining materials used in the construction of a compartment. The drive for highly insulated linings in buildings for energy efficiency has, as a result, meant that the HRR required for flashover has been markedly reduced and as a consequence, so has the time for escape.

The data employed to obtain Eq. 2.7 was taken from both small and full-scale compartments, of cubical dimensions with the fire centrally located (Lee, 1982) and later (Mowrer and Williamson, 1987) investigated the effect of fire position with regard to the HRR required for flashover. They concluded that the heat release required for flashover was less for a fire next to the wall, and least for the corner position.

2.2.3 HEAT RELEASE RATE CALCULATION

While the HRR time-histories for complex items may be estimated from their constituent materials and arrangements, such a procedure is subject to a degree of uncertainty. It was not until the development of oxygen consumption calorimetry (Huggett, 1980), and particularly the larger-scale calorimeters (furniture calorimeter (Babrauskas et al., 1991b) and full-room calorimeter, that allowed the HRR time-histories for items of furniture to be accurately measured.

Furniture calorimeters and room calorimeters operate in essentially a similar manner to the cone calorimeter (Babrauskas, 1995). An item (or items) of furniture are burnt under a hood, which collects and continuously removes the products of combustion, measuring their temperature and flow-rate (room calorimeter collects the products of combustion in hood upon exiting the compartment)**.** The products of combustion are continuously analysed for their O_2, CO_2 and CO concentrations, which are used to determine the HRR based on oxygen deficiency.

If the simplest method of HRR calculation ($\dot{m}_b \Delta H_c$) may be written in terms of the inlet air flow, for as long as all the oxygen in that flow is consumed during the combustion processes of the fuel Eq.2.8 :

$$\dot{Q}_C = \dot{m}_b \Delta H_c . r \quad \text{(kW)} \tag{2.8}$$

where, ΔH_c is the heat of combustion and r is the stoichiometric F/A ratio. Thornton and later (Huggett, 1980) found that the term $\Delta H_c.r$ (the heat of combustion per unit mass of air - $\Delta H_{c,air}$) is approximately constant for many hydrocarbons (≈3.1

kJ.g^{-1}), and is the heat of combustion per unit mass of air termed $\Delta H_{c,air}$. As the oxygen concentration in air is constant, a similar heat of combustion may be defined in terms of oxygen $\Delta H_{c,ox}$ (≈13.1 kJ.g^{-1}).

In order to account for the reduction in HRR by the incomplete consumption of oxygen, Eq. 2.8 may be re-written as:

$$\dot{Q}_C = (0.21 - \eta_{O_2}) \times \dot{V}_a \times 1000 \times \rho_{O_2} \times \Delta H_{c,ox} \text{ (kW)} \tag{2.9}$$

where η_{O_2} is the measured 'scrubbed' oxygen volume fraction, $\dot{V}_a$ is the volume flow rate of air entering the compartment (m^3.s^{-1}) and ρ_{O_2} is the density of oxygen at normal temperature and pressure (kg.m^{-3}). The numerical constant is required to maintain units as $\Delta H_{c,ox}$ is usually expressed in kJ.g^{-1}. As the O_2 concentration of the exhaust products is required in the calculation, Eq. 2.9 is equally suited to HRR determinations in well-ventilated conditions. This forms the basis for oxygen consumption calorimetry.

(Janssens, 2002) published equations in his review paper on calorimetry, based on the number of combustion products measured in the exhaust, estimating that even under the worst conditions, the error by ignoring CO generation in oxygen consumption calorimetry is <5%. However, oxygen consumption calorimetry is typically carried out under well-ventilated conditions, where CO production will generally be low. The ventilation-controlled conditions encountered in compartment fires can produce significantly larger quantities of CO (in addition to unburnt hydrocarbons and soot), which all serve to reduce the HRR, making efficiency correction all the more necessary. A general review of HRR calculation methods was published by (Janssens, 2002) which includes procedures, equations and details of both small and large scale apparatus. A similar paper has been written by (Babrauskas, 1995) specific to cone calorimetry.

2.2.4 FULLY DEVELOPED FIRE

Once a fire has reached flashover, the fully-developed stage is characterised by comparatively constant HRRs, temperatures, burning rates and species concentrations. This section highlights some of the most notable work carried out over the last few decades in post-flashover compartment fire-dynamics, in this the most researched stage due to its quasi-steady state characteristics. The fully-developed fire is generally considered to be related to property protection rather than life protection (for the compartment of origin) as survival past flashover is impossible. However, life protection still remains an important issue, products of combustion will travel from the compartment of origin, and present in life threatening quantities in remote areas of the building, and a number of studies (Gottuk, 1992a; Gottuk et al., 1995; Gottuk et al., 1992; Gottuk, 1992b; Gottuk, 1995) have investigated the toxic species transport from the compartment of origin.

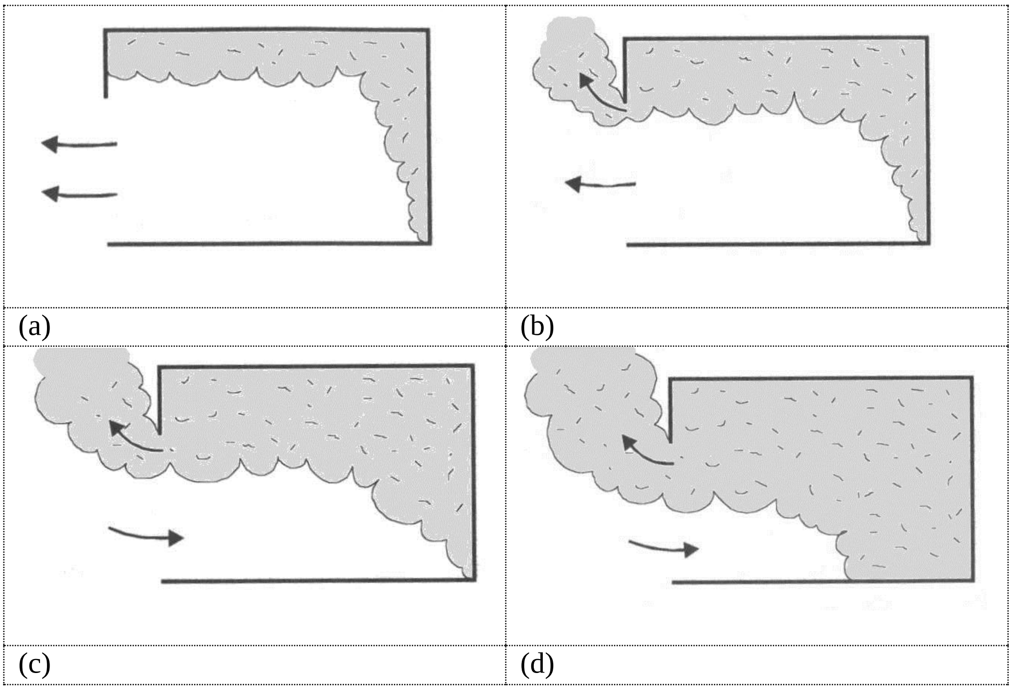

(a)
(b)
(c)
(d)

Figure 2-2 Air and product flows encountered during the growth (a, b & c) and fully-developed (d) phases of a compartment fire.

As a fire develops within a compartment, hot combustion products accumulate under the ceiling, while fresh air is entrained at low levels to support combustion. As the hot products build up under the ceiling, a distinct interface will form between the fire products and cool air below. With continued burning, the interface will descend until it reaches a vent, at which point combustion products will begin to flow out. Eventually, proximate equilibrium is established between the outflow of fire products and the inflow of air in figure 2-2. This bi-directional flow is separated by a neutral plane, where it is assumed that there is no flow, although realistically there is some turbulent mixing due to shear forces between the opposing flows.

The first major study into the rate of air entrainment into a fire compartment, was conducted in the late 1950s by (Kawagoe, 1958) noting that the basis of the calculations used stems back to work by Y.C Yesmann in 1911 (Babrauskas and Williamson, 1978) for window flows. Kawagoe's model assumed that:

- The burning compartment was at uniform temperature.
- The movement of gases (in and out of the compartment) was caused by a static pressure field induced by the temperature difference between the hot fire compartment and cool atmosphere.

By applying Bernoulli's equation to the two gas flows, Kawagoe (1958) derived an expression that linked the air flow into a compartment to the vent opening dimensions.

$$\dot{m}_a \approx \frac{2}{3} A_v H_v^{1/2} C_d \rho_a (2g)^{1/2} \left(\frac{(\rho_a - \rho_g)/\rho_a}{\left[1 + (\rho_a/\rho_g)^{1/3}\right]^3} \right)^{1/2} \quad \text{(kg.s}^{-1}\text{)} \tag{2.10}$$

where, A_v, H_v and C_d are the area, height and discharge coefficient of the opening vent, while ρ_a and ρ_g are the ambient air and internal flue gases densities respectively. The substitution of typical values of air and product density, discharge coefficient and gravity, allowed Kawagoe to approximate the inflow of air as:

$$\dot{m}_a \approx 0.52 A_v H_v^{1/2} \quad \text{(kg.s}^{-1}\text{)} \tag{2.11}$$

Because of the assumptions made, Kawagoe's flow model is only really suited to the fully-developed stage of a compartment fire. In order to find an expression that was more suitable over a wider range of conditions**,** (Rockett, 1976) developed Kawagoe's work, by deriving flow equations using more realistic assumptions, making their work more relevant to the earlier stages of a fire history. In this respect, by assuming that the temperature within a compartment was no longer uniform (with a steep thermal gradient existing between the upper and lower-layers), the work of (Rockett, 1976) was the most relevant. Additionally, by employing plume-entrainment theory to establish the height of the thermal discontinuity, (Rockett, 1976) was the first to introduce the effect of convective entrainment within an enclosure. This moves away from the idea that the inflow of air is controlled by a static pressure differential between two layers of dissimilar temperature, but rather that it is due to the air-entraining abilities of the fire plume.

In systematic fire studies, one popular technique is the use of a separate air entrainment compartment often placed below the main combustion room. This allows of a measurable sealed air supply system, eliminating the uncertainty associated with estimating the air flow to the compartment. This technique was deployed in published work in (Andrews et al., 2005b; Andrews et al., 2005a; Gottuk, 1992a; Gottuk et al., 1995; Gottuk et al., 1992; Gottuk, 1992b; Gottuk, 1995; Lattimer, 1996; Lattimer et al., 2005; Lattimer et al., 1994; Lattimer et al., 1998) and the author of this work (Aljumaiah et al., 2010a; Aljumaiah et al., 2010b; Aljumaiah et al., 2010c; Aljumaiah et al., 2011b; Aljumaiah et al., 2011a; Aljumaiah et al., 2008; Aljumaiah et al., 2010d).

2.2.6 COMBUSTION STOICHIOMETRY & SPECIES YIELDS

2.2.6.1 Basic stoichiometry

A classic example to introduce combustion stoichiometry is the combustion of methane under ideal conditions, where there is sufficient oxygen to enable all the carbon and hydrogen atoms in the fuel to be fully oxidised into carbon dioxide and water respectively (i.e. complete combustion):

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2$$

It can be seen that for every molecule of Methane (CH_4), 2 molecules of oxygen are required. This is often expressed as ratio of masses in experimental work as follows; for every 16grams of methane, 64grams of oxygen or ≈275grams of air are required for the complete or *stoichiometric* combustion of the fuel (i.e. a fuel to air ratio of 0.0582).

If there isn’t sufficient air to allow complete combustion, products of incomplete combustion will be produced - in the form of CO, H_2, unburnt hydrocarbons and soot. If only 1 molecule of oxygen is available for combustion, the air mass will be ≈138grams and thus the fuel to air ratio will be 0.1164. These conditions may be termed **fuel-rich** or **under-ventilated fire**.

Alternately, if there was more air than required for the fuel to burn completely, unreacted oxygen would be found in the combustion products. While combustion would still be complete, the fuel to air ratio would reflect this additional air, and give a value less than that for stoichiometric combustion. These conditions are usually referred to as **fuel-lean** or **over-ventilated fire**.

The earlier methane example may be extended to ta more complex fuel more relevant to fires, and burning in an ideal complete combustion as follows:

$$\text{Fuel [C, H, O, N, Cl, F, Br] + Air} \rightarrow \text{Products [}CO_2\text{, }H_2O\text{, }N_2\text{, }Cl_2\text{, }F_2\text{ Br]}$$

Nevertheless, in a realistic fire scenario the products are not limited to the ideal combustion products, and most likely will include the following:

$$CO_2\text{, CO, }H_2O\text{, UHC, Soot (C), }N_2\text{, HCN, HCL, HF, HB, e.t.}$$

As different fuels' chemical compositions will require different amounts of air for complete combustion, it is advantageous to relate the actual combustion conditions to those required for complete combustion. This would give a good indication of the actual combustion conditions present, the likely combustion products formed and the efficiency of combustion. This indication is given by the *equivalence ratio* (ϕ), and is calculated as in Eq. 2.12.

$$\phi = \frac{\text{F/A}_{actual}}{\text{F/A}_{stoichiometric}} \tag{2.12}$$

where, F/A is the ratio of fuel to air by mass.

Although the equivalence ratio concept is relatively clearly defined in most combustion studies; some slight variations do exist in the fire literature. Below are some of specified definitions used by different researchers:

Plume Equivalence Ratio (PER): the ratio of the gaseous fuel generation rate at the fuel surface to the air entrainment rate into the flame between the fuel surface and the hot layer/cold layer interface normalized by the stoichiometric ratio for the fuel. (Beyler, 1983; Bryner et al., 1994; Pitts, 1994)

Upper Layer Equivalence Ratio*:* the ratio of the mass of gas in the upper layer derived from the fuel divided by that introduced from air normalized by the stoichiometric ratio for the fuel. (Gottuk, 2002; Morehart, 1991; Pitts et al., 1994)

Global Equivalence Ratio (GER): The ratio of the fuel mass loss rate within the compartment to the air flow rate into the compartment, normalized by the stoichiometric ratio for the fuel (Gottuk, 2002; Pitts et al., 1994)

Another measure of the quantity of fuel relative to the oxygen/air available for oxidation is the mixture fraction. It has a one to one relationship to the equivalence ratio. The Fuel mixture fraction can be given as:

$$\mathrm{f} = \frac{\mathrm{m}_{\text{fuel atoms}}}{\mathrm{m}_{mixture}} \qquad (2.13)$$

where, $\mathrm{m}_{\text{fuel atoms}}$ is the mass of atoms that were originally fuel, and

$\mathrm{m}_{mixture}$ is the mass of the gaseous mixture.

It is often preferred by modern computational field developers, as it provides an easier mathematical expression to be implemented in computer codes. In addition, it allows an easier computation of the conservation of species and adding/removing extra variables to the mixture such as soot and CO. However, the equivalence ratio is more adopted by experimentalists, as it provides the data with a clearly defined fuel lean and fuel rich regions at ϕ =1, excluding irrelevant zones of the theoretical mixture fraction. Figure 2-3 provides an example the 1:1 relationship between mixture fraction and fuel equivalence ratio in Methane-Air mixture, and Heptane-Air mixture.

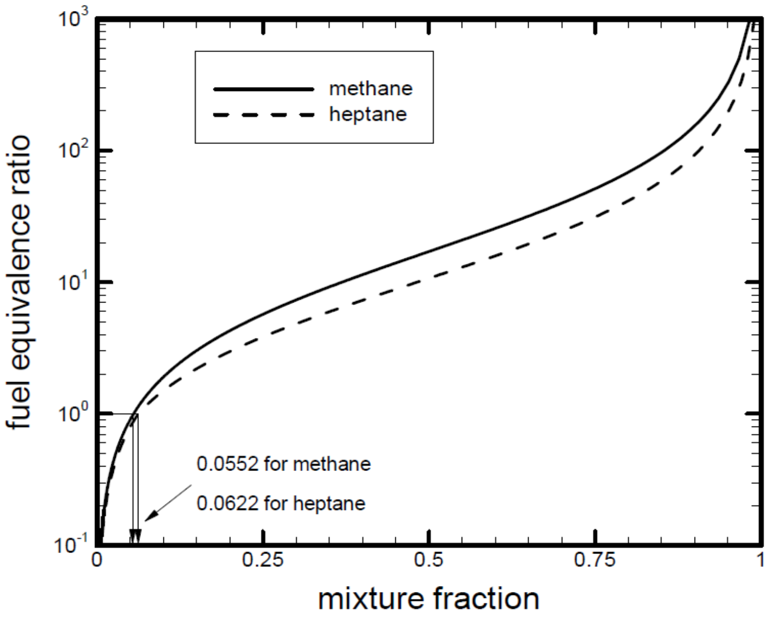


Figure 2-3: Direct conversion between mixture fraction and equivalence ratio adopted from (Bundy et al., 2007).

2.2.6.2 Species yields

In fire studies, a major aim is to be able to quantitatively predict the combustion product species. It has been found useful to report the resultant species mass originating from the fire process in terms of the mass loss of the fuel. This is different from the burning (reaction) rate of the fuel, as not all of the fuel will react. In other words the system studied could be fuel-rich and have unburnt fuel. The yield of species *i* can be expressed as:

$$Y_i = \frac{mi}{mf} \qquad (\mathrm{g.g^{-1}}) \tag{2.14}$$

where, *mi* is the mass of species *i* produced, and *mf* is the mass of mass lost in gasification.

A more useful way to calculate the yield Y_i of any species *i* experimentally from a two-layer system, may be determined as given by (Gottuk, 2002):

$$Y_i = \frac{X_{i,wet}\left(\dot{m}_f + \dot{m}_a\right)M_i}{\dot{m}_f M_{mix}} \quad (\text{g.g}^{-1}) \qquad (2.15)$$

where, $X_{i,wet}$ is the wet concentration (mole fraction) of species i,

M_i is its molecular mass,

M_{mix} is the molecular mass of the combustion product mixture (assumed air),

$\dot{m}_f$ is the mass volatilisation rate of the fuel (g.s^{-1}) and

$\dot{m}_a$ is the air-entrainment rate into the upper-layer (g.s^{-1}).

Simplifying the expression presented by Gottuk by replacing the mass ratio of fuel and air with the *A/F* provides the expression in Eq. 2.16 which is similar to the *Emission Indices* commonly used in engine research (ISO-8178, 2006). This form of the equation is more convenient when *A/F* is determined from gas analysis using carbon balance techniques.

$$Y_i = Cg_i \times \frac{MW_i}{MW_{air}} \times \left(1 + {}^{A}\!/_{F}\right) \quad (\text{kg.kg}^{-1}) \qquad (2.16)$$

where, C_{gi} is the concentration of the component, which if measured in ppm or %, should be multiplied by 10^{-6} or 10^{-2} respectively, and

$\frac{MW_i}{MW_{air}}$ is ratio of molecular weight of the toxic species to the molecular weight of the whole sample gas.

(Gottuk, 2002) also present the following mathematical expression for calculating the Oxygen depletion per mass of fuel consumed:

$$Y_{O_2} = \frac{0.21\dot{m}_a\left(\frac{M_{O_2}}{M_a}\right) - X_{O_2,wet}\left(\dot{m}_b + \dot{m}_a\right)\left(\frac{M_{O_2}}{M_{mix}}\right)}{\dot{m}_b} \quad (\text{g.g}^{-1}\text{fuel}) \qquad (2.17)$$

It should be noted that both Eq.2.15 and Eq. 2.17 require species concentrations to be measured *wet*. However, to prevent instrument damage, water removal from the exhaust gas sample is often necessary. Therefore, some species (usually CO_2, CO and O_2) will be measured *dry* and therefore, their measured concentrations will be higher than if measured *wet*. The relationship between the wet and dry concentrations is given by:

$$X_{i,wet} = \left(1 - X_{H_2O,wet}\right) X_{i,dry} \tag{2.18}$$

As reliable water measurements are difficult to obtain (Gottuk, 2002), Gottuk made the conversion between *dry* and *wet* gas concentrations by assuming that the molar ratio *C*, between water and carbon dioxide remains constant regardless of equivalence ratio (value determined from stoichiometric calculations i.e. $\phi = 1$). This allows to be re-arranged to:

$$X_{i,wet} = \frac{X_{i,dry}}{1 + CX_{CO_2,dry}} \tag{2.19}$$

This assumption was found to give an error of between 1 and 5%, as the dry CO_2 mole fraction increased from 0.01 to 0.2 (Gottuk, 1992a).

2.2.6.3 Species yields as a function of equivalence ratio

In fires, as in any other combustion system, there exists a strong relationship between the production of species and the Equivalence ratio. Generally speaking, the production of the species CO_2, H_2O, and N_2 will be near their ideal "complete" yields in well-ventilated fires. However, during under-ventilated "fuel rich" fires, the combustion products will include significant amounts of CO, UHC, soot, and if the fuel contains Nitrogen HCN may be present. Figure 2.4 shows the effect of under-ventilation on the species production for a variety of fuels, burnt in a simple hood configuration.

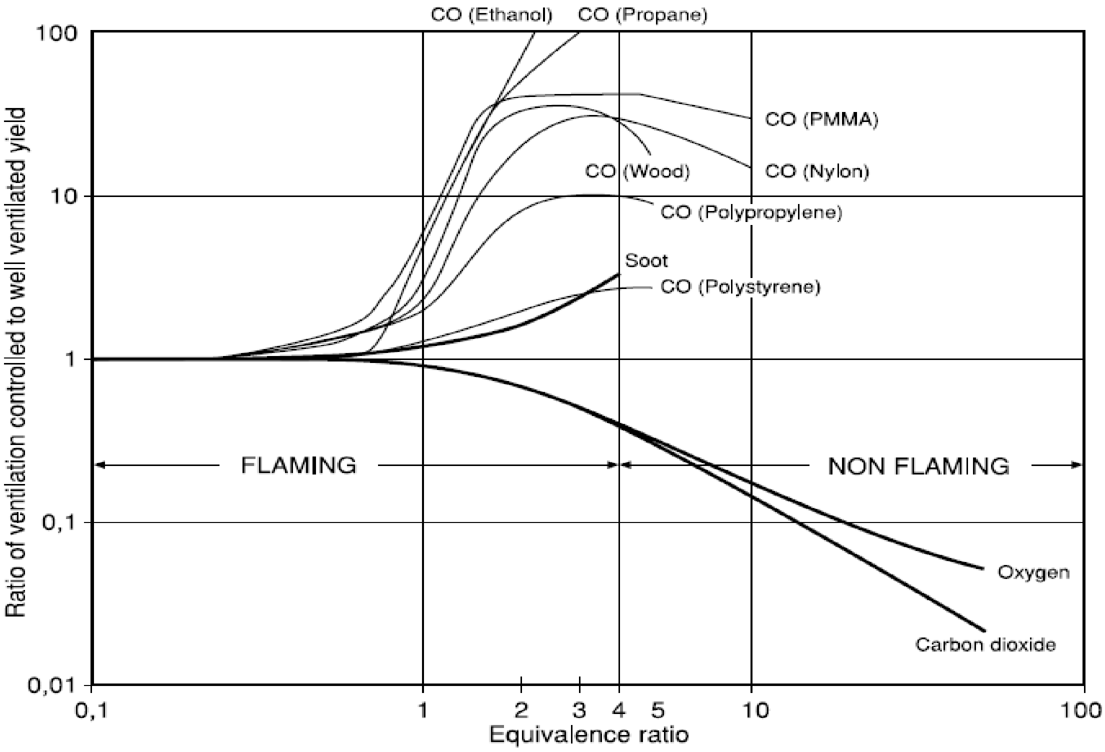


Figure 2-4: Effect of under-ventilation on yields of Oxygen, CO2, and CO for many materials, adopted from (Tewarson, 2002).

(Tewarson, 2002) reports the first data set on the effect of Equivalence ratio on the species production, his work was followed by Beyler, Gottuk, Pitts, and others. A compiled set of his original results is provided in Table 2-2, while further discussion on the validity and accuracy of these results will be discussed in the later parts of this Chapter.

However, the mechanism of incomplete combustion species production in compartment fires is not only limited to the equivalence ratio effect. (Andrews, 2007) explains CO generation in fires is from the same two routes as CO emissions from any combustion equipment: *Equilibrium CO* and *Inefficient Combustion CO*.

CO is a normal product of combustion and equilibrium CO can be calculated at the equilibrium adiabatic flame temperature. It is very large for rich mixtures and much lower, but still significant for lean mixtures. Nevertheless, in *inefficient combustion*, if, all of a hydrocarbon fuel is not fully burnt, i.e. does not reach equilibrium, then CO arises through partially burnt fuel and incomplete oxidation. (Andrews, 2007) explains, in fire conditions inefficient combustion is normally due to three reasons:

a) Inadequate residence time so that equilibrium is not achieved.

b) Poor fuel/air mixing – the poor mixing gives rise to rich local regions that have high equilibrium CO, which then do not find enough oxygen in the mixing zone to burn out. The closer the overall mixture is to stoichiometric the higher is this source of CO.

c) Quenching of the flame due to heat extraction (cooling) before combustion is completed to equilibrium. Note that cooling after equilibrium has been reached will reduce the CO, as equilibrium CO is lower at lower temperatures for the same excess air.

2.2.6.4 Combustion efficiency

An important feature of under ventilated fires is the high inefficiencies of the combustion process due to the poor fuel/air mixing, flame quenching, and inadequate residence time highlighted earlier. The quantification of the inefficiencies in the combustion process in compartment fire is recognised as a significant factor affecting the type of smoke products.

The efficiency of combustion (χ or ηcomb) may be defined as the ratio of the actual chemical HRR to the HRR for complete combustion (Tewarson, 2002)). This definition may also be written in terms of the ratio of heats of combustion (ΔHc,eff and ΔHc).

$$\eta_{comb} = \frac{\dot{Q}_{c,eff}}{\dot{Q}_c} \, or \, \frac{\Delta H_{c,eff}}{\Delta H_c} \tag{2.20}$$

While the value ΔHc for a specified fuel may be determined experimentally using bomb calorimetry (or theoretically using thermo-chemistry techniques), ΔHc,eff requires techniques such as oxygen consumption or carbon dioxide calorimetry for its evaluation for a variety of specified combustion conditions.

Furthermore, as the production of CO_2 is the greatest contributor to the actual HRR (greatest heat of formation ΔHf), many experimental determinations of the combustion efficiency have been focussed on measurements of CO_2 and/or CO concentrations (Beyler, 1986b). In fact, the most recent ISO standards describing the measurement of

Inefficiencies in compartment fires provide Eq. 2.21 for estimating the combustion efficiency:

$$Effecincy = \frac{100\ \times [CO_2]}{([CO_2] +\ [CO])} \tag{2.21}$$

While this method gives a reasonable estimation of the combustion efficiency, it neglects the contribution to the overall inefficiency by unburnt hydrocarbon emissions. Unburnt hydrocarbon emissions must represent a significant contribution to the overall inefficiency (particularly for under-ventilated conditions) as they represent un-released energy content and have (in the case of pure hydrocarbons) utilised energy from the flame to reach a vaporized state. In this respect, UHC could be considered to be endothermic products. In other areas of combustion research, such as engine emissions research, the unburnt hydrocarbon emissions are included in the experimental calculation combustion inefficiency, as explained in (Li, 2007). Thus, the overall combustion inefficiency is the combined inefficiencies of CO, UHC, and soot emissions as follows:

$$1 - \eta_c = \left(Y_{CO} \times \frac{CV_{CO}}{CV_{Fuel}}\right) + \left(Y_{UHC} \times \frac{CV_{UHC}}{CV_{Fuel}}\right) + \left(Y_{Soot} \times \frac{CV_{Carbon}}{CV_{Fuel}}\right) \tag{2.22}$$

The inclusion of the energy content of the UHC is particularly essential in under-ventilated hydrocarbon pool fires. The author has shown in (Aljumaiah et al., 2011a; Aljumaiah et al., 2010d) how the later method provided a more accurate approach towards quantifying the energy locked in the unburnt hydrocarbons. It can be argued that the ISO method may provide a good estimate of the efficiency in previous experimental work as in the hood experiments because of the good air/fuel mixing in that experimental set up, which is not a realistic fire condition.

Table 2-2: Maximum theoretical yields and experimentally determined yields for well ventilated and under ventilated fires adopted from (Tewarson, 2002).

Fuel	**Chemical Structure**	**Max. Theoretical Yield**			**Well Ventilated Fire (ϕ < 1)**				**Ventilation Controlled Fire (ϕ > 1)**	
		$Y_{CO\ max}$	$Y_{CO_2\ max}$	$Y_{O_2\ max}$	$Y_{CO\ max}$	$Y_{CO_2\ max}$	$Y_{s\ max}$	$Y_{HCl\ max}$	$Y_{CO\ max}$	$Y_{H_2\ max}$
Propane	C_3H_8	1.91	3.00	3.64	2.85	0.005	0.024	NA	0.23	0.011
Acetylene	C_2H_2	2.15	3.39	3.69	2.6	0.042	0.096	NA	-	-
Ethanol	C_2H_5OH	1.22	1.91	2.09	1.77	0.001	0.008	NA	0.22	0.0098
Heptane	C_7H_{16}	1.96	3.08	3.52	2.85	0.01	0.037	NA	-	-
Polystyrene	C_8H_8	2.15	3.38	3.08	2.3	0.06	0.16	NA	-	-
Nylon	$C_6H_{11}NO$	1.48	2.32	2.61	2.06	0.038	0.075	NA	-	-
Polyurethane (PU)	$CH_{1.7}N_{0.07}O_{0.32}$	1.41	2.21	2.05	1.5	0.031	0.23	NA	-	-
Polymethyl methacrylate	$C_5H_8O_2$	1.4	2.2	1.92	2.1	0.01	0.022	NA	0.19	0.032
Wood (pine)	$C_{0.95}H_{2.4}O$	0.89	1.4	1.13	1.33	0.005	0.015	NA	0.14	0.0024
Polyvinyl chloride (PVC)	C_2H_3Cl	0.903	1.42	1.42	0.46	0.063	0.14	0.5	0.4	-

NA= Not Applicable - = Not measured

2.2.7 CHARACTERIZATION OF COMPARTMENT FIRES

The different stages of a compartment fire exhibit different combustion conditions. The most important parameters used in distinguishing the different conditions are heat fluxes, oxygen concentration, equivalence ratio, and combustion efficiency (Purser et al., 2010). The differences in the combustion conditions have great influence on the toxic species yields in the fire effluent. It has been recognised that a careful classification of compartment fires is essential for fire studies (Babrauskas et al., 1991b). The earliest accepted classification of compartment fires in relation to toxic species production is found in an old British standard PD6503 (PD6503, 1988). This classification was further detailed in the SFPE (Purser, 2002). And the most up to date classification is found in (ISO-19706, 2005). The latest version of the classification is presented in table 2-3. And the following sections will discuss the applicability of these classified stages to real fire scenarios and comment on the sub categories.

2.2.7.1 Non-flaming and smouldering fires

This category includes three sub stages, 1a. *Self-sustained smouldering*, 1b. *Oxidative external radiation*, and 1c. *Anaerobic external radiation* (ISO-19706, 2005). In all the three sub stages little or no effect is exhibited from the compartment shape on the decomposition process. The main drive in these fires is the local heat, and the availability of air. The hot layer temperature and oxygen levels have limited effect, as the fires are not large enough to form a hot upper layer temperature and reduce the oxygen level in the enclosure.

Stage 1a represents self-sustaining smouldering combustion most common in porous material or charring cellular materials such as wood or cotton. In such fires, exothermic oxidation of the porous material drives the endothermic thermal decomposition of adjacent un-decomposed material, thus the overall product yields depend on the combined effects of the two processes. One of the most determining factors of such phenomena is the rate of air supply, which may result in an increased rate of decomposition ultimately leading to flaming combustion.

Stage 1b is the most common form of thermal decomposition in fires. During which, oxidative thermal decomposition occurs leading to reaction at the materials surface or gas phase. In the absence of large ignition sources it is often the precursor to flaming combustion. It usual occurs in most materials at temperatures exceeding 300 °C.

The final stage noted as 1c is the simplest pyrolysis process in fire studies. It occurs when enough heat is applied to cause material decomposition in an inert atmosphere. The products are usually limited range of organic compound often resembling the parent polymer. It can be argued these types of fire are not rapidly hazardous. However, decomposition under these conditions results in a range of irritant products as well as CO levels which may be significant hazard on larger scale times.

2.2.7.2 Well ventilated flaming fires

In general, most flaming fires start well ventilated, until the fire growth is limited by the enclosure size and air supply. These fires depend on the compartment geometry greatly. In cases where the compartment is very large with high ceilings such as large warehouses or big atriums the fire will continue to grow and it will be unlikely the fire will become under-ventilated. In these cases the fire hazard is greater from heat and fire spread than from smoke products. In smaller compartments the fire will build up a hot smoke layer and the feedback mechanism will accelerate the fire until it reaches flashover, or fully developed fires. After which, the fire will most likely be an under-ventilated fire and will develop into stage 3 in the classification.

Most of our credible knowledge on compartment fires comes from large scale fire calorimeter tests, in which well ventilated flaming fires are the dominant mode of combustion. Other experimental set up such as in the hood experiments also simulate combustion conditions which fall into this types of fires. Thus, most of the reported data correspond to this type of fires, although it can be argued this type is the least hazardous in terms of fire toxicity.

The combustion efficiency in well ventilated fires is relatively high. Although the >95% estimate reported in the standard is questionable, due to the fact the method used relay solely on CO/CO_2 levels. The main cause of combustion inefficiency and incomplete combustion products in this type of fires is the under-ventilated regions within the flaming zone. Local variations of the equivalence ratio and poor Air/Fuel mixing may occur in localised regions especially if the fire is large.

2.2.7.3 Under-ventilated flaming fires

3a *low ventilation room fires*

Most modern buildings in the UK and Europe consist of low ceiling energy efficient layouts. In such buildings the dominant fire type is 3a *low ventilated room fires*. During which the fire grows in a small enclosure with hot smoke filling up the upper layer relatively quickly thus accelerating the fire growth rate. Once the fire grows beyond a certain size, the upper smoke layer descends towards the lower part of the compartment. Thus, higher proportion of the flame is burning in oxygen depleted environment. The supply rate of fresh air in the lower part of the compartment will provide enough air for the fire to continue growing, while the burning zone will become more inefficient. The rate of air supply required for burning to the rate of fuel mass loss will decrease. Hence, the fire global equivalence ratio will exceed unity characterising the combustion as fuel rich. Consequently the rate of production of carbon dioxide and oxides of nitrogen will decrease, while other incomplete combustion products will increase. This includes carbon monoxide, hydrogen cyanide, volatile organic compounds, and organic irritants. This category of fires can be further divided into three common scenarios as follows: fires in small enclosed compartments, fires in larger enclosed compartments, and fires in a limited ventilation compartment.

In cases where a small enclosed room is involved, the fire grows quickly to self-extinguish from lack of oxygen in the compartment. In these fires, the hazard from fire smoke and toxic gases is generally higher than that of heat exposure.

Another similar type of fires is where a larger enclosed compartment is involved. This is a typical scenario in a modern flat where the exterior windows and doors are closed, but interior doors are open. During which the fire will grow significantly as a well-ventilated fire, until it reaches a stage where most of the oxygen is consumed. These fires may self-extinguish after a relatively longer period of time. However, the toxic species and incomplete combustion products are generated at a much higher rate. The burning in the fire plume occurs with very low efficiency and the air supply is often mixed with circulated fire smoke products. The main hazard from this type of fire is smoke and toxicants followed by heat for the occupants of the room of origin. Nonetheless, for occupants outside the room of origin the main hazard is toxic smoke.

Another common under-ventilated fire scenario is when fresh air is continuously supplied to the lower layer. In these fires, the air supply usually allows the fire to burn until the available fuel is consumed. One common occurrence of this type is a compartment fire with an opening leading to another compartment that has an external opening. In such situation, the fire grows until it becomes fuel rich in the main compartment of origin, after which the fire growth rate may stabilise, depending on the air supply, or observe an oscillating behaviour. In these fires, the smoke hazard is at its highest, and experimental work representing these conditions suggest a CO production yields of 0.24 g/g (Purser, 2000) In these circumstances the fire is not likely to self-extinguish, and the amount of toxic species and irritant gases will be produced until the fire runs out of fuel, or the fire fighters arrive.

3b *post flashover fires*

This type of fire occurs when there is sufficient fuel load and ventilation for the fire to reach flashover conditions. Once the upper layer temperature is around 500-600 °C, a sudden growth rate of the fire occurs. Thus causing the fire to turn into ventilation controlled rather than fuel controlled fire. The huge increase in the fire growth causes the fire process to turn into fuel rich combustion, since the air supply is limited. These fires generally produced very hot smoke with significant amount of toxicants. The main reason distinguishing 3b from 3a is the fire size which tends to be much larger in 3b and the smoke temperature. According to (Purser et al., 2010) very limited information is available on post flashover fires smoke and toxic species production rate.

Table 2-3: ISO19706 classification of fire types in relation to fire toxicity.

Fire type	**Heat flux to fuel surface kW/m2**	**Max. Temperature °C**		**Oxygen volume %**		**Fuel/air equivalence ratio (plume)**	**[CO] [CO2] v/v**	$\frac{100 \times [CO_2]}{([CO_2] + [CO])}$
		Fuel surface	**Upper layer**	**Entrained**	**Exhausted**			
1. Non-flaming								
1-A. self-sustaining (smouldering)	n.a.	450 to 800	25 to 85 **d**	20	0.20	—	0.1 to 1	50 to 90
1-B. oxidative pyrolysis from externally applied radiation	—	300 to 600**a**	**b**	20	20	< 1	**C**	**C**
1-C. anaerobic pyrolysis from externally applied radiation	—	100 to 500	**b**	0	0	>> 1	**C**	**C**
2.Well-ventilated flaming **d**	0 to 60	350 to 650	50 to 500	20	0.20	< 1	< 0.05**e**	> 95
3. Under-ventilated flaming **f**								
3-A. small, localized fire, generally in a poorly ventilated compartment	0 to 30	300 to 600 **a**	50 to 500	15 to 20	5 to 10	> 1	0.2 to 0.4	70 to 80
3-B. post-flashover fire	50 to 150	350 to 650 **g**	> 600	< 15	< 5	> 1 **h**	0.1 to 0.4**i**	70 to 90

a The upper limit is lower than for well-ventilated flaming combustion of a given combustible.

b The temperature in the upper layer of the fire room is most likely determined by the source of the externally applied radiation and room geometry.

c There are few data; but for pyrolysis, this ratio is expected to vary widely depending on the material chemistry and the local ventilation and thermal conditions.

d The fire's oxygen consumption is small compared to that in the room or the inflow, the flame tip is below the hot gas upper layer or the upper layer is not yet significantly vitiated to increase the CO yield significantly, the flames are not truncated by contact with another object, and the burning rate is controlled by the availability of fuel.

e The ratio may be up to an order of magnitude higher for materials that are fire-resistant. There is no significant increase in this ratio for equivalence ratios up to ≈ 0.75. Between ≈ 0.75 and 1, some increase in this ratio may occur.

f The fire's oxygen demand is limited by the ventilation opening(s); the flames extend into the upper layer.

g Assumed to be similar to well-ventilated flaming.

h The plume equivalence ratio has not been measured; the use of a global equivalence ratio is inappropriate.

i Instances of lower ratios have been measured. Generally, these result from secondary combustion outside the room vent.

2.3 COMPARTMENT FIRE SMOKE & TOXIC EFFLUENT

This section will provide an overview of the main toxic gases produced from combustion process in limited ventilation fires. It is generally accepted that the term toxic gases is used to describe all incomplete combustion products of fires including acute lethal toxicity and sub lethal irritant toxicity. Given this assumption, toxic fire products can be classified into two main categories; asphyxiant gases, and irritant gases. The latter further categorized into acidic gases, and organic irritants. In addition, to the low oxygen levels, and relatively high levels of carbon dioxide CO_2 these gases collectively pose the toxic hazard in under ventilated compartment fires.

2.3.1 ASPHYXIANT GASES

Asphyxia can be defined as the deficient supply of oxygen to the human body. Accordingly, in this work, as in most fire studies, asphyxiant gases are defined as gases which prevent the oxygen uptake in cells, resulting in loss of consciousness and death. Asphyxiant gases have been the focus of most of the early fire toxicity studies. They are well defined and their impact on fire victims is well understood. The main asphyxiant gases are Carbon Monoxide CO, and Hydrogen Cyanide HCN. Nevertheless, it is vital to consider that low oxygen levels and High levels of carbon dioxide in fire environment enhance the asphyxiant gases effects significantly. In fact, low oxygen levels <15% and/or high carbon dioxide levels >5%, which are very common in under ventilated fires, can be considered asphyxiant in their own right (Purser, 2010a).

2.3.1.1 Carbon Monoxide (CO)

Carbon monoxide has for long been recognized as the leading cause of death from fire gases (Alexeeff, 1986; Edgerley, 1982; Gordon L, 1987; Gormsen et al., 1984; Gottuk, 1992a; ISO-27368, 2008; Kaplan et al., 1984; Levin, 1996; Levin et al., 1987; Purser, 1984; Purser, 1992; Sayers and Davenport, 1930; Wieczorek, 2003; Yoshida et al., 1991). It is a primary product of inefficient combustion regardless of the fuel type, thus it is presence in high concentrations common across all under ventilated fire. Various studies indicate that CO is the ultimate cause of death through toxic asphyxia; this is only challenged by HCN in limited reports (Ferrari et al., 2001). CO acts by combining with haemoglobin to form carboxyhemoglobin (COHb). Haemoglobin's main objective is to carry oxygen in the form of oxyhemoglobin.

Table 2-4: Summarised effect of CO inhalation on humans adapted from (Purser, 2010).

Blood Saturation % COHb	**(Stewart, 1974)**	**(Sayers and Davenport, 1930)**	**(Purser, 1984; Purser, 2002; Purser et al., 1984; Purser and Woolley, 1983)**
0.3-0.7	Normal range due to endogenous production		
1-5	Increase in cardiac output to compensate for reduction in oxygen carrying capacity of blood.		
5-9	Exercise tolerance reduced, visual light threshold increased, less exercise required to induce chest pains in angina patients	minimal symptoms <10 %	
16-20	Headache, abnormal visual evoked response, may be lethal for patients with compromised cardiac function.	Tightness across forehead and headache experienced 10-20%.	
20-30	Throbbing headache; nausea; abnormal fine manual dexterity	Throbbing headache.	
30-40	Severe headache; nausea and vomiting syncope (fainting)	Severe headache; generalised weakness, visual changes; dizziness, nausea, vomiting, and collapse.	30 % caused confusion, collapse and coma in active animals during 30 min. exposure with nausea after.
40-50		Syncope, tachycardia (rapid heartbeat) and tachypnoea (rabid breathing)	40 % caused coma, bardycarida (slow heartbeat), arrhythmias in resting animals during 30 min. exposure
50+	Coma; convulsions	Coma and convulsions	
60-70	Lethal if not treated	Death from cardiac depression and respiratory failure	

The affinity of haemoglobin for CO is extremely high, and therefore the formation of COHb is extremely aggressive and favourable to the formation of oxyhemoglobin. Consequently, formation of COHb leads to a reduction in oxygen supply to different body tissues, and most importantly brain tissue (Purser, 2002). The reduction in oxygen supply is not only caused by the reduction of haemoglobin available to carry oxygen in the form of oxyhemoglobin, but also because the ability of the remaining oxyhemoglobin to release oxygen to the tissue is impaired due to a leftward shift of the oxygen dissociation curve (Purser, 2002). Since haemoglobin affinity for CO is high, CO toxic effect is considered cumulative as more CO inhalation results in increased formation of COHb. Table 2-4 shows a summary of the reported effects of COHb levels in the blood for human and non-human subjects.

It is estimated that as COHb levels reach 15% in the human blood, headache is experienced after short periods (15-20 minutes). Once COHb levels reach concentrations of 30%-40% incapacitation and loss of consciousness is predicted to occur. Lastly, COHb levels above 50% are considered fatal (Smith, 1985). Table 2-4 provides a summary of the reported effects of COHb levels in human and non-human subjects (Purser, 2010).

2.3.1.2 Hydrogen Cyanide (HCN)

Hydrogen cyanide is frequently reported as one of the leading causes of death from fire smoke (AEGL, 2002; Kallonen, 1990; Levin, 1996; Levin et al., 1987; Morikawa et al., 1995; Purser and Purser, 2008; Tuovinen et al., 2004). In fact, recent studies (Ferrari et al., 2001), suggest that HCN is challenging CO as a leading cause of death in fire victims. HCN is an incomplete combustion product of combustible fuel containing Nitrogen. Although, it is not as commonly produced as CO in compartment fires, its high toxicity (25 times more than CO) make it one of the main component of fire toxicity hazards in compartment fires. Its high toxicity is mainly due to the production of cyanide ion (CN-) formed by hydrolysis in the blood (Purser, 2002). The cyanide ion is then distributed to the extracellular fluid of tissue and different organs. Furthermore, the toxic effect produced by HCN can be explained in two interacting mechanisms. One is by combining with the ferric ion in mitochondrial cytochrome oxidase, therefore preventing electron transport in the cytochrome system and disabling the use of O_2 in the cells. The other mechanism is characterized by a brief stimulation followed by severe depression of the respiratory frequency, associated with severe starvation of oxygen in the body, resulting respiratory arrest then death.

The complex mechanisms by which HCN affects the human body, along with the relatively expensive CN^- are main reasons for limiting large scale and routine testing for the effect of HCN on fire victims (Purser, 2002). Nevertheless, recent reports suggest an increasing role of HCN lethality in the death of fire victims. (Purser, 2010a) provides a list of the known effects of HCN exposure on human and non-human pyramids.

Table 2-5: Incapacitation due to HCN inhalation adapted from (Purser, 2010a).

HCN Level (ppm)	**Species & Effect**	**Source**
100	Loss of Consciousness after 23-30 min in primates and humans	(Kimmerle, 1974; Purser et al., 1984)
200	Loss of Consciousness after approximately 2 min.	
300+	Death occurs ‘Rapidly’	(Kimmerle, 1974)
444	a man survived an accidental exposure	(Bonsall, 1984)
530	A man, Barcroft, survived a 1.5 min. exposure his dog exposed at the same time died	(Barcroft, 1931)
539	Suggested 10 min. LC50 in humans	(McNamara, 1976)
1000	One breath may cause loss of consciousness	(Purser, 2002)

2.3.2 IRRITANT GASES

Unlike asphyxiant gases, irritant gases had little attention in fire studies (Purser, 2002). Little information is available on their rate of production in fires, and the knowledge on how they affect human body is an emerging research area (Hull and Stec, 2010). The reasons behind the lack of knowledge on these gases can be attributed to several factors: first of which is the lack of adequate instrumentation and means of quantification for these gases in previous studies. The use of advanced gas analysis equipment such as the FTIR, and better sampling techniques in fire studies was very limited in the past due to cost and expertise. This is now changing as the standards of research in the field are improving. The second major factor is the priority given to understanding the lethal cause of fire casualties, rather than attempting to study the fire smoke hazard in terms of impairment of escape and the fire conditions leading to inhaling the lethal amounts of

CO and other toxic gases. A third factor is the adoption of the lethal concentration limits and lethal dose, as the main assessment method in fire toxicity studies. This is now changing, and will be discussed further in the toxicity assessment section.

Fortunately, extensive work on these gases was carried out by regulating authorities for exposure limits during work hours and industrial accidents. Detailed tenability limits provided by medical committees in the UK, USA and Europe can form basis of an alternative approach for assessing irritant gases produced in fires. The Control of Substances Hazardous to Health (COSHH, 2007) short term exposure limits (STELs) provided by the health and safety executive in the UK, the Immediately Dangerous to Life or Health Concentrations (IDLH) (NIOSH, 1994), by the National Institute for Occupational Safety and Health (NIOSH) in the USA, and the Acute Exposure Guideline Limits (AEGLs) (AEGL, 2010a) by the National Academy of Science in the USA cover a wide range of dangerous substances in a robust manner. They are regularly updated and form statuary limits, and their applicability to fire studies will be explored in details in the toxicity assessment sections.

Irritant gases are commonly classified, based on their source and molecular structure, into organic and inorganic irritants. Inorganic irritants include; Hydrogen halides, Nitrogen oxides, and Sulfur dioxide, while organic irritants include: Acrolein, Formaldehyde, Benzene etc. Some of which are common in most compartment fires, while others are only produced from specific materials. Nonetheless, there is evidence that the use of modern fire retardants as well as new synthesis polymers have increased the quantity of irritant species in compartment fires (Purser, 2010b).

An overview of the known irritant gases is provided in this section detailing the chemical properties, and its known effects on the human body, while the means of assessment are discussed in the relevant section.

Hydrogen halides:

2.3.2.1 Hydrogen chloride (HCl),

Hydrogen Chloride is a strong colourless acid, which dissociate entirely in water. Its molecular weight is 36.4 g/mol and its boiling point is -85°C. It acts on the human body through the acidity caused by H+ ion, similar to HBr, nonetheless due to its size and electron configuration it is considered a stronger irritant than other Hydrogen Fluoride. (Purser, 2010b). It is a respiratory irritant and very corrosive. Although its solubility in water is considered high, it is still lower than HBr and HF making less effectively scrubbed to the nasal passage and more penetration to the lungs (AEGL, 2004a). HCl is commonly produced from the burning of Poly Vinyl Chloride (PVC), as well as other chloride containing materials. According to (Hull and Stec, 2010) limited work is done on its effects on humans, resulted in a long controversy on what should be considered safe exposure limits. They also explain, the information available suggests 10 ppm of HCl is tolerable for a short period of exposure, while exposure to 50-100 ppm caused severe irritation accompanied by chest pain and choughs. In addition, throat irritation is reported at 35 ppm for short term exposure by the AEGL guide.

2.3.2.2 Hydrogen bromide (HBr)

Hydrogen Bromide is another strong Hydrogen Halide usually produced by the incomplete combustion of brominated flame retardants in compartment fires. It is gas at room temperature, its molecular weight is 80.9 g/mol, and its boiling point is -66.38^{O}C. it is a slightly larger molecule than HCl, and significantly larger than HF, and Similar to HCl its hazard comes from the high acidity caused by the H+ (Purser, 2010b). It is highly soluble in water, and its irritancy is first noticed through the nasal passage before penetrating to the lower respiratory system at higher concentrations. There are no reports on human exposure to HBr; however the threshold limits are derived from animal exposure data, which gave good predictions of tolerable limits for a wide range of organic and inorganic irritants. (Purser, 2010b).

2.3.2.3 Hydrogen Fluoride (HF)

Hydrogen Fluoride is the smallest in size of the hydrogen halides reported in fire studies; it is a colourless weak acid. Unlike HCl and HBr its toxicity is not driven by its acidity (AEGL, 2004b; Purser, 2010b). Its molecular weight is 20.09 and its boiling point is 19.5 C. It is extremely reactive in water, producing heat and hydrofluoric acid.

It is an extreme irritant to the skin, eyes, and the nasal passage. No data is available on its acute toxicity in humans; however limited studies are carried out on its irritancy. No human exposure relevant to its level of production during fires is available, however one report suggests notable irritation to the upper and lower respiratory system at 2.0-6.3 ppm exposure for one hour (Lund et al., 1997; Lund et al., 1999), extrapolation of animal exposure data provide the known threshold limits in recent (AEGL) reports.

Nitric Oxides

2.3.2.4 Nitric oxide (NO)

Nitrogen oxide is a colourless non-flammable gas. Its molecular weight is 30.01 and its boiling point is -151.7 °C. At high concentrations it reacts by combining with O_2 to form Nitrogen dioxide; however this is not as common reaction due to the low concentrations of NO. At low concentrations it has some medical application to treat breathing problem. It is commonly used for acute reparatory distress syndrome (ARDS), hence it was the subject of extensive study at concentration levels relative to its therapeutic effect and no studies relevant to fire exposure are available (AEGL, 2006). NO is administrated to ARDS levels of 20-80 ppm for periods of 4-48 hours with no known side effects. However, at high levels it dissolves in water forming nitric and nitrous acids. In the blood it combines with oxyhemoglobin to form methaemoglobin between 5-20 times faster than oxygen giving effects similar to hypoxia. However levels of 1000 ppm are reported in tobacco smoke with no harm. The (AEGL, 2006) committees have not set threshold limits for NO, due to the lack of studies on high exposure and the assumption that NO will be oxidized at high levels to NO_2. Therefore, the threshold limits are recommended to be the NO_2 threshold limits.

2.3.2.5 Nitrogen dioxide (NO_2)

Nitrogen dioxide is a non-flammable reddish-brown gas, its molecular weight is 46.01 and its boiling point is 21.15 °C. It is the most common form of nitrogen oxides, and it has the greatest impact on human health (AEGL, 2008a). It is heavier than air, and reacts with water. Its molecule have a phase dependence structure, while N_2O_4 structure preferred in the condensed phase, most of the nitrogen dioxide is converted to NO_2 in gas phase. NO_2 causes severe irritation to mucous membranes resulting in coughing and dyspnea. Exposure at high levels results in pulmonary edema, resulting in chest pain coughs, dyspnea, and cyanosis as reported in (NIOSH, 1976). It is a common product of fossil fuel combustion, and a major contributor to modern day air pollution. Hence, its health effect has been extensively studied. Exposure to 0.4 is noticeable, while levels of 15-25 are proven to cause respiratory and nasal irritation. Furthermore, levels between 25-75 ppm cause what is described as “reversible pneumonia and bronchiolitis” by the AEGL guide. Fatality is reported at 150-300 ppm (AEGL, 2008a).

Organic Irritants

2.3.2.6 Acrolein C_3H_4O

Acrolein is the simplest aldehyde; it is a colourless or yellowish liquid at ambient temperature and pressure. It has an acrid, pungent odour and is highly irritating to mucous membranes, especially the upper respiratory tract and eyes (AEGL, 2010b). Its chemical formula is C_3H_4O, its molecular weight is 56.06 g mol^{-1}, and its boiling point is $52.5^{o}C$. The largest sources of human exposure to Acrolein are from incomplete combustion of organic materials in fires, tobacco smoke, and the burning of fat-containing foods, and little information is available on its acute toxicity to human adults. One study reported by (Henderson and Haggard, 1943) suggests exposure to 150 ppm for 10 minutes is lethal. Nonetheless, irritation studies provide sufficient details on its harmful effect. Table 2-6 shows a summary of exposure studies to Acrolein provided by the AEGL Volume 8. This study was carried on healthy population of young adults for a one hour exposure. Table 2-7 shows a summary from another study conducted on a similar population for 10 and 20 minutes exposure to 0.3 Acrolein. It is crucial to acknowledge that these studies are carried on young adults in good health conditions, which is not always the case for fire victims as noted earlier.

Table 2-6: Effect tresholds in human volunteers exposed to acrolein adapted from (AEGL, 2010).

Effect	**Measurement**
Annoyance	0.09 ppm
Very Slight Eye Irritation	0.09 ppm
Nose Irritation	0.15 ppm
Doubling of Blinking Rate	0.26 ppm
10% Decrease in Respiratory Rate	0.3 ppm
Throat Irritation	0.43 ppm
25% Decrease in Respiratory Rate	0.6 ppm

Table 2-7: Effect of duration of exposure to 0.3 ppm level of acrolein in human volunteers from (AEGL, 2010b).

Effect	**% at 10 [m]**	**% at 20 [m]**
Wish to Leave the Room	50	72
Moderate Eye Irritation	18	35
Severe Eye Irritation	3	18
Moderate Nose Irritation	7	19
Severe Nose Irritation	1	4
Moderate Throat Irritation	1	2
Severe Throat Irritation	0	1
Doubling of Blinking Rate	66	70
10-15 % Decrease in Respiratory Rate	47	60

2.3.2.7 Formaldehyde CH_2O

Formaldehyde is a flammable colourless gas. It has been extensively studied (AEGL, 2008b; Amdur, 1960; Barnes and Speicher, 1942; Bender et al., 1983; Nagorny et al., 1979), and has been recently classified as a cancerous gas (NTP, 2011). It is usually present in its gas phase, its boiling point is -19°C and its molecular weight is 30.03 g/mole. Its flammability range is 7-75 % at 25°C, and its ignition temperature is 300°C. It has a distinct pungent suffocating odour, and it is noticeable at levels between 0.05 and 0.18 ppm (AEGL, 2008b). At levels exceeding 0.1 ppm, some individuals may experience adverse effects such as watery eyes; burning sensations in the eyes, nose, and throat; coughing; wheezing; nausea; and skin irritation (Institute, 2011). It is a naturally occurring compound found in several fruits in amounts of 3.3 to 26.3 ppm. It is also, found in fabrics, particle board plywood, office furniture and other consumer products. Human exposure to formaldehyde has been studied extensively. The (AEGL, 2008b) documents more than 23 clinical studies, most of which are conducted to study its irritant effect (Bender et al., 1983), reports exposure of healthy adult subjects to 0.35 to 0.9 for six minutes caused an average response of none to slight for eye irritation effect. In addition, the subject's response was slight to moderate eye irritation for exposure levels of 1.0 ppm for six minutes duration. Another study by (Stephens et al., 1961) in which healthy students were exposed to 0,1,3,4,5 ppm of formaldehyde for 5 minutes, suggests 1 ppm is the threshold for detection and 5 ppm exposure produces severe eye irritation. Finally, (Barnes and Speicher, 1942) exposed healthy subjects to 20 ppm for several minutes. In their findings they report lacrimation starts within 15-30 s followed by severe eye, nose and throat irritation which made the progress with the study unbearable. (Barnes & Speicher, 1942). No data are available on human acute exposure to Formaldehyde, however the available animal toxicity studies are used to estimate life threatening levels. Nagorny reports no deaths in mice subjects after 2 hours exposure to 98 ppm, however exposure to 410 ppm for the same time period was lethal to more than half the mice. They also report rats exposure to 350 and 478 for a four hour period, with the first group recording no deaths, and the second group half population fatality (Nagorny et al., 1979).

Formaldehyde can be described as a primary irritant that is scrubbed in the anterior nasal passages, from which the primary action of irritancy involves activation of sensory nerve fibres, causing the trigeminal nerve to reflexively induce bronchoconstriction through the vagus nerve (Amdur, 1960). Although this mechanism is observed in guinea pigs, it's not confirmed on human exposure studies. In addition, formaldehyde is also reported to be a highly cytotoxic respiratory tract irritant, although the exact mechanism of its irritant, corrosive, and cytotoxic effect is not fully understood (AEGL, 2008b). An essential fact, regarding formaldehyde effect, is that it is not a dose related effect. Most studies report the harmful effects of exposure to Formaldehyde is based on the level of concentration the subject is exposed to rather than quantity of dose inhaled during the same period of time.

2.3.2.8 Benzene C_6H_6

Benzene is a colourless liquid in ambient pressure and temperate. Its natural source is petroleum and natural gas, and it is an intermediate component in a wide range of industries. Its molecular weight is 78.114 g/mole, and its boiling temperature is 80.1 °C. It is regarded as highly flammable, and its explosive limits in air are 1.4%-8.0%. There exist many reports on human deaths due to high exposure of Benzene, but most of which lack accurate details on concentration levels and exposure time. Therefore, they are of limited usefulness for this research. The only available information on its lethality to humans is an estimate provided by (Flury, 1928) and later by (Gerarde, 1960) of acute lethality to be 20,000 ppm for 5-10 min. exposure and 7500 ppm for 30-60 min. Exposure to high concentrations of benzene is irritating to mucous membranes of the eye, nose, and reparatory tract. Gerrard reports exposures 50-150 ppm for 5 hours results in headache, lassitude, and weariness. He also adds, exposure to levels higher than 250 ppm can result in central nervous system depression (Gerrard, 1960). More studies are reported in (AEGL, 2009b) report on animal exposure and long term cancerous effects of benzene which are of significant importance to the long term health of the professionals in the fire investigation field.

2.3.2.9 Acetaldehyde C_2H_4O

Acetaldehyde is a colourless volatile liquid at ambient pressure and temperature. Its boiling point is 20°C, and it’s highly flammable and explosive in air with explosive limits of 4-57% (AEGL, 2009a). Acetaldehyde is a natural compound found in a range of fruits, vegetables, and plants. Its main source of exposure is through forest fires and biomass combustion. It is an intermediate in the production of other chemicals in the chemical industry. Available information on its toxicity is relatively limited, no acute (lethal) exposure reports are available; however there exist some studies on short term exposure effects. A study by (Silverman et al., 1946) reports majority of the subject studied reported severe eye irritation at nominal concentration 50 ppm for 15 minutes exposure and discomfort and mild resistance to work at 25 ppm exposure for the same period. More data are available on animal subjects from which the AEGL levels are derived.

2.3.2.10 Acetic Acid CH_3COOH

Acetic Acid is an organic weak acid. It is a colourless liquid with a distinctive sour taste and pungent smell. It is one of the simplest carboxylic acids, and forms the main component of vinegar. Its boiling temperature is 118 °C, its melting point is 16 °C, and has a molecular weight of 60.05 g/mole. Acetic Acid is flammable, with an explosive limit of 5.4-16% (NIOSH, 1992). It is an intermediate in many industries and one of its early formation methods is Acetaldehyde oxidation, a reaction that seems to be likely in fire effluents. It is irritant to the eyes, and mucous membranes. Furthermore at higher concentrations it is considered very corrosive to the skin, and can cause skin burns and permanent eye damage. No detailed studies on human exposure to Acetic Acid were found, however the potency limits are derived from animal exposure studies (AEGL, 2010a).

2.4 FIRE TOXIC SMOKE GENERATION STUDIES

This section will report a summary of the published experimental work done specifically to provide smoke toxicity data. It starts the pioneering fundamental studies commonly referred to as the hood experiments. This is followed by systematic studies in reduced scale enclosures, often preferred in academic work. After which, an insight into major studies carried out by governmental or semi-governmental agencies in the full scale fire studies section. The final subsection will provide an overview on the smaller apparatus commonly referred to as bench scale studies. The results from each major study are reported according to its objectives. This is followed by a critical analysis on the validity of the results and its contribution to our understanding of fire products.

2.4.1 HOOD EXPERIMENTS

The first systematic studies on the fundamental products of combustion in fires were conducted by (Beyler, 1983). In his work the production of major species from a range of hydrocarbon fuels was investigated using a burner with a controlled fuel supply, and a one meter diameter gas collection hood. In his work, Beyler assumed that species production rate is insensitive to flame structure, and air to fuel ratio can be defined for steady state burning. From these assumptions, by varying the fuel supply to the burner, and the distance between the burner and the hood, he managed to reach steady state burning conditions with different equivalence ratios. Based on this simplified set up, he established the first use of the global equivalence ratio that effectively meant the upper layer equivalence ratio was equal to the plume equivalence ratio during steady state burning. Figure 2-5, show the simplified set up used by Beyler.

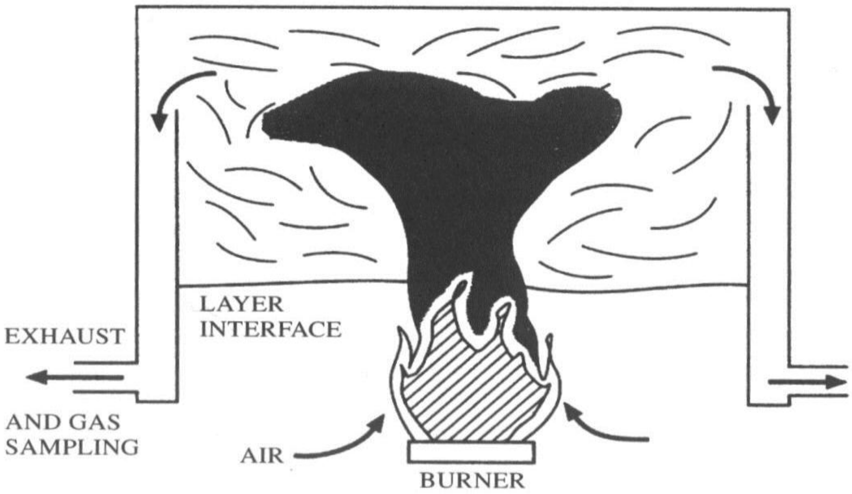


Figure 2-5: Beyler's experimental set up adopted from (Beyler, 1986a)

The gas sampling was taken from the exhaust stream, using a gas sampling probe with an aspirated thermocouple. Beyler's results showed that species yields correlated well with the equivalence ratio. He examined different hydrocarbon fuels to study the effect of chemical structure. By normalising the CO yields to the maximum theoretical CO yield for the fuel, he found that carbon monoxide production for under ventilated conditions ranked according to oxygenated hydrocarbons > hydrocarbons > aromatics. Although, different levels of CO were observed for various fuels, the correlations were qualitatively similar. Below equivalence ratio of 0.6 near zero CO production was reported. Above ϕ of 0.6, carbon monoxide yield increased as the ϕ increased, and, for most fuels, CO tended to level off at ϕ >1.2. Figure 2-6 shows the CO as a function of equivalence ratio from Beyler's experiments

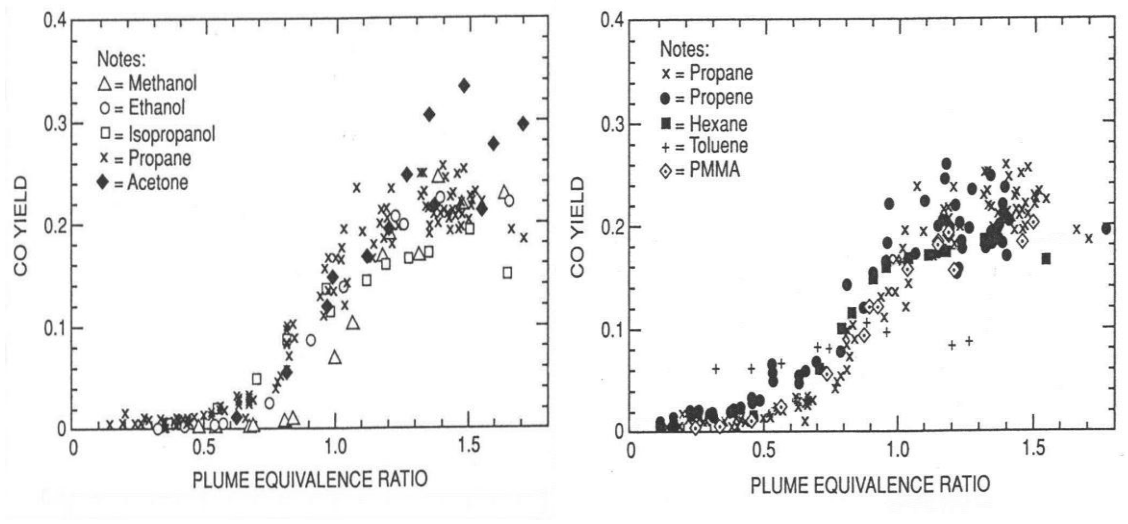


Figure 2-6: CO yields as a function of equivalence ratio from Beyler's experiments. Adopted from (Beyler, 1983).

Using the same hood system adjusted by adding a load cell instead of the continuously fed burner (Beyler, 1986a) further investigated the products from burning solid fuels such as: polyethylene, Poly (methyl methacrylate), and Pine wood. The findings of this study expanded the initial findings of the earlier work done on liquid fuels. Beyler's concluded that normalized carbon monoxide yield results support the earlier observation that oxygenated hydrocarbons produce carbon monoxide more efficiently than hydrocarbons under fuel rich conditions. The maximum CO yields reported for this work were 0.18, 0.2, and 0.14 g/g for Polyethylene, Poly (methyl methacrylate), and Pine wood respectively.

(Toner, 1987) carried out similar hood-type experiments but using a different experimental setup. The hood used was a 1.2 m cube insulated on the inside with ceramic fibre insulation. The layer in the hood formed to the lower edges where layer gases were allowed to spill out. Gas sampling was done using an uncooled stainless steel probe inserted up into the layer. Detailed gas species measurements were made using a gas chromatograph system. The upper layer equivalence ratio was determined from conservation of atoms using the chemical species measurements, the composition of the fuel and the metered fuel flow rate. The work was done on natural gas fires ranging from 20 kW to 200 kW over a 19 cm diameter burner. The layer in the hood was allowed to form and reach a steady condition before gas sampling was performed. Toner concluded that species concentrations are well correlated to the upper layer equivalence ratio and relatively insensitive to temperature for the range studied (210 to 600 °C). Despite, the slightly different equivalence ratios definition used by Toner, the correlations obtained were similar to the correlations obtained by Beyler for different fuels.

(Morehart, 1991) extended the work carried out by Toner using the same facilities in Caltech but with a larger hood. The collection hood used by Morehart was 1.8 m square and 1.2 m high. It was significantly larger than the earlier one used by Toner. In his work, Morhart attempted to establish a steady state burning conditions with an upper layer equivalence ration different to that of the plume equivalence ratio. He achieved this, buy running the methane burner at a constant flow rate, and then introduces fresh air at a constant rate to the upper layer trapped in the collection hood. Once the mixture reaches a steady state in the upper layer, a measurement was possible that produced a different equivalence ratio to that of the fire plume. This allowed several upper layer equivalence ratio scenarios to be produced for a single plume equivalence ratio. The results showed that the dependency of CO on the upper layer equivalence ratio is solid, while the plume equivalence ratio was set constant. Figure: 2-7 shows Toner, and Morehart results compared, noting that in Toner's work the plume and upper layer equivalence ratios were the same, while in Morehart work the data is presented for the upper layer equivalence ratio.

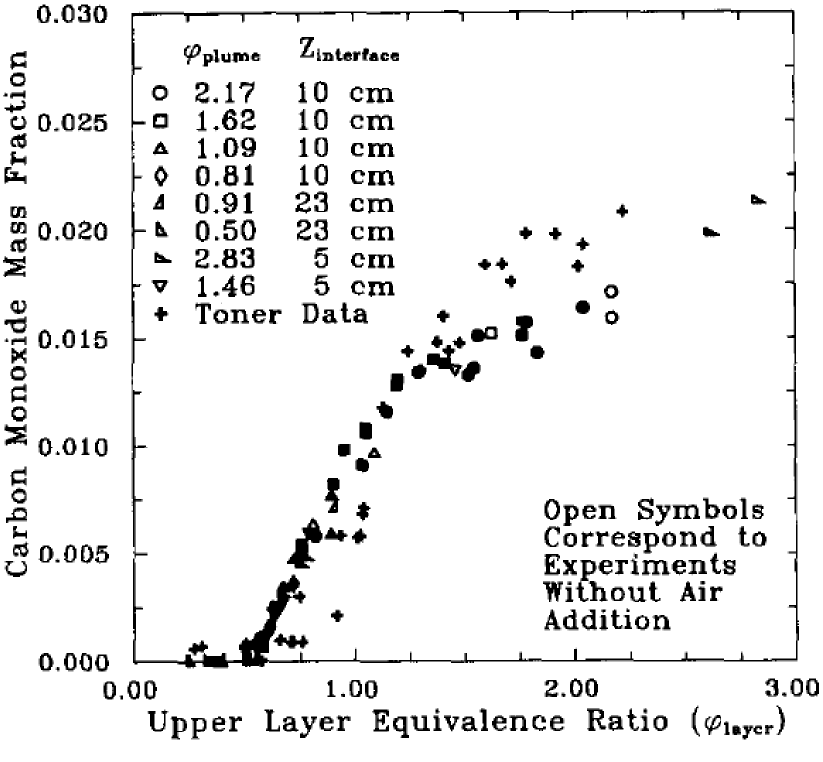


Figure 2-7: Morehart and Toner data from their hood experiments adapted from (Morehart et al., 1992).

Morehart data seemed to show lower CO yields than that of Toner, this can be attributed to the temperature difference in the upper layer temperature in Morehart work. Morehart explains, the use of a large, un-insulated hood, caused the upper layer temperature to be 120-200 °C, lower than that of Toner. In fact, Morehart reports that limited tests were carried out with an insulation added to the hood, and no addition of air to the upper layer to verify the difference in temperature and CO yields. The resulting conditions were an upper layer equivalence ratio of 1.45 and 400 °C temperatures and a CO yield within the range of Toner's data.

Although, these studies provided important basis for correlating the species production to the equivalence ratio, they are widely considered too simple to represent real fire conditions. The flaws of this approach include:

- The air supply to the lower part of the combustion in these experiments is infinite, which is not the case in real compartment fires.
- The heat losses are significant in the hood experiments set up. The relatively open set up allows heat radiation to the lab space in comparison to compartment fires where the heat is contained resulting in higher wall and upper layer temperatures.
- The hood experiment do not include ceiling and wall flame jets, or vitiated flames as often the case in fuel rich compartment fires.
- Finally, the results obtained from these tests are only representative of steady state conditions in the hood set up, which is often not the case in transient compartment fires.

2.4.3 REDUCED SCALE ENCLOSURE STUDIES (RSE)

Reduced scale enclosure studies are popular in systematic studies on combustion conditions, species production, and ventilation dependant behaviour in compartment fires. Much of our knowledge was gained from studies such as: (Andrews et al., 2000c; Andrews et al., 2000b; Andrews et al., 2000a; Bundy et al., 2007; Floyd and McGrattan, 2009; Gottuk, 1992a; Gottuk et al., 1995; Gottuk et al., 1992; Gottuk, 1992b; Gottuk, 1995; Hisahiro, 1988; Huang et al., 2009; Kim et al., 1993; Lattimer, 1996; Utiskul et al., 2005; Weckman and Sobiesiak, 1989; Yung, 1991), which were conducted in various lab size enclosures. Its repeatability, relatively higher accuracy, and low cost in comparison with Full scale studies made it the preferred approach in most academic studies. A large proportion of the previous studies concentrated on CO production in compartment fires.

Typically, reduced scale enclosures consist of a compartment size equivalent to 1/3 to 2/5 the (ISO-9705, 2011) room fire test size. It provides the researcher with the opportunity to replicate different fire conditions such as different upper layer temperatures, ventilation rates, and fuel distribution to a limited extent. These parameters can alter the fire behaviour significantly, and cannot be replicated in smaller scale tests. Nevertheless, it is vital to recognize the limitations of the each study, based on the methodology used and the assumptions made. In this section a survey of the most important studies conducted in reduced scales compartments are presented.

(Tewarson, 1985) was among the first researchers to correlate the global equivalence ratio to major species yields. In his 1985 publication Tewarson reported that CO, CO_2, and O_2 yields correlated well to the fire equivalence ratio. The presented data were obtained from a relatively small scale apparatus at Factory Mutual Research Corporation, and a compilation of earlier published work in the literature which include (Tewarson, 1972a; Tewarson, 1972b). In total, the presented results were obtained from seven different enclosures ranging from 0.21 to 21.8 m3 in volume. The ventilation was through a range of openings which included single and dual vertical and horizontal openings. The fire fuels were cellulosic fibreboard and pine wood cribs, and the exhaust was collected in a hood where a sample was extracted and analysed for CO, CO_2, O_2, and UHC, in addition to gas temperature. In addition to correlating the major species production to the global equivalence ratio, Tewarson raised key questions in regards to cellulosic fuel combustion products in under-ventilated compartment fires. He reports that significant amount of oxygenated combustion products are produced in under-ventilated wood crib fires which affect the standardised heat release rates calculation in fires. He argues, since the accepted definition of heat release rate does not take into account combustion efficiency and incomplete combustion products, it does not represent the real value of heat released from the fire (Tewarson, 1980; Tewarson, 1994). Tewarson discussion was focused on the effect the oxygenated products had on the heat release rate value; however an even more important aspect, from a toxicology point of view, was the very high irritancy these oxygenated products pose, which was not discussed in his work.

In Tewarson reported data, The CO_2 and O_2 yields are relatively constant for equivalence ratios up to about 1.7 and 1.4, respectively, and then decrease sharply as the equivalence ratio increases. The CO yield correlates with the equivalence ratio but with a fair amount of scatter in the data. With increasing equivalence ratio, the CO yield increases and, similar to Beyler's correlation for ponderosa pine, appears to be levelling out to a value of about 1.4 for under-ventilated conditions. However, the quality of Tewarson's data and correlations is compromised by the fact that the air entrainment rate used to calculate the mass air-to-fuel ratio was not measured directly, but was estimated from the ventilation parameter, Ah^2, where A is the cross sectional area and h is the height of the vent. It can be argued that, enclosure fire work performed with a single ventilation opening through which hot air flows in and upper layer gases flow out. The two-flow situation and the changing location of the layer interface make accurate flow measurements difficult.

In addition, Tewarson, compiled data obtained from the small scale flammability apparatus (ASTM-E2058, 2009) and fire research institute 0.022 m^3 enclosure among other tests methods to provide the most significant data base for species production in (Tewarson, 2002). Some of this data has been adopted by the British Standards Institute for the guidance on fire design in safety engineering (PD-7974-1, 2002) and the Charted Institution of Building Services Engineers Guide (CIBSE, 2003). He also examined correlations for the combustion efficiencies in (Tewarson et al., 1993)). Nevertheless, the majority of the published data falls in the relatively well ventilated flaming regime, and no significant information was found in (Tewarson, 2002) on irritant species production.

In his work in (Tewarson, 2002) Tewarson, classifies the results from the work done in the ASTM apparatus into species yield from ventilation-controlled (VC) and well-ventilated (WV), he concludes; the ratios of oxygen and carbon dioxide were independent of the chemical composition of the materials, while the ratios of carbon monoxide and hydrocarbons did exhibit a dependence on the chemical structure of the materials. This is agrees with the earlier findings of Beyler, for his work under the hood. Tewarson suggests the following relationship for calculating CO yields:

$$\frac{(Y_{CO})_{VC}}{(Y_{CO})_{WV}} = 1 + \frac{a}{exp^{\left(2.5\,\phi^{-\xi}\right)}} \tag{2.23}$$

where a and ξ are coefficients which are material dependent. No values for the coefficients for propane were reported by Tewarson, and similar correlations were proposed for the other major species.

At NIST, (Bryner et al., 1994) conducted an extensive study on the formation of carbon monoxide in compartment fires, using a natural gas burner in a reduced scale enclosure. The RSE was 40% of the standard ISO room, measuring 0.98 m wide, 0.98 m tall, and 1.46 m deep, and had a door opening of 0.48 m wide by 0.81 m tall. A total of 125 fires were tested ranging from 7 to 650 kW in heat release rate, and 0.2 to 4.2 in global equivalence ratio. Gas sampling was made at two locations, at the front and the rear of the upper layer. The measured gases were CO, CO_2, O_2, and UHC. The UHC measurements were only added for the latter half of the test series, and its low range calibration 0.1% was not suitable for under ventilated hydrocarbon fires. The results show, very high CO levels of up to 3.5 % in fires exceeding 400 kW in HRR, and an equivalence ratio > 2. The temperatures reached levels of 600 °C, and near zero oxygen levels were reported. The uniformity of the upper layer was questioned in their work, as higher temperatures, and CO levels were observed at the front of the compartment in comparison to the rear of the reduced scale enclosure. The authors hypothesise that additional oxygen is fed directly into the upper layer of the compartment from the door way, resulting in oxygen reaction with unburnt hydrocarbons forming additional carbon monoxide instead of fully oxidizing carbon dioxide. In addition this additional burning of unburnt fuel resulted in energy release thus, increasing the temperature. The final conclusion was that these results obtained from RSE fires, indicate that higher levels of carbon monoxide may be generated in post-flashover scenarios than suggested by hood experiments or other compartment studies assuming uniformed two layer structure. In addition, they argued current fire modelling including the GRE do not simulate temperature effect and gas no uniformities.

(Gottuk, 1992a) carried out RSE experiments using a special test set up that separated the incoming and exiting flows and generated upper layer gas temperatures similar to those obtained in actual fires. The test apparatus consisted of a 1.2 m by 1.5 m cross-section by 1.2 m high fire chamber, with a 1.2 by 1.5 by 0.3 m high air distribution plenum below the fire chamber. The test apparatus was designed so air was entrained into the compartment through a fixed diameter inlet duct located at the base of the compartment and exhaust gases were vented through a variable opening in the upper frontal portion of the compartment. This allowed air to be entrained into the base of the fire over the entire circumference. The area of the exhaust vent ranged between 404 cm^2 and 1615 cm^2. The experiments were performed using liquid n-hexane in circular pans ranging in diameter from 15 to 28 cm located at centre of the compartment. In this test setup, Gottuk simulated an ideal two-layer system, in which the actual air mass flow rate into and combustion species out of the compartment could be determined accurately the experimental configuration is shown in figure 2-8.

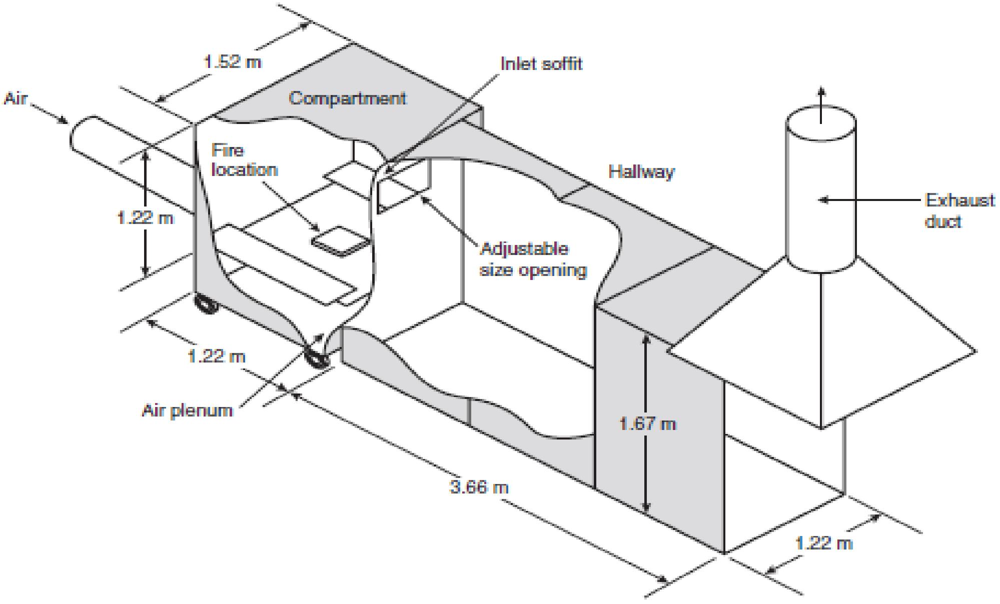


Figure 2-8: Gottuk experimental configuration adapted from (Gottuk, 2002)

In his work, Gottuk investigated four fuels, hexane, PMMA, spruce, and flexible polyurethane foam. He reports based on a series of measurements within the upper layer, a well-mixed, uniform layer existed; and therefore all measurements were performed by positioning a sampling probe horizontally 0.13 m into the compartment through the centre of the exhaust vent. The results showed that empirical correlations between the upper layer yield of major species and the plume equivalence ratio existed. It also showed that the production of CO is primarily dependent on the compartment equivalence ratio and upper layer temperature. He continues to explain, further analysis of the results indicated that increased compartment temperature affects the upper layer species yields in two ways: 1) the generation of species in the plume is changed, and 2) the oxidation of post flame gases in the layer is affected. Qualitatively correlations similar to the ones produced by Beyler were provided with a correction account for temperature effect. Based on the results from hexane fires, Gottuk proposed Eq. 2.24 and Eq. 2.25 for predicting CO from compartment fires based on equivalence ratio:

T > 625 °C $$Y_{CO} = (0.22/180) * \tan^{-1}[10 * (\phi - 1.25)] + 0.11 \quad (2.24)$$

T < 525 °C $$Y_{CO} = (0.19/180) * \tan^{-1}[10 * (\phi - 0.8)] + 0.095 \quad (2.25)$$

where, the result of the inverse tangent function is in degrees.

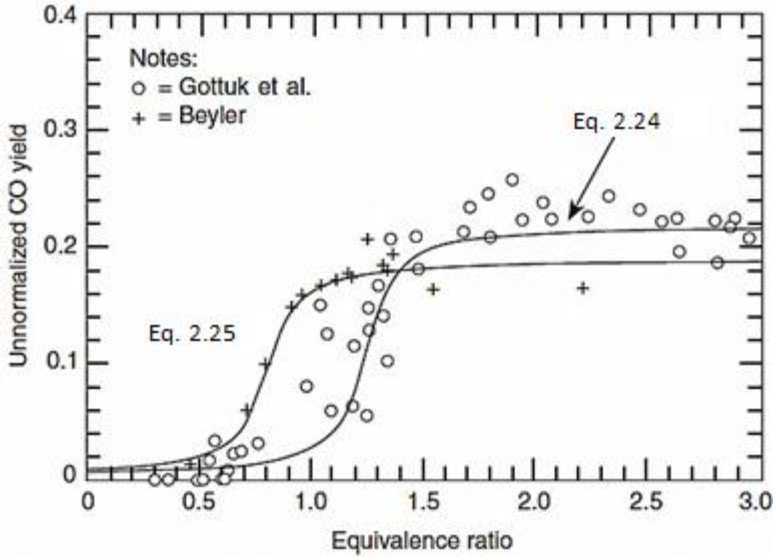


Figure 2-9: Gottuk and Beyler hexane results, along with Gottuk proposed correlation (Gottuk, 2002).

Gottuk observed external flames through the compartment vent. He argued external burning may affect the levels of CO in addition to the upper layer temperature and equivalence ratio. (Lattimar, 1996) investigated the effect of oxygen entrainment on the transport of CO in building fire. Using a RSE, similar to the one used by Gottuk, connected to hallway forming a L-shape configuration Lattimer investigated the CO, CO_2, UHC and O_2 levels in three locations. Inside the compartment, the hallway, and post hallway in the exhaust duct. In his work, Lattimer hypothesized that CO transport is most significantly affected by the oxygen entrainment into the compartment fire gases entering the hallway. Using a fixed size opening connecting the compartment to the hallway, the oxygen entrainment was varied by changing the depth of the oxygen deficient hallway upper-layer. A sketch of Lattimer experimental configuration is shown in Figure 2-10.

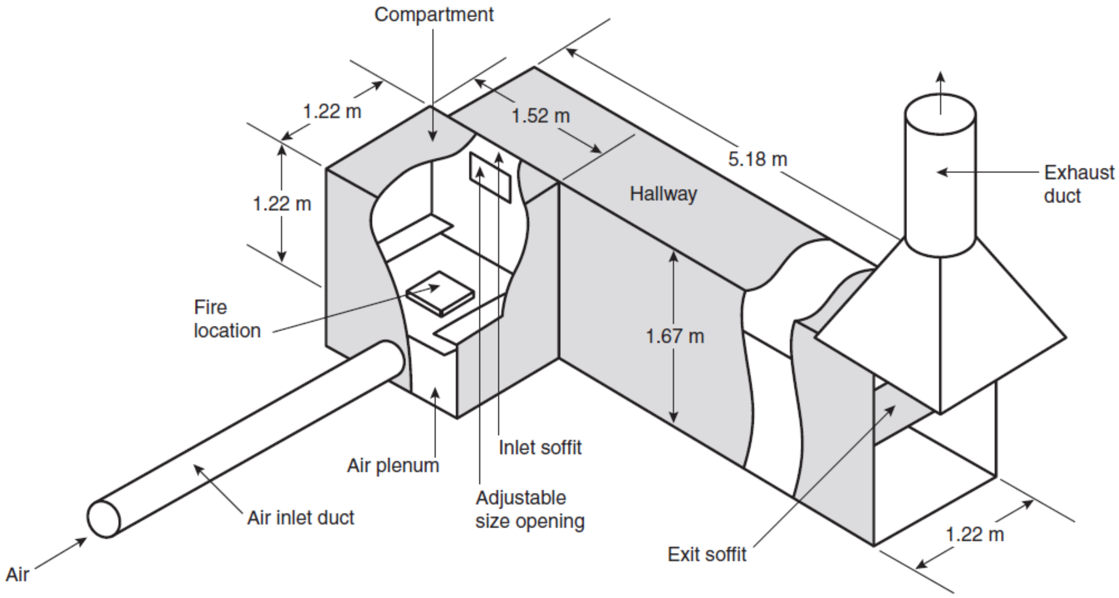


Figure 2-10: Experimental set up used by Lattimer 1996 adopted from (Gottuk, 2002).

Lattimer's (Lattimer, 1996; Lattimer et al., 1994) results show that in tests where compartment fire gases entered the hallway completely surrounded by oxygen deficient combustion gases, the post hallway CO yields were around 23% higher than CO yields measured inside the compartment, despite the presence of external burning. In tests where deep upper layers were present in the hallway, geometric effects were not observed to significantly affect the transported levels of CO, in fact, the CO level was a affected by compartment stoichiometry and external burning. He continues to explain, since the compartment was on the side of the hallway, the movement of the combustion products within the hallway was non-uniform. Gases containing high levels of CO were travelling across the hallway and then down the side of the hallway opposite to the fire compartment. On a final observation he reports, during steady state burning, the CO concentrations were 2.0-2.3% in the hallway.

The increased interest in the use of global equivalence ratio as a determent factor for estimating CO from fires, led (Pitts, 1995) to review the available information obtained from systematic studies on the formation of CO, and the applicability of the global equivalence ratio (GER) concept to real compartment fires. He concludes that the available evidence is that the correlation between CO formation and fire equivalence ratio is robust; nevertheless the applicability of the equivalence ratio to real scenario has its limitations. He explains it is important to acknowledge the effect of different fire scenarios and conditions on the fire, and the reliability of species production correlation to equivalence ratio. In his review, Pitts identified three upper layer temperature ranges that affected the applicability of the equivalence ratio concept along with other factors such as fresh air entrainment to the upper layer and the existence of fire load in the upper layer. His findings and recommendations are summarised below:

In conditions where the fire upper layer temperature is less than 425 °C, the use of GER concept is very appropriate. There is no evidence from the surveyed literature to dispute this, and it is believed that the upper layer is non-reactive. In fires where the upper layer is hotter than 625 °C, and fuel lean in terms of GER, the applicability of the GER concept is also appropriate. However, (Pitts, 1996) continue to explain that when the upper layer is hotter than 625 °C, and fuel rich in terms of GER, the applicability of the GER correlations to species have to be limited to cases where the only route to the fire plume is through the lower layer of the compartment. i.e. if there is a direct fresh air entrainment to the upper layer temperature the GER concept application is questionable as further chemical reaction and oxidation may exist. In addition, he continues to explain if, there exist a significant amount of combustible material such as wood in the upper layer, further pyrolysis and decomposition may occur in fires with a hot upper layer temperature, thus resulting in more CO production than expected by the simple GER correlations. Another fire conditions where the application of the GER concept should be treated with caution is in fires with a GER > 0.5 upper layer, and an intermediate temperatures ranging from 425-625 °C. In these circumstances, the reactions within the upper layer itself are possible and will be dependent on the layer residence time. Thus, the applicability of the GER should be corrected for temperature dependence. And more work should be done to identify these corrections.

Wieczorek studied carbon monoxide production and transport in compartment fires from a different prospective (Wieczorek, 2003). In his work a reduced scale enclosure, equivalent in size to 1/3 of ISO 9705 room test, adjacent to a 6 m long hallway were used. The compartment was fitted with a continuously fed n-hexane burner to generate limited ventilation compartment fires. A range of heat release rates ranging from 50 kW to 500 kW, along with four ventilation conditions with an opening area of 0.06, 0.15, 0.2, and 0.54 m^2. Uniformly distributed sampling rakes were used to map the species levels in the compartment door, and the adjacent hallway. In his work Wieczorek argues, that predictive techniques based on GER were not adequate for conditions where the plume equivalence ratio was different to that of the GER, or the upper layer equivalence ratio. He introduces a new parameter called non-dimensional heat release rate $\tilde{Q}$. The new parameter is based on the fuel load and geometrical parameters of the enclosure. He further explains this methodology is appropriate where no uniform upper layer is present, and the GER is not determined. Although detailed species concentration and mapping was provided for the hallway and compartment door, only steady state single point measurement were used for the correlation developed.

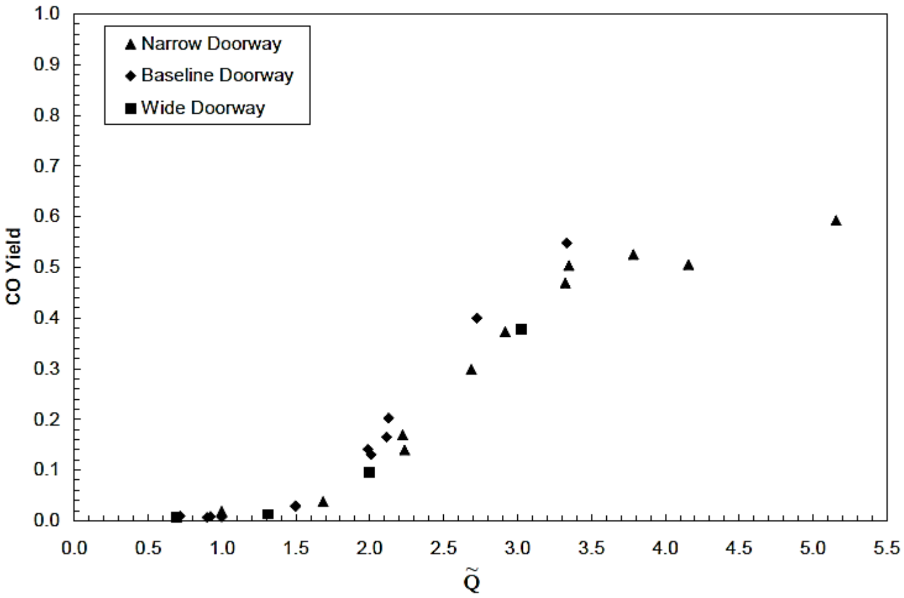


Figure 2-11: CO yield as a function of none dimensional heat release rate (Wieczorek, 2003).

Wieczorek proposed non-dimensional heat release rate is defined as the Ideal heat release rate (assuming complete combustion) divided by the flame extension heat release rate (taken as the flame reach the compartment doorway). As shown in equation Eq. 2.26:

$$\tilde{Q} = \frac{\dot{Q}_{ideal}}{\dot{Q}_{Flame\ Extension}} \tag{2.26}$$

where;

$$\dot{Q}_{ideal} = \dot{m}_{fuel}\ \Delta\ H_c \tag{2.27}$$

And $\dot{Q}_{Flame\ Extension}$ is an experimentally determined heat release rate corresponding to the flame reaching the door for each ventilation condition. However, it can be argued that since the ventilation opening is constant, and the fuel flow is variable producing the idealised heat release, and the flame extension heat release, this new parameter is another expression of the combustion stoichiometry. In addition, the use of a continuously fed burner made the fourth condition, least ventilation, not possible. Wieczorek explains since the opening area of the fourth ventilation condition was smaller than the burner area, therefore making the reaction zone (flames) outside the fuel rich compartment in the adjacent hallway.

Another more recent study was conducted by (Utiskul, 2005; Utiskul and Quintiere, 2005; Utiskul et al., 2005) to examine the behaviour of fully developed compartment fires. In his work, Utiskul examined different fire behaviour characteristics such as extinction, oscillation, fire area shrinkage, and response of fuel to thermal and oxygen effect. The experimental work was complemented with the development of one zone model for compartment fires with a single ventilation opening. Although this work was not directly related to combustion products, or fire products toxicity, it's important as it examines important criteria associated with ventilation controlled fires. The experimental work was carried out in a RSE measuring 40, 40, 120 cm, fitted with top and bottom vents (Utiskul, 2005). Perhaps the most significant finding of the experimental work was the identification of burning behaviour regimes based on the heptane pool fires tests.

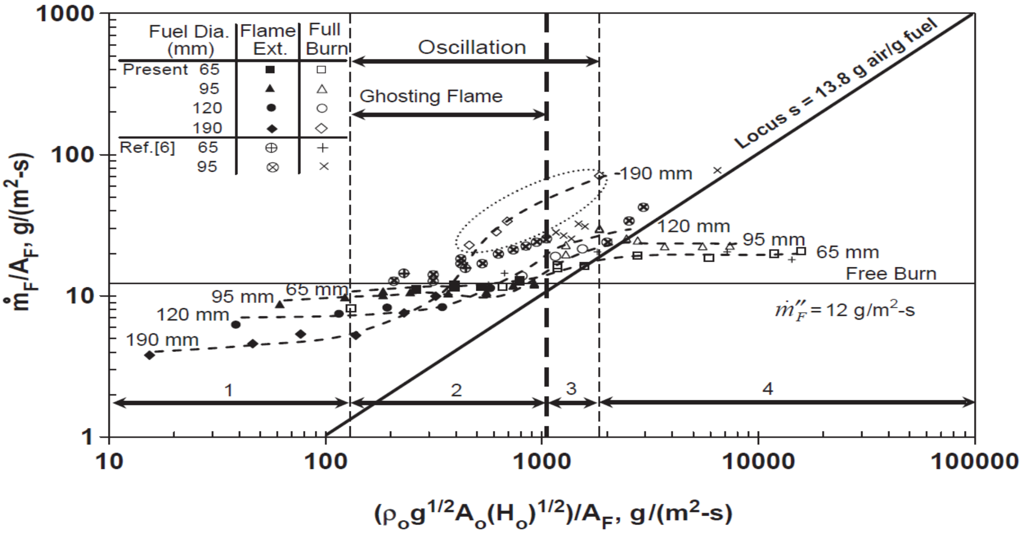


Figure 2-12: Compartment fuel mass loss rate versus ventilation parameter(Utiskul et al., 2005)

In his dimensionless analysis Utiskul explains, compartment burning rate depends on two dimensionless groups; the ratio of vent flow to the fuel flow, and the wall heat loss to fuel flow. The criterion adopted in their work was the vent flow to the fuel flow, which was is presented in Figure 2-12. On that figure, the oscillating burning, ghosting burning, and flame extension regimes were characterised by the fuel mass loss rate divided by the fuel surface area versus fuel surface ventilation parameter.

(Utiskul, 2005) work was the second in fire literature to refer to ghosting flames behaviour in low ventilation hydrocarbon compartment fires. The first was the pioneering study by Sugawa (Sugawa, 1991). In his work, Sugawa investigated fire behaviour under poor-ventilation conditions using a methyl alcohol 30 cm diameter pool as the fire source. Around 40 tests were carried out in the RSE enclosure measuring 2, 3, 0.6 m. the box was mapped with gas and temperature sampling vertical rakes distributed in 10 locations. A small observation window/door was used as the ventilation source measuring 60 by 60 cm. Sugawa’s works concentrated on the flame shape and ghosting flames phenomena. No detailed discussion on the species production rates from these burning conditions was provided. The ghosting flames behaviour was observed in this work, and was discussed extensively by the author in (Aljumaiah, 2011C). It will be shown in Chapter 8, that it exhibits a strong dependency on the hydrocarbon fuel physical properties, and upper layer temperature.

More recently, a major project on limited ventilation hydrocarbon fires was conducted by NIST (Bundy et al., 2007; Ko et al., 2009) The aim of the study was to generate detailed information on ventilation controlled pool fires, useful for validating fire CFD models. A range of hydrocarbon fuels including: Natural gas, Heptane, Toluene, Methanol, Ethanol, and Polystyrene were studied in a 1.4 m^3 reduced scale enclosure. The RSE was equivalent to 2/5 of the ISO 9705 room in size, and had two open door configurations which were equivalent to 0.388, and 0.194 m^3 in area. A sketch of the compartment used is shown in figure 2-13. Four different burners were used all continuously fed by the gas or liquid fuel except for the polystyrene pallets which were burnt in a pan. The heat release rates were measured using oxygen calorimetry method introduced by (Huggett, 1980) as well as the theoretical heat release rate obtained from the fuel flow. Gas samples were taking from two locations at the front and rear upper layer in the compartment, and analysed using oxygen paramagnetic analyser, non-dispersive infrared (NDIR), flame ionisation detector (FID), and gas chromatograph

(GC), for O_2, CO_2, CO, and UHC. In addition, gravimetric soot sampling system was used to measure the soot mass fraction. Soot samples were sampled over periods of 60 s to 300 s, at a standard flow rate of 2.75 L/min. The last piece of equipment used in their work was an optical extinction soot measurement, using laser transmission.

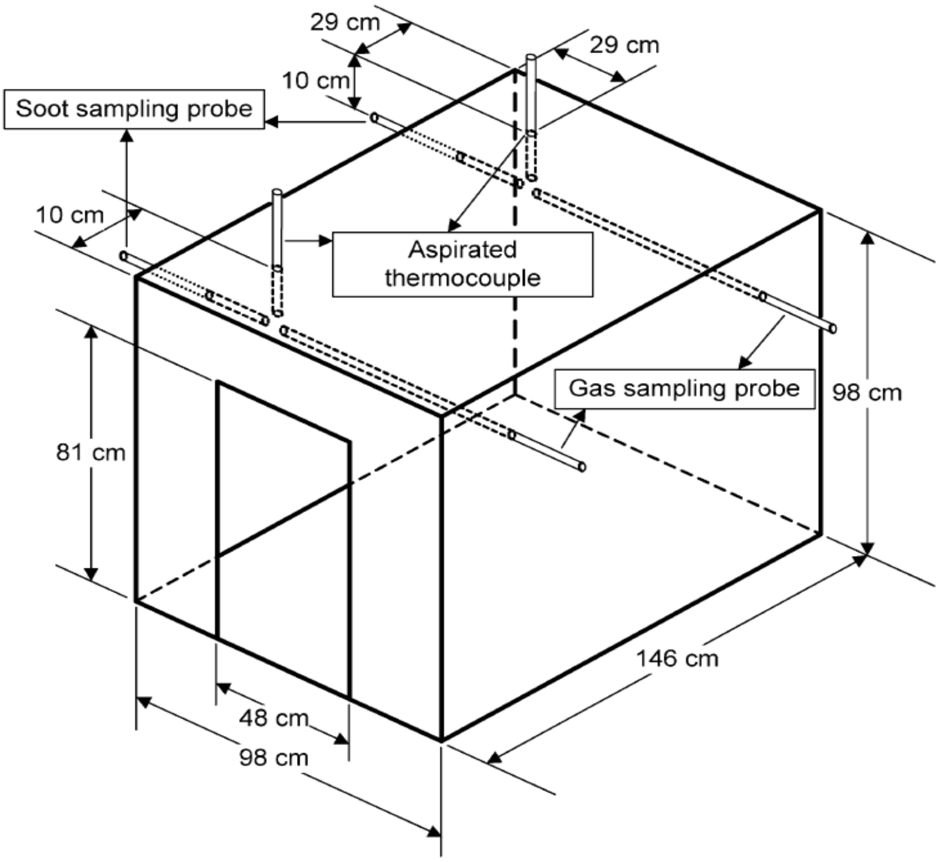


Figure 2-13: Sketch showing the dimensions and sampling locations of the RSE used by NIST (Bundy et al., 2007).

The measured mass fraction of the gas species were reported as a function of the mixture fraction. In addition CO yields were reported as a function of the local equivalence ratio. The results suggests the local composition as a function of the mixture fraction adequately collapses hundreds of species measurements from an variety of compartment conditions with varying heat release rates and spatial locations into a few coherent lines or bands. They also report significant fraction of carbon is turned into soot in the upper layer of smoky compartment fires, and the inclusion of soot in the mixture fraction analysis improves the identification fuel rich conditions.

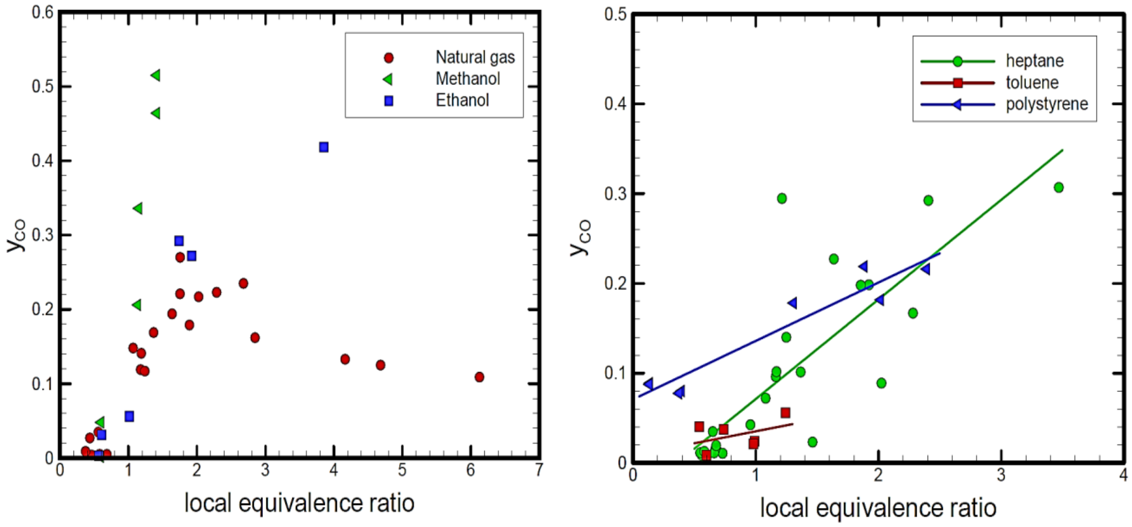


Figure 2-14CO yields vs equivalence ratio from the NIST study (Bundy et al., 2007)

The CO yields for the six fuels investigated are shown in a plot against the equivalence ratio in Figure 2-14. In general, the lighter fuels such as ethanol and methanol had the highest CO yields, while toluene showed the lowest CO yields. A significant scatter of heptane CO yields existed, while CO yields from the natural gas tests were decreasing after the equivalence ratio of 3. The yields of CO and soot in the upper layer of the reduced-scale compartment fires were related to the local equivalence ratio for fires burning ethanol, heptane, toluene and polystyrene, over a wide range of fire sizes, but significant scatter precludes use of the data for CO prediction; the relationship was non-linear in fires burning methanol and natural gas. In addition, the ratio of CO yield to soot yield was found to be approximately independent of local equivalence ratio for the smoky fuels. However, no discussion on the temperature effect on the soot formation a topic frequently studied in engine research studies as in (Akihama et al., 2001). The author of this work presented parts of this thesis and in (Aljumaiah et al., 2011a; Aljumaiah et al., 2010d) highlighting the burning behaviour of hydrocarbon fuels in a much lower ventilation, and heat release rate intensity, resulting in much lower soot yields and higher UHC productions.

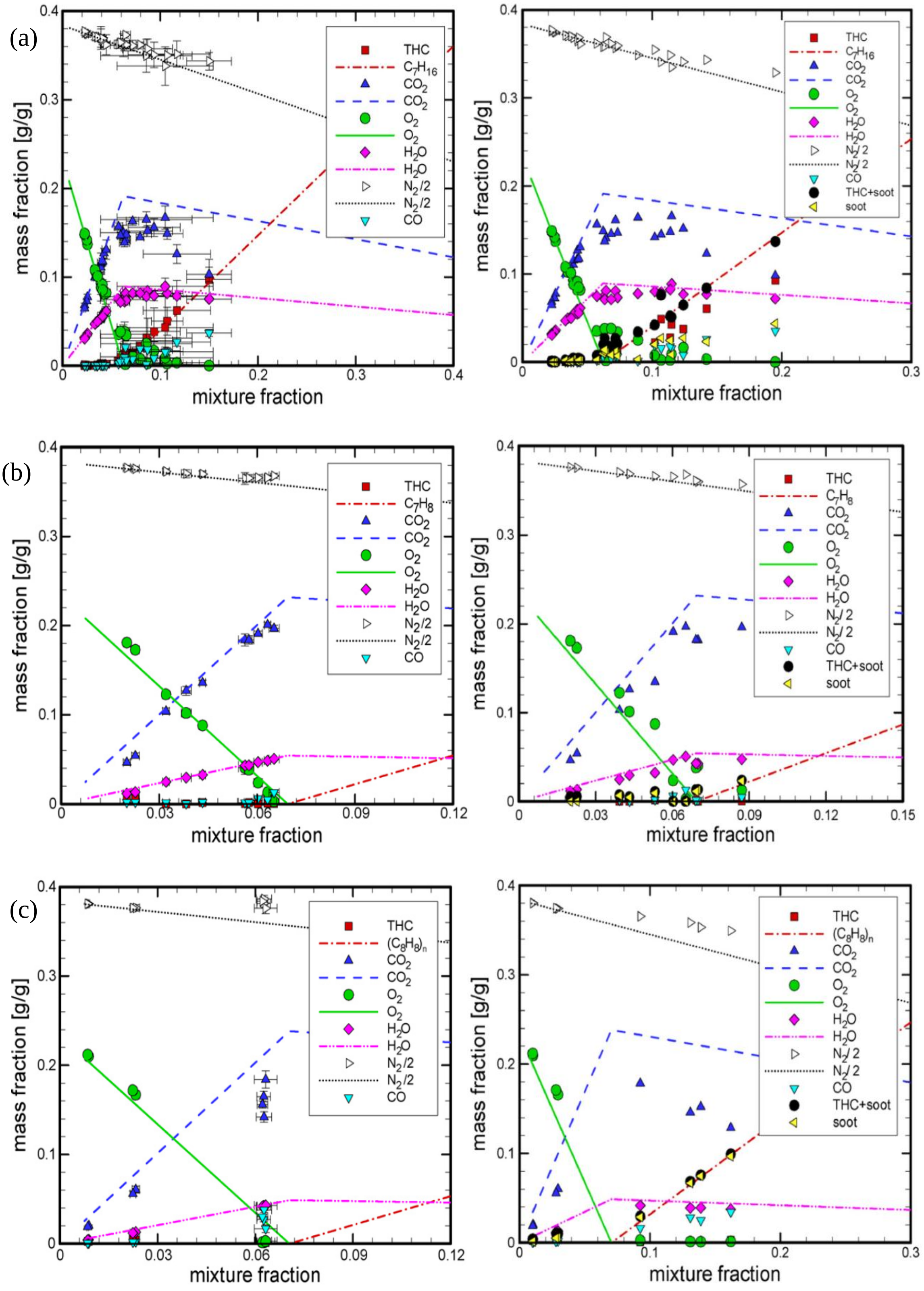


Figure 2-15: Averaged quasi-steady state mass fraction measurements as a function of the mixture fraction for Heptane (a), Toluene (b), and Polystyrene (c) without inclusion of soot (Left) and with the inclusion of soot (Right) (Ko, 2009).

2.4.3 FULL SCALE STUDIES

Full scale tests, such as ISO9705, are the most accredited approach for obtaining data on toxic fire smoke from compartment fires. The results obtained from these tests are often regarded as the bench mark smaller apparatus results should be compared to and validated against. This section will report few of the major room scale studies on combustion products.

One of the earliest full scale studies devoted for obtaining toxic smoke data was conducted by NIST and published in (Babrauskas et al., 1991a; Babrauskas et al., 1991b). In that study, tests were conducted in a room scale compartments in order to validate smaller scale toxicity apparatus. The validation criteria were individual toxic species yield, animal exposure study, and toxic potency measurement using the N gas model. The tests compartment configuration consisted of a burn room, connected to a corridor, leading to a target room which had an opening to the atmosphere. The burn room was 2.13 m^3 in size, 2.4m wide, 3.7 m, long and 2.4m high. The corridor was 2.4 m wide, 4.6 long, and 2.4 m high. The doors between the burn room and target room were identical 1.5m^2 in area, 2.03 m high, and 0.76 m wide each. Gas sampling was made at the entrance of the target room, where a sample of the upper layer was taken for animal exposure analysis, and another sample was take for the gas analysers. The gas analysers were a paramagnetic O_2 analyser, Infra-red CO_2 and CO analysers, and Ion chromatography (IC) for HCl, HBr, and HCN. The IC analyser required limited samples, and no continuous results were possible. The Fuels investigated were wood, rigid polyurethane (RPU), and polyvinyl chloride (PVC) cribs. They measured 23 kg, 1.0 kg, and 16 kg respectively. For the PVC test a 450 kW gas burner was used since it was not able to sustain burning on its own. The toxic species yields measured results are summarised in the table 2-8.

The toxic species yields results from (Babrauskas et al., 1991a) were reported to agree with other results in the project obtained using bench scale and medium scale setup with a factor of three. The weakness of this study include, it represents a highly ventilated fires due to the large amount of available ventilation and fuel load configuration. It appears that only the PVC tests were fuel rich at some stage, due to the use of the 450kW gas burner. In addition, the authors report due to difficulties in measurements handling, some yields were based on calculated estimates and not direct measurements, which makes the integrity of the results under question. And finally, the degree of acceptance as factor of three represents a very high error margin.

Table 2-8: Major species yields from the NIST 1991 full scale study (Babruskas et al., 1991a).

Test		Y_{CO}	Y_{CO2}	Y_{HCl}	Y_{HCN}
Wood	Analytical DF2	0.091	1.2	-	-
	Animal DF1	0.072	1.2	-	-
	Animal DF2	0.12	1.8	-	-
RP	Analytical RPU	0.14	2.2	-	0.009
	Animal RPU 1	0.12	1.5	-	0.005
	Animal RPU 2	0.10	2.2	-	0.011
PVC	Analytical PVC 1	0.25	0.96	0.12	-
	Analytical PVC 2	0.19	0.67	0.22	-
	Animal PVC 1	0.43	1.1	0.19	-
	Animal PVC 2	0.29	0.78	0.18	-
	Animal PVC 3	0.47	0.32	0.09	-

(Chamberlain, 1996) investigated large scale diesel pool fires for the purpose of generating experimental data for fire models validations. In his work, the compartment used was 135m^3 in volume, 3.91 m high, 3.54m wide, and 9.8m long. A fully open wall was the configuration used for fuel controlled tests, whiles vent areas of 5 and 12 m^2 were used for ventilation controlled tests. About 20 kg of diesel were used in each test. The fuel was loaded into 1m^2 steel pans, arranged in different configurations. The test configuration variables included using 6 or 12 fuel pans located in the middle or near the wall, and the use of small or large vent. The diesel fuel had a boiling range of 165-360 °C, and calibration tests suggested the overall burning rate was 0.03 kg/m^2/s. A failed attempt was made to measure the rate of fuel mass loss rate (burning rate), by placing a load cell underneath one of the central pans, therefore, the measure of burning rate is derived from the total time to a marked drop in fire intensity due to fuel depletion.

In an analysis of the most intense tests, highest fuel load, and largest vent configuration of the reported experiments, the pan radiometer measured constant radiation throughout the majority of the test period and there was no evidence of increased burning due to increased radiative feedback from the hot upper layer, a phenomenon which often reported in compartment fires literature. This observation strongly suggests that the mechanism of radiative feedback which controls the burning rate had maximised, and that the fire had attained its peak value of fuel loss rate. In addition, a significant feature of his work was the very high temperatures reported, which reached 1350 °C above the fire plume before the thermocouples failed. These high temperatures were associated with a sudden increase in soot concentrations, Chamberlien hypothesised that unburnt fuel in the fire plume was pyrolysed to soot more readily at these high temperatures. This can be assumed to be a function of highly insulated compartment fires, were heat build-up is significantly more than open fires.

In general, Chamberlien concludes, these experiments showed that fire severity in large-scale hydrocarbon pool fires is worse in over-ventilated, but confined conditions. The burning rate of ventilation controlled pool fires is self-limiting and the fire tends to settle in near stoichiometric, but slightly under-ventilated regime. However, the measure of severity in his work was heat flux and gas temperature, and no detailed discussion was provided on toxic emissions. The limited information provided on gas measurements, show that CO percentage increased from ≈ 0.5 % in the test with a large ventilation opening 12m^2, to ≈ 4.0% in the smaller ventilation opening of 5m^2.

A more advanced effort was conducted in the TOXFIRE project (Lönnermark et al., 1996), in which full-scale tests were performed at the Swedish National Testing and Research Institute, SP, (Blomqvist and Lönnermark, 2001)using an ISO 9705 room with solid and liquid fuel sources. The compartment ventilation was varied by maintaining the same door width and changing the sill height. The door was 0.8 m wide and 2.0 m high, however the height was reduced to 0.89 m, 0.68 m, 0.56 m, and 0.45m in order to achieve under ventilated conditions. The ventilation rate was expressed as global equivalence ratio, metered using a specifically developed phi meter. Five fuel types were investigated, polypropene (PP), Nylon 66, (Ny), tetramethyl-thiuram monosulfide (TMTM), chlorobenzene (CB), and chloronitrobenzoic acid (CNBA). Gas sampling was extracted from across the upper layer of smoke at the door, using a FTIR for CO_2, CO, HCN, HCl, and SO_2, a FID for total unburnt hydrocarbons UHC, and a chemiluminescene for NO_x. Another sampling location was in the duct of the collection hood, where a CO/CO_2 analyser and a FID for UHC were used. The results were presented as data points for sampled periods where they equivalence ratio was constant. Figure 2-16 shows the yields of HCN, CO, and UHC from the selected tests. The project was expanded by considering an even larger test facility simulating a storage compartment. Similar fire loads were examined and the results from the two tests were compared. In general, it was noted that the ISO room test had hotter upper layer temperatures than the storage room tests; this resulted in relatively higher toxic yields in the ISO room tests. No further discussion was provided on the results by the authors. Nevertheless, the authors conclude that combustion products yields show strong dependence on the equivalence ratio, and material chemical composition. They also acknowledge the temperature effect on the combustion chemistry. They argue that it is possible to measure a global equivalence ratio in large scale compartment fires and perform under-ventilated condition in the ISO 9705 room fire test. However, prolonged steady state high equivalence ratios burning was not possible from the configuration used. They also noted that larger tests simulating storage facility did not reach under ventilated conditions. The final remark was that highly ventilated compartment fire tests performed in the ISO 9705 room produced toxic yields similar to that obtained from free burning pool fires, and large storage facility.

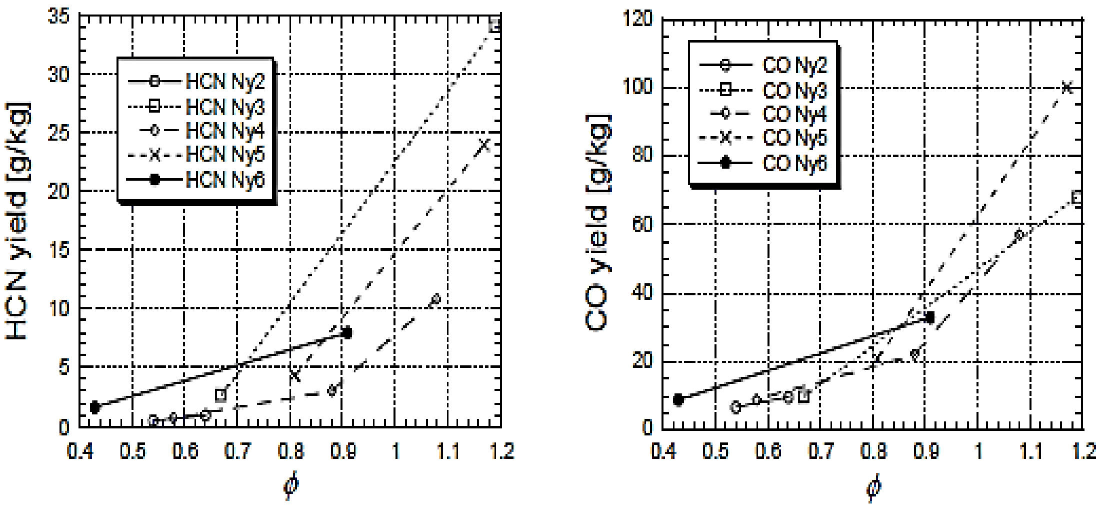


Figure 2-16: HCN and CO yields as a function of the fire equivalence ratio in Nylon tests (Blomqvist and Lönnermark, 2001).

The TOXFIRE was one of the early works in fire studies to attempt comprehensive online toxic smoke data analysis. The authors report that technical difficulties have restricted them from obtaining continuous measurements. Therefore, a sampling period approach was used to report the data for the stable measurements periods. The use of the FTIR was challenging, as it was a new approach in fire studies, and difficulties were reported in water presence causing IR-spectrum interference between different species. As well as, exceeding the calibrated range for some of the measured species, this also interferes with other species spectrum. As a consequence of the difficulties, some important data had to be excluded such as CO measurements in the TM/TM tests. Figures 2-16, and 2-17 show some of the data obtained through the TOXFIRE project.

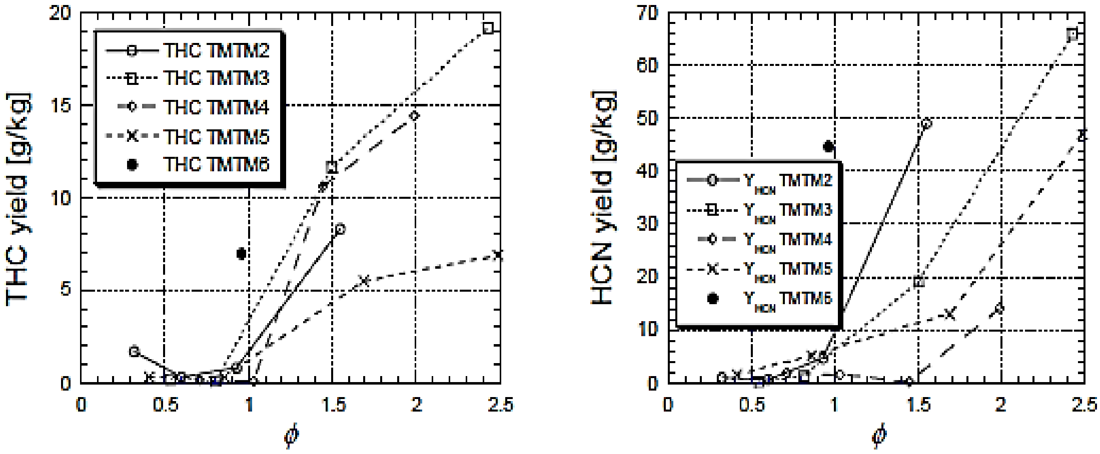


Figure 2-17: THC and HCN yields as a function of the fire equivalence ratio in TM/TM tests (Blomqvist and Lönnermark, 2001).

More recently, a technical paper on the most advanced attempt to investigate toxic smoke components in real-scale compartment fires was published in (Gann et al., 2010). The published paper is based on an earlier project concluded in NIST technical note 1345 (Gann et al., 2003). Despite significant efforts made by the research team, the results were of little value as unusual uncertainty in the FTIR measurements, reaching 378 %, was reported hammering the credibility of the results. In addition, to the FTIR uncertainties, the CO yields measured using standard NDIR were significantly lower than expected for post flashover fires as the highest CO yield was 0.15 kg/kg in comparison to 0.2 kg/kg often reported in earlier studies. The malfunction of the results, was acknowledged by the authors of the report, and highlighted by critics such as (Hirschler, 2005), nevertheless, this work remains the most technically advanced project and a lot can be learnt from the reported experimental work. An overview of the test series is provided in this section.

The experimental set up represented a room corridor structure as shown in figure 2-18. The room dimensions were 2.44 m wide, 2.44 m high, and 3.66 m long, while the corridor was 9.75 m long with the same width and height as the room. The corridor opened to the open, while the room to corridor door measured 0.76 m wide and 2.0 m high. The fuels investigated were a sofa made of upholstered cushions weighing 15.4 kg, a particleboard bookcase weighing 27.5 kg, a rigid polyvinyl chloride (PVC) sheet added to some book cases tests, and household wiring cable consisting of copper insulated with nylon and PVC weighing around 77 kg in total. A downward facing propane burner was used to ignite the sofa, an upward burner was used to ignite the bookcases from below, and twin burners were used for igniting the electrical cables. Gas sampling was made at four locations as shown in Figure 2-18 one inside the room, a couple just outside the room corridor and a fourth location at the far end of the corridor. The two sampling location near the door were chosen to investigate the gas composition after the jet flames region coming out through the door.

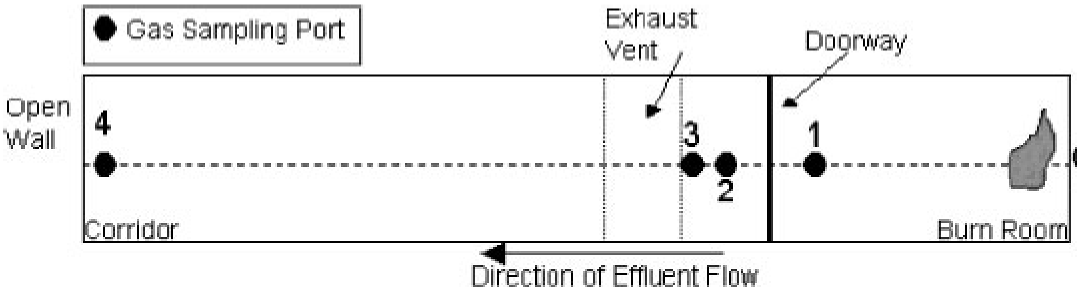


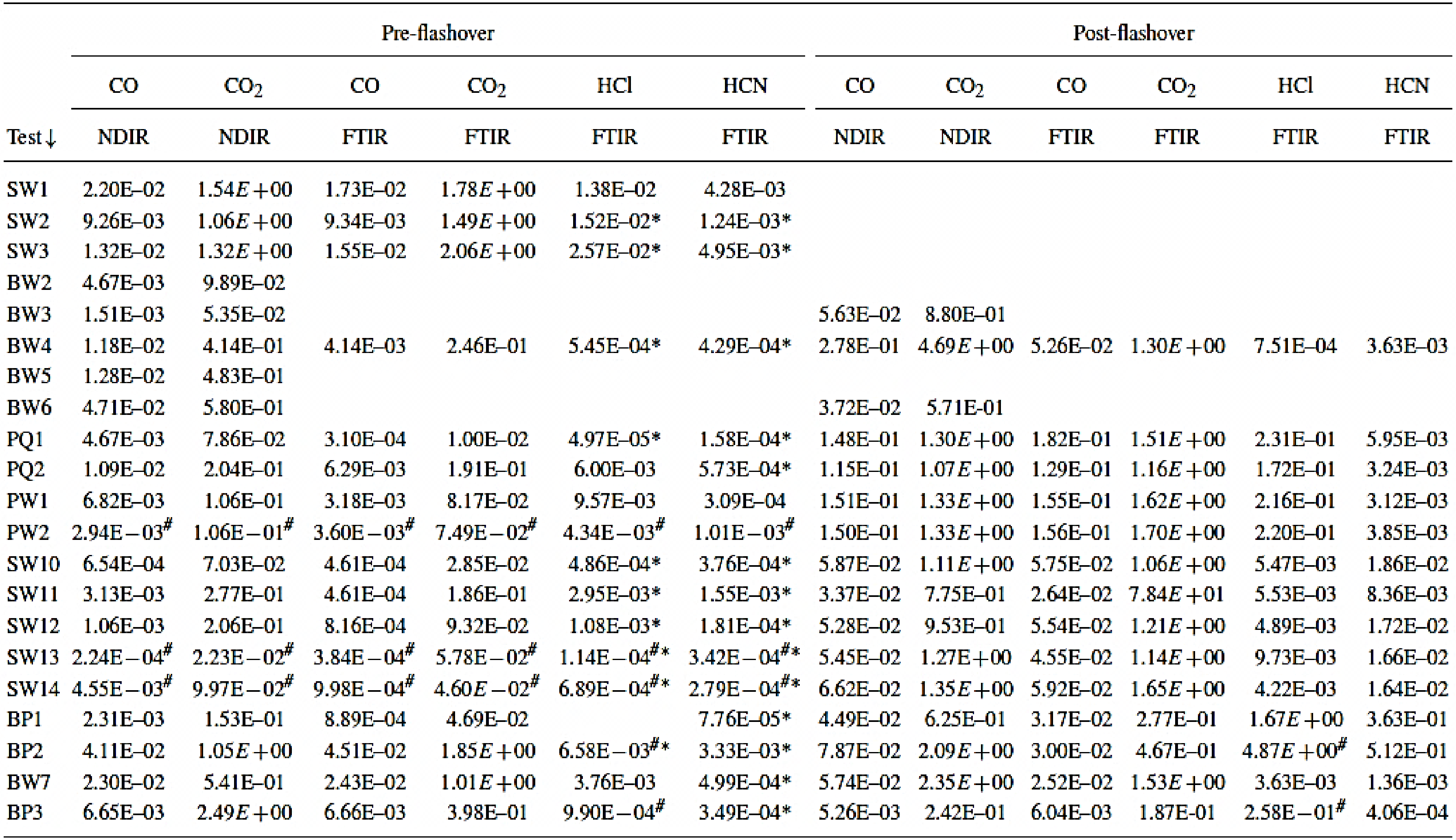
Figure 2-18: room corridor configuration in (Gann, 2010) study.

The smoke analysers included a non-dispersive infrared (NDIR) for CO and CO_2 measurements, a paramagnetic analyser for oxygen measurements, two Midac Illuminator FTIR spectrometers for CO, CO_2, HCN, HCl, HF, HBr, NO, NO_2, CH_2O (formaldehyde), and CH_2=CH-CH=O (acrolein) measurements, and a soot sampling system. The tests were coded to for the test variables; the first letter of the code represented the fuel type. S was used for Sofa fires, B for Bookcase fires, and P for Power cables. The other variables represented the location of the fire load in the room, and the test sequence number. The majority of the results are reported in detail in table 2-9, however as mentioned earlier the credibility of the reported data is very low. In addition, two sofa tests were carried out in a closed door. The results from those tests are reported in table 2-10. Possible reason for the huge uncertainty in the FTIR results of their work is the variation in the closeness of the signal to the background level, and the degree of spectral interference from other species. These factors among others will be discussed further in the experimental section of this thesis. The authors acknowledge the short comes of their work and summarise their prospective on the use of FTIR in fire research studies in the following points:

- The application of FTIR spectroscopy to fire testing requires the constant attention of an experienced professional, at a level well beyond the traditional fire instrumentation.
- The use of small optical path length, limited the sensitivity of the apparatus but it was still possible to detected important major gases.
- The long heated lines used in accordance with the SFAIR project recommendations (Hakkarainen et al., 2000), allowed the measurement of HCl a compound usually difficult to detect.

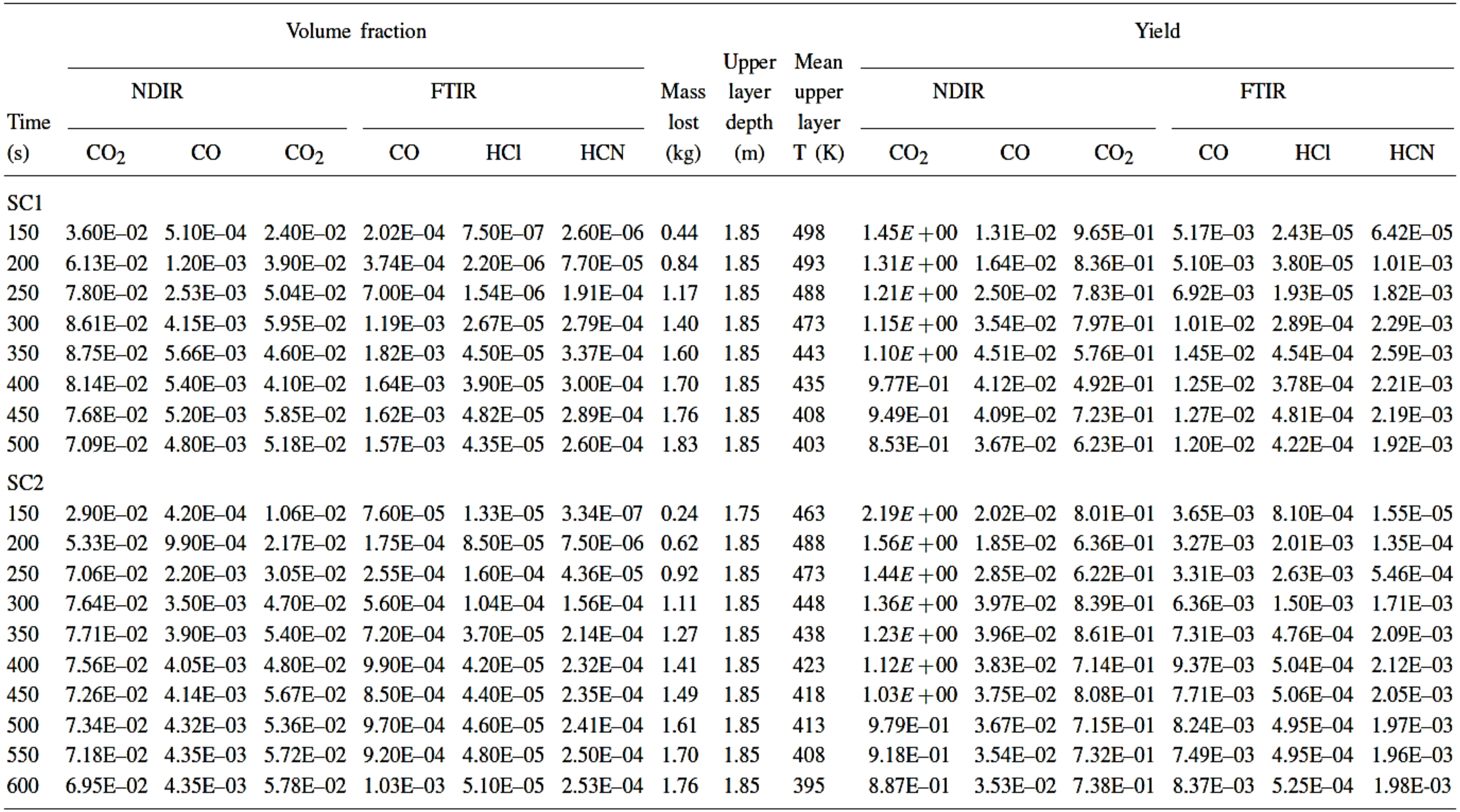
The authors of the NIST report conclude their work by acknowledging the most disappointing deficit of the project, the unexpected low CO yields in comparison to earlier studies. They also report not being able to measure significant irritants such as acrolein, formaldehyde, and NO_2, and arguably discard them as of not significance. Their point of view towards these irritants may be misleading as they form a significant proportion of the impairment of escape hazard, and as detailed in this thesis, medical studies reviewed by work exposure medical committees suggest that even the lowest concentrations may result in serious irritation and potentially damaging conditions resulting in impairing escape large proportions of fire victims.

Table 2-9: Average yields for pre flashover, and post flashover in the NIST full scale study (Gann et al., 2010).



	Pre-flashover						Post-flashover					
	CO	CO_2	CO	CO_2	HCl	HCN	CO	CO_2	CO	CO_2	HCl	HCN
Test↓	NDIR	NDIR	FTIR	FTIR	FTIR	FTIR	NDIR	NDIR	FTIR	FTIR	FTIR	FTIR
SW1	2.20E–02	1.54E+00	1.73E–02	1.78E+00	1.38E–02	4.28E–03						
SW2	9.26E–03	1.06E+00	9.34E–03	1.49E+00	1.52E–02*	1.24E–03*						
SW3	1.32E–02	1.32E+00	1.55E–02	2.06E+00	2.57E–02*	4.95E–03*						
BW2	4.67E–03	9.89E–02										
BW3	1.51E–03	5.35E–02					5.63E–02	8.80E–01				
BW4	1.18E–02	4.14E–01	4.14E–03	2.46E–01	5.45E–04*	4.29E–04*	2.78E–01	4.69E+00	5.26E–02	1.30E+00	7.51E–04	3.63E–03
BW5	1.28E–02	4.83E–01										
BW6	4.71E–02	5.80E–01					3.72E–02	5.71E-01				
PQ1	4.67E–03	7.86E–02	3.10E–04	1.00E–02	4.97E–05*	1.58E–04*	1.48E–01	1.30E+00	1.82E–01	1.51E+00	2.31E–01	5.95E–03
PQ2	1.09E–02	2.04E–01	6.29E–03	1.91E–01	6.00E–03	5.73E–04*	1.15E–01	1.07E+00	1.29E–01	1.16E+00	1.72E–01	3.24E–03
PW1	6.82E–03	1.06E–01	3.18E–03	8.17E–02	9.57E–03	3.09E–04	1.51E–01	1.33E+00	1.55E–01	1.62E+00	2.16E–01	3.12E–03
PW2	2.94E–03$^{\#}$	1.06E–01$^{\#}$	3.60E–03$^{\#}$	7.49E–02$^{\#}$	4.34E–03$^{\#}$	1.01E–03$^{\#}$	1.50E–01	1.33E+00	1.56E–01	1.70E+00	2.20E–01	3.85E–03
SW10	6.54E–04	7.03E–02	4.61E–04	2.85E–02	4.86E–04*	3.76E–04*	5.87E–02	1.11E+00	5.75E–02	1.06E+00	5.47E–03	1.86E–02
SW11	3.13E–03	2.77E–01	4.61E–04	1.86E–01	2.95E–03*	1.55E–03*	3.37E–02	7.75E–01	2.64E–02	7.84E+01	5.53E–03	8.36E–03
SW12	1.06E–03	2.06E–01	8.16E–04	9.32E–02	1.08E–03*	1.81E–04*	5.28E–02	9.53E–01	5.54E–02	1.21E+00	4.89E–03	1.72E–02
SW13	2.24E–04$^{\#}$	2.23E–02$^{\#}$	3.84E–04$^{\#}$	5.78E–02$^{\#}$	1.14E–04$^{\#*}$	3.42E–04$^{\#*}$	5.45E–02	1.27E+00	4.55E–02	1.14E+00	9.73E–03	1.66E–02
SW14	4.55E–03$^{\#}$	9.97E–02$^{\#}$	9.98E–04$^{\#}$	4.60E–02$^{\#}$	6.89E–04$^{\#*}$	2.79E–04$^{\#*}$	6.62E–02	1.35E+00	5.92E–02	1.65E+00	4.22E–03	1.64E–02
BP1	2.31E–03	1.53E–01	8.89E–04	4.69E–02		7.76E–05*	4.49E–02	6.25E–01	3.17E–02	2.77E–01	1.67E+00	3.63E–01
BP2	4.11E–02	1.05E+00	4.51E–02	1.85E+00	6.58E–03$^{\#*}$	3.33E–03*	7.87E–02	2.09E+00	3.00E–02	4.67E–01	4.87E+00$^{\#}$	5.12E–01
BW7	2.30E–02	5.41E–01	2.43E–02	1.01E+00	3.76E–03	4.99E–04*	5.74E–02	2.35E+00	2.52E–02	1.53E+00	3.63E–03	1.36E–03
BP3	6.65E–03	2.49E+00	6.66E–03	3.98E–01	9.90E–04$^{\#}$	3.49E–04*	5.26E–03	2.42E–01	6.04E–03	1.87E-01	2.58E–01$^{\#}$	4.06E–04

Table 2-10: Major toxic species volume fraction and yields for the closed door tests (Gann et al., 2010).



Time	Volume fraction						Mass	Upper	Mean	Yield					
	NDIR			FTIR			lost	layer	upper	NDIR			FTIR		
(s)	CO_2	CO	CO_2	CO	HCl	HCN	(kg)	depth (m)	layer T (K)	CO_2	CO	CO_2	CO	HCl	HCN
SC1															
150	3.60E–02	5.10E–04	2.40E–02	2.02E–04	7.50E–07	2.60E–06	0.44	1.85	498	1.45E+00	1.31E–02	9.65E–01	5.17E–03	2.43E–05	6.42E–05
200	6.13E–02	1.20E–03	3.90E–02	3.74E–04	2.20E–06	7.70E–05	0.84	1.85	493	1.31E+00	1.64E–02	8.36E–01	5.10E–03	3.80E–05	1.01E–03
250	7.80E–02	2.53E–03	5.04E–02	7.00E–04	1.54E–06	1.91E–04	1.17	1.85	488	1.21E+00	2.50E–02	7.83E–01	6.92E–03	1.93E–05	1.82E–03
300	8.61E–02	4.15E–03	5.95E–02	1.19E–03	2.67E–05	2.79E–04	1.40	1.85	473	1.15E+00	3.54E–02	7.97E–01	1.01E–02	2.89E–04	2.29E–03
350	8.75E–02	5.66E–03	4.60E–02	1.82E–03	4.50E–05	3.37E–04	1.60	1.85	443	1.10E+00	4.51E–02	5.76E–01	1.45E–02	4.54E–04	2.59E–03
400	8.14E–02	5.40E–03	4.10E–02	1.64E–03	3.90E–05	3.00E–04	1.70	1.85	435	9.77E–01	4.12E–02	4.92E–01	1.25E–02	3.78E–04	2.21E–03
450	7.68E–02	5.20E–03	5.85E–02	1.62E–03	4.82E–05	2.89E–04	1.76	1.85	408	9.49E–01	4.09E–02	7.23E–01	1.27E–02	4.81E–04	2.19E–03
500	7.09E–02	4.80E–03	5.18E–02	1.57E–03	4.35E–05	2.60E–04	1.83	1.85	403	8.53E–01	3.67E–02	6.23E–01	1.20E–02	4.22E–04	1.92E–03
SC2															
150	2.90E–02	4.20E–04	1.06E–02	7.60E–05	1.33E–05	3.34E–07	0.24	1.75	463	2.19E+00	2.02E–02	8.01E–01	3.65E–03	8.10E–04	1.55E–05
200	5.33E–02	9.90E–04	2.17E–02	1.75E–04	8.50E–05	7.50E–06	0.62	1.85	488	1.56E+00	1.85E–02	6.36E–01	3.27E–03	2.01E–03	1.35E–04
250	7.06E–02	2.20E–03	3.05E–02	2.55E–04	1.60E–04	4.36E–05	0.92	1.85	473	1.44E+00	2.85E–02	6.22E–01	3.31E–03	2.63E–03	5.46E–04
300	7.64E–02	3.50E–03	4.70E–02	5.60E–04	1.04E–04	1.56E–04	1.11	1.85	448	1.36E+00	3.97E–02	8.39E–01	6.36E–03	1.50E–03	1.71E–03
350	7.71E–02	3.90E–03	5.40E–02	7.20E–04	3.70E–05	2.14E–04	1.27	1.85	438	1.23E+00	3.96E–02	8.61E–01	7.31E–03	4.76E–04	2.09E–03
400	7.56E–02	4.05E–03	4.80E–02	9.90E–04	4.20E–05	2.32E–04	1.41	1.85	423	1.12E+00	3.83E–02	7.14E–01	9.37E–03	5.04E–04	2.12E–03
450	7.26E–02	4.14E–03	5.67E–02	8.50E–04	4.40E–05	2.35E–04	1.49	1.85	418	1.03E+00	3.75E–02	8.08E–01	7.71E–03	5.06E–04	2.05E–03
500	7.34E–02	4.32E–03	5.36E–02	9.70E–04	4.60E–05	2.41E–04	1.61	1.85	413	9.79E–01	3.67E–02	7.15E–01	8.24E–03	4.95E–04	1.97E–03
550	7.18E–02	4.35E–03	5.72E–02	9.20E–04	4.80E–05	2.50E–04	1.70	1.85	408	9.18E–01	3.54E–02	7.32E–01	7.49E–03	4.95E–04	1.96E–03
600	6.95E–02	4.35E–03	5.78E–02	1.03E–03	5.10E–05	2.53E–04	1.76	1.85	395	8.87E–01	3.53E–02	7.38E–01	8.37E–03	5.25E–04	1.98E–03

2.4.4 BENCH SCALE STUDIES

The use of bench scale apparatus is the most debatable method for obtaining toxic smoke data. Nonetheless, it is the preferred method by building authorities and regulators, because it generates repeatable and relatively more accurate measurements of the toxic products of a given sample, in comparison to the lower accuracy and high cost regularly incurred in larger scale tests. However it's often criticised for not representing real fire conditions. However, data obtained from different apparatus can be useful once the combustion conditions under which the apparatus performs is correlated to the nearest fire conditions observed in compartment fires. This can be achieved by relating the test methods to the ISO fire stages classification presented earlier in section 2.2.7. This was the basis on which an extensive review of the current use of bench scales apparatus for fire toxicity measurements conducted by (Hull, 2008). In addition, several publications attempted to compare the measured toxic yields from bench scale apparatus to larger scale studies reporting some degree of success in establishing some validation of the bench-scale results, as in (Babrauskas et al., 1991b; Hull et al., 2005; Hull et al., 2008a; Stec et al., 2009) among others.

This section will provide some highlight of the most commonly used bench scale apparatus for obtaining fire smoke data. Hull explains in (Hull, 2010; Hull and Paul, 2007) smoke generation methods can be classified into two main categories: closed cabinet tests, and flow through tests. In closed cabinet tests, the fire load sample is decomposed by a heat source and the resulting smoke accumulates within the cabinet. As a result, the O_2 level will decrease in the cabinet resulting in higher toxic yields. One problem in this type of tests is that the smoke layer do not always accumulate in a uniform upper layer, but rather circulate in the small compartment due to natural convection. Therefore, the extracted sample for analysis is highly dependent on the location of the sampling port in the compartment. This group of tests represent well ventilated fires at the initial stages, and turn into a representative of the later stages of a fire, but without any indication to how the measured yield varies with fire condition. Examples of this type of testing include: the NBS/NIST smoke box, NIST radiant furnace method (ASTM E1678), and NIST Cup test. In the other group of tests, the flow through tests, a sample is decomposed in a furnace with or without flaming over a flowing air which derives the combustion products towards the gas sampling ports. The most credible test of this group is the purser furnace test currently adopted in two similar versions in (BS7990) and (ISO19700). Other variations of the test include IEC 60695-7-50, DIN 53436, and PN-88/B-02855. In most cases, the variations of the test are limited to the number of analysers used for sampling the toxic yields, and the temperature at which the furnace operates. The ISO19700 test is shown in figure 2-19, it consists of a furnace, a moving sample boat, a primary and secondary air supplies. The control of the primary air supply, along with the rate at which the sample moves, provides control on the desired burning rate, and estimated equivalence ratio. The reported results from this particular apparatus appear to be more consistent with larger scale tests, such as the standard ISO room (Hull et al., 2005; Hull et al., 2008a; Stec et al., 2009). However, the test is limited in the choice of combustibles and fire conditions.

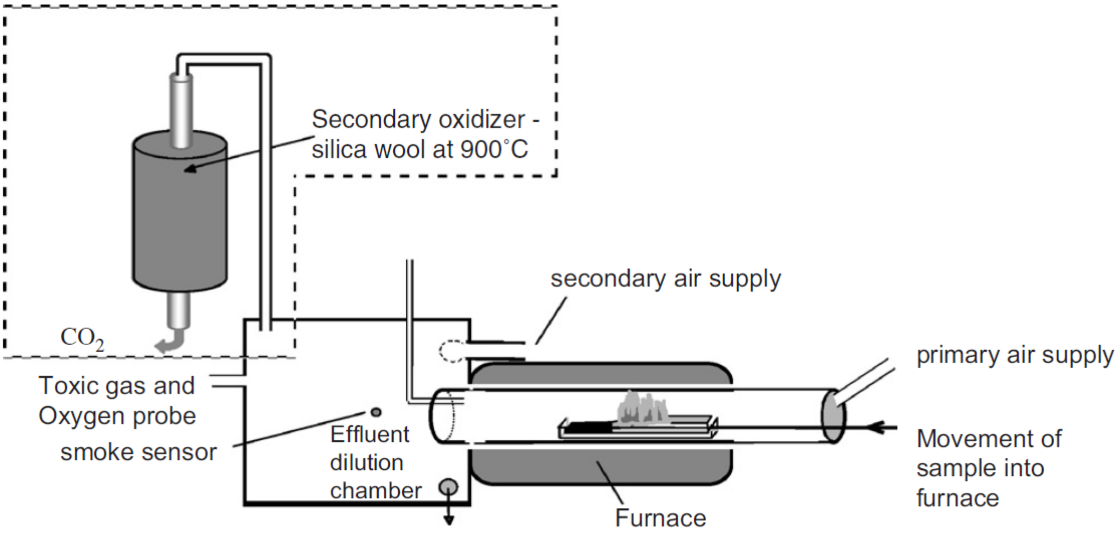


Figure 2-19: Purser furnace, now recognised as ISO19700, BS7990.

A summary of the bench-scale apparatus and their applicability to fire stages or conditions is provided in table 2-11. In general, despite providing useful results, bench scale apparatus comes short from simulating important phenomena associated with compartment fires, such as smouldering combustion, or the poor mixing in under-ventilated fires. In addition, other reported factors which affect the toxic yields composition, such as the effect of upper layer temperature and transient conditions in fire development are eliminated in these tests, as it provides the results for a single furnace temperature, which make the obtained results even more limited in its application to fire engineering. Finally, other bench-scale tests which were not included in this short analysis such as the cone calorimeter and the flame propagation apparatus, are not intended for fire toxicity studies, but occasionally used for fire smoke analysis by researcher as a compliment to the main fire tests. The results from these tests do not represent under-ventilated condition, but rather freely ventilated fires.

In conclusion, bench scale tests may be useful for identifying new toxicants for newly developed materials. However, awareness of the test conditions must be noted by the researcher in order to make accurate conclusions. The use of its results however, is not very credible in fire modelling or other fire engineering assessment methods, as it does not represent complete conditions of a real fire.

Table 2-11: A summarised list of the currently used fire toxicity appartus, summarised from (Hull, 2008).

Informal name	**Test Code**	**Fire Stage** [a]	**Heat Source** [b]	**Ventilation Type** [c]	**Ref.**
NBS smoke	prEN 2824	1b	R	N	(prEN-2824, 2009)
Box Test		2-3a	R+F	N	
NIST Radiant USA Buildings	ASTM E1678	2	R	N	(ASTM-E1678, 2010)
NIST Cup USA General		1b,2,3a	C	N	
Russia General	GOST 12.1012	1b,2,3a	R	N	(Gost-12.1012, 1984)
Japan Buildings	JIS A 1321	3a	F	F	(JIS-A-1321, 1976)
China Buildings	GA 132	1b,21,3b	T	F	(GA-132, 1996)
Purser Furnace	BS 7990	1b,2,3a,3b	T	F	(BS-7990, 2003)
	ISO 19700	1b,2,3a,3b	T	F	(ISO-19700, 2006)
	IEC 60695-7	1b,2,3a,3b	T	F	(IEC-60695, 2002)
Cone Calorimeter	ISO 5660	1b, 2	R	N	(ISO-5560, 2002)
Fire Propagation test	ASTM E2058	1a, 1b, 2, 3a, 3b	R	F	(ASTM-E2058, 2009)

[a] The fire stage refers to the ISO fire classification presented in Table 2-3.

[b] The main source of heat in the test, R= Radiant, P= Pilot flame, C=Crucible, F=flame, T= tube furnace.

[c] Air supply to the combustion zone type, N= natural, F= Forced.

2.5 QUANTIFICATION OF TOXIC HAZARDS FROM FIRE EFFLUENT

In general, the increased importance of quantifying toxicity hazard in fire safety engineering is a result of the move from prescriptive standards to performance based fire codes that require a thorough hazard assessment. A major component in any modern fire hazard assessment is the estimates of toxic species quantities and distribution throughout the building of interest. The estimates of the toxic species are based on our knowledge of toxic species yields obtained from experimental work. Based on those yields, the design fire products are typically assessed using toxic potency end limits. The aim of this assessment is to provide a reasonable estimate of the Available Safe Escape Time (ASET) and making sure it allows for the Required Safe Escape Time (RSET) for the building occupants (Purser, 2003; Purser and Bensilum, 2001). In modern toxicity assessments, a set of toxic potency limits are needed for the evaluation of the accumulated lethal/impairing dose. However, this is considered a developing research area. And, most of our knowledge was gained through the available literature which consists of two different approaches towards measuring the toxic effect of fire effluent. The first approach was based on evaluating new materials in an attempt to identify super toxicants, and relay on animal exposure to identify the lethality of the material burning in certain combustion conditions, the second approach however, was to assume that a limited number of toxicants that can be measured and quantified from different fire conditions, and thus the effect on human could be assessed based on evaluating their levels. This section will report the development of the toxicity assessment method, starting with the animal exposure studies, and moving on to more detailed discussion on the currently accepted chemical analysis based toxicity assessment.

2.5.1 TOXIC POTENCY BASED ON ANIMAL EXPOSURE STUDIES

In most animal exposure tests, the toxicological effect end point was lethality. The smoke lethality is commonly expressed as lethal concentration or lethal loading. The lethal concentration LC_{50} value is defined as the mass loading or combusted mass of the sample per unit chamber volume (gm^{-3}) that kills 50% of the test animal during a fixed exposure time and a post exposure observation period (Gann, 2004a; ISO-1344, 2004;

Neviaser and Gann, 2004) The lethal loading on the other hand, is defined as the mass loading (g) in the furnace that kills 50% of the test animals as a result of a fixed exposure time. The later expression, is not of a useful use in fire hazard analyses, but strictly used for material evaluation. In addition, to the lethality measure, a limited number of studies were conducted to investigate the incapacitation effect IC_{50}. Similar to the earlier lethal LC_{50} expression, the IC_{50} is defined as the mass loading or combusted mass of the sample per unit chamber volume (gm^{-3}) that incapacitates 50% of the test animals (Gann, 2004a) animal based tests include the NIST cup furnace, the NIST radiant furnace test (ASTM 1678), and the tube furnace NFX 70-100, and the confidence limits reported from various testing labs are typically as high as 95%. Examples of the data generated from animal based toxicity studies are shown in table 2-12. The presented results are an extracted sample from a major review by (Neviaser and Gann, 2004). The results are presented in two classifications well ventilated and oxidative pyrolysis (Vitiated combustion), for each material. In theory, the smaller the toxic dose the more toxic the material, this suggest an unusual ultra-toxic levels produced from Fluorpolymers UHTP. Other highly toxic materials include Epoxy, and PVC plasticized, especially for oxidative pyrolysis.

Table 2-12: a typical sample of animal based toxicity tests results obtained using different methods expressed as LC50 and IC50 in gm-3.

Material		**Well Ventilated**			**Oxidative Pyrolysis**		
		Min.	**Avg.**	**Max**	**Min.**	**Avg.**	**Max.**
LC_{50}	Epoxy	1.5	7.3	15.8	8.9	11.0	13.1
	PVC plasticized	20.1	26.2	22.3	11.8	22.9	34.4
	PVC	16.8	20.0	23.2	13.2	16.1	19.3
	Wood	34.8	40.2	45.1	30.8	36.1	41.0
	Fluorpolymers	19.0	27.4	35.8	17.8	25.4	33.5
	Fluorpolymers UHTP	0.0	0.1	0.9	0.1	0.4	1.0
IC_{50}	Epoxy	5.2	6.2	7.3	3.3	4.1	5.0
	PVC plasticized	4.9	7.1	9.3	2.8	3.4	4.0
	PVC	8.6	12.2	16.3	6.1	13.5	20.4
	Wood	17.5	21.4	25.3	12.2	15.3	18.5
	Fluorpolymers	6.9	14.8	21.9	7.9	19.9	19.9
	Fluorpolymers UHTP	0.1	0.6	1.0	0.3	0.7	1.5

Animal based testing advocates argue that it provides direct toxicity determination, provides the chance to observe the toxicological effect, and detects unusual toxic species (super toxicants) (Hull and Paul, 2007). However, the argument against the animal exposure studies is overwhelming for various reasons. They include; the reported difficulties in translating animal tests data such as rats, mice, dogs, monkeys, and baboon into humans because of the different respiratory volume rats and airway dimensions especially for cases where the main toxicants are irritant gases. Another reason is, although lethality is a well-defined end point, animal based tests are not generally capable of predicting incapacitation, this is due to the fact that the measured incapacitation end point is too close to the lethal level, thus making it too risky for application to humans. In fact, the more appropriate methods to investigate incapacitation in animals such as: trained escape response, and maze escape methods are rarely used in fire toxicity animal exposure studies for reasons of complexity and cost (Hull and Paul, 2007). Finally the most compelling argument against the animal studies is the legal limitations over the routine use of animals in fire smoke toxicity studies in the European Union and other jurisdictions.

It is also worth pointing out that toxicity is not a material inherited property, and a single measure of toxicity for each material is a misleading approach, thus more interest was put into investigating the individual components of the toxic effluent.

2.5.2 TOXIC POTENCY BASED ON CHEMICAL ANALYSIS

The general view in toxic potency based on chemical analysis is to assume an additive behaviour of individual toxicants present in fire effluent. The toxicants concentrations are then expressed as a fraction of the lethal concentration for 50% of the population for a 30 min. exposure LC_{50}. The result of the added fractions forms an estimated dose or concentration which is predicted to be lethal. The earliest assumption of the additive behaviour of the different gases was in a model by (Tsuchiya and Sumi, 1972), further advancements were made by (Hartzell, 1989; Hartzell et al., 1985a; Hartzell et al., 1983; Hartzell et al., 1985b; Hartzell et al., 1985c; Levin, 1996; Levin et al., 1987), and (Purser, 1989; Purser, 2000; Purser, 2002).

2.5.2.1 Levin N-Gas Model

The basic concept on which most models are derived is the additive toxic effect of the investigated gases. The second major assumption was that a limited number of gases (N) are responsible for the most of the toxic effect in fires. Based on these assumptions, Levin specifically designed LC_{50} experiments to investigate individual asphyxiant and irritant gases, in addition to combination mixtures of two and three of the toxic gases in terms of their lethal effect. From that work, Levin introduced a 7 gas model in (Levin, 1996), which she describes as predicts the toxic potency of the combustion products of materials based on the toxicological interactions of the fire gases. The latest version of the Levin N-gas model for predicting total death during and after exposure is shown in Eq. 2.28, while the constants proposed in the equation are given in table 2-13.

$$\begin{aligned}\mathrm{N-Gas\ Value} \\ &= \frac{m\,[\mathrm{CO}]}{[\mathrm{CO_2}]-b} + \frac{21-[\mathrm{O_2}]}{21-\mathrm{LC_{50}\ O_2}} + \left(\frac{[\mathrm{HCN}]}{\mathrm{LC_{50}HCN}} \times \frac{0.4[\mathrm{NO_2}]}{\mathrm{LC_{50}\ NO_2}}\right) \\ &+ 0.4\left(\frac{[\mathrm{NO_2}]}{\mathrm{LC_{50}NO_2}}\right) + \frac{[\mathrm{HCl}]}{\mathrm{LC_{50}HCl}} + \frac{[\mathrm{HBr}]}{\mathrm{LC_{50}\ HBr}}\end{aligned} \tag{2.28}$$

A major feature in Levin’s N gas model is that it accounts for the carbon dioxide enhancing effect on carbon monoxide lethal toxicity. The estimated effect of carbon dioxide was concluded from a series of a combined CO and $\mathrm{CO_2}$ exposure experiments. Levin explains; the effect of $\mathrm{CO_2}$ on CO toxicity peaks at 5 %, after which the $\mathrm{CO_2}$ effect decreases. The effect is represented by constants *m* and *b* in E.q. 2.28, which represent the slope and intercepts of the combination gas toxicity curve. Another consideration was a corrective term for the protective effect of nitrogen dioxide on nitrogen cyanide toxicity.

Table 2-13: Constants and LC50 concentrations for use in the Levin N-gas model.

Gas	**LC_{50}**
For $[\mathrm{CO_2}] \leq 5\%$	m=-18 and b=122000
For $[\mathrm{CO_2}] < 5\%$	m=23 and b =-38600
Oxygen depletion	21-5.4 – 15.6 % depletion
HCN	150 ppm
HCl	3700 ppm
HBr	3000 ppm
$\mathrm{NO_2}$	200 ppm

Although, this model was a major advancement in fire toxicity modelling, it had few weaknesses. The first flaw in the model was the limitation of the correcting factor for carbon dioxide effect to carbon monoxide. It appears that Levin concluded the major toxic effect from fire effluent in carbon monoxide, hence limited the carbon dioxide effect to carbon monoxide. Also, the correction factors applied for the protective effect of nitrogen dioxide on hydrogen cyanide only works for nitrogen dioxide levels of around 200 ppm, which may not be realistic, as some studies suggest nitric oxide is the leading oxidant product from fires(Purser and Purser, 2008). The mathematical expression, as given in this model, would result in negating the hydrogen cyanide effect for cases where little or no nitrogen dioxide is present, while it would enhance the hydrogen cyanide effect for levels higher than 200 ppm, both cases are incorrect. The final flaw in the model, is the assumption that low oxygen hypoxia is linearly related to decreased oxygen concentration, when in practice it is established it is a not linear relationship (Purser, 2010a; Purser, 2010c)

2.5.2.2 Purser FED model

Based on earlier work by Levin, and Hertzell, purser further refined the toxic potency predictive model into the Fraction Effective Dose model. The new model, agrees with the earlier N gas model, in that the effect of different gases apart from CO_2 is additive, and the toxic potency end-point LC_{50} for 30 min. exposures in rats. However, the changes include a different approach in representing the hyperventilation caused from CO_2 inhalation, where V_{CO_2} is a multiple of all the toxic terms and not only CO. In addition, the representation of low oxygen hypoxia was replaced by an additive term that accounts for the effect of oxygen depletion in an exponential function. Another correction was to modify the NO_2 effect on HCN by taking into account all the NO_x. The final, change was to allow for all detectable inorganic acid gases and organic irritants to be considered, instead of limiting the analysis to 7 gases. The resulting function is shown in E.q. 2.29. and the rats 30 min. LC_{50} proposed for use in this model are given in table 2-14.

Table 2-14: LC50 concentration for use in the Purser LC50 FED model.

Gas	**LC$_{50}$**
CO	5400 ppm
HCN	165 ppm
HCl	3800 ppm
HF	2900 ppm
HBr	3000 ppm
SO_2	400 ppm
NO_2	1700 ppm
Acrolein	150 ppm
Formaldehyde	750 pmm
Hypoxia using the function provided	21-5.4=15.6 % depletion

$$\mathrm{FED} = \left(\frac{[\mathrm{CO}]}{\mathrm{CO_{LC50}}} + \frac{\mathrm{HCN} - \mathrm{NO_x}}{\mathrm{HCN_{LC50}}} + \frac{[\text{each acid gas}]}{\mathrm{LC_{50}}\ \text{each acid gas}} + \frac{[\text{each organic irritant}]}{\mathrm{LC_{50}}\ \text{Each irritant gas}}\right) \times \mathrm{V_{CO_2}} + \mathrm{A} + \frac{1}{\text{hypoxia function}} \tag{2.29}$$

where,

$\mathrm{V_{CO_2}}$ is a multiplication factor for CO_2 driven hyperventilation:

$$= 1 + \frac{(\exp(0.14 \times [CO_2] - 1))}{2} \tag{2.30}$$

A is an acidosis factor given as:

$$= ([CO_2] \times 0.05) - 0.02 \tag{2.31}$$

Hypoxia function expressed as:

$$= \exp(8.13 - 0.54\ \times [21 - \mathrm{O_2}]) \tag{2.32}$$

This model provides a better mathematical representation of the toxic gases interactions generated from a fire test. However, in order to not misuse their application, it is important to understand the reasoning behind the proposed model, and the correct application of each fire toxicity model. The N-gas models, and the Purser FED model, are essentially a replacement models to the animal testing protocol in bench scale testing. They are developed for the purpose of being used to generate a comparable outcome to the LC_{50} (gm^{-3}), material dependant endpoint explained in the earlier section, therefore eliminating the need for animal based tests. Purser explains; when the FED is equal to unity, death is predicted, and the mass loss exposure dose for the material producing these gases is then equal to the LC_{t50} for the material decomposed in the same test conditions. He summarises in (Purser, 2002) the usefulness of the FED model as follows:

- In a small test, and only using chemical effluent analysis it is now enabled to estimate of the likely approximate toxic potency of combustion products of the material, without the use of animals.
- Where a test involved chemical gas analysis, and animal exposure, it is possible to validate if a limited number of gases are accountable for the toxic effect, or if there exists additional toxicants.
- If the toxic effect can be accounted for from a limited number of toxicants (as often reported), it is then possible to estimate the toxic potency from larger scale tests using only chemical analysis.
- Based on bench-scale tests results obtained through, chemical analysis, or animal exposure, the material LC_{50} expressed in (gm^{-3}) allows for predicting the toxicity in full scale tests based on the full scale test mass loss data.
- Finally, when gas analytical data are available from full-scale tests, a rough **estimate** of the toxic potencies of the burnt material is provided.

Although great effort was put into developing the earlier models, they remained of little help to human exposure scenarios, or fire safety engineering in general. The toxic effect remains estimated, and the use of lethality as an end-point is highly controversial for human safety purposes. Therefore, more work mainly through the ISO committees, was put into developing modified toxicity assessment models more relative to humans, and capable of estimating the Available Escape Time (ASET). The basic principles of additive behaviour of the toxic species remains a core assumption, while other sub-lethal endpoints other than the lethality end-point currently adopted in the fire research community are being investigated.

2.5.2.3 ISO 1344: 2004

(ISO-1344, 2004): estimation of the lethal toxic potency of fire effluents is the earliest ISO document addressing fire effluent toxicity. It provides guidance on the application of Eq. 2.28 and Eq. 2.29, provided by Levin and Purser, to evaluate toxic effluent from new materials and products to assist in their research and development. It utilises the application of the earlier models in materials research, but provides no useful information on its applicability to humans, and no information on the sub lethal toxicity. In the latest version of this standard two variables are defined the FED (Fractional Effective Dose), and the LC_{50} of the material in gm^{-3}. The FED is presented as L_{FED} in order to eliminate confusion, and imply lethality. The calculated term from Eq. 2.28 and Eq. 2.29, is integrated over time and presented as L_{FED} as shown in Eq. 2.33.

$$L_{FED} = \sum_{i=1}^{n} \int_{0}^{t} \frac{C_i}{(C,t)_i}\, dt \tag{2.33}$$

Where, C_i is the concentration expressed in microliters per litres (the volumetric expression of ppm) of the toxic species i.

$(C,t)_i$ is the concentration-time product expressed in microliters per litre times minutes for the specific exposure dose required to produce the toxicological effect. i.e. the 30 min. LC_{50} of the toxic species, as in table 2-14.

In effect, L_{FED}, is equivalent to the N quantity in Levin's model, and FED in Purser's model, nevertheless, once L_{FED} is calculated it is then used to calculate the LC_{50} of the given material sample based on the following expression:

$$\mathrm{LC}_{50} = \frac{\mathrm{M}}{\mathrm{L}_{\mathrm{FED}} \times \mathrm{V}} \tag{2.34}$$

where, M is the specific mass loss, in grams. and,

V is the total air volume in cubic meters.

2.5.2.4 ISO 13571: 2007

The most relevant toxicity assessment models to humans are provided in (ISO-13571, 2007): Life-threatening components of fire - Guidance for the estimation of time available for escape using fire data. The standard provides four major models for calculating different fire associated hazards which may prevent escape. The hazards considered are: toxic gases, irritant gases, heat, and smoke obscuration. The standard does not provide a clear instruction on how these hazards assessments may be combined, but it suggest that each effect may be estimated independently. The end point of the toxic effect was chosen to be incapacitation. Arguably, it is the first time a credible fire related standard approves the use of sub-lethal point as a potency assessment threshold. However, incapacitation is yet another extreme end of lethal effect, and its use as a measure is debatable.

Asphyxiant gases FED

The first part of the standard covers assessing asphyxiant products of a fire. It builds on the earlier ISO1344 fraction effective dose methodology, assuming similar principles of the additive effect of the toxicants, and duration dependant dose build up. The first mathematical expression in the standard Eq. 2.35 is in effect the same in concept as Eq. 2.33 in the ISO1344. It represents the general form of the fractional effective dose methodology, with the expectation that the in this model the incapacitation dose is taken instead of the lethal dose. The standard leaves a chance for the expert to identify the total number of asphyxiant toxicants involved in the assessment.

$$FED = \sum_{i=1}^{n} \int_{0}^{t} \frac{C_i}{(C,t)_i} \, dt \tag{2.35}$$

where, C_i is the expected exposure level, and

$(C,t)_i$ is the incapacitation dose.

The standard states: “all available evidence supports the working hypothesis that in a typical fire atmosphere CO and HCN are the only asphyxiant combustion products that exert significant effect". Therefore, a general assumption was made that the two gases form the majority of the asphyxia effect; accordingly the standard provided the expanded version of the in Eq. 2.36. In this equation the value of 35000 ppm per minute is taken as the incapacitation dose for carbon monoxide, and the incapacitation term for HCN is represented in an exponential expression. In addition, the standard suggests where CO_2 levels are significant (<2%), hyperventilation effect caused by increased CO_2 should also be taking into consideration. The term V_{CO_2} from Eq. 2.37 representing the CO_2 effect should be multiplied by Eq. 2.36 at each time increment.

$$FED = \sum_{i=1}^{t_2} \frac{[CO]}{35{,}000} \Delta t + \sum_{i=1}^{t_2} \frac{\exp(\frac{[HCN]}{43})}{220} \Delta t \tag{2.36}$$

where, $[CO]$ is the average concentration of CO expressed in ppm, and

[HCN] is the average concentration of HCN expressed in ppm, and

Δt is the time increment, expressed in minutes.

$$V_{CO_2} = exp \frac{[CO_2]}{5} \tag{2.37}$$

where, $[CO_2]$ is the average volume percentage of CO_2.

The standard mentions that O_2 depletion may contribute to the asphyxiation effect, however its contribution is only significant for levels less than 13%, a level not likely for human exposure mostly occurring far from the fire origin. Nevertheless, it refers the reader to the earlier ISO1344 for considering the oxygen depletion effect where necessary. The CO incapacitation levels were based on baboon tests, while the HCN expression was derived from studies on monkeys. The estimated uncertainties in Eq. 2.36 and 2.37 are ±35%, and 20% respectively. The irritant gases are assumed to have negligible effect on the fraction effective dose; however they form the core of the second model the fraction effective concentration.

Irritant gases FEC

The second model in the standard is the irritant gases model. It accounts for the effects of sensory/upper-respiratory, and pulmonary irritants. The model is based on the fractional effective concentration concept shown in Eq. 2.38. Similar to earlier models, additive effect is assumed to combine the effect of different species, however, the effective concentration FEC concept is fundamentally different to the earlier FED, in that it assumes the toxic effect occurs instantaneously after inhalation. The irritation occurring in the upper-respiratory-tract and other body tissue is triggered upon first contact with the irritant species. The time-dependant effect is negligible in comparison to the severe effects incurred upon contact. Therefore, unlike the FED, the FEC is calculated for each time increment independently, from earlier history. Once the summation of the irritant species normalised to the incapacitation effect reaches one, it is estimated the toxic gas will cause incapacitation, and prevent escape.

$$\begin{aligned} FEC = {} & \frac{[HCl]}{IC_{50,HCl}} + \frac{[HBr]}{IC_{50,HBr}} + \frac{[HF]}{IC_{50,HF}} + \frac{[SO_2]}{IC_{50,SO_2}} + \frac{[NO_2]}{IC_{50,NO_2}} \\ & + \frac{[Acrolien]}{IC_{50,Acrolien}} + \frac{[Formaldehyde]}{IC_{50,Formaldehyde}} + \sum \frac{irritant\ [i]}{IC_{50,irritant\ i}} \end{aligned} \tag{2.38}$$

where, [i], is the average concentration expressed in ppm, and,

$IC_{50,irritant\ i}$ is the concentration of each irritant gas that is expected to cause incapacitation and prevent escape, expressed in ppm.

The ISO13571, suggests the uncertainty in the FEC model is 50%, and provides suggested data for use as IC_{50} concentrations that represent incapacitation. The FED, and FEC end point data from the ISO 13571 are summarised in table 2-15. Nevertheless, they represent a level well beyond the safe limit that shall be insured for occupant’s safety. This meant the toxicity assessment of fire products, remained an active research area. Some of the arguments on alternative assessment methods are presented in the following section.

Table 2-15: ISO13571 Incapacitation limits for different gases.

Gas	**IC_{50}**
CO	35000 ppm
HCl	1000 ppm
HF	500 ppm
HBr	1000 ppm
SO_2	150 ppm
NO_2	250 ppm
Acrolein	30 ppm
Formaldehyde	250 pmm

2.5.2.5 Alternative toxicity assessment models

In fire studies, toxic smoke assessment has been a recurring topic. The limited available information on the toxic smoke irritant components, and their quantification methods, have always caused uncertainty in identifying the toxic components. In addition, the difficulties in identifying toxic effects points lower than lethality was another major obstacle in developing suitable models for human exposure. The lethality measure adopted in the early N gas and Purser FED model were criticized for excluding the irritation and incapacitation effect, which is a significant hazard in fire smoke. Nonetheless, they remained the main stream toxicity assessment models for fire hazard calculation, despite being originally proposed for materials research studies. In their early forms, (Purser, 2010c) proposed that a fraction of the FED (0.1) should be considered in performance based designs to maintain a safe escape. However, this was displaced by the new incapacitation model proposed in ISO 13571.

Nevertheless, new information gained from other research venues, namely work exposure laws and guidelines, in Europe and North America in the past decade is reshaping the view on toxic fire effluent. The gases exposure limits approved by medical committees, suggest a higher role the irritant species play in harming fire casualties and preventing escape. The work exposure guidelines, namely Acute Exposure Guideline Levels (AEGL) by the U.S Environmental Protection Agency, and the Workplace Exposure Limits (WELs) in the Control of Substances Hazardous to Health Regulations (COSHH) by the Health and Safety Executive (HSE) in the UK show that even small amounts of irritant gases can cause serious damage more relevant to impairing escape. The data in these documents shown in table 2-17, suggest that substances such as Acrolein and Formaldehyde are severely irritant. The data in these documents are more conservative than the ISO13571 incapacitation data, and provide a logical alternative for predicting impairment of escape, since predicting incapacitation is not a safety measure.

(Andrews et al., 2007; Andrews et al., 2005b) pointed out the need for more conservative fire products toxicity assessment more relevant to impairment of escape and safe evacuation. The limited data in their work was normalised against Short Time Exposure Limits (STEL) values and LC_{50}. Their results showed that if impairment of escape was to be considered as the main hazard from fire effluent, several irritant species are present in significant quantities that make the common consideration of carbon monoxide as the main leading toxicological hazard questionable. The gases reported include Benzene, Formaldehyde, Acrolein, and their combined contribution to the overall COSHH based toxicity was more than 70% in most cases. This views on the toxicological assessment is shared by other researchers in the field, as (Purser, 2002) suggest a lower limit for estimating the irritant effect as impairing escape, lower than the incapacitation limit provided in ISO13571. The latest lower limit provided by Purser in (Purser, 2010c) is shown in table 2-16. In his proposal Purser suggests using this lower limit in Eq. 2.38 for developing an impairment of escape level instead of the incapacitation approach in table 2-16.

Table 2-16: Impairment of escape due to irritation effect, proposed by (Purser, 2010).

Gas	**Impairment of Escape**
HCl	200 ppm
HF	200 ppm
HBr	200 ppm
SO_2	24 ppm
NO_2	70 ppm
Acrolein	4 ppm
Formaldehyde	6 pmm

As part of this work, a compiled summary of the available limits for toxic smoke assessment is presented in table 2-17 for comparison. In the summarised table, a comparison of the LC50 and IC50 proposed by the ISO standards, and the limits approved by the work exposure committees is presented. The AEGL level 2 for 10 min. exposure, and the STEL 15 min. exposure limits are proposed in this work to be adopted as the limit on which fire toxicity assessment is made. The decision to adopt one of these limits is supported by the following:

First, the definitions of the AEGL-2 and STEL 15 min. explicitly indicate they are approved for accidental exposure and to allow for escape. The AEGL 10 min. (2) is defined as: "the airborne concentration (expressed as ppm or mg/m3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape." (AEGL), while, the Control of Hazardous Substances Hazardous to Health Short Term Exposure Limits is defined as "maximum exposure permitted over a 15-min. reference period, designed to protect against immediate acute ill-health effects" (COSHH).

Secondly, the exposure limits are binding legal limits in the UK and Europe, while the ISO recommended limits are recommended as a standard at a global level. Thirdly, although COSHH and AEGL limits may seem conservatives, they are approved by medical committees, to be the levels after which long term damage, and impairment of escape is predicted, while in the ISO recommended limits, a fraction of the dose or concentration is suggested as the safe limit. Finally, in fire engineering application, there is a need for relative safety areas, as well as clear escape routes. The conservative quantification shall allow the design of highly ventilated relative safe area essential for phased evacuation.

In addition, the adoption of these conservative limits will spot the light on important toxicants, such as Acrolein and Formaldehyde, which are often ignored or discounted in fire toxicity research. An example of this is found in a recent publication, by NIST, in which the authors stated: "The yields of CO_2, CO, HCl, HCN, and soot were determined. Other toxicants (NO2, formaldehyde, and acrolein), whose concentrations were below the detection limits, were of **limited importance** relative to the detected toxicants." (Gann, 2010). The mentioned statement is misleading, and inaccurate if the toxicological effect was to prevent escape, rather than cause death.

In the following table 2-17, the final two columns are used to highlight the inconsistency between assessing the fire products from a lethal endpoint as in LC_{50} ISO1344, and assessing the toxic components using an impairment of escape measure such as COSHH STEL or AEGL-2. The LC_{50} value is divided by the STEL or AEGL-2, to show that for toxicants such as HBr, the lethal concentration is more than 1250 times the impairment of escape concentration, whereas for CO the lethal concentration was only 27 times the impairment of escape concentration. This means, although, HBr is not likely to be lethal in most fires, it is in effect a major contributor to the impairment of escape from fires. The same concept applies for Formaldehyde, Acrolein, Hydrogen Fluoride, and Hydrogen Chloride. This suggests, that the view that CO is the major hazard in fire products, is solely based on lethal endpoint, and more gases are of concern if human safety is to be considered in toxic smoke studies. The irritant species suspected of being major contributors to the impairment of escape hazard, and neglected in previous toxicity assessment methods are identified in red. The measure used in this analysis, was that if the lethal limit, is more than 100 times the impairment of escape limit, the toxic components would have been most likely neglected due to toxicological endpoint being too high.

Table 2-17: a summary and comparison of potential toxicity assessment limits for fire gases.

Toxic Gas	CAS Number	Formula	LC_{50} ISO1344	IC_{50} ISO13571	COSHH W.E.L.		AEGL 10 m.			AEGL 30 m.			IDLH	$\frac{LC_{50}}{15\ min.\ STEL}$	$\frac{LC_{50}}{AEGL\ 10m\ (2)}$
					15 Min. STEL	8 hours TWA	1	2	3	1	2	3			
Carbon monoxide	630-08-0	CO	5,400	35,000	200	30	-	420	1700	-	150	600	1200	27	13
Nitric oxide	10102-43-9	NO	2,500	2,500	35	-	-	-	-	-	-	-	100	71	-
Nitrogen dioxide	10102-44-0	NO_2	170	170	5	-	0.5	20	34	0.5	15	25	20	34	9
Ammonia	7664-41-7	NH_3	750	750	35	25	30	220	2700	30	220	1600	300	21	3
Hydrogen cyanide	74-90-8	HCN	165	165	10	-	2.5	17	27	2.5	10	21	50	17	10
Hydrogen chloride	7647-01-0	HCl	3,800	1,000	5	1	1.8	100	620	1.8	43	210	100	760	38
Hydrogen fluoride	7664-39-3	HF	2,900	500	3	1.8	1	95	170	1	34	62	30	967	31
Hydrogen bromide	10035-10-6	HBr	3,800	1,000	3	-	2	250	740	1	50	250	50	1267	15
Sulfur dioxide	744-09-5	SO_2	1400	150	5		0.2	0.75	30	0.2	0.75	30	100	280	1867
Benzene	71-43-2	C_6H_6	-	-	3	1	130	200	-	73	1100	5600	500	-	-
Toluene	108-88-3	C_7H_8	-	-	100	50	200	3100	-	200	1600	6100	500	-	-
Xylenes	1330-20-7	C_8H_{10}	-	-	100	50	130	2500	-	130	1300	3600	900	-	-
Methanol	67-56-1	CH_3OH	-	-	250	200	670	11000	-	670	4000	14000	-	-	-
Acetaldehyde	75-07-0	C_2H_4O	4,000	2,000	50	20	45	340	1100	45	340	1100	200	80	12
Formaldehyde	50-00-0	CH_2O	750	250	2	2	0.9	14	100	0.9	14	70	20	375	54
Acrolein	107-02-8	C_3H_5O	150	30	0.3	0.1	0	0.44	6.2	0	0.01	2.5	2	500	341
Formic acid	64-18-6	CH_2O_2	1600	800	-	5	-	-	-	-	-	-	30	-	-
Acetic acid	64-19-7	$C_2H_4O_2$	11,000	-	15	-	-	-	-	-	-	-	50	733	-

2.6 COMPUTER SIMULATION OF FIRE HAZARD AND TOXIC PRODUCTS

The use of deterministic fire models, have grown considerably in the past few decades. Their popularity comes from the recent move towards performance based designs and the exponential increase in computational ability (Grewolls, 2010; Yeoh and Yuen, 2009). If used correctly, computer models can provide a cost effective solution in establishing a safe performance design. Its uses include, assessing the possible safe evacuation in a building, assessing the best conditions for fire fighting activities, validating compartmentation, and predicting toxicity levels for humans or the environment.

Based on the objective of the investigation, a choice on the model type is made. The prominent types are Zone models, such as CFAST, and CFD models such as FDS. Zone models are based on correlations derived from typical fuel mass loss rate. In a zone model simulation, the compartment is divided into upper and lower zone, and based on the mass loss rate provided; levels of temperatures and major toxic species CO_2, CO, and Oxygen are predicted in the upper layer. The irritant species levels are estimated based on CO_2 levels, which is questionable. However, the simplicity and ease of use make them a popular choice for simple hazard analysis.

More comprehensive analysis is generally performed using 3D CFD models, which are capable of providing detailed flow patterns, temperature levels, and to a limited extent species production. However, a major consideration in CFD simulation approach is the high computational cost, which limits users and developers of the models (Mcgrattan, 2005). The complexity of the fire problem, which includes heat, flow, and chemistry analysis along with the typical large domains, make it very challenging to balance, the amount of details required and the available computational cost. Nonetheless, the computational cost is decreasing over the long term, and it is predicted that CFD written codes will be the most dominant fire models. The most widely used CFD code in the past decade is the Fire Dynamics Simulator (FDS) developed by NIST (Mcgrattan, 2008). A short description on its latest version FDS5 is provided in Appendix 1, it is provided along with the basic CFD assumptions currently in use in order to establish the capabilities and limitations in such models.

2.7 CONCLUSIONS

In order to provide foundations for this research, this chapter covered a spectrum of topics relevant to this work. It started with a short background, and historical overview on the development of fire science studies, and how this shaped the existing patterns in the field. This was followed by the theoretical background of the established knowledge on compartment fires. This was followed by a fruitful investigation of the knowledge on compartment fire toxic effluents components, enhanced by the reported information from the AEGLs medical committees' reports. This was followed by a literature survey of the fire studies on combustion products conducted using the hood experiments, reduced scale enclosures, and large scale tests. The final sections of this chapter reported current fire smoke toxicity assessment models, and an overview of the current fire modelling approach in combustion products. The following conclusions can be drawn from the reported studies:

- There exists a good understanding of the physical phenomena of fire, in terms of major characteristics and behaviour in relatively highly ventilated compartment fires. This is reflected in the good amount of credible information provided in section 2.2. Based on the ISO classification of fire stages, the upper layer temperatures and the fire equivalence ratio, are the main features which characterise a compartment fire with regards to its toxic products generation.
- Although, little information is known on the sub-lethal toxic effects of fire effluent in the fire research classic literature, a wealth of information is available on most of the toxic species relevant to fire studies, in the governmental reports provided by medical committees, for the purpose of developing work exposure guidelines, in Europe and North America.
- Significant amount of research was carried out on carbon monoxide production in compartment fires, but little or no information is provided on other incomplete irritant species. The available information suggests a strong dependence on fire equivalence ratio, and a less degree of independence on upper layer temperature.
- In fire research, a wide range of compartments configurations were used, in order to study different phenomena. The data from different sizes compartments, forced and natural ventilation configurations support the hypothesis, that

combustion products are highly dependent on the fire equivalence ratio and upper layer temperature.

- The evaluation of toxic products generated in ventilation controlled fires is a developing venue in fire research. The generally accepted biological endpoint in fire smoke hazard assessment in fire research is lethality. This is now being revised, and disputed. This work will show the short comes of the lethality measure in terms of predicting impairment of escape.
- The existing fire toxicity assessment models were developed for various reasons; therefore, careful consideration should be taken before they can be implemented in fire models.
- Toxic fire products, often regarded as less important toxicants, such as Formaldehyde, Acrolein, and Benzene are extremely irritant, even at very low concentrations, causing breathing difficulties, eye irritation, and impairing escape. This is consistent with reported experience from fire survivors, thus better standards of research are required for quantifying and assessing the fire smoke hazard to include these species.

3. CHAPTER 3: METHODOLOGY

Introduction:

In this Chapter the experimental methods, data analysis methods, and toxicity assessment methods, are described in details. In addition, a toxic model is proposed suitable for computationally inexpensive modelling. The first section describes the main experimental compartments used in this work. This is followed by a detailed description of the gas analysis equipment used in section 3.2. The mathematical tools for the quantification of the gases and fire characteristics are presented in the gas analysis technique section, which also include, important aspects on tests repeatability and FTIR results validation, and. The final parts of this chapter cover the toxicity assessment method used, and a proposed CO equivalent toxicity method.

The majority of the tests in this project were carried out in the University of Leeds reduced scale toxicity tests enclosure. This compartment, originally built in 1996 by Deansfield fabrications, was modified and upgraded several times over the past decade. Work on the earlier setup was published in (Andrews et al., 2000c; Andrews et al., 2000b; Andrews et al., 2000a). The latest modifications to the experimental set up include the addition of the online FTIR system, which is a key component of this work.

In addition to the core work done using the fire toxicity compartment, further testing was carried out in the gas fired furnace facility, in order to investigate combustion products and burning behaviour in the later stages of a compartment fire. Although it’s a standard facility for materials performance testing, it was modified for the purpose of this work. The final fire testing apparatus used was a standard cone calorimeter, in which primarily testing was carried out to investigate material behaviour, before the larger scale tests were performed. The same set of data analysers, and data acquisition system was used throughout this work.

3.1 EXPERIMENTAL:

3.1.1 EXPERIMENTAL COMPARTMENTS:

3.1.1.1 Reduced Scale fire toxicity compartment:

The Enclosed fire compartment, illustrated in Figure 3.1, consists of a 1.4m x 0.96m x 1.25m high fire compartment, and a 1.4m x 0.96m x 0.25m high air-distribution plenum situated below the compartment. It is one of three adjacent compartments separated by sealed walls making up the large fire testing platform shown in Figure 3.2. Although the air-sealed dividing walls between the compartments were removable for different compartment volumes, only the centre compartment, shown in Figure 3.1 was used in this study.

The fire compartment was internally lined on three walls with 25mm thick Triton Kaowool 1260 insulation board. An observation window fitted on the front wall, which was used in earlier work of smaller fuel loads, is covered externally using the same insulation material.

In all the tests in this rig, forced air entrainment was fed through the air inlet port to the air distribution plenum below the enclosed compartment, and then to the enclosed fire compartment through the four slots on the enclosed compartment floor. Using compressed air, the air feed was kept constant for each test. The pressure regulating air supply was measured using Endress & Hauser T-MAS AT533 mass flow meter. The air flows used in this work ranged from 10kg/hr to 70 kg/hr resulting in ventilation rates corresponding to 5 Air Changes per Hour (ACH) to 38 ACH.

A suspended ceiling, measuring 0.825m by 1.21m and positioned at 1.12m above the compartment floor, and 5 cm below the enclosed compartment roof, was used with leakage gaps at the four sides of the suspended ceiling. A 152mm diameter exhaust-port was situated above a suspended ceiling. The exhaust port was positioned centrally on the roof of the fire compartment and housed a multi-hole ‘X’ gas-sample probe, with 36 sample holes on centres of equal area, to allow sampling of the fire-gases. The multi-hole gas sampler is shown in figure 3.8.

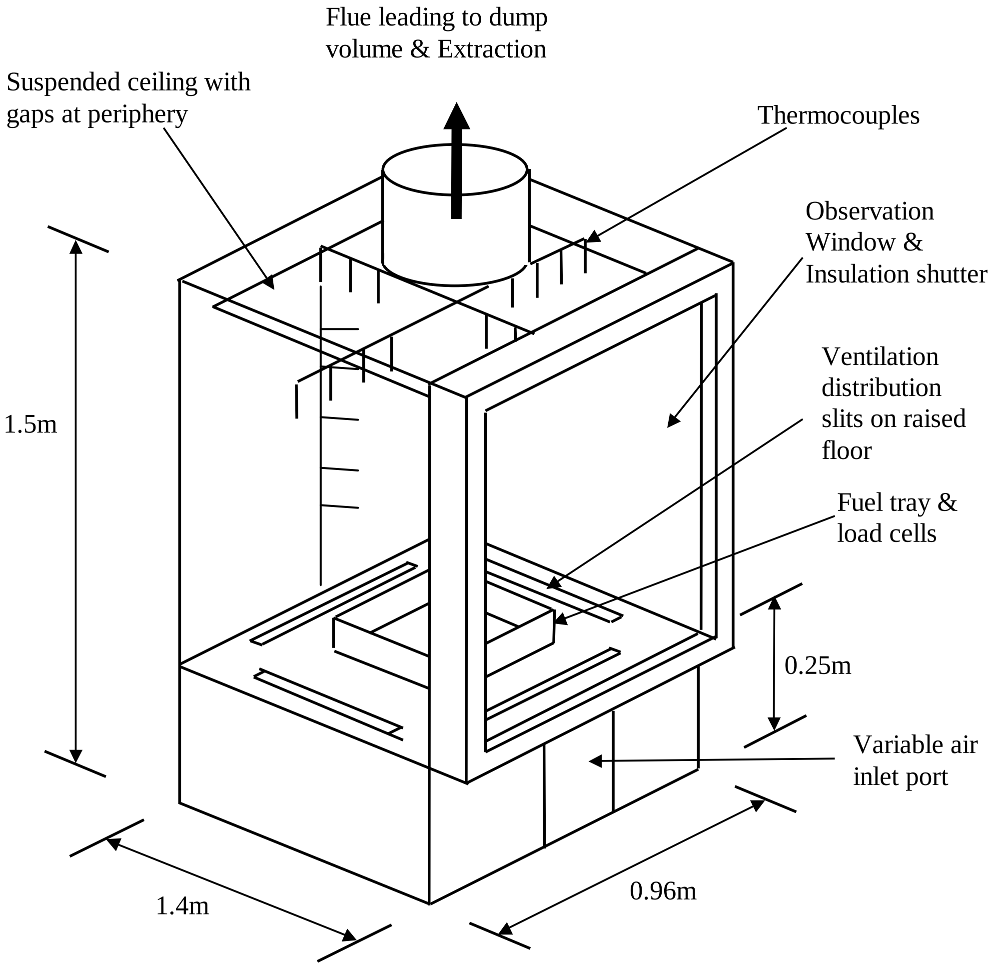
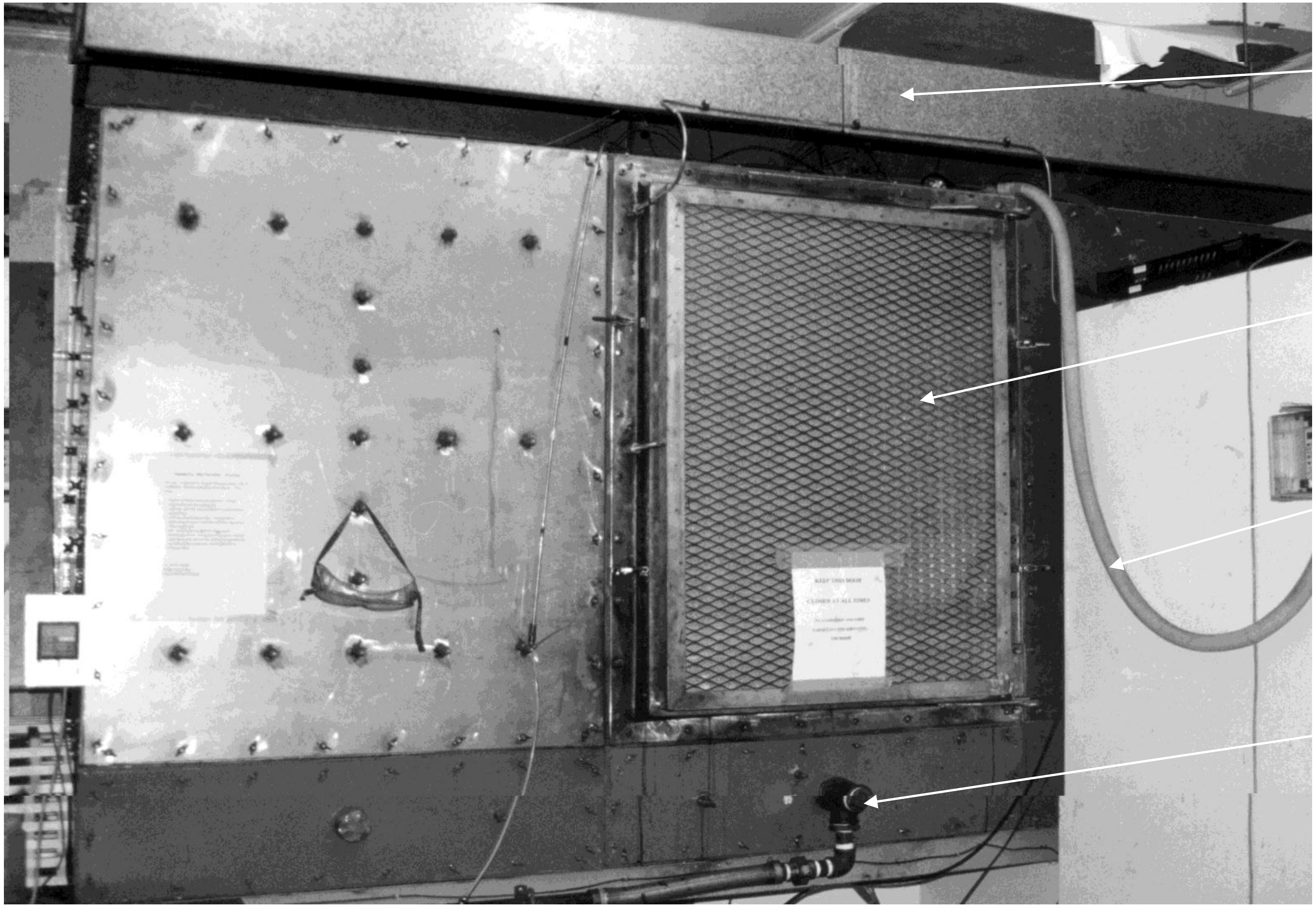


Figure 3-1: A sketch of the reduced scale enclosure.

For clarity, side and roof panels have been removed, whilst suspended ceiling has been shown as transparent.

- Details of the thermocouple arrangements may be found in Figure 3-4 – Figure 3.6.
- Details of the suspended ceiling and upper compartment may be found in Figure 3-3.



Extraction Hood

Observation window & insulated shutter

Heated gas sampling line

Air inlet for forced ventilation experiments

Figure 3-2 A Picture of the reduced scale compartment sealed door, forced ventilation port, and extraction hood.

Once the combustion products passed through the sampling port, they were extracted into a dump volume where a large hood (measuring 3m x 1.5m, situated 90mm above the roof of the compartment). Extraction system was then deployed to transport the fire products to the atmosphere through a 10m high, 381mm (15") diameter vertical chimney. The extraction was provided by a 381mm (15") bifurcated fan, manufactured by Halifax Fan Manufacturing Co. Ltd., which provided a free air-flow rate of around $0.8917m^3.s^{-1}$ at maximum speed of 1425rpm.

This experimental configuration is similar in size, to several reported reduced scale enclosures, reported in Chapter 2. However, the critical features of the suspended ceiling, and the controlled air flow, make this an ideal set up for accurate quantification of combustion products in compartment fires. The suspended ceiling allows the air to accumulate and the upper smoke layer temperature to be accurately measured. While, the separate air entrainment plume and measured air feed, as in Gottuk, and Lattimar work, excludes the uncertainties associated with the estimating air mass flow. In addition, this set up, allows for studying fires with a very low ventilations (air starved) conditions, where the minimum amount of ventilation to sustain burning is provided. This is an area not studies before, and it represents a common problem in the UK, where small fires in a sealed room, are a major cause of death.

Temperature monitoring

The temperatures within the enclosure was monitored using 26 type K mineral insulated exposed hot junction, 1.5mm bead, 613 stainless steel sheathed thermocouples from TC Ltd. The measured temperatures were not corrected for radiation losses and poor convective heat transfer; this is expected to result in an experimental error of around 5% (Shaddix, 1999). Since, wall temperatures and gas velocity measurements in the thermocouple region were not possible in this work; the measured values were accepted with this uncertainty.

The thermocouples were divided into:

- Rear vertical thermocouple tree (Figure 3-4) consisting of 10 thermocouples each separated by 0.1m, the lowest thermocouple being 0.15m from the compartments floor and the highest 1.05m from the floor, with the tree located centrally on the rear compartment wall and the thermocouple beads located 0.175m from the rear wall (0.2m less 0.025m lining).

- Central vertical thermocouple tree (Figure 3-5), situated vertically above the test fires, consisting of 7 thermocouples each separated by 0.1m, the lowest being 0.45m from the compartments floor and the highest 1.05m above the compartments floor.
- 9 thermocouples were situated 1.05m above the compartments floor (0.07m below the suspended ceiling – see Figure 3-6). The results from these thermocouples were averaged every 5s and the result was used as the upper-layer temperature. The difference between the maximum and minimum temperature was 15% during the growth stage, and decreased to less than 10% during more steady parts of the test.
- An additional thermocouple was placed in the exhaust sample probe housing to measure the exhaust temperature. And another thermocouple measured, the air temperature in the air entrainment compartment, beneath the major compartment, to validate that no burning occurs in air distribution enclosure.

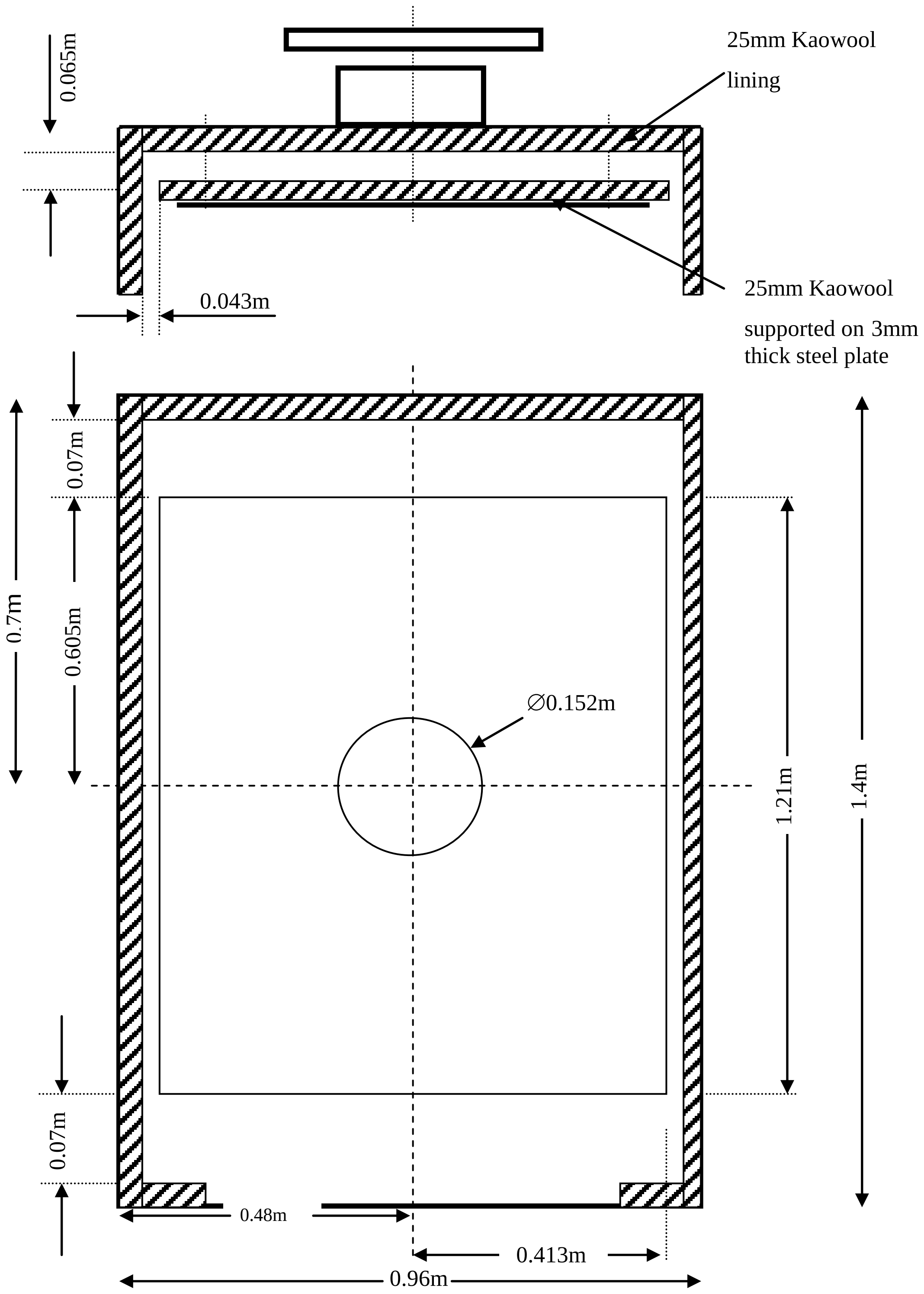
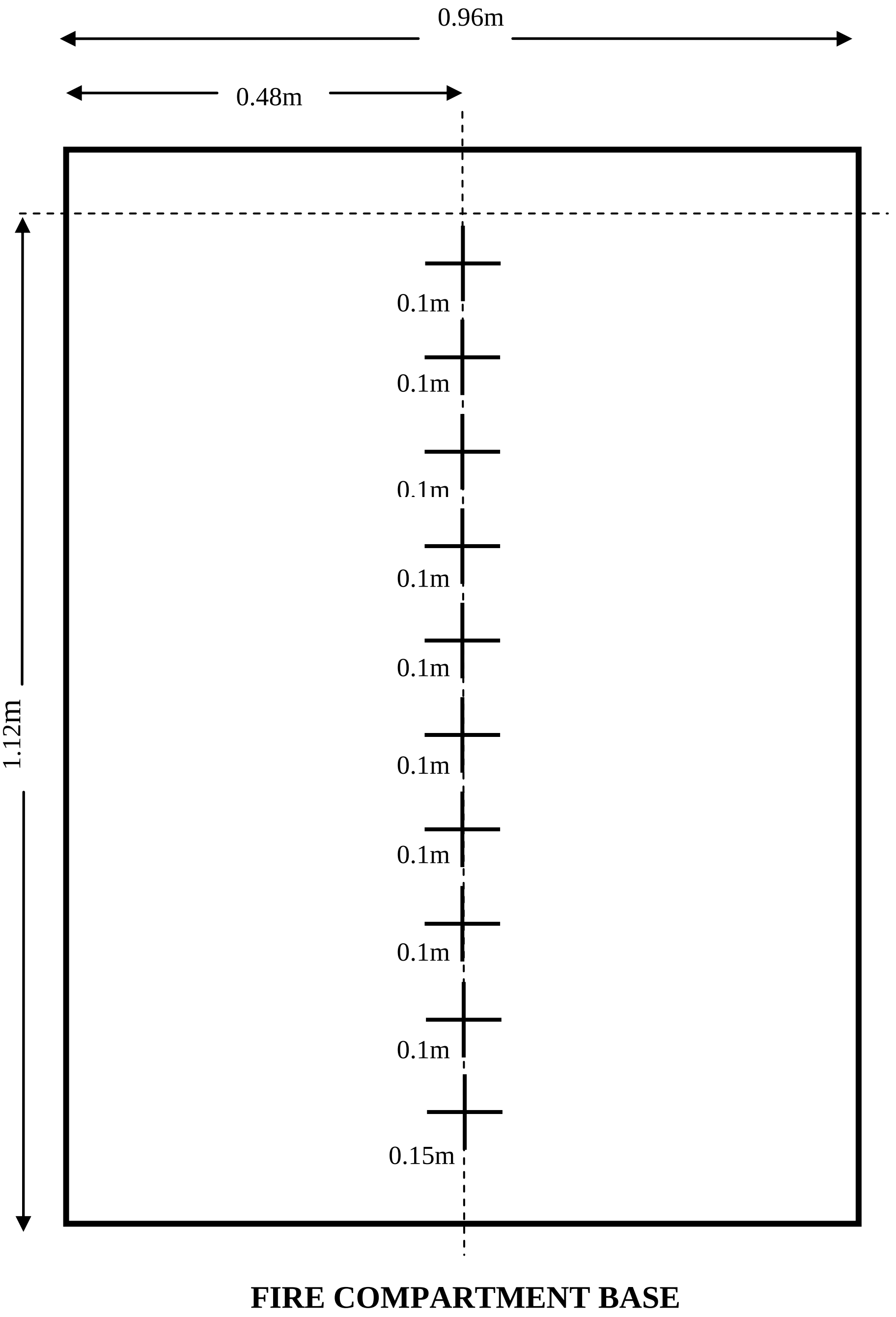
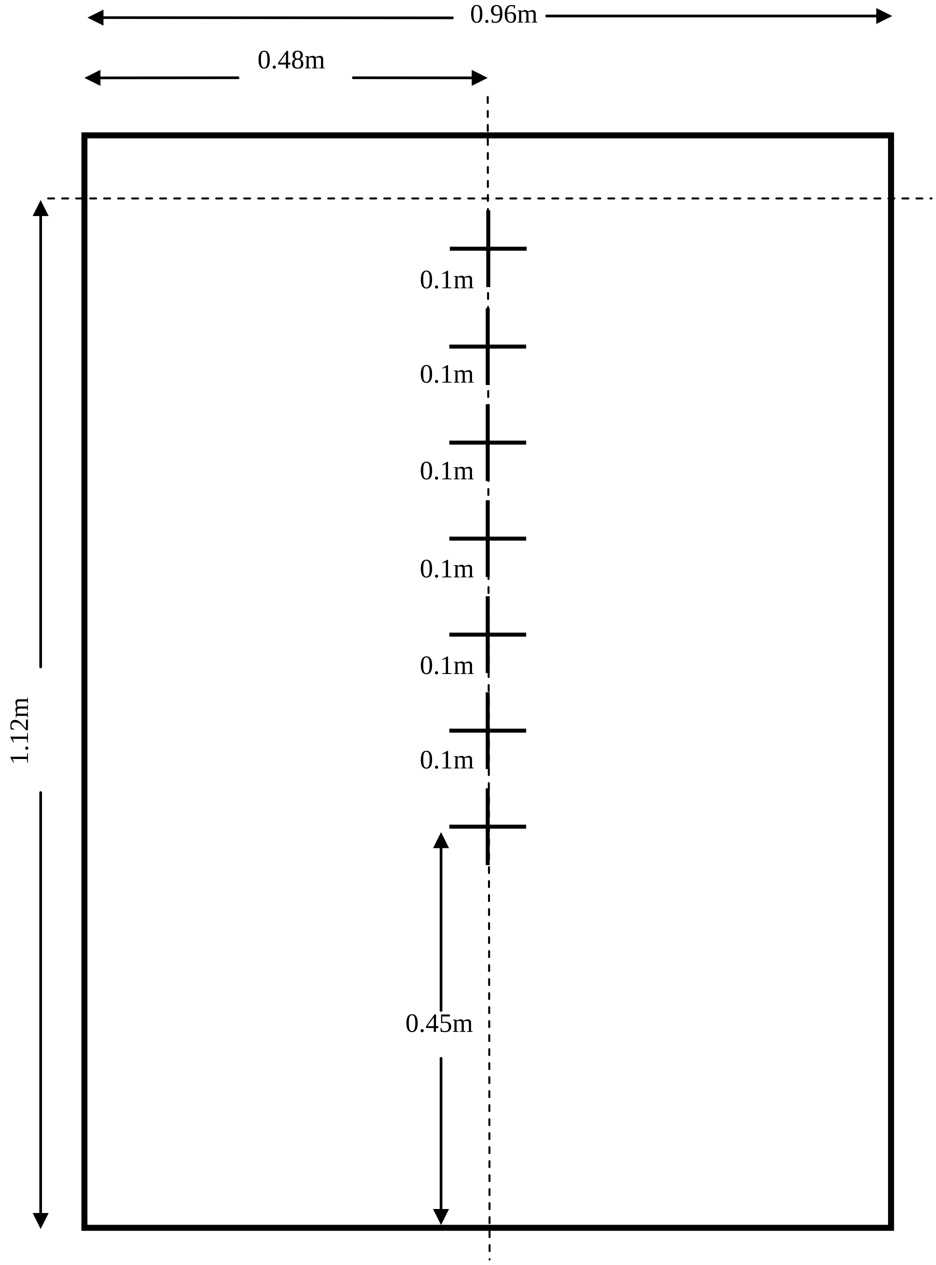


Figure 3-3: Suspended ceiling details (not to scale).



- View displayed is from the front of the compartment (as if looking through the open door).
- Upper dotted line indicates the height of the suspended ceiling above the compartment base (Figure 3-3).
- Thermocouple beads placed 0.175m from inside surface of rear wall, so that the rearmost thermocouple in the ceiling array (Figure 3.6) also became the uppermost thermocouple in the rear vertical tree.

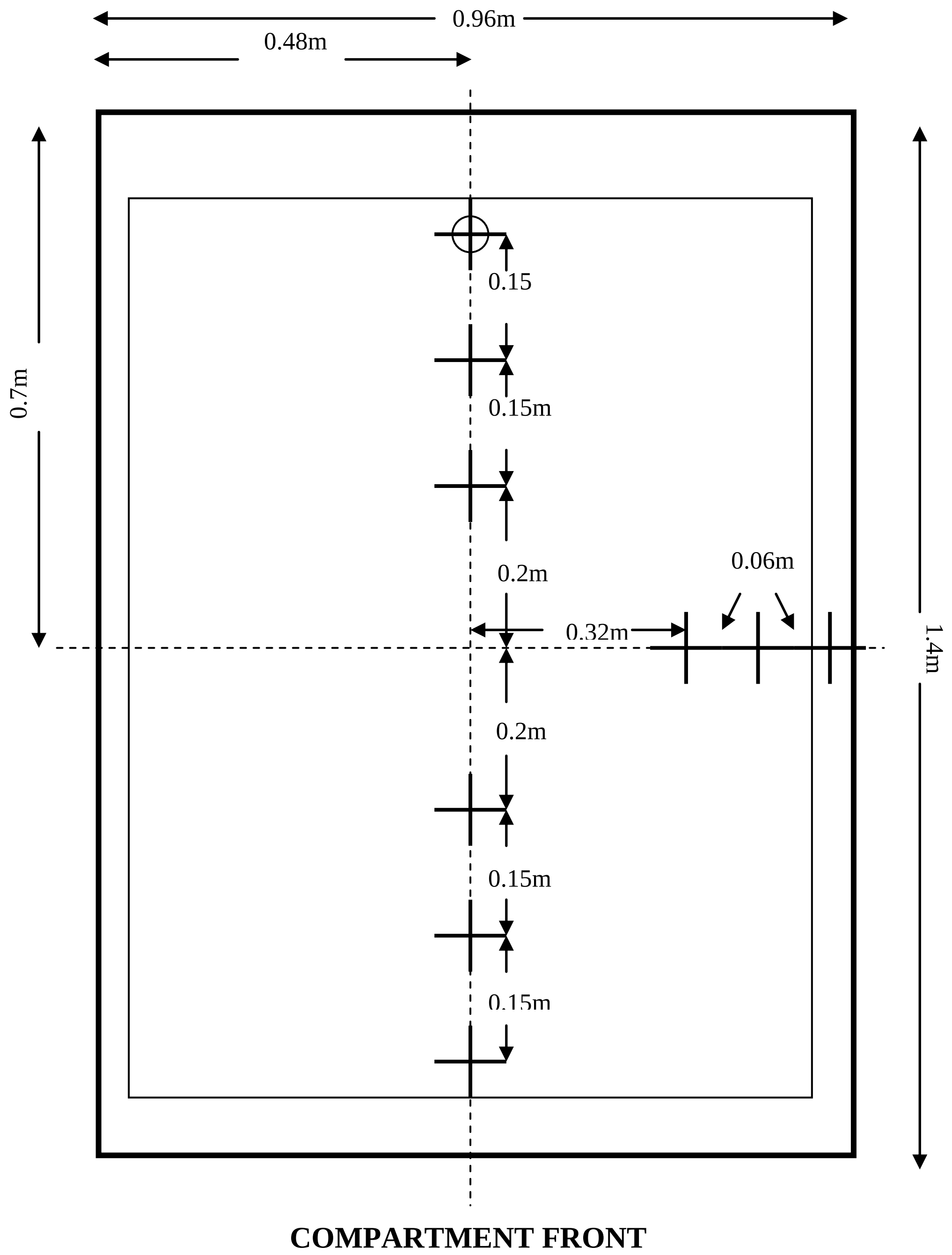
Figure 3-4: Rear thermocouple tree.



FIRE COMPARTMENT BASE

- View displayed is from the front of the compartment.
- Upper dotted line indicates the height of the suspended ceiling above the compartment base (Figure 3-3).
- Thermocouple beads placed 0.675m from inside surface of rear wall, so that the tree was centrally located in the compartment, directly above the fire plume.

Figure 3-5: Central thermocouples tree.



- Circle indicated around the uppermost thermocouple on the diagram indicates the position of the thermocouple tips of the rear vertical tree (Figure 3-4).
- Inner rectangle indicates the approximate size and position of the suspended ceiling (Figure 3-3 for more detailed measurements).
- All thermocouple beads are situated 70mm below suspended ceiling (1.05m above floor)

Figure 3-6: Upper layer thermocouples distribution.

3.1.1.2 Gas fired furnace:

This compartment is a 1.6m^3 ceramic lined furnace, heated by a natural gas burner, which has a very wide flame stability range and could generate any desired furnace temperature. The furnace is fitted with a single burner port of 150mm diameter that is located about 300mm above the floor and 300mm from the corner. This burner location was to avoid direct burner impact on the fire load which was placed in the centre of the furnace. The furnace is 1.3 m high, 1 m wide, and 1.2 deep fitted with a 150 mm exhaust port at the top and a mechanical extraction of a measured 5 m/s. The furnace was designed as an indicative fire test furnace that used the burner to follow the various standard fire temperature-time test scenarios. In addition, the furnace was fitted, with a total of 32 thermocouples, which provided detailed information on the temperature profile during the tests. The peak temperature was designed to be 1150^{o}C, as in the test methods. Higher or lower temperatures could easily be achieved. However, by limiting the burner air flow and modulating the burner natural gas flow any furnace temperature could be achieved. Further details on the furnace properties and the development of this part of the work, is provided in the Chapter 5. A sketch of the furnace is provided in figure 3-7.

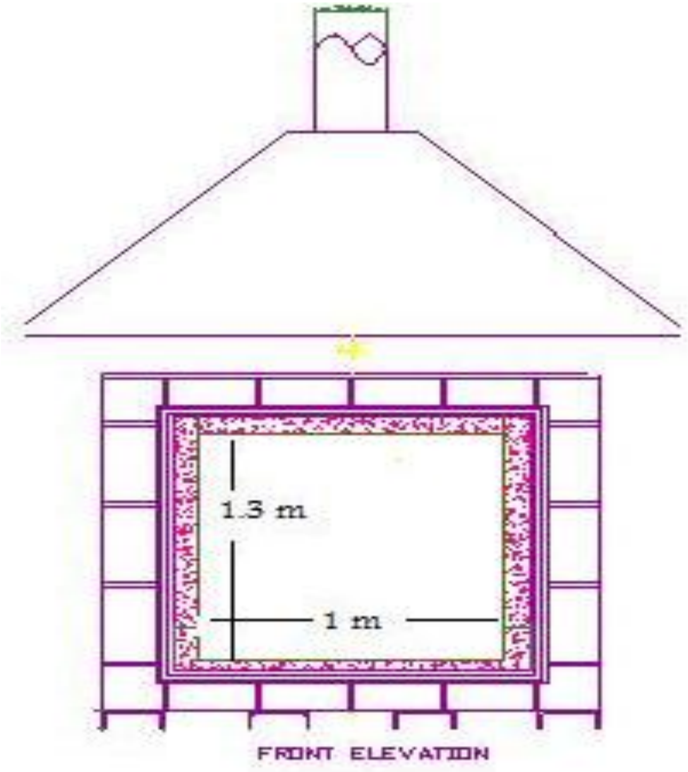


Figure 3-7: Gas fired 1.6 m^3 furnace.

3.1.2 GAS ANALYSIS EQUIPMENT:

As mentioned earlier, the combustion products leaving the fire compartment were sampled using an multi-hole ‘X’ sample probe (Figure 3.8), and the gases transported to the different analysers through a stainless steel filter assembly (Balston filter products model 3856) and via a 10m filtered Teflon transmission line. The line was electrically heated to 180^{o}C (above the dew points of the sampled gases), thus preventing water and hydrocarbons condensation in transmission to the analysers leading instrument damage.

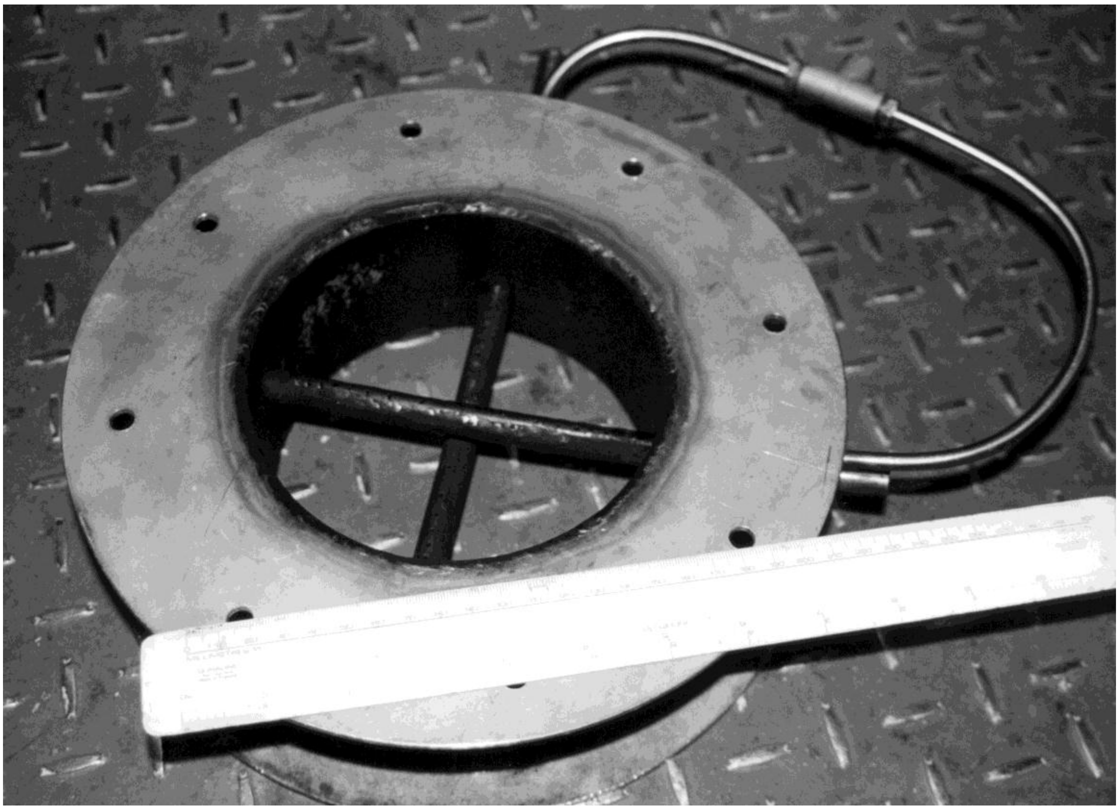


Figure 3-8: Picture of the X-hole sample probe.

Condensed water within the lines can lead to the removal of nitrogen dioxide, thus reducing the overall NO_x measurement, while condensed hydrocarbons will lower the unburnt hydrocarbon measurement. Therefore, before entering the analysers, the sample was first passed into a heated oven containing a pump and filter maintained at 190^{o}C. The sample line for CO2, CO, and O_2, was passed through a refrigeration cooler (operating at 2^{o}C) to remove water vapour, before entering the analysers. Additionally a bypass line capable of circumventing all instrumentation was employed to enable the control of the sample flow rate. A separate heated sample line, filter, and pump were used for providing the FTIR sample. Figure 3.9 shows a sketch summarising the analyser's connections, and sampling lines. Pictures of the different analysers used in this work can be found in Appendix A.

Between tests, the transmission line and instrumentation was purged and cleaned with compressed air from a Signal Instruments A580 air-purifier and filter, and the first filter in the transmission path manually cleaned and oven dried. This air-supply was also used as the supply for any analyser that required an uncontaminated air-supply for their operation such as the FID.

All data from the gas analysis instrumentation, except FTIR, were transferred to an MSTM Excel spread sheet every 5s on a PC via an IOTech Multiscan/1200 isolated data acquisition system.

3.1.2.1 Flame Ionisation Detector (FID):

The first analyser in the gas sampling system is the Flame Ionization detector 520 series, manufactured by Analysis Automation limited. Generally, it has high sensitivity and wide range of linearity. It responds to any molecule with a carbon-hydrogen bond but responds poorly to compounds such as H_2S, CCl_4 or NH_3. It functions as follows, as the gas sample enters the FID it is burnt in a hydrogen air flame where ions and free electrons were formed in the flame. The charged particles produced a current flow between two electrodes in the detector which resulted in a current flow with greater strength than the signal produced by the pure carrier gas and the fuel gas flame alone. The signal differential provides information about the sample. In principle, it has a detection range of 0.1ppm to almost 100%, however the instrument used in this work was calibrated for a maximum range of 10%.

3.1.2.2 Chemi-luminescent:

The second analyser in the set of analysers was the Chemi-luminescent apparatus; it operates on the reaction of NO with Ozone O_3. When the nitric oxide (NO) reacts with Ozone, it is oxidizes to form NO_2 in an excited state. A small fraction of the excited state molecules decay, by giving off light, near the infrared portion of the spectrum, hence the concentration of NOx in the sample is determined by the amount of light emitted being measured by the analyser.

3.1.2.3None-Dispersive Infra-Red Spectrometer (NDIR):

The NDIR equipment used in this work was manufactured by Hartmann and Braun. It was connected to the cold sample line. In order to condensate the water present in the sample the sampling line was cooled to around $2^{o}C$. CO and CO_2 are then detected by passing the sample gas through an infrared spectrometer. The equipment reads Carbon dioxide for a range of 0-20% and Carbon monoxide from 0-2000ppm and 0-3% with a resolution of 0.00001%.

3.1.2.4 Paramagnetic O_2 analyser:

The cold sample line was also attached to a paramagnetic oxygen spectrometer. That consisted of a pair of magnets, creating a magnetic field across an interface. Since oxygen is magnetic, once it is introduced to a magnetic field, its dipole will align with the field and strengthen it. The resolution of the equipment used was 0.01%. The detector measurements were taken from dry analysis, as such they need to be converted to wet analysis if they are to be used for comparison.

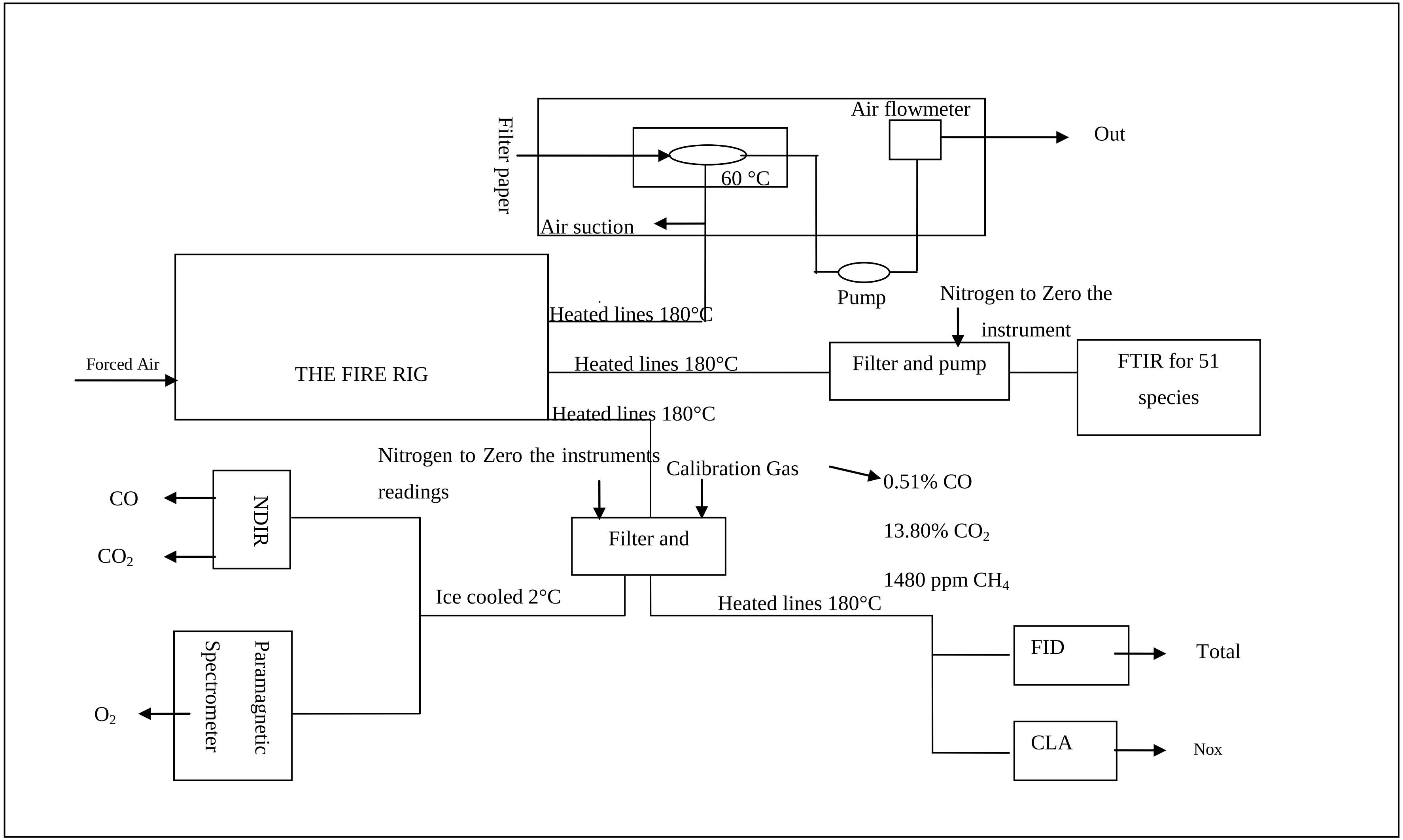


Figure 3-9: A schematic sketch of the analysers used.

3.1.2.5 Fourier Transform Infra-Red Spectrometer (FTIR):

The most important gas analyser used in this work was the CR-Series portable FTIR manufactured by TEMET GASMETThe FTIR In this section a short overview on the development of the FTIR techniques and its operating principles is provided. The development of Fourier Transform Infrared spectroscopy (FTIR) in the early 1970s provided a significant advancement in infrared analytical capabilities for monitoring and quantifying pollutants and toxic gases. This technique offered a number of advantages over conventional infrared systems, including sensitivity, speed and improved data processing. The technique is in principle a combination of Fourier Transform, which is a mathematical technique of expressing a wave signal in a summation of sins and cosines, and Infrared, which the range of invisible radiation wavelengths from about 750 nanometres, just longer than red in the visible spectrum, to 1 millimetre, on the border of the microwave region.

The model used in this work had a typical 2 ppm resolution with an accuracy of 2% and a precision that is 0.01% of the measurement range. Part of this uncertainty comes from the calibration gases used for obtaining reference spectra and part of it is from the analysis algorithm used in Calcmet software. When adding concentrations (e.g. NO_x = NO_2 + NO) it will be SQRT(0.02^2+ 0.02^2) and the same concept is extended when summing the hydrocarbon components. The 2% uncertinity is given by the analysis software developers.

The basic components of a typical FTIR are shown schematically in Figure 3.10. It operates as follows: the infrared source emits a broad band of different wavelength of infrared radiation. The IR source used in the Temet GASMET FTIR CR-series is a SiC ceramic at a temperature of 1275 ºC. The IR radiation goes through an interferometer that modulates the infrared radiation. The interferometer performs an optical inverse fourier transform on the entering IR radiation. The modulated IR beam passes through the gas sample where it is absorbed to various extents at different wavelengths by the various molecules present. Finally the intensity of the IR beam is detected by a detector, which is a liquid-nitrogen cooled MCT (Mercury-Cadmium-Telluride) detector in this work. The detected signal is digitised and Fourier transformed by the computer to get the IR spectrum of the sample gas.

Figure 3-10: A sketch of the basic FTIR components.

Nevertheless, the unique part of an FTIR spectrometer is the interferometer. A Michelson type plane mirror interferometer configuration is displayed in Figure 3-11. Infrared radiation from the source is collected and collimated (made parallel) before it strikes the beam splitter. The beam-splitter transmits one half of the radiation, and reflects the other half. Both transmitted and reflected beams strike mirrors, which reflect the two beams back to the beam-splitter. Thus, one half of the infrared radiation that finally goes to the sample gas has first been reflected from the beam-splitter to the *moving* mirror, and then back to the beam-splitter. The other half of the infrared radiation going to the sample has first gone through the beam-splitter and then reflected from the *fixed* mirror back to the beam-splitter. When these two optical paths are reunited, interference occurs at the beam-splitter because of the optical path difference caused by the scanning of the moving mirror.

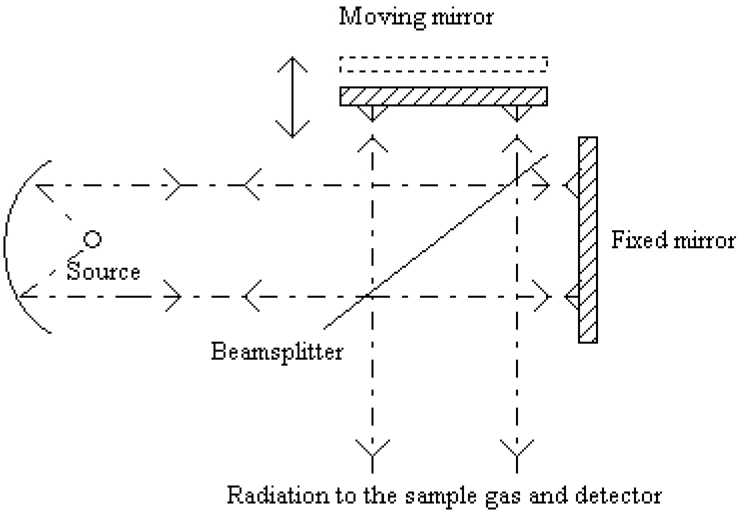


Figure 3-11: Michelson interferometer.

The optical path length difference between the two optical paths of a Michelson interferometer is two times the displacement of the moving mirror. The interference signal measured by the detector as a function of the optical path length difference is called the interferogram. A typical interferogram produced by the interferometer is shown in Figure 3-12. The graph shows the intensity of the infrared radiation as a function of the displacement of the moving mirror. At the peak position, the optical path length is exactly the same for the radiation that comes from the moving mirror as it is for the radiation that comes from the fixed mirror.

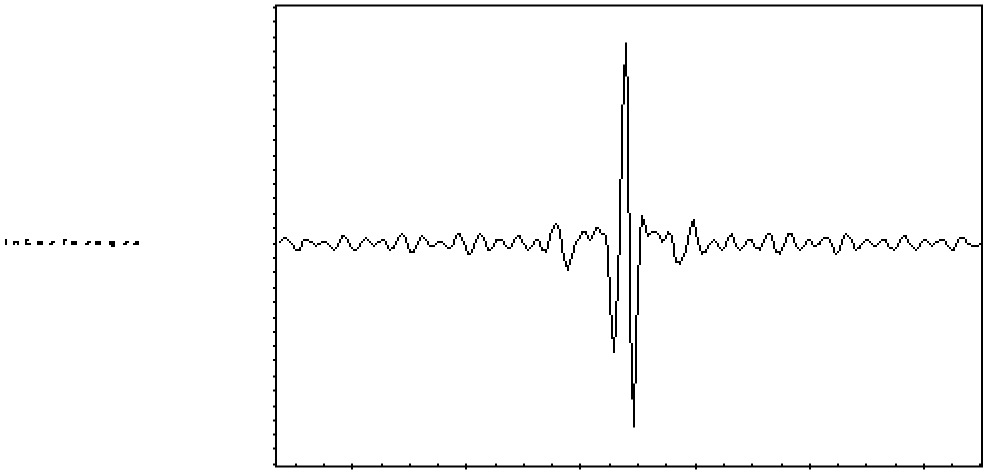


Figure 3-12: A typical interferogram.

The spectrum can be computed from the interferogram by performing a Fourier transform. The Fourier transform is performed by the same computer that ultimately performs the quantitative analysis of the spectrum. The degree of absorption of infrared radiation at each wavelength is quantitatively related to the number of absorbing molecules in the sample gas. Since there is a linear relationship between the absorbance and the number of absorbing molecules, multicomponent quantitative analysis of gas mixtures is feasible. To perform multicomponent analysis the processes starts with the sample spectrum. In addition, a reference spectrum of all the gas components that may exist in the sample is needed, if these components are to be analysed. A reference spectrum is a spectrum of one single gas component of specific concentration. In multicomponent analysis it is advised to try to combine these reference spectra with appropriate multipliers in order to get a spectrum that is as close as possible to the sample spectrum. If we succeed in forming a spectrum similar to the sample spectrum, we get the concentration of each gas component in the sample gas using the multipliers of the reference spectra, provided that we know the concentrations of the reference gases. This is crucial in fire studies, where a wide range of toxicants co-exists. Therefore, it was attempted to use one of the largest libraries calibrated by the manufacturers to detected 51 species, in order to obtain the best possible solution accuracy.

For example, suppose we have a sample spectrum and reference spectra like those shown in Figure 3-13. In this case, we know that the sample gas consists of gases Reference 1 and Reference 2. We have the reference spectra available and we know that these reference spectra represent concentrations of 10 ppm and 8 ppm respectively. To find out the concentration of each component in the sample gas, we try to form the measured sample spectrum using a linear combination of the reference spectra. We find out that if we multiply the spectrum Reference 1 by 5 and the spectrum Reference 2 by 2, and combine these two spectra, we get a spectrum that is similar to the sample spectrum. Accordingly, the sample gas contains reference gas 1 at five times the amount in the reference spectrum 1, and reference gas 2 at two times the amount in the reference spectrum 2. The analysis indicates that the sample indeed consists of these two reference gases. The concentration of the reference gas 1 in the sample is found to be 50 ppm, and the concentration of the reference gas 2 in the sample is 16 ppm.

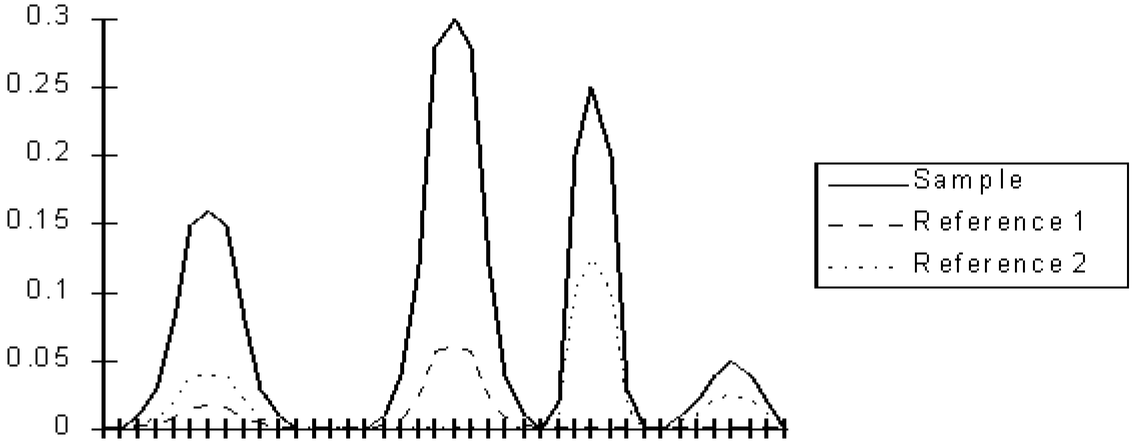


Figure 3-13: An example of spectra for multi-component analysis.

This multi-component ability of FTIR means that theoretically, any spectrum obtained with the FTIR can be reprocessed at a future date to determine the concentration of any newly calibrated gases. Therefore it is worth saving the spectra obtained from FTIR since they potentially contain so much information about the sample gas.

Finally, the detector cell, sample line, pump and filter were all heated so that no species was lost during the analysis and so that high molecular weight hydrocarbons could be detected.. The zero had to be set using nitrogen before the experiment commenced. The FTIR calibration for the range of the gases tested is presented in table 3.1 in the following page. It should be noted however, in cases where the measured quantity exceeded the calibration range; the measurement residual was checked for validation of the accuracy of the measurement. The measurement residual is an indication of the fit between the sample spectrum and the spectrum calculated from the analysis results. In cases, where the residual was less than 0.01 were deemed accurate. Higher, residuals meant there was probably a good chance that other, un-calibrated compound co-existed in the same spectrum, thus interfered with the measurment and further re analysis was required.

Table 3-1: FTIR calibrated range for the 51 species.

Species	Range		Species	Range	
Water vapor	50	%	1,3,5-trimethylbenzene	500	ppm
CO_2	30	%	Ethylbenzene	*200	ppm
CO	20000	ppm	Indene	*500	ppm
N_2O	500	ppm	Methanol	500	ppm
NO	2000	ppm	Ethanol	500	ppm
NO_2	1000	ppm	Propanol	500	ppm
SO_2	1000	ppm	Butanol	*200	ppm
COS	200	ppm	MTBE	500	ppm
NH_3	500	ppm	Dimethyl Ether	*200	ppm
HCN	500	ppm	Formaldehyde	500	ppm
HCl	500	ppm	Acetaldehyde	200	ppm
HF	200	ppm	Formic acid	200	ppm
Methane CH_4	1000	ppm	Acetic acid	500	ppm
Ethane C_2H_6	500	ppm	Acrolein	500	ppm
Propane C_3H_8	500	ppm	Naphthalene	500	ppm
Butane C_4H_{10}	500	ppm	1-ethylnaphthalene	500	ppm
Pentane C_5H_{12}	500	ppm	Sulfur hexafluoride	50	ppm
Iso-pentane C_5H_{12}	*200	ppm	i-Butane	*100	ppm
Hexane C_6H_{14}	500	ppm	1-Butene	*500	ppm
Heptane C_7H_{16}	500	ppm	Tran-2-Butene	*100	ppm
Octane C_8H_{18}	*200	ppm	Cis-2-Butene	*150	ppm
Iso-octane C_8H_{18}	*500	ppm	i-ButeneC_4H_8	*150	ppm
Cetane $C_{16}H_{34}$	*200	ppm	PenteneC_5H_{10}	*250	ppm
Acetylene C_2H_2	500	ppm	HexeneC_6H_{12}	*500	ppm
Ethylene C_2H_4	500	ppm	HepteneC_7H_{14}	*500	ppm
Propene C_3H_6	500	ppm	OcteneC_8H_{16}	*500	ppm
1,3-Butadiene	500	ppm	Nonene C_9H_{18}	*500	ppm
Benzene	500	ppm	Cyclopropane C_3H_6	*500	ppm
Toluene	500	ppm	Cyclohexane C_6H1_2	*500	ppm
m-xylene	500	ppm	Alpha-pinene	*500	ppm
o-xylene	500	ppm	NO_x	3000	ppm
p-xylene	500	ppm	THC	1000	ppm
1,2,3-trimethylbenzene	500	ppm	TMB	1500	ppm
1,2,4-trimethylbenzene	500	ppm	* = Generic libraries used		

3.1.3 SOOT SAMPLING EQUIPMENT:

A direct sample of the exhaust gases via the multi-hole ‘X’ sample probe shown earlier, was used in an attempt to obtain soot concentrations measurement using a Richard Oliver heated filter paper soot sample system.

The gravimetric measurement of particulates was carried out in a batch sampling process for the duration of a test, using a Richard Oliver heated filter paper soot sample system. This system essentially utilised a pump to draw specified volumes of exhaust products at controlled flow rates through a filter paper (Whatman GF/F glass fibre filter papers - 25mm sample spot size) in a heated oven. The ability to control both the sample volume and flow rate allowed the mass of particulates deposited to be controlled over the sampling period; too small a sample volume would result in there being insufficient mass collected on the filter paper to obtain an accurate measurement of the mass, while too large a sample volume would result in the collection of too much particulate mass, which would fall from the filter paper inside the oven resulting in an underestimate of the concentration. Furthermore, if a high flow rate was utilised (preferable to give as many samples as possible for transient data); the risk of damaging the filter becomes significant.

Sampling above the water vapour saturation temperature is needed to ensure that particulate concentration is reported on an unambiguous basis (wet) and to avoid damage of the filter paper. In the present work, the filter housing was heated to 90^{o}C (as opposed to 50^{o}C used in diesel engine emissions – where the technique originates). A temperature of 90^{o}C is above the dew point of the products of combustion at any equivalence ratio in the fire gas sample and hence no condensation could occur.

Before each test, a suitable number of filter papers (for soot measurements to be carried out for the duration of the fire) were placed in a desiccator (to remove any water mass) for approximately 12 hours. These papers were numbered and weighed on a Mettler semi-analytical balance (10 μg resolution) and returned to the desiccator. Each filter paper was placed in turn into the heated filter paper housing and the flow rate and volume were set to 5 litres.min^{-1} and 15 litres respectively (giving a sample duration of 3min. and a sample mass of approximately 1-2 mg). At the end of the sample duration, each paper was returned to the desiccator. After a further 12 hours, the papers were reweighed, so the particulate mass and hence concentration (g.m^{-3}) could be determined at number of points during the fire's duration.

3.1.4 GENERAL EXPERIMENTAL PROCEDURES IN BRIEF:

In this work, every test was treated as a compartment fire. In general a fire test required a day of measurements and monitoring, and half a working day in preparation. Depending on the test variables, fuel type, and ventilation conditions the tests actual duration ranged from 30 min. to 6 hours. A general description of the experimental procedure is given here, however more details are provided in the relevant chapters.

- At about 2 hours before the start of the test, the FTIR is turned, and left to warm up. Once stabilised the interferometer is purged using nitrogen gas for about 15 min. at a later stage the sample cell is purged with liquid nitrogen for about 2-3 minutes.
- At about 1 hour before the start of the test, the heated lines, analysers and associated instrumentation, were turned on to allow them to warm up as recommended by the manufacturer's guidelines.
- The extraction system was turned on, and remained on throughout the test and for a least an hour afterward to ensure the safe removal of all combustion products from the compartment.
- The required fuel tray (and ignition tray in the case of crib fires) was placed in the centre of the load cell array, and the load-meter tared to give a zero reading.
- The PC was turned on and the data-logging programs were started and linked to a MS™ Excel template used to contain the calibrations for the instrumentation.
- The gas analysers were calibrated using air and a precise gas mixture and for the zero and span settings respectively.
- The fuel tray was filled with the desired fuel to the mass required (for liquid fuels).
- The air flow feed was set to the desired, flow rate and monitored continuously throughout the test.
- The spreadsheet calibrations were adjusted, so that the gas analysers' zero and span settings and the fuel mass, read accurately in the MS™ Excel template.

- The fuel was ignited and the compartment door closed immediately. The downloading of the data-loggers into the MS™ Excel template and a stopwatch were also triggered simultaneously.
- Measurements were recorded at 5s intervals automatically by the MS™ Excel template of the exhaust gas composition, fuel mass and compartment temperatures. At the same time, the resulting FTIR data is saved in txt format, while the test spectrum is stored for future reference.
- Once the test is over, the compartment was kept closed until the morning after.

This was a general procedure for most of the tests, however some tests required special preparation which will be highlighted in the relevant chapters.

3.2 GAS ANALYSIS TECHNIQUES:

3.2.1 CROSS ANALYSERS CHECKING

The first measure to validate the results was to examine the concentration of CO, CO_2, and UHC, obtained from the FTIR and compare them to the results obtained using the NDIR, and FID. In general the agreement was satisfactory, with less than 5% difference in most tests. In cases where disagreement occurred, further steps were taking to investigate the cause of the inconsistency. The first step was to re-analyse the FTIR stored spectrum. The second was to double check the analyser’s performance using calibration gases. And the final step was to reassess the experimental set up, to identify if there was any pressure drop, leakage, or blockage in the gas sampling system. Inconsistency between the analysers was noticed in two tests, and after re analysing the FTIR data, and consulting the manufacturers, it was deemed, that the malfunction of the data was most probably due an experimental error, where a blockage occurred in the FTIR sampling line. A decision was made to scale the FTIR data, to match the CO, and CO2 from the NDIR, and the scaled results for rest of the species concentrations fell into the expected pattern.

3.2.2 CARBON BALANCE FOR CALCULATING AFR AND Ø

A major feature of this work is the precise and adequate quantification of the combustion products. One advantage of this is the ability to back calculate the process air to fuel ratio using carbon balance techniques. This was a useful exercise for tests were direct measurement of the fuel mass loss rate was possible, and a metered air to fuel ratio was calculated. It showed that the AFR calculated using carbon balance techniques, agrees to a very reasonable level with the AFR calculated from the mass loss rate, and air supply rate. . The carbon balance technique used in this work, was adopted from mathematical equations developed by (Chan, 1996) for fuel containing *CHONS* elements. The mathematical expression, presented in Appendix B, was implemented in an Excell spread sheet which calculated the estimated AFR for each test. This is the first time, the Chan equations are used in fire research, and it provided good agreement with the meter AFR, in all the tests investigated.

An example is shown for a wood crib fire tests in Figure 14. The presented tests, shows very good agreement, between the back calculated, and mass based AFR, with the only difference is the slight fluctuations caused by the partial collapse of the crib in the later stages of the fire. The more useful use of this technique however, was evident from tests where no direct mass loss rate was possible, due to fuel set up. The carbon balance based AFR allowed the researcher to investigate hanging fire loads, and furnace burning conditions with high confidence in the calculated yields

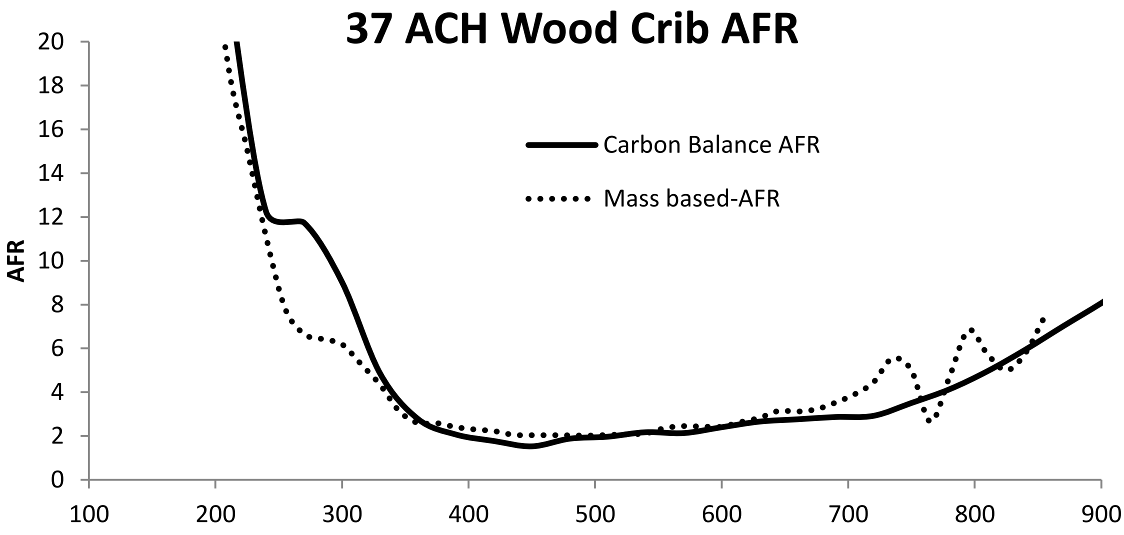


Figure 3-14: Metered and gas analysis based AFR in a 37 ACH wood crib test.

3.2.3 SPECIES YIELDS CALCULATION

Once the air to fuel ratio is established, and the concentration was measured, E.q. 2.16 was used to compute the species production rate in kg/kg. The experimental configuration, allowed a direct measurement of the estimated yield of species over time. Unlike most earlier studies, which concluded the results from each test to the peak value of the yield, these tests provide a wealth of information on different fire stages and combustion conditions. The species yields are typically presented against the equivalence ratio calculated using E.q. 2.12. This allowed comparison with the previously reported yields, often presented against the equivalence ratio. However, the results from this work, suggest in addition to the equivalence ratio effect, a strong dependence on the upper layer temperatures, as will be shown later.

3.2.4 HEAT RELEASE RATE FROM GAS ANALYSIS

The heat release rate was calculated using oxygen calorimetry first introduced by (Huggett, 1980). E.q. 2.9 was used to estimate the Heat Release Rate (HRR). However, in most cases the calculated results did not agree with the theoretical heat release rate derived from the fire load mass loss rate. This was to be expected, as most of these fires were under ventilated and very inefficient fires. In this work, the oxygen based heat release rate is deemed the actual HRR, and once the yields are quantified, it was shown that when combustion efficiency is taken into consideration, the theoretical (mass loss based) heat release should be much closer to the oxygen analysis heat release rate. The author has shown in (Aljumaiah et al., 2010a; Aljumaiah et al., 2011b) how the combustion efficiency is very low in these conditions, and how adjusting the theoretical heat release rate provides similar results to oxygen calorimeter heat release rate.

An example is shown in Figure 3-15, where a wood crib fire was very inefficient, during most of the test period.

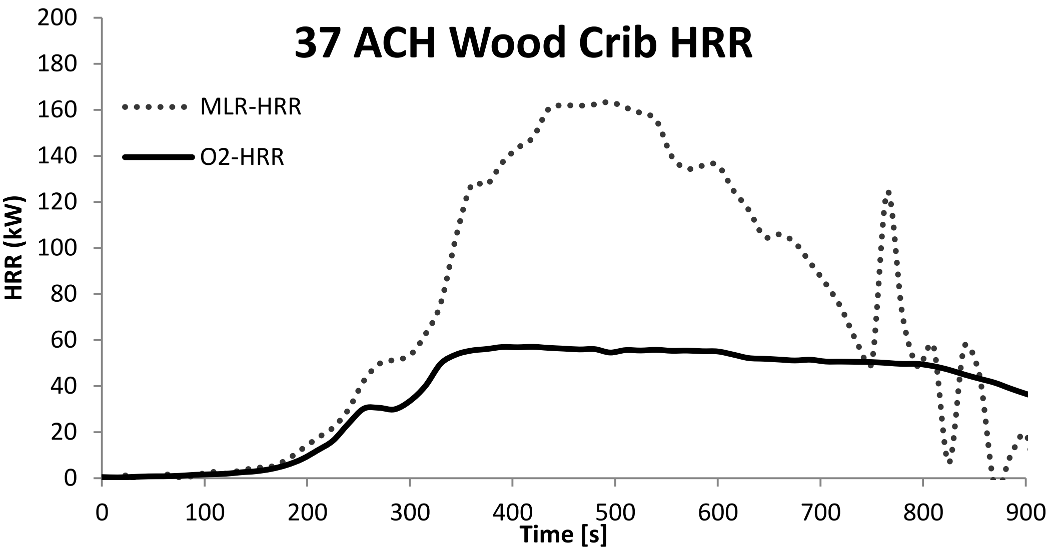


Figure 3-15: HRR over time in a wood crib test.

3.2.5 COMBUSTION EFFICIENCY

Combustion efficiency is another fundamental feature of compartment fires, often overlooked by fire researchers. Its quantification can be through calculating the theoretical heat release rate, and comparing it to the actual heat release rate measured using oxygen consumption. Alternatively, calculating the energy locked in the incomplete combustion products as in E.q. 2.22, in the background section. The latter method is adopted in this work, where no direct mass loss was measured in the test.

3.3 FIRE TOXICITY ASSESSMENT:

3.3.1 N GAS MODEL USED IN THIS WORK

The general assumption, as shown in section 2.2, in fire research, is to assume additive behaviour of the fire toxic smoke components effects. This was adopted in almost all the toxicity assessment models reviewed. More importantly, it was shown that the toxicological endpoint used in the toxic effluent assessment is the crucial conceptual basis of the model. In this work, two measures are investigated; lethality, based on LC_{50} rat data in line with the ISO1344, and Impairment of escape in humans, based on

COSHH Short Term Exposure Limit (STEL) for 15 min. exposure limit. These two endpoints are the most important, as the lethality indicated severe death, and the impairment of escape can provide a relative safety zone.

In addition, it was shown in previous fire toxicity assessment models, a major deterministic factor in model development was the objective and use of the model. For example, the N-gas, Purser FED, and ISO1344, were developed for materials research, therefore, rat lethality and a time-dependant cumulative dose were considered to present data consistent with earlier animal exposure studies.

On the other hand, the ISO13571, FEC, methodologies for impairment of escape were developed for estimating the toxic smoke levels at which incapacitation or impairment of escape in humans was predicted due to irritant species, therefore a different toxicological endpoint was used, and a fractional effective concentration was adopted instead of the fractional effective dose methodology. Nonetheless, they are developed to evaluate the human exposure to these gases, and not the fire source. Applying these models would be miss leading, without clearly defined objectives and interpretations.

In this work, as the toxic effluent do not represent a case of human exposure, nor a material toxicity assessment, but rather combustion process conditions monitoring, representing a fire source. In addition, a major objective of this work, is quantifying the different toxic species, and compare them to establish their relative importance for hazard assessment.. Therefore, a modified fractional effective concentration approach is used to give the ability, to rank and asses the different gases at any part of the fire. In addition, it would allow the researcher to compare the toxic gas species relative to their expected effect, Lethal in LC_{50} or Irritant in $COSHH_{15}$. Eq. 3.1 and Eq. 3.2, show the models used in this work, while the limits LC_{50} and $COSHH_{15}$, are found in Table 2.17.

In addition, this model, allows predicting how much the total toxic composition is in terms of irritation, and lethality. It provides an estimate on how much should the fire products should be diluted in order to provide safe escape for occupants. And most importantly, it allows the researcher to produce a time history of the fire showing the composition of the toxic dose, during different phases of the fire development as shown by the author in (Aljumaiah et al., 2010a; Aljumaiah et al., 2010b; Aljumaiah et al., 2010c; Aljumaiah et al., 2011b), and will be shown in the following chapters.

$$N-LC_{50}=\frac{[CO]}{LC_{50,CO}}+\frac{[HCl]}{LC_{50,HCl}}+\frac{[HBr]}{LC_{50,HBr}}+\frac{[HF]}{LC_{50,HF}}+\frac{[SO_2]}{LC_{50,SO_2}}+\frac{[NO_2]}{LC_{50,NO_2}}+\frac{[Acrolien]}{LC_{50,Acrolien}}+\frac{[Formaldehyde]}{LC_{50,Formaldehyde}}+\sum\frac{Speciies\ [i]}{IC_{50,Species\ i}} \tag{3.1}$$

where, LC_{50} of a toxic species i, is the lethal concentration provided in ISO1344, and reviewed in chapter 2 and,

$[i]$ is the measured concentration of the gas.

$$N-COSHH=\frac{[CO]}{COSHH_{15\ min.CO}}+\frac{[HCl]}{COSHH_{15\ min.HCl}}+\frac{[HBr]}{COSHH_{15\ min.\ HBr}}+\frac{[HF]}{COSHH_{15\ min,HF}}+\frac{[SO_2]}{COSHH_{15\ min.SO_2}}+\frac{[NO_2]}{COSHH_{15\ min.NO_2}}+\frac{[Acrolien]}{COSHH_{15\ min.Acrolien}}+\frac{[Formaldehyde]}{COSHH_{15\ min.\ Formaldehyde}}+\sum\frac{Speciies\ [i]}{COSHH_{15\ min.,Species\ i}} \tag{3.2}$$

where, $COSHH_{15\ min.}$ of a toxic species i, is the Short Term Exposure Limit STEL and,

$[i]$ is the measured concentration of the gas.

3.4 FIRE TESTS VARIABLES:

A major feature of this work is the special configuration suitable for studying under-ventilated fires conditions. The focus of this work was to generate data in the least studied of under ventilated fires. However, characterising the fire in terms of ventilation rate is not a clearly defined area. Nonetheless, one possible expression which may relate to any other compartment is the air changes per hour. It is a frequently used, global measure in building services, air quality control, and air conditioning industry. In fact, it is also used in some fire standards for setting up the extraction rate during fires. The (CIBSE, 2003)guide suggests smoke control system operating at 10 ACH for car park fires, and basement fires. (Andrews et al., 2005b) estimated current design guides, allow for a leakage representative of around 5 ACH. This, assumes a closed room, and only design leakage is taken into consideration. In addition, once a window is partly opened, or a door is not closed properly the leakage area will be in the order of 10-20 in terms of ACH. It is around these scenarios that this work is carried out. Lower rates representing a fully enclosed room, were investigated by (Andrews et al., 2007; Andrews et al., 2005b; Andrews et al., 2005a), however those tests were possible, due to the small loading used. It will be shown in this work, fire would self extinguish in most cases in tests where the air ventilation rate was 5ACH or less.

Furthermore, it is important to note that, the ventilation rate, is by no means a measure of fire vitiation, this is because these tests are started naturally simulating accidental fire development, unlike smaller scale tests, where heat is imposed on the sample. Thus, the fire vitiation is a function of the growth rate of the fire, and the amount of ventilation. It will be shown in some tests, that the lowest ventilation tests self extinguished, and some of the relatively higher ventilation tests, produced significantly higher toxicants.

In addition, the tests second major variable, was the type of fire load. The investigation starts with wood cribs, which are then burnt in the furnace to investigate further the different conditions effect on the same fuel. This is followed, by further testing on cotton towels, acrylic curtains, and a range of hydrocarbon pool fires, which included Kerosene, Heptane, Toluene, and Diesel. Further details on the choice of materials, and fuel configuration is provided in each chapter..

4. CHAPTER 4:
WOOD CRIB COMPARTMENT FIRES

This chapter is based on the following publication:

Aljumaiah, O., G. E. Andrews, B. G. Mustafa, H. Al-qattan, V. Shah and H. N. Phylaktou,(*2011a)*, Air Starved Wood Crib Compartment Fire Heat Release and Toxic Gas Yields, In *Proceedings of the 10th International Symposium on Fire Safety Science, Maryland, USA,* edited by Spearpoint, 2011, International Association for Fire Safety Science.

ABSTRACT

Pine wood crib fires (4.6 kg) were investigated in a 1.6 m^3 fire compartment with air ventilation between 3 and 40 air changes per hour (ACH). The cribs were 380 mm tall and 300 mm square. The fires rapidly self-extinguished at 3ACH and struggled to continue to propagate at 5 ACH, where only 15 % of the initial crib mass was burnt. For 11, 21 and 37 ACH the cribs burned completely and the oxygen consumption HRR increased with ventilation. All three fully burned fires had rich equivalence ratios for most of the fire duration and associated high CO yields. Extremely toxic levels of CO, acrolein, formaldehyde and benzene were generated and the total toxic N on an LC_{50} basis was over 30. The combustion efficiency was very low due to the very high CO and total hydrocarbon emissions and this led to a major difference in the HRR by mass loss and that by oxygen consumption. The results demonstrate the severe toxic conditions that occur in ventilation restricted fires with wood as the main fire load.

4.1 INTRODUCTION

The majority of fire fatalities are caused by inhalation of toxic gases in fire smoke (National Statistics, 2009; National Statistics, 2010; USFA, 2005; USFA, 2011). Not only does smoke reduce the visibility of occupants in compartment fires, but it also is an irritant which causes respiratory problems. (Purser, 2002) showed that in most fires the main toxic products are CO, HCN and irritant or acidic gases and the amount of each depends on the thermal decomposition of the fire load, which depends on the temperature and oxygen supply. However, HCN and HCl and HBr are normally low unless the fire load contains organic N, Cl or Br compounds (Hartzell, 2001; Hull and Stec, 2010; Hull et al., 2008b; Purser, 2010b), which was not the case in this chapter. There are very few measurements of irritant and acidic gases in compartment wood fires and the present work uses heated Fourier transform infra-red spectroscopy (FTIR) specifically to investigate these gases.

The effect of toxic smoke can be lethal; therefore, it is normally measured by the LC_{50} toxic limits (Babrauskas et al., 1998; Babrauskas et al., 1992; Levin, 1996)for 50 % deaths after 30 min exposure. However, toxic gases are often described by survivors of fires as acidic and/or irritant gases and these slow the movement of people and can lead indirectly to their death (Purser, 2002). CO is the most common gas that kills people in fires, but this has no odour or irritant effect on people. (Andrews et al., 2007; Andrews et al., 2005b; Andrews et al., 2005a)have used COSHH 15 min exposure standards [9] as well as LC_{50} to access fire toxicity. COSHH is the European standard on occupational exposure limits, which are statutory law in Europe, and are similar to the equivalent US limits. These COSHH 15 min levels represent an impairment of the means of escape, whereas the LC_{50} limits are for 50 % people dying in a fire after 30 min exposure. The USA has introduced the Acute Exposure Guideline Levels (AEGL) with three exposure levels: 1 for non-disabling and essentially similar to the COSHH 8 h levels; 2 for disabling and impairment of escape based on 10 min exposure which is similar to the COSHH 15 min exposure limit; and 3 for life threatening health effects which are similar to LC_{50}. The $COSHH_{15min}$ (HSE, 2005) limits have been largely ignored in fire toxicity, apart from in the work of the authors, but are the best data set for assessing multi-component toxicity with a legally agreed methodology, which is similar to the LC_{50} N-gas method in (Levin, 1996).

A summarised selection of the toxicity assessment limits discussed earlier are compared in Table 4-1. The data for LC$_{50}$ depends on which dataset is used and which animal exposure is used (Purser, 2010c). However, the data uncertainty is no more than a factor of 2 for most gases, but the ratio of the LC$_{50}$ to impairment of escape limits are not consistent by a factor of 8. For the LC$_{50}$ to COSHH$_{15}$ limits the ratios are again not consistent and vary by a factor close to 100. This means that the relative toxicity for LC$_{50}$ of the different gases is completely different when impairment of means of escape limits are compared. In applying the toxic concentrations in Table 4-1 to the complex mixtures of toxic gases from fires the combined toxicity will be different for LC$_{50}$ than for the three methods of assessing the impairment of escape, because there is no consistency in the relative toxicities. LC$_{50}$ will always place a greater relative emphasis on CO and COSHH$_{15}$ will always place a greater relative emphasis on acrolein. AEGL-2 is in agreement with this assessment of a much greater toxicity associated with acrolein than is given in LC$_{50}$. This means that the gas concentrations that control death are quite different from those that impair escape. The AEGL-2 escape impairment limits in Table 1 are in most cases similar to COSHH$_{15}$, but for benzene and HCl there are large differences.

Table 4-1: Toxicity assessment methods and their ratios (all concentrations are ppm).

Toxic gas	**15 min exposure limit COSHH**	**AEGL-2 10 min escape impairment**	**SFPE conc. impair escape**	**LC$_{50}$ 30 min**	**LC$_{50}$ /Impair**	**LC$_{50}$/ AEGL-2**	**LC$_{50}$/ COSHH$_{15}$**
CO	200	420		3,000		17	15
NO_2	5	20	70	350	5	17.5	70
HCN	10	17		135		8	13.5
C_6H_6	3	2000		10.000		5	3333
CH_2O	2	14	6	250	42	18	125
C_3H_5O	0.3	0.44	4	135	34	307	1000
CH_2O_2	5						
SO_2	5	0.75	24	500	20.8	667	100
HCl	5	100	200	3,700	18.5	370	740

Most current information on toxic gases in fires has been obtained from well-ventilated compartment fires that simulate room fires with an open door or window or are freely-ventilated fires such as in the cone calorimeter. These essentially test the fire propagating properties of the material at conditions that represent the start of a fire, where ambient temperatures are low and the fire entrained gases are air with 21 %

oxygen. These tests are suitable to rank material for fire safety purposes with tests under the same conditions (Purser, 2000). However, they do not represent the behaviour of these materials in real fires, especially in the later stages of fires. Hence, toxicity measurements made in these reference tests may not be valid for use in computer modelling of fires in compartments. In a compartment fire the oxygen is depleted as the fire temperature rises and in the later stages of fires the conditions are high temperature, low oxygen and rich mixtures. This is the area of fire development that was investigated in the present work.

Information on fire toxicity has also been obtained by simulating the fire equivalence ratio in a tube furnace (BS-7990, 2003). This has the problem that the fire temperature is separated from the fire equivalence ratio and this is not how real fires behave. In a closed room fire compartment with fire resistant walls, floor and ceiling, a closed fire door and closed double glazed windows, the air ventilation of the fire is very low and this was simulated in the present work. The present work follows the procedure in a tube furnace where the ventilation is imposed by using a forced fixed air mass flow which can be referred to in air changes per hour (ACH) ventilation terms. However, realistic fires are generated where the fire temperature and equivalence ratio are linked and not separated. The Purser furnace method overcomes one disadvantage of the cone calorimeter method in that free ventilation is replaced by a controlled ventilation and controlled fire equivalence ratio.

In real compartment fires temperature, ventilation and equivalence ratio are all interdependent, which is why the present procedure was developed to give a better link between fire temperature and oxygen in studies of material behavior in fires, as well as to burn more realistic larger fire loads than in the Purser furnace method. Its principles are similar to the Purser method but on a more practical scale. It imposes the fire ventilation which is fixed, as in the Purser method, but generates a high fire temperature by heat release from the fire load and not through external heat supply.

4.2 EXPERIMENTAL SET UP

A 1.6 m^3 enclosed fire compartment presented in details in section 3.1.1.1, was used. with similar dimensions to that used by (Bundy et al., 2007). The principle of air entry at floor level and fire products exiting near the ceiling level was first introduced (Gottuk, 1992a) and this has been used in this work. The principle of supplying the air ventilation at a fixed rate to the fire compartment was developed in (Andrews et al., 2007; Andrews et al., 2005b; Andrews et al., 2005a) and has also been used in studies of pool fires by (Utiskul et al., 2005). Although most compartment fires have an open door compartment (Chamberlain, 1996; Gross and Robertson, 1965; Tewarson, 1985) they are usually of full room height which controls the pressure difference that entrains air into the fire. In smaller compartments such as the present with a 1.5 m height natural ventilation would result in lower ventilation rates than real compartment fires and the forced ventilation technique overcomes this problem. In the fully developed fire stage of compartment fires the ventilation rate is normally relatively constant and fixed by the room height and the area of the open door (Chamberlain, 1996; Gross and Robertson, 1965; Tewarson, 1985) and hence the present procedures are not far away from real compartment fires.

A fixed air ventilation rate was set for each fire and 3–37 air changes per hour (ACH) were used. The bottom end of this range represents air starved fires and top end represents well ventilated fires with an open door. The air was fed into a plenum chamber under the compartment and from there into the fire compartment through four slots at the edge of the compartment. The fire gases flowed along the flat metal ceiling to exit the compartment through a small gap between the edge of the ceiling and the compartment walls. The fire products then flowed along the rear of the ceiling to exit through a 150 mm diameter short chimney discharge. Gas samples were taken from the short chimney and were the mean composition of the ceiling gases. The compartment had horizontal and vertical thermocouples arrays to determine the fire compartment mean ceiling temperature. The compartment had a high temperature glass door that was closed immediately after the methanol was ignited. The initial stages of the fire development could be photographed through the window, but this soon became covered in soot and an outer cover was closed over the window to prevent radiative heat loss.

Raw fire ceiling gases were sampled via 190 ºC heated sample lines and passed to a 190 ºC heated filter and pump and then to a heated FID for total hydrocarbon analysis. A heated chemiluminescence NOx analyser was used and after a 2 ºC water condenser the sample gas went to a NDIR analysers for CO and CO_2 and a paramagnetic analyser for oxygen. The oxygen analysis together with the air ventilation mass flow rate was used to determine the fire oxygen consumption and from this the HRR. The HRR was also determined by fire load mass loss measurements, as the crib was supported on a tray that rested on load cells in the air plenum chamber. The difference in the two HRR was large and this was due to the high combustion inefficiency. The gas analysis for CO_2, CO, HC and O_2 was used to determine the A/F by carbon balance, using the procedures of Chan and Zhu (Chan, 1996), together with the combustion inefficiency as the sum of the energy content of the CO and HC. The fire equivalence ratio was determined from the A/F by carbon balance using the stoichiometric A/F for the pine wood. The pine wood sticks were analysed for their HCO composition using an elemental analyzer, which gave the composition as 47.25 % C, 47.07 % O and 5.68 % H. This gave the chemical formula as $CH_{1.44}O_{0.75}$ where 1.44 is the H/C ratio and 0.75 is the O/C ratio. The stoichiometric A/F ratio for this composition is 5.34/1 and this was used in all the determinations of the fire equivalence ratio.

A heated TEMET GASMET CR-Series portable FTIR was used for acidic and irritant toxic gas analysis. This had a separate heated sample line, filter and pump and the FTIR sample cell was also heated at 190 ºC so that all analysis was on a hot wet basis and no acidic gases were lost by condensation. The FTIR was calibrated for over 50 species, including most of the toxic gases of interest in fire toxicity. The FTIR had a liquid nitrogen cooled detector and this gave at least 2 ppm resolution on all species. CO was calibrated to 10 % but other toxic species were calibrated to 500 ppm. The high level CO calibration was important in the present work where peak CO levels of 9 % were recorded. The parallel NDIR CO analyser was not designed to measure higher than 3 % CO and this instrument was off-scale for most of the results with ventilation levels of 11 ACH or above.

4.3 FIRE LOAD PINE WOOD CRIBS

The 4.6 kg pine wood cribs were identical for each fire, so that the only variable was the fire compartment ventilation rate. The cribs were three times the size of those that (Andrews et al., 2007; Andrews et al., 2005b; Andrews et al., 2005a) have previously investigated, and this was to bring the fire loads closer to reality. A feature of the work with smaller cribs was that the fires had mainly lean equivalence ratios and the rich mixtures that often occur with ventilation restricted fires as in (Chamberlain, 1996; Gross and Robertson, 1965; Tewarson, 1985) were not encountered. The calorific value of pine is 17 MJ/kg and this gives 78 MJ of energy in the 4.8 kg pine cribs. The fire loading referenced to the floor area and compartment volume was 58 MJ/m^2 and 3.6 kg/m^2 or 50 MJ/m^3 and 3.1 kg/m^3 respectively. These are very light fire loads compared with the practical range for a wood processing factory of 200–800 MJ/m^2 (Buchanan, 2001), although there are some practical fire load conditions as low as 40 MJ/m^2 (Buchanan, 2001), Other fire protection design guides quote low, medium and high fire loads (PD-7974-0, 2002). Typical minimum fire loads are 230 MJ/m^2 as applied for example to a hospital (PD-7974-0, 2002). The description of fire loads as a ratio to the floor area is not very realistic when the ceiling height of rooms can vary. The fire development is dependent on the air available and increases with the height of a room. However, a standard room is about 2.5m high so that fire loading in terms of floor area could simply be interpreted as a ratio to the compartment volume using this standard ceiling height. This gives 80–320 MJ/m^3 for wood processing factories (Buchanan, 2001) and 16 MJ/m^3 for the lightest fire loads (PD-7974-0, 2002). It is considered that the volume based fire loading used in the present work is representative of a lightly loaded fire. The results show much higher toxic levels than in our previous work (Andrews et al., 2007; Andrews et al., 2005b; Andrews et al., 2005a) with smaller cribs and this shows that fire loading is an important parameter in fire toxicity.

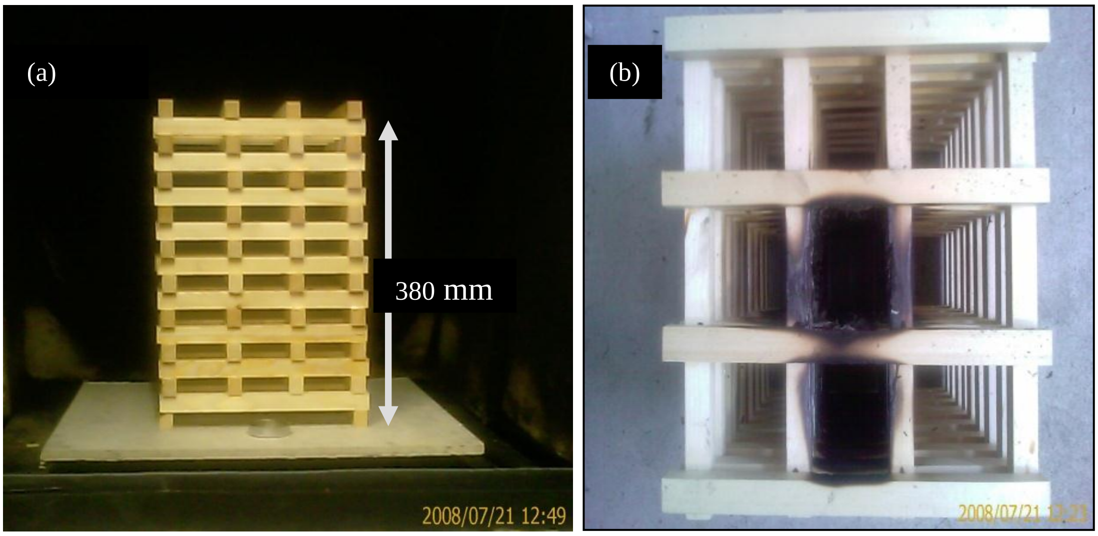


Figure 4-1: (a) Crib construction; (b) partially burned crib at 5 ACH.

The pine cribs were made of 74 sticks 300 mm long and 20 mm square cross section. The crib was made in layers of four sticks with the next layer at 90° to the previous one. The total height of the 19 layers was 380 mm and the gap between the sticks was 73 mm. The crib before burning is shown in Fig. 4-1a. The cribs were ignited by placing a small 50 mm diameter pool of 5 mm deep methanol in the centre of the crib beneath one of the pine sticks and the same position was used for each fire. The energy in the methanol was 0.4 % of the total crib heat release and hence was negligible in the fire heat release rate. Time zero in the experiments was when the compartment door was closed after placing the ignited methanol in place.

4.4 RESULTS

4.4.1 TYPICAL 4.8 KG PINE WOOD CRIB COMPARTMENT FIRE RESULTS FOR 11 ACH

The main features of the ventilation controlled compartment fires for the 4.8 kg pine wood cribs are shown in Fig. 4-2 for 11 ACH. There was good agreement with the carbon balance equivalence ratio results and the metered air and fuel consumption rates. The results in Fig. 4-2 show a rapid fire development with the ceiling temperature increasing as the oxygen level was depleted and the CO_2 increased. There were three phases in the fire: the initial growth phase, main flaming combustion phase and finally a char burn out phase or smoldering combustion phase, which extended well beyond the time shown in Fig. 4-2. At 2500 s 90 % of the initial mass had been burnt, but the remaining 10 % took a further 5000s to burn out completely. This smoldering combustion phase started soon after the 1500 s time when the temperature started to fall and the oxygen to increase sharply. There was also a reduction in the toxic CO and in the total unburned hydrocarbons at this point. The mean fire equivalence ratio was different in the three phases with initially lean combustion followed by very rich conditions throughout the main flaming period of the fire and then a return to lean combustion after 1500 s when smoldering combustion was the main fire mode. It will be shown later that the toxic emissions during the first flaming fire development lean burning phase were quite different from those in the smoldering combustion lean burning phase of the fire, so that equivalence ratio is not the sole governing factor in the toxic emissions.

A key feature in Fig. 4-2, which was present at all the ventilations, was that the oxygen was never near 0 % even though the overall equivalence ratio was rich. The reason for this, as shown in Fig. 4-2, was the very high CO and total unburned hydrocarbons that occurred during the rich burning phase. The CO and HC contribute to the combustion efficiency, which is discussed later. The presence of significant oxygen during the rich high temperature fire mode leads to significant acrolein formation in this phase of the fire, as detailed later, which was unexpected as this is normally associated with lean low temperature fires.

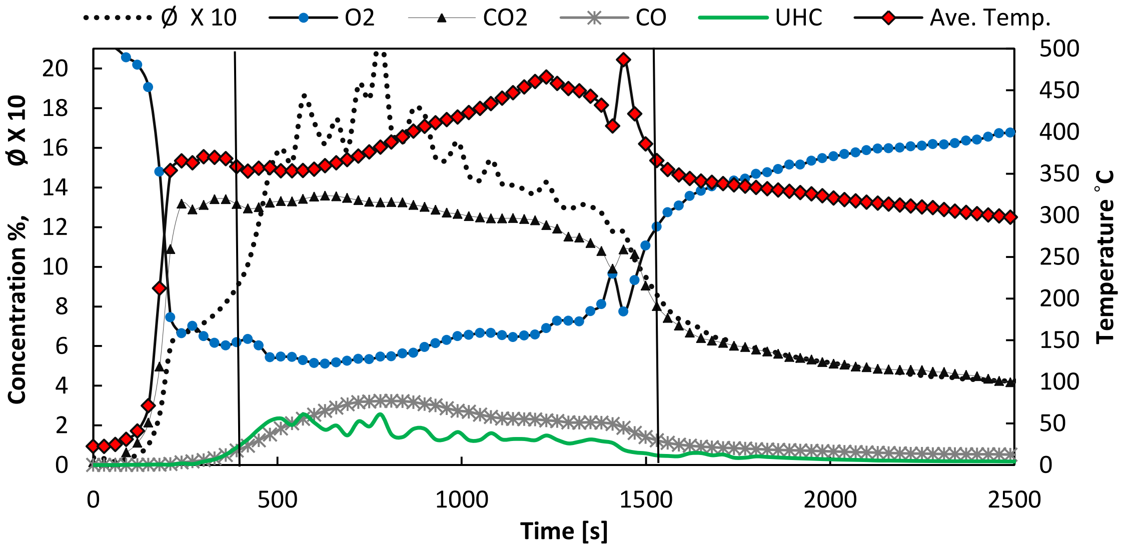


Figure 4-2: characteristics for 4.8 kg pine wood crib with 11ACH ventilation.

Similar results were obtained for each ventilation rate. The results show the influence of the ventilation rate on all the key fire parameters. For ventilation less than 11 ACH the crib was only partially burned, as shown in Fig. 2b for 5 ACH. The 5 ACH fire did burn sufficiently to record fire data for at least one hour, but only 17 % of the initial mass was burned and most of this in the first 20 min, as shown in Fig. 4-3. At 3 ACH the fire self extinguished very early in the fire. The crib did start to burn, but the lack of oxygen supply could not sustain the flame for more than 5 min. The results for this low ventilation have not been included in the graphs. In previous work (Andrews et al., 2007; Andrews et al., 2005b; Andrews et al., 2005a)with 1.5 kg pine wood cribs, ventilation rates as low as 1 ACH could sustain a crib fire burnt lean throughout the duration. It is considered that in the present work the heat losses to the higher wood sticks resulted in cooling the post flame gases to a level that was too low to ignite the pine sticks higher up the crib. In this work there were 19 vertical layers of pine sticks compared with 10 layers, of the same stick 20 mm square cross section, in the 1.5 kg crib fires.

4.4.2 COMPARTMENT WEIGHT LOSS AND RATE OF MASS CONSUMPTION

The pine crib mass loss and rate of mass loss are shown in Fig. 4 for the four ventilation rates of 5, 11, 21 and 37 ACH. Figure 4 shows that at 5 ACH there was only a partial burn and most of this was in the Phase 3 of smoldering char combustion after about 500

s. 11 ACH was the lowest ventilation at which all the crib was burned and increasing the ventilation simply increased the rate at which the crib burned and decreased the duration of the high heat release flaming combustion phase of the fire. If combustion is complete the mass burning rate should be a linear function of the air mass flow rate as the potential heat release is ~3 MJ/kg of air irrespective of the fire load. For a given fire material, increasing the air ventilation should increase the mass burn rate linearly with the ACH. Fig. 4b shows this is not the case as increasing ACH from 11 to 21 does not double the peak mass loss rate. The reason is that all the fuel is not burned due to the presence of richer than stoichiometric mixtures, as shown in the combustion efficiency results. During most of these fires, in the Phase 2 rich burning flaming mode the pine cribs are being gasified to CO and H_2 as well as unburned volatile hydrocarbons and soot. These release heat when they encounter air outside the ceiling hot gas discharge. In a real fire this is seen as external flames from windows or roofs.

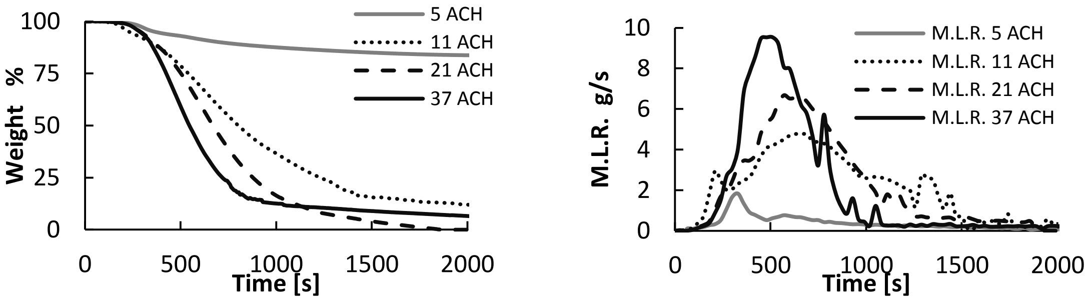


Figure 4-3: Pine wood crib: (a) mass loss; (b) rate of mass loss for 5, 11, 21, and 37 ACH ventilation.

4.4.3 COMPARTMENT AVERAGE CEILING TEMPERATURE

The mean ceiling temperature is shown for all the air ventilations as a function of time and equivalence ratio in Fig. 4-4. There was a rapid temperature rise in the initial first lean burning phase and the peak temperature in this phase was limited by the air ventilation. All the fires showed a subsequent fall in temperature, which for 11–37 ACH was due to rich lower temperature combustion. This was followed by the peak temperature which occurred as the fire moved to near stoichiometric burning at lower mass burning rates in the final stages of flaming combustion before the transition to smoldering combustion. In the initial lean phase, the fire was hotter than in the final lean phase due to flaming combustion in the first lean phase and smoldering combustion in the final lean phase. Most of the 5 ACH fire occurred as smoldering combustion.

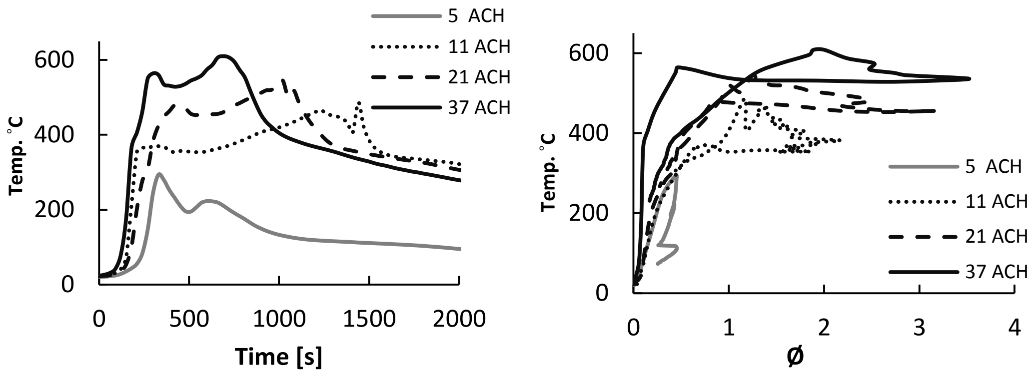


Figure 4-4: Compartment mean ceiling temperature as a function of: (a) time; (b) equivalence ratio.

4.4.4 COMPARTMENT OXYGEN AND OXYGEN BASED HEAT RELEASE RATE (HRR)

The variation of oxygen with time for all the fire ventilations is shown in Fig. 4-5a. The HRR in Fig. 4-5b has been derived by oxygen mass consumption. There was very poor agreement between the HRR based on the wood mass consumption (shown later) and that based on oxygen consumption. The reason was the very poor combustion efficiency that is reflected in the high CO and HC emissions in Fig 4. When the mass loss based HRR is corrected for the poor combustion efficiency there was much better agreement with the oxygen consumption based HRR. The peak HRR by oxygen consumption for 37 ACH was 50 KW compared with 170 kW by mass consumption. The low combustion efficiency and high CO and HC that accounted for the unreleased energy are shown in Fig. 4-3 and for all the ventilations in Fig. 4-6. The high CO was due to the rich fire equivalence ratio, which was >1 for 20 min duration in Fig. 4, during which 85 % of the original mass was burned. This was the flaming combustion mode of the fire and this was where the toxic gases were at their highest, as shown later.

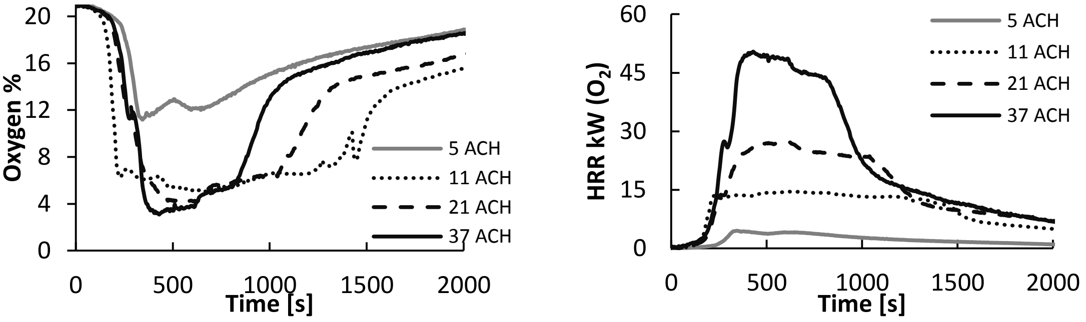


Figure 4-5: (a) Compartment oxygen (b) oxygen consumption based HRR as a function of time.

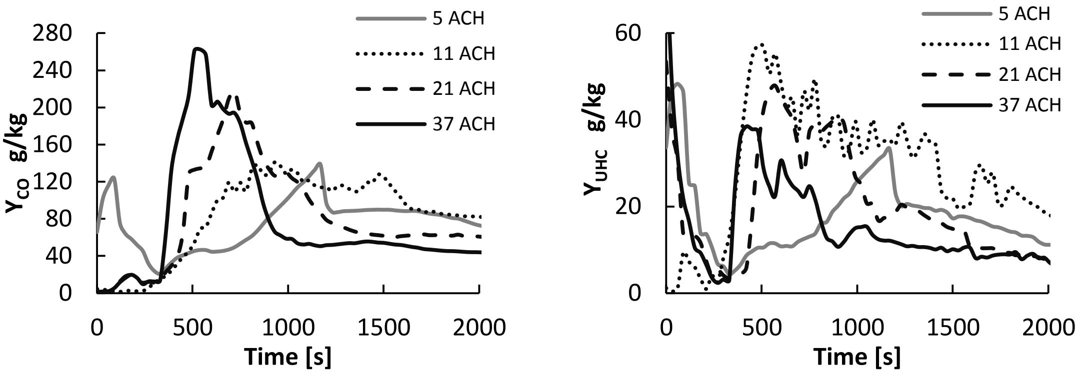


Figure 4-6: (a) Carbon monoxide and (b) total unburned hydrocarbons yields (g/kg) as a function of time.

4.4.5 CARBON MONOXIDE AND TOTAL UNBURNED HYDROCARBON YIELDS

The carbon monoxide and total unburned hydrocarbon concentrations were converted to mass yields as g/kg and are shown in Fig. 4-6. Eq. 2.16 was used to calculate the CO, UHC, and all the toxic species yields in this chapter. The MW weight of the exhaust was taken to that of air, which would be accurate to 1%. Figure 4-6 shows that CO yields are relatively low in the initial lean combustion phase, very high in the rich flaming combustion phase and relatively low in the final smoldering lean burning phase of the fires. The peak CO yield for 37 ACH was 250 g/kg which is much greater than the 4 g/kg for freely ventilated pine wood fires (Quintiere, 1998). Quintiere quotes a value for pine wood in under-ventilated rich combustion of 138 g/kg and he also shows data for the increase in CO yield with equivalence ratio. For wood with a peak rich equivalence ratio of 4 the yield was 50 times that for a freely ventilated fire (4 g/kg) and this would give a peak yield of 200 g/kg, which is close to the present results for 21 and 37 ACH, where the peak equivalence ratio was 3–3.5, as shown in Fig. 4-7. (Purser et al., 1994) for the steady state tube furnace reported yields of 170 g/kg for pine wood rich combustion at 450 ºC, in reasonable agreement with the present results. However, these laboratory methods do not show the strong dependence of CO yield on ventilation shown in Fig. 4-6. Higher ventilation creates richer mixtures, as shown in Fig. 8a. Ventilation also increases the temperature, as shown in Fig. 4-4 and this occurs for the same rich equivalence ratio as shown in Fig. 4-4b. In furnace tests with wood, Purser et al. (Purser et al., 1994) showed that an increase in furnace temperature from 350 to 400 ºC increased the CO yield by a factor of 2 for the same ventilation. Fig. 5b shows for the same equivalence ratio of 2 that the temperature increased from 350 ºC to 600 ºC as the ventilation increased from 11 to 37 ACH. The peak CO yield in Fig. 4-6a increased from 140 to 260 g/kg over the same temperature change. This is a significant influence of temperature, but much lower than that found in the furnace work of Purser for a 50 ºC temperature increase. The increase in CO with temperature is a reflection of the increase in equilibrium CO with higher flame temperatures.

4.4.6 COMBUSTION EFFICIENCY, FIRE EQUIVALENCE RATIO AND MASS LOSS BASED HRR

The hydrocarbon (methane equivalent) yields in Fig. 4-6b are very significant and show that a substantial part of the fire load was volatilised but not burned in these fires. The HC results show a high yield during the period when the wood is being heated by the methanol accelerant, when there is little mass combustion. These volatiles suddenly ignite and burn out to zero and this gas flame is followed by heat release from the main wood flaming combustion at 200 s from the ignition of the accelerant. This occurs at the same time as this flaming combustion is driving the overall equivalence ratio rich, as shown in Fig. 4-57b. The subsequent high yield of HC is due to the inefficient combustion in the rich combustion.

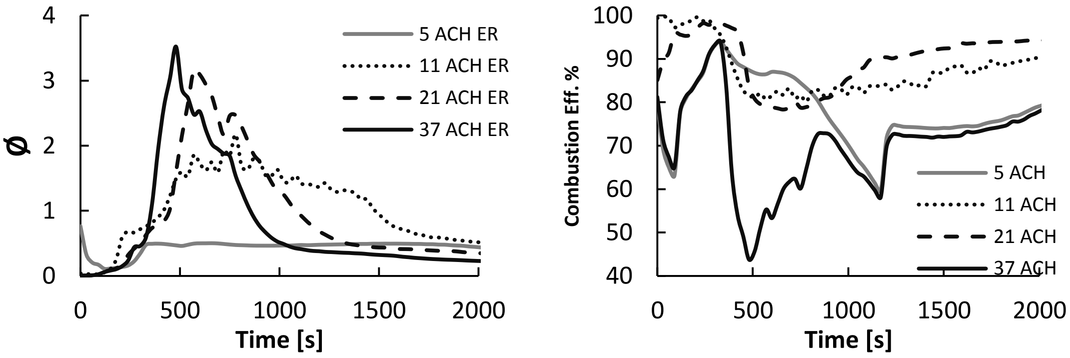


Figure 4-7: (a) Combustion efficiency and (b) fire equivalence ratio as a function of time.

The energy content of the hydrocarbons together with the energy content of the CO represent a combustion inefficiency. The combustion efficiency variations with time are shown in Fig. 8b. These efficiencies will be high, as no account has been taken of the hydrogen or the soot energy content. However, the results show very low combustion efficiencies for all ventilation rates, but there was a decrease in the combustion efficiency as the ventilation was increased and this was related to the richer mixtures that were generated, as shown in Fig. 9a. The consequence of the very low combustion efficiencies is that not all the energy content in the fire load is released in the compartment fire, the CO, unburned hydrocarbons, hydrogen and soot energy is released outside the compartment as the discharge gases combine with external air. Consequently, there is a major difference between oxygen consumption based heat release, Fig. 4-5b, and that based on the fire load mass loss rate in Fig. 4-8b. If the peak HRR for 37 ACH of 170 kW in Fig. 4-8b is combined with the combustion efficiency of 45 % in Fig. 8b and 9a, the oxygen consumption HRR should be 76 kW. However, Fig. 6b shows it was 50 kW, implying that the real combustion efficiency was 29 %, due to very high hydrogen and soot emissions. The soot emissions were measured in the experiments and were very high, but these measurements will be reported separately.

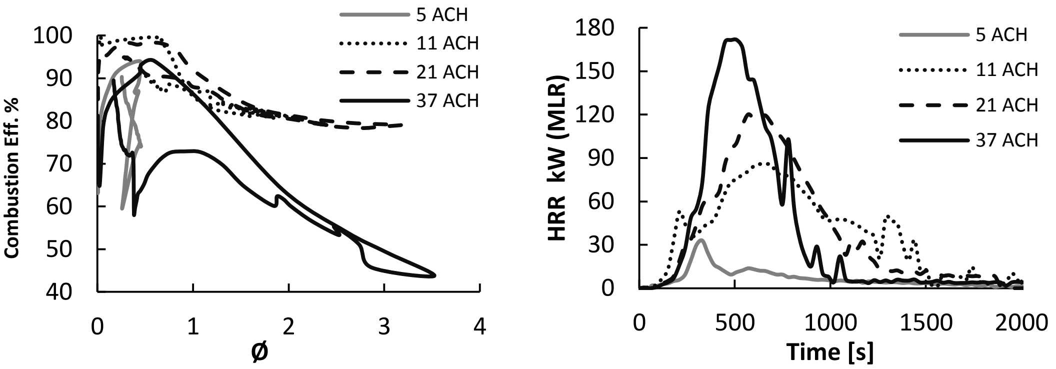


Figure 4-8: . (a) Combustion efficiency (CO + HC energy loss) as a function of time and (b) mass loss based HRR.

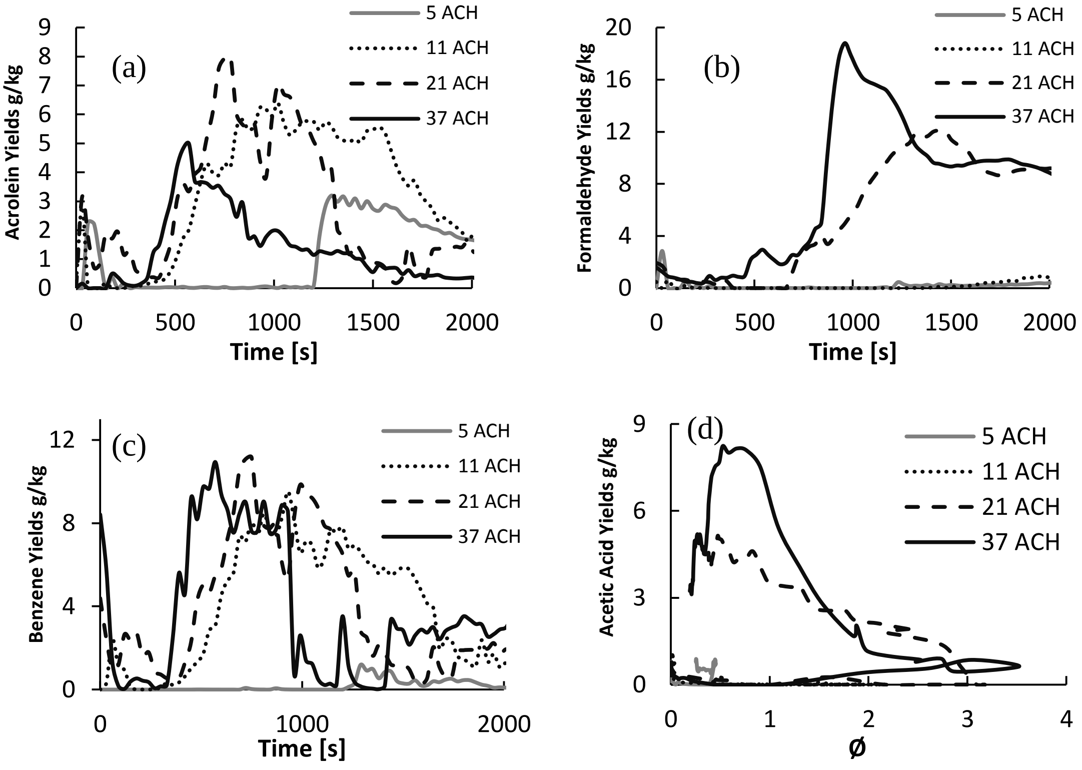


Figure 4-9: Yields of : (a) acrolein; (b) formaldehyde; (c), benzene; (d) acetic acid.

4.4.7 ACIDIC AND IRRITANT GAS YIELDS

The acidic and irritant toxic gases acrolein, formaldehyde, benzene and acetic acid were all determined by the FTIR and were significant toxic gases in addition to the CO that has been discussed above. Their yields as g/kg are presented as a function of time in Fig. 10. There were other toxics generated including formic acid, toluene, methyl benzene, HCN, NO_2 and SO_2, but space does not permit this data to be included.

Acrolein, formaldehyde and acetic acid were all formed in the rich flaming combustion phase of the fire. They are products of the partial oxidation of volatiles. The oxygen present during the rich combustion was essential for their formation. Benzene is part of the unburned hydrocarbons and its yield is about 20 % of the total hydrocarbon yield and indicates very strong production of benzene in pine wood fires.

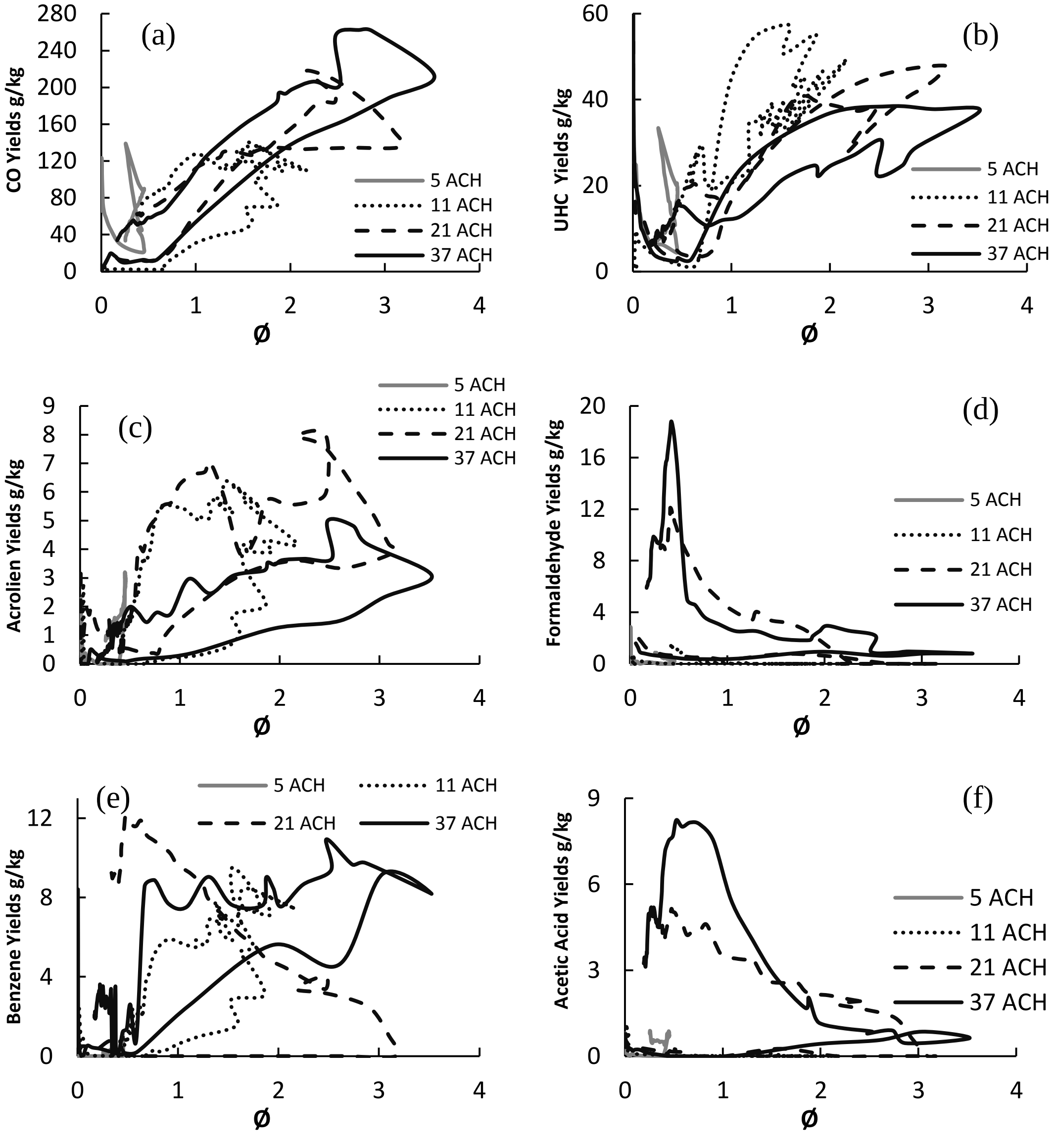


Figure 4-10: Toxic yields as a fucntion of the fire equivalence ratio.

4.4.8 TOXIC YIELDS AS A FUNCTION OF EQUIVALENCE RATIO

The yields of CO, HC, acrolein, formaldehyde, benzene and acetic acid are shown as a function of equivalence ratio in Fig. 4-10 a–f. For CO and total hydrocarbons the high yields are for the rich flaming combustion phase. The results show two yields for the same equivalence ratio, the lower yield was for the fire growth and the higher yield was for the later stages of the fire where temperatures were higher. In the lean region the initial lean fire growth was low in CO yield but the smoldering combustion char burn out phase had much higher CO yields for the same equivalence ratio. Formaldehyde and acetic acid yields were high in the lean smoldering combustion end phase of the fire, but acrolein yield was high across the range of equivalence ratios, apart from in the initial lean flaming part of the fire. Benzene was low in the initial lean part of the fire and high in the flaming rich fire and the smoldering fire phase.

4.4.9 PEAK FIRE PROPERTIES AS A FUNCTION OF VENTILATION RATE IN ACH

Figure 4-11 shows the peak value of various fire parameters as a function of the ventilation ratio in ACH. Peak fire temperature, mass loss rate and HRR all increase with increase of ACH. This is a reflection of the increased fire load combustion rate with the air mass flow increase, as a result of ~3 MJ of heat release for every kg of air supplied to a fire, provided there is sufficient oxygen to burn the fire load. This is a problem area as the minimum oxygen decreases as the ventilation increases as shown in Fig. 4-11. This leads to rich combustion in the fire with very poor combustion efficiency. This is shown as the peak CO and HC yields increase with ventilation in a linear relationship, as shown in Fig. 4-11.

Toxic yields also increase with ventilation as shown in Fig. 4-11 for acrolein and formaldehyde, but the trends are not linear. Acrolein has a decreased yield for the highest ventilation, as shown in Figs. 4-9a, 4-10c and 4-11. High temperatures and low oxygen are not conducive to acrolein formation and increasing the ventilation increases the temperature and reduces the oxygen, which results in lower acrolein formation for the 37 ACH ventilation. Formaldedyde is not generated significantly until the ventilation was above 11 ACH and then increased for 37 ACH. Formaldehyde was generated towards the end of the fires in the lean smoldering char combustion phase. This phase occurred much later in the fire and at lower temperatures.

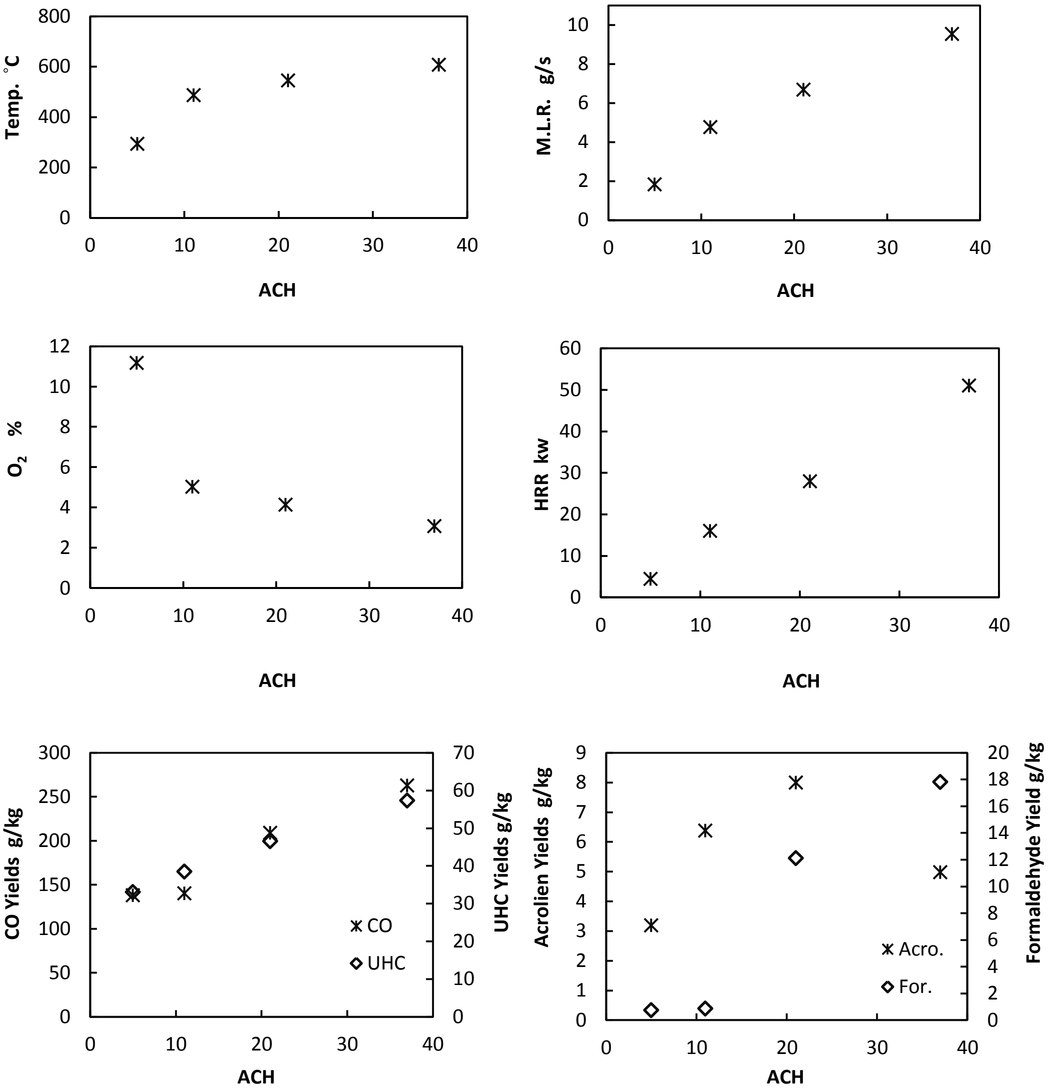
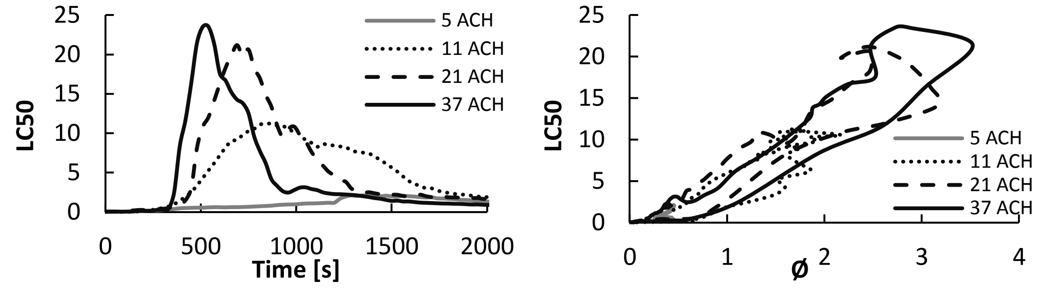


Figure 4-11: Peak fire properties as a function of the air ventilation of the fire in ACH.

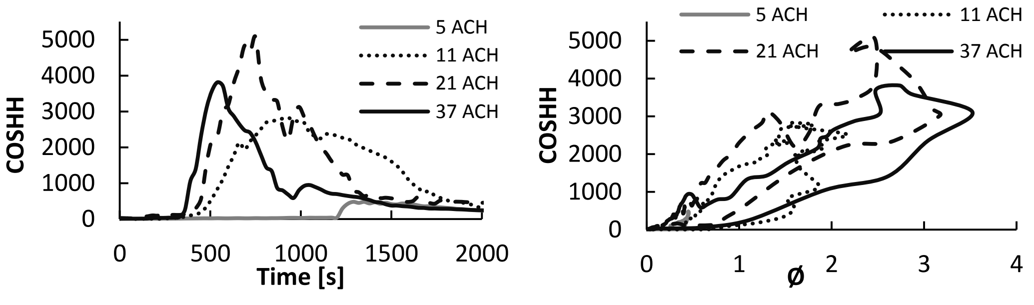
4.4.10 TOTAL TOXICITY N ON A LC$_{50}$ AND COSHH$_{15MIN}$ BASIS

All the toxic species measured by the FTIR were normalised to their LC$_{50}$ or COSHH$_{15min}$ toxic limits and these were summated to give the total toxicity ratio N. This is shown as a function of time and equivalence ratio in Fig. 4-12 for LC$_{50}$ toxicity and in Fig. 4-13 for COSHH$_{15nin}$ toxicity. The results show extremely high toxicity levels on both LC$_{50}$ and COSHH$_{15min}$ basis, as expected from the very high yields of the toxic species. When the two toxicity assessment methods are compared they give identical shaped curves as a function of time for the same ventilation, as can be seen by comparing Figs. 4-12a and 4-13a. For the lowest ventilation the overall toxicity was low, as the fire was lean throughout and most of the time was in the smoldering char burning mode. However, for 11 ACH and higher, toxic levels increased with ventilation and all three higher ventilation fires had LC$_{50}$ N values above 10 and COSHH$_{15\ min}$ above 2000. All the peak toxcities occurred in the flaming rich combustion phase of the fire as shown in Fig. 4-12b and 4-13b. The intial lean combustion had little toxicity, but the final smoldering lean combustion had relative high toxicity for a long period with LC$_{50}$ values between 1 and 5 and COSHH$_{15min}$ values between 10 and 1000.



(a) (b)

Figure 4-12: Normalised total toxicity N as a function of: (a) time; (b) equivalence ratio for 5–37 ACH..

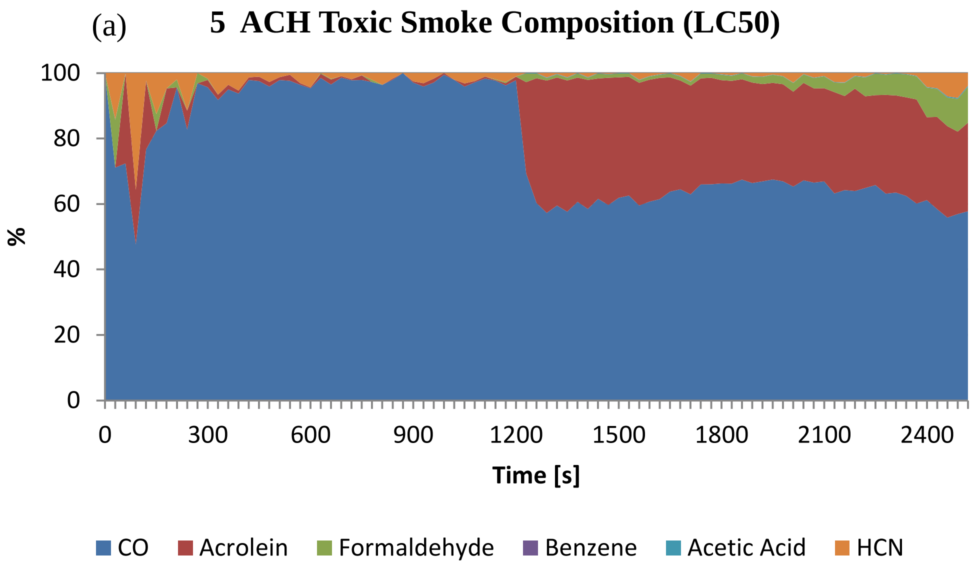


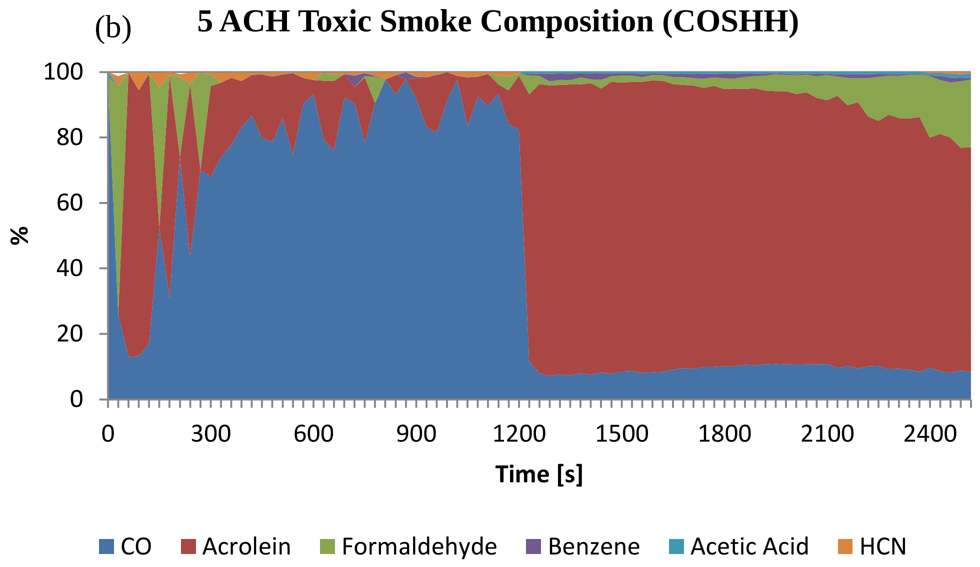
(a) (b)

Figure 4-13: Total normalised COSHH15min toxicity as a function of: (a) time; (b) equivalence ratio.

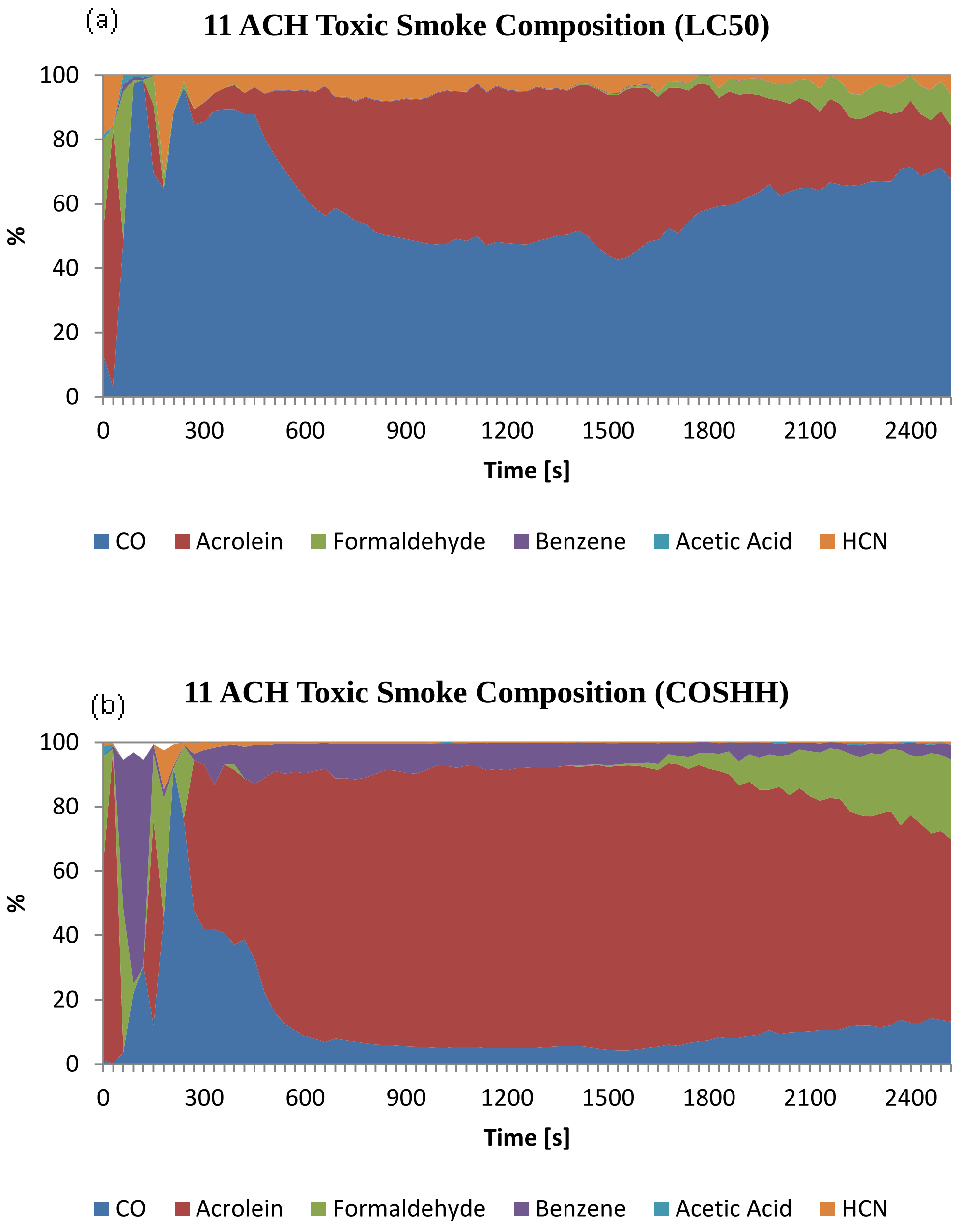
Smoke leaking from such fires (around door areas for example) would be extremely toxic and would require dilution by a factor of at least 1000 before it did not impair escape or by a factor of about 30 to make the risk of death unlikely. The species with greatest contribution to the overall toxicity are shown in Fig. 4-14 to 4-18. All fires were simlar and showed CO, acrolein, formaldehyde and benzene as the key toxic species on both LC_{50} and $COSHH_{15min}$ basis. The main difference was that CO was more important for the LC_{50} assessment, whereas acrolein was more important on a $COSHH_{15min}$ basis. Acrolein and formaldehyde were important species for both methods of assessment. Formaldehyde was more important in the last phase of smoldering char combustion and acrolein was very important in the flaming combustion phase of the fire.

(a)



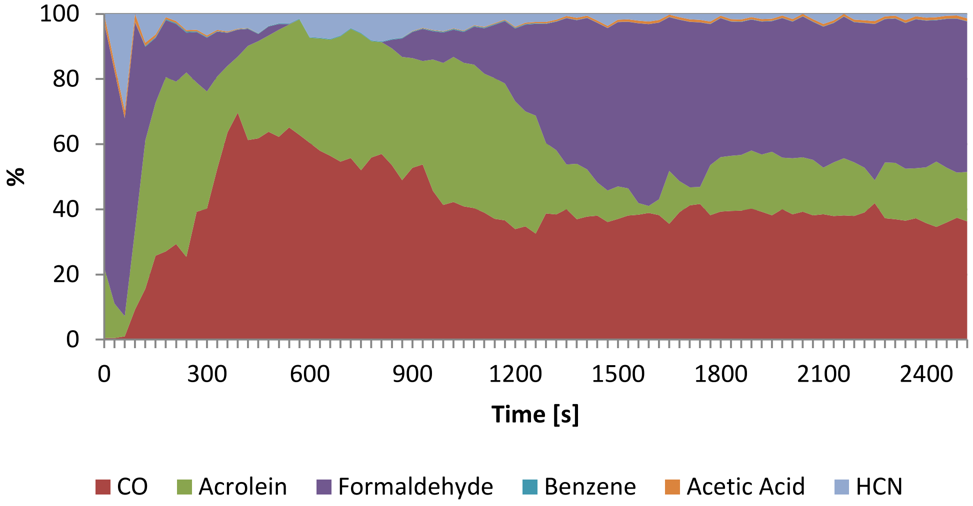


4-14: Contribution of the major toxic species to the overall toxicity at 5 ACH for: (a) LC50; (b) COSHH15min.



4-15: Contribution of the major toxic species to the overall toxicity at 11 ACH for (a) LC50; (b) COSHH15min.

(a) 21 ACH Toxic Smoke Composition (LC50)



(b) 21 ACH Toxic Smoke Composition (COSHH)

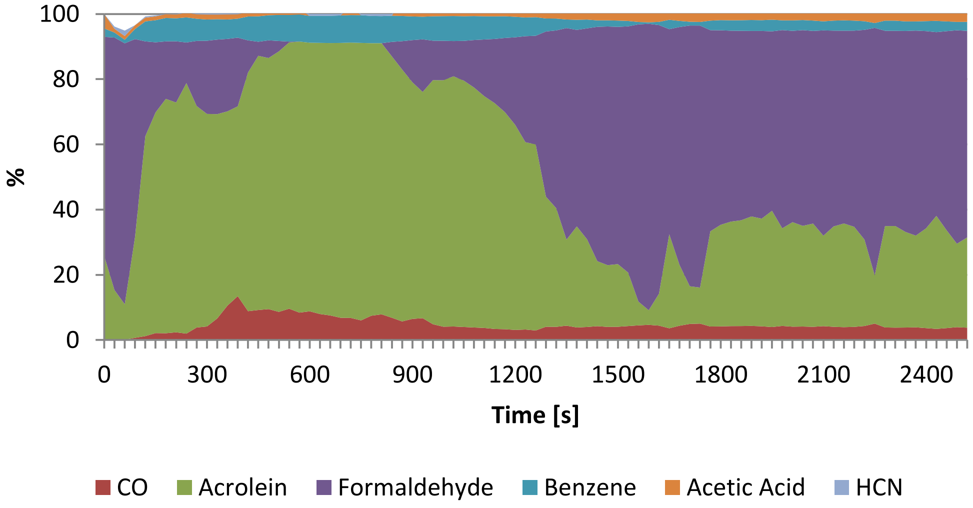
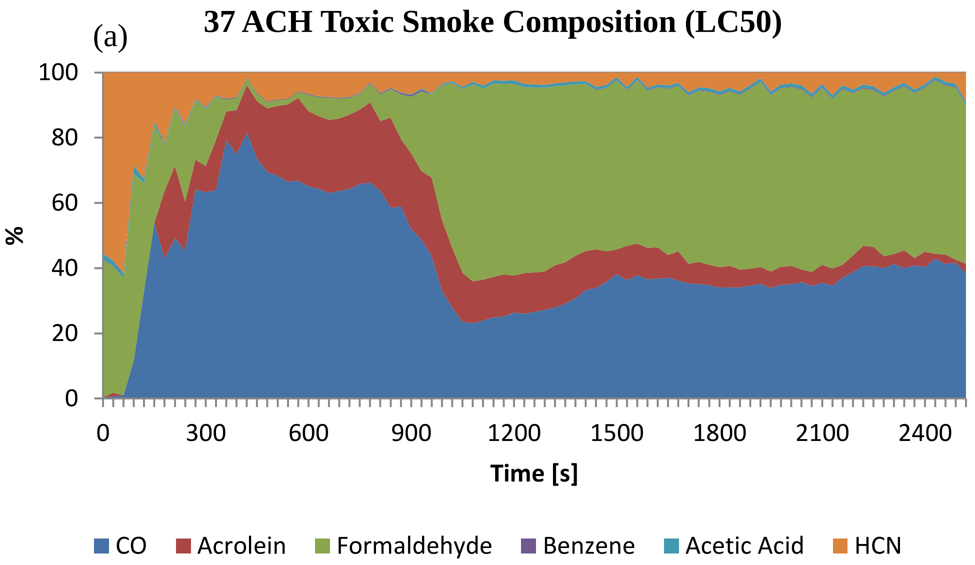


Figure 4-16: Contribution of the major toxic species to the overall toxicity at 21 ACH for: (a) LC50; (b) COSHH15min.



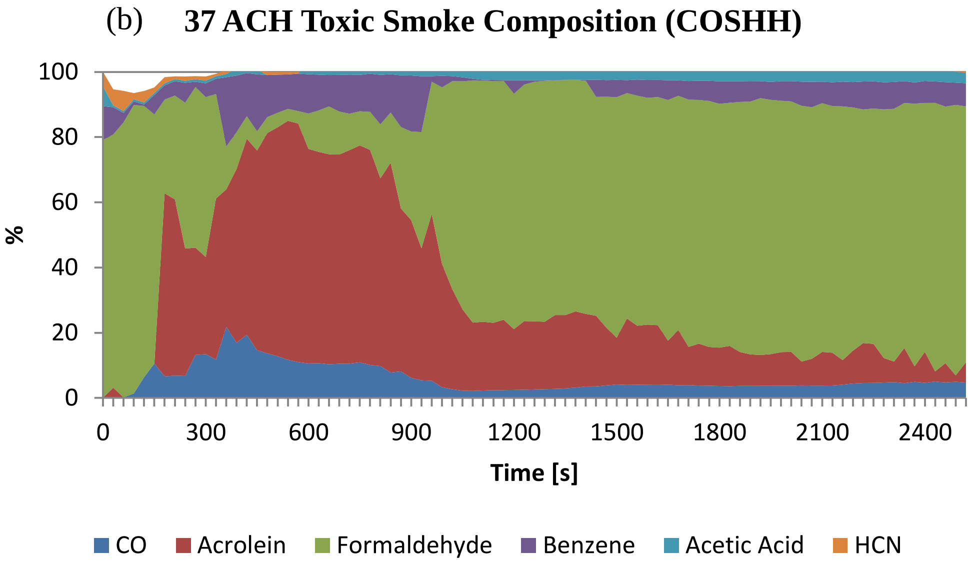


Figure 4-17: Contribution of the major toxic species to the overall toxicity at 21 ACH for: (a) LC50; (b) COSHH15min.

4.5 CONCLUSIONS

Lightly loaded wood crib fires in a ventilation controlled compartment fire did not develop at 3 ACH and only partially burned at 5 ACH. For complete combustion of the fire load 11 ACH was required.

For 11–37 ACH the peak fire temperature, HRR and mass burn rate all increased linearly with ACH. All fires with 11 ACH or greater rapidly generated rich combustion with peak equivalence ratios of 3. This phase had the highest temperature, greatest toxic yields and lowest combustion efficiencies.

As the ventilation went higher, this meant higher temperatures, and higher burning rate. The results from these conditions were the most toxic. However, interestingly, the irritant products seem to slightly decrease in the same conditions.

Irritation levels reached 3000 to 4000 thousands the proposed safe limits, this indicate highlights the relative importance of the irritant species detected in relation to human safety, and suggests more work need to be done to fully understand the interaction between the irritants.

Toxic gas yields for CO were up to 250 g/kg and there were very high acrolein yields and significant yields of formaldehyde and benzene. Peak LC_{50} N values were >10 for long periods in the fires.

In the self extinguished 5 ACH test, CO formed a major component of the toxic effluent both in terms of lethality and irritation. In the 11 ACH test, CO was still a major component of the lethal concentration, however it was displaced to second place by acrolein in terms of irritation. In the 21 ACH test, CO is a minor component of the irrition measure, however it still forms about half of the lethal dose. Acrolein and formaldehyde dominate the irritation scale, with formaldehyde apparently forming during the later stages of a fire. In the test with the highest intensity, 37 ACH, CO was not a major factor in terms of irritation, however, it still formed slightly more than half of the lethal dose during the flaming periods of the test.

5. CHAPTER 5:

WOOD CRIBS IN FURNACE

This chapter is based on two publications:

Aljumaiah, O., G. E. Andrews, A. Abdullahi, B. Mustafa and H. N. Phylaktou,(*2010a)*, Wood Crib Fires under High Temperature Low Oxygen Conditions, In *Proceedings of the Sixth International Seminar on Fire and Explosion Hazards, Leeds,* edited by D. Bradley, G. Makhviladze and V. Molkov, 2011, Research Publishing Services, ISBN: 978-981-08-7724-8, DOI: 10.3850/978-981-08-7724-8_15-05

Aljumaiah, O., J. Jordan, G. E. Andrews and H. N. Phylaktou,(*2008)*, The Development of a Technique for the Combustion of Wood in a High Temperature Low Oxygen Compartment, In *Proceedings of the Saudi International Innovation Confrence, Leeds, U.K.,* ISBN: 978-0-9559241-2-5.

ABSTRACT

Pine wood crib fires were investigated in a compartment fire under post-flashover conditions using a natural gas (NG) burner to rapidly generate 500^{o}C furnace temperature and oxygen levels of 12%. The subsequent fire temperatures were 600-700^{o}C, with oxygen levels below 5%. These conditions reproduce the circumstances in fires when fire gases suddenly encounter wood that has not contributed to the heat release that gave rise to the flashover conditions. Two pine crib fires were investigated, one with three times the fire load of the first and this resulted in rich overall combustion compared with lean overall combustion at the lower fire load. The combustion efficiency was high and the yield of toxic products was low for the low fire load lean combustion case. However, for the high fire load with rich combustion the wood was mainly gasified and the combustion efficiency was very low. Extreme fire toxicity conditions were generated in this post-flashover rich combustion case, as well as the circumstances for backdraft explosions.

5.1 INTRODUCTION

(Purser, 2002) has classified fires in terms of their characteristics of ventilation and oxygen levels during burning. This work is concerned with his fire classification 3b for post flashover fires in large compartments where the fire temperature is >700^{o}C and the hot gases are 500-1000^{o}C and combustion occurs with initial oxygen levels <15% and final oxygen levels 0-12%. Pine wood cribs burning after flashover in a compartment fire were investigated using a natural gas (NG) burner to rapidly generate 500^{o}C furnace temperature and oxygen levels of 12%. Flashover normally occurs at about 600^{o}C hot layer temperature in compartment fires with restricted ventilation. The temperatures in the present work were in the 600-700^{o}C range with oxygen levels below 5% and hence the post flashover conditions were generated.

Most fire tests for toxicity and heat release rate are based on freely ventilated fires such as the cone calorimeter or the corner fire test (Ostman, 2006). These essentially test the fire propagating properties of the material at conditions that represent the start of a fire, where ambient temperatures are low and the fire entrained gases are air with 21% oxygen. These tests are suitable to rank materials for fire safety purposes with tests under the same conditions (Ostman, 2006). However, they do not represent the behaviour of these materials in real fires, especially in the later stages of fire development. Hence, toxicity measurements made in these reference tests may not be valid for use in computer modelling of fires in compartments. In a compartment fire the oxygen is depleted as the fire temperature rises and can result in post flahover conditions of high temperature and low oxygen. This is the phase of fire development that was investigated in the present work.

The Purser test furnace approach (BS-7990, 2003) for fire toxicity studies aims to reproduce the later stages of compartment fires in terms of the fire temperature. However, the fire temperature is created using electrical heat and this burns the fire load at high temperature with air delivered to the fire with 21% oxygen. The fire equivalence ratio is changed by the rate of feed of the fire load at fixed air supply. The Purser furnace technique produces a fire where the fire equivalence ratio is decoupled from the fire temperature and the ventilation rate. In the cone calorimeter test the test specimens are burnt under conditions of the later stages of a fire as the electrically generated radiant heat represents the effect of a surrounding fire radiation on the burning of the test specimen. However, there is plentiful air supply with 21% oxygen and this does not normally occur in developed compartment fires. The Purser furnace method (BS-7990, 2003) overcomes one disadvantage of the cone calorimeter method in that free ventilation is replaced by controlled ventilation and controlled fire equivalence ratio.

In real compartment fires temperature, ventilation and equivalence ratio are all interdependent. The present procedure was developed to give a better link between fire temperature and oxygen in studies of material behaviour in fires, as well as to burn larger (more realistic) fire loads than in the Purser furnace method. The principles are similar to the Purser method but on a more practical scale. It imposes the fire ventilation which is fixed, as in the Purser method, but generates a high fire temperature by gas flame combustion so that the self-induced oxygen depletion that accompanies high fire temperatures is reproduced.

The general situation in post flashover oxygen deprived fires is well known, with the generation of high levels of CO, unburnt hydrocarbons and other dangerous species, which contribute to the risk of backdraft if a door is opened to a room fire under these conditions. However, very little quantitative data exists from measurements in compartment fires under these conditions and this work was aimed at providing quantitative data that could be used to validate computer models of this type of fire.

5.1.1 FLAMMABILITY IN HIGH TEMPERATURES

Fuel properties such as the lower oxygen concentration that are needed for flame propagation and ignition can be significantly different under high temperature conditions than for ambient air as the oxidant. Most zone and CFD models assume flame extinction at oxygen levels corresponding to tests at ambient temperature in freely ventilated fires. The lower oxygen concentration for flame extinction decreases as the fire temperature increases in a compartment fire. This difference must be addressed in fire models or flame extinction and unburned hydrocarbon and CO emissions will be predicted at conditions where the flame will not extinguish in reality.

(Beyler, 2002) suggested the following equation for the limit oxygen level as a function of the fire temperature.

$$Yo_2 = \frac{\overline{C_p}(T_f - T_m)}{\Delta H / r_{O_2}} \tag{5.11}$$

where, YO_2 is the oxygen mass fraction,

C_p is the specific heat with an average of 1.1 kJ/kg /K ,

T_f is the critical flame temperature of 1425 ^{O}C, and

T_m is the ambient temperature and $\Delta H/rO_2$ is the specific oxygen energy release of 13100 KJ/kg fuel.

This is the approach used in the FDS fire CFD code (McGrattan et al., 2008b). The oxygen concentration as a function of fire temperature is shown in Fig. 1a. The critical temperature of 1425 ^{O}C is rather high and if lean limit critical flame temperatures are used then 1500 K (Ali and Andrews, 1987) is more appropriate and 1125 ^{O}C (Ali and Andrews, 1987) would correspond better to modern lean flammability measurement methods. The critical oxygen level as a function of temperature is shown on this basis in Fig. 5-1. There is a very significant difference in the critical oxygen level between the two approaches and the use of Eq. 5.1 and a 1425 ^{O}C limit temperature in FDS could underestimate the flammable burning range of volatiles released from fire loads.

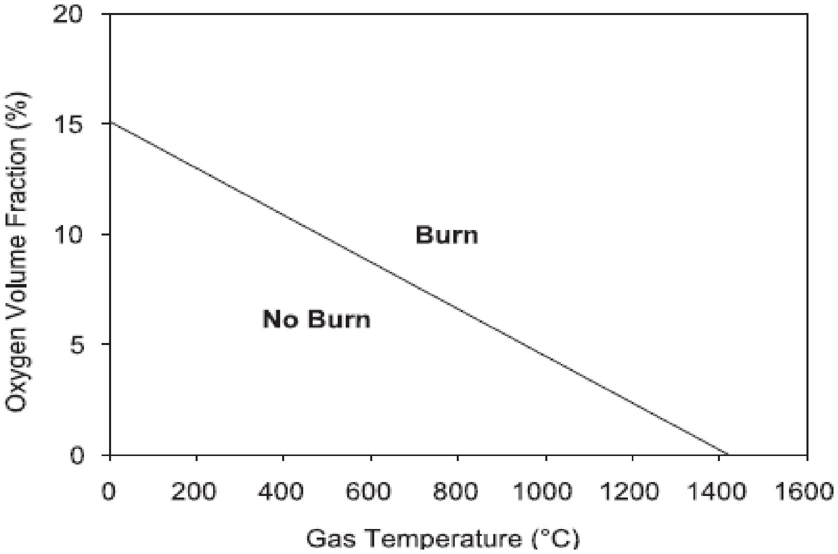


Figure 5-1: FDS Burn or No Burn zones in the flame extension model adapted from (McGrattan et al., 2008b).

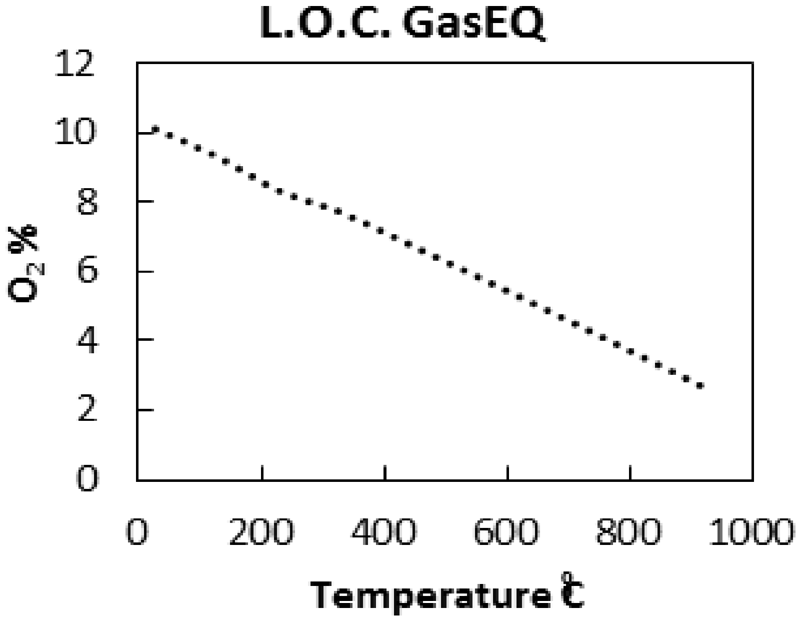


Figure 5-2: limits of flame temperature prediction of the influence of fire temperature on limiting oxygen for a critical temperature 1225 ^{O}C.

The above critical temperature considerations are for hydrocarbon flames, which are produced by pyrolysis in fires. However, for enclosed fires with rich mixtures, gasification of wood occurs, which produces CO and hydrogen together with hydrocarbons. These conditions occurred in the present work with the higher fire load. Flaming combustion is then controlled by the flammability of hydrogen and CO mixtures. This was observed in the present work with the complete absence of the yellow soot laden hydrocarbon flames. Hydrogen has a critical oxygen level of 5% at ambient air conditions and a critical lean flammability temperature of about 425 ^{O}C, which would result in a zero oxygen critical condition for fire temperatures higher than this for globally rich combustion. None of these considerations of rich combustion under post-flashover conditions is included in current fire CFD codes such as FDS.

5.2 THE DEVELOPMENT OF A TECHNIQUE HIGH TEMPERATURE LOW OXYGEN ENVIRONMENT

5.2.1 EQUIPMENTS

The tests were carried out in a 1.6m^3 ceramic lined furnace that was heated by a natural gas burner, which had a very wide flame stability range and could generate any desired furnace temperature. The furnace was fitted with a single burner port of 150mm diameter that was located about 300mm above the floor and 300mm from the corner. This burner location was chosen to avoid direct burner impact on the fire load which was placed in the centre of the furnace. The furnace was 1.3 m high, 1 m wide, and 1.2 deep fitted with a 150 mm exhaust port at the top. The furnace was designed as an indicative fire test furnace that used the burner to follow the various standard fire temperature-time test scenarios. By limiting the burner air flow and modulating the burner natural gas flow any furnace temperature could be achieved.

A sample of the exhaust was extracted from the furnace exit flue and transported to a gas analysis system via 190^{o}C heated sample lines, heated pump and more heated lines to the gas analysis instruments. The gas analyser system was manufactured by Signal Instruments and consisted of a Flame ionisation detector, Chemiluminescence Analyser, Infra-red Spectrometer, and Paramagnetic Spectrometer. To record the unburned hydrocarbons, NOx, CO, CO_2, and O_2 levels in the exhaust. The furnace was also fitted with 20 thermocouples spread over the furnace volume. These were all averaged to provide the mean furnace temperature that is reported in this work.

The fire load investigated was a pine wood crib consisting of 50 sticks. Each stick was 30 x 2 x 2 cm. and each crib weighed approximately 3 kg and was centered in the furnace compartment. These cribs have been used in previous compartment fires by Andrews et al [4,5] using a different 1.5 m^3 enclosed fire test facility that was ventilated by a forced air flow that could achieve 1 – 40 air changes per hour in the enclosed fire space. The use of the same crib and furnace size in the present work was to enable comparison of the wooden crib fires for the two situations.

A similar crib was made for each fire test at the different temperatures and these were all nominally identical. The pine wood samples were supported on 20cm bricks and were centered in a 40cm x 40cm steel tray. The initial work for the first three tests was carried out with the cribs supported on a wire mesh so that furnace gases could flow through the crib. They were also ignited with 100g of kerosene, placed in the furnace and then the furnace was closed up and the burner rapidly fired. This was the ignition procedure used on the enclosed fire rig without a burner, as discussed above. However, it was noticed that as soon as the burner was lit the kerosene pool fire went out, presumably through lack of oxygen. It was decided in a repeat test at 400K to not use any kerosene accelerant and to place the fire load on a solid tray, as used in the other enclosed fire rig. It will be shown that there was little difference in the results and hence this simpler method of fire tests is recommended for future work. Essentially the present work shows that the wooden crib ignites by a process of auto-ignition and an initial accelerant is not necessary.

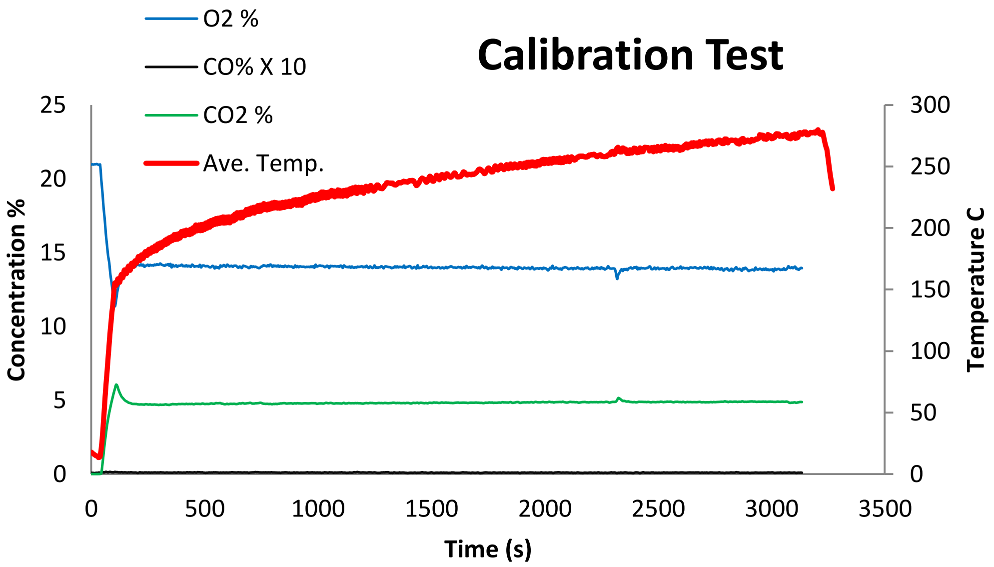
The methane and air flows were calibrated to achieve the temperature and oxygen profiles desired. The initial 3 tests were carried out at a relatively low air flow rate to the burner, which was set to achieve similar compartment ventilation rates as in the earlier work on a conventional fire enclosure with no burner. Temperatures of up to 500^{o}C were achieved but with very low associated oxygen, due to the high heat losses to the walls and the consequent use of relatively rich burner conditions. Higher temperatures could not be achieved without the oxygen being reduced to zero. This was not practical as the wood needs oxygen in the surrounding gases if it is to ignite. Consequently it was decided that the furnace test conditions should be those used to achieve the standard fire test curve, which involved the use of a much higher air flow to the burner. The temperature rise in the furnace was also much faster. The greater heat input at this condition, with the same heat flux to the walls, resulted in higher furnace temperatures and associated higher oxygen levels. The furnace could then achieve temperatures of 500^{o}C or higher with adequate oxygen for the wooden crib to undergo auto-ignition.

The initial conditions used in the tests, where 80l/m of methane and 1000 l/m of air which produced an average temperature of 300^{o}C and Oxygen level of 14 %. 100l/m of methane and 1000l/m of air produced an average temperature of 400^{o}C and an Oxygen level of 11.8 %. 135 l/m and 1250 l/m of air to achieve an average temperature of 500^{o}C and Oxygen level of 8.5%. Furthermore, 110l/m of methane and 1000 l/m of air produced a temperature of 400 C and 8.5% Oxygen. The Final Test was carried out at flow condition that followed the standard temperature curve.

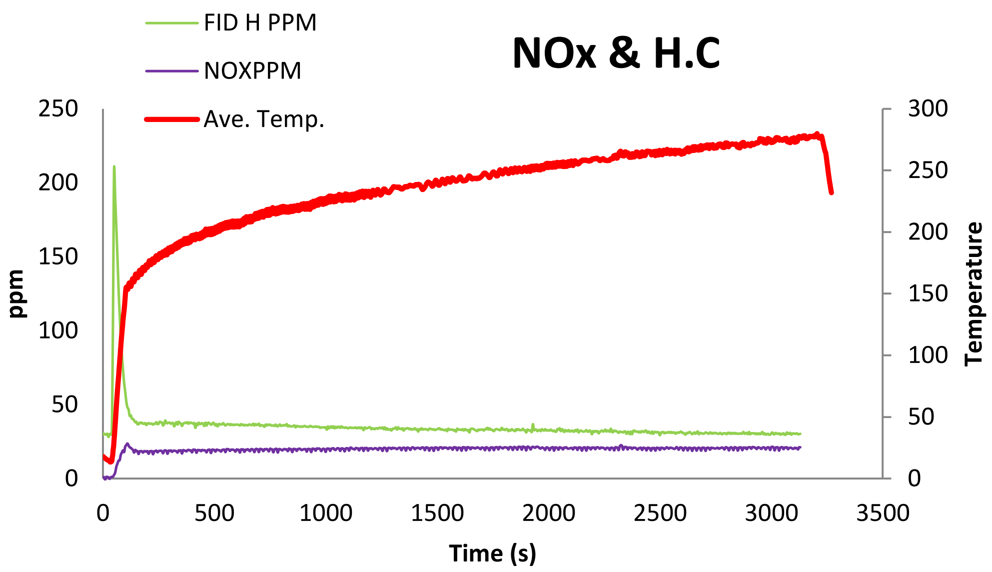
5.2.2 PRIMARILY TESTING AND DEVELOPMENT

Calibration test

A series of calibration Tests were performed to examine the oxygen consumption and temperature rise at different flow rates of methane and air. The first calibration, shown in Fig. 5-3 was at 80 l/m of methane and 1000 l/m of air. As shown in the graphs 3 and 4 below, this amount of fuel led to about 280 C and an Oxygen level of 14 % in the exhaust. The results of this calibration showed the that burner conditions were rapidly stabilized with no change in oxygen, CO_2, CO, HC and NOx emissions with time after the 100s of burner operation. These are the reference conditions and changes of these parameters with the wooden crib present will represent heat release and oxygen consumption by the wood. The temperature was not constant and this was because of the thermal mass of the furnace walls, which extracted heat from the flame. As the walls heated up less heat was extracted and hence the furnace temperature increased. The chemical energy in terms of fuel flow into the furnace was constant, but the heat transferred to the walls was the variable that resulted in the variable furnace temperature with time. In the wooden crib tests the initial temperature was taken as that when the wood first showed oxygen consumption.



5-3: Initial furnace calibration main gases and average temperature.



5-4: Initial furnace calibration NO_x, UHC and average temperature.

Test 1:

This test was started with 100 grams of kerosene in attempt to ignite the crib from the start. The kerosene flame self-extinguished due to the limited amount of kerosene and the limited oxygen level. The gas composition results are shown in Fig. 5-5 and these show that after 1500 seconds a slow oxidation phase started shown by the slow decrease in the Oxygen levels in, and the slow rise in the Carbon monoxide and Carbon dioxide levels in the exhaust. At 2040 seconds a very sudden rise in the compartment temperature occurred associated with a huge drop in the Oxygen levels in the exhaust. Also CO and CO_2 increased, which indicated that fast oxidation flaming combustion had started. This period of intense combustions lasted for about 500 seconds before the oxygen levels and the CO and CO_2 levels start recovering to their initial levels. Also, the average temperature curve started to follow its initial pattern. However, the Oxygen levels do not reach the initial condition maintained by the burner. This indicates another phase of combustion with slow heat release after the main flaming combustion. This is the smouldering combustion of the wood.

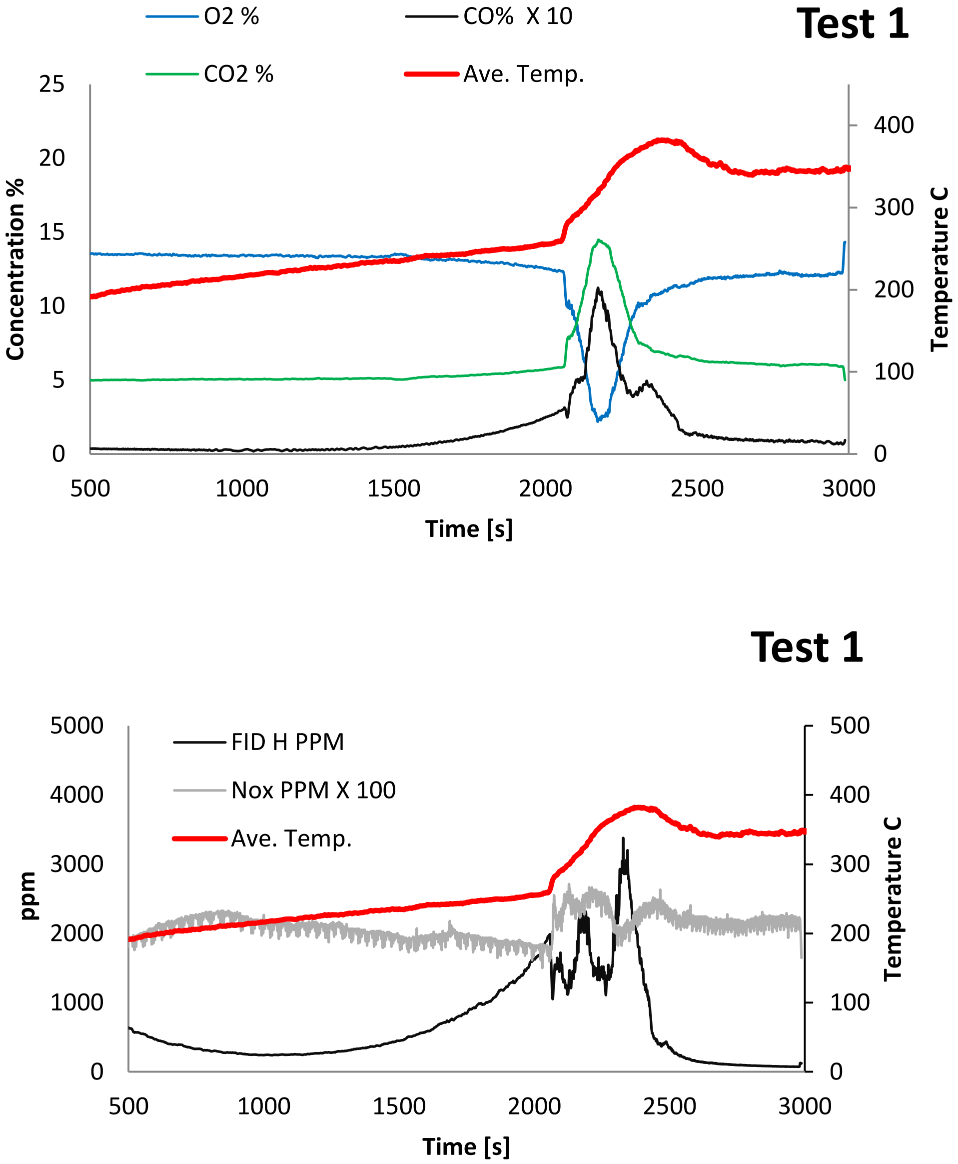
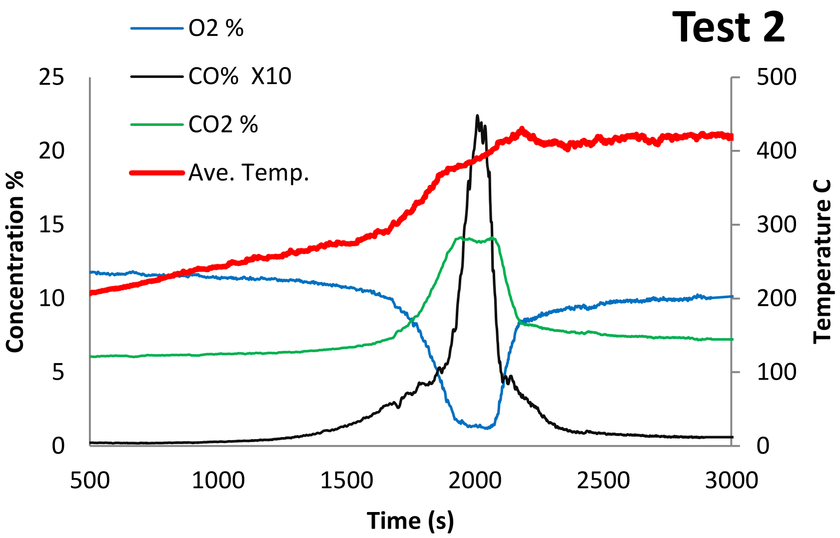


Figure 5-5: Combustion of wood at the Test 1 furnace calibration conditions in Fig. 5-3.

These results show that the key features of the crib fire was a long delay period of 2100s during which the temperature of the furnace increased from 200 to 270°C and the oxygen decreased from 14% to 13%. It may be concluded that the autoignition time of wood at these test conditions with 270°C and 13% oxygen was 2100s (33 mins). Air starved fires can give rise to these low fire temperatures that lead to long fire development times. The autoignition temperature rise was proceeded by an increase in CO and HC. However, at the point of ignition the CO was 2% and the HC 0.2%, due to thermal pyrolysis of the wood. However, these CO and HC levels are below the flammable range and hence ignition did not occur through autoignition of the evolved gases but by autoignition of the wood. This is further confirmed by the NOx emissions, which showed only a small rise after the wood ignited. This does indicates that the main event was not flaming combustion in the conventional sense, as this would give rise to significant NOx generation. Once the wood ignited there was a fast burning phase which came to an abrupt end, shown by the decrease in fire temperature and associated sudden decrease in HC and CO. However, the fire was not extinguished as the oxygen level was below that from the gas burner in Fig. 5-3 and the CO was not zero but the HC were very low Also the fire temperature continued to be well above that due to the burner alone. This is indicative of smouldering combustion, which would continue beyond the recorded time in Fig. 5-5. The next day there was no wood left unburnt in the furnace.

Test 2:

Test 2 was carried out at similar conditions to test 1, but the burner methane flow was raised from 80 to 100 l/m to achieve a higher temperature and lower Oxygen levels. The Oxygen level was stable around 11.8 % and the temperature reached 400 ^{o}C in the calibration tests. However, in the fire tests the wood ignited at 300^{o}C when the oxygen level was 10%, as shown in Fig.5-6. The results show the slow oxidization phase started at 1250 seconds and the main combustion phase started at 1600 seconds and lasted about 600 seconds. The Oxygen levels in this test have not reached 11.8 % after the main combustion phase which again indicates a smoldering phase of combustion.



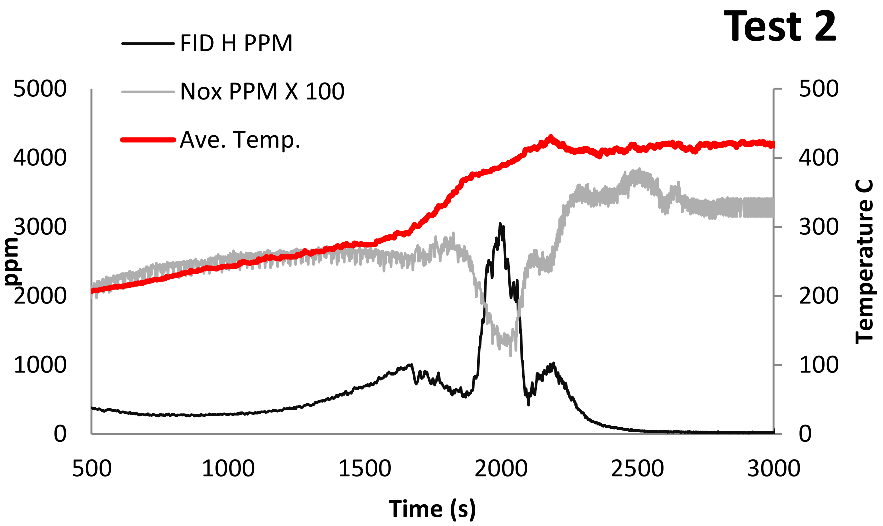


Figure 5-6: The fire gas composition and temperature profiles for Test 2 at 300 ^{O}C and 12% initial oxygen..

Test 3:

Test 3 was started with kerosene which was quickly extinguished, as in the previous tests. 135 l/m of methane and 1250 l/m of air were used in an attempt to achieve 500^{o} C. The results are shown in Fig. 5-7 which shows that the slow oxidation phase started at around 500 seconds and the main combustion started at 800 seconds. Similarly to the previous tests the oxygen levels were relatively lower than expected at the end of the test which suggests another phase of smoldering combustion. A feature of these results, which is also shown in the tests 1 and 2 results, is a large increase in CO and HC during the main heat release phase. This indicates pyrolysis of the wood to evolve these gases, which are not burning due to lack of oxygen. An unusual feature of all the results is that during this phase of combustion the NOx decreases significantly. A possible explanation of this is the occurrence of reburn chemistry, which occurs in local rich mixtures where NOx formed upstream (at the burner in this case) is reduced by reaction with hydrocarbons in the absence of oxygen. The final smoldering combustion phase was very clean at these conditions as the CO and HC was very low, but there was clearly consumption of oxygen and production of CO_2 relative to the levels of the burner at the calibration conditions.

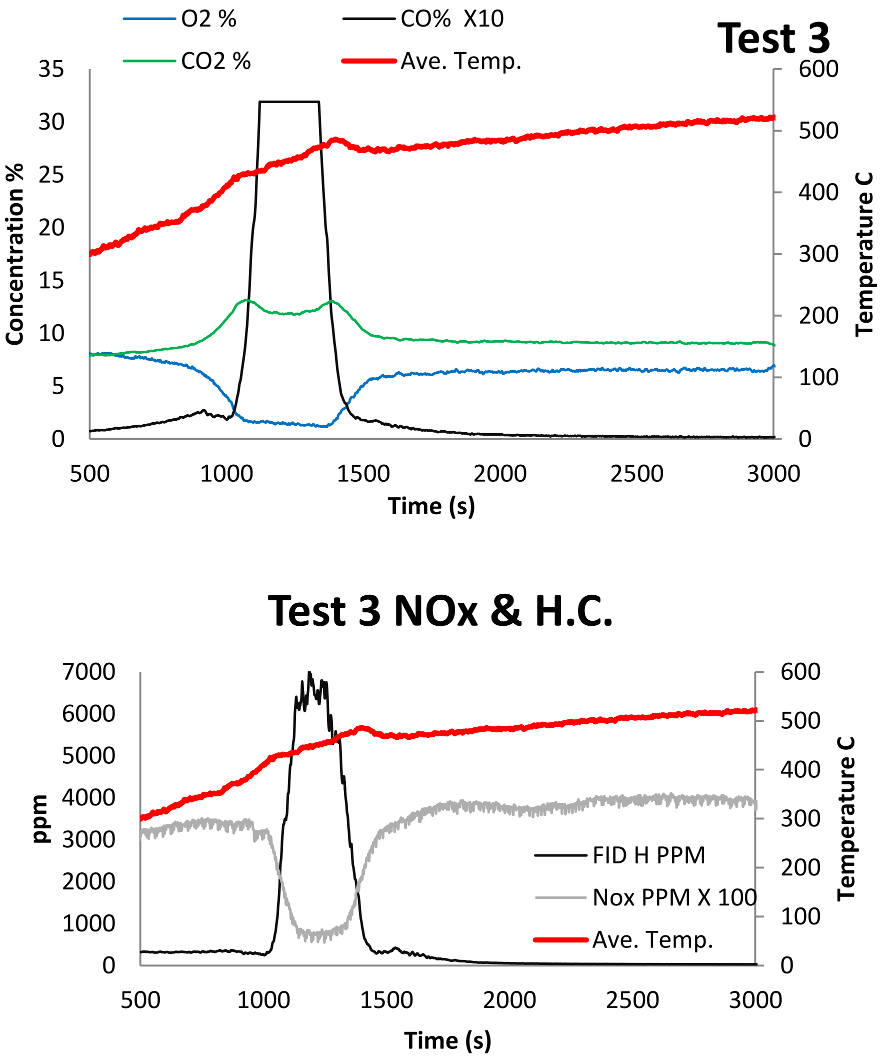


Figure 5-7: Fire gases composition and temperature for Test 3 with 400oC and 7% oxygen at the ignition time.

Test 4:

Test 4 was different from the previous tests, and no kerosene was used. At this stage the focus was purely on auto ignition of the wood. The results are shown in Fig. 5-8 In this test the oxygen level of the burner was 8.5 %. And the temperature was expected to reach 400C. However, a slow oxidation phase starts after 500 seconds and a main combustion phase is observed after 1500 seconds. This intense combustion phase lasted for about 800 seconds. This was relatively longer than the previous tests. Also the oxygen level stables at 6.5 % after this stage which suggest a slower smouldering combustion phase. The hydrocarbon results in this test were unusual, relative to the previous tests as they indicated two phases of the main combustion: production of HC followed by sudden consumption and then further generation. There was no equivalent variation in CO emissions and it is not known what caused this HC variation.

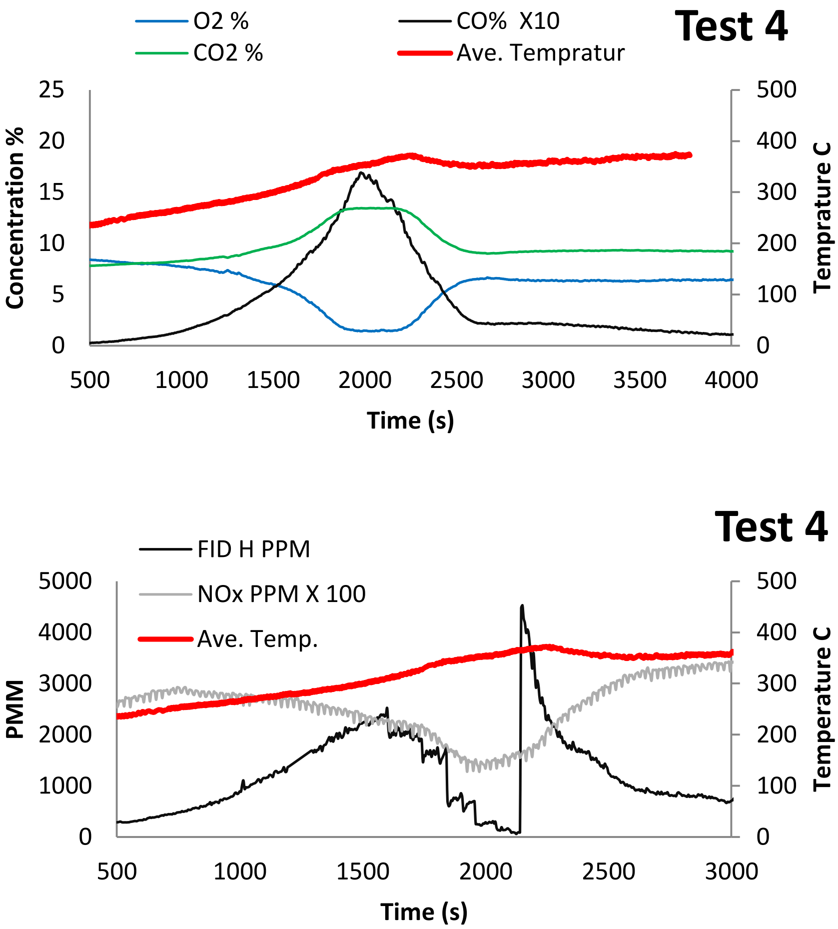


Figure 5-8: Test 4 fire gas composition and temperature at crib ignition conditions of about 6% oxygen and 300 ^{O}C with an ignition delay of about 1500s.

Test 5:

In the previous tests, the delay time to ignition was relatively long and the slow oxidation process have been recognised. Adding to this, the ignition have always occured before the desired temperature. Mainly this is due to heating of the furnace and heat loss to the walls. This suggested another technique in which a high burner airflow with an increasing methane flow rates. The relevant high heat input resulted in high temperatures for a given oxygen level due to the methane flow heat input. The former burner conditions were the heat loss to the walls of the compartment and delay in temperature rise. This was by increasing the methane flow in attempt to follow the standard fire test curve. This results in a faster heating and variable oxygen concentration, as shown in Fig. 5-8 where a limited oxidation process is shown to start followed by the main combustion phase after 550 seconds delay with a duration of about 560 seconds. The temperature at the ignition point was 550^{0}C and the oxygen was 8%. These results show that there was possibly no smouldering combustion phase as the oxygen and CO_2 levels after the main heat release was that of the burner. Also CO and HC levels were close to zero. Thus at this higher initial temperature all the wood load may be consumed in the main combustion phase.

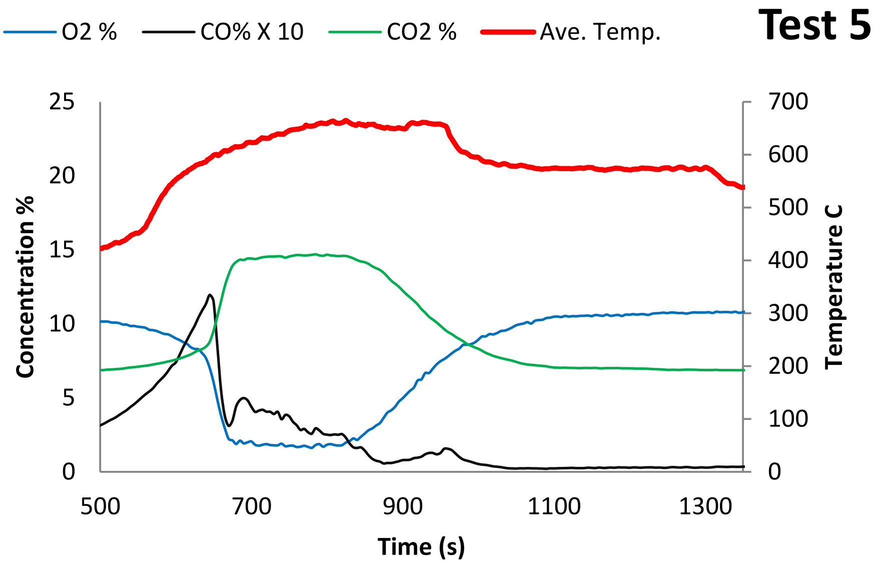


Figure 5-9: Fire gas composition and temperature for a temperature at main ignition of 550 ^{O}C and oxygen of 8%.

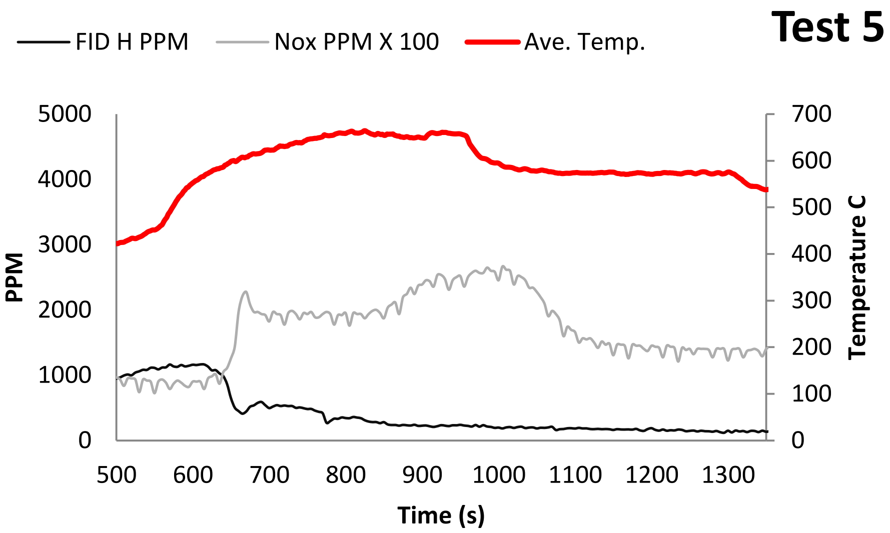


Figure 5-10: UHC levels and NO_X levels in Test 5.

The results are summarized in Table 5-1. This shows that the ignition delay may be correlated with the temperature at the ignition point and not be strongly dependent on the oxygen level. The results at 300^0C with two different oxygen levels have a similar ignition delay. During the main combustion the minimum oxygen level is similar for most of the fires and is probably controlled by the fire load, which was constant for all the fires. The main burn time would be expected to decrease as the fire initial temperature increased. This does not consistently occur and the evidence at 300^oC is that the fire burn time is also dependent on the oxygen level with shorter burn times for higher oxygen levels.

Table 5-1: Summary of the primarily testing results.

T ^{c}o	O_2%	Ignition delay [s]	Min. O_2 %	Main burn time [s]	Peak fire T ^{o}C	Peak heat Release kW
270	13	2100	3	200	390	30
300	10	1600	1	500	420	28
300	6	1500	2	800	380	18
400	7	800	1	500	500	25
550	8	550	2	560	670	60

5.2.3 CONCLUSIONS

A method for investigating the combustion of wood in the later stages of compartment fires has been developed. This has shown that once the initial fire has consumed oxygen and raised the temperature, the rest of the wood fire load would ignite by auto ignition after a delay period. The heat release rate of the wood was higher than when the wood burns under standard fire conditions and the fire consumption rate is faster so that for a fixed fire load the fire duration was shorter. These results are considered to be important for the modeling of the later stages of compartment fires. Further work is required to understand and model this autoignition mode of fire propagation. The following sections will descripe the actuall tests made using this method to investigate fire products toxicity.

5.3 EXPERIMENTAL SETUP

Pine wood cribs were burned in a 1.6 m^3 (1.3 m high, 1 m wide and 1.2 m deep) ceramic fire brick lined compartment, which was an indicative fire test furnace. The furnace had two observation windows which enabled the wood combustion to be observed and photographed. A natural gas burner was used that could follow the standard fire furnace temperature time curve (BS-476-22, 1987)by manually adjusting the fuel flow rate to the burner for a fixed air flow rate. The procedure was to use the air flow rate necessary to achieve the standard fire temperature-time curve, but to hold the burner fuel flow at a level that achieved the required fire temperature. The fire ventilation was then set in this work at that used in indicative fire tests and this was a relatively high ventilation rate of 38 air changes per hour (ACH) which is typical of the well ventilated fires that lead to flashover. In this work the fire temperature was chosen to be 500^oC so that the heat release from the combustion of the wood generated temperatures that would represent flashover conditions. The equipment could generate any fire temperature up to 1200^oC or down to 200^oC.

The furnace was fitted with a 150 mm exhaust port at the top close to the front wall of the furnace. The gases were assumed to be well mixed by the exhaust position and a single hole sample probe was used at the exhaust port and prior to the downstream entrained air dilution. The burner (Ali and Andrews, 1987) was recessed from the furnace in a 162mm diameter pipe with its separate ignition system and flame detector.

The combustion efficiency was very high and hot burned gases entered the furnace. This burner was offset from the furnace centre so that there was no direct burner jet interaction with the wood crib. The furnace was fitted with 20 thermocouples spread over the furnace volume. These were all averaged to provide the mean furnace temperature that is reported in this work.

The cribs had no ignition source other than the furnace 500°C temperature and this temperature was reached in 190 s from ignition of the gas burner. Time zero in the reported results is the auto ignition time of the wood, determined from a decrease in oxygen and increase in CO_2 and CO as the wood ignited. There was no other air supply other than that for the burner so that the furnace oxygen level was that of the lean burner combustion at 12%. Other combinations of temperature and oxygen could be generated but this condition was used initially as it is typically of compartment fire conditions pre-flashover. The fire load expressed as a load per compartment volume, using 18 MJ/kg for the CV of pine wood, were 35 MJ/m^3 for the 3 kg crib and 104 MJ/m^3 for the 9 kg crib. Typical fire loads [4] are a minimum of 230 MJ/m^2 for a hospital, which with a typically 2.5 m room height converts to 92 MJ/m^3. The equivalent figure for a shop is 240 MJ/m^3. The 3 kg crib is a very low fire load, but the 9 kg crib is representative of light fire loads in buildings. A 21 kg crib would be required to represent the fire loading in a shop.

The fire loads investigated were pine wood cribs consisting of 48 sticks and 84 sticks respectively. Each stick in the 3 kg crib was 30x2x2 cm and the second crib weighed 9 kg with 60x2x2 cm sticks, both cribs were the same height using 12 layers of wood with four sticks per layer in the 3 kg crib and 7 sticks per layer in the 9 kg crib. Both cribs had the same stick spacing per layer of 8 cm. The similar construction of the two cribs ensured that they should have the same HRR in a free fire with the wider crib simply burning for longer. The cribs were located with the bottom surface 15 cm above the furnace floor and supported on a metal plate with sides to catch any crib debris that collapsed in the later stages of burning. The top of the crib was 29 cm above the furnace floor with a furnace height of 1.3 m. The pine wood was analysed using an elemental analyser to be 47.25% carbon, 47.07% oxygen and 5.68% hydrogen. This converts to $CH_{1.442}O_{0.746}$ and the stoichiometric A/F ratio by mass was 5.34/1. This has been used to convert the air/fuel ratio of the fire into a fire global equivalence ratio. The air/fuel ratio of the fire was determined by carbon balance of the mean exhaust gas sample, using the method of (Chan, 1996) for HCO fuels.

The HRR was determined by oxygen consumption. In the present work the NG burner was operated at 110 kW. The oxygen consumption calorimetry method, which requires the air mass flow and the A/F ratio by mass to be determined, gave good agreement (<5% difference) with the HRR based on the natural gas mass flow rate to the burner and the calorific value of natural gas. The burner air/fuel ratio by mass was 34.2/1 or an equivalence ratio of 0.49. The natural gas burner was stable down to an equivalence ratio of 0.1.

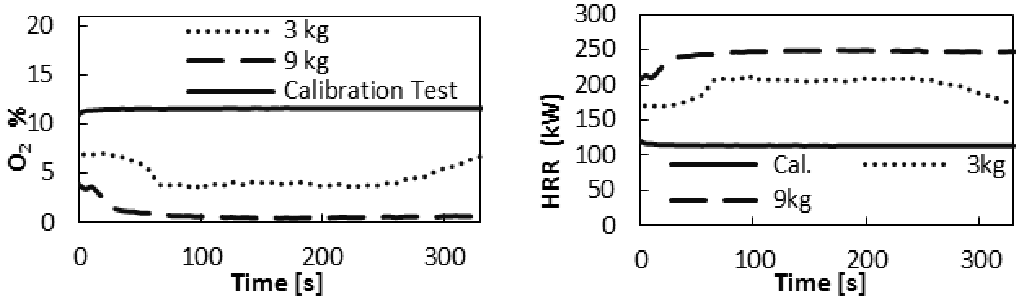
The fire product gases were sampled from the 162 mm diameter flue into a 190^{o}C heated sample line and then passed through a heated pump and filter into a Signal Instruments gas analysis system that consisted of a heated FID detector for total HC analysis, a heated chemiluminescence NOx detector and finally through a water condenser and then to a NDIR analyzer for CO and CO_2 and a paramagnetic oxygen analyzer for the oxygen analysis used in the HRR measurements. The FID was not calibrated for the very high HC emission levels encountered in this work and this resulted in no measurements above 1% HC. Consequently all the HC reported were from the FTIR analysis.

A second heated sample line was linked to a heated filter and heated sample pump and then to a heated TEMET GASMET CR-Series portable FTIR analyzer, which is approved for legislated emissions measurement in the UK. This had a 190^{o}C heated interferometry cell and this prevented any sample losses due to condensation or removal by dissolving in condensed water in the refrigerated condensers used upstream of conventional NDIR analysers. This FTIR was precalibrated by the manufacturers for over 50 species that occur in fire product gases. It had a sensitivity for most species of 2 ppm using a liquid nitrogen cooled detector. The FTIR did not measure all the hydrocarbons present but if all 50+ hydrocarbon species that were analysed and calibrated were added together then a pseudo total HC measurement is made, each FTIR species was multiplied by its carbon number to yield a total that was C1 equivalent. Calibration of the FTIR HC measurement with that of a FID in a compartment fire with low HC emissions gave good agreement.

5.4 RESULTS

5.4.1 FLAME OBSERVATIONS, OXYGEN AND HRR.

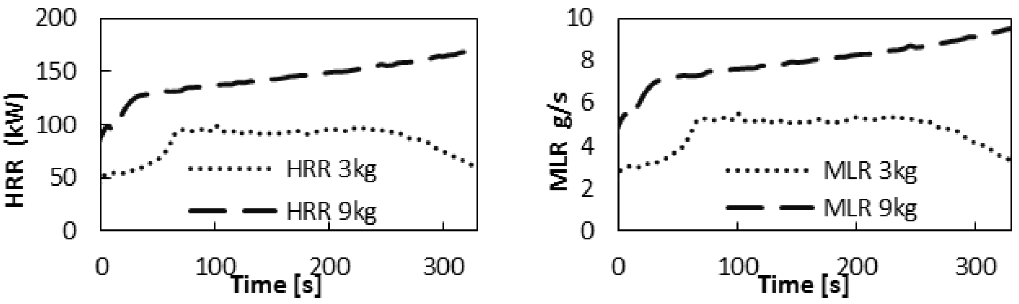
Observations of the crib flames through the two furnace windows showed that the normal luminous flames from wood combustion were absent. Ignition of the wood was by autoignition. Detailed pictures are found in Appendix D. The 3 and 9 kg fires behaved differently and this was because the 3 kg crib had an overall lean equivalence ratio and the 9 kg crib had overall rich combustion, as will be shown later. The oxygen levels and the oxygen consumption heat release rates (HRR) are shown in Fig. 2. This shows the main period of burning for the 3 kg fire but only the first stage of burning for the 9 kg fire as burning continued at the steady state HRR shown in Fig. 2. The steady state oxygen levels were 4% for the 3kg crib and <0.5% for the 9 kg crib. The 'Cal.' line is the furnace condition prior to the ignition of the wood crib and the reduction in oxygen outflow when the crib ignited was used to determine the heat release.



(a) (b)

Figure 5-11: Oxygen (a) and heat release rate (b) over time.

For the 3 kg crib there was a light blue 'ghosting' flame, which coincided with high CO emissions at the start of the wood combustion. This was the main period of heat release from the wood, as shown in Fig. 5-11, and occurred with no collapse of the crib. It was followed by a glowing red combustion of the wood with no visible external flames and during this phase the crib gradually collapsed. It is considered that the two phases of the 3 kg wood combustion are gasification and smoldering or char combustion. The wood HRR was lower during this glowing combustion phase, as shown for the 3 kg results in Fig.3b after 250 s. The mass loss rates are shown in Fig. 3b and are converted from Fig. 3a by dividing the oxygen based HRR by the product



(a) (b)

Figure 5-12: HRR at 500°C for pine cribs (a) and the mass burning rate of the cribs (b).

of the CV of 18 MJ/kg for pine wood and the combustion efficiency (see later). The mass loss rate is higher for the 9 kg fire, but much of this mass loss was gasification and not combustion as this was limited by oxygen availability. The 9 kg fire continued to burn for 1400 s at <0.5% oxygen and a HRR of between 120 and 170 kW from the wood combustion. Only the first phase of burning is shown in this work. The 9 kg fire did not have a red glowing phase and the fire was entirely in light blue flames signifying CO combustion. The fire was thus dominated by gasification of the wood.

5.4.2 GLOBAL EQUIVALENCE RATIO DURING THE CONSTANT HRR PERIOD

The global fire equivalence ratios based on carbon balance from the mean gas analysis are shown as a function of time in Fig. 4. This is the combined natural gas and wood crib equivalence ratio. The natural gas only equivalence ratio was 0.49, as detailed above. The stoichiometric A/F ratio was taken as the average on a mass burning rate basis between natural gas and pine wood. These results show that the two fire loads burned with different global equivalence ratios, lean for the 3 kg crib and rich for the 9 kg crib.

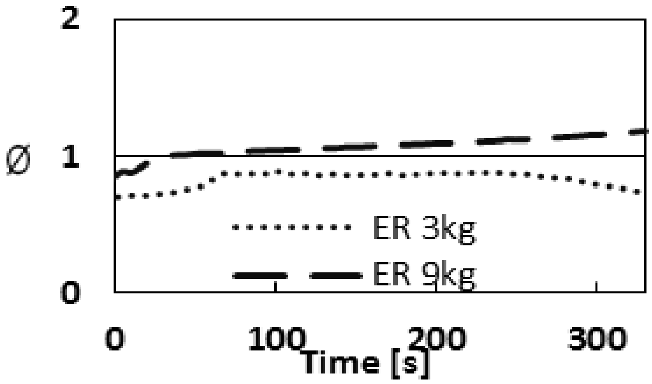


Figure 5-13: fire global equivalence ratio by carbon balance.

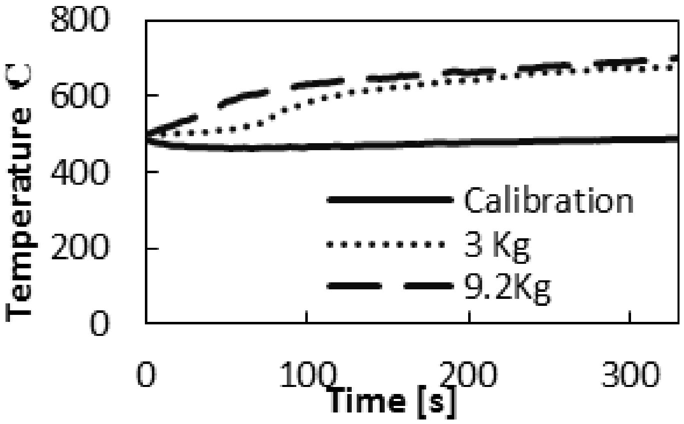


Figure 5-14: mean compartment temperature.

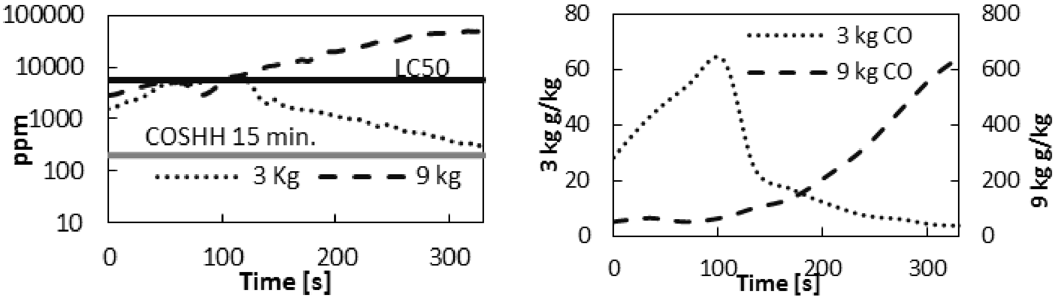
5.4.3 COMPARTMENT TEMPERATURES

The reference (Cal.) compartment temperature with the gas burner is shown in Fig. 5 to slowly rise from about 470 to 500°C. The NG fuel mass flow was constant and the rise in temperature was due to the gradual build up of heat in the furnace walls. With the pine cribs the temperature rose faster with the 9kg crib, due to its greater HRR. However, after 250s there was only a 30°C higher temperature for the 9kg crib than. The reasons for the small difference in temperatures was that the 9kg crib was gasifying the wood and not generating heat release, due to lack of oxygen.

Flashover is normally taken to occur at about 600°C and this was achieved in 50 s for the 9 kg crib when 0.8 kg had been burnt and 110s for the 3kg crib when 0.4 kg had been burnt. The 3kg crib fire had a lean global equivalence ratio post flashover with oxygen present that resulted in low CO and other toxic emissions, but for the 9 kg crib a rich global equivalence ratio was generated with high CO. The aim of creating flashover conditions using a natural gas burner to has been demonstrated.

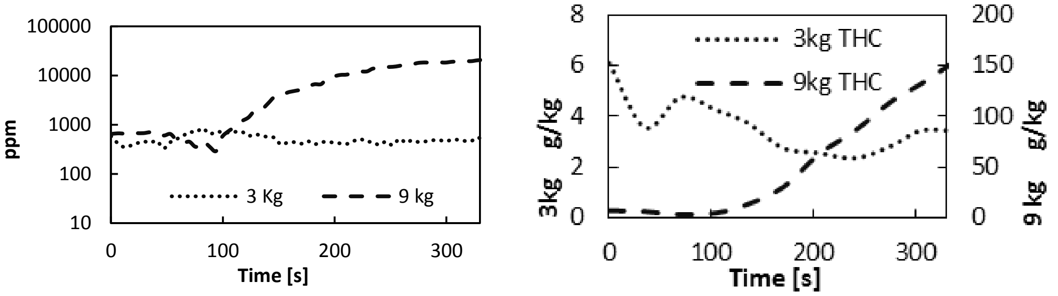
5.4.4 CO AND TOTAL HYDROCARBON (HC) EMISSIONS AND COMBUSTION EFFICIENCY

The CO and HC emissions (ppm) and yields (g/kg) are shown in Figs. 5-15 and 5-16 and both show that there was a large difference between the CO and HC for 3 and 9 kg cribs. The reason for this was the difference in the fire global equivalence ratio shown in Fig. 5-13. The 3 kg pine crib was lean throughout all the combustion period and the emissions decrease as the fire temperature increases, as there is always excess oxygen present. However, for the 9 kg fire the global fire equivalence ratio goes from lean to rich after 100 s. Prior to this the mass burn rate was lower and the global equivalence ratio was lean and the CO and HC for the first 100 s were similar for both crib fires.



(a) (b)

Figure 5-15: . CO ppm (a) and yield g/kg (b) emissions as a function of the time from autoignition of the pine crib for 3 and 9 kg cribs.



(a) (b)

Figure 5-16: Total HC by FTIR ppm (a) and yield g/kg (b) emissions as a function of time from autoignition of the pine crib for 3 and 9 kg cribs..

Figures 5-15 and 5-16, show that the rich combustion with the 9 kg crib resulted in very high CO and HC emissions. In contrast the lean high temperature combustion with the 3 kg crib resulted in very efficient combustion and very low CO and HC emissions. The levels of CO and HC are sufficiently high that a gas explosion would occur if air was added by opening a door and hence the conditions for back-draught were generated. If the gases escaped the fire through a broken window then they are the source of the external flames that are seen in many post flashover fires, where entrained external air provides the oxidant.

The summation of the CO and HC yields enables the combustion efficiency to be determined using the calorific value of CO and taking HC as methane. This is shown in Fig. 5-17. For the 3 kg lean combustion fire the combustion efficiency was >98%

throughout the fire and >99% after the first 120 s following autoignition, when the temperature was below 600^{o}C and the HRR was still increasing. For the 9 kg crib the CO and HC emissions were very high and this results in very low combustion efficiencies of <<98%, once the fire has a significantly rich overall equivalence ratio after 100 s. The combustion efficiency deteriorates due to the equivalence ratio becoming richer as the fire develops, as shown in Fig. 4. In practice the 9 kg crib results are closer to reality as the fire loading is close to that of a relative low fire load as discussed above. The 3 kg crib fire load is unrealistically low and would not normally be encountered in real fires with practical fire loadings.

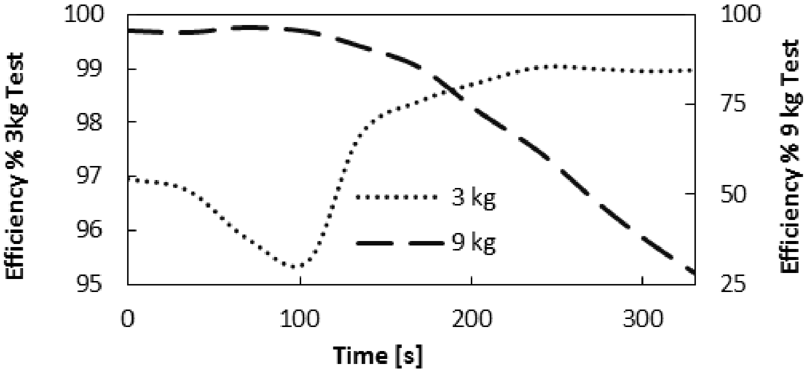
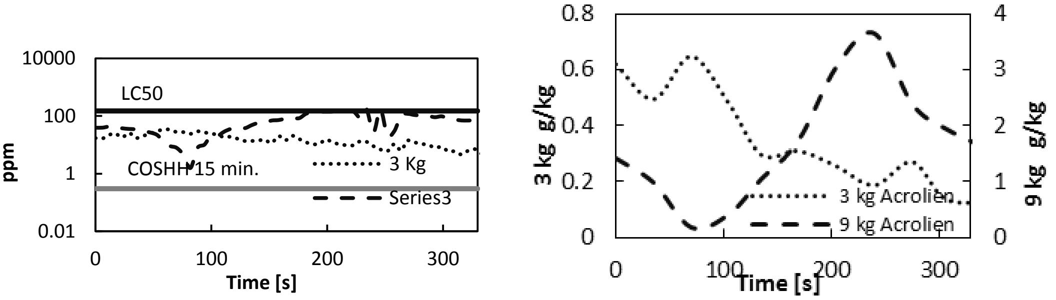


Figure 5-17: Combustion efficiency as a function of time from auto ignition of the wood for the 3 (LH scale) and 9 kg (RH scale) pine wood cribs..

Associated with rich combustion and the high levels of CO would be hydrogen which was generated by the gasification reactions in rich combustion. For equilibrium conditions the water gas shift reaction can be used to compute the levels of hydrogen from the CO levels. For natural gas, the equivalence ratios in Fig. 4 would give rise to hydrogen levels increasing from near zero to 7.5% for Ø=1.5 at the end of the measurement period. This 9 kg test is close to reality in terms of its loading per m^3 but is well below the most highly loaded fire scenarios. It may thus be concluded that in high temperature air starved fires after flashover the remaining fire load undergoes gasification and this leaves a very flammable gaseous atmosphere of CO, HC and H_2, which gives rise to the phenomena of back-draught when a door is open and air added to the fire. Explosive propagation of the fire then occurs.

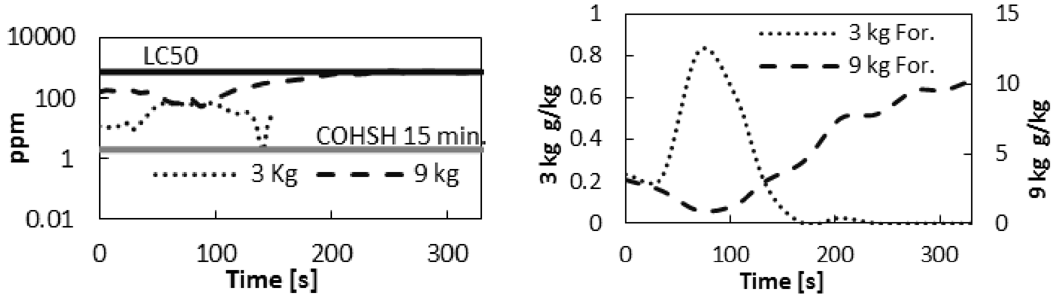
5.4.5 TOXIC EMISSIONS

The LC_{50} toxic limits reflect conditions that will cause death and the $COSHH_{15min}$ limits reflect conditions that will impair escape. The CO toxic emissions are shown in Fig. 6a with these toxic limits shown. The CO emissions for the 3 kg crib fire were lower than the $COSHH_{15min}$ limits for most of the fire, whereas the CO emissions for the 9 kg crib fire resulted in CO levels considerably higher than the LC_{50} limit. This shows the critical importance of fire loading in air starved post flashover fires. The other key toxic emissions are shown in Figs. 5-18 and 5-19. For Acrolein Fig. 5-18 shows that the emissions were so high for the 9 kg crib that the LC_{50} limit was exceeded by a factor of 5, but for the 3kg fire the acrolein emissions were above the $COSHH_{15}$ but well below LC_{50}. Similar results were found for formaldehyde as shown in Fig. 10 and these two gases plus CO dominated the total toxicity N that is shown in Fig. 5-20. This shows that the total toxicity N for the 9 kg fire was an order of magnitude higher than for the 3 kg fire, due to the rich mixtures that occurred. Also the toxicity was higher the richer the fire became, whereas for the 3 kg fire the toxicity peaked during the period the fire HRR increased to its maximum value.



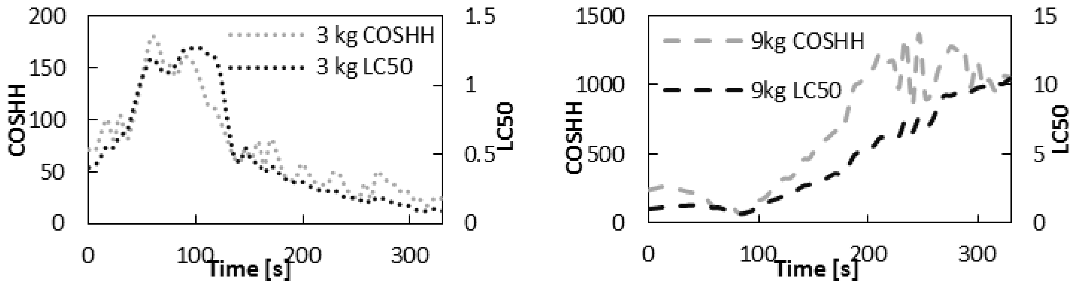
(a) (b)

Figure 5-18: Acrolein emissions for 3 and 9 kg crib fires (a) ppm (b) yield g/kg.



(a) (b)

Figure 5-19: Formaldehyde emissions for the 3 and 9 kg fires (a) ppm (b) yield g/kg.



(a) (b)

Figure 5-20: Total normalised toxicity N for LC50 and COSHH15min

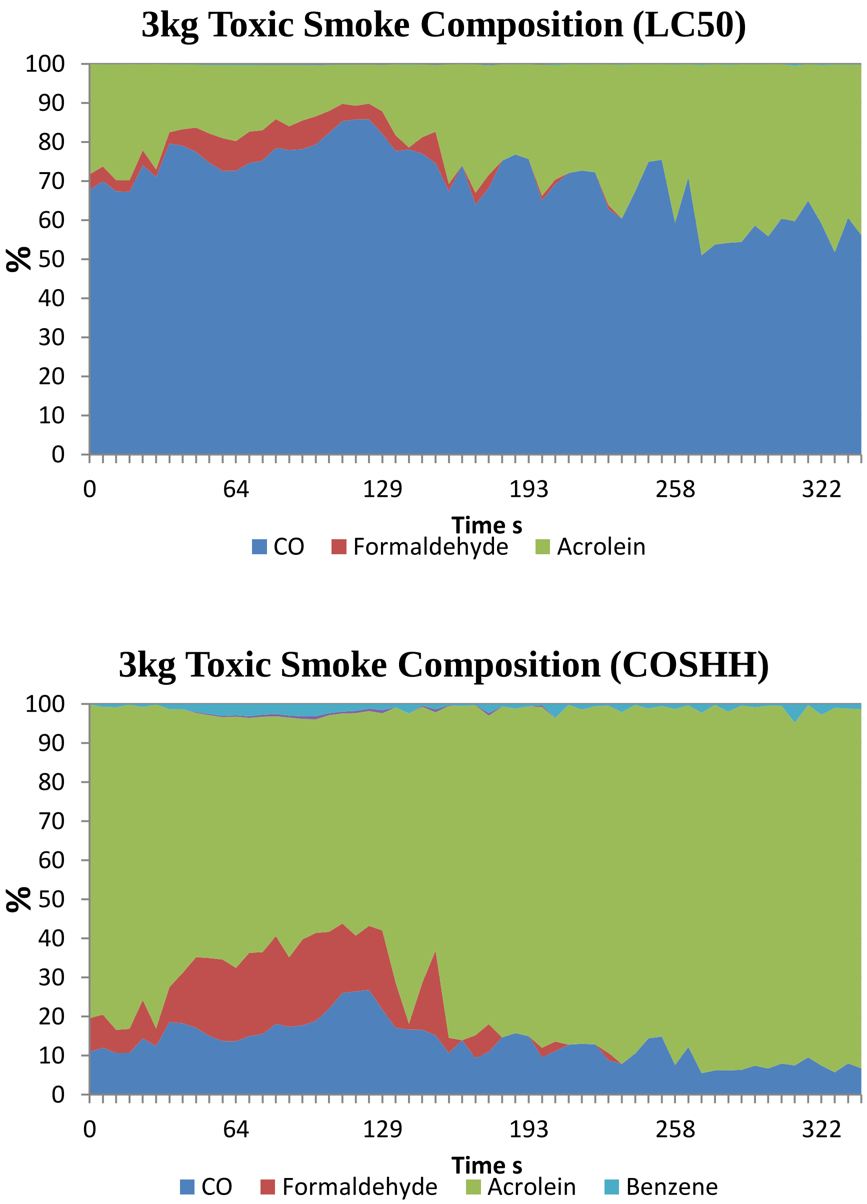


Figure 5-21: Toxicity contributions for 3 kg wood crib fire (a) LC50 (b) COSHH15min.

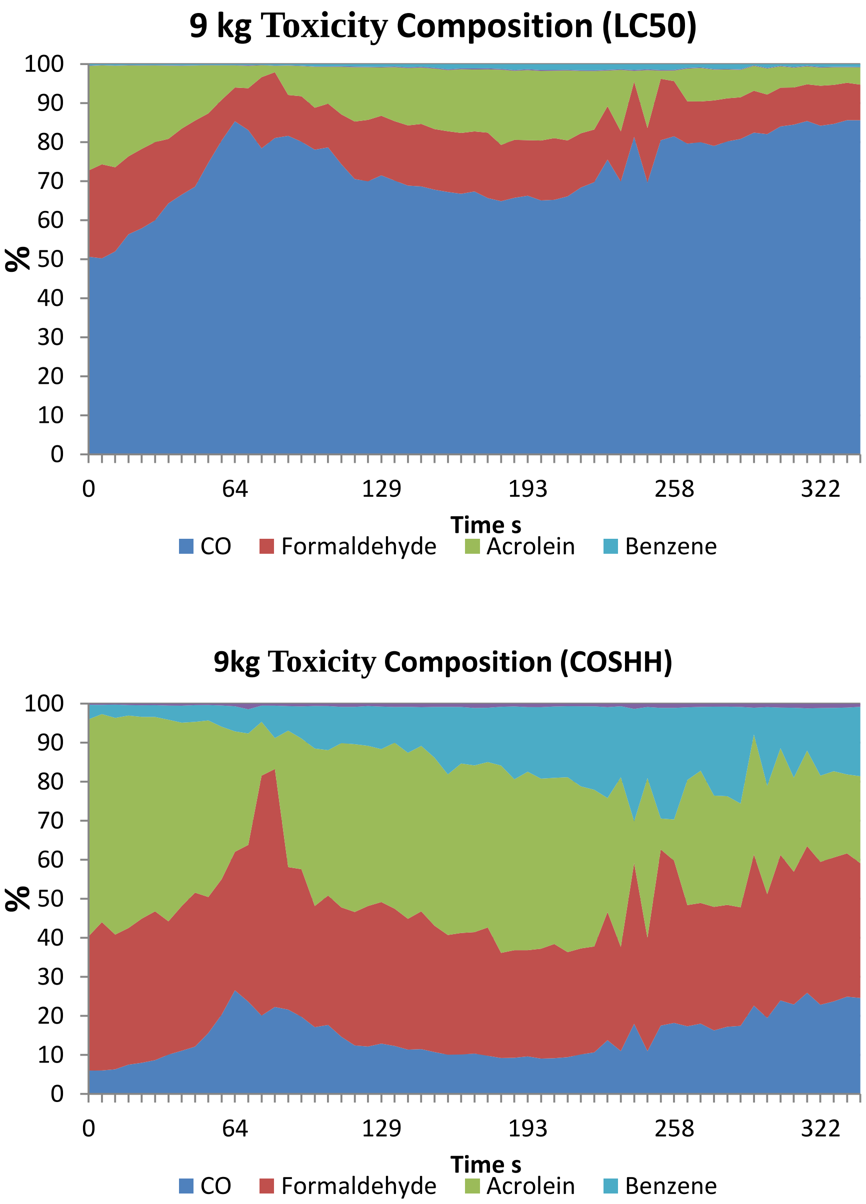


Figure 5-22: Toxicity contribution for 9 kg wood crib fire (a) LC50 (b) COSHH15min.

The major contribution to the total toxicity are shown on an LC_{50} and $COSHH_{15min}$ basis in Figs 12 and 13 for the 3 and 9 kg crib fires respectively. For the 3 kg fire with lean burning and relatively low total N, the toxicity was dominated by CO on an LC_{50} basis and acrolein on a $COSHH_{15min}$ basis. Formaldehyde was the third most important toxic gas, but its contribution never exceeded 10% on an LC50 basis and 20% on a $COSHH_{15min}$ basis. For the 9 kg crib the toxicity was dominated by CO on an LC50 basis, but formaldehyde was more significant. However, on a $COSHH_{15min}$ basis acrolein and formaldehyde have a similar contribution and CO was the third most important toxic gas. Benzene was also a significant contribution to the toxicity in these rich burning gasification type fires. The differences between LC_{50} and $COSHH_{15min}$ toxic assessments in these fires show that the relative importance of the four toxic gases are different for death than for impairment of escape. For wood fires CO dominates in relation to death and for impairment of escape the other three gases are more important.

5.4 CONCLUSION

The use of a gas burner to rapidly generate 500^oC fire temperatures with high residual oxygen (12%) in a closed 1.6 m^3 compartment fire with 38 ACH was shown to generate post flashover conditions in the presence of a wood crib fire load. The wood was ignited by autoignition and there was no conventional flaming combustion, but gasification of the wood occurred with subsequent CO and HC combustion. A faint blue flame from the CO combustion was observed above the crib. Travelling flames around the compartmnet were also detected.

The pine wood crib loading had a great influence on the fire development due to a low load generating lean combustion and a high load rich combustion. For fire loadings similar to a lightly loaded compartment fire, very rich combustion occurred with gasification of the wood resulting in very high levels of CO, HC and the toxic gases acrolein, formaldehyde and benzene. In these fires gasification of the fire load was occurring generating very high levels of CO and HC, which give back-draught conditions.

The work carried out using this techniques provides new data on post flashover conditions relative to backgraught phenomena frequently reported by fire and rescue services. The composition of the vapourised fuel was reported in details, in the form of toxic incomplete combustion products, and unburnt hydrocarbons. Further research is required to provide more details on other types of fuels.

6. CHAPTER 6:
FOLDED COTTON TOWELS

This chapter is based on the following publication:

Aljumaiah, O., G. E. Andrews, Alshammari, Burell, Cox and H. N. Phylaktou,(*2010c)*, Toxic Emissions from Folded Cotton Towel Fires in a Low Ventilation Compartment, In *Proceedings of the Proceedings of the Sixth International Seminar on Fire and Explosion Hazards, Leeds,* edited by D. Bradley, G. Makhviladze and V. Molkov, 2011, Research Publishing Services, ISBN: 978-981-08-7724-8, DOI: 10.3850/978-981-08-7724-8_11-07.

ABSTRACT

The toxic gases from low temperature smoldering combustion were investigated using folded cotton towels. An enclosed 1.6 m3 fire test facility was used with a controllable air flow inlet at floor level and fire gases discharge at ceiling level. 2kg of folded cotton bath towels were burned in the compartment with a ventilation rate of 11 and 21 air changes per hour (ACH), which produced smoldering combustion. The situation simulated the conditions in an enclosed cupboard fire. The smoldering combustion heat release rate peaked at 5 kW and was 2 kW in the later stages. CO, formaldehyde and acrolein were the most significant toxic species. The toxicity level doubled at the lower ventilation rate. The total toxicity normalised to the LC50 limit were 1.5 – 3. On a COSHH15 min basis the total N was between 400 and 900 and these gases would seriously impair escape from fire.

6.1 INTRODUCTION

The Rose Park Nursing home fire in Edinburgh in 2004 killed 14 people through toxic gases from a fire in a cupboard containing a fuel load with a large textile component (BBC, 2007). This is a fire scenario that has received relatively little study and this present work was undertaken to investigate toxic gases released under these low ventilation conditions with stored textiles as a significant fire load. Under these air starvation fire circumstances, (Andrews et al., 2007; Andrews et al., 2005b; Andrews et al., 2005a) have shown for pool fires, wood and acrylic blanket fires that the gases acrolein and formaldehyde can be of more importance than CO in terms of the overall toxicity in terms of irritant gases that would impair escape. Textiles such as cotton towels have a HCO composition similar to wood and hence their toxic gases may be related, although their burning rates are quite different.

Over 70% of fire fatalities are caused by inhalation of toxic gases present in fire smoke(National Statistics, 2010; USFA, 2005). Not only does smoke reduce the visibility in compartment fires, but it also is an irritant which causes respiratory problems. Purser [5, 6] showed that in most fires the main toxic products are CO with irritant and acidic gases and the amount of each depend on the thermal decomposition of the fire load, which depends on the temperature and oxygen supply. Acrolein and formaldehyde have an irritant activity in fires and hence influence the impairment of escape However, HCN, HCl and HBr are normally low unless the fire load contains organic N, Cl or Br compounds (Purser, 2002; Purser, 2010b), which was not the case in the present work. (Andrews et al., 2007; Andrews et al., 2005b; Andrews et al., 2005a) have shown that for fire loads with mainly acrylic textile fire loads then HCN is a dominant toxic gas and for fires with electric cables that use PVC as the outer cable material have very high toxic yields of HCl (Gann et al., 2010)

Most of our knowledge (Purser, 2002; Purser, 2010b) on toxic gases from fires is from fast burning fires in well ventilated compartments, where CO dominates the toxicity in under ventilated (fuel rich) conditions. These occur at high air flow ventilation of the fire, as this increases the combustion rate. The present work concentrates on fires with low air flow rates that produce low upper layer temperature lean combustion fires. For some fire loads low air flow rates produce low temperature smoldering combustion and this occurred in the present work using a common textile fire load, folded cotton towels. The low temperature of smoldering fires is crucial in the development of fire toxicity, as the fires are very lean and there is no contribution to CO from equilibrium CO. Lean combustion in fires is often taken to have low toxic yields due to the presence of oxygen. However, this only applies at high fire temperatures and in low temperature fires CO yield is dominated by combustion inefficiency sources and can be higher CO than for rich combustion. This was shown by the authors for pool fires in air starved enclosures (Andrews et al., 2000b; Andrews et al., 2000a). Lean combustion at higher temperatures, generated using higher ventilation, gives lower CO than low temperature ventilation restricted fires (Gottuk, 1992b).

All the literature on the influence of ventilation on compartment fires shows higher CO levels than equilibrium in the lean equivalence ratio region and close to equilibrium in the rich fire region (Andrews et al., 2000a). These features can only be generated in experiments that reproduce the essential features of real ventilation controlled compartment fires. The use of the cone calorimeter for toxic yield determinations can give unrealistically low yields (Hull, 2010) as it is a freely ventilated fire and has a radiant heat flux that corresponds to a high temperature fire. The Purser Furnace (Hull, 2010; Stec et al., 2009) test enables the fire global equivalence ratio to be varied so that the toxic yields can be determined as a function of the fire equivalence ratio. However, this test imposes a fire temperature of 600^{o}C using an electrically heated furnace enclosure and in reality the fire temperature is a function of the fire global equivalence ratio. This tube furnace test is intended to replicate the flaming combustion conditions in fairly well-developed compartment fires, where the upper layer is typically 400-700C. The result is that the furnace test usually gives low or negligible toxic yields for lean fire equivalence ratios and this is only valid for high temperature well ventilated fires. The present work will show high CO yields for very lean fire global equivalence ratios.

6.1.1 TOXICITY ASSESSMENTS FOR FIRE GASES

The LC_{50} 30-minute exposure gas concentrations are the most common toxic gas assessment used in fire toxicity and these aim to predict the concentrations at which 50% of people will die in the fire if exposed to the concentration for 30 minutes (Purser, 2010c). However, the objective of fire protection is to get all occupants out alive. Hence, there is a requirement for toxic gas concentration data that will not impair escape. COSHH [15] is the European standard on occupational exposure limits, which are statutory law in Europe, and are similar to the equivalent US short term exposure limits. The $COSHH_{15\ min}$ toxic gas concentration represent a no harm condition for 15 minutes and hence no impairment of escape. The USA has introduced the Acute Exposure Guideline Levels (AEGL) with three exposure levels: 1 for non-disabling and essentially similar to the COSHH 8 hour levels; 2 for disabling and impairment of escape based on 10 minute exposure, which are similar to the $COSHH_{15min}$ levels; and 3 for life threatening health effects which are similar to LC_{50}.

The COSHH limits have been largely ignored in fire toxicity, apart from in the work of the author, but are the best data set for assessing multi-component toxicity with a legally agreed methodology which is similar to the LC_{50} N-gas method (Levin, 1996). The assessment methods of fire toxic gases are compared in Table 1 for the major toxic species for the present folded cotton towel fires. AEGL-2 and $COSHH_{15min}$ have a similar assessment for the relative toxicity of CO and acrolein, whereas LC_{50} requires over 100 times the concentration of acrolein to cause death compared with the concentration to impair the means of escape. All three methods have quite different assessment levels for formaldehyde with $COSHH_{15min}$ being 1% of the LC_{50} limit and about 10% of the AEGL-2 limit. There are also major disagreements over the role of benzene, with only $COSHH_{15min}$ giving this a significant role in fire toxicity. It is clear that the toxic gases that are important in death in fires are the same as those that impair escape, but their relative importance is quite different. Acrolein is a major toxic gas in regard to impairment of escape on a COSHH and AEGL-2 basis, but has little contribution to death. Similarly formaldehyde is much more important for impairment of escape than it is for death. These conclusions will be supported by the results of the present work and have been found in other experimental fires (Andrews et al., 2007; Andrews et al., 2005b; Andrews et al., 2005a).

Table 6-1: Critical toxic gas concentration ppm for three assessment methods.

	LC_{50} 30 min.	**$COSHH_{15min}$**	**AEGL-2**
CO	3,000	200	420
Acrolein (A)	135	0.3	0.44
Formaldehyde (FMA)	250	2	14
Benzene (B)	10,000	3	2000

6.1.2 PREVIOUS WORK ON FOLDED COTTON TOWEL FIRES

(Andrews et al., 2007) have investigated the toxic emissions from single 0.6 kg folded cotton towel in a storage situation. The influence of the ventilation of the closed fire compartment was investigated using air changes per hour (ACH) of 1, 3, 11 and 40. 1. Three ACH represent a closed room with limited ventilation scenario, 11 ACH is a leaky room on an air flow basis and 40 ACH requires a door or window to be open to achieve the air flow. The fire initiation simulated an arson case with 0.08kg of kerosene poured on top of the towel. This gave a high heat release at the start of the fire but left a smoldering cotton towel fire once the initial kerosene had burnt off. The fires lasted around an hour apart from in the higher ventilation case where the fire duration was 30 minutes. The results are summarized in Tables 6-2 and 6-3 in terms of the relative contribution to the total normalized toxicity, N, on a $\text{COSHH}_{15\text{min}}$ and 30 minutes LC_{50} basis respectively.

Table 6-2: The major toxic species as a percentage of the overall toxicity N for COSHH 15 min. (HSE, 2005) toxic limits.

(ACH)	A	FMA	CO	B	*N COSHH 15 min.*	*A*	*FMA*	*CO*	*B*	*N COSHH 15 min.*
	Max. HRR					Smoldering				
1.1	74	22	1	0	*585*	*77*	*20*	*3*	*0*	*613*
2.7	32	51	2	6	*145*	*31*	*50*	*7*	*4*	*150*
10.7	59	16	7	15	*62*	*33*	*16*	*20*	*14*	*41*
40	39	17	9	17	*17*	*40*	*18*	*35*	*4*	*8*

Table 6-3: The major toxic species as a percentage of the overall toxicity N for 30 minutes LC50 toxic limits (HSE, 2005).

(ACH)	A	FMA	CO	N LC_{50}	*A*	*FMA*	*CO*	*N* LC_{50}
	Max. HRR				Smoldering 35			
1.1	24	57	17	1.81	*17*	*35*	*46*	*2.74*
2.7	8	76	16	1.00	*2*	*19*	*79*	*3.13*
10.7	9	19	67	0.43	*8*	*35*	*56*	*1.96*
40	5	10	48	0.21	*0*	*4*	*70*	*0.27*

The results are given for two stages in the fires, maximum HRR or minimum oxygen and for smoldering combustion 35 minutes after the start of the fire. The peak HRR was contributed to by the kerosene accelerant. The LC_{50} results in Table 6-3 show that the smoldering phase of the fire had a greater toxicity then that at the highest HRR, for all ventilation rates and the highest toxicity was for the lowest ventilation rates. For smoldering combustion CO dominated the total toxicity, formaldehyde was a very significant contributor whilst acrolein was of little importance. However, on a $COSHH_{15min}$ basis the total normalized toxicity N was similar at the maximum HRR and in the smoldering phase of the fire. The two low ventilation fires were much more toxic than the two higher ventilation fires and this toxicity was dominated by acrolein and formaldehyde, with CO of little importance. Also benzene was a significant contributor to the total toxicity. These toxicity results for gases that would impair escape are quite different conclusions than for gases that would cause death. The principle difference was the relative role of acrolein and CO, as discussed above and summarized in Table 6-1.

The present work was undertaken to investigate a higher cotton fire load, using three bath towels with a fire load of 2.1 kg. It will be shown that the higher fire load simply increased the duration of the fire in proportion to the increased mass and the fires were about 3hours in duration, compared with one hour for a single towel. Most of the fire duration was in the smoldering phase. The use of 0.2kg of kerosene to start the fire were investigated as a representation of arson conditions and this was compared with the use of 0.01 kg of ethanol to simulate an a lower energy accidental ignition source. The investigation into the Edinburgh Rose Park nursing home fire (BBC, 2007) is not yet in the public domain, due to legal actions. However, autoignition of the towels, contaminated with oils used for skin treatment, is now considered a likely ignition source for the fire. This scenario is likely to result in a smoldering fire which may develop into a flaming fire if sufficient ventilation is available. The use of a very small quantity of accelerant simulated this condition in the present work.

6.2 EXPERIMENTAL TECHNIQUES

An enclosed fire test facility (fire rig) with a volume of $1.6m^3$ (1.4m x 0.92m x 1.22m) was used with a controllable air flow inlet at floor level and fire emissions ventilation at ceiling level. The fire product gases were well mixed at the final exit duct and mean toxic gas samples were taken from this location. The fire rig had 25mm thick high insulated walls attached to a steel backing wall. There was a high temperature air sealed glass door, which could be used to observe the early stages of a fire. The fire rig was fitted with an outer door with 25mm thick insulation. The fire compartment had several bare bead thermocouples with one array 70mm below the ceiling and a vertical array on the rear wall and on the centerline. The term ‘fire temperature’ has been used in this work to refer to the average ceiling or upper layer temperature.

The air was fed from a compressor through a thermal mass flow meter into the fire enclosure, through a plenum chamber under the fire rig floor. The air inlet to the fire compartment was through four slots on the floor which were situated at the base of each wall. In this work 2.1 kg of folded cotton bath towels was burned in the compartment with ventilation rates of 10.7 and 21.4 air changes per hour. The previous work with 1 and 3 ACH, summarized in Tables 2 and 3, showed extremely high toxic gas levels on both an LC_{50} and $COSHH_{15min}$ basis and further experimental work at these very low ventilations was considered to be too dangerous.

Two fire initiation modes were investigated at 11 ACH. The first simulated an arson case and used 200g of kerosene poured on top of the three folded curtains; this was greater than the 80g used in the previous single folded cotton towel fires [4]. The second fire at 11 ACH was initiated using a small 10g ethanol pool fire placed at the bottom corner of the three folded towels. This fire initiation mode was intended to reproduce an accidental start to the fire and the accelerant had a negligible energy release compared to the fire load, whereas the use of 200g of kerosene had 10% of the total fire load energy. The 10g ethanol fire initiation was also used for the 3 folded cotton towel fire with 21 ACH.

Mixed raw fire gases were sampled from the fire compartment ceiling outlet duct via $190^{o}C$ heated sample lines and a heated filter and pump and then to a heated FID for total hydrocarbon analysis, a heated chemiluminescence NOx analyser and through a 20C condenser to NDIR analysers for CO and CO2 and paramagnetic analyser for oxygen. A heated TEMET GASMET CR-Series portable FTIR was also used for acidic and irritant toxic gas analysis. This had a separate $190^{o}C$ heated line, filter and pump and the FTIR sample cell was also heated so all analysis was on a hot wet basis. The FTIR was calibrated for over 50 species, including most of the toxic gases of interest in fire toxicity. The FTIR had a liquid nitrogen cooled detector and this gave at least 2ppm resolution on all species. The elemental composition of the cotton towel used is shown in Table 4, where it is compared with the composition of the cotton towels used in the previous work (Andrews et al., 2007) The present cotton was similar in composition to cellulose, $CH_{1.67}O_{0.83}$. The cotton towels were dyed blue and the diazo dye used was a source of HCN, but these were not sufficiently high to be of major toxic gas concern.

Table 6-4: Cotton towel elemental composition and stoichiometric A/F.

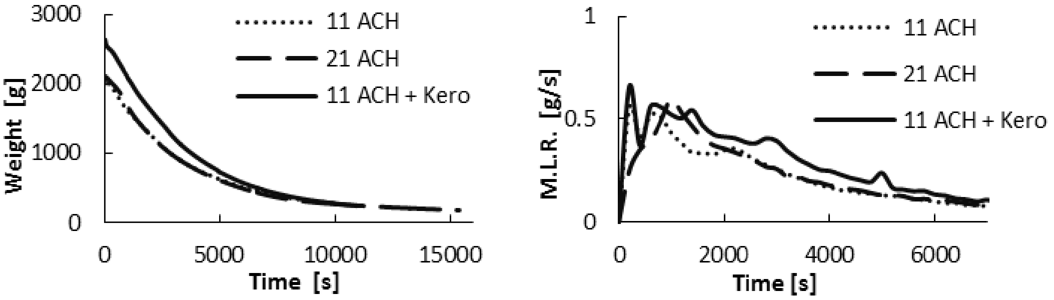
Fire Load	**Carbon**	**Hydrogen**	**Oxygen**	**CH_yO_z**	**A/F Ø=1**	**CV MJ/kg**
Cotton (Andrews et al., 2007)	38.1%	6.25%	55.65%	$CH_{1.97}O_{1.10}$	4.13	16.1
Cotton Towels	43.5%	7.6%	48.9%	$CH_{2.10}O_{0.84}$	5.54	

6.3 RESULTS

6.3.1 MASS LOSS, HEAT RELEASE RATES (HRR) AND TEMPERATURES

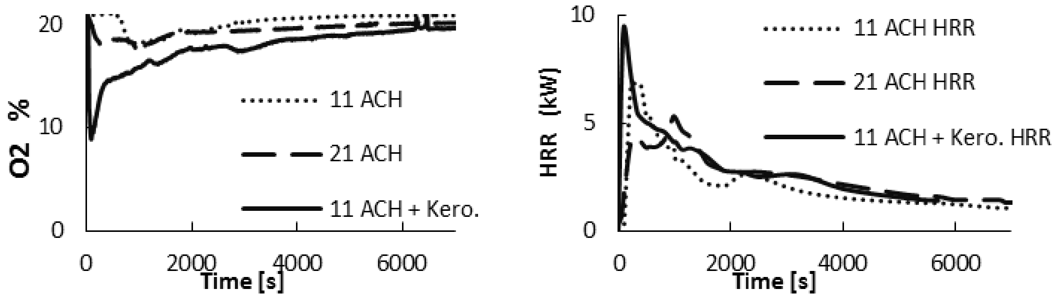
Figures 6-1 to 6-44 show that at 11ACH the initial fire development with the accelerant was very fast compared with no significant accelerant, but only lasted about 200s. There was a peak initial temperature of 300°C with the accelerant compared with 120°C for the negligible accelerant case. However, the effect of the accelerant was that a larger hotter cotton towel fire resulted for all the rest of the fire burn period. Compartment temperatures were 50 – 100°C hotter and oxygen based HRR were consistently higher for the fire started with 0.2 kg of kerosene poured on top of the towels. Fig. 6-3 shows that the oxygen levels were very high for compartment fires, indicating very lean overall fire equivalence ratios as detailed later.

The oxygen mass consumption based heat release was considerably lower than that based on the mass loss rate, especially in the early stages of the fire. This was due to the low combustion efficiency, due to the low fire temperatures shown in Fig. 6-4 and associated low CO and HC oxidation rates. Figure 6-3(b) shows that when the oxygen based HRR was corrected for the combustion efficiency the HRR was then in better agreement with that based on the mass loss rate. The folded cotton towel fires had two phases consisting of a volatile burning phase up to about 5000s and a slower char oxidation phase at low HRR. The toxic emissions all peaked in the faster burning volatile release phase of the fire and it will be shown that there was little toxicity associated with the fire gases during the char burning phase. The influence of doubling the ventilation rate on the smoldering fire development was small for the same 20g ethanol accelerant as fire temperatures and mass loss rates were the same.



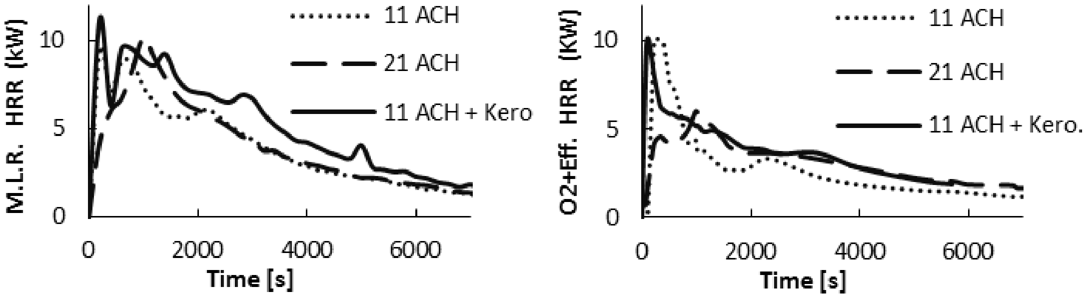
(a) (b)

Figure 6-1: Cotton towel fire weight loss (a) and rate of weight loss (b).



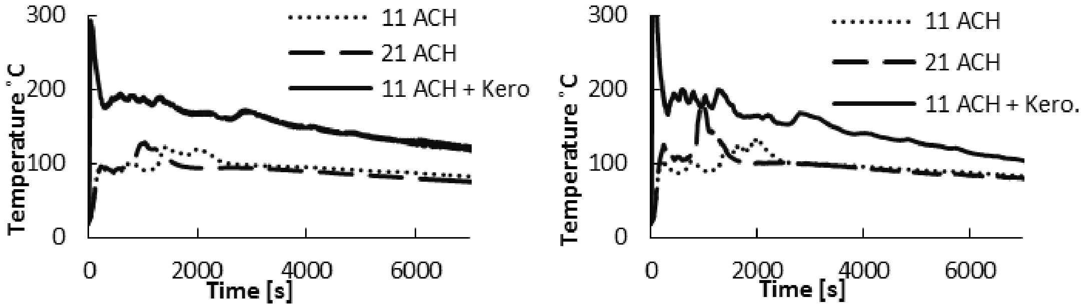
(a) (b)

Figure 6-2: Oxygen concentrations (a) and oxygen consumption derived HRR (b).



(a) (b)

Figure 6-3: HRR derived from the mass loss rate and Calorific Value (a), compared to that derived from oxygen consumption and corrected for combustion inefficiency (b).

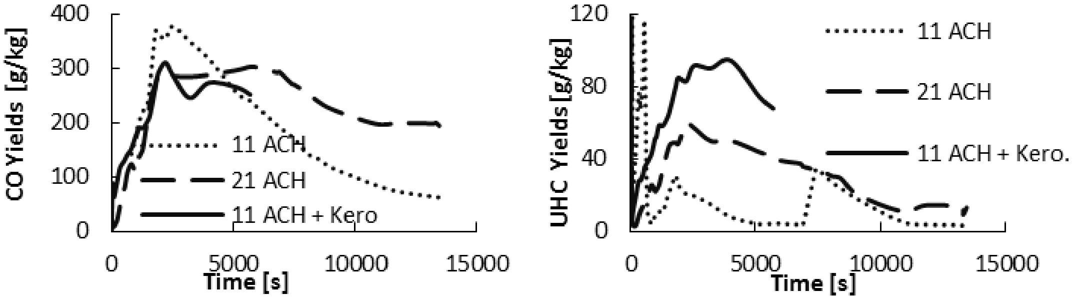


(a) (b)

Figure 6-4: mean upper layer temperature (a) and peak temperature above the fire (b).

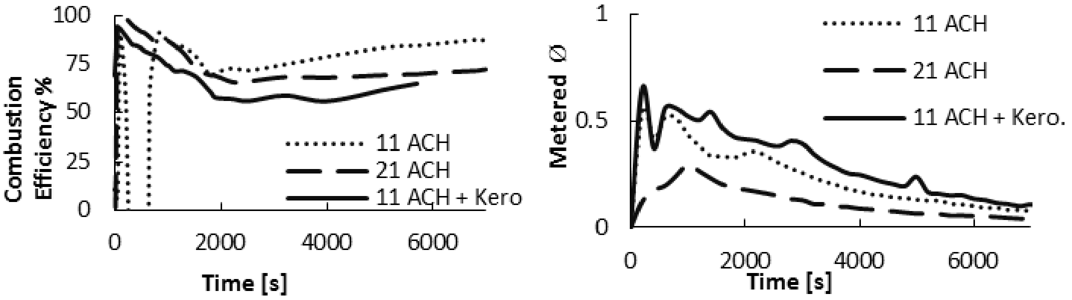
6.3.2 CO, HYDROCARBON, FIRE EQUIVALENCE RATIO AND COMBUSTION EFFICIENCY

The CO and total hydrocarbon yields and the combustion efficiency, computed from the energy content of the CO and HC are shown in Figs. 6-5 and 6-6. The fire equivalence ratio by carbon balance from the CO, HC and CO2 is shown in Fig. 6-6b. These results show very high yields of CO and very low combustion efficiencies for the very lean combustion conditions of the smoldering cotton towel fires. These results demonstrate that it is not necessary to have rich combustion conditions in fires to have high CO yields, if the fire temperature is low enough to produce very inefficient combustion.



(a) (b)

Figure 6-5: CO (a) and total hydrocarbon, UHC, (b) yields in g/kg.

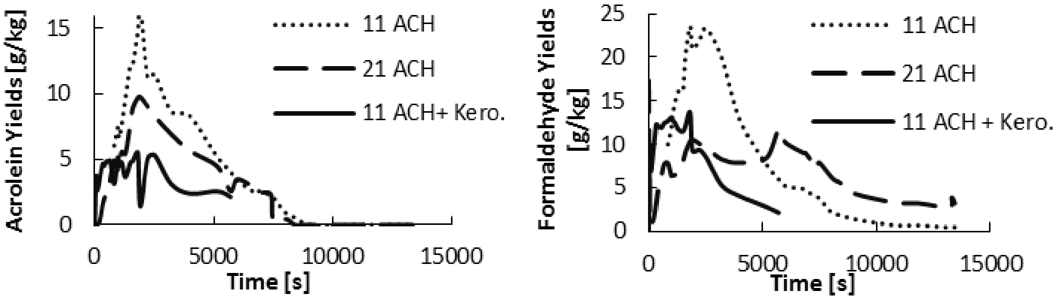


(a) (b)

Figure 6-6: Combustion efficiency from CO and UHC (a) and equivalence ratio (b).

6.3.3 TOXIC YIELDS OF ACROLEIN AND FORMALDEHYDE

The yields of the two major toxic gases in addition to CO are shown in Fig. 6-7. The toxic gases were at a peak in the early stages of the smoldering combustion and CO, formaldehyde and acrolein were the most significant with peak levels of 8000, 500 and 150 ppm respectively at the lower flow rate and 5000, 200 and 100 ppm at the higher ventilation. The toxicity was thus worse at the lower ventilation rates in these smoldering fires and this is also shown in the yield results in Figs. 6-5(a) and 6-7. These results also show that with 200g of kerosene accelerant at 11 ACH the toxic emissions were lower than for the low accelerant fire. These lower yields of CO, acrolein and formaldehyde in these fires were considered to be due to their higher fire temperatures.

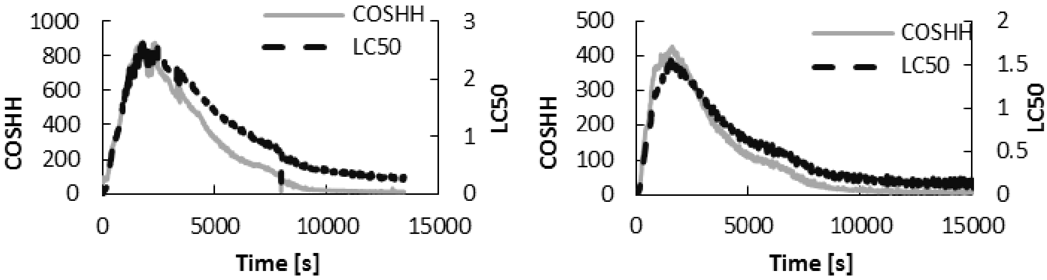


(a) (b)

Figure 6-7: Toxic yields g/kg Vs time for acrolein (a) and formaldehyde (b).

6.3.5 TOTAL TOXICITY N RATIO FOR COSHH$_{15MIN}$ AND LC$_{50}$

The total N was determined by taking the ratio n of the FTIR measured individual toxic gas and dividing by either the COSHH$_{15min}$ or 30 minutes LC$_{50}$ concentration. For all 30 toxic gases measured by the FTIR the individual n values were summated to give the total N ratio and these are shown in Fig. 6-8 as a function of time, for the fires started with a small amount of ethanol accelerant. The results show that the variation of N with time is very similar for the COSHH$_{15min}$ and LC$_{50}$ toxic assessments. Lethal levels of 30 minute exposure toxicity (LC$_{50}$ $N>1$) were produced in these low temperature smoldering fires from 10 to 100 minutes from the start of the fire and the COSHH$_{15min}$ toxicity levels indicate that escape would be impaired for the entire duration of the fire. As these smoldering fires lasted over 3 hours and were only limited by the initial 2kg load of cotton towels, it is clear there would be time for death to occur for anyone in a room under these smoldering combustion conditions. However, the dilution required to prevent 30 minute LC$_{50}$ exposure levels from being lethal was relatively low at about 3 and hence only people close to the source of this fire would be at risk of death. Impairment of escape would be a much more significant effect of these toxic gases when they leaked from the smoldering fire room, as dilution by over 100 would be required before these gases did not impair escape.



(a) (b)

Figure 6-8: Comparison of the total toxicity N for COSHH15min and LC50 for 11 ACH (a) and 21 ACH (b) for 20g of ethanol as the fire initiator.

Figure 6-8 shows a very significant influence of the smoldering fire ventilation on toxicity with the lower ventilation rate of 11 ACH having about twice the peak toxic N to that for 21 ACH. This was mainly due to higher acrolein and formaldehyde yields, as shown in Fig. 7 and higher CO yield, as shown in Fig. 6-5b. Fig. 9 shows similar peak toxicity N of about 850 as for the tests with a much smaller quantity of accelerant. Also the time when the peak toxicity occurred was different for $COSHH_{15min}$ and LC_{50}, whereas in Fig. 6-8 the two peak Ns were very similar and peak at the same time. This was mainly due to earlier generation of peak acrolein and formaldehyde, as shown in Fig. 6-7. There was no change in the time at which peak CO occurred and this is why the $COSHH_{15min}$ peak N occurred sooner. It is considered that the 200^{o}C fire compartment temperature in this period, compared with 100^{o}C for the small ethanol accelerant, was responsible for the higher aldehyde production.

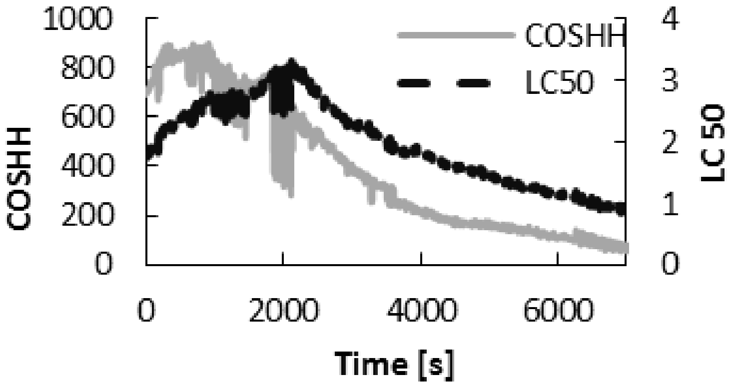


Figure 6-9: Toxicity N for COSHH15min and LC50 for 11ACH with 0.2 kg of kerosene as an accelerant.

6.1.1 MAJOR CONTRIBUTING GASES TO THE TOTAL TOXICITY N

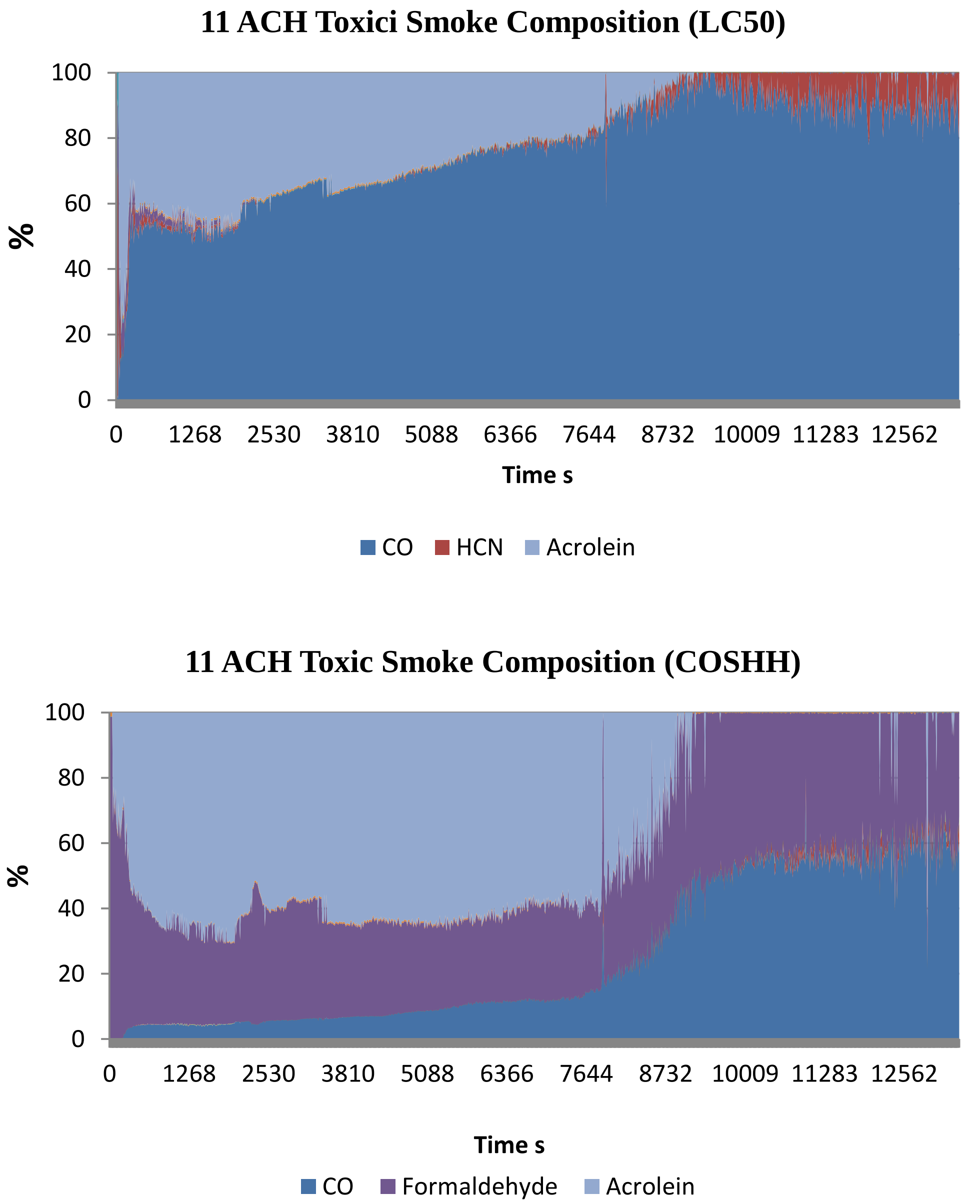
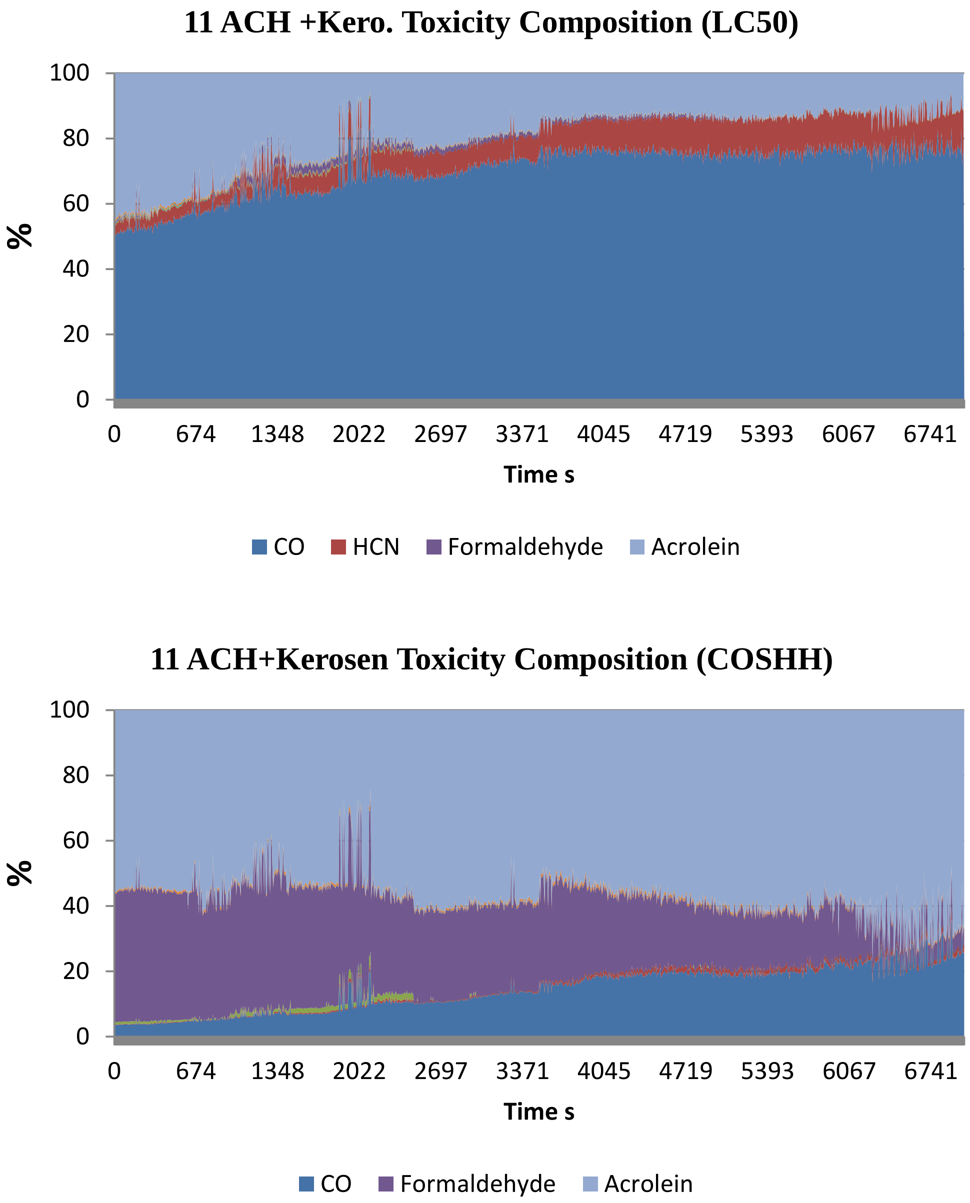
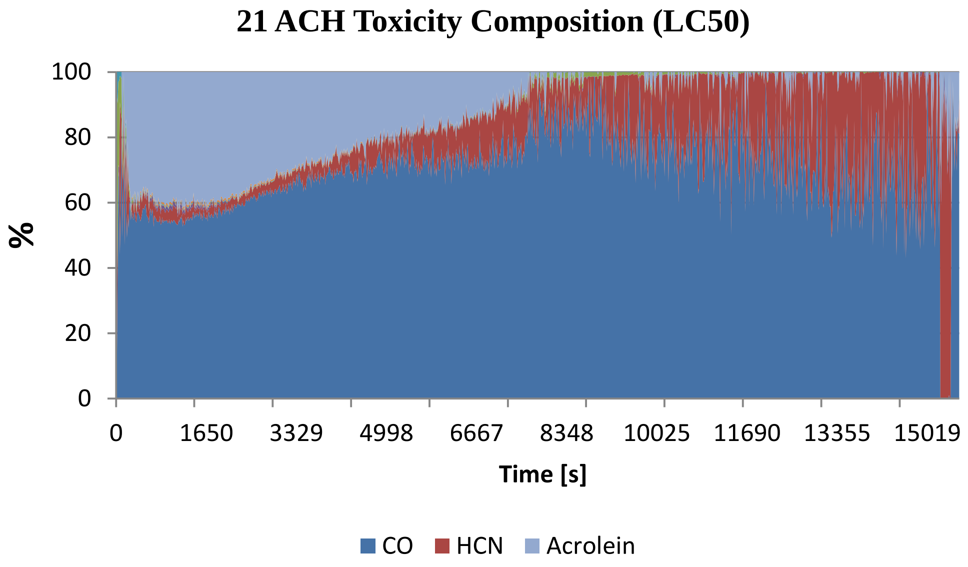
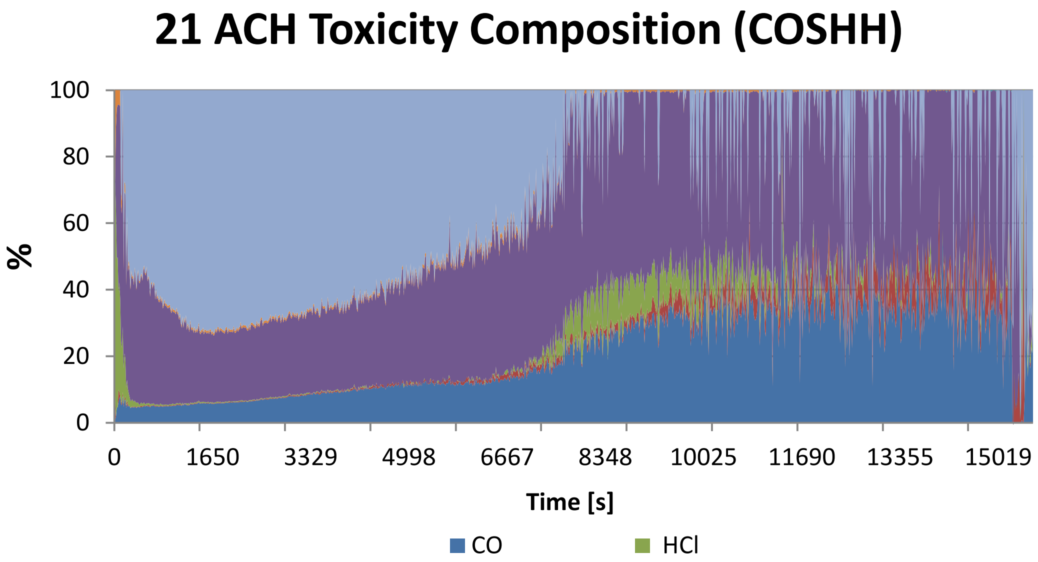


Figure 6-10: Percentage contribution to total N for 11ACH with 20g ethanol accelerant for COSHH15min (a) and LC50 (b).



6-11 : Percentage contribution to total N for 11ACH with Kerosene accelerant for COSHH15min (a) and LC50 (b).





6-12 Percentage contribution to total N for 11ACH with 20g ethanol accelerant for COSHH15min (a) and LC50 (b).

Figures 6-10 to 6-12, show that, for 11ACH with low accelerant use, on an LC_{50} basis CO was the most important toxic gas and was 50% of the toxicity in the early stages of smoldering combustion and 80% in the later stages. Acrolein was the next most significant toxic species accounting for 40% of the total toxicity in the early stages of smoldering combustion. However, on a COSHH 15 min. basis acrolein was the most important toxic gas accounting for 60% of the toxicity in the early stages of smoldering combustion, with no contribution after 9000s when the temperatures were lower temperatures. However, formaldehyde then increased from 30% of the total toxicity in the early stages of smoldering combustion and increasing to 50% in the later stages. CO was only a 10% contribution to total toxicity in the early stages, but was 50% in the later stages. This was the case for both ventilation rates. For all the fires the three dominant toxic gases were CO, acrolein and formaldehyde. Acrolein was the main toxic gas that would impair the means of escape, but CO levels were sufficient to cause death.

6.4 CONCLUSIONS

- Smoldering folded cotton towel fires in a closed compartment with 11 and 21ACH ventilation were investigated. The test conditions simulated scenarios relating to the Rose Park Nursing home fire where 14 people died from toxic gases with a fire that did not spread from the compartment.
- The smoldering fires burnt at low compartment temperatures of 100^{o}C peak temperature and the fires continued for several hours. Previous work with 1/3 of the cotton loading lasted 1/3 the time of these fires and hence it may be concluded that the duration of smoldering fires is proportional to the fire load.
- The combustion efficiency of the fires was very low, due to the low temperatures, which resulted in a major difference in oxygen and mass loss based HRR.
- All the fires burnt very lean and high CO emissions were due to inefficient low temperature combustion and not to equilibrium CO. It is thus possible to generate high CO levels without having rich burning high temperature fire [6].
- Acrolein and formaldehyde were the dominant toxic gases in addition to CO. The ventilation level had a major impact on the total toxicity and the reduction from 21 to 11 ACH increased the peak total toxic N by a factor of 2 and it would be expected that lower ventilation rates would increase the toxicity further.

7. CHAPTER 7: ACRYLIC CURTAINS

This chapter is based on the following publication:

Aljumaiah, O., G. E. Andrews, Alqahtani, B. Husain, P. Singh and H. N. Phylaktou,(*2010b)*, Air Starved Acrylic Curtain Fire Toxic Gases using an FTIR, In *Proceedings of the Sixth International Seminar on Fire and Explosion Hazards, Leeds,* edited by D. Bradley, G. Makhviladze and V. Molkov, 2011, Research Publishing Services, ISBN: 978-981-08-7724-8, DOI: 10.3850/978-981-08-7724-8_11-08.

ABSTRACT

Fire retarded acrylic curtains are a significant fire load in many domestic and hotel fires and give rise to the release of the toxic gas HCN, in addition to other irritant and acidic gases. This work studied the toxic gases from acrylic curtain fires in a 1.6 m^3 compartment fire with controlled ventilation at 5-37 air changes per hour (ACH). The fires were initiated by a small 10g pool fire of ethanol and the pool ignition was at the bottom of the curtains. The fire spread was rapid and peak mean compartment temperatures were 350-500^{o}C depending on the ACH. Peak HRR increased from 6 to 50 kW as the ventilation increased. All the fires generated rich equivalence ratios of between 1.5 and 2.5 depending on the ACH. Toxic products were analysed using FTIR and peak CO yields were 0.15 with 0.026 for HCN, 0.045 for formaldehyde and 0.01 for acrolein. The LC_{50} total toxicity peak was 45, indicating extremely toxic conditions for air starved acrylic curtain fires. The peak yields were similar to those for rich mixtures in tube furnaces with N containing polymers such as polyamides.

7.1 INTRODUCTION

The effect of toxic smoke can be lethal (National Statistics, 2010; Purser, 2002; USFA, 2005; USFA, 2011) and this is normally measured by the LC_{50} toxic limits (Babrauskas et al., 1998; Levin, 1996; Purser, 2002) for 50% deaths after 30 minutes exposure. However, toxic gases are often described by survivors of fires as acidic and/or irritant gases and these slow the movement of people and can lead indirectly to their death [1]. CO is the most common gas that kills people in fires, but this is has no odour or irritant effect on people. (Andrews et al., 2007; Andrews et al., 2005b; Andrews et al., 2005a)have used COSHH 15 min exposure standards (HSE, 2005) as well as LC_{50} to access fire toxicity. COSHH is the European standard for occupational exposure limits, which are similar to the equivalent US limits. These COSHH 15 min levels represent no harm and hence no impairment of the means of escape, whereas the LC_{50} limits are for 50% people dying in a fire. In between these there are limits whereby escape is impaired (Purser, 2002). The USA has introduced the Acute Exposure Guideline Levels (AEGL) with three exposure levels: 1 for non-disabling and essentially similar to the COSHH 15 min levels; 2 for disabling and impairment of escape; and 3 for life threatening health effects and are similar to LC_{50}. The COSHH limits have been largely ignored in fire toxicity, apart from in the work of the Andrews et al., but are the best data set for assessing multi-component toxicity with a legally agreed methodology, which is similar to the LC_{50} N-gas method.

The various assessment methods of fire toxic gases are compared in Table 7-1. The ratios of the LC50 to impairment of escape limits are not consistent. For the LC_{50} to $COSHH_{15}$ limits the ratios are again not consistent and vary by a factor close to 100. In applying the toxic concentrations in Table 1 to the complex mixtures of toxic gases from fires the combined toxicity will be different for LC_{50} than for the three methods of assessing the impairment of escape, because there is no consistency in the relative toxicities. LC_{50} will always place a greater relative emphasis on CO and $COSHH_{15}$ will always place a greater relative emphasis on acrolein and AEGL-2 is in agreement with this assessment of a much greater toxicity associated with acrolein than is given in LC_{50}. This means that the gas concentrations that control death are quite different from those that impair escape. The AEGL-2 escape impairment limits in Table 1 are in most cases similar to $COSHH_{15}$, but for benzene and HCl there are large differences. Formic acid is a highly irritant gas but there is no impairment of escape concentration information or LC_{50} data, but the COSHH limits of 5ppm indicate a significant potential impact on impairment of escape.

Table 7-1: Summarised toxicity assesment limits related to acrylic curtains tests.

Toxic Gas	**15 Min Exposure Limit COSHH**	**AEGL-2 10 min. Escape Impairment**	**Purser Impairment of Escape.**	**LC_{50} 30 min**	**LC_{50} /Impair**	**LC_{50}/ AEGL -2**	**LC_{50}/ $COSHH_{15}$**
CO	200	420		3,000		17	15
NO_2	5	20	70	350	5	17.5	70
HCN	10	17]		135		8	13.5
C_6H_6	3	2000		10.000		5	3333
CH_2O	2	14	6	250	42	18	125
C_3H_5O	0.3	0.44	4	135	34	307	1000
CH_2O_2	5						
SO_2	5	0.75	24	500	20.8	667	100
HCl	5	100	200	3,700	18.5	370	740

Most current information on toxic gases in fires has been obtained from well ventilated compartment fires that simulate room fires with an open door or window or are freely ventilated fires such as in the Cone Calorimeter. Information on fire toxicity has also been obtained by simulating the fire equivalence ratio in a tube furnace (BS-7990, 2003).This has the problem that the fire temperature is separated from the fire equivalence ratio and this is not how real fires behave. In a closed room fire compartment with fire resistance walls, floor and ceiling, a closed fire door and closed double glazed windows, the air ventilation of the fire is very low and this was simulated in the present work. Acrylic curtain fires were studied and HCN will be shown to be a major toxic gas in addition to CO and other irritant and acid gases (Ferrari et al., 2001) showed that HCN was as lethal as CO in most fire victims.

7.2 EXPERIMENTAL TECHNIQUE

Acrylic curtains are a common domestic fire load which gives rise to rapid fire spread. Commercial acrylic curtains were used with cotton lining (38% cotton, 62% acrylic by mass). Four identical 1.4 kg curtains were burned at different ventilation rates simulating 5, 11, 21, 37 air changes per hour. The fire load was 1.04 kg/m^2 which is a relatively lightly loaded compartment fire. The curtains were folded over a hanger and the fire mass consumption rate was determined by oxygen consumption calorimetry. The elemental composition was COHN and an elemental analyser was used to determine this composition, as detailed in Table 7-2. The curtains were fire retarded and the methods used decrease volatile formation and increase char production(Horrocks, 2001). For acrylic materials the fire retardant usually involves a halogenated comonomer with antimony compounds (Horrocks, 2001).

Table 7-2: Elemental analysis of the acrylic curtains.

Curtain Composition		**C %**	**O %**	**H %**	**N %**	**Elemental Formula**	**Stoich. A/F**	**CV MJ/kg**
Acrylic	62%	62.73	4.94	4.57	28.06	$CH_{1.1}O_{0.3}N_{0.27}$	6.7	28
Cotton	38%	42.93	5.44	51.22	0.41			18
Weighted average		55.2	22.3	5.1	17.6	100		24.2

A 1.56 m^3 enclosed fire compartment was used as described in section 3.1.1.1. A fixed air ventilation rate for each fire and this was set to achieve 5-37 air changes per hour (ACH). The air was fed into a plenum chamber under the compartment and fed into the fire compartment through four slots at the edge of the compartment. The fire gases flowed along the flat metal ceiling to exit the compartment along the edges through a small gap between the edge of the ceiling and the compartment walls. The fire products then flowed along the rear of the ceiling to exit through a 150mm diameter short pipe discharge. The gas samples were taken from here and were assumed to be well mixed and to represent the mean composition of the ceiling gases. The compartment had horizontal and vertical thermocouples arrays to determine the fire compartment mean ceiling temperature. The compartment had a high temperature glass door that was closed immediately after the methanol was ignited. The initial stages of the fire development could be photographed through the window, but this soon became covered in soot and an outer cover was closed to prevent radiative heat loss.

The curtains were folded on an 80 cm high beam. 10 mg of methanol in a 50mm diameter pool was used as an accelerant. The accelerant was placed next to one of the curtains sides on the inside void of the folded curtains. The curtain arrangement before the fire is shown in Fig. 7-1 and the appearance of the curtains at the end of the fires is also shown in Fig. 7-1. This shows that the completeness of burning of the curtains increased as the ventilation increased. At the lowest ventilation of 5.6 ACH the curtain was only partially burned, with some original curtain material remaining. The fire debris after the test was weighed to determine the total mass of curtain burned in the fire and this increased from 0.72 kg at 5.6 ACH to 1.0 kg at 37 ACH, which is 51% and 71% of the fire initial load respectively. The action of the fire retardant was to produce a char that burned very slowly and the char still had the form of the original curtains at the end of the test, as shown in Fig. 7-1.

Figure 7-1: Pictures of the curtain set up, ignition, debris after the four fires.

Raw fire ceiling gases were sampled via 190°C heated sample lines and passed to a heated filter and pump and then to a heated FID for total hydrocarbon analysis, a heated chemiluminescence NOx analyser and through a 2^0C condenser to NDIR analysers for CO and CO_2 and a paramagnetic analyser for oxygen. A heated TEMET GASMET CR-Series portable FTIR was also used for acidic and irritant toxic gas analysis. This had a separate heated line, filter and pump and the FTIR sample cell was also heated so all analysis was on a hot wet basis. The FTIR was calibrated for over 50 species, including most of the toxic gases of interest in fire toxicity. Only HBr was missing from the calibration and thus the use of bromine based fire retardants could not be detected from the presence of HBr. The FTIR had a liquid nitrogen cooled detector and this gave at least 2 ppm resolution on all species.

7.3 RESULTS

7.3.1 FIRE TEMPERATURE

Average upper layer temperatures are shown in Fig. 7-2. There was a sudden increase in temperature after the first 100 seconds representing the fire propagation through the folded curtains. The 21 ACH test reached the highest temperature at about 500°C, followed by the highest ventilation of 37 ACH, where the mean ceiling temperature reached 480°C. The 5 ACH test had the lowest recorded temperature mainly due to the insufficient air feed and fire self extinguishment occurred just after the peak HRR and minimum oxygen condition. The unstable burning at 11 ACH, shown in Fig. 7-2, was due to near extinguishment followed by re-ignition.

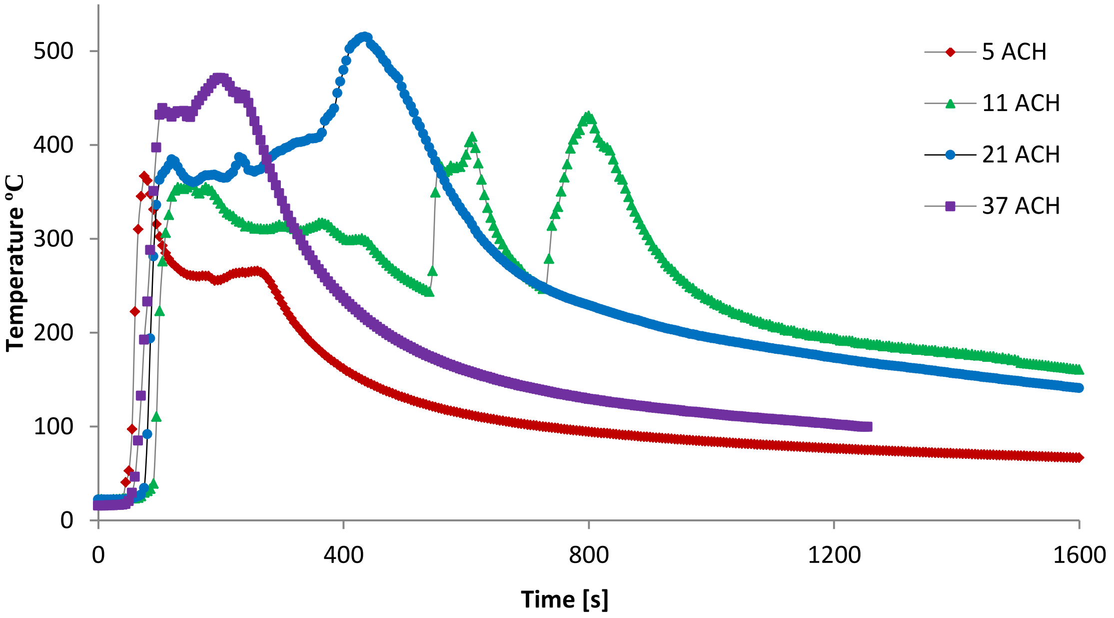


Figure 7-2average upper layer tempera rue as a function of the fire duration.

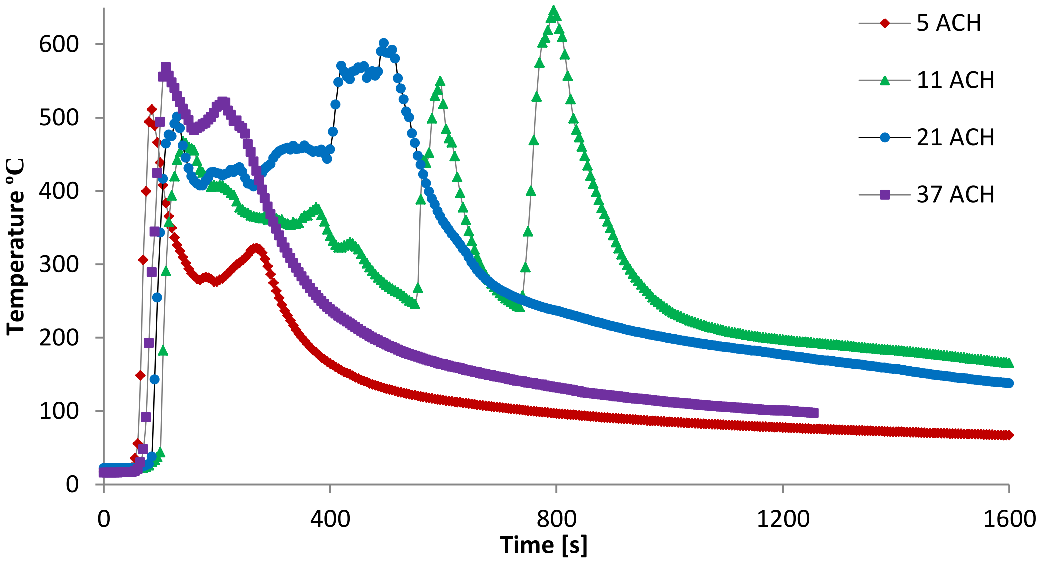


Figure 7-3: The temperature directly above the fire load as a function of time.

The temperature just above the the curtains are shown in Fig. 7-3 and showed relatively higher temperatures than for the mean ceiling layer temperature, with the same general characteristics as in Fig. 7-2. Fig. 7-3 shows the 21 ACH test to have temperatures approaching 600°C while the highest ventilation test of 37 ACH peaked at 560°C. This is close to flash over conditions from just one fire retarded acrylic curtain for a compartment fire load that is less than in most domestic room fires.

7.3.2 OXYGEN DEPLETION AND HEAT RELEASE RATE (HRR)

The oxygen depletion is shown in Fig. 7-4 and the heat release rate (HRR) by oxygen mass consumption is shown in Fig. 7-5. The highest HRR of 50 KW occurred at the highest ventilation. The lower ventilation fires showed longer burning stages with the 11 air changes test lasting the longest at more than 900 s. For 5 ACH the fire was self extinguished with a substantial proportion of the original curtain material unburned.

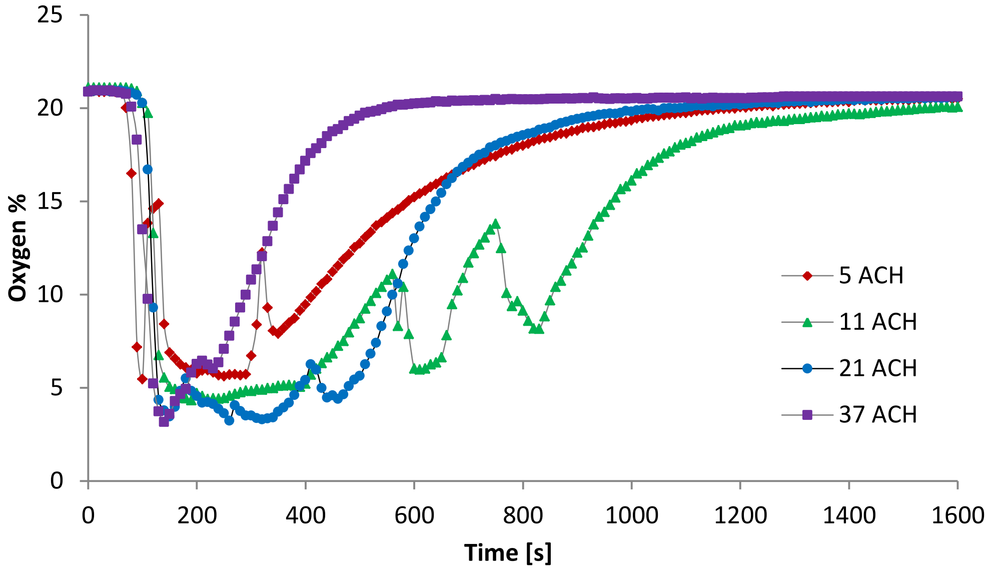


Figure 7-4: Oxygen concentration as a function of time in the four tests.

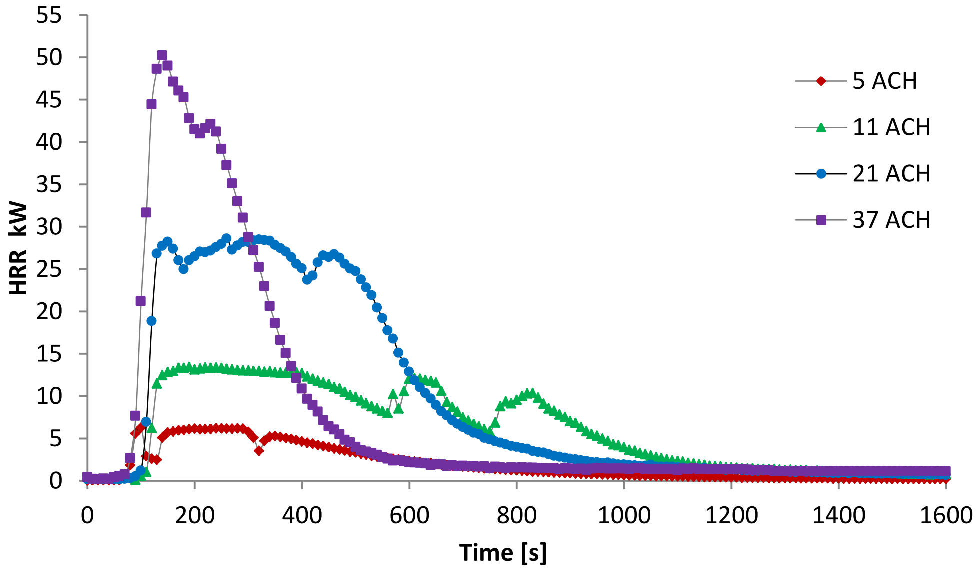


Figure 7-5: Heat release rate as a function of time in the four tests.

7.3.3 EQUIVALENCE RATIO VARIATION WITH TIME

The mean fire equivalence ratio was computed by carbon balance from the raw ceiling layer gas composition (Chan, 1996). The CO, total unburnt hydrocarbons (THC) and the CO_2 analysis were all required as part of the computation, as well as the elemental composition of the fire load given above. The mean ceiling layer equivalence ratio in the acrylic curtain fires are shown as a function of time in Fig. 7-6.

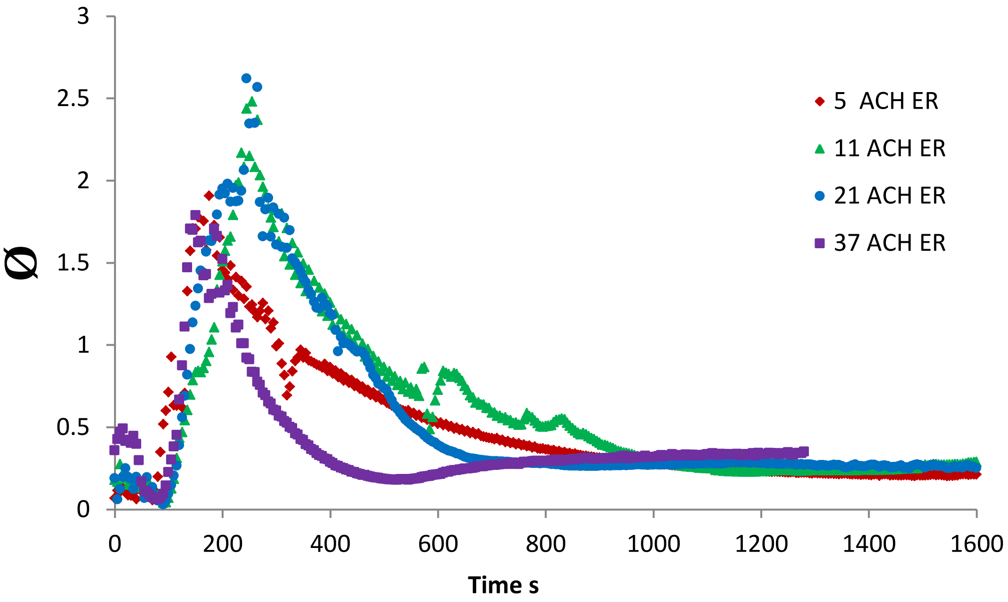


Figure 7-6 mean ceiling layer equivalence ratio as function of time.

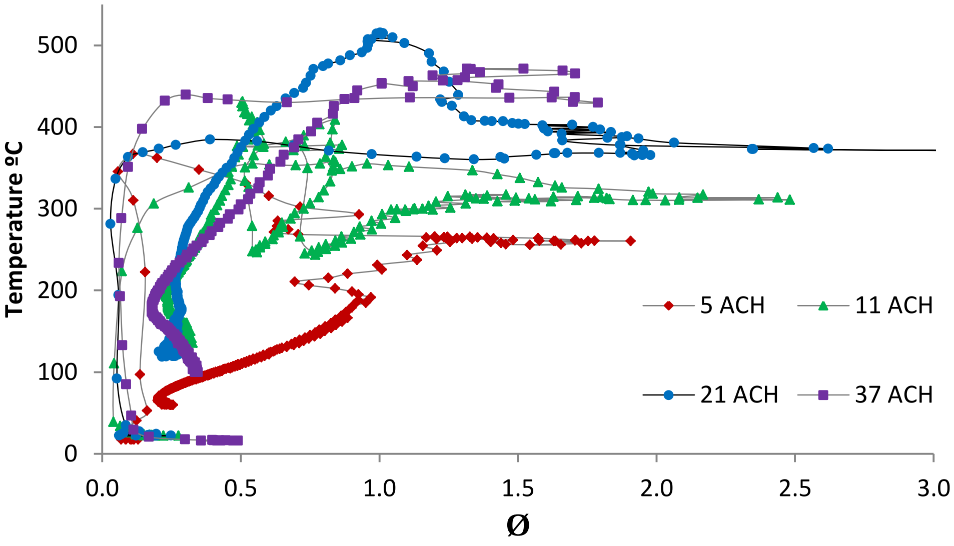


Figure 7-7: mean ceiling layer fire temperature as a function of equivalence ratio.

This shows that all the fires, after a slow ignition phase, had a rapid flame development leading to rich combustion. This was due to rapid combustion of the cotton lining and combustion of volatiles released from the acrylic curtains, which melt at >220°C and pyrolyse at 290^{o}C (Horrocks, 2001). The period for which the fire was rich was greatest for the 11 and 21 ACH tests and the toxicity of these tests is examined in detail. There was a later slower lean combustion phase, which was the char burn out phase of the fire. All the HRRs were below 10 KW in this slow char burning phase of the fire, when the ceiling layer was 100-200^{o}C. The highest air flow of 37 ACH had the least period of rich combustion and the decay period of the fire was longer and all in the lean region, which gave more rapid char burn out.

A surprising feature of the results was that the extensive rich periods in the fire were accompanied by significant oxygen levels of about 4%, as shown in Fig. 7-4. The reason was that the CO and THC levels were so high that the combustion inefficiency was high, as detailed later, and all the oxygen had not been consumed in the fire. The mean ceiling fire temperature is shown as a function of equivalence ratio in Fig.8. This shows a rapid increase in temperature during the initial lean combustion, then a period of relative stable peak temperature across a wide range of equivalence ratios and finally a decay in temperature. There were lower temperatures for the same overall Ø in the fire decay char combustion region. For 21 ACH the peak temperature occurred for near stoichiometric mixtures and declined for rich mixtures. These results show that for the same equivalence ratio there were times when the fire temperature was different and this controlled the toxic emissions from the fire.

7.3.4 CO AND UHC YIELDS AND THE COMBUSTION INEFFICIENCY

The CO yields are shown as a function of time and equivalence ratio in Figs. 7-8 and 7-9. The initial stages of the fire had lower CO than the later stages, for the same equivalence ratio. This was due to char burning (Horrocks, 2001) in the later stages producing more CO than from the volatile burning in the early stages of the fire, for the same temperature. The total unburnt hydrocarbon (UHC) yields are shown in Figs. 7-10 and 7-11. These are much higher in the initial volatile burning phase and lower in the char burning phase. The combustion efficiency results, which are computed from the energy content of the CO and UHC, are shown in Figs. 7-12 and 7-1314. Very inefficient combustion occurred for all rich mixtures and this depressed the HRR. In the lean burning char burn out region combustion efficiencies were higher, even though the HRR was low, as shown in Fig. 7-5.

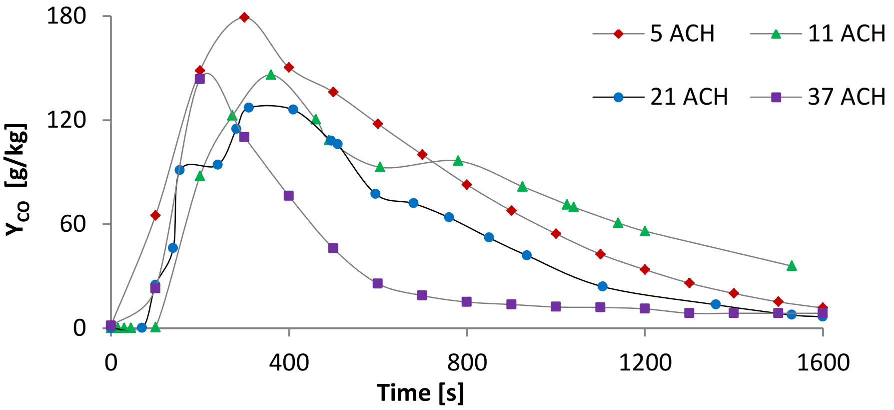


Figure 7-8: CO yield against time.

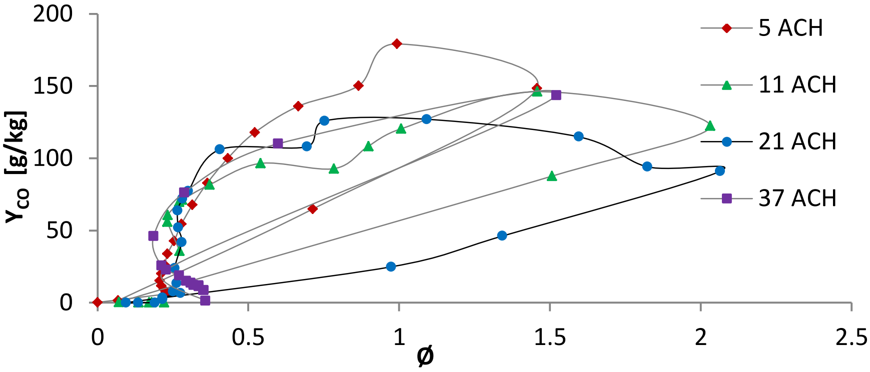


Figure 7-9: CO yields against fire equivalence ratio.

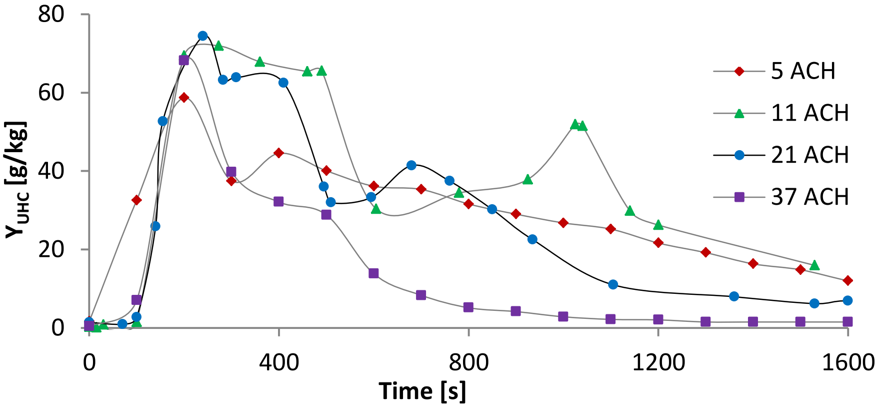


Figure 7-10: UHC yields against time.

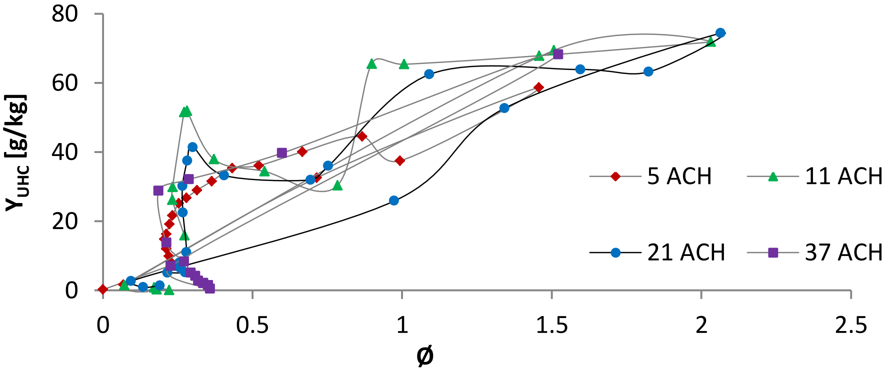


Figure 7-11: UHC yield v. equivalence ratio.

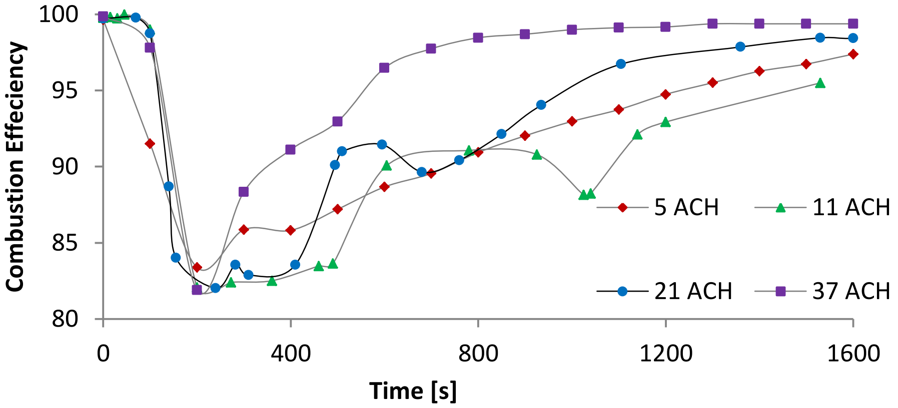


Figure 7-12: Combustion efficiency v. time

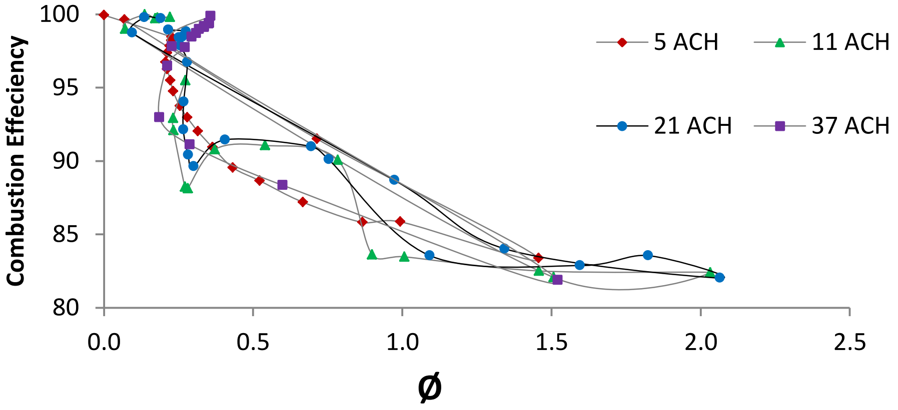


Figure 7-13: Combustion efficiency v. equivalence ratio.

7.3.5 TOXIC GAS YIELDS AND THEIR VARIATION WITH EQUIVALENCE RATIO

The dominant toxic gases were HCN, acrolein and formaldehyde. Their variation with time in the fire and with the fire equivalence ratio are shown in Figs 7-14 to 7-19 for 11 and 21 ACH. The HCN peaks in the volatile burning phase of the fire, but continues to be generated through the char burning phase. This shows that there is a continuous generation of HCN through the fire. The peak HCN yield occurs for rich mixtures and hence correlates well with the CO yields. There was still an influence of the fire temperature, with low CO and HCN for the higher temperatures early in the fire at the same equivalence ratio as later in the fire, when temperatures were lower.

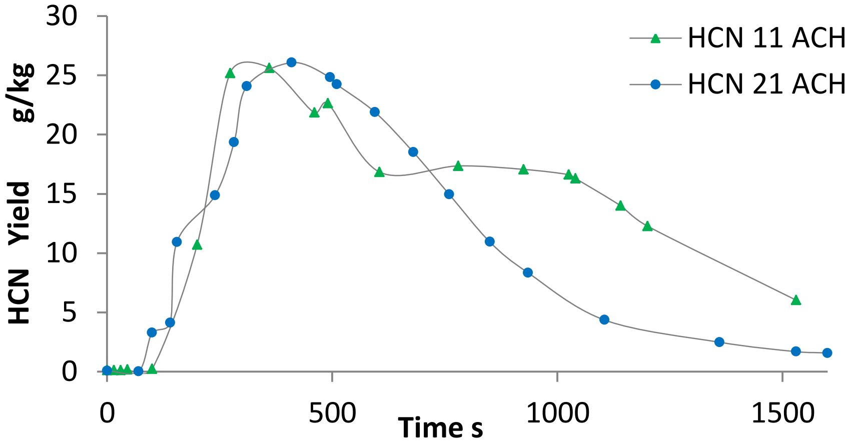


Figure 7-14: HCN yield v time from start of fire.

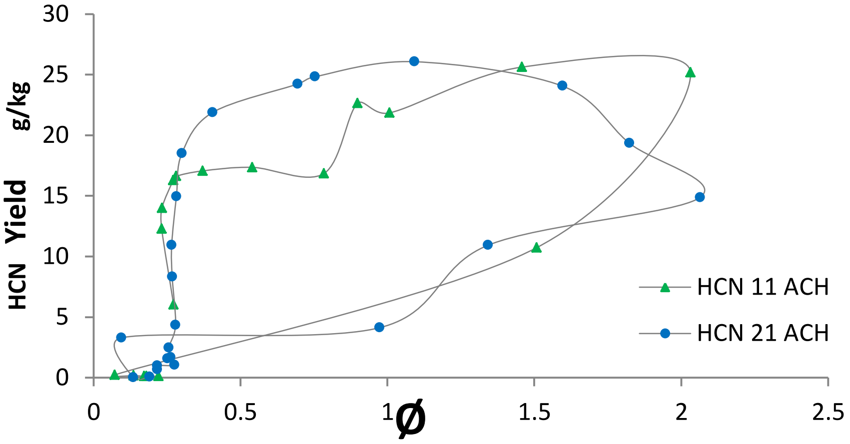


Figure 7-15: HCN yield v. equivalence ratio.

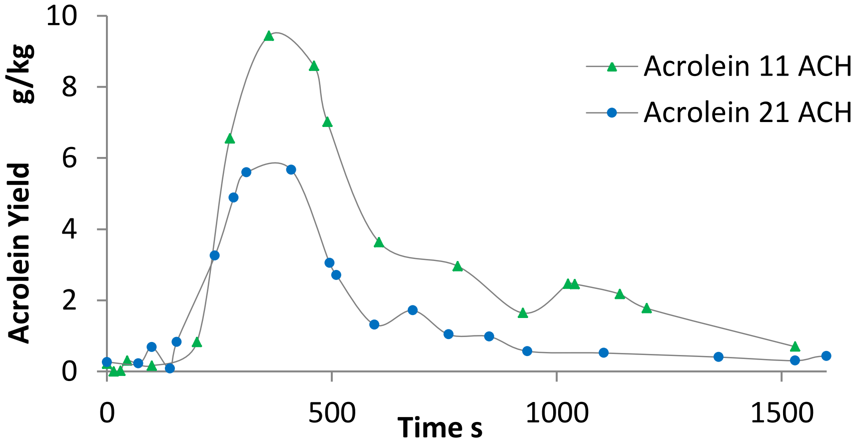


Figure 7-16: Acrolein yield v. time from start of fire.

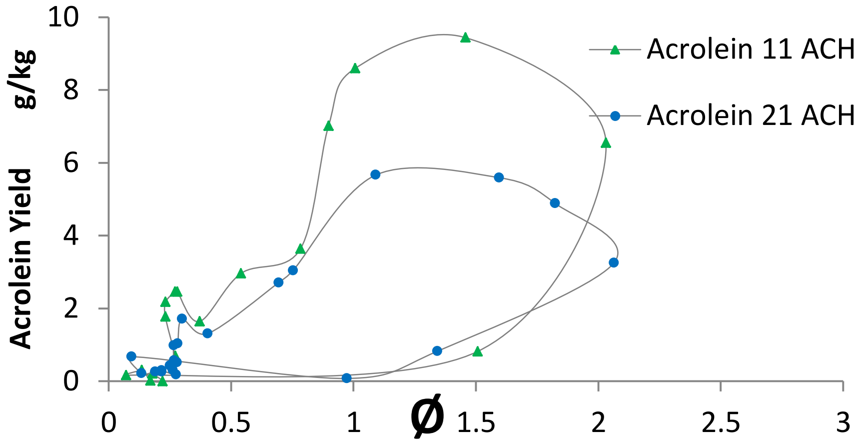


Figure 7-17: Acrolein v. equivalence ratio.

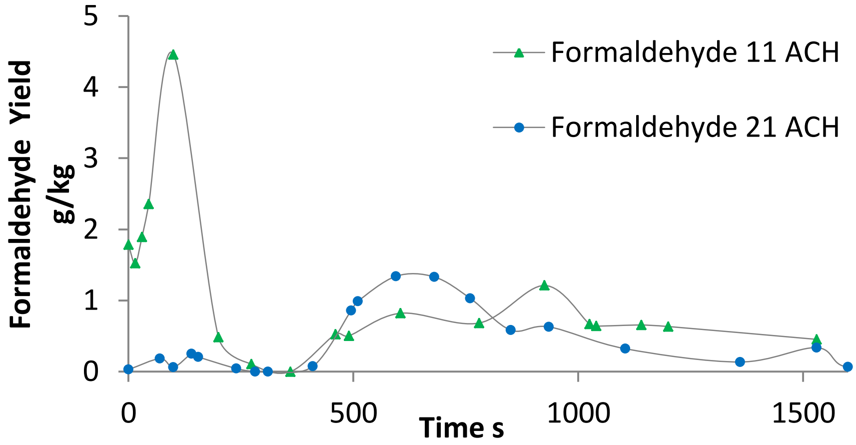


Figure 7-18: Formaldehyde yield v. time.

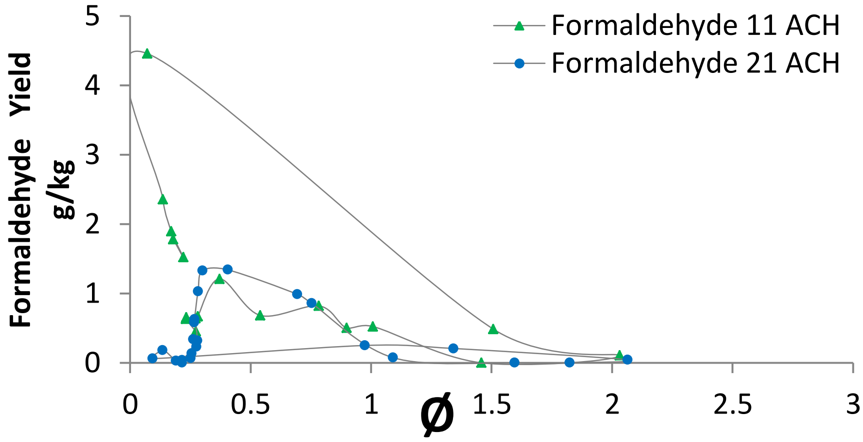


Figure 7-19: Formaldehyde yield vs equivalence ratio.

The organic nitrogen in the acrylic part of the curtains gives rise to the production of HCN. The peak yield was 26 g/kg and in concentration was 6-7,000 ppm. The present fire load was only 62% by mass acrylic and the rest was the cotton lining. As all the HCN can be considered to originate from the fuel bound nitrogen in the acrylic portion of the curtain, then the yield of HCN from the acrylic should be increased to 42 g/kg. This peak yield is compared in Table 2 with that in other work on fire toxicity for fire loads with organically bound nitrogen, such as nylon or polyurethane (PU). Table 7-3 shows that the present results are towards the higher end of the published range and only the Purser tube furnace results ,at an equivalence ratio of 2.0, are higher at 66 g/kg for polyamide. The difference in the present results was the high HCN yield for lean Ø, which was not found by Blomqvist or Hull. The associated CO yields in the work of Blomqvist were a peak of about 80 compared with 120-200 in the present work. The presence of the 100KW burner in the ISO9705 room fire test, used by Blomqvist, results in higher fire temperatures.

Table 7-3: Comparison of published HCN yields in fires.

Source	**Test Method**	**Material**	**Peak HCN Yield g/kg**	**CO g/kg**	**Ø**
This work	1.6 m^3 Room	Acrylic	42	120-200	1.5-2
(Blomqvist, 2005)	ISO9750 Room	Nylon 66 6.3% Fuel N	35	80	1.2
(Babrauskas et al., 1991a)	NBS Cup	Rigid PU	18		
	Cone Cal.	Rigid PU	4.5		
	ISO9750 Room	Rigid PU	10	120	
(Gann et al., 2010)	Furniture Calorimeter	Sofa	15	51	
		Book Case	2.5	46	
		Electric Cable	4	15	
(Duquesne et al., 2000)	Purser Tube Furnace	PU	14	250	
(Hull, 2010)	Cone Calorimeter	Polyamide 6.6	5		
	ISO9750 Room	Polyamide 6.6	35		1.2
	Purser Tube Furnace	Polyamide 6.6	65		2.0
	Purser Tube Furnace	Polyamide 6.6	<1		<1.0
(Horrocks, 2001)	NBS Cup	PU foam	1.7		
	NBS Cup	PU foam fire retarded	5.2		

Table 7-3 shows that the freely ventilated fires used in cone calorimeters, furniture calorimeters and the NBS cupe method all give low HCN yields, which are unrealistic for real fires as the rich mixtures necessary to generate conversion of fuel N to HCN are not present. Fire confinement is required to generate the rich condition for HCN formation.

7.3.6 TOTAL TOXICITY N AND THE MAIN TOXIC GASES

The toxic gas concentration was divided by the LC50 limit and the COSHH limits and their sum made the overall toxicity, N. The two total toxic N values for LC_{50} and $COSHH_{15min}$ are compared in Figs 22 and 23 for 11 and 21 ACH respectively. These results show the same shape for the time dependence of the toxicity, thus the two toxic assessment methods identify the same stage in the fire as the most toxic and this is close to the time for peak HCN and acrolein yields. Figs 24-27 show the relative contribution to the total toxicity on an LC_{50} and $COSHH_{15min}$ basis for 11 and 21 ACH. These show that on an LC_{50} basis HCN was the dominant threat, accounting for almost 70% of N. CO had almost 20% of N and acrolein was most of the remaining toxicity. For COSHH based N the dominant toxicity was from acrolein with HCN the next most important and then CO. Formaldehyde was important at the start of the fires but had only a small contribution to the total N for the rest of the fire time.

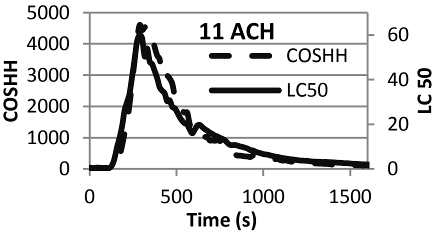


Fig. 22 Total toxicity N for 11 ACH for LC_{50} and $COSHH_{15min}$ toxicity data.

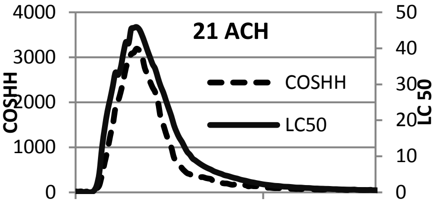


Fig. 23 Total toxicity N for 22 ACH for LC_{50} and $COSHH_{15min}$ toxicity data

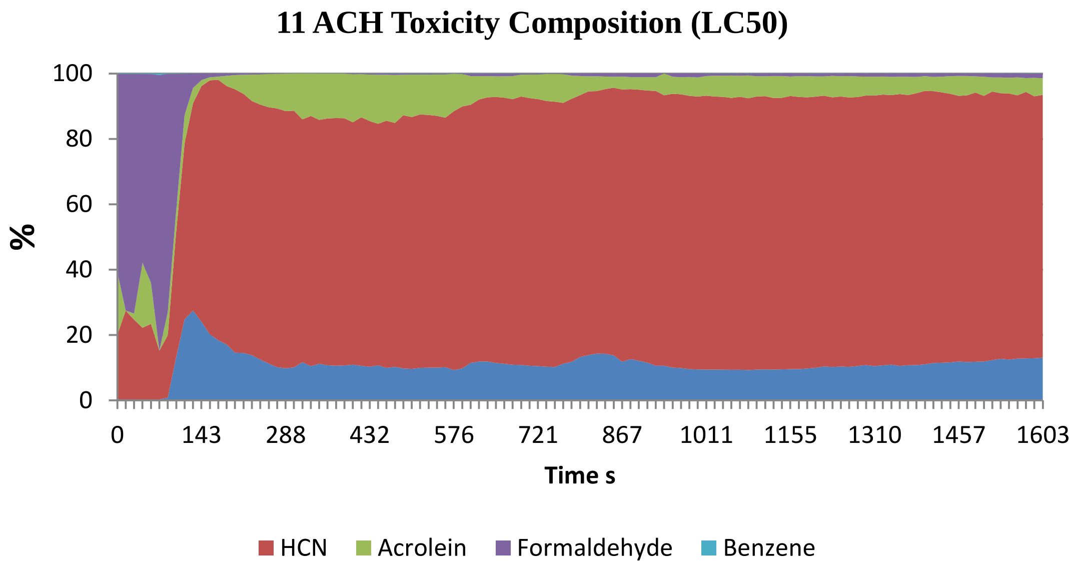


Figure 7-20: LC50 relative toxicity for 11 ACH

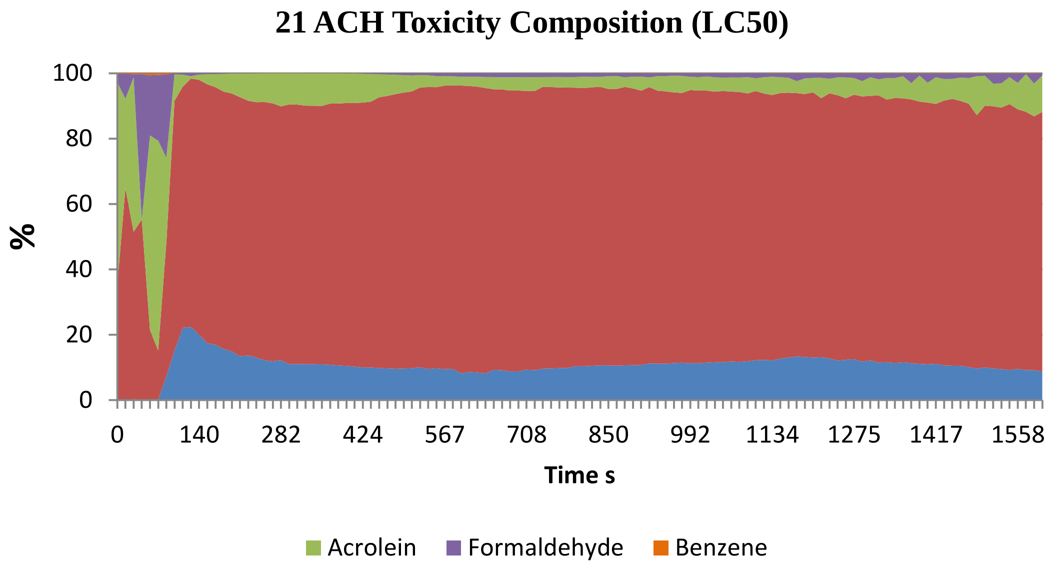


Figure 7-21: LC50 relative toxicity for 21 ACH

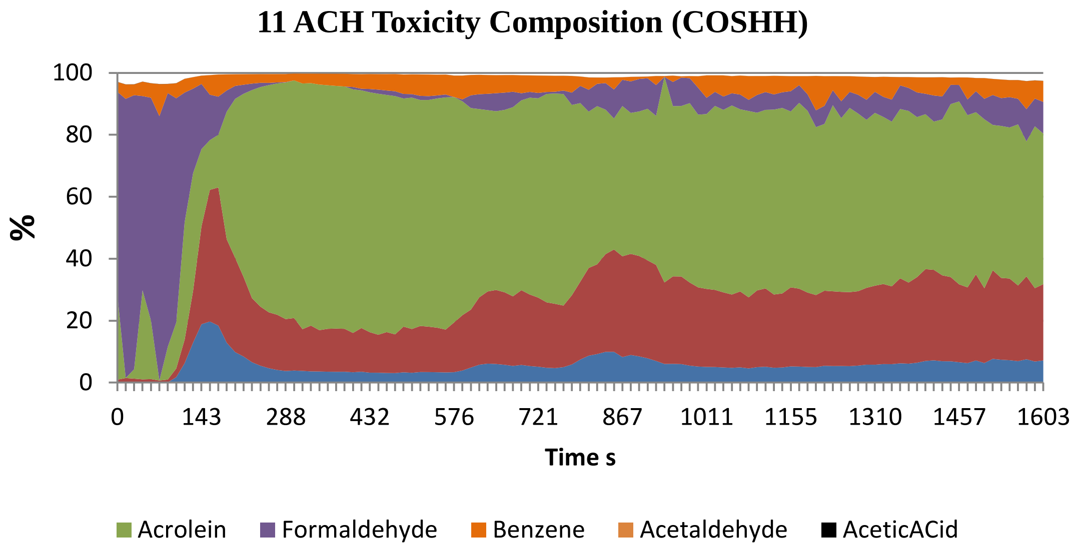


Figure 7-22: COSHH15min relative toxicity for 11 ACH.

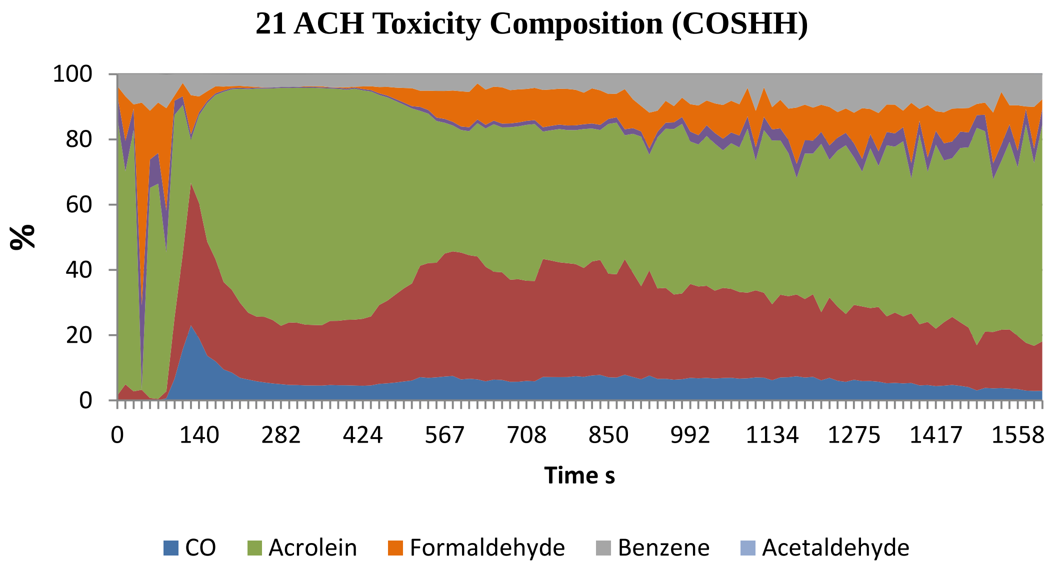


Figure 7-23: COSHH15min relative toxicity for 21 ACH.

The two toxic gas criteria do not have the same relative assessment of toxicity. The ratio of LC_{50} / $COSHH_{15\ min}$ for CO is 15 and for HCN is 13.5, so the relative assessment of the toxicity of these two gases is similar. However, for acrolein the ratio is 1000 and this means that $COSHH_{15min}$ places a much greater emphasis on the presence of acrolein. Thus the two toxic gas assessment methods will give different relative results for which toxic gas is most important. LC_{50} relates to deaths in fires and COSHH to the safe escape from fire with no toxic gas harm. The total N for all the toxic gases under the COSHH limits is a measure of the amount of air entrainment required to occur into the fire gases before they are safe to inhale.

7.4 CONCLUSIONS

Commercial fire retarded acrylic curtains with a cotton lining burn rapidly when ignited by a small pilot flame and in an enclosure with controlled air supply, generates temperatures of up to 500^{o}C. Peak HRR increased from 6 to 50 kW as the ventilation increased form 5 to 37 ACH. All the fires generated rich equivalence ratios of between 1.5 and 2.5 depending on the ACH. Peak CO yields were 0.15 with 0.026 for HCN, 0.045 for formaldehyde and 0.01 for acrolein. The LC50 total toxicity peak was 45, indicating extremely toxic conditions for air starved acrylic curtain fires. The fires showed two stages: a rapid initial combustion of the cotton and volatile release from the acrylic followed by a slow char burn out stage. This resulted in toxic gas yields that were not uniquely correlated by the equivalence ratio. The difference was due to the temperature of the fire in the two phases and this shows that toxic yields are both a function of equivalence ratio and temperature.

8. CHAPTER 8:

HYDROCARBON POOL FIRES

This chapter is based on two publications:

Aljumaiah, O., H. N. Phylaktou, G. E. Andrews, I. Heath and J. Ledger,(*2010d)*, Ghosting Flames in a Low Ventilation Compartment with Kerosene Pool Fires, In *Proceedings of the International Congress Combustion and Fire Dynamics, Santander, Spain,* edited by J. Capote and D. Alvear, 2010, University De Cantabria, ISBN: 978-84-86116-23-1.

Aljumaiah, O., G. E. Andrews, H. N. Phylaktou and A. Jimenez (2011b). "Low Ventilation Pool Fires." Journal of Hazardous Materials

ABSTRACT

Pool fires in low ventilation compartments give rise to ghosting flames and their toxic and particulate emissions were investigated for 400mm square pool fires in a 1.6 m^3 compartment with ventilation of 10.6 air changes per hour or 0.035 kg/m^2s air mass flow rate per pool surface area. This was within the ventilation range which has been shown to give ghosting flames for heptane pool fires (Utiskul et al., 2005). Four liquid fuels were compared: heptane, toluene, kerosene and diesel. The results show that the fires took place with very low combustion efficiency, particularly for kerosene. Rich mixtures were created with relatively low temperatures that produced low soot emissions.

8.1 INTRODUCTION

Hydrocarbon Pool fires are a common petrochemical fire hazard (Chamberlain, 1996), but most work in this area is for freely ventilated pool fires. For pool fires in compartments with a door open and relatively high ventilation, fire temperatures can be in excess of 1000^{o}C with associated high soot emissions (Utiskul et al., 2005). For well ventilated compartment fires (Bundy et al., 2007; Ko et al., 2009) used a small scale compartment of 2m^3 which was very similar in size to that of the present work (1.6 m3) and of (Gottuk, 1992b) who used a 2.2 m^3 compartment to investigate ventilation controlled heptane pool fires. The present 1.6 m^3 compartment was first used by (Andrews et al., 2000b; Andrews et al., 2000a) to study air starved pool fires. (Gottuk, 1992b)also used relatively large ventilation openings and generated rich mixtures with high yields of CO for heptane pool fires, similar to the findings of (Chamberlain, 1996) and (Ko et al, 2009). Apart from the work of (Andrews et al., 2000b; Andrews et al., 2000a) and the more recent work of (Utiskul et al., 2005) the behaviour of pool fires with very restricted ventilation has had limited study. It will be shown in the present work that the fire temperatures and toxic emissions are quite different than well ventilated compartment fires.

(Ko et al., 2009) and (Gottuk, 1992b) have shown for well ventilated compartment heptane and toluene pool fires that rich global fire equivalence ratios occur with CO and soot yields of >0.1 for most of the rich pool fires investigated and peak fire temperatures were also in excess of 1000^{o}C. This is in agreement with the work of (Chamberlain, 1996) even though the test rig was much smaller at 2 m^3 compared with 96 m^3 in the work of (Chamberlain, 1996). It is clear that ventilation controls the compartment temperature and that full scale tests are not necessary to generate the high temperature and high soot conditions of large scale compartment fire tests. This justifies the use of small scale compartments for studying pool fire toxicity.

In contrast to well ventilated compartment pool fires, which have flames attached to the pool in a similar manner to free pool files, pool fires in low ventilation compartments give rise to ghosting flames (Utiskul et al., 2005). 400mm square pool fires were investigated with ventilation restricted to 10 air changes per hour or 0.035 kg/m^{2}s as air mass flow rate per pool surface area. This was mainly within the ventilation range identified by (Utiskul et al., 2005) as that which gave ghosting flames for heptane pool fires. The present work investigated toxic and particulate emissions under these air starved pool fire ghosting flame conditions.

(Andrews et al., 2000b; Andrews et al., 2000a) introduced a ventilation parameter Kin that is the air in leakage equivalent total inlet open area, Av, divided by the cross sectional area of a cubic room of equivalent volume (V) to the test room. They showed that Kin would range from 0.09% to 0.6% if the design guides (10) for passive fire protection and fire doors were followed. They studied Kin of 0, 0.1% and 1% in the same equipment as in the present work. The lowest value of Kin that has been studied prior to this work was 1.32% in the work of (Sugawa, 1991), 1.7% by (Peatross and Beyler, 1997) and 1.9% by (Audiunnin et al., 1997). All of these investigators used pool fires as the fire load and all found ghosting flames occurred.

Ghosting flames are flames detached from the surface of the pool that travel towards the oxygen rich areas and sometimes stabilize near the ventilation vents. (Sugawa, 1991) first reported ghosting flames in his work on poor ventilation compartment fires. Then (Gottuk, 1992b) reported similar phenomena in his work where hexane pool fires were burnt in a compartment with relatively high ventilation and he reported stabilized flames near the exhaust window. More recently, (Utiskul et al., 2005)conducted a study on small pool fires in an enclosure. The ghosting flame regime was related to a fuel mass loss rate ratio to a ventilation parameter (Utiskul et al., 2005) which gave ghosting flames for heptane at from 0.12 – 1 kga/(m^{2}s). They correlated this ventilation parameter against a fuel consumption parameter, the fuel mass consumption rate divided by the pool surface area. Ghosting flames occurred between 5 and 30 gf/(m^{2}s), for free flames the burning rate was 12 gf/(m^{2}s). In this work four different types of hydrocarbon fuels were investigated at 0.035 kga/(m^{2}s), which was below that ghosting flame range of (Utiskul et al., 2005) and in their self-extinction regime. The phenomenon of ghosting flames was investigated for different fuel volatility at very low air ventilation. In addition, an analysis of the fire products including major gas species, soot and particulates was undertaken. In contrast to the ghosting flame regime, compartment pool fires that are well ventilated (Bundy et al., 2007) have burn rates from 19 – 140 g/(sm^2) for heptane and toluene pool fires (Bundy et al., 2007), well above the ghosting flame regime (Utiskul et al., 2005).

8.2 EXPERIMENTAL TECHNIQUES

A 1.56 m^3 enclosed fire test facility, 1.4m x 0.92m x 1.22m, was used, as described in section 3.1.1.1, with separated entrained air inlet at floor level and fire product exit at ceiling level .The compartment was fitted with a Pyrex window for the entire area of the front of the compartment. This was also fitted with an insulated cover door to stop radiative heat losses from the fire. The window observations were used to determine visually the transition to ghosting flames. 400mm square pool fires of Kerosene, Diesel, Heptane, and Toluene pool were investigated. The fire load rested on load cells to determine the mass loss rate. The initial pool fuel mass was 2.4 kg, which gave a depth of 20mm in the 40mm deep 400mm square pan. This fuel mass together with the weight of the pan was higher than the capability of the load cells to measure and no measured fuel mass loss was available in these tests. The fuel mass consumption was derived from the oxygen consumption HRR and the combustion efficiency, as discussed later.

The properties of the four liquid fuels used are summarized in Table 1. Most previous work on pool fires in compartments, apart from the work of Chamberlain, 1996), has used pure hydrocarbons that are very volatile, such as heptane or hexane or toluene [1, 4, 6]. In this work two pure hydrocarbon pool fires are compared with the more common kerosene and diesel pool fires hazards. Volatility is the main difference in the fuels as combustion stoichiometry was very similar at close to 14.6 A/F by mass. The higher specific heat capacity of heptane relative to the other fuels gives a lower temperature rise for a given heat flux from the fire. However, this will be completely offset by the lower boiling point. Heptane and toluene pools will boil in the fire much sooner than kerosene and diesel. This will be shown to be a particular problem with the heptane pool fires which became unstable towards the end of the fires due to the boiling pool.

The forced ventilation air was metered using a thermal mass flow meter and fed through a plenum chamber under the fire enclosure floor, with air admission to the fire chamber through four long slots on the floor at the base of each wall. The four pool fire fuels were compared at 10.6 air changes an hour, which in the present compartment was an air flow rate of 20 kg/hour. This is a low ventilation rate typical of a closed room with door leakage area . The ventilation rate corresponded to a Kin of approximately 0.04%, by calibration of the air flow in fires with varied Kin.

The fire product gases flowed across the ceiling and were exhausted from the fire through four slots around the periphery of the ceiling and then along the rear of the ceiling to an exit of 162mm diameter on the centerline. The gases were well mixed at this point and the gas samples, taken as representative of the fire ceiling product gases, were sampled through heated lines from this discharge duct prior to any dilution with ambient air. After the discharge duct the gases were diluted with entrained ambient air in a large discharge cowl that fed a vertical flue with an extract fan for discharge through the test room roof to ambient air

Gas samples for toxic gases and particulate analysis were taken through uncooled stainless steel tubes into 190^{o}C heated sample lines. Three sample probes were used simultaneously, all with 190^{o}C heated sample lines. One was fed via a heated filter and pump to a conventional emissions analysis system with heated FID for total hydrocarbons, heated chemiluminescence NO_x analyser and through a 2^{o}C refrigerated condenser to NDIR analysers for CO and CO_2 and a paramagnetic analyser for oxygen. The second heated sample line was linked to a heated filter and heated sample pump and then to a heated TEMET GASMET CR-Series portable FTIR, the results of which will be reported separately.

Table 8-1: Properties of the four fuels used in the pool fires.

	H/C	**Boiling Temp.^{o}C**	**Flash Point C**	**Lower FL %**	**Higher FL %**	**LHV kJ/kg**	**CV MJ/kg**	**Specific Heat Capacity KJ/kg.K**
Heptane		98.4	-4	1	6.7	317	44.6	2.20
Toluene		110.4	4	1.27	7.1	360	40.5	1.67
Kerosene	1.92	150-260	46	0.7	6	256	43.1	1.99
Diesel	1.88	160-360	52	0.4	1.7	228	43.2	1.88

The third heated sample line was used to take an exhaust sample to a heated filter paper particulate sampler. The sample was thermally cooled to 70^{o}C in an oven, so that unburned fuel could condense onto the particulate matter, but water vapor would not. The filter paper housing was separately heated to 70^{o}C to avoid water condensation. The filter was weighed to 10μg resolution before and after the test and the mass collected was divided by the total sample volume to yield the particulate mass concentration Cp in g/m3, which was converted, using Eq. 8.1, to a particulate yield using the A/F by mass determined by carbon balance from the gas analysis. The density of the exhaust gases in the sample can be taken as that of air to better than 1% accuracy for hydrocarbon type combustion products. In this work this density was 1.18 kg/m3 at the pressure and temperature of the sample gas flow meter.

$$\text{Particulate yield} = \left[\frac{\text{Cp}}{1.18}\right] \times \left[1 + \frac{\text{A}}{\text{F}}\right] \text{g/kg} \tag{8.1}$$

The A/F ratio was determined by carbon balance using the (Spindt, 1965) equation which specifies the fuel composition in terms of the H/C ratio, listed in Table 1. The gaseous toxic yields are also based on this A/F by carbon balance. The yields, Yg, of CO and total unburned hydrocarbons, HC, are given by E.q. 8.2. The measured concentration as a fraction by volume is Cg The constant M is the molecular weight ratio of the toxic species to that of the exhaust sample gases, which are take to be air, which is accurate for hydrocarbon combustion to <1% error. M is 0.991 for CO and 0.555 for HC, taken as CH_4 equivalent as the FID measures total HC as C1 equivalent.

$$\text{Y} = \text{Cg M}\left(1 + {}^{A}\!/_{F}\right) \text{ kg/kg} \tag{8.2}$$

In this work it will be shown that the emissions of CO and HC were very high and the combustion efficiency was very low, which reduced the heat release rate. The combustion inefficiency was determined from the energy content in the unburned CO and HC, as in Eq. 8.3

$$1 - \eta\text{c} = \left(\text{YCO x } \frac{\text{CV CO}}{\text{CV fuel}}\right) + (\text{YCH4}) + \left(\text{YSoot x} \frac{\text{CVCarbon}}{\text{CVfuel}}\right) \tag{8.3}$$

Here, CV is the calorific value of the unburned CO or HC or soot. The CV of unburnt fuel was taken as the same as the fuel. The soot term in the present work will be shown to be low and for the highest soot emitting pool fire was less than 2% of the fuel, which is relatively low compared to well ventilated pool fires [2] and it is not very significant in the combustion efficiency calculations here, but is significant when the soot yield is >>2%.

8.3 RESULTS

8.3.1 HEAT RELEASE RATE (HRR) AND MASS LOSS RATES (MLR)

The HRR was computed from the oxygen mass consumption This was based on the metered mass flow of air into the compartment (oxygen is 23.2% by mass) less the oxygen mass flow in the exhaust calculated from the exhaust mass flow rate (air + fuel [derived as in Fig. 8.2]) times the oxygen concentration on a mass basis. The HRR is shown as a function of time for the four pool fires in Fig. 8.1a and as a function of the global fire equivalence ratio (as discussed later) in Fig. 8.1b for a ventilation rate of 10.6 air changes per hour. The HRR increases with the global fire equivalence ratio for all four fuels but kerosene behaved differently as the highest HRR was for a very rich mixture. The reason for this was the poor combustion efficiency, which is discussed later. This resulted in the effective burning zone equivalence ratio being close to stoichiometric when the overall equivalence ratio was rich. For a global fire equivalence ratio of stoichiometric the highest HRR was heptane, then diesel then toluene and finally kerosene. Most of these differences were due to combustion efficiency differences that are reported below.

The mass loss rate was computed from the oxygen consumption HRR divided by the combustion efficiency and is shown as a function of time in Fig. 8.2. The large difference in the trends between Fig. 8.1 and 8.2 was due to the very significant differences in combustion efficiency presented later. Two distinctive phases of combustion occured: the early growth and inital burning was followed by a more stable steady state burning in the later stages of the fire. The peak heat release rate was achieved in the later stages and was similar for all fuels at 15.5, 13.5, 15.4, and 14.2 kW for Heptane, Toluene, Kerosene, and Diesel respectively. These are relatively low heat release rates compared with pool fires with higher ventilation. For kerosene there was a third stage with a sudden increase in the mass loss rate towards the end of the fire. This was also present in the metered mass loss rate measurements. This late peak MLR was underestimated as the HC were greater than 10% and offscale in the FID measurement system used. The increase in mass loss did not correspond with a large increase in HRR as the vaporised fuel was not burnt, due to lack of oxygen.

The heptane pool fires showed two periods of fluctuating mass loss at around 500s and 1500s, which was not exhited with any of the other three fuels. The first unstable period was due to the transition to ghosting flame combustion and the second was associated with the liquid pool boiling towards the end of the test. Heptane has the lowest boiling point and is the most volatile of the four fuels, as evidenced by its lowest flash point in Table 8.1. It will be shown later that the second unstable phase was due to very large fluctuations in HC and CO and hence produce a fluctuating combustion efficiency with little fluctuation in the HRR, as shown in Fig. 8.1.

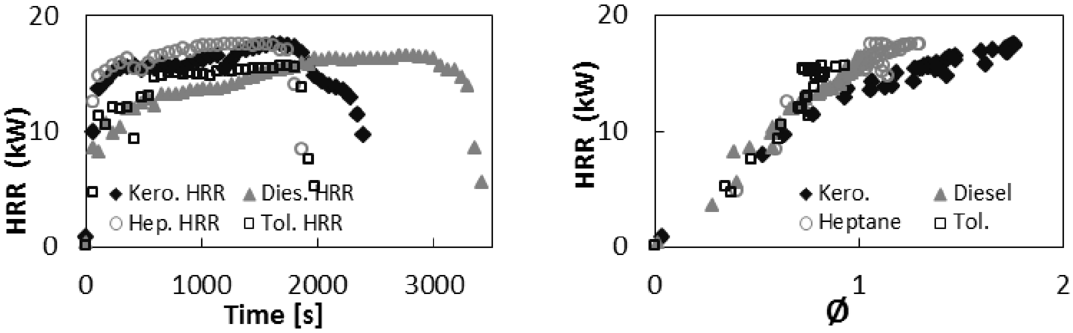


Figure 8-1: Heat release rate as a function of time (a) and equivalence ratio (b).

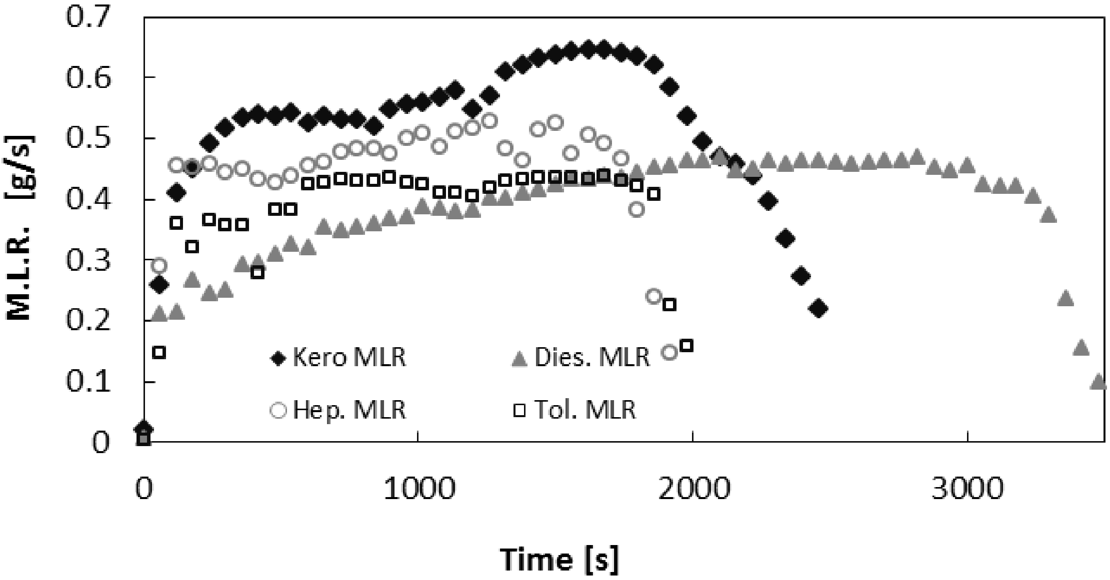


Figure 8-2: Mass Loss Rate g/s as a function of time for the four fuels.

8.3.2 MEAN CEILING TEMPERATURES AND EVIDENCE FOR GHOSTING FLAMES

The average upper layer temperature measurements are shown in Fig. 8.3. This shows a similar temperature history for all four fuels. It also indicate that the fuel burning times varied between the fuels, even though the initial mass of fuel and the ventilation air flow rate were the same. The time to burn the fuel was less than 2000 seconds for the Toluene and Heptane tests, while the Diesel test had the longest duration stretching to almost 3500 seconds.

Fig. 8.4a shows the temperature measurements for the Heptane fire 40 cm above the surface of the pool (Mid) and 30 cm above the ventilation slot at the rear of the compartment (Rear). It shows a high peak temperature above the pool at the beginning of the fire followed by a drop in temperature then a steady slow increase over the course of the burning which corresponds with the mean ceiling temperature increase. At the same time the rear temperature readings (above the ventilation slot) showed a slower increase at the beginning of the tests, due to this region being locally lean as it is above the air inlet. This was followed by an increase in temperature which is considered to mark the transition to ghosting flames which are stabilized at the ventilation slots rather than the fuel surface, but effectively mean that all the area of the compartment is involved in unsteady ghosting flames instead of the flames being confined above the pool. This interpretation was confirmed by visual observations through the high temperature window. Similarly, the Diesel pool fire is shown in Fig. 8.4b where a similar phenomenon to that of the heptane fire occurs but much later in the fire.

All four fuels showed a similar ghosting flame phenomena and the results are summarised in Table 8.2. This shows that the ceiling temperature at which ghosting flames first occurred increased as the fuel boiling point increased and the fire duration decreased as the boiling point decreased.

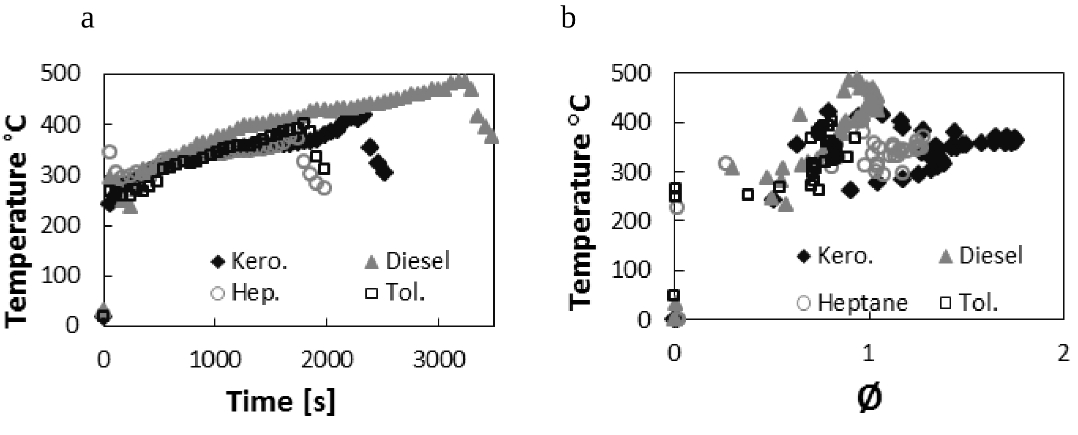


Figure 8-3: Average upper layer temperatures as a function of time (a) and global equivalence ratio (b).

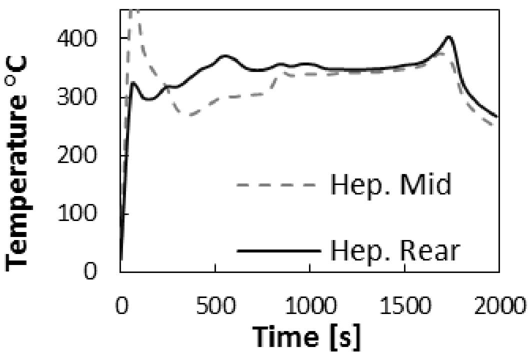


Figure 8-4: Temperatures above the pool surface and at the rear vent of the compartment for Heptane and Diesel Tests..

Table 8-2: Summary of the conditions and time for the onset of ghosting combustion.

	Boiling Temp. °C	LHV kJ/kg	CV MJ/kg	Start of Ghosting Flames s	Start of Ghosting Temp. °C	Fire Duration [s]
Heptane	98.4	317	44.6	320	320	1880
Toluene	110.4	360	40.5	360	290	1970
Kerosene	150-260	256	43.1	480	350	2420
Diesel	160-360	228	43.2	1680	430	3500

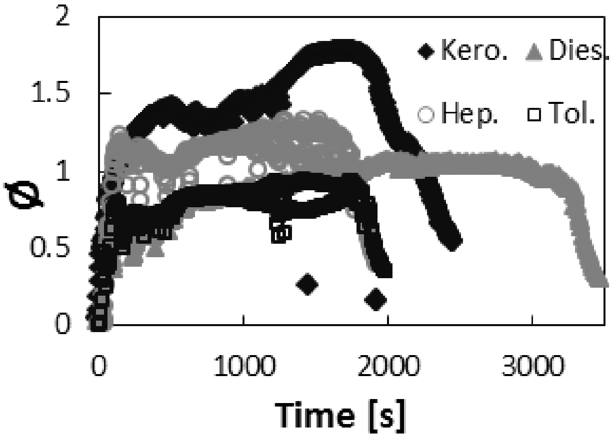


Figure 8-5: Equivalence ratio as a function of time in the four tests.

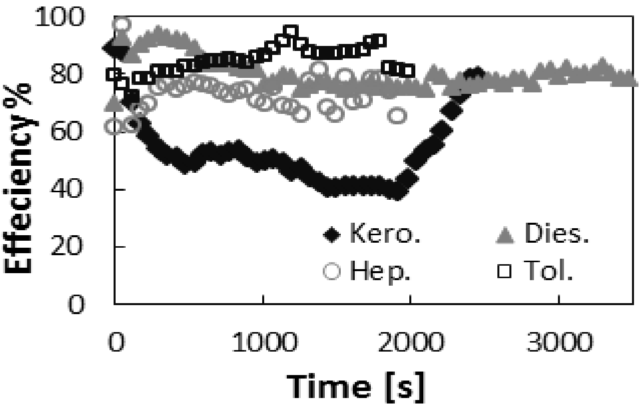


Figure 8-6: Combustion inefficiency as function of time in the four tests.

8.3.3 EQUIVALENCE RATIO AND COMBUSTION INEFFICIENCY

The global equivalence ratio was determined by carbon balance from the CO_2, CO and total HC emissions. The results are shown in Fig. 8.5 for all four fuels as a function of time. These results were unexpected as there is no correlation with fuel volatility. Kerosene formed the richest global equivalence ratio and toluene and diesel were lean for most of the fire, although diesel was stoichiometric by the end phase of the fire. Heptane formed rich mixtures, but to a lesser extent than kerosene. The combustion efficiency results are shown in Fig. 8.6 and these were very low, particularly for kerosene fires. The effective burning equivalence ratio is given by the product of the overall equivalence ratio and the combustion efficiency and at the richest overall mixture this gives 0.91 for heptane, 0.72 for toluene, 0.68 for kerosene and 0.75 for diesel. However, this is the mean burning equivalence ratio and above the pool the local equivalence ratio will be richer. It is likely that extinction of the pool fire starts with extinction above the pool and the heat of the compartment vaporizes fuel leading to overall fire extinction. A feature of the low combustion efficiency in these pool fires is that there is oxygen present during rich combustion, as shown in Fig. 8.7 for all the fuels tested.

8.3.4 CO AND HC YIELDS

The yields of CO and HC are shown as a function of time and equivalence ratio in Fig. 8.8. The equivalence ratio plots have an increase in yield as the fire becomes hotter and richer and then a decrease as the fire moves to extinction with increase in oxygen levels. Both yields are very high for both lean and rich mixtures for all the fuels. For lean mixtures the high yields are due to low temperature combustion, for rich mixtures the high yields of CO are due to equilibrium CO as well as low temperature inefficient combustion CO. There would also be high levels of hydrogen associated with the rich mixtures, which are calculated assuming water gas equilibrium in the Spindt [15] equation used for the computation of equivalence ratio. The rich high yields of HC are due to low temperature inefficient combustion. The ability of kerosene and diesel to burn much richer than for heptane and toluene was due to the wide range of boiling point hydrocarbons in these practical fuels compared with the single boiling point fuels. This was mainly driven by inefficient combustion of the rich mixtures, particularly for kerosene where the effective burning zone equivalence ratio was lean even though the overall mixture was rich. Heat from the fire was vaporizing kerosene that was not burning. The higher final boiling point for diesel led to much lower hydrocarbon levels and leaner overall mixtures. For the more volatile single component fuels the fire vaporized the fuels earlier in the fire and they reached a rich quench position sooner.

Associated with the high yields of CO and HC are very high toxicity levels. CO toxicity for LC50 is 3,000 ppm and peak levels in the fire were between 7 and 17 times this critical toxicity level for all four fuels. CO was highest for heptane and lowest for toluene, with kerosene less than diesel as shown in Fig. 8.8a. Hydrocarbon levels were also very high for all fuels with kerosene much higher than for the other fuels, as shown in Fig. 8.8c. This was mainly due to the much richer mixtures that occurred with kerosene as shown in Fig. 8.8d. Within these high hydrocarbon levels were many toxic hydrocarbons such as benzene. The low temperature combustion also gave rise to large concentrations of toxic aldehydes including acrolein and formaldehyde.

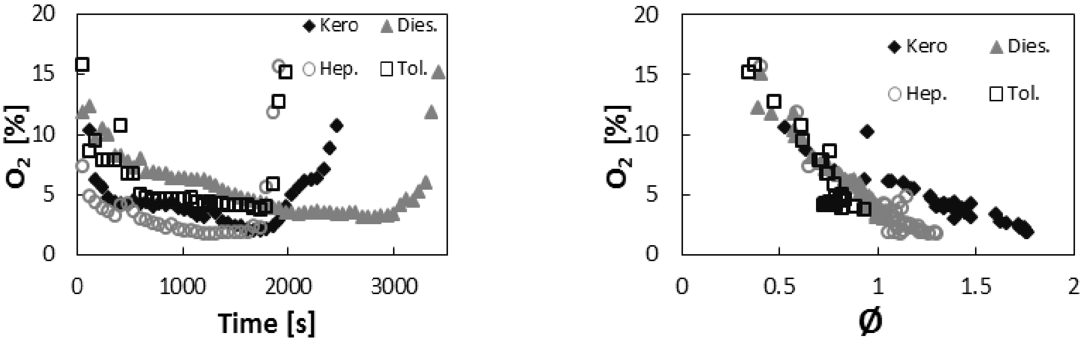


Figure 8-7: Oxygen concentration as a function of time (a) and equivalence ratio (b).

8.3.5 PARTICULATE YIELDS AND COMPOSITION

The particulate yields are shown in Fig. 8.8a as a function the time and in Fig. 8.8b as the carbon fraction by TGA analysis as a function of the global fire equivalence ratio for the midpoint of the sample period. Each heated particulate filter paper sample involved about a five minute sample period and then a short period to change the filter paper. Sufficient filters were obtained to enable the time variation of the particulate yields to be determined. The A/F by mass required for the conversion of the particle

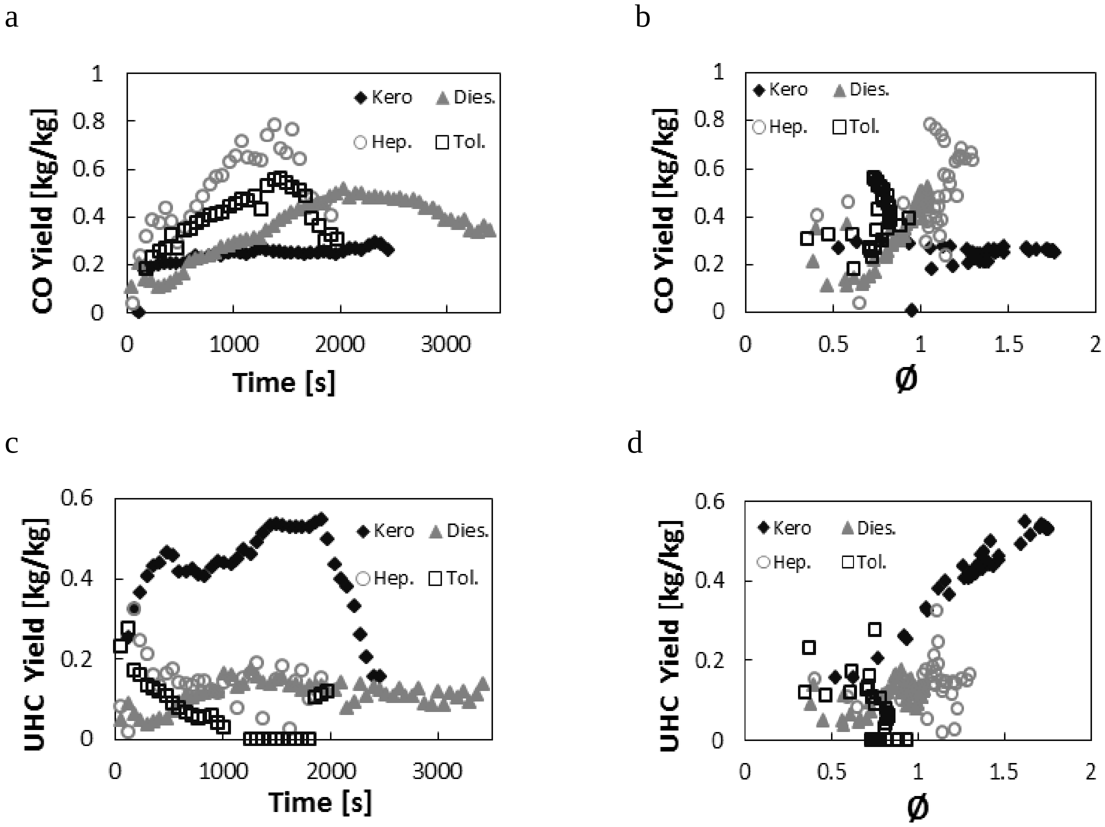


Figure 9 CO and HC yields as a function of time and equivalence ratio

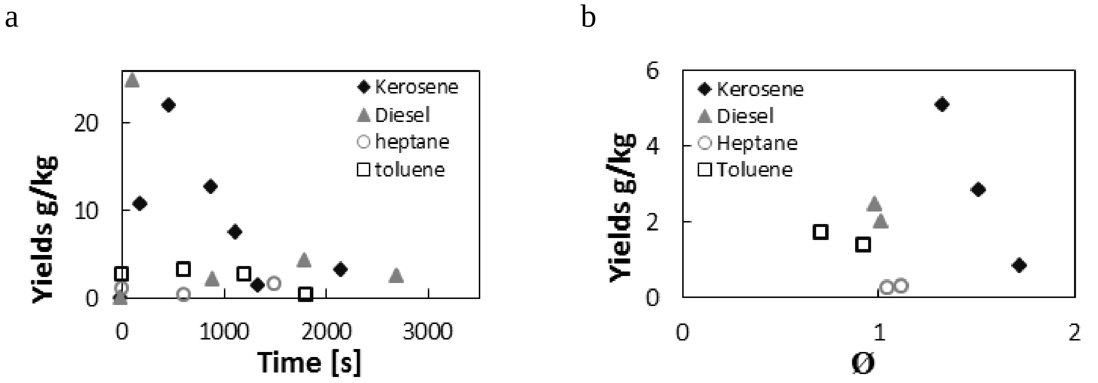


Figure 8-8: Particulates yields as a function of time (a) and carbon yield as a function of equivalence ratio (b)

concentration to yield in Eq. 8.1 was taken as the mean A/F during the sample period. The particulate yields were unexpectedly low for rich mixtures and the highest value was 2.5% for diesel and 2.2% for kerosene in the early stages of the fire when the global equivalence ratio was around stoichiometric for kerosene and lean for diesel. Particulate yields for heptane and toluene were very low at <0.4%. The low particulate yields are considered to be due to low temperature rich combustion, which is a known phenomenon in diesel engines and used to achieve low soot emissions at low power low temperature conditions(Akihama et al., 2001). The particulate yields of (Chamberlain, 1996) and (Utiskul et al., 2005) were much higher due to the high combustion temperatures with the higher ventilation of the fires.

Table 8-3: Thermal Gravimetric Analysis of some of the Particle Filters.

Fuel	Time [S]	Particulate [g/kg]	Carbon [g/kg]	Volatile [g/kg]	Carbon [%]	Volatile [%]
Heptane	300	0.9	0.20	0.70	22	78
	1800	0.9	0.25	0.65	29	71
Toluene	300	1.6	1.0	0.6	63	37
	1800	1.75	1.06	0.69	60	40
Kerosene	300	6.53	4.73	1.8	72	28
	1200	5.67	3.10	2.57	55	45
	1800	2.46	1.09	1.37	44	56
Diesel	1800	3.15	1.83	1.32	58	42
	2900	3.01	1.54	1.45	50	50

Some of the filter papers were analysed using thermal gravimetric analysis to determine the volatile and soot fractions of the particulate and the results are summarized in Table 3. The heptane particulates were dominated by the volatile fraction and in contrast toluene was dominated by carbon, as expected from the high soot forming tendency of aromatic compounds. For kerosene and diesel pool fires the carbon and volatile fractions were of near equal importance. The carbon yield has been plotted as a function of the global fire equivalence ratio in Fig. 11b. The three kerosene samples show the reduction in soot that occurs as the mixtures becomes richer due to the reduced temperatures and low oxygen concentrations (Akihama et al., 2001). For the other fuels the samples were closer to stoichiometric and for the same equivalence ratio the ranking of the fuels for soot yields was as expected with the pure n-alkane heptane with the least, then toluene and then diesel with the highest soot.

8.4 CONCLUSIONS

Pool fires in air starved compartment fire conditions have ghosting flames which detach from the surface of the pool and burn closer to the inlet air ports. These fire conditions have relatively low temperatures with very poor combustion efficiency and very high yields of CO and HC, with associated high toxicity levels that are of the order of a factor of 10 greater than LC50 limits for CO, benzene, acrolein and formaldehyde. The rich low temperature fire conditions produced relatively low particulate emissions as carbon formation kinetics are low under low temperature rich combustion conditions.

9. CHAPTER 9:

CONCLUSIONS AND FUTURE WORK:

9.1 MAIN FINDINGS AND CONCLUSIONS:

In conclusion, this work provides quality data on the toxic effluent in limited ventilation control fire. One of the most detailed data sets are presented for a variety of burning conditions and materials. The major gaseous species were reported to agree with the established literature. Other products of incomplete combustion were in most cases reported for the first time. Thus, the data was analysed in details, and ranked in terms of lethality and irritancy. A summarised overview is given below, for the different sections of this work.

First, an in depth survey of the fire toxicity modelling, potency limits, and overlooked irritant effects were provided. This was followed by analysis and discussion on the current fire toxicity assessment models, and their applicability for different branches in fire research. A compelling argument is put forward for the use of more conservative potency limits in relation to fire safety engineering.

Furthermore, experimental work done on wood crib fires, over a ventilation range of 3 ACH to 37 ACH, yielded the following:

- Wood crib fires self extinguished at 3 ACH and 5 ACH.
- Wood cribs burnt at 11 to 37 ACH completed to burn in very inefficient way, reaching 40% combustion efficiency for the 37 ACH fire.
- The fire products in these tests were of extreme toxicity peaking at 25 times the lethal exposure dose, and 3000 the irritancy threshold adopted in this work.
- The main gases produced in these tests were CO, Acrolein, Formaldehyde, Benzene, and to a limited extent HCN.
- They rank in terms of their lethal amount:
  CO> Formaldehyde>Acrolein>HCN.

- The rank in terms of their irritation amountcrolein>Formaldehyde>CO>Benzene.

Further testing on wood cribs in the fire furnace simulating the later stages of a fire, yielded the following:

- Wood pyrolysis in the later stages of a fire is fundamentally different from flaming combustion. Visual observation documented in the Appendix of this work, shows the wood crib being gasified, while flames are travelling around the compartment following oxygen rich zones.
- Nevertheless, the same combustion products, noting that the sampling was made outside the reaction zone.
- The Major toxicants in terms of lethality were:
  CO>Acrolien>Formaldehyde
- The toxicants ranking due to irritancy was:
  Acrolein>Formaldehyde>CO>Benzene.

Testing carried out on folded cotton towels represented an overlooked scenario in fire research, where a small localised fire smoulders for several hours giving an identified amount of toxicants. This work attempted to quantify this process, and altered one scenario by pouring significant amount of accelerant. The tests yielded the following:

- Despite burning for long hours, these tests did not progress at any stage into a more sever fire. The low intensity combustion process however, was very inefficient producing significant yields of toxicants, comparable to flaming scenarios.
- The 21 ACH smouldering fire, gave almost double the amount given by the 10 ACH fire. The peak LC50 was almost 3 times the lethal limit, while the irritant measure was around 800.
- Despite using an accelerant, and testing the other 2 tests at different ventilation rates, the fires were burning for a long period of time more than 3 hours, at oxygen levels near 20%.
- During the long period of burning the incomplete products of combustion were extremely high, with Formaldehyde yields reaching 25 g/kg, and Acrolien peaking at 15 g/kg.

- The toxic species ranking in terms of lethality was:
  CO>ACrolein>HCN.
- The toxic species ranking in terms of irritancy was:
  Acrolein>Formaldehyde> CO.

Another group of tests was the Acrylic Curtains tests, where a 2.4 kg curtain was hanged inside the reduced scale compartment. The range of ventilation investigated was 5 ACH, 11ACH, 21, ACH, and 37 ACH.

- The 5 ACH only burnt less than half the sample, while the 11 ACH tests exhibited an interesting behaviour where the fire was oscillating lacking oxygen. The 11 ACH burnt almost 75% of the sample through three phases of burning and self extinguishment. The higher ventilation fires, were burnt almost completely, and in a relatively short time.
- The main toxicant in these tests was HCN, which dominated the LC50 toxicity measure accounting for more than 80%.
- In terms of irritancy Acrolein was the leading toxicant, followed by HCN and formaldehyde.
- Surprisingly CO was not noticed to account for any significant effect, >5% of the toxic assessment.
- The total lethality measure on LC_{50} was extremely high, peaking at 60 times the lethal limit, while the irritant measure was in the range of 4000.

The final group of testing was on Hydrocarbon pool fires. They were burnt in a unique set up, simulating conditions never studied before. The restricted amount of ventilation, and the relative high fuel load, caused the pool fire behaviour to turn into a ghosting flame fire. The burning was unusually cold for a hydrocarbon pool fire, and upper layer temperatures were in the range of 300- 500 ^{O}C. This caused the fire to self inert the main pool surface, and continue evaporate the fuel. This was an extremely hazardous scenario, causing significant threat of explosion. The measured unburnt hydrocarbon off scaled the FID equipment exceeding the calibrated range of 10%. This unusual behaviour, shifted the focus of that analysis into a more fundamental investigation on fuel properties, and burning behaviour. The main reason behind this, was that it was deemed unlikely that such unburnt hydrocarbon amounts would reach any fire victim. They would most likely be oxidised near the vent. Nevertheless, this was an intresting part of the research, which opened venues for further research into the topic of ghosting fires.

On a final note, a limited number of tests were not included in the final report, but did not provide an qualitative addition to the knowledge gained.

9.2 RECOMMENDATIONS AND FUTURE WORK:

The first major recommendation from this work is to validate and implement CO equivalent toxicity variable in current computer fire models using the experimental data provided. This variable representing the total incomplete combustion products according to their toxicology effect can then be combined with O_2 depletion and CO_2 levels already established to provide a suitable amount of information which can be assessed for human exposure as in the FED, or FEC models.

A Second recommendation would be to further investigate other fire load materials, in order to asses if there exists, any critical toxicant in more complex fuels, which may increase the overall toxic effect. This will provide computer modellers, and the scientific community more options to consider for the design fire modelling used in fire strategy and risk assessment.

A third recommendation is to expand the work on the already done tests by investigating if the hot gases composition changes when travelling complex building or long corridors. The main considerations would be investigating the effect of mixing with fresh air and the dynamic temperature change that the hot gases go through before reaching remote areas in the building. This can be done experimentally, by expanding the current set up and installing a mixing duct for the exhaust gases to travel through. In which, a fresh air can be introduced at different rates and the smoke composition can then be analysed and compared to existing data.

In addition, the adoption of the Short Term Exposure Limits is an essential requirement for hazard analysis for the purpose of human safety. It has been the lethal limits that dominated the fire research for too long, and an immediate change is required.

On a final note, the FTIR is a powerful tool in gas analysis research, however, good background, knowledge, and training is needed in order to make good use of the equipment. Projects such as (Gann, 2010), and (TOXFIRE, 2001) have incurred significant cost, with little reward due to mishandling of the apparatus. It is the good quality lab scale research that can allow for learning, analysis, and interpretation.

REFERENCES

AEGL, Committee on Acute Exposure Guideline Levels Committee on Toxicology Board on Environmental Studies and Toxicology. (2002). Acute Exposure Guideline Levels for Selected Airborne Chemicals (HCN). **2** The National Academies Press. Washington, DC.

AEGL, Committee on Acute Exposure Guideline Levels Committee on Toxicology Board on Environmental Studies and Toxicology. (2004a). Acute Exposure Guideline Levels for Selected Airborne Chemicals (HCL). **4** The National Academies Press. Washington, DC.

AEGL, Committee on Acute Exposure Guideline Levels Committee on Toxicology Board on Environmental Studies and Toxicology. (2004b). Acute Exposure Guideline Levels for Selected Airborne Chemicals (HF). **4** The National Academies Press. Washington, DC.

AEGL, Committee on Acute Exposure Guideline Levels Committee on Toxicology Board on Environmental Studies and Toxicology. (2006). Acute Exposure Guideline Levels for Selected Airborne Chemicals (Nitric Oxide). The National Academies Press. Washington, DC.

AEGL, Committee on Acute Exposure Guideline Levels Committee on Toxicology Board on Environmental Studies and Toxicology. (2008a). Acute Exposure Guideline Levels for Selected Airborne Chemicals (NO2 N2O4). The National Academies Press. Washington, DC.

AEGL, Committee on Acute Exposure Guideline Levels Committee on Toxicology Board on Environmental Studies and Toxicology. (2008b). Interim Acute Exposure Guideline Levels for Selected Airborne Chemicals (Formaldehyde). **7** The National Academies Press. Washington, DC.

AEGL, Committee on Acute Exposure Guideline Levels Committee on Toxicology Board on Environmental Studies and Toxicology. (2009a). Interim Acute Exposure Guideline Levels for Selected Airborne Chemicals (Acetaldehyde). **7** The National Academies Press. Washington, DC.

AEGL, Committee on Acute Exposure Guideline Levels Committee on Toxicology Board on Environmental Studies and Toxicology. (2009b). Interim Acute

Exposure Guideline Levels for Selected Airborne Chemicals (Benzene). **7** The National Academies Press. Washington, DC.

AEGL, Committee on Acute Exposure Guideline Levels Committee on Toxicology Board on Environmental Studies and Toxicology. (2010a). Acute Exposure Guideline Levels for Selected Airborne Chemicals. **8** The National Academies Press. Washington, DC.

AEGL, Committee on Acute Exposure Guideline Levels Committee on Toxicology Board on Environmental Studies and Toxicology. (2010b). Acute Exposure Guideline Levels for Selected Airborne Chemicals (Acrolein). **8** The National Academies Press. Washington, DC.

Akihama, Kazuhiro, Yoshiki Takatori, Kazuhisa Inagaki, Shizuo Sasaki and Anthony M. Dean (2001). "Mechanism of the Smokeless Rich Diesel Combustion by Reducing Temperature." SAE Technical Paper 2001-01-0655. DOI: 10.4271/2001-01-0655.

Alexeeff, George V. (1986). "Smoke and toxicant production during thermal degradation." Fire and Materials **10**(2): 71-77. DOI: 10.1002/fam.810100205.

Ali, A.F and G. Andrews (1987). Conical grid plate flame stabilizers: influence of the number of holes. ASME IGTI International Congress on Gas Turbines. Anaheim, USA, American Society of Mechanical Engineers. **1987**.

Aljumaiah, O., G. E. Andrews, H.N. Phylaktou and A. Jimenez (2011a). "Low Ventilation Pool Fires." Journal of Hazardous Materials.

Aljumaiah, O., G.E. Andrews, A. Abdullahi, B. Mustafa and H.N. Phylaktou,(*2010a)*, Wood Crib Fires under High Temperature Low Oxygen Conditions, In *Proceedings of the Sixth International Seminar on Fire and Explosion Hazards, Leeds,* Edited by D. Bradley, G. Makhviladze and V Molkov, 2011, Published by Research Publishing Services, ISBN: 978-981-08-7724-8, DOI: 10.3850/978-981-08-7724-8_15-05.

Aljumaiah, O., G.E. Andrews, Alqahtani, B. Husain, P. Singh and H.N. Phylaktou,(*2010b)*, Air Starved Acrylic Curtain Fire Toxic Gases using an FTIR, In *Proceedings of the Sixth International Seminar on Fire and Explosion Hazards, Leeds,* Edited by D. Bradley, G. Makhviladze and V Molkov, 2011, Published by Research Publishing Services, ISBN: 978-981-08-7724-8, DOI: 10.3850/978-981-08-7724-8_11-08.

Aljumaiah, O., G.E. Andrews, Alshammari, Burell, Cox and H.N. Phylaktou,(*2010c)*, Toxic Emissions from Folded Cotton Towel Fires in a Low Ventilation Compartment, In *Proceedings of the Proceedings of the Sixth International Seminar on Fire and Explosion Hazards, Leeds,* Edited by D. Bradley, G. Makhviladze and V Molkov, 2011, Published by Research Publishing Services, ISBN: 978-981-08-7724-8, DOI: 10.3850/978-981-08-7724-8_11-07.

Aljumaiah, O., G.E. Andrews, B.G. Mustafa, H. Al-qattan, V. Shah and H.N. Phylaktou,(*2011b),* Air Starved Wood Crib Compartment Fire Heat Release and Toxic Gas Yields, In *Proceedings of the 10th International Symposium on Fire Safety Science, Maryland, USA,* Edited by Spearpoint, 2011, Published by International Association for Fire Safety Science,

Aljumaiah, O., J. Jordan, G.E. Andrews and H.N. Phylaktou,(*2008),* The Development of a Technique for the Combustion of Wood in a High Temperature Low Oxygen Compartment, In *Proceedings of the Saudi International Innovation Confrence, Leeds, U.K.,* Edited by Alshahrani, Published by ISBN: 978-0-9559241-2-5,

Aljumaiah, O., H.N. Phylaktou, G.E. Andrews, I. Heath and J. Ledger,(*2010d),* Ghosting Flames in a Low Ventilation Compartment with Kerosene Pool Fires, In *Proceedings of the International Congress Combustion and Fire Dynamics, Santander, Spain,* Edited by J Capote and D. Alvear, 2010, Published by University De Cantabria, ISBN: 978-84-86116-23-1,

Amdur, M.O. (1960). "The response of guinea pigs to inhalation of formaldehyde and formic acid alone and with a sodium chloride aerosol." Int. Air Pollut. **3**: 201-220.

Anderson, J.D. (1995). Computational fluid dynamics: the basics with applications, McGraw-Hill.

Andrews, G. E. (2007). Combustion Fundamentals. Leeds, University of Leeds.

Andrews, G. E., J. Ledger and H. N. Phylaktou,(*2000a),* Pool Fires in a Low Ventilation Enclosure, In *Proceedings of the IChemE Symposium on Hazards XV: The Process, Its Safety and the Environment,* Edited by 2000, Published by

Andrews, G. E., J. Ledger and H.N. Phylaktou,(*2000b),* The Gravimetric Determination of soot yields in enclosed pool fires, In *Proceedings of the Third International Seminar on Fire and Explosion Hazards, Windermere,* Edited by D. Bradley, T.

Graham and G. Makhviladze, 2000, Published by Centre for Research in Fire and Explosion Studies at the University of Central Lancashire,

Andrews, G.E., S. Boulter, B. Daham, M.D. Mmolawa, G. Burrell, J. Ledger and H.N. Phylaktou,(*2007)*, Toxic Gas Measurments Using FTIR for Combustion of COH Materials in Air Starved Enclosed Fires, In *Proceedings of the Third European Combustion Meeting, Chania, Crete* Edited by I Gokalp, 2007, Published by Greek Secion of the Combustion Inistitute,

Andrews, G.E., B. Daham, M.D. Mmolawa, S. Boulter, J. Mitchell, G. Burrell, J. Ledger, W. Gunamusa, R.A. Boreham and H.N. Phylaktou,(*2005a)*, FTIR Investigations of Toxic Gases In Air Starved Enclosed Fires, In *Proceedings of the Eighth International Symposium on Fire Safety Science, Beijing*, Edited by D. Gottuk and B. Lattimer, 2005, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.8-1035

Andrews, G.E., B. Daham, MD. Mmolawa, S. Boulter, J. Mitchell, G. Burrell, W. Gunamusa and H.N. Phylkaktou,(*2005b)*, Toxic Emissions from Air Straved Fires, In *Proceedings of the Eigth International Symposium on Fire Saftey Science*, Edited by D. Gottuk and B. Lattimer, 2005, Published by DOI: 10.3801/IAFSS.FSS.8-1035.

Andrews, G.E., J. Ledger and H.N. Phylaktou,(*2000c)*, Enclosed Pool Fires in Low Ventilation Enclosures: Flame Temperatures and Global Heat Loss Using Gas Analysis, In *Proceedings of the Sixth International Symposium on Fire Safety Science, Poitiers*, Edited by M Curtat, 2000, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.6-591

ASTM-E1678. (2010). Standard method for measuring smoke toxicity for use in fire hazard analysis. American Society for Testing and Materials.

ASTM-E2058 (2009). Standard Test Methods for Measurement of Synthetic Polymer Material Flammability Using a Fire Propagation Apparatus. American Society for Testing and Materials.

Audiunnin, I Such, malet and Casselmann,(*1997)*, A Real Scenario for a Ghosting Flame, In *Proceedings of the Fifth Int. Symp. On Fire Safety Science,* Edited by Published by

Babrauskas, Harris, R. Gann, B. Levin and B Paabo. (1991a). NIST Technical Report 1284: The Role of Bench-Scale Test Data in Assessing Real-Scale Fire Toxicity.

NIST Technical Reports. United States Department of Commerce. Gaithersburg. NIST.

Babrauskas, R. Harris, R. Gann, B. Levin, Peacok and S. Yusa (1998). "A methodolgy for obtaining and using toxic Potency data for fire analysis." Fire Saftey Journal(31): 345-359.

Babrauskas, Vytenis (1980). "Estimating room flashover potential." Fire Technology **16**(2): 94-103. DOI: 10.1007/bf02351801.

Babrauskas, Vytenis (1995). "The generation of CO in bench-scale fire tests and the prediction for real-scale fires." Fire and Materials **19**(5): 205-213. DOI: 10.1002/fam.810190503.

Babrauskas, Vytenis, Richard H. Harris, Emil Braun, Barbara C. Levin, Maya Paabo and Richard G. Gann (1991b). "Large-Scale Validation of Bench-Scale Fire Toxicity Tests." Journal of Fire Sciences **9**(2): 125-148. DOI: 10.1177/073490419100900203.

Babrauskas, Vytenis, Barbara C. Levin, Richard G. Gann, Maya Paabo, Richard H. Harris, Richard D. Peacock and Shyuitsu Yusa (1992). "Toxic potency measurement for fire hazard analysis." Fire Technology **28**(2): 163-167. DOI: 10.1007/bf01857942.

Babrauskas, Vytenis and Robert Brady Williamson (1978). "Post-flashover compartment fires: Basis of a theoretical model." Fire and Materials **2**(2): 39-53. DOI: 10.1002/fam.810020202.

Barcroft (1931). Journal Hygiene **31**: 1-34.

Barnes, E.C. and H.W. Speicher (1942). "The determination of formaldehyde in air." J. Ind. Hyg. Toxicolgy **24**: 10-17.

BBC. (2007). "Rose Park Fire." from http:/news.bbc.co.uk/1/hi/Scotland/3448091.stm.

Bender, J.R., L.S. Mullin, G.J. Grapel and W.E. Wilson (1983). "Eye irritation response of humans to formaldehyde." Am. Ind. Hyg. Assoc. J. **44**: 463-465.

Beyler, C. (1983). Development and Burning of a Layer of Products of Invomplete Combustion Generated by a Buoyand Diffusion Flame. Applied Sciences. Cambridge, Massachuttes, Harvard University **Doctor of Philosophy**.

Beyler, C.,*(1986a),* Major Species Production by Solid Fuels in a Two layer Compartment Fire Environment, In *Proceedings of the First Initernational Symposium on Fire Safety Science,* Edited by C. Grant and P. Pagni, 1986, Published by Hemisphere Publishing Corporation, DOI: 10.3801/IAFSS.FSS.1-497

Beyler, C. (2002). Flammability Limits of Premixed and Diffusion Flames. SFPE Handbook of Fire Protection Engineering. Ed. DiNenno. Quincy, Massachusetts, National Fire Protection Association**:** 2-172-2186.

Beyler, Craig L. (1986b). "Major species production by diffusion flames in a two-layer compartment fire environment." Fire Safety Journal **10**(1): 47-56. DOI: Doi: 10.1016/0379-7112(86)90031-7.

Blomqvist, P. (2005). Emissions from Fires: Consequences for Human Safety and the Enviroment. Department of Fire Safety Engineering. Lund, Lund University. **Doctor of Philosophy**.

Blomqvist, Per and Anders Lönnermark (2001). "Characterization of the combustion products in large-scale fire tests: comparison of three experimental configurations." Fire and Materials **25**(2): 71-81. DOI: 10.1002/fam.761.

Bonsall, J.L. (1984). Human Toxicology **3**: 57-60.

Bradley, Derek (1992). "How fast can we burn?" Symposium (International) on Combustion **24**(1): 247-262. DOI: 10.1016/s0082-0784(06)80034-2.

Bryner, Nelson P., Erik Johnsson and W. Pitts. (1994). NIST Interagency Report 5568: Carbon Monoxide Production in Compartment Fires-Reduced-Scale Enclosure Test Facility. NIST Interagency Report. United States Department of Commerce. Gaithersburg. NIST.

BS-476-22. (1987). Fire Tests on Building Materials and Structures. Methods for Determining of the Fire Resistance of Non-Loadbearing Elements of Construction. British Standards Inistitution. London.

BS 7990. (2003). Tube furnace method for determination of toxic products yields in fire effluent. British Standards Inistitution. London.

Buchanan, Andrew H. (2001). Fire Engineering Design Guide. Canterbury, University of Canterbury.

Bullen, M. L. and P. H. Thomas (1979). "Compartment fires with non-cellulosic fuels." Symposium (International) on Combustion **17**(1): 1139-1148. DOI: 10.1016/s0082-0784(79)80108-3.

Bundy, Matthew, Anthony Hamins, Erik Johnsson, Sung Chan Kim, Gwon Hyun Ko and David B. Lenhert. (2007). NIST Technical Note 1483: Measurments of Heat and Combustion Products in Reduced-Scale Ventilation-Limited Compartment

Fires. NIST Technical Notes. United States Department of Commerce. Gaithersburg. NIST.

Chamberlain (1996). "The Hazards Posed by Large-Scale Pool Fires in Offshore Platforms." IchemE **74**: 81-87.

Chan, S.H. (1996). "An Exhaust Emmissions based Air-Fuel Ratio Calculation For Internal Combustion Engines." IMech Auto Eng. **210**: 273-280.

CIBSE Guide E. (2003). Fire Engineering: CIBSE Guide E. Charted Inisititution of Building Services Engineers. London.

COSHH. (2007). List of approved workplace exposure limits (as consolidated with amendments October 2007). Health and Safety Commission. HSE, UK.

Cox, G. (1995). Combustion Fundamentals of Fire. London, Academic.

Drysdale, D. D.,*(2010)*, The origins of fire safety engineering in the UK, In *Proceedings of the Fire Safety Engineering in the UK: The State of the Art, Edinburgh*, Edited by R. Carvel, Published by University of Edinburgh,

Drysdale, Dougal (1998). An Introduction to Fire Dynamics. Chichester, John Wiley & Sons.

Duquesne, Sophie, Miche Le Bras, Serge Bourbigot, René Delobel, Franck Poutch, Giovanni Camino, Berend Eling, Chris Lindsay and Toon Roels (2000). "Analysis of Fire Gases Released from Polyurethane and Fire-Retarded Polyurethane Coatings." Journal of Fire Sciences **18**(6): 456-482. DOI: 10.1106/6crg-q8vd-pv3g-eldd.

Edgerley, P. G. (1982). "Toxic gas tests in perspective." Fire and Materials **6**(2): 72-75. DOI: 10.1002/fam.810060207.

Ferrari, Luis A., Miriam G. Arado, Leda Giannuzzi, Guido Mastrantonio and Manuel A. Guatelli (2001). "Hydrogen cyanide and carbon monoxide in blood of convicted dead in a polyurethane combustion: a proposition for the data analysis." Forensic Science International **121**(1-2): 140-143. DOI: 10.1016/s0379-0738(01)00464-9.

Fleischmann, C.M. and A.R. Parkes,*(1997)*, Effects Of Ventilation On The Compartment Enhanced Mass Loss Rate., In *Proceedings of the Fifth International Symposium on Fire Safety Science, Melbourne*, Edited by Y. Hasemi, 1997, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.5-415

Floyd, J. E. and K. B. McGrattan (2009). "Extending the mixture fraction concept to address under-ventilated fires." Fire Safety Journal **44**(3): 291-300. DOI: DOI: 10.1016/j.firesaf.2008.07.002.

Flury, F. (1928). "Moderne gewerbliche vergiftungen in pharmakologisch-toxicologischer hinsicht." Archiv. F. Experiment. Path. U. Pharmakol. **138**: 65-82.

GA-132. (1996). Smoke and toxicity of fire effluents. China.

Gann, Richard, Jason Averill, Erik Johnsson, Marc Nyden and Richard Peacock. (2003). NIST Technical Note 1453: Smoke Component Yields from Room-scale Fire Tests. NIST Technical Notes. United States Department of Commerce. Gaithersburg. NIST.

Gann, Richard G. (2004a). "Estimating Data for Incapacitation of People by Fire Smoke." Fire Technology **40**(2): 201-207. DOI: 10.1023/b:fire.0000016843.38848.37.

Gann, Richard G. (2004b). "Sublethal Effects of Fire Smoke." Fire Technology **40**(2): 95-99. DOI: 10.1023/b:fire.0000016898.88522.79.

Gann, Richard G., Jason D. Averill, Erik L. Johnsson, Marc R. Nyden and Richard D. Peacock (2010). "Fire effluent component yields from room-scale fire tests." Fire and Materials **34**(6): 285-314. DOI: 10.1002/fam.1024.

Gerarde, H.W. (1960). Toxicology and biochemistry of aromatic hydrocarbon. New York, USA, Elsvier Publishing Company.

Gordon L, Nelson (1987). "Regulatory aspects of fire toxicology." Toxicology **47**(1-2): 181-199. DOI: 10.1016/0300-483x(87)90167-3.

Gormsen, H., N. Jeppesen and A. Lund (1984). "The causes of death in fire victims." Forensic Science International **24**(2): 107-111. DOI: 10.1016/0379-0738(84)90090-2.

(1984). UDSSR Imo Standard Fb/353, Toxic potency of effluents.

Gottuk, D. (1992a). Generation of Carbon Monoxide in Compartment Fires. Mechanical Engineering. Blacksburg, VA, Virginia Polytechnic Inst. and State University. **Doctor of Philosophy**.

Gottuk, Daniel T., Richard J. Roby and Craig L. Beyler (1995). "The role of temperature on carbon monoxide production in compartment fires." Fire Safety Journal **24**(4): 315-331. DOI: Doi: 10.1016/0379-7112(95)00027-5.

Gottuk, Daniel T., Richard J. Roby, Michelle J. Peatross and Craig L. Beyler (1992). "Carbon Monoxide Production in Compartment Fires." Journal of Fire Protection Engineering **4**(4): 133-150. DOI: 10.1177/104239159200400402.

Gottuk, Lattimer (2002). Effect of Combustion Conditions on Species Production. SFPE Handbook of Fire Protection Engineering. Ed. DiNenno. Quincy, Massachusetts, National Fire Protection Association**:** 85-146.

Gottuk, Richard J. Roby & Craig L. Beyler (1992b). A Study of Carbon Momoxide and Smoke Yields from Compartment Fires with External burning. Twenty Fourth Symposium on Combustion.

Gottuk, Richard J. Roby & Craig L. Beyler (1995). "The Role of Temperature on Carbon Monoxide Production in Compartment Fires." Fire Saftey Journal **24**: 315-331.

Graham, T. L., G. M. Makhviladze and J. P. Roberts (1995). "On the theory of flashover development." Fire Safety Journal **25**(3): 229-259. DOI: 10.1016/0379-7112(95)00049-6.

Grewolls, K. (2010). Computer simulation of fire hazards and evacuation. Fire Toxicity. Ed. T. R. Hull and A. A. Stec. Cambridge, Woodhead Publishing Limited**:** 607-618.

Gross, D. and A. F. Robertson (1965). "Experimental fires in enclosures." Symposium (International) on Combustion **10**(1): 931-942. DOI: 10.1016/s0082-0784(65)80236-3.

Hagglund, B., R. Jasson and B. Onnermark. (1974). Fire development in residential rooms after ignition from nuclear explosion. FOA Report. C 20016-D6 (A3) Stockholm.

Hakkarainen, Tuula, Esko Mikkola, Jan Laperre, Francis Gensous, Peter Fardell, Yannick Le Tallec, Claudio Baiocchi, Keith Paul, Margaret Simonson, Caroline Deleu and Edwin Metcalfe (2000). "Smoke gas analysis by Fourier transform infrared spectroscopy – summary of the SAFIR project results." Fire and Materials **24**(2): 101-112. DOI: 10.1002/1099-1018(200003/04)24:2<101::aid-fam729>3.0.co;2-2.

Hall, John. (2010). The Total Cost of Fire in the United States. National Fire Protection Association. Quincy, MA.

Hall, John R. (2004a). "How Many People are Exposed to Sublethal Fire Smoke?" Fire Technology **40**(2): 101-116. DOI: 10.1023/b:fire.0000016838.96609.94.

Hall, John R. (2004b). "How Many People Can Be Saved from Home Fires if Given More Time to Escape?" Fire Technology **40**(2): 117-126. DOI: 10.1023/B:FIRE.0000016839.11376.b3.

Harmathy, T.Z. (1978). "Mechanism of burning of fully-developed compartment fires." Combustion and Flame **31**(0): 265-273. DOI: 10.1016/0010-2180(78)90139-6.

Hartzell, G. E., S. C. Packham and W. G. Switzer (1983). "Assessment of toxic hazards of smoke: Toxicological potency and intoxication rate thresholds." Fire and Materials **7**(3): 128-131. DOI: 10.1002/fam.810070306.

Hartzell, G.E. (2001). "Engineering analysis of hazards to life safety in fires the fire effluent toxicity component." Safety Science(38): 147-155.

Hartzell, G.E., S.C. Packham, A.F. Grand and W.G. Switzer (1985a). "Modeling of Toxicological Effects of Fire Gases: Iii. Quantification of Post-Exposure Lethality of Rats From Exposure To HCl Atmospheres." Journal of Fire Sciences **3**(3): 195-207. DOI: 10.1177/073490418500300304.

Hartzell, G.E., D.N. Priest and W.G. Switzer (1985b). "Modeling of Toxicological Effects of Fire Gases: Ii. Mathematical Modeling of Intoxication of Rats By Carbon Monoxide and Hydrogen Cyanide." Journal of Fire Sciences **3**(2): 115-128. DOI: 10.1177/073490418500300204.

Hartzell, G.E., W.G. Switzer and D.N. Priest (1985c). "Modeling of Toxicological Effects of Fire Gases: V. Mathematical Modeling of Intoxication of Rats By Combined Carbon Monoxide and Hydrogen Cyanide Atmospheres." Journal of Fire Sciences **3**(5): 330-342. DOI: 10.1177/073490418500300504.

Hartzell, Gordon E. (1989). "Prediction of the Toxic Effects of Fire Effluents." Journal of Fire Sciences **7**(3): 179-193. DOI: 10.1177/073490418900700303.

Henderson, Y. and H.W. Haggard (1943). Noxious Gases. New York, Reinhold Publishing Co.

Heselden, A.J.M. and S.J. Melinek. (1975). The early stages of fire growth in a compartment. Fire Research Note. 1029

Heskstad, G. (1982). Engineeering relations for fire plumes. Technology Report 82-8

Hirschler, Marcelo M. (1987). "Fire Hazard and Toxic Potency of the Smoke from Burning Materials." Journal of Fire Sciences **5**(5): 289-307. DOI: 10.1177/073490418700500501.

Hirschler, Marcelo M. (2005). "Analysis of work on smoke component yields from room-scale fire tests." Fire and Materials **29**(5): 303-314. DOI: 10.1002/fam.887.

Hisahiro, Takeda (1988). "Experimental investigation of fire behavior in a 1/6 scale dual opening compartment." Symposium (International) on Combustion **21**(1): 137-142. DOI: 10.1016/s0082-0784(88)80240-6.

Holborn, P. G., S. R. Bishop, D. D. Drysdale and A. N. Beard (1993). "Experimental and theoretical models of flashover." Fire Safety Journal **21**(3): 257-266. DOI: 10.1016/0379-7112(93)90030-t.

Holborn, P. G., P. F. Nolan and J. Golt (2003). "An analysis of fatal unintentional dwelling fires investigated by London Fire Brigade between 1996 and 2000." Fire Safety Journal **38**(1): 1-42. DOI: 10.1016/s0379-7112(02)00049-8.

Horrocks, A.R. (2001). Textiles. Fire Retardant Materials. Ed. A.R. Horrocks, Woodhead Publishing**:** 128-181.

Hostikka, S. (2011). FDS+Evac Evacuation Model: Recent Developments. 2011 Fire and Evacuation Modeling Technical Conference. Baltimore, Maryland.

HSE. (2005). Control of Substances Hazardous to Health Regulations: EH40/2005 Workplace exposure limits. HSE Books. UK Health and Safety Executive.

Huang, Hong, Ryozo Ooka, Naian Liu, Linhe Zhang, Zhihua Deng and Shinsuke Kato (2009). "Experimental study of fire growth in a reduced-scale compartment under different approaching external wind conditions." Fire Safety Journal **44**(3): 311-321. DOI: DOI: 10.1016/j.firesaf.2008.07.005.

Huggett, Clayton (1980). "Estimation of rate of heat release by means of oxygen consumption measurements." Fire and Materials **4**(2): 61-65. DOI: 10.1002/fam.810040202.

Hull, T. R. (2010). Bench-scale Generation of Fire Effluent. Fire Toxicity. Ed. T. R. Hull and A. A. Stec. Cambridge, Woodhead Publishing Limited**:** 424-461.

Hull, T. R. and A. A. Stec (2010). Introduction to Fire Toxicity. Fire Toxicity. Ed. T. R. Hull and A. A. Stec. Cambridge, Woodhead Publishing Limited**:** 1-25.

Hull, T. Richard, Krzysztof Lebek, Maddalena Pezzani and Silvio Messa (2008a). "Comparison of toxic product yields of burning cables in bench and large-scale experiments." Fire Safety Journal **43**(2): 140-150. DOI: DOI: 10.1016/j.firesaf.2007.06.004.

Hull, T. Richard and Keith T. Paul (2007). "Bench-scale assessment of combustion toxicity--A critical analysis of current protocols." Fire Safety Journal **42**(5): 340-365.

Hull, T.R., K. Lebek and K.T. Paul,(*2005)*, Correlation Of Toxic Product Yields From Tube Furnace Tests And Large Scale Fires., In *Proceedings of the Eighth International Symposium on Fire Safety Science, Beijing,* Edited by D. Gottuk and B. Lattimer, 2005, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.8-1059

Hull, T.R., A.A. Stec and K.T. Paul,(*2008b)*, Hydrogen Chloride in Fires, In *Proceedings of the Ninth International Symposium on Fire Safety Science, Karlsruhe,* Edited by B. Karlsson, 2009, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.9-665

IEC60695-7-50. (2002). Fire hazard testing—part 7-50: toxicity of fire effluents—estimation of toxic potency: apparatus and test method. International Electrotechnical Commission.

Institute, National Cancer. (2011, 06/10/2011). "Formaldehyde and Cancer Risk." Retrieved 10th of August, 2011, from http://www.cancer.gov/cancertopics/factsheet/Risk/formaldehyde#r3.

ISO 1344. (2004). Estimation of the lethal toxic potency of fire effluents. International Standards Orgnisation. Geneva.

ISO 5660. (2002). Reaction to fire tests heat release, smoke production, and mass loss rate (Cone calorimeter dynamic measurment). International Standards Orgnisation. Geneva.

ISO 8178. (2006). Reciprocating internal combustion engines -- Exhaust emission measurement -- Part 1: Test-bed measurement of gaseous and particulate exhaust emissions. International Standards Orgnisation. Geneva.

ISO 9705. (2011). Fire tests -- Full-scale room test for surface products. International Standards Orgnisation. Geneva.

ISO 13571. (2007). Life-threatening components of fire - Guidlines for the estimation of time available for escape using fire data. International Standards Orgnisation. Geneva.

ISO 13943. (2008). Fire safety - Vocabulary. International Standards Orgnisation. Geneva.

ISO 19700. (2006). Controlled equivalence ratio method for the etermination of hazardous components of fire effluents. International Standards Orgnisation. Geneva.

ISO 19706. (2005). Guidlines for assesing the fire threat to people. International Standards Orgnisation. Geneva.

ISO 27368. (2008). Analysis of blood for asphyxiant toxicants - Carbon monoxide and hydrogen cyanide. International Standards Orgnisation. Geneva.

Janssens, M. (2002). Calorimetry. SFPE Handbook of Fire Protection Engineering. Ed. DiNenno. Quincy, Massachusetts, National Fire Protection Association**:** 3-38.

JIS A 1321. (1976). Semi-non-combustible and fire retarded building materials conforming to the building standards Law. Ministry of Construction. Japan.

Jones, Walter W., G.P. Forney, Richard Peacock and Paul A. Reneke. (2000). A Technical Reference for CFAST: An Engineering for Estimating Fire and Smoke Transport. National Inistitute of Standards and Technology. Gaithersburg, MD.

Kallonen, Raija (1990). "Smoke Gas Analysis by FTIR Method. Preliminary Investigation." Journal of Fire Sciences **8**(5): 343-360. DOI: 10.1177/073490419000800503.

Kaplan, Harold L., Arthur F. Grand and Gordon E. Hartzell (1984). "Toxicity and the smoke problem." Fire Safety Journal **7**(1): 11-23. DOI: Doi: 10.1016/0379-7112(84)90004-3.

Karlsson and Quintiere (1999a). Introduction. Enclosure Fire Dynamics. CRC Press.

Karlsson and Quintiere (1999b). A Qualitative Description of Enclosure Fires. Enclosure Fire Dynamics. CRC Press.

Karlsson, Björn and James G. Quintiere (1999c). Enclosure Fire Dynamics. London, Boca Raton.

Kawagoe, Kunio. (1958). Fire behaviour in rooms. Tokyo. Bbuilding Research Inistitute.

Kim, Kwang Ill, Hideo Ohtani and Yoichi Uehara (1993). "Experimental study on oscillating behaviour in a small-scale compartment fire." Fire Safety Journal **20**(4): 377-384. DOI: Doi: 10.1016/0379-7112(93)90056-v.

Kimmerle, G. (1974). Journal of combustion Toxicolgy **1**: 4.

Ko, Gwon Hyun, Anthony Hamins, Matthew Bundy, Erik L. Johnsson, Sung Chan Kim and David B. Lenhert (2009). "Mixture fraction analysis of combustion products in the upper layer of reduced-scale compartment fires." Combustion and Flame **156**(2): 467-476. DOI: DOI: 10.1016/j.combustflame.2008.08.012.

Lattimer, B. (1996). The Transport of High Concentrations of Carbon Monoxide to Locations Remote from the Burning Compartment. Mechanical Engineering. Blacksburg, VA, Virginia Polytechnic Inst. and State University. **Doctor of Philosophy**.

Lattimer, Brian, Uri Vandsburger and Richard Roby (2005). "Species Transport from Post-Flashover Fires." Fire Technology **41**(4): 235-254. DOI: 10.1007/s10694-005-3731-x.

Lattimer, Brian Y., David S. Ewens, Uri Vandsburger and Richard J. Roby (1994). "Transport and Oxidation of Compartment Fire Exhaust Gases in an Adjacent Corridor." Journal of Fire Protection Engineering **6**(4): 163-180. DOI: 10.1177/104239159400600403.

Lattimer, Brian Y., Uri Vandsburger and Richard J. Roby (1998). "Carbon Monoxide Levels in Structure Fires: Effects of Wood in the Upper Layer of a Post-Flashover Compartment Fire." Fire Technology **34**(4): 325-355. DOI: 10.1023/a:1015366527753.

Lee, B.T. (1982). Quarter scale modeling of room fire tests of interior finish. National Bureau of Standards.

Levin, B. (1996). "New research avenues in toxicology: 7-gas N-gas model, toxicant suppressants, and genetic toxicology." Toxicology **115**(1-3): 89-106. DOI: 10.1016/s0300-483x(96)03497-x.

Levin, Barbara C., Maya Paabo, Joshua L. Gurman and Steven E. Harris (1987). "Effects of exposure to single or multiple combinations of the predominant toxic gases and low oxygen atmospheres produced in fires." Fundamental and Applied Toxicology **9**(2): 236-250. DOI: 10.1016/0272-0590(87)90046-7.

Lönnermark, Anders, Per Blomqvist, Margret Månsson and Henry Persson (1996). "TOXFIRE – Fire Characteristics and Smoke Gas Analyses in Under-ventilated Large-scale Combustion Experiments – Tests in the ISO 9705 Room." SP Swedish National Testing and Research Institute(SP Report 1996:45).

Lund, K., J. Ekstrand, J. Boe, P. Søstrand and J. Kongerud (1997). "Exposure to hydrogen fluoride: an experimental study in humans of concentrations of fluoride in plasma, symptoms, and lung function." Occup Environ Med **54**(1): 32-37.

Lund, K., M. Refsnes, T. Sandstrøm, P. Søstrand, P. Schwarze, J. Boe and J. Kongerud (1999). "Increased CD3 positive cells in bronchoalveolar lavage fluid after hydrogen fluoride inhalation." Scand J Work Environ Health **25**(4): 326-334.

Marchant, E. W. (1976). Some aspects of human behaviour and esape route design. 5th International Fire Protection Seminar. Karlsruhe.

Martin, S. B. and S. J. Wiersma. (1979). An experimental study of flashover criteria forcompartment fires. **Final Report** Stanford Research Inistitute. Stanford.

McGrattan, K. (2008). FDS Future Development. O. Aljumaiah. Leeds.

McGrattan, K., B. Klein, S. Hostikka and J. Floyd (2008a). Fire Dynamics Simulator 5, User's Guide.

Mcgrattan, K.B.,*(2005)*, Fire Modeling: Where Are We? Where Are We Going?, In *Proceedings of the Eighth International Symposium on Fire Safety Science, Beijing*, Edited by D. Gottuk and B. Lattimer, 2005, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.8-53.

McGrattan, Kenvin, H. Baum, R. Rehm, S. Hostikka and J Floyd (2008b). Fire Dynamics Simulator 5 Technical Reference Guide. Washington.

McNamara, B.P. (1976). Estimates of the Toxicity of Hydrocyanic Acid Vapors in Man. Edgewood Arsenal, Aberdeen Proving Ground, MD.

Morehart, J. H. (1991). Species Produced in Fires Burning in two-layered and Homogenous Vitated Enviroments. Engineering and Applied Sciences. Pasadena, California, USA, California Inistitute of Technology. **Doctor of Philosophy**.

Morehart, J. H., E. E. Zukoski and T. Kubota (1992). "Chemical species produced in fires near the limit of flammability." Fire Safety Journal **19**(2-3): 177-188. DOI: 10.1016/0379-7112(92)90032-8.

Morikawa, T., T. Okada, M. Kajiwara, Y. Sato and Y. Tsuda (1995). "Toxicity of Gases from Full-Scale Room Fires Involving Fire Retardant Contents." Journal of Fire Sciences **13**(1): 23-42. DOI: 10.1177/073490419501300102.

Mowrer, Frederick W. and Robert Brady Williamson (1987). "Estimating room temperatures from fires along walls and in corners." Fire Technology **23**(2): 133-145. DOI: 10.1007/bf01040428.

Nagorny, P.A., Zh.A. Sudakova and S.M. Schablenko (1979). "On the general toxic and allergic action of formaldehyde." Gig. Tr. Prof. Zabol. **1**: 27-30.

National Statistics. (2007). Fire Statistics, United Kingdom 2005. Department for Communities and Local Government. London.

National Statistics. (2008). Fire Statistics, United Kingdom 2006. Department for Communities and Local Government. London.

National Statistics. (2009). Fire Statistics, United Kingdom 2007. Department for Communities and Local Government. London.

National Statistics. (2010). Fire Statistics, United Kingdom 2008. Department for Communities and Local Government. London.

Neviaser, Julie L. and Richard G. Gann (2004). "Evaluation of Toxic Potency Values for Smoke from Products and Materials." Fire Technology **40**(2): 177-199. DOI: 10.1023/b:fire.0000016842.67144.12.

NIOSH. (1976). NIOSH criteria for a reommended standard occupational exposure to osides of nitrogen. US Department of Health. Washington, DC. National Inistiute for Occupational Safety and Health.

NIOSH. (1992). Acetic Acid Fact Sheets. US Department of Health. Washington, DC. National Inistiute for Occupational Safety and Health.

NIOSH, Publications and Products. (1994). Chemical Listing and Documentation of Revised IDLH Values (as of 3/1/95). Documentation for Immediately Dangerous To Life or Health Concentrations (IDLHs).

NTP. (2011). 12th Report on Carcinogens. National toxicology program. US Department of Health.

ODPM. (2006). The Economic Cost of Fire: Estimates for 2004. The Economic Cost of Fire. Office of the Deputy Prime Minister. London. ODPM.

Ostman, B.A. (2006). Flammability of Wood Products. Flammability Testing of Materials used in Construction, Transport, and Mining. CRC Press.

PD6503. (1988). Toxicity of combustion products. Guide to the relevance of small-scale tests for measuring the toxicity of combustion products of materials and composites. British Standards Inistitution. London.

PD 7974-0. (2002). Application of fire safety engineering principles to the design of buildings - Guide to design framework and fire safety engineering procedures. British Standards Inistitution. London.

PD 7974-1. (2002). Application of fire safety engineering principles to the design of buildings - Initiation and development of fire within the enclosure of origin. British Standards Inistitution. London.

Peatross, M.J. and C.L. Beyler,*(1997)*, Ventilation Effects on Compartment Fire Characterization., In *Proceedings of the Fifth International Symposium on Fire Safety Science, Melbourne,* Edited by Y. Hasemi, 1997, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.5-403

Pitts, William M. (1995). "The global equivalence ratio concept and the formation mechanisms of carbon monoxide in enclosure fires." Progress in Energy and Combustion Science **21**(3): 197-237. DOI: 10.1016/0360-1285(95)00004-2.

Pitts, William M., Erik L. Johnsson and Nelson P. Bryner (1994). "Carbon monoxide formation in fires by high-temperature anaerobic wood pyrolysis." Symposium (International) on Combustion **25**(1): 1455-1462. DOI: 10.1016/s0082-0784(06)80789-7.

Pitts, Williams M. (1994). "Application of thermodynamic and detailed chemical kinetic modeling to understanding combustion product generation in enclosure fires." Fire Safety Journal **23**(3): 271-303. DOI: 10.1016/0379-7112(94)90032-9.

prEN-2824. (2009). Burning behaviour, determination of smoke density and gas components in the smoke of materials under the influence of radiating Heat and flames—test equipment apparatus and media. Aero space series.

Purser, D.,*(1989)*, Modelling Toxic And Physical Hazard In Fire, In *Proceedings of the Second International Symposium on Fire Safety Science, Tokyo,* Edited by T. Wakamatsu, Y. Hasemi, A. Sekizawa, P. Seeger, P. Pagni and C. Grant, 1989, Published by Hamisphere Publishing Corporation, DOI: 10.3801/IAFSS.FSS.2-391

Purser, D. A. (2002). Toxic assessment of combustion products. SFPE Handbook of Fire Protection Engineering. Ed. DiNenno. Quincy, Massachusetts, National Fire Protection Association**:** 85-146.

Purser, D. A. and M. Bensilum (2001). "Quantification of behaviour for engineering design standards and escape time calculations." Safety Science **38**(2): 157-182. DOI: 10.1016/s0925-7535(00)00066-7.

Purser, D.A. (1992). "The evolution of toxic effluents in fires and the assessment of toxic hazard." Toxicology Letters **64-65**(0): 247-255. DOI: 10.1016/0378-4274(92)90196-q.

Purser, D.A.,*(2003)*, ASET and RSET: addressing some issues in relation to occupant behaviour and tenability, In *Proceedings of the Seventh International*

Symposium on Fire Safety Science, Worcester, Edited by D. Evans, 2003, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.7-91

Purser, D.A. (2010a). Asphyxiant Components of Fire Effluent. Fire Toxicity. Ed. T. R. Hull and A. A. Stec. Cambridge, Woodhead Publishing Limited**:** 118-198.

Purser, D.A. (2010b). Hazards from Smoke and Irritants. Fire Toxicity. Ed. T. R. Hull and A. A. Stec. Cambridge, Woodhead Publishing Limited**:** 51-117.

Purser, D.A. (2010c). Toxic hazard calculation models for use with fire effluent data. Fire Toxicity. Ed. T. R. Hull and A. A. Stec. Cambridge, Woodhead Publishing Limited**:** 580-610.

Purser, D.A., P.J. Fardell, J. Rowley, S. Vollam and Bridgeman (1994). An improved tube furnace method for the generation and measurement of toxic combustion products under a wide range of fire conditions. Flame Retardant Confrence, Interscience Communication**:** 263-274.

Purser, D.A., P. Grimshaw and K.R. Berrill (1984). Arch. Environ. Health **39**: 394-400.

Purser, D.A. and J.A. Purser,(*2008)*, HCN yields and fate of fuel nitrogen for materials under different combustion conditions in the ISO 19700 tube furnace and large - scale fires, In *Proceedings of the Ninth International Symposium on Fire Safety Science, Karlsruhe,* Edited by B. Karlsson, 2009, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.9-1117

Purser, D.A., A. A. Stec and T. R. Hull (2010). Fire Scenarios and Combustion Conditions. Fire Toxicity. Ed. T. R. Hull and A. A. Stec. Cambridge, Woodhead Publishing Limited**:** 26-47.

Purser, D.A. and W.D. Woolley (1983). "Biological Studies of Combustion Atmospheres." Journal of Fire Sciences **1**(2): 118-144. DOI: 10.1177/073490418300100204.

Purser, David A. (1984). "A Bioassay Model for Testing the Incapacitating Effects of Exposure To Combustion Product Atmospheres Using Cynomolgus Monkeys." Journal of Fire Sciences **2**(1): 20-36. DOI: 10.1177/073490418400200104.

Purser, David A. (2000). "Toxic product yields and hazard assessment for fully enclosed design fires." Polymer International **49**(10): 1232-1255. DOI: 10.1002/1097-0126(200010)49:10<1232::aid-pi543>3.0.co;2-t.

Quintiere, J., B. J. McCaffrey and T. Kashiwagi (1978). "A Scaling Study of a Corridor Subject to a Room Fire." Combustion Science and Technology **18**(1-2): 1-19. DOI: 10.1080/00102207808946835.

Quintiere, J.G. (1998). Principles of fire behavior, Delmar Publishers.

Rockett, John A. (1976). "Fire Induced Gas Flow in an Enclosure." Combustion Science and Technology **12**(4-6): 165-175. DOI: 10.1080/00102207608946717.

Sayers, P.R. and S.J. Davenport. (1930). Review of Carbon Monoxide Poisoning. Public Health Bulletin. Wasington, DC. U.S. Government Printing Office.

Schifiliti, R. (2002). Design of Detection Systems. SFPE Handbook of Fire Protection Engineering. Ed. DiNenno. Quincy, Massachusetts, National Fire Protection Association**:** 85-146.

Shaddix, C.R. (1999). Correcting Thermocouple Measurements for Radiation Loss. 33rd National Heat Transfer Confrence. Albuquerque, NM.

Silverman, L., H.F. Schulte and F.W. First (1946). "Further Studies on Sensory Response to Certain Industrial Solvent Vapors." Journal of Industrial Hygiene and Toxicology **28**(6): 262-266.

Smith, D. A. (1985). "Smoke and toxicity." Fire and Materials **9**(4): 167-170. DOI: 10.1002/fam.810090404.

Spindt (1965). "An Exhaust Ratios from Exhaust Gas analysis." SAE paper **74**.

Stec, A. A., T. R. Hull, J. A. Purser and D. A. Purser (2009). "Comparison of toxic product yields from bench-scale to ISO room." Fire Safety Journal **44**(1): 62-70. DOI: DOI: 10.1016/j.firesaf.2008.03.005.

Stephens, E.R., E.R. Darley, O.C. Taylor and W.E. Scott (1961). "Photochemical reaction products in air pollution." Int. Air Water Pollut. **4**: 79-100.

Stewart, R.D (1974). Journal of combustion Toxicolgy **1**: 167-176.

Sugawa (1991). "Burning Behaviour in a poor-ventilation compartment fire-Ghosting fire." Nuclear Engineering and Design **125**: 347-352.

Takeda, Hisahiro and Kazuo Akita (1981). "Critical phenomenon in compartment fires with liquid fuels." Symposium (International) on Combustion **18**(1): 519-527. DOI: 10.1016/s0082-0784(81)80057-4.

Tewarson, A. (1972a). "Some observations on experimental fires in enclosures, part II-Ethyl alcohol and paraffin oil." Combustion and Flame **19**(3): 363-371. DOI: Doi: 10.1016/0010-2180(72)90006-5.

Tewarson, A. (1972b). "Some observations on experimental fires in enclosures. Part I: Cellulosic materials." Combustion and Flame **19**(1): 101-111. DOI: Doi: 10.1016/s0010-2180(72)80090-7.

Tewarson, A. (1980). "Heat release rate in fires." Fire and Materials **4**(4): 185-191. DOI: 10.1002/fam.810040405.

Tewarson, A. (1985). "Fully developed enclosure fires of wood cribs." Symposium (International) on Combustion **20**(1): 1555-1566. DOI: 10.1016/s0082-0784(85)80650-0.

Tewarson, A. (1994). "A response to “Comment on chemical efficiency of combustion as reported by Tewarson et al.”." Combustion and Flame **98**(1-2): 177-178. DOI: 10.1016/0010-2180(94)90208-9.

Tewarson, A. (2002). Generation of Heat and Chemical Compounds in Fires. SFPE Handbook of Fire Protection Engineering. Ed. DiNenno. Quincy, Massachusetts, National Fire Protection Association**:** 85-146.

Tewarson, A., F. H. Jiang and T. Morikawa (1993). "Ventilation-controlled combustion of polymers." Combustion and Flame **95**(1-2): 151-169. DOI: 10.1016/0010-2180(93)90058-b.

Thomas, P. H. (1974). Fires in Enclosure. Heat Transfer in Fires. Ed. P.L. Blackshear. New York, John Wiley and Sons**:** 73-94.

Thomas, P. H. (1980). "Fires and flashover in rooms -- A simplified theory." Fire Safety Journal **3**(1): 67-76. DOI: Doi: 10.1016/0379-7112(80)90009-0.

Toner, S. (1987). Entrainment, Chemistry, and Structure of Fire Plumes. Engineering and Applied Sciences. Pasadena, California, USA, California Inistitute of Technology. **Doctor of Philosophy**.

Tsuchiya, Y. and K. Sumi (1972). "Evaluation of the Toxicity of Combustion Products." Journal of Fire and Flammability **3**: 46-50.

Tuovinen, Heimo, Per Blomqvist and Fikret Saric (2004). "Modelling of hydrogen cyanide formation in room fires." Fire Safety Journal **39**(8): 737-755. DOI: DOI: 10.1016/j.firesaf.2004.07.003.

USFA. (2005). Fatal Fires. Fires in the United States. U.S. Department of Homeland Security/Federal Emergency Management Agency United States/Fire Administration/National Fire Data Center. Emmitsburg, Maryland.

USFA. (2009). Fires in the United States 2003-2007. Fires in the United States. U.S. Department of Homeland Security/Federal Emergency Management Agency

United States/Fire Administration/National Fire Data Center. Emmitsburg, Maryland.

USFA. (2011). Civilian Fire Fatalities in Residential Buildings. Topical Fire Report Series. U.S. Department of Homeland Security/Federal Emergency Management Agency United States/Fire Administration/National Fire Data Center. Emmitsburg, Maryland.

Utiskul, Y. (2005). Theoretical and Experimental study on Fully Developed Compartment Fires. Fire Protection Engineering. College Park, University of Maryland. **Doctor of Philosophy**.

Utiskul, Y. and J.G. Quintiere,(*2005),* Generalizations On Compartment Fires From Small-scale Experiments For Low Ventilation Conditions, In *Proceedings of the Eighth International Symposium on Fire Safety Science, Beijing,* Edited by D. Gottuk and B. Lattimer, 2005, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.8-1229

Utiskul, Yunyong, James G. Quintiere, Ali S. Rangwala, Brian A. Ringwelski, Kaoru Wakatsuki and Tomohiro Naruse (2005). "Compartment fire phenomena under limited ventilation." Fire Safety Journal **40**(4): 367-390. DOI: 10.1016/j.firesaf.2005.02.002.

Wade, C. A. (2004). A User's Guide to BRANZFIRE 2004. Building Research Association of New Zeland. Wellington.

Walton, W.D. (1985). ASET-B A Room Fire Program for Personal computers. National Bureau of Standards. Washington, DC.

Waterman, T. (1968). "Room flashover—Criteria and synthesis." Fire Technology **4**(1): 25-31. DOI: 10.1007/bf02588603.

Weckman, E. J. and A. Sobiesiak (1989). "The oscillatory behaviour of medium-scale pool fires." Symposium (International) on Combustion **22**(1): 1299-1310. DOI: 10.1016/s0082-0784(89)80141-9.

Wieczorek, C.J. (2003). Carbon Monoxide Generation and Transport From Compartment Fires. Mining and Minerals Engineering. Blackburg, VA, Virginia Polytechnic Inistitute and State University. **Doctor of Philosophy**.

Yeoh, Guan Heng and Kwok Kit Yuen (2009). Computational Fluid Dynamics in Fire Engineering, Butterworth-Heinemann.

Yoshida, M., J. Adachi, T. Watabiki, Y. Tatsuno and N. Ishida (1991). "A study on house fire victims: Age, carboxyhemoglobin, hydrogen cyanide and hemolysis."

Forensic Science International **52**(1): 13-20. DOI: 10.1016/0379-0738(91)90091-v.

Yung, D. (1991). "Small-scale compartment fire experiments with PMMA cribs." Fire Safety Journal **17**(4): 301-313. DOI: Doi: 10.1016/0379-7112(91)90025-t.

Bibliography

AEGL, Committee on Acute Exposure Guideline Levels Committee on Toxicology Board on Environmental Studies and Toxicology. (2010). Acute Exposure Guideline Levels for Selected Airborne Chemicals (CO). 8 The National Academies Press. Washington, DC.

Alarie, Yves (2002). "Toxicity of Fire Smoke." Critical Reviews in Toxicology 32(4): 259-289. DOI: 10.1080/20024091064246.

Alvares, N. J., K. L. Foote and P. J. Pagni (1984). "Forced Ventilated Enclosure Fires." Combustion Science and Technology 39(1-6): 55-81. DOI: 10.1080/00102208408923783.

Andersson, Petra, Lars Rosell, Margaret Simonson and Viktor Emanuelsson (2004). "Small and Large Scale Fire Experiments with Electric Cables under Well-Ventilated and Vitiated Conditions." Fire Technology 40(3): 247-262. DOI: 10.1023/b:fire.0000026879.07753.86.

Ashgriz and Mostaghimi. (2002). "An Introduction to Computational Fluid Dynamics." Fluid Flow Handbook, from http://www.mie.utoronto.ca/labs/MUSSL/cfd20.pdf.

Audouin, L. and B. Tourniaire,(2000), New Estimation Of The Thermal Interface Height In Forced-ventilation Enclosure Fires, In Proceedings of the Sixth International Symposium on Fire Safety Science, Poitiers, Edited by M Curtat, 2000, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.6-567

Babrauskas, Vytenis (1980). "Flame lengths under ceilings." Fire and Materials 4(3): 119-126. DOI: 10.1002/fam.810040304.

Babrauskas, Vytenis (1981). "A closed-form approximation for post-flashover compartment fire temperatures." Fire Safety Journal 4(1): 63-73. DOI: Doi: 10.1016/0379-7112(81)90005-9.

Babrauskas, Vytenis (1986). "Free burning fires." Fire Safety Journal 11(1-2): 33-51. DOI: Doi: 10.1016/0379-7112(86)90051-2.

Babrauskas, Vytenis (1989). "Toxic Hazard from Fires: A Simple Assessment Method." Fire Safety Journal(20): 1-14.

Babrauskas, Vytenis (1991). "Effective measurement techniques for heat, smoke, and toxic fire gases." Fire Safety Journal 17(1): 13-26. DOI: Doi: 10.1016/0379-7112(91)90010-v.

Babrauskas, Vytenis (1996). "Fire Modeling Tools for FSE: Are They Good Enough?" Journal of Fire Protection Engineering 8(2): 87-93. DOI: 10.1177/104239159600800203.

Babrauskas, Vytenis (1997). "Sandwich panel performance in full-scale and bench-scale fire tests." Fire and Materials 21(2): 53-65. DOI: 10.1002/(sici)1099-1018(199703)21:2<53::aid-fam593>3.0.co;2-8.

Babrauskas, Vytenis (2000). "Fire safety improvements in the combustion toxicity area: is there a role for LC50 tests?" Fire and Materials 24(2): 113-119. DOI: 10.1002/1099-1018(200003/04)24:2<113::aid-fam730>3.0.co;2-l.

Babrauskas, Vytenis and Richard D. Peacock (1992). "Heat release rate: The single most important variable in fire hazard." Fire Safety Journal 18(3): 255-272. DOI: Doi: 10.1016/0379-7112(92)90019-9.

Babrauskas, Vytenis, Richard D. Peacock and Paul A. Reneke (2003). "Defining flashover for fire hazard calculations: Part II." Fire Safety Journal 38(7): 613-622. DOI: Doi: 10.1016/s0379-7112(03)00027-4.

Beard, Alan N. (2010). "Flashover and boundary properties." Fire Safety Journal 45(2): 116-121. DOI: DOI: 10.1016/j.firesaf.2009.12.002.

Becker, W. and H. Sand (1988). "The contribution of materials to fire gas toxicity. A critical review of methods of assessment." Fire and Materials 13(1): 130-137. DOI: 10.1002/fam.810130118.

Bensilum, M. and D.A. Purser,(2003), An Object-oriented Building Evacuation Model Combining Pre-movement And Movement Behaviours For Performance-based Design., In Proceedings of the Seventh International Symposium on Fire Safety Science, Worcester, Edited by D. Evans, 2003, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.7-941

Bilbao, R., J. F. Mastral, M. E. Aldea, J. Ceamanos, M. Betrán and J. A. Lana (2001). "Experimental and theoretical study of the ignition and smoldering of wood including convective effects." Combustion and Flame 126(1-2): 1363-1372. DOI: Doi: 10.1016/s0010-2180(01)00251-6.

Bishop, S. R., P. G. Holborn, A. N. Beard and D. D. Drysdale (1993). "Nonlinear dynamics of flashover in compartment fires." Fire Safety Journal 21(1): 11-45. DOI: Doi: 10.1016/0379-7112(93)90003-9.

Biteau, H., T. Steinhaus, C. Schemel, A. Simeoni, G. Marlair, N. Bal and J.L Torero,(2008), Calculation Methods for the Heat Release Rate of Materials of Unknown Composition, In Proceedings of the Ninth International Symposium on Fire Safety Science, Karlsruhe, Edited by B. Karlsson, 2009, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.9-1165

Blevins, Linda G., Michael W. Renfro, Kent H. Lyle, Normand M. Laurendeau and Jay P. Gore (1999). "Experimental study of temperature and CH radical location in partially premixed CH4/air coflow flames." Combustion and Flame 118(4): 684-696. DOI: 10.1016/s0010-2180(99)00023-1.

Blomqvist, Per, Tommy Hertzberg, Heimo Tuovinen, Karine Arrhenius and Lars Rosell (2007). "Detailed determination of smoke gas contents using a small-scale controlled equivalence ratio tube furnace method." Fire and Materials 31(8): 495-521. DOI: 10.1002/fam.946.

Bøhm, Benny and Bo Musse Rasmussen (1987). "The development of a small-scale fire compartment in order to determine thermal exposure inside and outside buildings." Fire Safety Journal 12(2): 103-108. DOI: Doi: 10.1016/0379-7112(87)90026-9.

Boonmee, N (2004). Theoretical and Experimental study of Autoigntion of Wood. Fire Protection Engineering. College Park, University of Maryland. Doctor of Philosophy.

Briggs, Peter J. (1993). "Smoke generation--Developments in international test methods and use of data for selection of materials and products." Fire Safety Journal 20(4): 341-351. DOI: Doi: 10.1016/0379-7112(93)90054-t.

Brohez, S., C. Delvosalle and G. Marlair (2004). "A two-thermocouples probe for radiation corrections of measured temperatures in compartment fires." Fire Safety Journal 39(5): 399-411. DOI: DOI: 10.1016/j.firesaf.2004.03.002.

Brohez, S., C. Delvosalle, G. Marlair and A. Tewarson,(2000), Soot Generation In Fires: An Important Parameter For Accurate Calculation Of Heat Release, In Proceedings of the Sixth International Symposium on Fire Safety Science, Poitiers, Edited by M Curtat, 2000, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.6-255

Brohez, S., G. Marlair and C. Delvosalle (2006). "Fire calorimetry relying on the use of the fire propagation apparatus. Part II: burning characteristics of selected chemical substances under fuel rich conditions." Fire and Materials 30(1): 35-50. DOI: 10.1002/fam.897.

Brown, S. K. and K. G. Martin (1985). "Toxic gas and smoke measurement with the British Fire Propagation test. I: Test conditions." Fire and Materials 9(2): 88-94. DOI: 10.1002/fam.810090206.

Bryant, Rodney A. (2009). "A comparison of gas velocity measurements in a full-scale enclosure fire." Fire Safety Journal 44(5): 793-800. DOI: DOI: 10.1016/j.firesaf.2009.03.010.

Bullen, M. L. (1977). A Combined overall and surface energy balance for fully developed ventilation controlled liquid fuel in fires in compartments. Fire Research. 1: 171-185.

Bullen, M. L. (1978). "A combined overall and surface energy balance for fully-developed ventilation-controlled liquid fuel fires in compartments." Fire Safety Journal 1(3): 171-185. DOI: Doi: 10.1016/0379-7112(78)90003-6.

Bustamante Valencia, Lucas, Thomas Rogaume, Eric Guillaume, Guillermo Rein and Jose L. Torero (2009). "Analysis of principal gas products during combustion of polyether polyurethane foam at different irradiance levels." Fire Safety Journal 44(7): 933-940. DOI: 10.1016/j.firesaf.2009.05.003.

Butler, Kathryn M. and George W. Mulholland (2004). "Generation and Transport of Smoke Components." Fire Technology 40(2): 149-176. DOI: 10.1023/b:fire.0000016841.07530.64.

Cetegen, B. M., E. E. Zukoski and T. Kubota (1984). "Entrainment in the Near and Far Field of Fire Plumes." Combustion Science and Technology 39(1-6): 305-331. DOI: 10.1080/00102208408923794.

Chalasani, N R, Miles Greiner and Ahti Suo-Anttila (2011). "Benchmarking of Container Analysis Fire Environment (CAFE) simulation using the memorial tunnel fire ventilation tests." Journal of Fire Protection Engineering. DOI: 10.1177/1042391511426212.

Chatris, J. M., J. Quintela, J. Folch, E. Planas, J. Arnaldos and J. Casal (2001). "Experimental study of burning rate in hydrocarbon pool fires." Combustion and Flame 126(1-2): 1373-1383. DOI: Doi: 10.1016/s0010-2180(01)00262-0.

Cheong, M.K., M.J. Spearpoint and C.M. Fleischmann (2009). "Calibrating an FDS Simulation of Goods-vehicle Fire Growth in a Tunnel Using the Runehamar Experiment." Journal of Fire Protection Engineering 19(3): 177-196. DOI: 10.1177/1042391508101981.

Cheung, Sherman, Richard K. K. Yuen, G. H. Yeoh and Grace Cheng (2004). "Contribution of soot particles on global radiative heat transfer in a two-compartment fire." Fire Safety Journal 39(5): 412-428. DOI: DOI: 10.1016/j.firesaf.2004.03.004.

Clarke, Frederic B. (1999). "The effects of brominated flame retardants on the elements of fire hazard: a re-examination of earlier results." Fire and Materials 23(3): 109-116. DOI: 10.1002/(sici)1099-1018(199905/06)23:3<109::aid-fam674>3.0.co;2-w.

Cleary, M. J. and J. H. Kent (2005). "Modelling of species in hood fires by conditional moment closure." Combustion and Flame 143(4): 357-368. DOI: DOI: 10.1016/j.combustflame.2005.08.013.

Cooper, Leonard Y. (1983). "A concept for estimating available safe egress time in fires." Fire Safety Journal 5(2): 135-144. DOI: Doi: 10.1016/0379-7112(83)90006-1.

Cooper, Leonard Y. (1984). "Smoke movement in rooms of fire involvement and adjacent spaces." Fire Safety Journal 7(1): 33-46. DOI: Doi: 10.1016/0379-7112(84)90006-7.

Croce, P. A. and Y. Xin (2005). "Scale modeling of quasi-steady wood crib fires in enclosures." Fire Safety Journal 40(3): 245-266. DOI: DOI: 10.1016/j.firesaf.2004.12.002.

Cuzzillo, B.R. and P.J. Pagni,(2000), The Myth Of Pyrophoric Carbon, In Proceedings of the Sixth International Symposium on Fire Safety Science, Poitiers, Edited by M Curtat, 2000, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.6-301

Delichatsios, Michael A., Gordon W. H. Silcock, Xijuan Liu, Mary Delichatsios and Yee-Ping Lee (2004). "Mass pyrolysis rates and excess pyrolysate in fully developed enclosure fires." Fire Safety Journal 39(1): 1-21. DOI: DOI: 10.1016/j.firesaf.2003.07.006.

Dembsey, N. A., P. J. Pagni and R. B. Williamson (1995). "Compartment fire experiments: Comparison with models." Fire Safety Journal 25(3): 187-227. DOI: Doi: 10.1016/0379-7112(96)00002-1.

Dillon, Scott Edward. (1998). Analysis of the ISO 9705 Room/Corner Test: Simulations, Correlations and Heat Flux Measurements. NIST. Gaithersburg, MD.

Emmons, H. W. (1984). "The Further History of Fire Science." Combustion Science and Technology 40(1-4): 167-174. DOI: 10.1080/00102208408923804.

Emmons, Howard W. (1981). "The growth of fire science." Fire Safety Journal 3(3): 95-106. DOI: Doi: 10.1016/0379-7112(81)90036-9.

Fardell, P. J. (2010). Sampling and Measurement of Toxic Fire Effluent. Fire Toxicity. Ed. T. R. Hull and A. A. Stec. Cambridge, Woodhead Publishing Limited: 385-423.

Fernandez-Pello, A. C. (1994). "The Challenge of Fire Prediction." Combustion Science and Technology 98(4-6): 281-290. DOI: 10.1080/00102209408935413.

Fitzpatrick, E. M., A. B. Ross, J. Bates, G. Andrews, J. M. Jones, H. Phylaktou, M. Pourkashanian and A. Williams (2007). "Emission of Oxygenated Species from the Combustion of Pine Wood and its Relation to Soot Formation." Process Safety and Environmental Protection 85(5): 430-440. DOI: 10.1205/psep07020.

Fleischmann, and Parkes,(1994), Effects of Ventilation on the Compartment enhanced mass loss rate, In Proceedings of the Fifth Int. Symp. On Fire Safety Science, Edited by Published by

Floyd, J. E., K. B. McGrattan, S. Hostikka and H. R. Baum (2003). "CFD Fire Simulation Using Mixture Fraction Combustion and Finite Volume Radiative Heat Transfer." Journal of Fire Protection Engineering 13(1): 11-36. DOI: 10.1177/1042391503013001002.

Foley, Marianne and Dougal Drysdale (1994). "Note: Smoke measurement and the cone calorimeter." Fire and Materials 18(6): 385-387. DOI: 10.1002/fam.810180606.

Foster, S., M. Chladna, C. Hsieh, I. Burgess and R. Plank (2007). "Thermal and structural behaviour of a full-scale composite building subject to a severe compartment fire." Fire Safety Journal 42(3): 183-199. DOI: 10.1016/j.firesaf.2006.07.002.

Friedman, R,(1986), Some Unresolved Fire Chemistry Problems, In Proceedings of the First Initernational Symposium on Fire Safety Science, Edited by C. Grant and P. Pagni, 1986, Published by Hemisphere Publishing Corporation, DOI: 10.3801/IAFSS.FSS.1-349

Fu, Zhuman and George Hadjisophocleous (2000). "A two-zone fire growth and smoke movement model for multi-compartment buildings." Fire Safety Journal 34(3): 257-285. DOI: Doi: 10.1016/s0379-7112(99)00045-4.

Gann, R.G.,(2008), On the Inclusion of Toxic Potency in Product Fire Performance, In Proceedings of the Ninth International Symposium on Fire Safety Science, Karlsruhe, Edited by B. Karlsson, 2009, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.9-677

Gann, Richard G., Vytenis Babrauskas, Stephen J. Grayson and Nathan D. Marsh (2011). "Hazards of combustion products: Toxicity, opacity, corrosivity, and heat release: The experts' views on capability and issues." Fire and Materials 35(2): 115-127. DOI: 10.1002/fam.1043.

Gann, Richard G., Vytenis Babrauskas, Richard D. Peacock and John R. Hall (1994). "Fire conditions for smoke toxicity measurement." Fire and Materials 18(3): 193-199. DOI: 10.1002/fam.810180306.

Gasmet (2005). User's Guide and Reference Manual. Finland, Gasmet Technologies.

Gerwolls, K., T. R. Hull, A. A. Stec and D. Purser,(2010), Fire Effluent Toxicity: Possibilities and Limitations of Modeling Hazards, In Proceedings of the Proceedings of the Sixth International Seminar on Fire and Explosion Hazards, Leeds, Edited by D. Bradley, G. Makhviladze and V Molkov, 2011, Published by Research Publishing Services, ISBN: 978-981-08-7724-8, DOI: 10.3850/978-981-08-7724-8_11-05.

Gobeau, Ledin and Lea. (2002). "Guidance for HSE InspectorsL Smoke movment n complex enclosed spaces-Assessment of Computaional Fluid Dynamics." from http://www.hse.gov.uk/research/hsl_pdf/2002/hsl02-29.pdf.

Gray, Peter (1990). "The need for fundamental Fire Research." Fire Safety Journal 16(5): 341-346. DOI: Doi: 10.1016/0379-7112(90)90006-z.

Gurman, Joshua L., Laura Baier and Barbara C. Levin (1987). "Polystyrenes: A review of the literature on the products of thermal decomposition and toxicity." Fire and Materials 11(3): 109-130. DOI: 10.1002/fam.810110302.

Hamins, Anthony, Erik Johnsson, Michelle Donnelly and Alexander Maranghides (2008). "Energy balance in a large compartment fire." Fire Safety Journal 43(3): 180-188. DOI: DOI: 10.1016/j.firesaf.2007.08.002.

Han, S. and W. Chow (2005). "Calculating FED and LC for testing toxicity of materials in bench-scale tests with a cone calorimeter." Polymer Testing 24(7): 920-924. DOI: 10.1016/j.polymertesting.2005.06.009.

Harmathy, T. Z. (1978). "Experimental study on the effect of ventilation on the burning of piles of solid fuels." Combustion and Flame 31(0): 259-264. DOI: 10.1016/0010-2180(78)90138-4.

Harmathy, T. Z. (1980). "Ventilation of fully-developed compartment fires." Combustion and Flame 37(0): 25-39. DOI: 10.1016/0010-2180(80)90069-3.

Harmathy, T. Z. (1981). "Some overlooked aspects of the severity of compartment fires." Fire Safety Journal 3(4): 261-271. DOI: Doi: 10.1016/0379-7112(81)90048-5.

Hartzell, G.E., A.F. Grand and W.G. Switzer,(1989), Studies On The Toxicity Of Smoke Containing Hydrogen Chloride., In Proceedings of the Second International Symposium on Fire Safety Science, Tokyo, Edited by T. Wakamatsu, Y. Hasemi, A. Sekizawa, P. Seeger, P. Pagni and C. Grant, 1989, Published by Hamisphere Publishing Corporation, DOI: 10.3801/IAFSS.FSS.2-371

Hartzell, Gordon E., Steven C. Packham and Walter G. Switzer (1983). "Toxic Products from Fires." American Industrial Hygiene Association Journal 44(4): 248-255. DOI: 10.1080/15298668391404743.

Hasofer, Abraham M. and Vaughan R. Beck (1997). "A Stochastic model for compartment fires." Fire Safety Journal 28(3): 207-225. DOI: Doi: 10.1016/s0379-7112(97)00079-9.

Hayasaka, H.,(1994), A Study On Pool Flame Structure Using Thermography., In Proceedings of the Fourth International Symposium on Fire Safety Science, Ottawa, Edited by T. Kashiwagi, 1994, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.4-125

Hayasaka, H.,(1997), Unsteady Burning Rates Of Small Pool Fires., In Proceedings of the Fifth International Symposium on Fire Safety Science, Melbourne, Edited by Y. Hasemi, 1997, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.5-499

Hietaniemi, Jukka, Raija Kallonen and Esko Mikkola (1999). "Burning characteristics of selected substances: production of heat, smoke and chemical species." Fire and Materials 23(4): 171-185. DOI: 10.1002/(sici)1099-1018(199907/08)23:4<171::aid-fam680>3.0.co;2-c.

Hilado, Carlos J., Heather J. Cumming and Anne M. Machado (1978). "Relative toxicity of pyrolysis gases from materials: Specific toxicants and special studies." Fire and Materials 2(4): 141-153. DOI: 10.1002/fam.810020402.

Hinkley, P. L., H. G. H. Wraight and C. R. Theobald (1984). "The contribution of flames under ceilings to fire spread in compartments." Fire Safety Journal 7(3): 227-242. DOI: Doi: 10.1016/0379-7112(84)90022-5.

Hirschler, M.M. and G.F. Smith,(1991), Investigation of a Smoke Toxicity Fire Model for Use on Wood, In Proceedings of the Third International Symposium on Fire Safety Science, Edinburgh, Edited by G. Cox and B. Langford, 1989, Published by Elsevier Science Publishers LTD, DOI: 10.3801/IAFSS.FSS.3-615

Hirschler, Marcelo M. (1991). "The measurement of smoke in rate of heat release equipment in a manner related to fire hazard." Fire Safety Journal 17(3): 239-258. DOI: Doi: 10.1016/0379-7112(91)90004-i.

Hirschler, Marcelo M. (1994). "Comparison of large-and small-scale heat release tests with electrical cables." Fire and Materials 18(2): 61-76. DOI: 10.1002/fam.810180202.

Hirschler, Marcelo M. and Arthur F. Grand (1993). "Comparison of the smoke toxicity of four vinyl wire and cable compounds using different test methods." Fire and Materials 17(2): 79-90. DOI: 10.1002/fam.810170205.

Hirschler, Marcelo M. and David A. Purser (1993). "Irritancy of the smoke (non-flaming mode) from materials used for coating wire and cable products, both in the presence and absence of halogens in their chemical composition." Fire and Materials 17(1): 7-20. DOI: 10.1002/fam.810170103.

Holborn, P. G., P. F. Nolan and J. Golt (2004). "An analysis of fire sizes, fire growth rates and times between events using data from fire investigations." Fire Safety Journal 39(6): 481-524. DOI: 10.1016/j.firesaf.2004.05.002.

Holborn, P. G., P. F. Nolan, J. Golt and N. Townsend (2002). "Fires in workplace premises: risk data." Fire Safety Journal 37(3): 303-327. DOI: 10.1016/s0379-7112(01)00055-8.

Hostikka, S. (2008). Development of fire simulation models for radiative heat transfer and probablistic risk assessment. Helsinki, Helsinki University of Technology. Doctor of Technology.

Hostikka, S., Mcgrattan, K.B. and Hamins, A.,(2003), Numerical Modeling Of Pool Fires Using Les And Finite Volume Method For Radiation., In Proceedings of the Seventh International Symposium on Fire Safety Science, Worcester, Edited by D. Evans, 2003, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.7-383

Hshieh, Fu-Yu and Robert R. Buch (1997). "Controlled-atmosphere cone calorimeter studies of silicones." Fire and Materials 21(6): 265-270. DOI: 10.1002/(sici)1099-1018(199711/12)21:6<265::aid-fam620>3.0.co;2-u.

Hu, L. H., N. K. Fong, L. Z. Yang, W. K. Chow, Y. Z. Li and R. Huo (2007). "Modeling fire-induced smoke spread and carbon monoxide transportation in a long channel: Fire Dynamics Simulator comparisons with measured data." Journal of Hazardous Materials 140(1-2): 293-298.

Hu, L. H., W. Peng and R. Huo (2008). "Critical wind velocity for arresting upwind gas and smoke dispersion induced by near-wall fire in a road tunnel." Journal of Hazardous Materials 150(1): 68-75.

Hu, Z., Y. Utiskul, J.G. Quintiere and A. Trouve,(2005), A Comparison Between Observed And Simulated Flame Structures In Poorly Ventilated Compartment Fires., In Proceedings of the Eighth International Symposium on Fire Safety Science, Beijing, Edited by D. Gottuk and B. Lattimer, 2005, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.8-1193

Hull, T. Richard, Rita E. Quinn, Irene G. Areri and David A. Purser (2002). "Combustion toxicity of fire retarded EVA." Polymer Degradation and Stability 77(2): 235-242.

Hyde, S.M. and J.B. Moss,(2003), Modelling Co Production In Vitiated Compartment Fires., In Proceedings of the Seventh International Symposium on Fire Safety Science, Worcester, Edited by D. Evans, 2003, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.7-395

ISO 19701. (2005). Methods for sampling and analysis of fire effluents. International Standards Orgnisation. Geneva.

ISO 19702. (2006). Toxicity testing of fire effluents - Guidance for analysis of gases and vapours in fire effluents using FTIR gas analysis. International Standards Orgnisation. Geneva.

ISO 19703. (2005). Generation and analysis of toxic gases in fire - Calculation of species yields, equivalence ratios and combustion efficiency in experimental fires. International Standards Orgnisation. Geneva.

Janssens, Marc (1991). "Rate of heat release of wood products." Fire Safety Journal 17(3): 217-238. DOI: Doi: 10.1016/0379-7112(91)90003-h.

Jolly, S. and K. Saito (1992). "Scale modeling of fires with emphasis on room flashover phenomenon." Fire Safety Journal 18(2): 139-182. DOI: Doi: 10.1016/0379-7112(92)90036-c.

Jones, Walter W. (1985). "A multicompartment model for the spread of fire, smoke and toxic gases." Fire Safety Journal 9(1): 55-79. DOI: Doi: 10.1016/0379-7112(85)90030-x.

Kaplan, Harold L. and Gordon E. Hartzell (1984). "Modeling of Toxicological Effects of Fire Gases: I. Incapacitating Effects of Narcotic Fire Gases." Journal of Fire Sciences 2(4): 286-305. DOI: 10.1177/073490418400200404.

Karlsson and Quintiere (1999a). Combustion Products. Enclosure Fire Dynamics. CRC Press.

Karlsson and Quintiere (1999b). Computer Modeling of Enclosure Fires. Enclosure Fire Dynamics. CRC Press.

Karlsson and Quintiere (1999c). Conservation Equations and Smoke Filling. Enclosure Fire Dynamics. CRC Press.

Karlsson and Quintiere (1999d). Energy Release Rates. Enclosure Fire Dynamics. CRC Press.

Karlsson and Quintiere (1999e). Gas Temperatures in Ventilated Enclosure Fires. Enclosure Fire Dynamics. CRC Press.

Karlsson, B. and J.G. Quintiere (2000). Enclosure fire dynamics, CRC Press.

Kashiwagi, T. and International Association for Fire Safety Science (1994). Fire safety science: proceedings of the fourth international symposium, International Association for Fire Safety Science.

Kawagoe, Kunio and Yuji Hasemi (1981). "Recent advances in fire physics in Japan." Fire Safety Journal 3(3): 149-162. DOI: Doi: 10.1016/0379-7112(81)90040-0.

Kliylii, U.O., Y.R. Sivathanu and G.M. Faeth,(1991), Carbon Monoxide And Soot Emissions From Buoyant Turbulent Diffusion Flames., In Proceedings of the Third International Symposium on Fire Safety Science, Edinburgh, Edited by G. Cox and B. Langford, 1989, Published by Elsevier Science Publishers LTD, DOI: 10.3801/IAFSS.FSS.3-625

Lennon, Tom, Danny Hopkin, Jamal El-Rimawi and Vadim Silberschmidt (2010). "Large scale natural fire tests on protected engineered timber floor systems." Fire Safety Journal 45(3): 168-182. DOI: DOI: 10.1016/j.firesaf.2010.02.006.

Lennon, Tom and David Moore (2003). "The natural fire safety concept--full-scale tests at Cardington." Fire Safety Journal 38(7): 623-643. DOI: Doi: 10.1016/s0379-7112(03)00028-6.

Lestari, F., A. R. Green, G. Chattopadhyay and A. J. Hayes (2006). "An alternative method for fire smoke toxicity assessment using human lung cells." Fire Safety Journal 41(8): 605-615. DOI: 10.1016/j.firesaf.2006.06.001.

Lewis, M.J., J.B. Moss and P.A. Rubini,(1997), Cfd Modelling Of Combustion And Heat Transfer In Compartment Fires. , In Proceedings of the Fifth International Symposium on Fire Safety Science, Melbourne, Edited by Y. Hasemi, 1997, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.5-463

Li, Hu, Gordon E. Andrews, Basil Daham, Margaret Bell, James Tate and Karl Ropkins (2007). "Impact of Traffic Conditions and Road Geometry on Real World Urban Emissions Using a SI Car." SAE Technical Paper 2007-01-0308. DOI: 10.4271/2007-01-0308.

Lomax, S. and R Simmons,(1986), The Formation of Carbon Monoxide from Diffusion Flames, In Proceedings of the First Initernational Symposium on Fire Safety Science, Edited by C. Grant and P. Pagni, 1986, Published by Hemisphere Publishing Corporation, DOI: 10.3801/IAFSS.FSS.1-441

Lönnermark, Anders, Per Olof Hedekvist and Haukur Ingason (2008). "Gas temperature measurements using fibre Bragg grating during fire experiments in a tunnel." Fire Safety Journal 43(2): 119-126. DOI: DOI: 10.1016/j.firesaf.2007.06.001.

Lundquist, Per, Lennart Rammer and Bo Sörbo (1989). "The role of hydrogen cyanide and carbon monoxide in fire casualties: A prospective study." Forensic Science International 43(1): 9-14. DOI: 10.1016/0379-0738(89)90116-3.

Luo, C., B. Z. Dlugogorski, B. Moghtaderi and E. M. Kennedy (2004). "Computational Study on Toxic Gases Released from Compartment Fires Suppressed with Halogenated Agents." Cybernetics and Systems 35(7-8): 607-625. DOI: 10.1080/01969720490499362.

Luo, M. and V.R. Beck,(1997), Stoichiometric Combustion Model With Oxygen Threshold Improved Predictions For Fire Simulation Using A Cfd Model., In Proceedings of the Fifth International Symposium on Fire Safety Science, Melbourne, Edited by Y. Hasemi, 1997, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.5-559

Lyon, Richard K. and Jerald A. Cole (2000). "Unmixed combustion: an alternative to fire." Combustion and Flame 121(1-2): 249-261. DOI: Doi: 10.1016/s0010-2180(99)00136-4.

Mahalingam, A., F. Jia, Z. Wang, M. K. Patel and E. R. Galea (2011). "Numerical investigation of tube furnace toxicity measurement method (ISO 19700)." Fire and Materials: n/a-n/a. DOI: 10.1002/fam.1079.

Mao, J., Y. H. Xi, G. Bai, H. M. Fan and H. Z. Ji (2011). "A model experimental study on backdraught in tunnel fires." Fire Safety Journal 46(4): 164-177. DOI: DOI: 10.1016/j.firesaf.2011.01.005.

Marchant, E. W. (1980). "Full-scale Fire tests with auromatic sprinkler in a patient room interim report no. NBSIR 79-1749 (June 1979): By John G. O'Neill and Warren D. Hayes, Jr., National Bureau of Standards, Washington." Fire Safety Journal 2(4): 284-285. DOI: Doi: 10.1016/0379-7112(79)90030-4.

Marsh, N., R. Gann, J. Averill and M.R. Nyden,(2008), Sensitivity of a Smoke Toxicity Test Method to Test Conditions, In Proceedings of the Ninth International Symposium on Fire Safety Science, Karlsruhe, Edited by B. Karlsson, 2009, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.9-687

Matala, A., S. Hostikka and J. Mangs,(2008), Estimation of pyrolysis model parameters for solid materials using thermogravimetric data, In Proceedings of the Ninth International Symposium on Fire Safety Science, Karlsruhe, Edited by B. Karlsson, 2009, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.9-1213

Merci, Bart and Karim Van Maele (2008). "Numerical simulations of full-scale enclosure fires in a small compartment with natural roof ventilation." Fire Safety Journal 43(7): 495-511. DOI: DOI: 10.1016/j.firesaf.2007.12.003.

Mikkola, E.,(1991), Charring of Wood Based Materials., In Proceedings of the Third International Symposium on Fire Safety Science, Edinburgh, Edited by G. Cox and B. Langford, 1989, Published by Elsevier Science Publishers LTD, DOI: 10.3801/IAFSS.FSS.3-547.

Miles, S.D., S. Kumar and G. Cox,(2000), Comparisons of 'blind Predictions' of a CFD Model With Experimental Data. , In Proceedings of the Sixth International Symposium on Fire Safety Science, Poitiers, Edited by M Curtat, 2000, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.6-543

Mitler, Henri E. (1985). "The Harvard fire model." Fire Safety Journal 9(1): 7-16. DOI: Doi: 10.1016/0379-7112(85)90026-8.

Morikawa, Tokio (1988). "Evolution of toxic gases from burning polymeric materials in a small-scale box model." Fire and Materials 12(2): 43-49. DOI: 10.1002/fam.810120202.

Mulholland, G.W. (1990). "Position Paper Regarding CO Yield" in FPETOOL: Fire Protection Engineering Tools for Hazard Estimation. H.E. Nelson. Gaithersburg, MD.

Mulholland, G.W., M.L. Janssens, S. Yusa, W. Twilley and V. Babrauskas,(1991), The Effect of Oxygen Concentration on CO and Smoke Produced by Flames., In Proceedings of the Third International Symposium on Fire Safety Science, Edinburgh, Edited by G. Cox and B. Langford, 1989, Published by Elsevier Science Publishers LTD, DOI: 10.3801/IAFSS.FSS.3-585

Murray, A. and Morell B.,(2010), How the fire engineering enabled the design of a state of the art regional sports facility, In Proceedings of the Fire Safety Engineering in the UK: The State of the Art, Edinburgh, Edited by R. Carvel, Published by University of Edinburgh,

Nakaya, I. and K. Akita (1983). "A simulation model for compartment fires." Fire Safety Journal 5(2): 157-165. DOI: Doi: 10.1016/0379-7112(83)90008-5.

Nakaya, Ichiroh (1987). "Prediction model of CO, CO2 and O2 concentrations in compartment fires using wood fuel." Fire and Materials 11(4): 173-178. DOI: 10.1002/fam.810110403.

National Statistics. (2011). Fire Statistics Monitor: April 2010 to March 2011. Department for Communities and Local Government. London.

Nicholson, John W. and Philip F. Nolan (1983). "The behaviour of thermoset polymers under fire conditions." Fire and Materials 7(2): 89-95. DOI: 10.1002/fam.810070207.

Novozhilov, V., D. J. E. Harvie, J. H. Kent, V. B. Apte and D. Pearson (1997). "A computational fluid dynamics study of wood fire extinguishment by water sprinkler." Fire Safety Journal 29(4): 259-282. DOI: Doi: 10.1016/s0379-7112(97)00027-1.

Ohmiya, Yusa, Sizuki, Koshikawa, and Delichatsios,(2002), Aerothermodynamics of fully involved enclosure fires having external flames, In Proceedings of the 7th International Symposium on Fire Safery Science, Edited by Published by

Olenick, Stephen M. and Douglas J. Carpenter (2003). "An Updated International Survey of Computer Models for Fire and Smoke." Journal of Fire Protection Engineering 13(2): 87-110. DOI: 10.1177/1042391503013002001.

Paabo, Maya and Barbara C. Levin (1987a). "A literature review of the chemical nature and toxicity of the decomposition products of polyethylenes." Fire and Materials 11(2): 55-70. DOI: 10.1002/fam.810110203.

Paabo, Maya and Barbara C. Levin (1987b). "A review of the literature on the gaseous products and toxicity generated from the pyrolysis and combustion of rigid polyurethane foams." Fire and Materials 11(1): 1-29. DOI: 10.1002/fam.810110102.

Park, Won Chan, Arvind Atreya and Howard R. Baum (2010). "Experimental and theoretical investigation of heat and mass transfer processes during wood pyrolysis." Combustion and Flame 157(3): 481-494. DOI: DOI: 10.1016/j.combustflame.2009.10.006.

Paul, K. T., T. R. Hull, K. Lebek and A. A. Stec (2008). "Fire smoke toxicity: The effect of nitrogen oxides." Fire Safety Journal 43(4): 243-251. DOI: DOI: 10.1016/j.firesaf.2007.10.003.

Pauluhn, J. (1992). "Modeling of toxicological effects of fire effluents: prediction of toxicity and evaluation of animal model." Toxicology Letters 64-65(0): 265-271. DOI: 10.1016/0378-4274(92)90198-s.

PD 7974-2. (2002). Application of fire safety engineering principles to the design of buildings - Spread of smoke and toxic gases within and beyond the enclosure of origin. British Standards Inistitution. London.

PD 7974-3. (2002). Application of fire safety engineering principles to the design of buildings - Structural response and fire spread beyond the enclosure of origin. British Standards Inistitution. London.

Peacock, Richard D., Jason D. Averill, Paul A. Reneke and Walter W. Jones (2004). "Characteristics of Fire Scenarios in Which Sublethal Effects of Smoke are Important." Fire Technology 40(2): 127-147. DOI: 10.1023/b:fire.0000016840.14947.61.

Peacock, Richard D. and Vytenis Babrauskas (1991). "Analysis of large-scale fire test data." Fire Safety Journal 17(5): 387-414. DOI: 10.1016/0379-7112(91)90019-u.

Peacock, Richard D., Walter W. Jones and Richard W. Bukowski (1993). "Verification of a model of fire and smoke transport." Fire Safety Journal 21(2): 89-129. DOI: Doi: 10.1016/0379-7112(93)90038-r.

Physchem. (2006). "Glossary Definition." Retrieved 02/09/2008, from http://physchem.ox.ac.uk/MSDS/glossary/.

Pierce, J. B. M. and J. B. Moss (2007). "Smoke production, radiation heat transfer and fire growth in a liquid-fuelled compartment fire." Fire Safety Journal 42(4): 310-320. DOI: DOI: 10.1016/j.firesaf.2006.11.006.

Pitts, W.,(1997a), An Algorithm for Estimating Carbon Monoxide Formation In Enclosure Fires., In Proceedings of the Fifth International Symposium on Fire Safety Science, Melbourne, Edited by Y. Hasemi, 1997, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.5-547

Pitts, W.M., Kudou, Y., Kojima, and Udea, (1997b). Backdraft and Various Backdraft related Phonomena observed in small compartment fires. 14th Joint Panel Meeting of the UJNR Panel on Fire Research and Safety. Japan.

Pope, N. D. and C. G. Bailey (2006). "Quantitative comparison of FDS and parametric fire curves with post-flashover compartment fire test data." Fire Safety Journal 41(2): 99-110. DOI: DOI: 10.1016/j.firesaf.2005.11.002.

Prager, F. H., G. Kimmerle, T. Maertins, M. Mann and J. Pauluhn (1994). "Toxicity of the combustion and decomposition products of polyurethanes." Fire and Materials 18(2): 107-119. DOI: 10.1002/fam.810180207.

Puri, R. and R.J. Santoro,(1991), The Role of Soot Particle Formation on The Production of Carbon Monoxide in Fires., In Proceedings of the Third International Symposium on Fire Safety Science, Edinburgh, Edited by G. Cox and B. Langford, 1989, Published by Elsevier Science Publishers LTD, DOI: 10.3801/IAFSS.FSS.3-595

Purser, David (1996). "Behavioural impairment in smoke environments." Toxicology 115(1-3): 25-40.

Quintiere, J. G., M. Birky, F. Macdonald and G. Smith (1982). "An analysis of smoldering fires in closed compartments and their hazard due to carbon monoxide." Fire and Materials 6(3-4): 99-110. DOI: 10.1002/fam.810060302.

Quintiere, J. G., B. J. McCaffrey and K. Den Braven (1979). "Experimental and theoretical analysis of quasi-steady small-scale enclosure fires." Symposium (International) on Combustion 17(1): 1125-1137. DOI: 10.1016/s0082-0784(79)80107-1.

Quintiere, J.G. (2006). Fundamentals of fire phenomena, John Wiley.

Quintiere, J.G., R.L. Alpert, R.A. Altenkirch and American Society of Mechanical Engineers. Heat Transfer Division (1983). Fire dynamics and heat transfer, American Society of Mechanical Engineers.

Quintiere, James G. (1982). "Smoke measurements: An assessment of correlations between laboratory and full-scale experiments." Fire and Materials 6(3-4): 145-160. DOI: 10.1002/fam.810060308.

Rasbash, D. J. and D. D. Drysdale (1982). "Fundamentals of smoke production." Fire Safety Journal 5(1): 77-86. DOI: Doi: 10.1016/0379-7112(82)90008-x.

Rasbash, D. J. and D. D. Drysdale (1983). "Theory of fire and fire processes." Fire and Materials 7(2): 79-88. DOI: 10.1002/fam.810070206.

Rasbash, D. J. and B. T. Pratt (1980). "Estimation of the smoke produced in fires." Fire Safety Journal 2(1): 23-37. DOI: 10.1016/0379-7112(79)90013-4.

Rein, Guillermo, Amnon Bar-Ilan, A. Carlos Fernandez-Pello and Norman Alvares (2006). "A Comparison of Three Models for the Simulation of Accidental Fires." Journal of Fire Protection Engineering 16(3): 183-209. DOI: 10.1177/1042391506056926.

Saito, F. (1982). "Toxicity test for fire resistive materials in Japan." Journal Combustion Toxicology 9: 194-205.

Sanghavi, Prachi, Kavi Bhalla and Veena Das (2009). "Fire-related deaths in India in 2001: a retrospective analysis of data." The Lancet 373(9671): 1282-1288. DOI: 10.1016/s0140-6736(09)60235-x.

Santo, Giulio and Francesco Tamanini (1981). "Influence of oxygen depletion on the radiative properties of PMMA flames." Symposium (International) on Combustion 18(1): 619-631. DOI: 10.1016/s0082-0784(81)80067-7.

Saso, Y., H. Gotoda and Y. Ogawa,(2005), Correlation of Toxic Product Yields From Tube Furnace Tests and Large Scale Fires., In Proceedings of the Eighth International Symposium on Fire Safety Science, Beijing, Edited by D. Gottuk and B. Lattimer, 2005, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.8-1013

Schnipper, Anette, Lene Smith-hansen and Erling Sonnich Thomsen (1995). "Reduced combustion efficiency of chlorinated compounds, resulting in higher yields of carbon monoxide." Fire and Materials 19(2): 61-64. DOI: 10.1002/fam.810190203.

Sinai, Y. L. (1999). "Comments on the role of leakages in field modelling of under-ventilated compartment fires." Fire Safety Journal 33(1): 11-20. DOI: Doi: 10.1016/s0379-7112(99)00005-3.

Smardz (2006). Validation of Fire Dynamics Simulator (FDS) for forced and natural convection flows, Ulster.

Stec, A. A., T. R. Hull, K. Lebek, J. A. Purser and D. A. Purser (2008a). "The effect of temperature and ventilation condition on the toxic product yields from burning polymers." Fire and Materials 32(1): 49-60. DOI: 10.1002/fam.955.

Stec, A.A., T.R. Hull, J.A. Purser, P. Blomqvist and K. Lebek,(2008b), A Comparison of Toxic Product Yields Obtained From Five Laboratories Using the Steady State Tube Furnace (ISO TS 19700), In Proceedings of the Ninth International Symposium on Fire Safety Science, Karlsruhe, Edited by B. Karlsson, 2009, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.9-653

Stec, Anna A., Peter Fardell, Per Blomqvist, Lucas Bustamante-Valencia, Laurent Saragoza and Eric Guillaume (2011). "Quantification of fire gases by FTIR: Experimental characterisation of calibration systems." Fire Safety Journal In Press, Corrected Proof. DOI: 10.1016/j.firesaf.2011.02.004.

Steckler, K. D., J. G. Quintiere and W. J. Rinkinen (1982). "Flow induced by fire in a compartment." Symposium (International) on Combustion 19(1): 913-920. DOI: 10.1016/s0082-0784(82)80267-1.

Steventon, Jill (1983). "Fire safety in hospitals." Ergonomics 26(8): 747-754. DOI: 10.1080/00140138308963396.

Sumi, K. (1984). "Toxicity of fire effluents: Application of test data." Fire and Materials 8(1): 1-5. DOI: 10.1002/fam.810080102.

Symington, I. S. Anderson, R. A. Oliver, J. S. Thomson, I. Harland, W. A. Kerr, J. W. (1978). "Cynide Exposure in Fires." The Lancet 312(8080): 91-92.

Takeda, Hisahiro (1983). "Mixing effect and combustion efficiency in compartment fires." Fire Safety Journal 5(3-4): 199-199. DOI: Doi: 10.1016/0379-7112(83)90018-8.

Takeda, Hisahiro and Kazuo Akita (1982). "New modeling of liquid or thermoplastic pool fires in compartment." Symposium (International) on Combustion 19(1): 897-904. DOI: 10.1016/s0082-0784(82)80265-8.

Tetteh, John, Ed Metcalfe, Sian Howells, Rob Withnall, Stanley Ames and Simon Vollam (1996). "Orthogonal Noise Annihilation for FTIR Spectroscopy in Fire Gas Analysis." Fire and Materials 20(1): 51-59. DOI: 10.1002/(sici)1099-1018(199601)20:1<51::aid-fam560>3.0.co;2-0.

Tewarson (1996). "Ventilation effects on combustion products." Toxicology 115(1-3): 145-156. DOI: 10.1016/s0300-483x(96)03503-2.

Tewarson, A.,(2008), Smoke Emissions in Fires, In Proceedings of the Ninth International Symposium on Fire Safety Science, Karlsruhe, Edited by B. Karlsson, 2009, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.9-1153

Tewarson, A., F. Chu and F.H. Jiang,(1994), Combustion of Halogenated Polymers., In Proceedings of the Fourth International Symposium on Fire Safety Science, Ottawa, Edited by T. Kashiwagi, 1994, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.4-515

Tewarson, A., J. L. Lee and R. F. Pion (1981). "The influence of oxygen concentration on fuel parameters for fire modeling." Symposium (International) on Combustion 18(1): 563-570. DOI: 10.1016/s0082-0784(81)80061-6.

Tewarson, A. and S. D. Ogden (1992). "Fire behavior of polymethylmethacrylate." Combustion and Flame 89(3-4): 237-259. DOI: Doi: 10.1016/0010-2180(92)90013-f.

Tewarson, A. and J. Steciak (1983). "Fire ventilation." Combustion and Flame 53(1-3): 123-134. DOI: 10.1016/0010-2180(83)90011-1.

Tewarson, Archibald (2004). "Combustion efficiency and its radiative component." Fire Safety Journal 39(2): 131-141. DOI: DOI: 10.1016/j.firesaf.2003.07.004.

Thomas, I.R. and I.D Bennetts,(2000), Fires In Enclosures with Single Ventilation Openings - Comparison Of Long And Wide Enclosures, In Proceedings of the Sixth International Symposium on Fire Safety Science, Poitiers, Edited by M Curtat, 2000, Published by International Association for Fire Safety Science, DOI: doi:10.3801/IAFSS.FSS.6-941

Thomas, Ian R., Khalid A.M. Moinuddin and Ian D. Bennetts (2007). "The Effect of Fuel Quantity and Location on Small Enclosure Fires." Journal of Fire Protection Engineering 17(2): 85-102. DOI: 10.1177/1042391506064908.

Thomas, P. H. (1981). "Fire modeling and fire behavior in rooms." Symposium (International) on Combustion 18(1): 503-518. DOI: 10.1016/s0082-0784(81)80056-2.

Thomas, P. H. (1983). "Modelling of compartment fires." Fire Safety Journal 5(3-4): 181-190. DOI: Doi: 10.1016/0379-7112(83)90016-4.

Thomas, P. H. and M. L. Bullen (1980). "Burning of fuels in fully-developed room fires." Fire Safety Journal 2(4): 275-281. DOI: Doi: 10.1016/0379-7112(79)90027-4.

Thomas, P. H., M. L. Bullen, J. G. Quintiere and B. J. McCaffrey (1980). "Flashover and instabilities in fire behavior." Combustion and Flame 38(0): 159-171. DOI: 10.1016/0010-2180(80)90048-6.

Thomas, P. H. and C. Ian Smith (2000). "A note on fully developed fires in large compartments." Fire Safety Journal 35(1): 67-69. DOI: Doi: 10.1016/s0379-7112(00)00012-6.

Thomas, Philip H. (2000). "Dimensional analysis: a magic art in fire research?" Fire Safety Journal 34(2): 111-141. DOI: Doi: 10.1016/s0379-7112(99)00054-5.

Tsuchiya, Y.,(1989), Relative Signigicance of NOx and HCN In Fire Gas, In Proceedings of the Second International Symposium on Fire Safety Science, Tokyo, Edited by T. Wakamatsu, Y. Hasemi, A. Sekizawa, P. Seeger, P. Pagni and C. Grant, 1989, Published by Hamisphere Publishing Corporation, DOI: 10.3801/IAFSS.FSS.2-381

Tsuchiya, Y.,(1994), CO/CO2 Ratios In Fire., In Proceedings of the Fourth International Symposium on Fire Safety Science, Ottawa, Edited by T. Kashiwagi, 1994, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.4-515

Tsuchiya, Yoshio (1982). "Methods of determining heat release rate: State-of-the-art." Fire Safety Journal 5(1): 49-57. DOI: 10.1016/0379-7112(82)90006-6.

Tuovinen, H,(1994), Modelling Of Laminar Diffusion Flames In Vitiated Environments., In Proceedings of the Fourth International Symposium on Fire Safety Science, Ottawa, Edited by T. Kashiwagi, 1994, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.4-113

Wakatsuki, Kaoru (2005). High Temperature Radiation Absorption of Fuel Molecules and an Evaluation of Its Influence on Pool Fire Modeling. Mechanical Engineering. College Park, University of Maryland. Doctor of Philosophy.

Wakefield, J.C. (2010). A Toxicological Review of the Products of Combustion. Health Protection Agency Chemical Hazards and Posons Division. Chilton. HPA.

Wang, H. Y. (2009). "Prediction of soot and carbon monoxide production in a ventilated tunnel fire by using a computer simulation." Fire Safety Journal 44(3): 394-406. DOI: DOI: 10.1016/j.firesaf.2008.08.007.

Wang, Lei and James G. Quintiere (2009). "An analysis of compartment fire doorway flows." Fire Safety Journal 44(5): 718-731. DOI: 10.1016/j.firesaf.2009.02.001.

Wang, Qi, Takaki Ishikawa, Tomomi Michiue, Bao-Li Zhu and Hitoshi Maeda (2011). "Evaluation of human brain damage in fire fatality by quantification of basic fibroblast growth factor (bFGF), glial fibrillary acidic protein (GFAP) and single-stranded DNA (ssDNA) immunoreactivities." Forensic Science International 211(1-3): 19-26. DOI: 10.1016/j.forsciint.2011.03.037.

Wang, Z., F. Jia and E. R. Galea (2007). "Predicting toxic gas concentrations resulting from enclosure fires using local equivalence ratio concept linked to fire field models." Fire and Materials 31(1): 27-51. DOI: 10.1002/fam.924.

Wang, Z., F. Jia, E. R. Galea and M. K. Patel (2010a). "Predicting toxic gas concentrations at locations remote from the fire source." Fire and Materials: n/a-n/a. DOI: 10.1002/fam.1069.

Wang, Zhaozhi, Fuchen Jia and E. R. Galea (2010b). "A generalized relationship between the normalized yields of carbon monoxide and hydrogen cyanide." Fire and Materials: n/a-n/a. DOI: 10.1002/fam.1076.

Welch, S., A. Jowsey, S. Deeny, R. Morgan and J. L. Torero (2007). "BRE large compartment fire tests--Characterising post-flashover fires for model validation." Fire Safety Journal 42(8): 548-567. DOI: DOI: 10.1016/j.firesaf.2007.04.002.

Welch, S. and S Paul,(2010), Prediction of toxic species in fire, In Proceedings of the Fire Safety Engineering in the UK: The State of the Art, Edinburgh, Edited by R. Carvel, Published by University of Edinburgh,

Wen, J. X. and L. Y. Huang (2000). "CFD modelling of confined jet fires under ventilation-controlled conditions." Fire Safety Journal 34(1): 1-24. DOI: Doi: 10.1016/s0379-7112(99)00052-1.

Weng, W. G. and W. C. Fan (2004). "Nonlinear analysis of the backdraft phenomenon in room fires." Fire Safety Journal 39(6): 447-464. DOI: DOI: 10.1016/j.firesaf.2004.04.001.

Wieczorek, C.J., U. Vandsburger, B. Lattimer and C. Mckay,(2000), The Applicability of Correlations Between the Species Formation and the Global Equivalence Ratio In a 1/2- Scaled ISO Compartment With Nongaseous Fuel, In Proceedings of the Sixth International Symposium on Fire Safety Science, Poitiers, Edited by M Curtat, 2000, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.6-965

Wieczorek, Christopher J., Uri Vandsburger and Jason Floyd (2004). "An Evaluation of the Global Equivalence Ratio Concept for Compartment Fires: Data Analysis Methods." Journal of Fire Protection Engineering 14(1): 9-31. DOI: 10.1177/1042391504034743.

Williams, S. J. and F. B. Clarke (1982). "Combustion product toxicity: Dependence on the mode of product generation." Fire and Materials 6(3-4): 161-162. DOI: 10.1002/fam.810060309.

Williams, S. J. and F. B. Clarke (1983). "Combustion product toxicity: Dependence on the mode of product generation." Fire and Materials 7(2): 96-97. DOI: 10.1002/fam.810070208.

Williamson, Robert Brady and Nicholas A. Dembsey (1993). "Advances in assessment methods for fire safety." Fire Safety Journal 20(1): 15-38. DOI: Doi: 10.1016/0379-7112(93)90010-n.

Woolley, W. D., S. A. Ames and P. J. Fardell (1979). "Chemical aspects of combustion toxicology of fires." Fire and Materials 3(2): 110-120. DOI: 10.1002/fam.810030210.

Woolley, W. D. and P. J. Fardell (1977). "The prediction of combustion products." Fire Safety Journal 1(1): 11-21. DOI: Doi: 10.1016/0379-7112(77)90004-2.

Woolley, W. D. and P. J. Fardell (1982). "Basic aspects of combustion toxicology." Fire Safety Journal 5(1): 29-48. DOI: 10.1016/0379-7112(82)90005-4.

Woolley, W. D. and P. J. Fardell (1990). "Toxicity of combustion products--Measurements and interpretations." Polymer Degradation and Stability 30(1): 123-140.

Woolley, W. D., P. J. Fardell, A. B. Atkinson and A. P. Verrall (1978). "Conversion of fuels containing nitrogen to oxides of nitrogen in hydrogen and methane flames." Fire and Materials 2(3): 122-131. DOI: 10.1002/fam.810020306.

Xing T, Stern. (2006). "Introduction to Computational Fluid Dynamics (CFD), University of Iowa." from http://css.engineering.uiowa.edu/~me_160/Lab/CFD_grid_postprocessing_2006.ppt.

Xue, H., J. C. Ho and Y. M. Cheng (2001). "Comparison of different combustion models in enclosure fire simulation." Fire Safety Journal 36(1): 37-54. DOI: Doi: 10.1016/s0379-7112(00)00043-6.

Yamada, S. and T. Tanaka,(1994), A Model For Predicting Concentrations Of Carbon Monoxide In Building Fires., In Proceedings of the Fourth International Symposium on Fire Safety Science, Ottawa, Edited by T. Kashiwagi, 1994, Published by International Association for Fire Safety Science, DOI: 10.3801/IAFSS.FSS.4-539

Yang, D., L. H. Hu, Y. Q. Jiang, R. Huo, S. Zhu and X. Y. Zhao (2010). "Comparison of FDS predictions by different combustion models with measured data for enclosure fires." Fire Safety Journal 45(5): 298-313. DOI: DOI: 10.1016/j.firesaf.2010.06.002.

Yeoh, G. H., R. K. K. Yuen, S. C. P. Chueng and W. K. Kwok (2003). "On modelling combustion, radiation and soot processes in compartment fires." Building and Environment 38(6): 771-785. DOI: 10.1016/s0360-1323(03)00022-2.

Yii, Ee H., Andrew H. Buchanan and Charles M. Fleischmann (2006). "Simulating the effects of fuel type and geometry on post-flashover fire temperatures." Fire Safety Journal 41(1): 62-75. DOI: DOI: 10.1016/j.firesaf.2005.09.001.

Yu, Hong-Zeng (1993). "A unified fire property data correlation scheme for combustibles burning under different ventilation/oxygen concentration conditions." Fire Safety Journal 20(2): 175-181. DOI: Doi: 10.1016/0379-7112(93)90036-p.

Yuan, Shusheng and Jian Zhang (2009). "Large eddy simulation of compartment fire with solid combustibles." Fire Safety Journal 44(3): 349-362. DOI: DOI: 10.1016/j.firesaf.2008.08.002.

Zou, G. W. and W. K. Chow (2005). "Evaluation of the Field Model, Fire Dynamics Simulator, for a Specific Experimental Scenario." Journal of Fire Protection Engineering 15(2): 77-92. DOI: 10.1177/1042391505047304.

Zukoski, E. E., J. H. Morehart, T. Kubota and S. J. Toner (1991). "Species production and heat release rates in two-layered natural gas fires." Combustion and Flame 83(3-4): 325-332. DOI: 10.1016/0010-2180(91)90079-q.

Appendix A

CFD Basic assumptions

In most Computational Fluid Dynamics CFD codes the conversation of mass, momentum, and energy for a Newtonian fluid are fundamental assumption. Eq. 2.39-2.41 represents the classic form of the conservation equations obtained from (Anderson, 1995):

Conservation of Mass

$$\frac{\partial \rho}{\partial t} + \nabla . \rho \mathbf{u} = \dot{\mathrm{m}}_{b}^{m} \qquad 2.39$$

Conservation of Momentum (Newton’s Second Law)

$$\frac{\partial}{\partial t}(\rho \mathbf{u}) + \nabla . \rho \mathbf{u}\mathbf{u} + \nabla p = \rho \mathrm{g} + \mathrm{f}_{b} + \nabla . \tau_{ij} \qquad 2.40$$

Conservation of Energy (First Law of Thermodynamics)

$$\frac{\partial}{\partial t}(\rho h) + \nabla . \rho h \boldsymbol{u} = \frac{D_P}{Dt} + \dot{q}''' - \dot{q}_b''' - \nabla . \dot{q}'' + \varepsilon \qquad 2.41$$

where, ρ is density, **u** is velocity, *T* is temperature, *p* is pressure, *m* is mass, f is force and *h* is sensible enthalpy.

The equations are presented here in a summarised format, using the notation; however, its implementation in computer codes requires the expanded forms. Once the variables are presented in the expanded form, and the domain (mesh) on which the required solution is identified, mathematical technique is then deployed to obtain the solution. Depending, on the type of the problem, number of variables, and the accuracy of the solution, the following model types were developed (Anderson, 1995; Cox, 1995; Yeoh and Yuen, 2009):

- Reynolds-Averaged Navier-Stokes, RANS models, where equations are time-averaged for all length scales considered, used for most of the fire models
- Large Eddy Simulation, LES models, where turbulences in the flow are only averaged at scales smaller than the mesh size. This requires higher computational capability than the RANS model, in addition to the need for a finer mesh.
- Direct Numerical Simulation, DNS models, where all the relevant scales which occur in the flow are resolved. However, this approach is not yet of practical use in modelling of building fires as it requires an extremely well resolved mesh.

The FDS model, investigated in this work comprises more than one of these techniques as will be shown in the following section.

Fire Dynamics Simulator (FDS)

Fire Dynamics Simulator FDS, is the most widely used CFD software for the prediction of fire development and smoke movement in buildings (McGrattan et al., 2008b; McGrattan et al., 2008a). The FDS user guide describes the code as an open-source CFD code, which:

“Solves numerically a form of the Navier-Stokes equations appropriate for low-speed, thermally-driven flow with an emphasis on smoke and heat transport from fires. The partial derivatives of the conservation equations of mass, momentum and energy are approximated as finite differences and the solution is updated in time on a three-dimensional, rectilinear grid. Thermal radiation is computed using a finite volume technique on the same grid as the flow solver. Lagrangian particles are used to simulate smoke movement, sprinklers discharge, and fuel spray.” (McGrattan et al., 2008a)

In order to be adequate for use in fire simulations, the model comprises three major components. The first is the Hydrodynamic model, which solves Navier-Stoke equations of the low speed flow. This hydrodynamic model is solved explicitly using a second order accurate predictor-corrector scheme, while turbulence is treated by the Smagorinsky form of Large Eddy Simulation (LES). The second major sub model in FDS is the radiation transport model. It predicts the radiate heat transfer, through the solution of the radiation transport of a grey gas. The radiation mathematical model, is specifically developed by the FDS developers, and uses a similar technique to the Finite Volume Method (FVM) typically used for convective transport. The radiation model, typically consumes 20% of the computational cost of a typical simulation. The third major component, and most relevant to this work, is the combustion model (McGrattan et al., 2008b)

The default combustion model in FDS deploys the mixture fraction concept, which is a quantity representing the fuel and the products of the combustion in the gas phase. This is the preferred approach by the developers and users, as it performs reasonably well, in large eddy simulations, where the grid is not fine enough to resolve the diffusion of fuel and oxygen. An alternative Direct Numerical Simulation (DNS), is also provided by the developers, which traces the individual gas species, and reaction according the specified Arrhenius reaction parameter. However, the very high computational cost, and very fine meshing, required for DNS simulations; make it an unfavourable approach in fire simulations (McGrattan et al., 2008a).

The mixture fraction model in FDS can be explained as follow, given a volume containing a mixture of gas species, the ratio of the mass of a subset of the species to the total mass present in the volume. For a combustion process, fresh air can be considered 0, while the fuel at the burner surface is almost 1. Once, the fuel and air mix, in the combustion zone, the combustion process will occur instantaneously. In earlier versions of FDS, 2-4, the single step mixture fraction was considered sufficient in describing the combustion process. However, this was upgraded by considering temperature as a third quantity. The consideration of temperature, allowed for predicting local extensions by considering oxygen-temperature levels, and subsequently, and flammability limits identified in (Beyler, 2002). The resulting, model was called mixture fraction with local extension.

The latest version of the mixture fraction model used in FDS is described as a two-step reaction with local extension mixture fraction model. Since, the assumption that complete combustion occurs in earlier models, an attempt was made to expand the same concept to address incomplete combustion in under ventilated fires. the proposed model includes the production of large amounts of CO in the first step of a two-step reaction, followed by a partial conversion to CO_2 if there is a sufficient amount of oxygen present. The user of the model is expected to provide the fuel composition, the expected soot and CO yields, based on this, the first reaction occurs, and the conversion of excess CO to CO_2 is done by the model where excess oxygen is present (McGrattan et al., 2008a).

The current configuration of the mixture fraction model, allows for the addition of extra variables as a combustion product. However, the developers argue any advantage gained from specifying a new variable, should outweigh, the computational expense incurred as a results of its addition. This is an approach to keep the model practical and popular for industry and users, who avoid more complex combustion models (McGrattan, 2008; Mcgrattan, 2005)

In all cases, the fuel mass fraction accounted for in the gas phase combustion model is provided by a pyrolysis model. The pyrolysis model yields char, water vapour, and fuel vapour fractions. FDS provides a selection of pyrolysis models for the modeller to choose from, they include: a gas burner with a specified heat release rate, a single and multi-step solid phase pyrolysis model with a prescribed reaction rates, and a liquid fuels models. The pyrolysis models, are another area of active research which may affect the combustion model greatly, however they are considered out of the scope of this work on toxic effluents, which focuses on the gas phase products.

Fire toxicity in computational models

The progress in fire toxicity modelling is impaired by the limitations of the existing models. One of the major limitations is that most models are not yet capable of predicting the fuel mass loss rate, and subsequent combustion reactions accurately (Grewolls, 2010) As a result, the current credible approach towards fire modelling, in both zone models, and CFD models, is to specify a t^2 design fire, according to the specifications in the British Standard (PD-7974-1, 2002), and Charted Engineering guide (CIBSE, 2003). This design fire, as mentioned earlier, specify toxic yields related to well ventilated fires, with a reference to CO being significantly higher (0.2 - 0.25 kg/kg) in vitiated conditions. In addition the design fires, only mentions major fire products, with emphasis on CO levels.

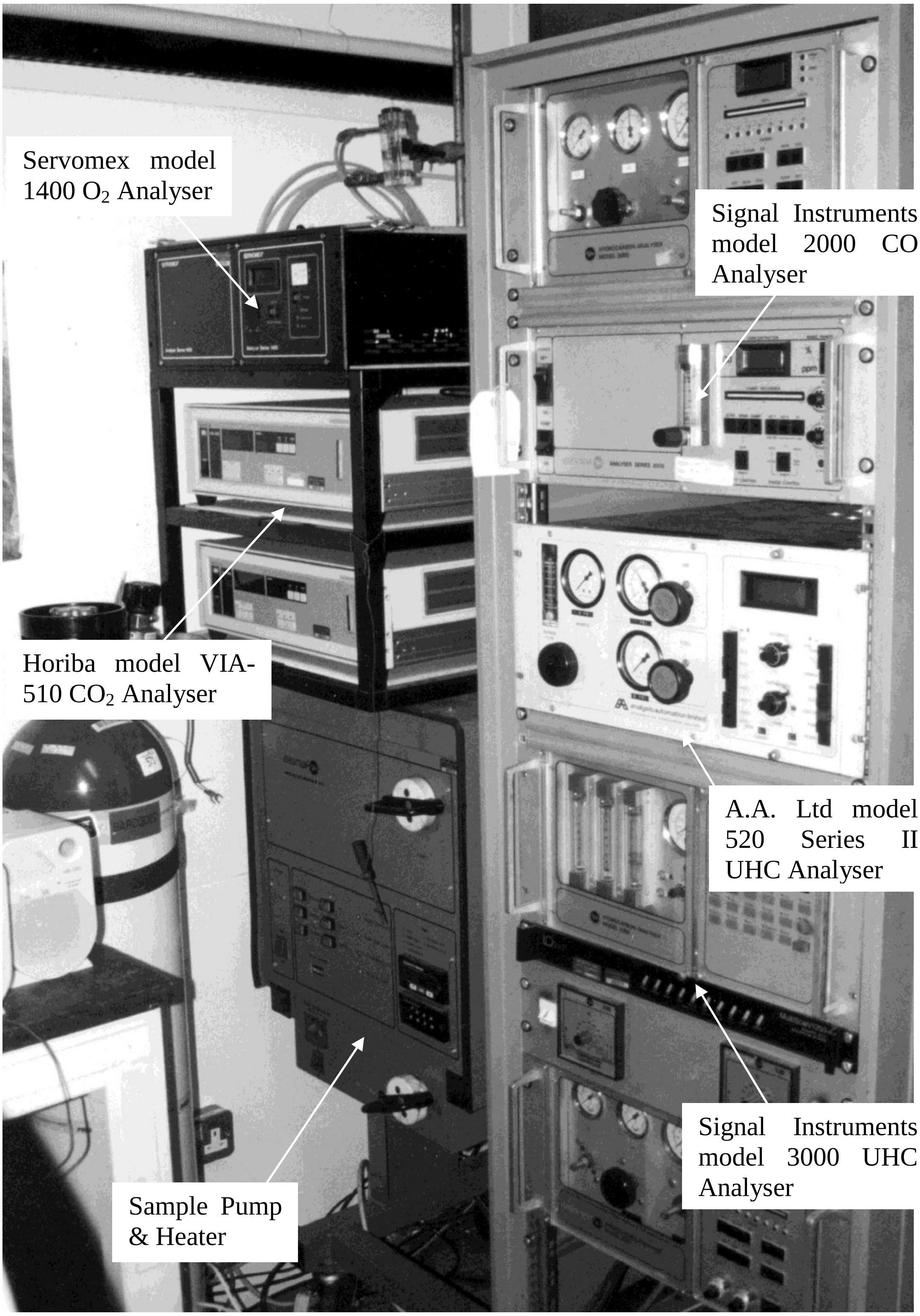
The recent development in FDS, allow for the application of a constant 0.25 g/kg CO yields more related to under ventilated conditions in the design fire, and at the same time, provide an alternative approach to the fixed heat release fire, by allowing the modeller to activate the multiphase pyrolysis model. Nonetheless, the validity of the model is not yet verified, and the detailed kinetics properties needed make it challenging for practical application by fire safety engineers. Therefore, the current best practice by engineers in the field can be described, as specifying a burner fire, growing over time to simulate t^2, and producing levels of CO equivalent to 0.25 kg/kg.

More recently, a FED value as prescribed in the ISO1344 was proposed in EVAC, an evacuation model associated with FDS, the FED quantity can be measured, at any location, simulating human exposure to the toxic gases and predicting incapacitation (Hostikka, 2011). However, the FED only considers CO, CO_2, and O_2 depletion. The developed FED is intended to be used as an alternative to the classic assessment based on CO levels, and visibility, however, this quantity is misleading, as it does not represent the hazard posed by irritants, nor it takes into account important asphyxiant such as HCN.

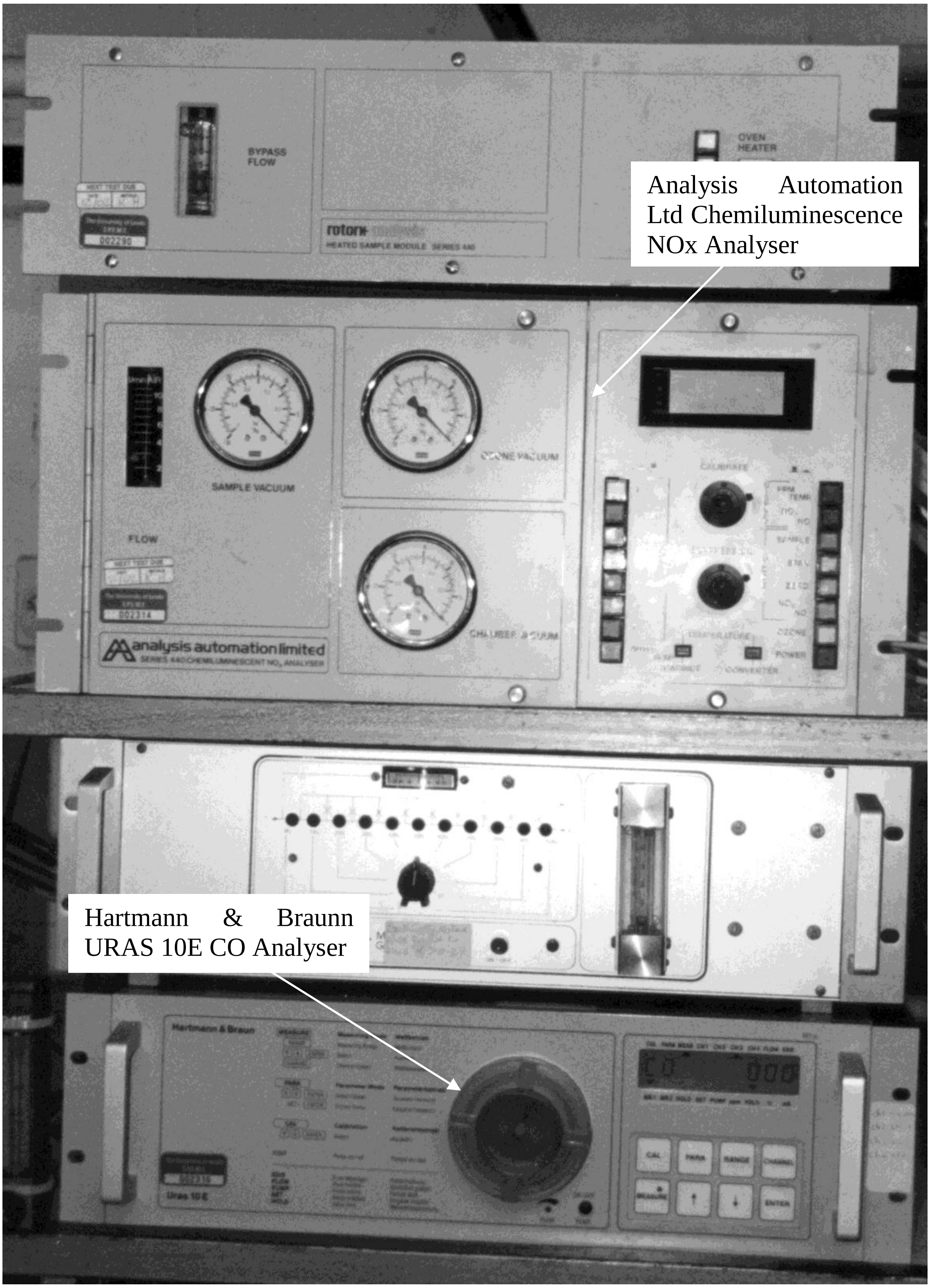
It is predicted that future fire models, shall be capable of predicting the toxic hazard in a more precise manner. However, better understanding and standards of research are needed in order to provide data useful for developing future models. At the same time, while current models are capable of predicting major species to a reasonable level, an estimate is needed to account for minor combustion species (irritants) produced in fires. Although, these species are considered minor in terms of effect on the fire source and fire development, they shall be regarded as important in terms of hazard posed to fire victims.

APPENDIX B

Pictures of gas analysers used in this work



Pictures of Gas Analysers used in this work:

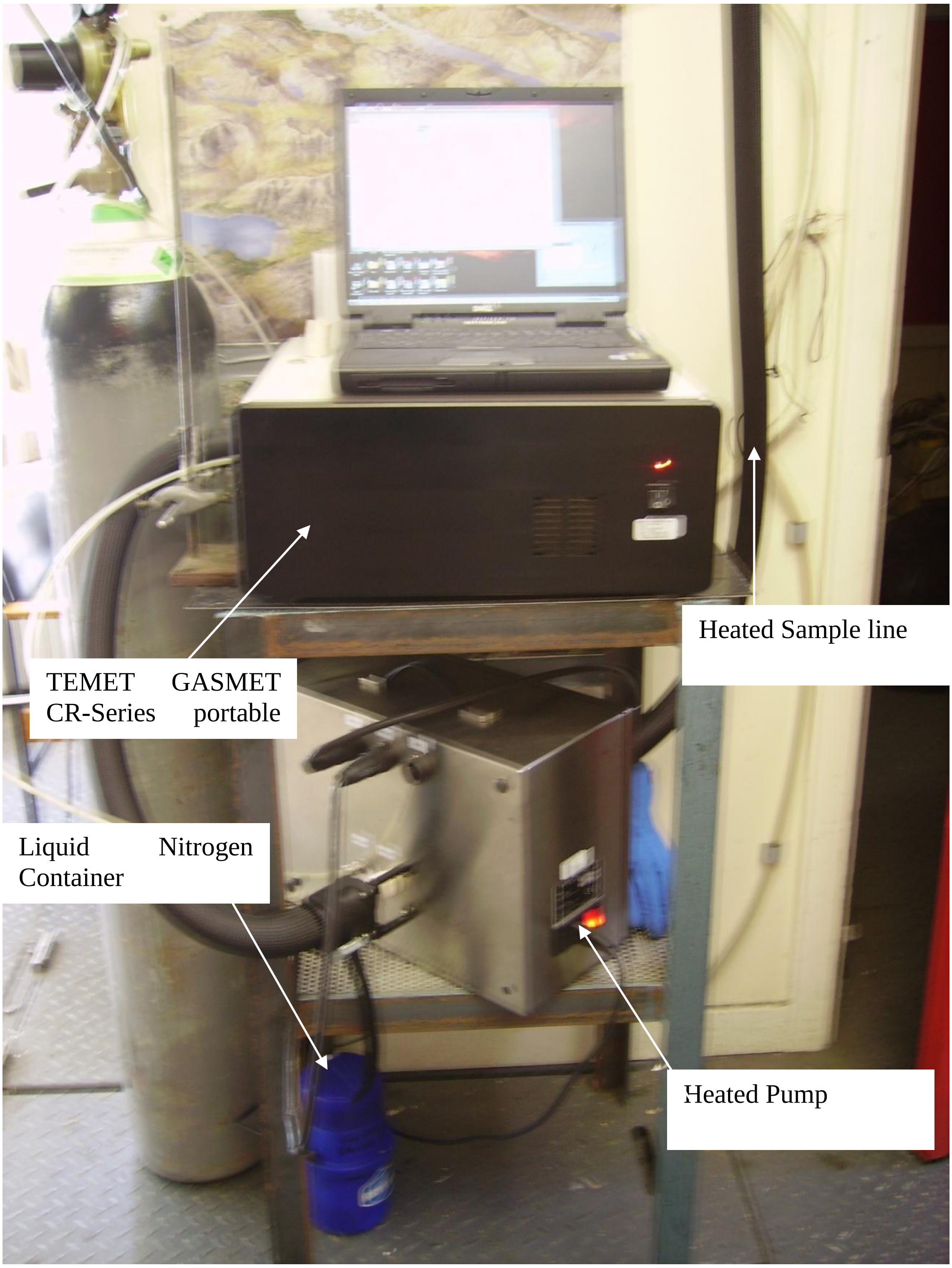


Analysis Automation Ltd Chemiluminescence NOx Analyser

Hartmann & Braunn URAS 10E CO Analyser

Pictures of gas analysers:

Portable FTIR, along with the pump, heated sample line, and liquid nitrogen container:



APPENDIX C

Chan equation for calculating AFR from an exhaust, for a fuel containing:

$$Fuel = C_{\alpha}H_{\beta}O_{\gamma}N_{\delta}$$

$$A/F_{Chan} = \frac{1}{12.011\alpha + 1.008\beta + 15.999\gamma + 14.007\delta} * \frac{\alpha A_1 - \gamma + (\beta K[CO_2])/2A_2 - (\alpha A_3 A_4)/2A_2}{2.0038 + A_5 - (A_5 K[CO_2])/A_2 + (0.0019A_3A_4)/2A_2 - 0.0019A_1}$$

Where:

$$K = \exp^{\left[2.743 - \frac{1.761}{0.001T_{eq}} - \frac{1.611}{(0.01T_{eq})^2} + \frac{0.2083}{(0.01T_{eq})^3}\right]}$$

T_{eq} = Equilibrium Temperature

$$A_1 = \frac{[CO] + 2[CO_2] + 2[O_2] + [NO_2] + 2[NO_2]}{[CO] + [CO_2] + [HC]}$$

$$A_2 = K[CO_2] + [CO]$$

$$A_3 = \frac{K[CO_2]}{[CO]([CO] + [CO_2] + [HC])}$$

$$A_4 = X[HC][CO]$$

$$A_5 = 4.7755\frac{P_V}{P_A - P_V}$$

$[\ ]$ = Volumetric concentrations in percent

X = Ratio of Elemental Hydrogen to Elemental Carbon

P_A = Atmospheric Pressure (atm)

P_V = Pressure of Water vapour (atm)

APPENDIX D

Furnace testing pictures:

3 kg set up:

9 kg crib: