



**Modelling and Evaluation of Fate and Occurrence of
Ash-forming and Trace Elements in Combustion of
Virgin and Treated Biomass**

Wahyu Meka

March 2020

Supervisors: Paul Fennell and Niall Mac Dowell

Mentor: Christopher Tighe

Department of Chemical Engineering

Imperial College London

This thesis is submitted for the degree of Doctor of Philosophy to the Imperial College of
Science, Technology, and Medicine

Abstract

The increase of global carbon emissions by 2.7% in 2018 from the 2015 level indicates that the utilisation of fossil fuel, particularly coal, as the primary energy source is still very significant worldwide. Many countries have made efforts to reduce their carbon emissions by replacing coal with biomass. The UK government has promoted the gradual transition from coal-firing to biomass-firing to achieve complete coal power plant shutdown by 2025. This transition program is also supported with several incentive schemes to encourage the current and planned future coal-firing power plants to utilise biomass.

However, several disadvantages are attributed to the utilisation of biomass as an energy source. Significant exploitation of woody biomass contributes to flooding, increasing carbon debts, and food security issues due to deforestation. Additionally, the use of herbaceous biomass causes operational problems in power plants due to severe ash deposition and corrosion.

Treated wood is abundantly available and is known to complement virgin biomass in combustion to mitigate the disadvantages associated with woody and herbaceous biomass combustion. In the EU, 52.9 million tonnes of waste wood is produced annually, 54% of which is utilised to produce electricity. However, treated wood contains trace elements (TE), e.g. arsenic, cadmium, copper, lead, nickel, etc. sourced from prior anthropogenic treatment, e.g. preservatives and paints. These elements are relatively volatile at high temperatures and are released to the atmosphere during combustion. Ingestion of these elements may harm human metabolism and pose other health risks to wildlife.

This thesis aims to develop a comprehensive model to predict the fate and the occurrence of trace elements (TEs) and ash-forming elements (AFEs) in combustion of treated wood and virgin wood. The combustion process considered is based on the biomass combustion operation in the 250-kW entrained-flow boiler in the UKCCSRC Pilot-scale Advanced Capture Technology (PACT) facility in Sheffield, UK. The developed model is designed to predict the downstream concentrations, the fate profiles, and the occurrence profiles each AFE and TE. The modelled downstream concentrations as the element concentrations in uncooled downstream gas are well validated by the experimental downstream concentrations measured with the online inductively-coupled plasma – mass spectrometer (ICP-MS). The modelled fate and occurrence profiles of each AFE and TE are in good agreement with the experimental results pertaining to the respective elements.

Declaration of Originality

I declare that

- the work presented in this thesis is primarily my own and otherwise appropriately referenced,
- I am the primary person responsible for the design, construction, and preparation of this manuscript, including the modelling results presented, and
- Any work carried out as part of a collaborative work has been explicitly stated in the text and the acknowledgements

Wahyu Meka, March 2020

Copyright Declaration

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives license. Researchers are free to copy, distribute, or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes, and that they do not alter, transform, or build upon it. For any reuse or distribution, researchers must make clear to others the licence term of this work.

Acknowledgement

In the name of Allah, the one and only lord of the universe, the most gracious, the most merciful

Blessings and peace of Allah be upon His last messenger, Prophet Muhammad

I would like to give enormous thanks to my mother, Meli Refina, my father, Kazuerman, my wife, Syadza Rifani Fitri, and my brother, Ridho Meka, for your never-ending support. I will never let you down.

I would like to thank my supervisors, Professor Paul Fennell and Dr Niall Mac Dowell, for giving me the opportunity to pursue this PhD and guiding me throughout my study at Imperial College London and my participation in the ONF project.

I would like to thank my mentor, Dr Christopher Tighe, for your guidance and advice.

I would like to thank Dr Salman Masoudi Soltani and Dr Mai Bui for guiding me at the early stage of my study and introducing me to the things a PhD student must and must not do.

I would like to thank to Dr Matthew Boot-Handford for supervising and guiding my study whilst Paul was on leave for his sabbatical. I would like to thank to Dr Thomas Hills for teaching me how to conduct ash acid digestion.

I would also like to thank Imperial College Chemical Engineering staffs for their support during my study: Thanks to Patricia Carry for training me in the analytical laboratory, thanks to Chin Lang for lending me laptops several times, thanks to Keith Walker and Ben Kitsnah for your help in the Chemical Engineering store, thanks to Susi Underwood for helping me to deal with my studentship status extension, and thanks to Viji Pilai and Anusha Sri-Pathmanathan for me helping me sorting out my financial problems.

I would like to thank my officemates and colleagues: Thanks to Dr Joseph Yao, Dr Clemens Patschke, Kazuaki Katayama, Shiladitya Ghosh, Husain Bahzad, Michael High, Patrick Brandl, Nixon Sunny, Jose Morales-Corona, Janet Skitt, Dr. Liya Zheng for all knowledge you share to me during my study, thanks to Dr Muhammad Andung Muntaha from KTH Royal Institute of Technology for teaching me basic coding of C++, thanks to Dr Janos Szuhanski, Dr Karen Finney, Dr Bijal Gudka, Professor Jenny Jones, Dr Juan Riaza, Dr Hannah Chalmers, and all other ONF project members that helped me during my study.

Acronyms

AFC – Ash-forming Compound

AFE – Ash-forming Element

AFGC – Ash-forming Gas Compound

AFLC – Ash-forming Liquid Compound

AFSC – Ash-forming solid Compound

CCA – Copper Chromium Arsenate

CFD – Computational Fluid Dynamic

CHP – Combined Heat and Power

EPA – Environmental Protection Agency

EU – European Union

FDA – Food and Drug Administration

FT – Fluid Temperature

HHV – High Heating Value

HT – Hemisphere Temperature

ICP – Inductively Coupled Plasma

IDT – Initial Deformation Temperature

LES – Large Eddy Simulation

LHV – Low Heating Value

ME – Major Element

MEX – Matlab Executable

MoDS – Model Development Suite

MSW – Municipal Solid Waste

MSVP – Multi-solids Progress Variables

ODE – Ordinary Differential Equation

OFA – Over-fired Air

PA – Primary Air

PACT – Pilot-scale Advanced Capture Technology

PAH – Polycyclic Aromatic Hydrocarbon

PM – Particulate Matter

PSD – Particle Size Distribution

RANS – Reynold-averaged Navier Stokes

RED – Renewable Energy Directive

SA – Secondary Air

SEM-EDXA – Scanning Electron Microscopy-Energy Dispersion X-Ray

SGTE – Scientific Group Thermodata Europe

ST – Sphere Temperature

TC – Trace Compound

TGC – Trace Gas Compound

TLC – Trace Liquid Compound

TSC – Trace Solid Compound

TE – Trace Element

VOC – Volatile Organic Compound

XML – Extensible Markup Language

XRF – X-ray Fluorescence

Table of Contents

Abstract.....	2
Declaration of Originality	3
Copyright Declaration.....	4
Acknowledgement	5
Acronyms.....	6
Table of Contents.....	8
List of Figures	10
List of Tables	23
Chapter 1 Introduction	24
1.1 Statement of the Problem.....	24
1.2 Project Aims and Objectives.....	30
1.3 Thesis Outline	31
Chapter 2 Literature Review: Biomass, Combustion Problems, and Model	33
2.1 Biomass Composition, Conversion, and Process.....	33
2.2 Ash Problems: Fouling, Corrosion, and Slagging	43
2.3 Trace Elements: Health Impact.....	51
2.4 Modelling Route	56
Chapter 3 Literature Review: Modelled Solid Fuel and Inorganic Element Origins and Distributions.....	61
3.1 White Wood.....	62
2.2 Recycled Wood.....	65
2.3 Rice Husk.....	71
2.4 Switchgrass	72
Chapter 4 Single-particle Combustion Model	73
4.1 Mathematical Concept of the Model.....	73
4.2 Case Study	88
3.4 Concluding Remarks.....	104
Chapter 5 Entrained-flow Combustion Model.....	107

5.1 Operating Conditions	108
5.2 Particle Aspect Ratio Profile.....	112
5.3 Mathematical Concept of the Model.....	116
5.4 Discussion and Validation of the Model Result.....	127
5.5 Concluding Remarks.....	134
Chapter 6 Fate and Occurrence Model	136
6.1 Model Assumptions	136
6.2 Mathematical Concept of the Model.....	139
6.3 Chemical Equilibrium Integration and Performance	143
6.4 Concluding Remarks.....	146
Chapter 7 Simplified Entrained-flow Combustion Model and Simplified Fate and Occurrence Model	148
7.1 Mathematical Concept of the Model.....	148
7.2 Chemical Equilibrium Integration	153
7.3 Model Result Discussion and Validation.....	155
7.4 Method of PACT ICP Measurements and Bulk Validation.....	177
7.5 Concluding Remarks.....	184
Chapter 8 Simplified Combustion and Chemical Equilibrium Model.....	186
8.1 CaO-SiO ₂ -K ₂ O Ternary Diagram and Model Setup	187
8.2 Discussion of the Model Result: Rice Husk	189
8.3 Discussion of the Model Result: Switchgrass.....	202
8.4 Concluding Remarks.....	212
Chapter 9 Conclusions and Future Work.....	219
9.1 Conclusions.....	219
9.2 Future Work: Model Comparison with the State of the Art and Room for Improvement	220
Bibliography	224
Appendix.....	244

List of Figures

Figure 1.1 Global Carbon Emissions	25
Figure 1.2 Global Temperature Anomaly Relative to Mean Global Temperature from 1951 to 1980.....	26
Figure 2.1 Result of Thermogravimetric Analysis of Pine Bark under $N_{2(g)}$ flowing at 200 ml min ⁻¹ at a Heating Rate of 15 K min ⁻¹	35
Figure 2.2 Char Combustion Regime (Logarithmic y-axis)	38
Figure 2.3 Schematic Diagram of AVV2.....	39
Figure 2.4 Schematic Diagram of Fluidised-bed Boiler: Circulating Fluidised-bed Boiler (left) and Bubbling Fluidised-bed Boiler (right).....	40
Figure 2.5 Schematic Diagram of Boiler 5	41
Figure 2.6 Schematic Diagram of Entrained-flow Boiler	42
Figure 2.7 Typical Locations of Fouling and Slagging in a Commercial Boiler	43
Figure 2.8 Routes for Biomass Ash Formation.....	44
Figure 2.9 Routes for Fouling and Agglomeration	46
Figure 2.10 Slagging Layers	47
Figure 2.11 Ash Fusion Measurement	49
Figure 2.12 Route of Chloride Deposition in Bark/Forest Residue Combustion and Chloride Deposition Prevention in Co-firing Forest Residue and Coal.....	51
Figure 2.13 Groups of TEs and Other Elements According to Their Volatility	54
Figure 3.1 The General Occurrence of AFEs in Woody Biomass	65
Figure 3.2 Penetration of a Solvent-borne Alkyd Primer into Sapwood Pine (Top), Beech Wood (Centre), and Meranti Wood (Bottom).....	68
Figure 3.3 TE Intake Pathways in Phytoremediation.....	69
Figure 3.4 Scanning Electron Micrographs of Outer Cortical Cells of Signal Grass and Rhodes Grass Root (V = Vacuole; CW = Cell Wall; C = Cytoplasm; MV = Vesicle)	70
Figure 4.1 The Radial and Axial Directions of a Cylindrical Particle for Intra-particle Numerical Calculations.....	75
Figure 4.2 The Discrete Intra-particle Parts of a Cylindrical Particle.....	76
Figure 4.3 Reaction routes during Wood Pyrolysis	80
Figure 4.4 Illustration of Nodes of Shrinking Particles	85
Figure 4.5 Discretisation of the Cylindrical Particle Radial Boundary Layers	86

Figure 4.6 Discretisation of the Cylindrical Particle Axial Boundary Layers	87
Figure 4.7 Modelling Route of Single-Particle Combustion Model	90
Figure 4.8 Comparison between Particle Surface Temperatures Obtained in This Work and in the Work of Mason <i>et al.</i>	93
Figure 4.9 Modelled Intra-particle Temperature Profiles at Particle Edge, Particle Centre, Particle Middle Cylindrical Surface, and Particle Base Centre, based on Mason <i>et al.</i>	94
Figure 4.10 Modelled Intra-particle CO _(g) Concentration Profile at Particle Edge, Particle Centre, Particle Middle Cylindrical Surface, and Particle Base Centre, based on Mason <i>et al.</i>	95
Figure 4.11 Modelled Intra-particle O _{2(g)} Concentration Profile at Particle Edge, Particle Centre, Particle Middle Cylindrical Surface, and Particle Base Centre, based on Mason <i>et al.</i>	96
Figure 4.12 Modelled Intra-particle Char Density Profile at Particle Edge, Particle Centre, Particle Middle Cylindrical Surface, and Particle Base Centre, based on Mason <i>et al.</i>	96
Figure 4.13 Modelled Intra-particle Temperature Contours at 2.763 s, based on Mason <i>et al.</i>	97
Figure 4.14 Modelled Intra-particle Temperature Contours at 6 s, based on Mason <i>et al.</i>	97
Figure 4.15 Combustion Setup of Lu <i>et al.</i>	98
Figure 4.16 Setup of Lewtak and Marek: 1. Biomass Particle; 2. Thermocouple; 3. Cool Shield Tube; 4. Reactor; 5. Gas Inlet; 6. High Speed Camera; 7. Quartz Window; 8. Gas Outlet	99
Figure 4.17 Comparison between the Temperature of the Particle Centre and Surface Obtained in This Work and the Temperature of the Particle Centre obtained in the Work of Lu <i>et al.</i>	100
Figure 4.18 Thermocouple Temperature Profile during the Early Combustion Stage with the Surrounding Gas Temperature at 1,250 K	101
Figure 4.19 The Thermally Affected Particle Body Radially Surrounding the Thermocouple Type B	102
Figure 4.20 Comparison between Fractional Residual Particle Mass Obtained in This Work and in the Work of Mehrabian <i>et al.</i>	103
Figure 4.21 Comparison between Particle Centre Temperature Obtained in This Work and in the Work of Lewtak and Marek	104
Figure 5.1 Three-dimensional diagram of the PACT Facility 250kW Combustion Unit	108
Figure 5.2 Process Flow Diagram for the PACT Facility 250kW Combustion Unit.....	109
Figure 5.3 Three-Dimensional Diagram of the PACT Facility 250kW Entrained-flow Burner	110

Figure 5.4 Two-dimensional Diagram of the Feed Introducer in the PACT Facility 250kW Entrained-flow Burner.....	110
Figure 5.5 Cumulative PSD of White Wood and Recycled Wood	113
Figure 5.6 Microscopic Image of White Wood.....	114
Figure 5.7 Particle Aspect Ratio as a Function of Particle Length	115
Figure 5.8 Cumulative Particle Length and Radius Distribution with 100-micron- increment Data Points	115
Figure 5.9 Cumulative Particle Length and Radius Distribution with 200-micron- increment Data Points	116
Figure 5.10 Discretisation of the PACT Facility Entrained-flow Burner	117
Figure 5.11 Combustion Model Structure of a Thin Slice with Discretised Particles	117
Figure 5.12 Particle Side Surface Area of Node $\left(\frac{m_s}{n}\right)$	120
Figure 5.13 Particle Base Surface Area of Node $\left(\frac{m}{n_s}\right)$	121
Figure 5.14 Heat Loss through Burner Wall	124
Figure 5.15 Validation of the Modelled Bulk Gas Temperature Profile of White Wood during Air-combustion in the PACT Entrained-flow Burner.....	128
Figure 5.16 Validation of Dry Molar Percentage Profile of the Modelled Bulk $O_{2(g)}$ Gas during Air-combustion of White Wood in the PACT Entrained-flow Burner.....	129
Figure 5.17 Centre Temperature Profiles of Modelled Particles of White Wood during Air-combustion in the PACT Entrained-flow Burner	130
Figure 5.18 Surface Temperature Profiles of Modelled Particles of White Wood during Air-combustion in the PACT Entrained-flow Burner	131
Figure 5.19 Velocity Profiles of Bulk Gas and Modelled Particles of White Wood during Air-combustion in the PACT Entrained-flow Burner	131
Figure 5.20 Residual Mass Fraction Profiles of Modelled Particles of White Wood during Air-combustion in the PACT Entrained-flow Burner	132
Figure 5.21 Validation of Modelled Bulk Gas Temperature Profile of White Wood during Oxy27-combustion in the PACT Entrained-flow Burner	133
Figure 5.22 Validation of Modelled Dry Molar Percentage Profile of Bulk $O_{2(g)}$ of White Wood during oxy27-combustion in the PACT Entrained-flow Burner	133
Figure 6.1 General Fate of AFEs and TEs during Falling of Particles in Burner	140
Figure 6.2 AFE and TE Model Structure in Thin Slice with Discretised Particle	141
Figure 6.3 Sobol Sequence Data for $AsO_{(g)}$ Molar Mass (y-axis) vs Temperature (x- axis).....	145
Figure 6.4 Deviations in Chemical Equilibrium Results for $AsO_{(g)}$, $PbO_{(g)}$, and $Cd_{(g)}$	145

Figure 6.5 White Wood Biot Numbers	147
Figure 7.1 Combustion Model Structure of a Thin Slice with Non-discretised Particle	149
Figure 7.2 AFE and TE Model Structure in a Thin Slice with Non-discretised Particle	152
Figure 7.3 Validation of the Modelled Bulk Gas Temperature Profile of White Wood during Air-combustion in the PACT Entrained-flow Burner	156
Figure 7.4 Validation of Dry Molar Percentage Profile of the Modelled Bulk $O_{2(g)}$ Gas during Air-combustion of White Wood in the PACT Entrained-flow Burner.....	156
Figure 7.5 Validation of the Modelled Bulk Gas Temperature Profile of White Wood during Oxy27-combustion in the PACT Entrained-flow Burner	157
Figure 7.6 Validation of Dry Molar Percentage Profile of the Modelled Bulk $O_{2(g)}$ Gas during Oxy27-combustion of White Wood in the PACT Entrained-flow Burner	158
Figure 7.7 Modelled Potassium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood	160
Figure 7.8 Modelled Potassium Fate Profiles in Air-combustion of White Wood and Recycled Wood.....	160
Figure 7.9 Modelled Potassium Bulk Occurrences in Air-combustion of White Wood.....	160
Figure 7.10 Modelled Potassium Bulk Occurrences in Oxy27-combustion of White Wood.....	161
Figure 7.11 Modelled Potassium Bulk Occurrences in Air-combustion of Recycled Wood.....	161
Figure 7.12 Modelled Calcium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood	164
Figure 7.13 Modelled Calcium Fate Profiles in Air-combustion of White Wood and Recycled Wood.....	164
Figure 7.14 Modelled Calcium Bulk Occurrences in Air-combustion of White Wood	164
Figure 7.15 Modelled Calcium Bulk Occurrences in Oxy27-combustion of White Wood.....	165
Figure 7.16 Modelled Calcium Bulk Occurrences in Air-combustion of Recycled Wood.....	165
Figure 7.17 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of White Wood	166
Figure 7.18 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of White Wood.....	166
Figure 7.19 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Recycled Wood	167

Figure 7.20 Modelled Silicon Fate Profiles in Air-combustion and Oxy27-combustion of White Wood	168
Figure 7.21 Modelled Silicon Fate Profiles in Air-combustion of White Wood and Recycled Wood.....	168
Figure 7.22 Modelled Silicon Bulk Occurrences in Air-combustion of White Wood	169
Figure 7.23 Modelled Silicon Bulk Occurrences in Oxy27-combustion of White Wood.....	169
Figure 7.24 Modelled Silicon Bulk Occurrences in Air-combustion of Recycled Wood.....	170
Figure 7.25 Modelled Silicon Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of White Wood	170
Figure 7.26 Modelled Silicon Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of White Wood.....	171
Figure 7.27 Modelled Silicon Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Recycled Wood	171
Figure 7.28 Modelled Copper Fate Profiles in Air-combustion and Oxy27-combustion of White Wood	172
Figure 7.29 Modelled Copper Fate Profiles in Air-combustion of White Wood and Recycled Wood.....	172
Figure 7.30 Modelled Copper Bulk Occurrences in Air-combustion of White Wood	173
Figure 7.31 Modelled Copper Bulk Occurrences in Oxy27-combustion of White Wood.....	173
Figure 7.32 Modelled Copper Bulk Occurrences in Air-combustion of Recycled Wood.....	174
Figure 7.33 Modelled Chromium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood	175
Figure 7.34 Modelled Chromium Fate Profiles in Air-combustion of White Wood and Recycled Wood	175
Figure 7.35 Modelled Chromium Bulk Occurrences in Air-combustion of White Wood.....	175
Figure 7.36 Modelled Chromium Bulk Occurrences in Oxy27-combustion of White Wood.....	176
Figure 7.37 Modelled Chromium Bulk Occurrences in Air-combustion of Recycled Wood.....	176
Figure 7.38 Flow Diagram of PACT Online ICP	177
Figure 7.39 Validation of Element Concentrations in Uncooled Downstream Gas during Air-combustion of White Wood (E: Experiment; M: Model)	178

Figure 7.40 Validation of Element Concentrations in Uncooled Downstream Gas during Oxy27-combustion of White Wood (E: Experiment; M: Model).....	179
Figure 7.41 Element Partition Based on On-line ICP Measurement in Air-combustion of White Wood	179
Figure 7.42 Element Partition Based on On-line ICP Measurement in Oxy27-combustion of White Wood	180
Figure 7.43 Modelled Liquid-to-solid Mass Ratio for Recycled Wood (L: Liquid; S: Solid).....	183
Figure 8.1 Liquidus Isotherm Lines within CaO-SiO ₂ -K ₂ O Ternary Phase Diagram.....	188
Figure 8.2 Modelled Temperature Profile of Bulk Gas during Rice Husk Combustion in the PACT Entrained-flow Burner.....	190
Figure 8.3 Modelled Dry Molar Percentage Profile of Bulk O _{2(g)} during Combustion of Rice Husk in the PACT Entrained-flow Burner	190
Figure 8.4 Modelled Potassium Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk.....	192
Figure 8.5 Modelled Potassium Bulk Occurrences in Air-combustion of Rice Husk	193
Figure 8.6 Modelled Potassium Bulk Occurrences in Oxy27-combustion of Rice Husk	193
Figure 8.7 SEM Images of Fouling Deposit Layers in Ensted Boiler.....	194
Figure 8.8 Modelled Potassium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Rice Husk	194
Figure 8.9 Modelled Potassium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Rice Husk.....	195
Figure 8.10 Modelled Calcium Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk.....	196
Figure 8.11 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Rice Husk	196
Figure 8.12 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Rice Husk.....	197
Figure 8.13 Modelled Silicon Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk.....	199
Figure 8.14 Modelled Silicon Bulk Occurrences in Air-combustion of Rice Husk.....	199
Figure 8.15 Bulk Composition of Rice Husk (Black Box) at Complete Combustion and Liquidus Isotherm Lines within CaO-SiO ₂ -K ₂ O Ternary Phase Diagram	200
Figure 8.16 A Fragment of Ash Deposit Generated in an Entrained-flow Boiler in Kardia Power Plant	200
Figure 8.17 Modelled Silicon Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Rice Husk	201

Figure 8.18 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Rice Husk.....	201
Figure 8.19 Particle Composition of Rice Husk (Black Box) at Complete Combustion and Liquidus Isotherm Lines within CaO-SiO ₂ -K ₂ O Ternary Phase Diagram	202
Figure 8.20 Modelled Temperature Profile of Bulk Gas during Switchgrass Combustion in the PACT Entrained-flow Burner.....	203
Figure 8.21 Modelled Dry Molar Percentage Profile of Bulk O _{2(g)} during Combustion of Switchgrass in the PACT Entrained-flow Burner	203
Figure 8.22 Modelled Potassium Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass	204
Figure 8.23 Modelled Potassium Bulk Occurrences in Air-combustion of Switchgrass	205
Figure 8.24 Modelled Potassium Bulk Occurrences in Oxy27-combustion of Switchgrass	205
Figure 8.25 Modelled Potassium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Switchgrass.....	206
Figure 8.26 Modelled Calcium Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass	208
Figure 8.27 Modelled Calcium Bulk Occurrences in Air-combustion of Switchgrass	209
Figure 8.28 Modelled Calcium Bulk Occurrences in Oxy27-combustion of Switchgrass	209
Figure 8.29 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Switchgrass.....	210
Figure 8.30 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Switchgrass	210
Figure 8.31 Modelled Silicon Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass	212
Figure 8.32 Bulk Composition of Switchgrass (Black Box) at Complete Combustion and Liquidus Isotherm Lines within CaO-SiO ₂ -K ₂ O Ternary Phase Diagram	213
Figure 8.33 Bulk Composition of Switchgrass (Black Box) at Complete Combustion and Liquidus Isotherm Lines within MgO-K ₂ O-SiO ₂ Ternary Phase Diagram.....	214
Figure 8.34 Modelled Silicon Bulk Occurrences in Air-combustion of Switchgrass	214
Figure 8.35 Modelled Silicon Bulk Occurrences in Oxy27-combustion of Switchgrass	215
Figure 8.36 Modelled Silicon Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Switchgrass.....	215
Figure 8.37 Modelled Silicon Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Switchgrass	216

Figure 9.1 A Power Plant with a Bark-combusting Grate-fired Boiler Integrated with a Fuel Dryer Unit in Boman <i>et al.</i> (2006).....	221
Figure B.1 Collision Integral as a Function of Temperature.....	253
Figure F.1 FactSage Main Window	268
Figure F.2 FactSage Equilib Module “Reactant” Window.....	268
Figure F.3 FactSage Equilib Module “Menu: last system” Window.....	269
Figure F.4 FactSage Equilib Module “Results” Window	269
Figure F.5 FactSage Equilib Module “List” Window.....	270
Figure G.1 MoDS Opening Window	272
Figure G.2 MoDS “Create new project” Window	273
Figure G.3 MoDS Blank Working Window	273
Figure G.4 MoDS “Add new model” Window.....	273
Figure G.5 Blank “Files” Tab of Model 1 MoDS Working Window.....	274
Figure G.6 “Files” Tab of Model 1 MoDS Working Window	275
Figure G.7 Successful Dry Run Notification in MoDS Dry Run Window.....	275
Figure G.8 Blank “Input Variables” Tab of Model 1 MoDS Working Window	276
Figure G.9 Selection of “Combust4.mac” in the MoDS “Choose a file from list” Window.....	276
Figure G.10 MoDS “Variable input file location specifier” Window	277
Figure G.11 “Input Variables” Tab of Model 1 MoDS Working Window	278
Figure G.12 Blank “Output Variables” Tab of Model 1 MoDS Working Window	278
Figure G.13 Selection of “Biomass_ALL.xml” in the MoDS “Choose a file from list” Window	279
Figure G.14 MoDS xml Data Import Window	279
Figure G.15 “Experimental Data” Tab of Simulation 1 MoDS Working Window	280
Figure G.16 “Select Cases” Tab of Simulation 1 MoDS Working Window	280
Figure G.17 “Select Variables” Tab of Simulation 1 MoDS Working Window	281
Figure G.18 “Configure Parameters” Tab of Simulation 1 MoDS Working Window	282
Figure G.19 “Configure Responses” Tab of Simulation 1 MoDS Working Window	282
Figure G.20 “” Tab of Simulation 1 MoDS Working Window	283
Figure G.21 “MPI Settings” Tab of Simulation 1 MoDS Working Window	284
Figure G.22 “Run Simulations” Tab of Simulation 1 MoDS Working Window	284

Figure G.23 “Read_previous_Alg_1” in “Setup Algorithms” Tab of Simulation 2 MoDS Working Window.....	285
Figure G.24 “HDMR _Alg_1” in “Setup Algorithms” Tab of Simulation 2 MoDS Working Window.....	286
Figure J.1 Modelled Sodium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood.....	297
Figure J.2 Modelled Sodium Fate Profiles in Air-combustion of White Wood and Recycled Wood.....	297
Figure J.3 Modelled Sodium Bulk Occurrences in Air-combustion of White Wood.....	298
Figure J.4 Modelled Sodium Bulk Occurrences in Oxy27-combustion of White Wood.....	298
Figure J.5 Modelled Sodium Bulk Occurrences in Air-combustion of Recycled Wood.....	299
Figure J.6 Modelled Magnesium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood.....	301
Figure J.7 Modelled Magnesium Fate Profiles in Air-combustion of White Wood and Recycled Wood.....	301
Figure J.8 Modelled Magnesium Bulk Occurrences in Air-combustion of White Wood.....	301
Figure J.9 Modelled Magnesium Bulk Occurrences in Oxy27-combustion of White Wood.....	302
Figure J.10 Modelled Magnesium Bulk Occurrences in Air-combustion of Recycled Wood.....	302
Figure J.11 Modelled Magnesium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of White Wood.....	303
Figure J.12 Modelled Magnesium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Recycled Wood.....	303
Figure J.13 Modelled Aluminium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood.....	305
Figure J.14 Modelled Aluminium Fate Profiles in Air-combustion of White Wood and Recycled Wood.....	305
Figure J.15 Modelled Aluminium Bulk Occurrences in Air-combustion of White Wood.....	306
Figure J.16 Modelled Aluminium Bulk Occurrences in Oxy27-combustion of White Wood.....	306
Figure J.17 Modelled Aluminium Bulk Occurrences in Air-combustion of Recycled Wood.....	307
Figure J.18 Modelled Aluminium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of White Wood.....	307

Figure J.19 Modelled Aluminium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of White Wood.....	308
Figure J.20 Modelled Iron Fate Profiles in Air-combustion and Oxy27-combustion of White Wood.....	310
Figure J.21 Modelled Iron Fate Profiles in Air-combustion of White Wood and Recycled Wood.....	310
Figure J.22 Modelled Iron Bulk Occurrences in Air-combustion of White Wood	310
Figure J.23 Modelled Iron Bulk Occurrences in Oxy27-combustion of White Wood	311
Figure J.24 Modelled Iron Bulk Occurrences in Air-combustion of Recycled Wood	311
Figure J.25 Modelled Arsenic Arsenic Profiles in Air-combustion and Oxy27-combustion of White Wood	312
Figure J.26 Modelled Arsenic Fate Profiles in Air-combustion of White Wood and Recycled Wood.....	312
Figure J.27 Modelled Arsenic Bulk Occurrences in Air-combustion of White Wood	313
Figure J.28 Modelled Arsenic Bulk Occurrences in Oxy27-combustion of White Wood.....	313
Figure J.29 Modelled Arsenic Bulk Occurrences in Air-combustion of Recycled Wood.....	314
Figure J.30 Modelled Cadmium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood	315
Figure J.31 Modelled Cadmium Fate Profiles in Air-combustion of White Wood and Recycled Wood	315
Figure J.32 Modelled Cadmium Bulk Occurrences in Air-combustion of White Wood.....	315
Figure J.33 Modelled Cadmium Bulk Occurrences in Oxy27-combustion of White Wood.....	316
Figure J.34 Modelled Cadmium Bulk Occurrences in Air-combustion of Recycled Wood.....	316
Figure J.35 Modelled Lead Fate Profiles in Air-combustion and Oxy27-combustion of White Wood.....	317
Figure J.36 Modelled Lead Fate Profiles in Air-combustion of White Wood and Recycled Wood.....	317
Figure J.37 Modelled Lead Bulk Occurrences in Air-combustion of White Wood	318
Figure J.38 Modelled Lead Bulk Occurrences in Oxy27-combustion of White Wood	318

Figure J.39 Modelled Lead Bulk Occurrences in Air-combustion of Recycled Wood	319
Figure J.40 Modelled Nickel Fate Profiles in Air-combustion and Oxy27-combustion of White Wood	320
Figure J.41 Modelled Nickel Fate Profiles in Air-combustion of White Wood and Recycled Wood	320
Figure J.42 Modelled Nickel Bulk Occurrences in Air-combustion of White Wood	320
Figure J.43 Modelled Nickel Bulk Occurrences in Oxy27-combustion of White Wood	321
Figure J.44 Modelled Nickel Bulk Occurrences in Air-combustion of Recycled Wood	321
Figure J.45 Modelled Vanadium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood	322
Figure J.46 Modelled Vanadium Fate Profiles in Air-combustion of White Wood and Recycled Wood	322
Figure J.47 Modelled Vanadium Bulk Occurrences in Air-combustion of White Wood	323
Figure J.48 Modelled Vanadium Bulk Occurrences in Oxy27-combustion of White Wood	323
Figure J.49 Modelled Vanadium Bulk Occurrences in Air-combustion of Recycled Wood	324
Figure J.50 Modelled Zinc Fate Profiles in Air-combustion and Oxy27-combustion of White Wood	325
Figure J.51 Modelled Zinc Fate Profiles in Air-combustion of White Wood and Recycled Wood	325
Figure J.52 Modelled Zinc Bulk Occurrences in Air-combustion of White Wood	325
Figure J.53 Modelled Zinc Bulk Occurrences in Oxy27-combustion of White Wood	326
Figure J.54 Modelled Zinc Bulk Occurrences in Air-combustion of Recycled Wood	326
Figure J.55 Modelled Mercury Fate Profiles in Air-combustion and Oxy27-combustion of White Wood	327
Figure J.56 Modelled Mercury Fate Profiles in Air-combustion of White Wood and Recycled Wood	327
Figure J.57 Modelled Mercury Bulk Occurrences in Air-combustion of White Wood	328
Figure J.58 Modelled Mercury Bulk Occurrences in Oxy27-combustion of White Wood	328

Figure J.59 Modelled Mercury Bulk Occurrences in Air-combustion of Recycled Wood.....	329
Figure K.1 Modelled Sodium Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk.....	331
Figure K.2 Modelled Sodium Bulk Occurrences in Air-combustion of Rice Husk	331
Figure K.3 Modelled Sodium Bulk Occurrences in Oxy27-combustion of Rice Husk	332
Figure K.4 Modelled Magnesium Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk.....	333
Figure K.5 Modelled Magnesium Bulk Occurrences in Air-combustion of Rice Husk	333
Figure K.6 Modelled Aluminium Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk.....	334
Figure K.7 Modelled Aluminium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Rice Husk	335
Figure K.8 Modelled Aluminium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Rice Husk.....	335
Figure K.9 Modelled Iron Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk	337
Figure K.10 Modelled Iron Bulk Occurrences in Air-combustion of Rice Husk	338
Figure K.11 Modelled Iron Bulk Occurrences in Oxy27-combustion of Rice Husk.....	338
Figure K.12 Modelled Iron Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Rice Husk.....	339
Figure K.13 Modelled Iron Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Rice Husk.....	339
Figure L.1 Modelled Sodium Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass	341
Figure L.2 Modelled Sodium Bulk Occurrences in Air-combustion of Switchgrass	341
Figure L.3 Modelled Sodium Bulk Occurrences in Oxy27-combustion of Switchgrass	342
Figure L.4 Modelled Magnesium Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass	344
Figure L.5 Modelled Magnesium Bulk Occurrences in Air-combustion of Switchgrass	344
Figure L.6 Modelled Magnesium Bulk Occurrences in Oxy27-combustion of Switchgrass	345
Figure L.7 Bulk Composition of Switchgrass (Black Box) at Complete Combustion and Liquidus Isotherm Lines within $CaO-P_2O_5-MgO$ Ternary Phase Diagram	346

Figure L.8 Modelled Magnesium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Switchgrass	347
Figure L.9 Modelled Magnesium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Switchgrass	347
Figure L.10 Modelled Aluminium Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass	348
Figure L.11 Modelled Aluminium Bulk Occurrences in Air-combustion of Switchgrass	349
Figure L.12 Modelled Aluminium Bulk Occurrences in Oxy27-combustion of Switchgrass	349
Figure L.13 Modelled Aluminium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Switchgrass	350
Figure L.14 Modelled Aluminium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Switchgrass	350
Figure L.15 Modelled Iron Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass	352
Figure L.16 Modelled Iron Bulk Occurrences in Air-combustion of Switchgrass	352
Figure L.17 Modelled Iron Bulk Occurrences in Oxy27-combustion of Switchgrass	353
Figure L.18 Modelled Iron Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Switchgrass	353

List of Tables

Table 2.1 General Classification of Types of Biomass as Solid Fuels.....	33
Table 2.2 Comparison of Coal Combustion Method Characteristics.....	37
Table 2.3 General Classification of Biomass Waste Wood as Solid Fuels	52
Table 2.4 General Classification of Biomass as Solid Fuels.....	52
Table 2.5 Health Impacts of Trace Elements	54
Table 2.6 Regulatory Limits for Trace Elements	55
Table 3.1 Characterisation of Modelled Biomass	61
Table 3.2 CFA Results of Rice Husk	71
Table 4.1 Wood Pyrolysis Gas Mass Fractions.....	81
Table 4.2 Numerical Parameters of Mason <i>et al.</i> 's Single-particle Combustion Model.....	89
Table 4.3 Initial Values of Mason <i>et al.</i> 's Single Particle Combustion Model.....	90
Table 4.4 Property Functions of Single-particle Combustion Model.....	91
Table 5.1 Inlet Gas Operating Conditions at the PACT Entrained-flow Burner.....	111
Table 7.1 Combustion Gas Heat Capacity Parameters.....	151
Table 8.1 Kinetic Parameters of Pyrolysis of Herbaceous Biomass	189
Table A.1 Combustion Gas Heat Capacity Parameters.....	245
Table A.2 Combustion Gas Viscosity Parameters	246
Table A.3 Combustion Gas Collision Parameters.....	247
Table A.4 Combustion Gas Interaction Energies	247
Table A.5 Permeabilities of Solids.....	248
Table A.6 Emissivities of Solids	248
Table C.1 Wood Pyrolysis Kinetic Parameter	258
Table C.2 Homogeneous Gas Reaction Kinetic Parameters	260
Table C.3 Heterogeneous Gas Reaction Kinetic Parameters	261
Table I.1 Stoichiometry of Reaction I.1 in Air-combustion	294
Table I.2 Stoichiometry of Reaction I.2 in Oxy27-combustion.....	295
Table M.2 Licenses of Figures and/or Tables Used.....	354

Chapter 1

Introduction

1.1 Statement of the Problem

The vast and overriding majority of experts and professionals believe that global warming is a real issue supported by scientific evidence. The Earth absorbs the sun's heat, which it releases to outer space at the same rate to maintain a constant temperature habitable to humans.¹ However, this heat balance has been disturbed due to anthropogenic phenomena and has caused global warming.

Anthropogenic phenomena, especially fossil fuel combustion, have been proven to be the most significant cause of global warming.² Fossil fuel exploitation transforms 'buried carbon' into carbon dioxide within seconds of a combustion process. In contrast, the reverse conversion of carbon dioxide back to 'buried carbon' requires a series of complex procedures that take a very long time. This imbalance in time required for the two stages of this carbon cycle to be completed has led to the accumulation of a significant amount of carbon dioxide in the atmosphere over half a century, as illustrated in Figure 1.1.³

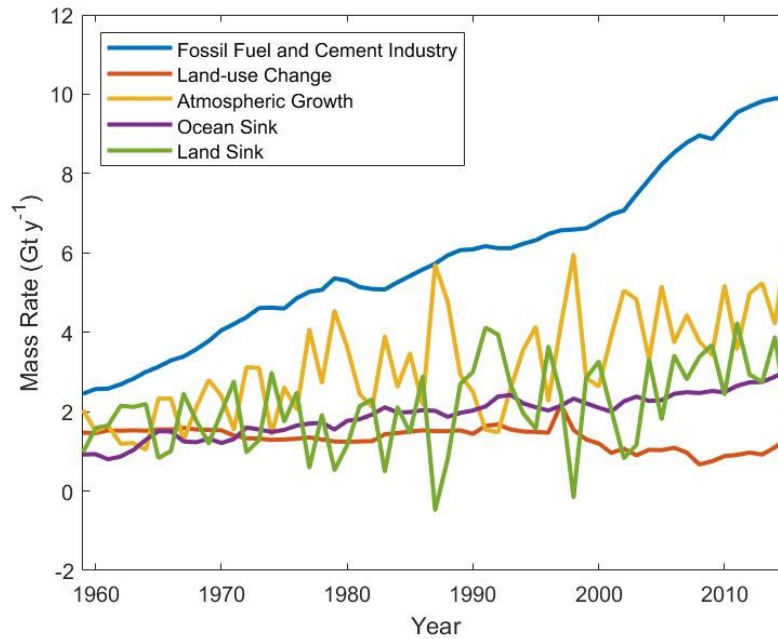


Figure 1.1 Global Carbon Emissions

The accumulation of carbon dioxide in the atmosphere increases global temperature due to the enhanced greenhouse-gas effect. The increase in global temperature since the last century is illustrated in Figure 1.2.⁴ The global temperature increase affected the ocean's physical properties between 1961 and 2003 to the extent that global ocean temperature rose by 0.1K and global sea-level rose at a rate of 1.8mm⁻¹. In addition, global energy demand is predicted to increase by more than twice its current level by 2040. Unless countermeasures are taken, the quantity of carbon dioxide in the atmosphere will increase by another 10 Gigatonnes (Gt) by 2040.⁵ This could potentially increase the global atmospheric temperature by between 1.1K and 6.4K, and global sea level by between 0.18m and 0.59m.⁶

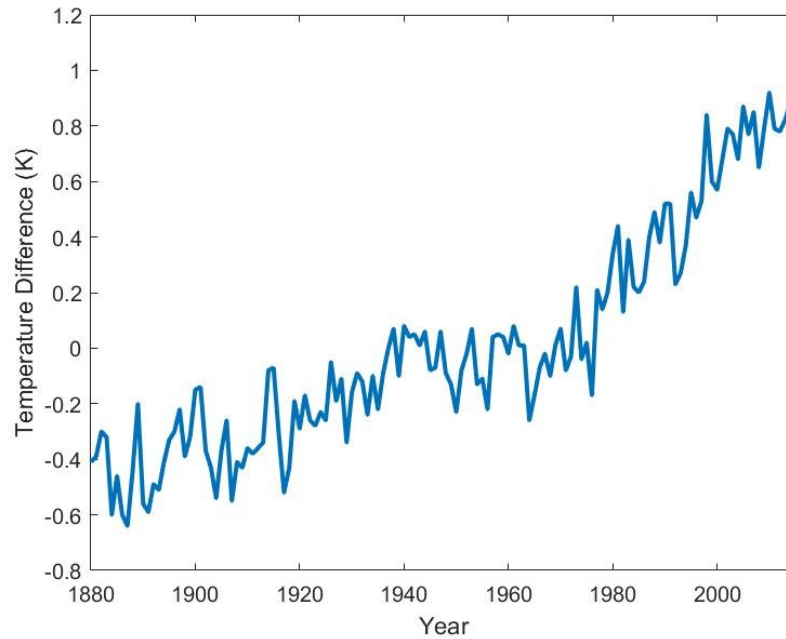


Figure 1.2 Global Temperature Anomaly Relative to Mean Global Temperature from 1951 to 1980

Regional and international actions are being made in an effort to reduce global temperature. The *Paris Agreement* within the United Nations Framework Convention on Climate Change, which was signed by almost 200 countries in 2016, is one of the most critical initiatives that have been drawn up to combat climate change. The Paris Agreement aimed to maintain the increase in global temperature well below 2°C and to deliver the changes necessary to limit the growth by 1.5°C. In the UK, the *Climate Change Act* was introduced in 2008 to limit UK net carbon emission by at least 80% of the 1990 value by 2050.

Intense efforts are required to fulfil the demands of the *Paris Agreement* and of the *Climate Change Act*. It has been reported that, globally, a third of oil reserves, half of gas reserves, and four-fifths of coal reserves cannot be exploited if the world is to achieve the goal of the *Paris Agreement*.⁷ Moreover, the UK government has introduced the *Carbon Budget* programme, which aims to suppress greenhouse gas emissions within five consecutive years. Also, some of the UK *Combined Heat and Power Incentives* programmes are designed to motivate energy industries to focus on energy production efficiency. For instance, an exemption to the *Climate Change Levy* is applied to fuel and energy tax if a 20% energy-saving threshold is achieved. As an external factor, the rise of the carbon price (a cost applied to carbon pollution) by 156% in 2018 could also force the energy industries to reduce their carbon emissions.⁸

However, a recent study reported a 2.7% increase in global carbon emission in 2018 from its 2015 value.⁹ This increase indicates that the current effort to reduce the global temperature is ineffectual, despite the *Paris Agreement*. The main contributors to the worldwide carbon emission increase are

China by 4.7%, the United States by 2.5%, and India by 6.3%. These contributions are sourced from massive utilisation of coal in power plants and oil in transportation to support the countries' economic growth.

The recent global increase in carbon emission due to fossil fuel utilisation has attracted attention to find and exploit another energy source. Biomass is well-known as one of the most suitable candidates to replace solid fossil fuels. Biomass is carbon-neutral, since the carbon it contains has been absorbed via photosynthesis. Biomass is also more operationally efficient than coal, since it is more reactive due to its lower density.¹⁰ Notably, a gradual transition from coal use to biomass use is encouraged in the UK through a plan to shut all coal power plants by 2025.¹¹ This gradual transition is also financially supported with the *Renewable Heat Incentive* included in the *Combined Heat and Power Incentives* programmes.

Similarly to coal among solid fuels, biomass also has different varieties, listed in Table 2.1. Amongst the listed varieties, woody and herbaceous biomass have been the most commonly used as solid fuels due to a number of advantages, e.g. availability and energy content. However, the combustion of both woody and herbaceous biomass also has disadvantages that limit the flexibility of their use as solid fuels.

Wood is mostly used as biomass solid fuel, particularly in countries that have few fossil fuel resources, due to its low cost and low carbon emissions.¹² Wood also offers other advantages in other aspects. During combustion, wood is considered less operationally problematic at high temperature since it is unlikely to form molten slag that is responsible for the formation of ash deposits and retards power plant efficiency.¹³ Besides, wood bottom ash may be used as a cement additive due to its substantial calcium content.¹⁴

However, the European Renewable Energy Directive (RED) has stated that use of half of Europe's annual forest harvest as biomass would supply only 10% of the European energy that is required to originate from renewable fuels.¹⁵ This harvest quantity would require a large area of forest as wood source. A tremendous amount of carbon is released during harvested wood combustion. Despite the eventual carbon absorption forestry in the future, the re-establishment of this takes years due to the time required for plantation and growth. Consequently, carbon may remain in the atmosphere for decades and warm the Earth in the same way as if fossil fuels were used.¹⁶

Additionally, economic predictions suggest possible future competition for land between the energy and the food sectors. It is estimated that around 1,500 million ha of land will be required for plantations and agriculture dedicated to the growth of biomass fuels for renewable energy by 2050 to meet the demands of the carbon tax on other businesses, even if that tax is implemented at the least stringent level of regulation.¹⁷

Herbaceous biomass is considered another potential alternative form of biomass solid fuel. Its structure avoids the issues regarding woody biomass. In comparison with woody biomass, herbaceous biomass is more widely abundant.¹⁸ A study has revealed that land that is surplus to the requirements of agriculture, mostly in developing countries, is available and in enough supply to meet energy demands by 2035. Energy crop productivity in developed countries is generally at around 5ton ha⁻¹, which suggests that land expansion might not be necessary.¹⁹ In developed countries where herbaceous biomass use is still particularly rare, e.g. Finland, herbaceous biomass is expected to become one of the most dominant energy sources in the future, and it does not present food security issues.²⁰

However, herbaceous biomass contributes to operational issues during combustion due to higher ash contents than woody biomass as exhibited in Table 3.1. High ash contents establish biomass rich in AFEs, TEs, and chlorine. The significant quantity of potassium and chlorines promotes intense fouling. Fouling occurs via potassium volatisation at high temperature and condensation at low temperature on probe surfaces as a liquid layer initiating ash deposition buildup. Condensed KCl within ash deposit induces corrosion at probe surfaces. When a significant quantity of sulphur present in the ash deposit interacts with the condensed KCl, corrosion is accelerated due to chlorine that is liberated as a sulphation product and attacks the probe surface.²¹ Herbaceous biomass also contains a significant quantity of silicon, often along with a considerable amount of phosphorus and calcium, which is responsible for slagging at high temperature on refractory materials.²²

Alternatively, the exploitation of waste wood, e.g. furniture waste or demolished buildings, as solid fuel provides a promising route towards biomass-based energy production at a considerable quantity without requirements to overcome the problems associated with land competition, carbon debt, and operational issues. Waste wood is relatively abundant due to increasing property business, particularly in developing countries. The waste wood annual reserve is currently at around 52.9 million tonnes in the EU, only 54% of which is converted to electricity.²³ Globally, the waste wood reserve is approximately 30 million m³ y⁻¹.²⁴ According to the Wood Recyclers Association, 4.5 million tonnes of waste wood are generated in the UK every year. Only around 2.1 million tonnes are converted into solid fuel, whilst the rest is exported and recycled.

However, waste-wood utilisation needs a thorough technical and environmental examination regarding its emission. Waste wood mostly originates from construction demolition and unused furniture, and it contains additives, e.g. preservatives, paints, and coatings. The additives are well absorbed and amalgamated with the wood at a cellular level. During combustion, hazardous elements in the additives or so-called trace elements (TEs), e.g. arsenic, cadmium, copper, etc. are partially volatilised to the atmosphere and remain in the bottom ash residue. Unfortunately, excessive intake of these elements to the human body causes complications such as congenital disability, organ failures, and metabolism disturbance.²⁵ Authorities such as the Environmental Protection Agency of the US and the European

Environment Agency set standards for emission limits that are precautionary to ensure that the TE emission concentrations of power plants do not exceed the standard. Also, bottom ash that contains trace elements is not suitable to be disposed of with virgin wood ash and requires an additional treatment process that can cost approximately \$180 ton⁻¹.²⁶

In order to predict the fate and occurrence of TEs in waste wood combustion, it is imperative firstly to understand the affecting parameters. The parameters are primarily the operating conditions of the combustion unit and the initial quantities of TEs in the waste wood. Various companies manufacture wood additives in different compositions. Also, use of different methods for application of additives leads to variability in the final additive concentration in the wood.

Chemical equilibrium calculation has been commonly used in a wide range of applications to predict the fate and occurrence of TEs. One of the main reasons of this common use is due to a lack of available kinetic data for TE kinetic reactions in literature. Niu *et al.*²⁷ compiled a list of all possible reactions involved during ash deposition. These reactions may be used qualitatively to deduce the origin of certain chemical compounds found in biomass ash. However, their work and that of many others have still been unable to incorporate kinetic data due to its availability.

Although the previous models with chemical equilibrium calculated on the prediction of fate and occurrence of TEs have been widely available, the operating conditions were often simplified. The previous models often predicted the fate and occurrence of TEs in solid fuel combustion in a single combustion unit or a series of combustion units at specific mean temperatures at certain positions or units.^{28,29,30} The use of mean temperatures underestimated the variable temperatures around specific positions or within units and did not reveal any information on the fate and occurrence of TEs between any neighbouring positions or units. The lack of fate and occurrence of TEs might have given a misleading impression that, for instance, there was no formation of concerned products, e.g. liquid compounds, between any neighbouring positions or units. Moreover, some models did not really reflect the actual combustion since the temperatures were of typical values.³¹

The previous models also used the initial quantities of TEs at any positions in a combustion unit for TE occurrence prediction that might have resulted in inaccurate TE partition.^{32,33} At locations farther from the combustion unit inlet, some portions of TEs are released from the solid fuel particles due to high temperatures. The remaining TEs might stay in the residual particles separated as bottom ash. Hence, when leaving the combustion units, the quantities of TEs in the gas phase are no longer the same, with those in the solid fuels and both TEs in the gas phase and TEs in the residual particles undergoing individual occurrence changes after the TE release positions.

Therefore, this problem statement concludes that a more comprehensive prediction method is required. The proposed method primarily addresses the simplification of the affecting parameters by considering

the fate and occurrence evolution within temperature profiles and separate calculations of fate and occurrence prediction in the solid fuel and gas phases. With the proposed method, a chemical correlation between the affecting parameters and the emission and retention of TEs is established.

1.2 Project Aims and Objectives

This thesis aims to begin to develop a comprehensive combustion model to examine the combustion of virgin and waste wood that follows a specific set of parameters to predict the fate and occurrence of TEs. The **entrained-flow combustion model** equipped with the **single-particle combustion model** was the initial modelling approach to accommodate the evaluation of both intra-particle profiles and burner profiles. These profiles were the parameters and platforms for the **fate and occurrence model**. Further simplification of the **entrained-flow combustion model** and the **single-particle combustion model** was necessary due to computational limitations. More details on the development of these models are found in Section 2.4. The model later was extended to focus on the evaluation of liquid phase formation based on the occurrence and fate of ash-forming elements (AFEs), e.g. potassium, silicon, calcium, etc. Chemical equilibrium is considered as the primary method to calculate the fate and occurrence of TEs, based on thermodynamic analyses. The work described in this thesis therefore aims to fulfil the following objectives:

- **Chemical Equilibrium Model Platform**
Most numerical-computing environments are equipped with proprietary languages. However, the majority of chemical equilibrium tools feature built-in user interfaces written in conventional languages, e.g. Fortran, C++, etc. There is therefore a language barrier between the two computational fields. Based on this language barrier, one objective of the work is to link computationally a numerical-computing environment and a chemical equilibrium tool, e.g. Matlab and FactSage.
- **AFE and TE Fate and Occurrence Prediction**
The research aims to predict the proportion of AFEs and TEs found in the bottom ash and in released gas and aerosols, and to predict the compounds in which they are found in bottom ash and released gases and aerosols.
- **Prediction of TE Concentrations as Element Concentrations in Uncooled Downstream Gas**
This objective is to predict and validate the concentrations of elements in uncooled downstream gas at a boiler outlet. These values are used to assess whether the combustion of waste wood leads to emissions of TEs at concentrations within the administrative emissions limits.
- **Liquid Phase Formation**
This objective is to predict the formation of liquid compounds within both solid fuels and bulk gas at specific locations within a boiler as a prediction of ash deposition.

1.3 Thesis Outline

This thesis incorporates nine chapters.

- The first chapter discusses the background of the work described in this thesis. The background arises from biomass utilisation in energy production to fulfil the need to reduce global carbon emissions whilst minimising biomass-associated problems by exploiting waste wood as a viable option. Further, this chapter explains the research aims based on this background.
- The second chapter presents a review of the literature for this thesis. This chapter categorises the review into several main general discussions, namely: biomass composition, conversion, and process; ash deposition problems; and trace elements. More detailed discussion of each of these facets is presented at the beginning of each subsequent chapter.
- The third chapter lists the solid fuels evaluated in this thesis and explains their general chemical properties based on the results of proximate analysis, ultimate analysis, ash analysis, and chemical fractionation analysis.
- The fourth chapter discusses the development of the **single-particle combustion model** with discretisation as the initial and fundamental approach of solid-fuel combustion in a boiler. The temperatures at the surface and centre of particles that are predicted by this model are validated with experimental results from the literature.
- The fifth chapter discusses the development of the **entrained-flow combustion model** in a PACT (Pilot-scale Advanced Capture Technology) entrained-flow boiler based on a plug-flow reactor. The single-particle combustion model introduced in the third chapter is included as the sub-model to calculate the thermal decomposition of particles. The boiler temperature and oxygen concentration calculated by the model are validated with the experimental results from white-wood combustion in the PACT entrained-flow boiler.
- The sixth chapter discusses the integration of chemical equilibrium and numerical-computing environments to produce a chemical equilibrium tool. Next, the AFE and TE **fate and occurrence model** is introduced. This is based on the model discussed in the fourth chapter. This chapter reveals that particle discretisation generates a costly computation.
- The seventh chapter discusses the development of the **simplified entrained-flow combustion model** based on the entrained-flow combustion model introduced in the fourth chapter. The simplified model aims to eliminate the expensive computation. The fate and occurrence of AFEs and TEs are modelled through use of the **simplified fate and occurrence model**, based on the simplified entrained-flow combustion model. The inorganic gas concentrations that are calculated by the model to be emitted at the boiler outlet are validated by comparison with experimental measurement.

- The eight chapter extends the use of both the simplified entrained-flow combustion model and the simplified fate and occurrence model for use with silicon-rich solid fuels, namely: rice husk and switchgrass. A similar discussion of the fate and occurrence profiles is presented to evaluate the formation of liquid compounds and their potential to initiate ash deposits.
- The ninth chapter draws together conclusions and recommends future work.

Chapter 2

Literature Review: Biomass, Combustion Problems, and Model

2.1 Biomass Composition, Conversion and Process

Biomass is comprehensively defined by Vassilev *et al.*³⁴ as:

“Biomass is contemporaneous (non-fossil), and complex biogenic organic-inorganic solid product generated by natural and anthropogenic (technogenic) processes, and comprises: (1) natural constituents originated from growing land- and water-based vegetation via photosynthesis or generated via animal and human food digestion; and (2) technogenic products derived via processing of the above natural constituents.”

As solid fuel, biomass is further classified into specific categories, as shown in Table 2.1. Biomass compositions show wide variability, which is due to many factors beyond the classifications shown in Table 2.1, namely: their growth mechanism, growth environment, the age of the plant at harvest, fertilisers and pesticide used, and harvesting time.^{35,36,37,38,39,40} Therefore, biomass characterisations, e.g. proximate and ultimate analysis, are necessary to ensure optimum combustion performance and avoid unnecessary operational and environmental issues.

Table 2.1 General Classification of Types of Biomass as Solid Fuels

Biomass Groups	Biomass Sub-groups, Varieties, and Species
Wood and Woody Biomass	Coniferous or deciduous; angiospermous or gymnospermous; soft or hard; stems, branches, foliage, bark, chips, lumps, pellets, briquettes, sawdust, sawmill and others from various wood species

Herbaceous and Agricultural Biomass	Annual or perennial and field-based or processed-based such as: (1) Grasses and flowers (alfalfa, arundo, bamboo, bana, brassica, cane, cynara, miscanthus, switchgrass, timothy, others); (2) Straws (barley, bean, flax, corn, mint, oat, rape, rice, rye, sesame, sunflower, wheat, others); (3) Other residues (fruits, shells, husks, hulls, pits, pips, grains, seeds, coir, stalks, cobs, kernels, bagasse, food, fodder, pulps, cakes, others)
Aquatic Biomass	Marine or freshwater algae; macroalgae (blue, green, blue-green, brown, red) or microalgae; seaweed, kelp, lakeweed, water hyacinth, others
Animal and Human Biomass Wastes	Bones, meat-bone meal, chicken litter, various manures, others
Contaminated Biomass and Industrial Biomass Wastes (semi-biomass)	Municipal solid waste, demolition wood, refuse-derived fuel, sewage sludge, hospital waste, paper-pulp sludge, waste papers, paperboard waste, chipboard, fibreboard, plywood, wood pallets and boxes, railway sleepers, tannery waste, others
Biomass Mixtures	Blends from the above varieties

Proximate analysis was initially designed to determine moisture, volatile, char and ash contents of coal.⁴¹ Since biomass has become a prevalent energy source and has a somewhat similar composition to coal, proximate analysis has been implemented frequently for biomass. However, the proximate and ultimate analysis results of biomass require careful interpretation. Even if two biomass pellets originate from the very same tree, their proximate and also ultimate compositions could potentially show different results because the pellets might primarily contain materials from different parts of the tree, e.g. one pellet mostly contains bark whilst the other mostly contains foliage.⁴² Therefore, proximate and ultimate analysis on a specific biomass fuel should be conducted multiple times to obtain representative data.

In practice, proximate analysis is a thermogravimetric measurement in which a solid fuel sample is heated at a constant heating rate under controlled atmospheric conditions. Sample mass is measured repeatedly until only residual solids are left. Further explanation regarding the way in which proximate analysis is conducted is given in ASTM D7582-15.⁴³ An example of a thermogravimetric measurement that has defined the solid fuel constituent mass fraction is given in Figure 2.1.⁴⁴

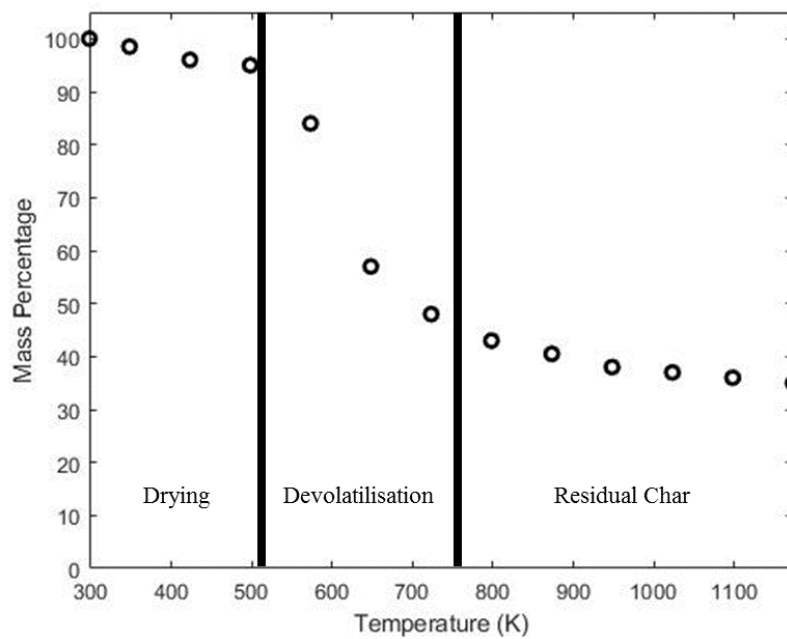


Figure 2.1 Result of Thermogravimetric Analysis of Pine Bark under $N_{2(g)}$ flowing at 200 ml min^{-1} at a Heating Rate of 15 K min^{-1}

Thermogravimetric measurement primarily consists of three major stages: *drying*, *volatilisation*, and *combustion* if oxygen ($O_{2(g)}$) is involved. In the *drying* stage, the mass of the sample slightly decreases due to moisture loss. After a short period of drying, subsequent significant loss of sample mass is a sign that the *drying* stage has ended and the *volatilisation* stage has begun. Finally, the remaining sample reaches a constant mass, which indicates that volatilisation has ended and the *residual char* stage has been reached. An extra stage entitled *remaining ash* is noted when the analysis is conducted in $O_{2(g)}$ -containing gas. The concentration of each proximate-analysis constituent, that is moisture, volatile matter, and char, is determined according to fractional mass loss within each stage.

Measurement of constituent compositions by proximate analysis, as exemplified in Table 3.1, provides essential information regarding solid fuel combustion performances. High moisture content indicates poor fuel quality, since the presence of moisture increases combustion delay time. High quantities of volatile matter are preferred since volatile matter increases overall reactivity. Excessive char content, retards combustion rate due to reliance on heterogeneous oxidation.

Another well-known characterisation method is ultimate analysis. The ultimate analysis method was also designed for coal characterisation. In ASTM D3176-15, ultimate analysis is defined as:⁴⁵

“Ultimate analysis in the case of coal and coke is the determination of carbon, hydrogen, nitrogen, and sulphur, as found in the gaseous products of its complete combustion, the determination of ash in the material as a whole, and the calculation of oxygen by difference.”

In typical ultimate analysis results, carbon makes up most of the biomass with a mass percentage at around 44% to 78%. Oxygen is in second place with a mass percentage above 40%. Hydrogen mass percentage is about 5% to 7%. In contrast, carbon content is significantly higher in coal at around 70% to 90%, whilst hydrogen content is only 3% to 6%. Both the hydrogen-to-carbon ratio (H/C) and the oxygen-to-carbon ratio (O/C) are often used to characterise solid fuel volatility. It has been proven experimentally that biomass with higher H/C and O/C than coal exhibits higher volatility.⁴⁶

Heating value is also used to characterise solid fuel. Heating value is measured as either higher heating value (HHV) or lower heating value (LHV). Both HHV and LHV are measured by calculating the enthalpy change between reactants and products, which consist of condensed water for HHV and gaseous water for LHV.⁴⁷ However, heating value measurement is more complicated and time-consuming to perform than proximate and ultimate analysis. Hence, it is more common to estimate heating value through calculation of correlations as functions of either proximate analysis results or ultimate analysis results, than to perform experiments.^{48,49,50}

Research on biomass was extended by many researchers from characterisations to combustion. Proximate and ultimate analysis are used to setup the optimum parameters of operating conditions in large-scale biomass combustion and estimate the speciation of each major element, e.g. carbon, hydrogen, and oxygen, in each biomass combustion thermal conversion reaction at particular combustion operating conditions.

A series of thermal conversion reactions occurs in biomass combustion. Biomass combustion is initiated with pyrolysis into volatile matter, tar, and char at high temperature. The released volatile matter is exothermically oxidised with $O_{2(g)}$ and converted into $CO_{2(g)}$ and $H_2O_{(g)}$. The tar does not create an operational problem in solid fuel combustion. During volatile matter volatilisation, the formed tar is simultaneously pyrolysed into char and oxidised into $CO_{2(g)}$ and $H_2O_{(g)}$. The $O_{2(g)}$ heterogeneously reacts with formed char to produce $CO_{2(g)}$. The char is also gasified with the $CO_{2(g)}$ and $H_2O_{(g)}$ released due to pyrolysis. Unlike gasification with $CO_{2(g)}$ and $H_2O_{(g)}$, solid fuel combustion is solely used to generate heat, since oxidation reactions are exothermic.

It is imperative to provide a sufficient amount of $O_{2(g)}$ to ensure complete conversion in solid-fuel combustion. The availability of $O_{2(g)}$ is represented by the air-fuel ratio, R_{AF} . R_{AF} is defined as the ratio of air mass to fuel mass. Under stoichiometric conditions, $R_{AF\ stoich}$ is defined such that $R_{AF\ stoich}$ kg of air is required to burn 1kg of solid fuel. The air-fuel equivalence ratio, λ , is calculated as shown in Equation 2.1.

$$\lambda = \frac{R_{AF}}{R_{AF\ stoich}} \quad (E2.1)$$

λ is ideally one. However, the formation of polycyclic aromatic hydrocarbons (PAHs), e.g. naphthalene, fluorine, phenanthrene, pyrene, etc., and volatile organic compounds (VOCs), e.g. formaldehyde, acetaldehyde, etc., are in practice often inevitable. The presence of PAHs and VOCs indicates that λ is actually less than one due to constraints of mixing and mass transfer.^{51,52} In practice, λ is always set at more than one to compensate for mixing and mass-transfer constraints and to minimise PAH and VOC emissions.⁵³

Solid fuel combustion on an industrial scale has been implemented since the early period of the Industrial Revolution. Since then, boilers have been playing the key role as solid fuel combustion equipment.⁵⁴ According to Krevelen⁵⁵ and Elliot⁵⁶, the combustion method of coal combustion are grouped into three categories, as listed in Table 2.2. It can be inferred from Table 2.2 that solid fuel particle sizes influence the required boiler types.

Table 2.2 Comparison of Coal Combustion Method Characteristics

Variables	Combustion Method		
	Fixed Bed (Grate-firing)	Fluidised Bed	Suspension Firing (Entrained-flow)
Particle Size			
Approximate Top Size	<5.08 cm	<80 mm ⁵⁷	180 μ m
Average Size	6.35 in	1.016 mm	45 μ m
System/Bed Temperature	815.6 °C (1,088.7 K)	815.6 – 982.2 °C (1,088.7 – 1,255.3 K)	>1,204.4 °C (1,477.6 K)
Particle Heating Rate	~0.6 °C s ⁻¹	~555 – 5,555 °C s ⁻¹	~555 – 555,555 °C s ⁻¹
Reaction Time			
Volatiles	~100 s	10 – 50 s	<0.1 s

Char	$\sim 1,000$ s	100 – 500 s	<1 s
Reactive Element			
Description	Diffusion-controlled	Diffusion-controlled	Chemically-controlled

As shown in Table 2.2, particle sizes affect volatilisation time. Fine particles are volatilised rapidly due to minor restrictions on intra-particle heat and mass transfer. In contrast, large particles need longer volatilisation time. Large particle volatilisation might potentially produce tar due to low particle temperatures in a high heating rate environment for a relatively considerable reaction duration. However, persistent contact with $O_{2(g)}$ converts the liquid tar into VOCs.

Char combustion, the last stage of solid-fuel combustion, is considered the slowest part of the process, since the reaction involves two reactants of different phases. Char combustion incorporates complex mechanisms, namely: $O_{2(g)}$ diffusion towards the char surface; $O_{2(g)}$ attachment to the char active site; $O_{2(g)}$ reaction with carbon at the char active site; and $CO_{(g)}$ release from the char surface.⁵⁸ However, some researchers believe that further $CO_{(g)}$ oxidation at the active sites on char surfaces may occur and directly release $CO_{2(g)}$ from the surface. The effect of diffusion and reaction on char combustion rates is illustrated in Figure 2.2.

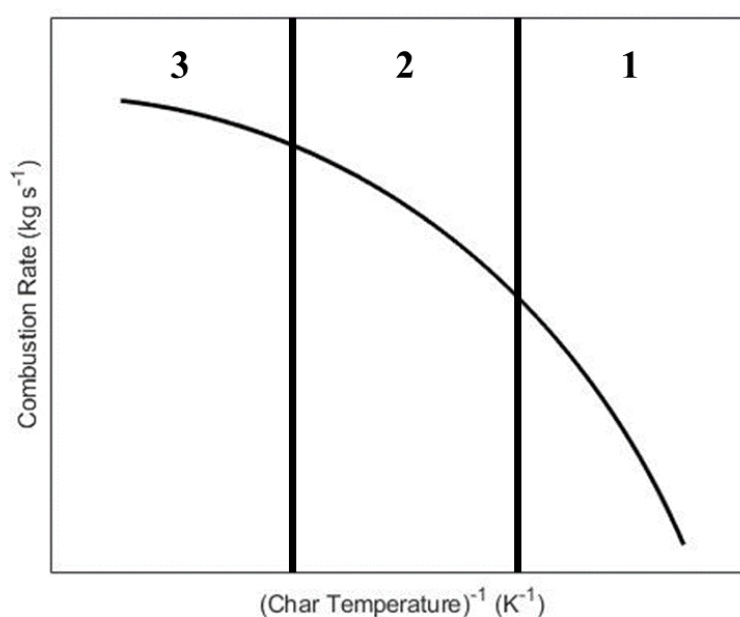


Figure 2.2 Char Combustion Regime (Logarithmic y-axis)

Figure 2.2 shows that char combustion rates are clustered into three regimes. In regime 1, heterogeneous reaction rates are slow due to the low temperature of the char. Under these conditions, the rate of gas

diffusion towards the char surface defines the reaction rate. As the temperature of the char increases, conditions are characterised as regime 2, in which both heterogeneous reaction rates and gas diffusion rates within particle bodies define the rate of reaction. In regime 3, heterogeneous reaction rates are extremely fast and dominate the rate of reaction due to very high char temperatures. Under these conditions, $O_{2(g)}$ is not present in the particle sub-surfaces since it has already been consumed at the particle surfaces.

Grate-firing boilers are the oldest form of solid-fuel combustion equipment. The majority of currently active grate-firing boilers in combined heat and power (CHP) plants have power ratings of 20 MW_e to 50 MW_e. Although grate-firing boilers were initially designed for coal combustion, the current applications of grate-firing boilers also include biomass combustion, e.g. AVV2 in Avedøre Power Station in Hvidovre, Denmark. AVV2 is a vibrating grate boiler combusting straw at an average mass flow rate of 6.55 kg s⁻¹ with a thermal capacity of 105 MW_{th}.⁵⁹ A schematic diagram of AVV2 is shown in Figure 2.3.⁶⁰

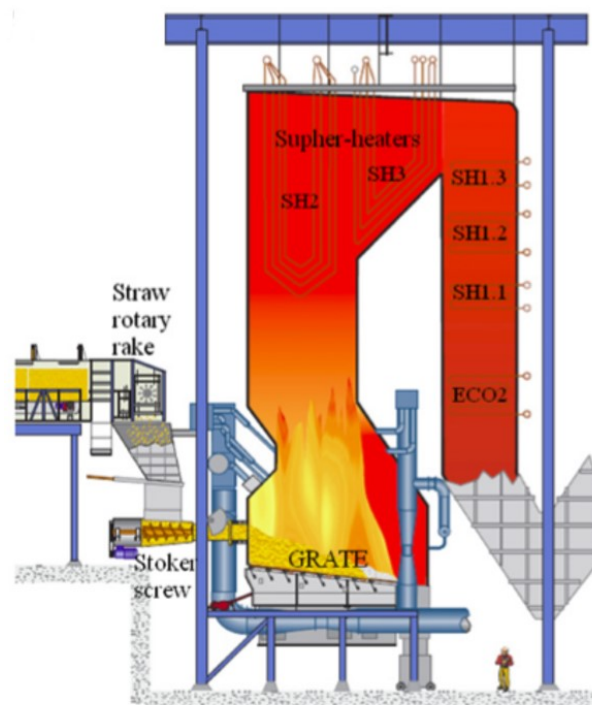


Figure 2.3 Schematic Diagram of AVV2

In a grate-firing boiler, solid fuel is introduced typically with a mechanical stoker. The stoker must be capable of spreading large particles and fine particles heterogeneously across the grate to minimise local heat formation. When the stoker drops the particles, large particles remain on the grate whilst fine particles may burn as they are carried above the grate by the air that flows upwards from below the grate.

Fluidised-bed boilers were a development of solid-gas reaction equipment that were introduced in the UK as solid-fuel combustors in the 1950s.⁶¹ In a fluidised-bed boiler, a bed that consists of solid fuel and bed material is retained at the bottom of the boiler. When air is introduced from the boiler base, the bed is “fluidised” and looks like a bubbling pond. The bed material distributes heat homogeneously throughout the bed. Improved heat distribution establishes a lower temperature, e.g. 1,073K to 1,173 K, in a fluidised-bed boiler than in a grate-firing boiler. Low temperature prevents NO_x formation and reduces the unnecessary costs of fitting boiler wall material that incorporates extreme heat resistance.⁶² Another advantage of the low temperature is that bed material such as limestone can be retained at its optimum condition to capture sulphur dioxide (SO_{2(g)}) that is released during combustion of sulphur-containing biomass.⁶³

Fluidised-bed boilers are generally categorised as circulating fluidised-bed boilers or bubbling fluidised-bed boilers, as shown in Figure 2.4.⁶⁴ Bubbling fluidised-bed boilers employ a suspended bed design due to the low gas flow rate, e.g. 1ms⁻¹ to 3ms⁻¹. In circulating fluidised-bed boilers, a substantial amount of bed is conveyed upward and departs from the boilers due to high gas flow rates, e.g. 3ms⁻¹ to 6ms⁻¹. Circulating fluidised-bed boilers are equipped with a cyclone gas-solid separator to separate the entrained solids from the gas. Lower cyclone outlets are connected to the bottom of the boiler to recycle the entrained solids back to the bed.

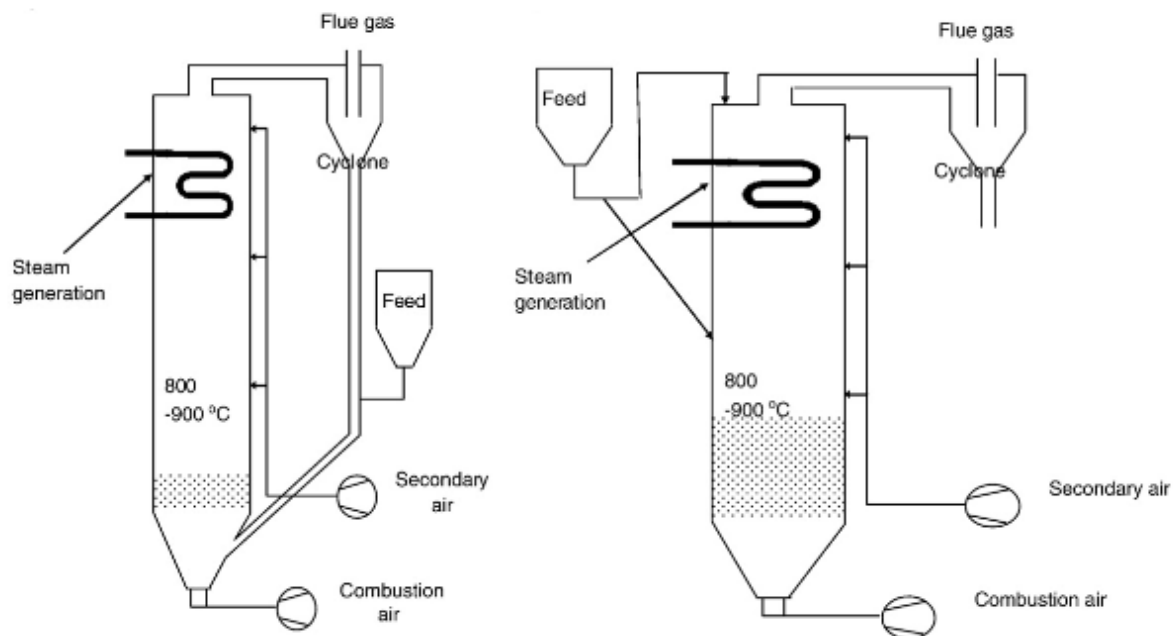


Figure 2.4 Schematic Diagram of Fluidised-bed Boiler: Circulating Fluidised-bed Boiler (left) and Bubbling Fluidised-bed Boiler (right)

Fluidised-bed boilers are compatible with biomass combustion. An example of biomass-fired fluidised-bed boiler is Boiler 5 operated by Mälarenergi in Västerås, Sweden, as shown in Figure 2.5. Boiler 5 is a circulating fluidised-bed boiler with a thermal capacity of 157 MW and bed temperature ranging from 1,073 K to 1,123 K. The fuel combusted in Boiler 5 is typically mixtures of wood, bark, forest residue, waste wood, and, sometimes, added with the bottom ash from Boiler 4 combusting a mixture of peat and coal.⁶⁵

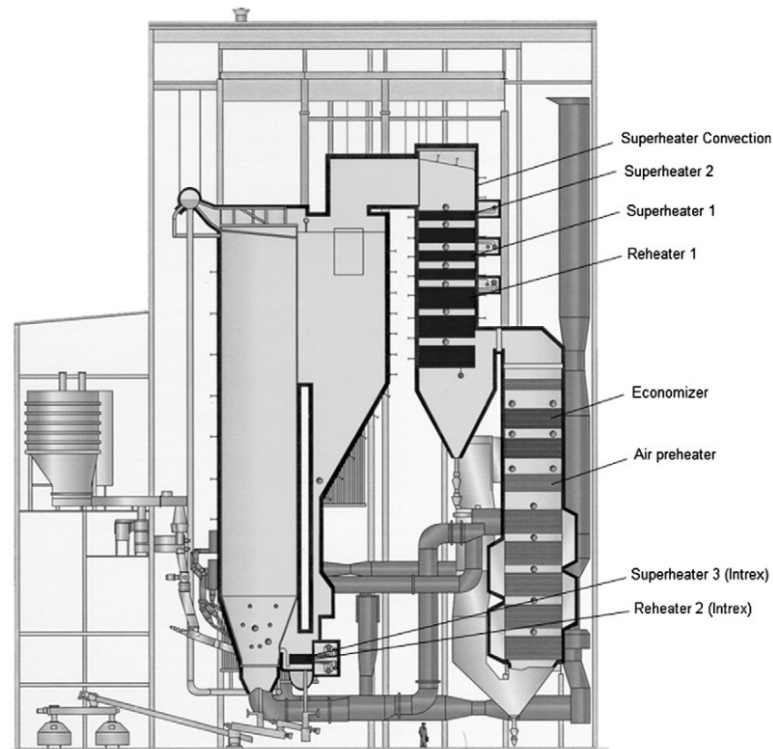


Figure 2.5 Schematic Diagram of Boiler 5

Unfortunately, bed agglomeration commonly occurs in biomass-fired fluidised-bed combustion. Due to operation at low temperatures, a sufficient amount of potassium and silicon might remain in bed. Both potassium and silicon might react to form low-melting-point alkali silicate. The formed alkali silicate melts at typical fluidised-bed boiler temperatures and promotes bed agglomeration, which causes bed defluidisation.⁶⁶ In the worst scenario, an entire plant has to be shut down and cleaned due to flow blockage and formation of channels in bed. The agglomeration is less likely to occur in coal combustion than in biomass combustion since biomass contains relatively larger amounts of potassium.⁶⁷

Entrained-flow boilers of large capacity up to 1,300MW are favoured in solid-fuel combustion. In comparison with grate-firing boilers, entrained-flow boilers have higher efficiency, of maximum 45%. The solid fuel is heated within milliseconds due to good thermal diffusion. Rapid combustion may establish peak temperatures that are higher than the maximum temperatures reached in grate-firing

boilers. Consequently, inorganic aerosols are formed faster than in grate-firing boilers, since the inorganic compounds are volatilised easily and nucleated at lower temperatures.⁶⁸ In general, the designs of entrained-flow boilers is shown in Figure 2.6.⁶⁹

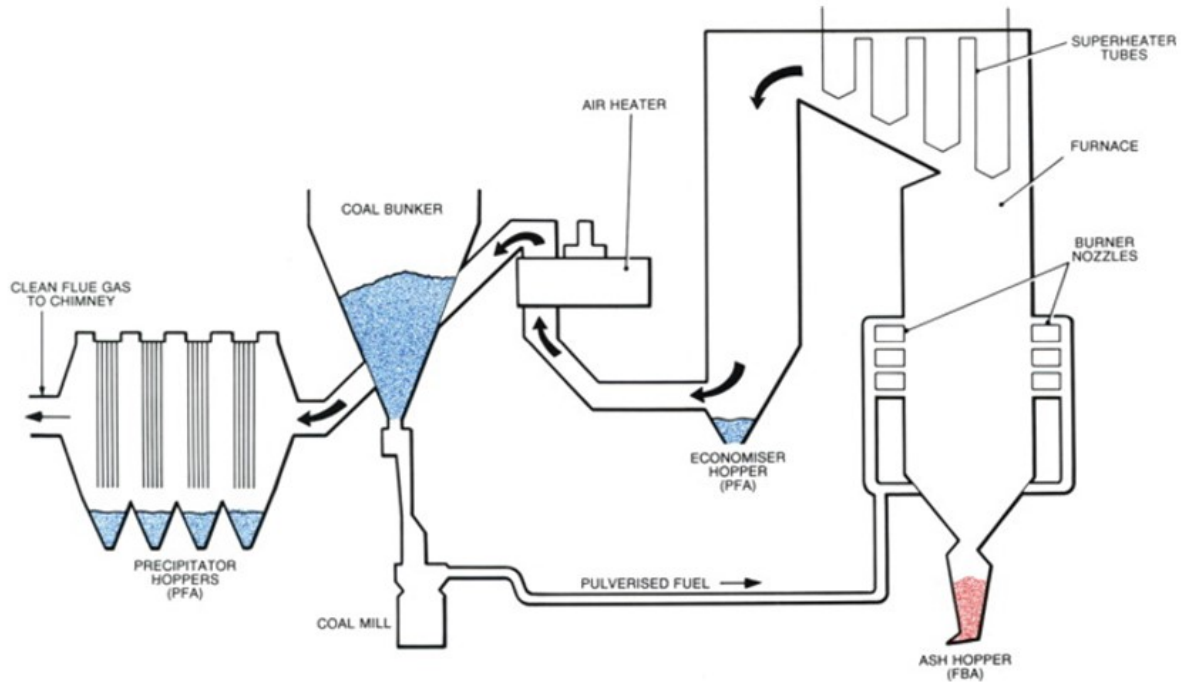


Figure 2.6 Schematic Diagram of Entrained-flow Boiler

Although entrained flow boilers are commonly used for coal combustion and coal co-combustion with biomass, few power plants utilise entrained flow boilers to fully combust biomass. An example is AMV2 in Amager Power Station in Amager, Denmark. AMV2 is an entrained-flow boiler with 12 feed burners at three levels; it was retrofitted in 2003 from coal combustion to biomass combustion and reduced in capacity by 30% due to this retrofitting. AMV2 co-combusts wood with straw at a maximum flow rate of 14.36 kg s^{-1} with thermal capacity of $250 \text{ MW}_{\text{th}}$.⁷⁰

Entrained-flow combustion equipment also exists with non-commercial designs, e.g. PACT facility entrained-flow burner. The entrained-flow burner at PACT facility is operated to combust coal and biomass at a maximum thermal capacity of 250 kW. Both solid fuel and gas enters the burner from the top and the flue gas leaves the burner from the lowest level of the burner. PACT facility entrained-flow burner is modelled in this thesis and further discussed in Chapter 5.

2.2 Ash Problems: Fouling, Corrosion, and Slagging

Biomass combustion is susceptible to operational problems associated with ash deposition and corrosion. Ash deposition reduces heat transfer efficiencies and increases average temperatures. The accumulation of ash deposit may block gas flow paths and establish localised pressure buildup mechanically damaging the boiler. The increasing average temperatures may thermally damage the boiler and reduce boiler lifetime and promote corrosion on heat transfer surfaces. In severe situations, boiler shutdown is required. Ash deposition is categorised as low-temperature deposition (fouling) and high-temperature deposition (slagging). Figure 2.7 exhibits the typical locations of both fouling and slagging in a commercial boiler.⁷¹

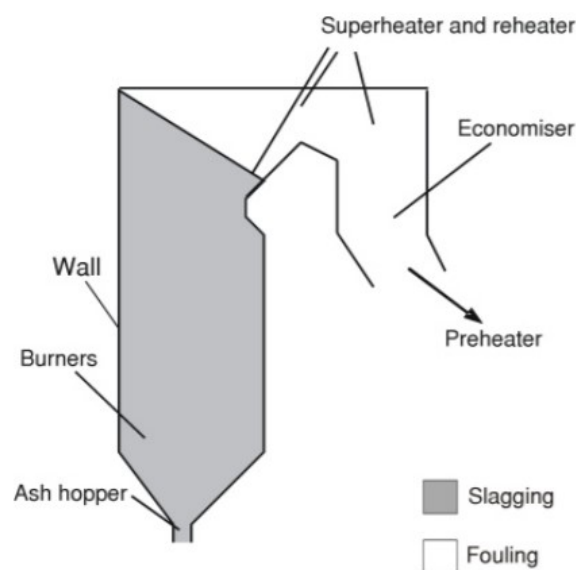


Figure 2.7 Typical Locations of Fouling and Slagging in a Commercial Boiler

Fouling is ash deposition on heat transfer surfaces of heat exchanger pipes at low temperatures and induced by the devolatilised silicon and alkali metals.^{72,73} Significant chlorine content in the biomass promotes rapid alkali-metal volatilisation by forming volatile potassium chloride ($\text{KCl}_{(g)}$) and sodium chloride ($\text{NaCl}_{(g)}$). At relatively low temperatures on heat transfer surfaces, $\text{KCl}_{(g)}$ and $\text{NaCl}_{(g)}$ are condensed and react with deposited silicon dioxide ($\text{SiO}_{2(s)}$) to form alkali metal silicates. Once the deposit is thick enough, it affects the power-plant efficiency.⁷⁴ Biomass with low sulphur content severely corrodes heat exchanger pipes due to the reaction of iron with $\text{KCl}_{(l)}$ on the surfaces of the pipes.⁷⁵ Biomass with a high sulphur content releases sulphur trioxide ($\text{SO}_{3(g)}$), which reacts with $\text{KCl}_{(l)}$ and therefore prevents corrosion through the formation of a barrier layer of potassium sulphate ($\text{K}_2\text{SO}_{4(s)}$). The chlorine subsequently leaves the deposit as gaseous hydrochloric acid ($\text{HCl}_{(g)}$).

Fouling is driven by the presence of ash particulates, the pathway to the formation of which is illustrated in Figure 2.8.⁷⁶ Volatile organo-metallic compounds are released during pyrolysis. Once char is formed, volatile compounds are released through the char's pores during char oxidation. At low temperatures, inorganic gases with high vaporisation temperatures are condensed into aerosols or submicron-sized particles. Some other inorganic gases might be condensed on to the residual particles' surfaces. Fouling routes of aerosols, submicron particles, and residual particles are described by three mechanisms, as shown in Figure 2.9, namely: alkali-metal-induced melting, silicate-induced melting, and agglomerations.⁷⁷

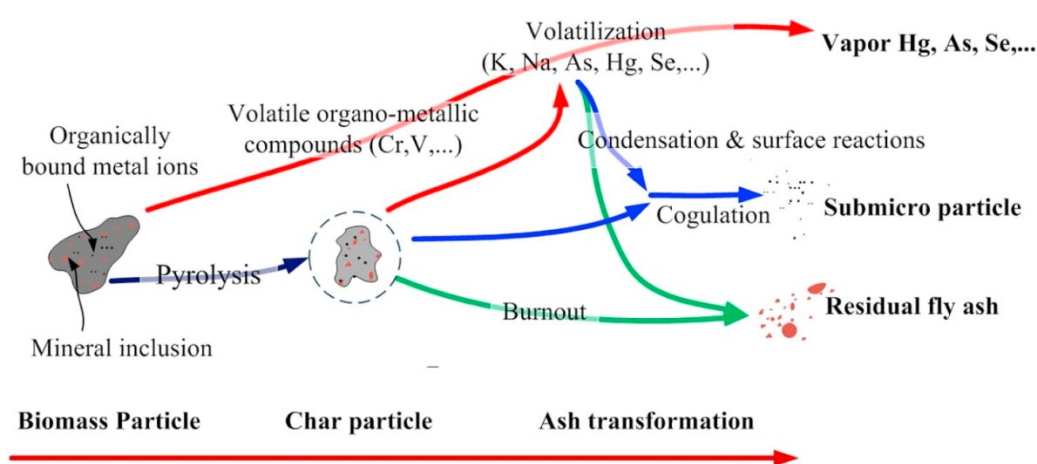


Figure 2.8 Routes for Biomass Ash Formation

The alkali-metal-induced melting strongly depends on the compositions of the released gases that flow around the heat transfer surfaces. It has been confirmed experimentally that $K_2SO_{4(s)}$ is mainly found in heat transfer ash deposits during the combustion of biomass that has low chlorine and high sulphur content, e.g. woody biomass. In contrast, $KCl_{(g)}$ has been commonly discovered in gas released from the combustion of herbaceous biomass that contains a significant amount of potassium and chlorine.⁷⁸

The alkali-metal-induced melting mechanism consists of sequential deposition. Alkali metal compounds are primarily released in the form of either hydroxides, chlorides, or sulphates.⁷⁹ At low temperatures, the released alkali metal compounds are condensed on heat transfer surfaces as sticky liquid layers due to the low temperature. Coarser aerosols and residual particles that impact the heat-exchanger surfaces are glued to the sticky layers and form the second layers. As the second layers become thicker, the adhesion becomes too weak to lead to further sticking of the coarse aerosols or residual particles. Then a new batch of alkali metal compounds is condensed and liquefied to form the third layers. This alkali-metal-induced melting mechanism enables the formation of deposits that contain alternating layers of fine and coarse ash particles. The growth of the alternating layers is predominantly driven by three different factors: inertial impaction of the residual particles,

thermophoresis of the coarser aerosols, and condensation of the alkali metal compounds. However, as the deposit layers thicken, they insulate the cooled exchanger pipes from the surrounding gas, and so the deposit surface temperature rises, reducing the role of condensation and thermophoresis.

Inertial impaction is defined as the flow within the gas of particles with sufficient inertia to flow towards the heat-exchanger pipe and impact on the pipe surface. The inertial impaction rate strongly depends on the probability of the particles sticking and the efficiency of particle capture. The particle sticking probability determines the likelihood that particles will stick on pipe surfaces and it is based on particle melt fractions and deposited ash compositions.^{80,81} The particle capture efficiency determines the probability of particle capture based on the distance of the particles from stagnation points. The highest inertial impaction rates are located at particle stagnation points. At larger than 50° from stagnation points, inertial impaction rates are considered negligible.

Thermophoresis is described as particle depositions that are induced by differences between gas temperatures and pipe-surface temperatures. Low temperatures at the pipe surface decrease the kinetic force of a particle and enhance the probability that the particle will flow slowly and be deposited on the pipe surface. Unlike inertial impaction, thermophoresis mostly affects finer particles.

Condensation refers to phase transformations of gas into liquid and solid aerosols at low temperatures on pipe surfaces. Three mechanisms of condensation may occur: vapours are heterogeneously condensed on pipe surfaces; vapours are nucleated into aerosols and thermophoretically deposited on pipe surfaces; and vapours are heterogeneously condensed on aerosols and thermophoretically deposited on pipe surfaces. Condensation establishes a more uniformly distributed and less coarse ash deposit than the former deposition factors. When liquid is formed on outer layers of ash deposits, inertial impaction rates become significant due to adhesive bonds in the liquid that reduce the probability of particle rebounds.

Alkali metal compounds are also condensed on the surfaces of coarse aerosols and residual particles. Condensed alkali metal compounds react with AFEs at the surface of coarse aerosols and residual particles to form other compounds, e.g. $\text{SiO}_{2(s)}$ and iron oxide ($\text{Fe}_2\text{O}_{3(s)}$).⁸² Liquefied surfaces glue the particles to one another and form clusters of agglomerated ash. Agglomerations in suspended beds, e.g. beds in fluidised-bed boilers, clog airflow and build channellings.⁸³

Silicate-induced melting occurs within ash particles that contain little potassium, e.g. residual particles. Liquid formation is mainly driven by the presence of silicon and aluminium. At high temperatures, $\text{SiO}_{2(l)}$ is formed on residual particle surfaces. Liquefied surfaces may promote sturdy construction of second layers of ash deposit.

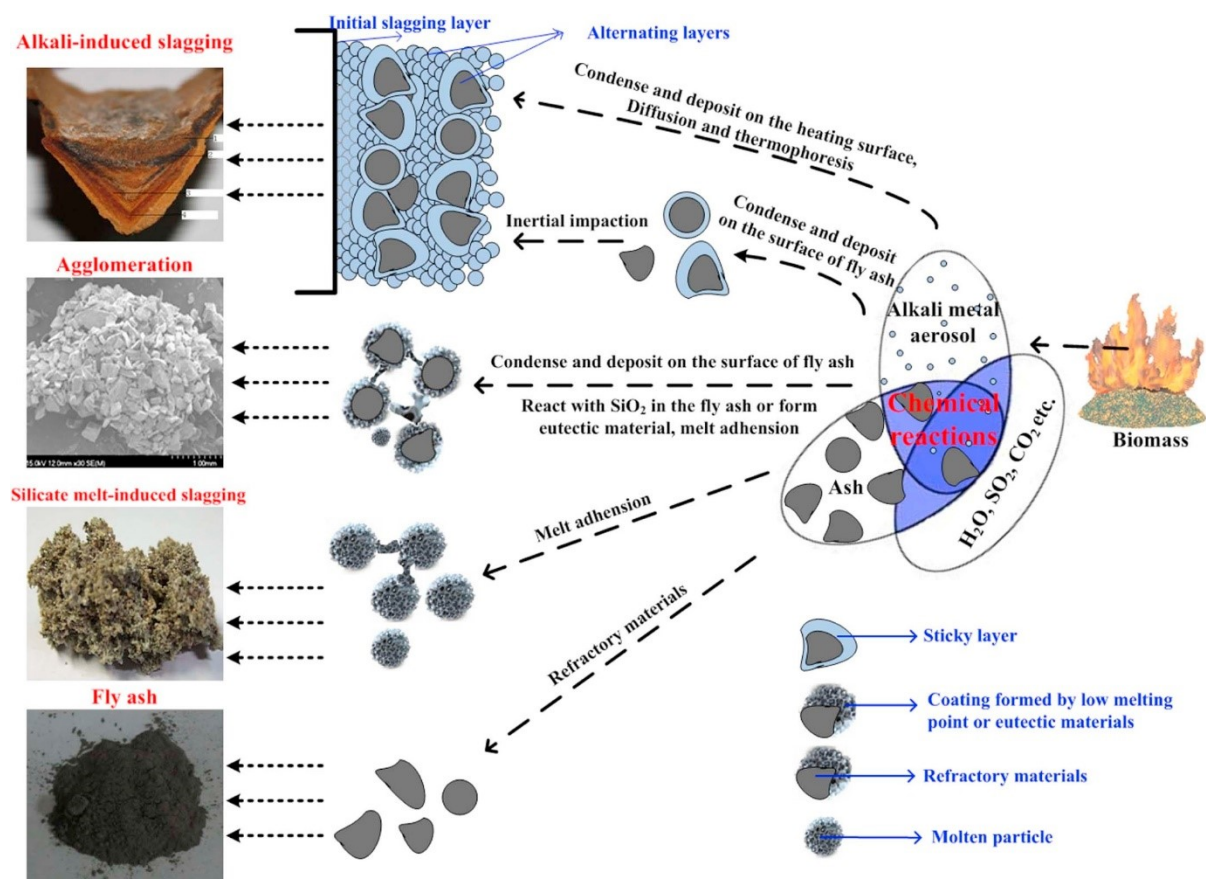


Figure 2.9 Routes for Fouling and Agglomeration⁸⁴

In a more comprehensive evaluation, the concentrations of AFEs vary along the heat transfer region in Figure 2.7 due to temperature variations. The heat transfer region consists of a series of heat exchanger pipe assembly ordered from the highest to the lowest temperature, e.g. superheater, reheater, and economiser. Potassium, sodium, and phosphorus are enriched at low temperature heat exchanger pipe assembly such as reheater and economiser since these elements vaporise easily from solid fuel during combustion and condenses at low temperatures. Aluminium, iron, silicon, calcium and magnesium have a substantially low tendency to volatilise and vaporise. Thus, the heat transfer region temperature variations do not significantly change the concentrations of aluminium, iron, silicon, calcium and magnesium in ash deposit in any heat exchanger pipe assembly.⁸⁴

Slagging is ash deposition on boiler refractory materials, e.g. the boiler wall or water wall tubes if available, due to the formation of molten ash at extremely hot temperatures mainly driven by radiative heat transfer.⁸⁵ There are three sequential slagging mechanisms on the refractory materials, namely: the van der Waals force, viscosity-induced adhesion, and surface-tension-driven growth. The flowing ash particles move towards and hit the refractory material surfaces due to turbulent diffusion and

thermophoresis. After hitting the surfaces, the ash particles rebound back to the main gas flow unless the ash particle viscosities are less than the ash particle critical viscosities. The remaining ash particles merge due to low surface tension and build ash deposit layers. Based on this mechanism, three distinctive ash layers are built on the refractory materials, as illustrated in Figure 2.10.⁸⁶

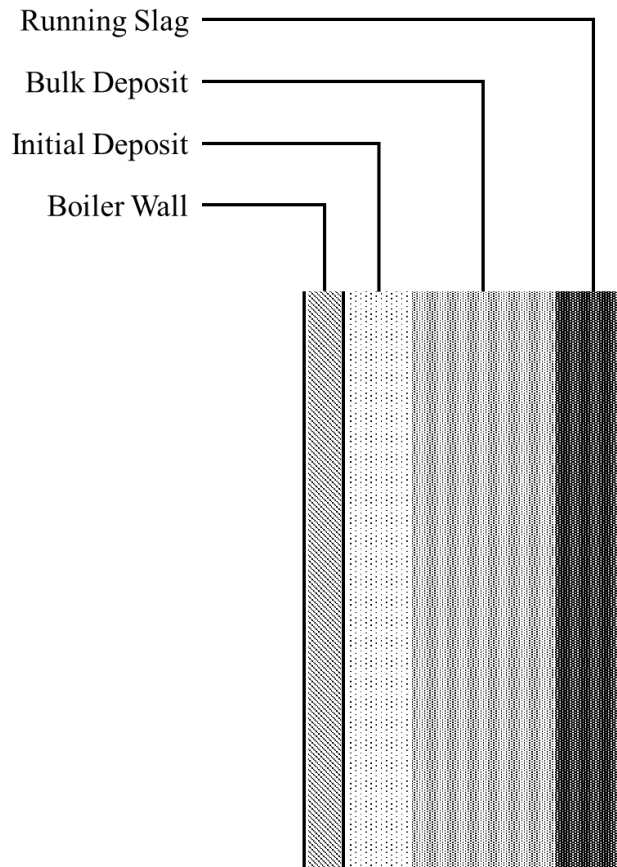


Figure 2.10 *Slagging Layers*

The initially formed layer adjacent to the boiler wall is the initial deposit layer, mostly containing fine ash particles. The temperatures are relatively cooler in the refractory material boundary layer than in the main gas flow. The low boundary layer temperatures promote fine ash particle deposition via thermophoresis due to temperature differences and are not likely to allow the deposited fine ash particles to sinter since the boundary layer temperatures are well below the fine ash particle melting temperatures. The thermal conductivity of the initial deposit layer is quite low, as the unsintered deposited fine ash particles form pores within the layer.⁸⁷

The bulk deposit layer is formed on the initial deposit layer surfaces when the initial deposit layer is thick and thermally resistive enough to achieve surface temperatures that allow viscosity-induced adhesion. The viscosity-induced adhesion occurs because the ash particles are sticky due to lower

particle viscosities than the critical particle viscosities.⁸⁸ Sticky conditions allow the bulk deposit layer to have higher densities and thermal conductivities than the initial deposit layer due to sintering.

As the bulk deposit keeps growing thicker, the deposit surface temperatures become hotter until the deposit stops growing due to the formation of the running slag layer, which is completely fused and molten. Due to the complete fusion, the layer is most dense and thermally conductive. The layer keeps flowing downward whilst fusing with any incoming arriving ash particles and eventually merging with residual particles as bottom ash.⁸⁶

The severity of slagging is practically assessed with severity indices as functions of the inorganic chemical compositions in the solid fuel. These indices have been developed over the years based on the behaviour of coal combustion. One of the most commonly used indices is the basic-to-acidic oxide ratios, $R_{BOx/AOx}$, calculated in Equation 2.1.⁸⁹

$$R_{BOx/AOx} = \frac{m_{BOx}}{m_{AOx}} \quad (E2.1)$$

m_{BOx} and m_{AOx} are the total masses of basic oxides and acidic oxides in kg, respectively. BOx is the summation of $Fe_2O_{3(s)}$, $CaO_{(s)}$, $MgO_{(s)}$, $K_2O_{(s)}$, and $Na_2O_{(s)}$. AOx is the summation of $SiO_{2(s)}$, $TiO_{2(s)}$, and $Al_2O_{3(s)}$. Equation 2.1 is often simplified by neglecting $K_2O_{(s)}$ and $Na_2O_{(s)}$ in BOx and $TiO_{2(s)}$ in AOx due to their negligible quantities. Another common index is sulphur index, R_S , calculated in Equation 2.2.

$$R_S = R_{BOx/AOx} \frac{m_S}{m_{fuel} - m_{H_2O(l)}} 100 \quad (E2.2)$$

m_S is the mass of sulphur in kg. m_{fuel} is the mass of solid fuel in kg. $m_{H_2O(l)}$ is the mass of moisture in kg. The severity of slagging is low when R_S is smaller than 0.6, medium when R_S is larger than 0.6 and smaller than 2, high when R_S is larger than 2 and smaller than 2.6, and very high when R_S is larger than 2.6.

The severity of slagging is also alternatively assessed with the ash fusibility index (AFI) as a function of initial deformation temperatures (IDTs) and hemisphere temperatures (HTs), calculated in Equation 2.3.

$$AFI = \frac{4(T_{ID}-273)+(T_H-273)}{5} + 273 \quad (E2.3)$$

AFI is the ash fusibility index in K. T_{ID} is the IDT in K. T_H is the hemisphere temperature in K. The severity of slagging is low when AFI is larger than 1,616 K, medium when AFI is larger than 1,505 K and smaller than 1,616 K, high when AFI is larger than 1,422 K and smaller than 1,505 K, and very high when AFI is smaller than 1,422 K.⁹⁰

IDTs and HTs are determined via ash fusion measurements visually represented through deformation of an ash pile, as illustrated in Figure 2.11. The ash pile is initially in the shape of a cone. The temperature is increased gradually to observe the effect of a hot environment on the pile's shape. The first deformation is shown in stage two, in which the cone peak becomes blunt and rounded. This occurs when the temperature is at IDT. When the temperature is at spherical temperatures (STs), stage three is reached and the pile collapses into a spherical shape. The pile becomes hemispherical in stage four, when the temperature is at HTs. Finally, the pile becomes flat at stage five, when the temperature reaches fluid temperatures (FT).⁹¹



Figure 2.11 Ash Fusion Measurement

The severity of fouling is assessed using the fouling index, F_U , calculated in Equation 2.4.

$$F_U = R_{BOx/AOx} \frac{m_{Na_2O(s)} + m_{K_2O(s)}}{m_{fuel}} 100 \quad (E2.4)$$

$m_{Na_2O(s)}$ is the mass of $Na_2O(s)$ in kg. $m_{K_2O(s)}$ is the mass of $K_2O(s)$ in kg. F_U is considered low when F_U is smaller than 0.6, medium when F_U is larger than 0.6 and smaller than 1.6, high when F_U is higher than 1.6 and smaller than 40, and very high when F_U is larger than 40.⁸⁹

However, some of the above indices might not be accurate for slagging in biomass combustion. Biomass is much more reactive than coal so that rapid devolatilisation might release significant quantities of ash-forming elements and should be considered as an important parameter. In Equation 2.1, BOx is supposed to reduce ash melting temperatures. However, the domination of $CaO(s)$, primarily relative to $K_2O(s)$, e.g. woody biomass, increases ash melting temperatures even if BOx is larger than AOx due to formation of high melting point calcium compounds, e.g. $Ca_2SiO_4(s)$.⁹² R_S might also be insufficient to estimate the slagging severity properly since most biomass does not contain significant quantities of sulphur.

Of all the slagging indices, *AFI* might be the most accurate index to predict biomass slagging. *AFI* simply relies on experimental observations whilst the former indices only correlate chemical compositions to ash fusibility without satisfactorily investigating the chemical synergy amongst the existing chemical compounds.⁹³

The inclusion of chlorine and sulphur compositions might improve the accuracy of the severity indices of biomass combustion since the release of alkali metals, such as those of the major AFEs in biomass, is dependent on chlorine and sulphur compositions. An improved fouling index formula includes chlorine and sulphur compositions, as shown in Equation 2.5.⁹⁴

$$F_U = \frac{m_{Na} + m_K}{2m_S + m_{Cl}} 100 \quad (E2.5)$$

The severity of corrosion on the surfaces of heat exchanger pipes is also assessed with sulphur-to-chlorine ratios, $R_{S/Cl}$, as functions of sulphur and chlorine compositions in the solid fuel, calculated in Equation 2.6.

$$R_{S/Cl} = \frac{m_S}{m_{Cl}} \quad (E2.6)$$

m_S is the mass of sulphur in kg. m_{Cl} is the mass of chlorine in kg. The severity of corrosion is low when $R_{S/Cl}$ is larger than 2 and high when smaller than 2.^{95,96} When $R_{S/Cl}$ is above 2, e.g. co-combustion of coal and bark, the quantity of sulphur originating from coal is adequate to convert all alkali chlorides into $HCl_{(g)}$ and prevent the condensation of chlorides on the surface of the heat exchanger pipes, as illustrated in Figure 2.12.⁹⁷ Above 4, the severity of corrosion is considered negligible.⁹⁸

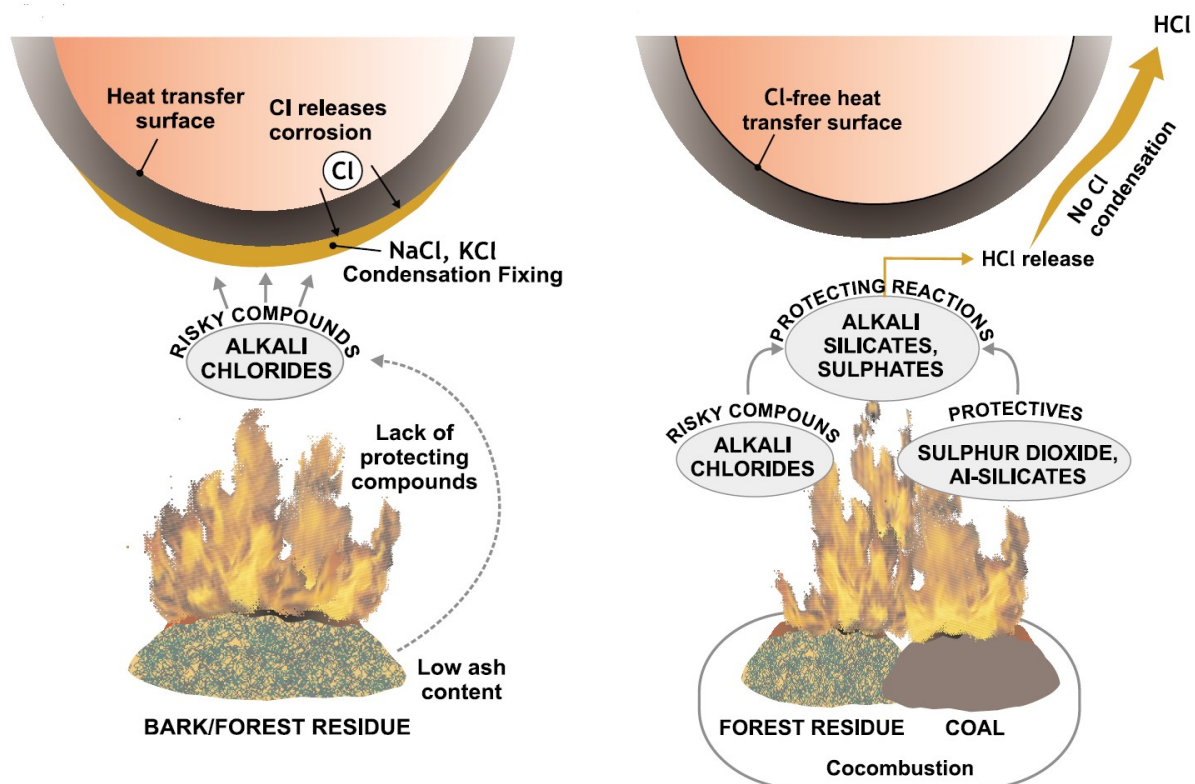


Figure 2.12 Route of Chloride Deposition in Bark/Forest Residue Combustion and Chloride Deposition Prevention in Co-firing Forest Residue and Coal

However, $R_{S/Cl}$ does not always reflect the actual severity of corrosion. Equation 2.6 might be accurate for biomass but not for coal or co-firing of coal with any other reactive solid fuel. An experiment on coal co-firing showed that negligible alkali chloride deposition was observed when $R_{S/Cl}$ was less than 2. This anomaly occurred since, unlike the organic-bound alkali metals in biomass, the alkali metals in coal are primarily mineral-bound and therefore more difficult to devolatilise by chloride since minerals are more thermally stable than organics.⁹⁹

Combustion of sulphur-rich biomass, e.g. wheat straw, also promotes corrosion at a specific condition. The released sulphur in the reducing atmosphere near the boiler burner zone undergoes sulfidation with alkali metals and forms alkali pyrosulphate. Alkali pyrosulphate melts at temperatures below 698 K on the surfaces of heat exchanger pipes and causes corrosion on the pipes.¹⁰⁰

2.3 Trace Elements: Health Impact

Waste wood that is regarded as contaminated biomass and industrial biomass waste is graded based on its inorganic composition and chemical treatment, as shown in Table 2.3.¹⁰¹ After publication of these gradings, Whitaker¹⁰² reported the classification of the most common waste wood found in the UK in

terms of WRAP grades and annual arising as listed in Table 2.4. The latter report may give brief information on the origin of UK waste wood.

Table 2.3 *General Classification of Biomass Waste Wood as Solid Fuels*

Waste Wood Grade	Typical Markets	Typical Sources of Raw Materials for Recycling	Materials within Wood Waste Grade	Typical Non-wood Content Prior to Processing
Grade A: Clean Recycled Wood	Manufacture of products such as animal bedding, horticultural mulches and the panel board sector	Distribution, retailing, packaging, secondary manufacture, e.g. joinery or pallets	Solid softwood and hardwood packaging waste, scrap pallets, packing waste, scrap pallets, packing cases, cable drums, off-cuts from joinery or manufacturing	Nails and metal fixings, minor amounts of paint, minor amounts of surface coatings
Grade B: Industrial Feedstock Grade	Industrial wood processing operations, such as the manufacture of panel products, including chipboard and MDF.	As Grade A, plus construction and demolition operations, and transfer stations	May contain up to 60% Grade A material as above, plus building and demolition materials and domestic furniture made from solid wood	Nails and metal fixings, some paints, plastics, glass, grit. Coatings, binders, glues. Limits on treated or coated materials as defined by WID
Grade C: Fuel Grade	Biomass fuel for use in the generation of electricity and/or heat in WID-compliant installations	As above, plus municipal collections, recycling centres, transfer stations, and civic amenity recycling sites	As above plus fencing products, flat-packed furniture and DIY materials. High content of chipboard, MDF, plywood, OSB and fibreboard	Nails and metal fixings, paints, coatings, glues, paper, plastics, rubber, coated, and treated timber
Grade D: Hazardous Waste	Requires disposal at special facilities	All of the above, plus fencing track work and transmission pole contractors	Fencing, transmission poles, railway sleepers, cooling towers	Copper-chrome-arsenate preservatives, treatments, creosote

Waste wood compositions are widely variable since waste wood is usually a mixture of different materials that originate from a wide range of sources, as shown in Table 2.5. An approach to obtain mean values of AFE and TE concentrations in a wide range of waste-wood feedstock has been conducted to generalise each AFE and TE concentration.¹⁰³ However, this approach is suitable only for rough estimations. Characterisations of the concentrations of each AFE and TE in waste wood are required to ensure accurate emission predictions.

Table 2.4 *General Classification of Biomass as Solid Fuels*

Sector	Material	Availability (10 ³ t)	Grade	Contaminants
Construction	Solid wood	560	Mostly A, some B	B: Formaldehyde and other resins, nails, and paint

	Particle/panel boards	270	Mostly B: particle board (17%), MDF (14%), OSB (6%), plywood (5%)	B: Formaldehyde and other resins, nails, and paint
	Other flooring	60	A or B, depending on treatment	A: Nails and paint
	Other	110	A or B	
Demolition	Demolition waste	1,100	Mostly C, some D	C: Plastics, melamine, formaldehyde and other resins. Heavy metal treatments; D: CCA, halogens, other preservatives
Commercial	Wooden packaging	500	A with small amounts of B: composite wood; small chance of C	A: Nails and paint; B: Formaldehyde and other resins; C: Methyl bromide in treated pallets
Industrial	Joinery and furniture waste	153	A: Solid wood	
	Joinery and furniture waste	240	Mostly B: particle board (56%), MDF (23%), plywood (21%)	B: Formaldehyde and other resins, nails, and paints
Local Authority	Total	560		
	Off-cuts		Mostly A, some B	B: Formaldehyde and other resins, nails, and paints
	Panel boards		B	B: Formaldehyde and other resins, nails, and paints
	Garden waste		A	Soil, stones, and debris

Each TE is volatilised at a certain partition in solid fuel combustion.¹⁰⁴ To characterise TE partitions, TEs are grouped into three classes according their volatility, namely: class 1, class 2, and class 3, as listed in Figure 2.13. Class 1 TEs include the elements equally distributed in bottom ash and fly ash. Class 2 TEs are the elements enriched in fly ash and remaining at much smaller portion in bottom ash. Class 3 TEs volatilise almost entirely and are not enriched in fly ash.¹⁰⁵

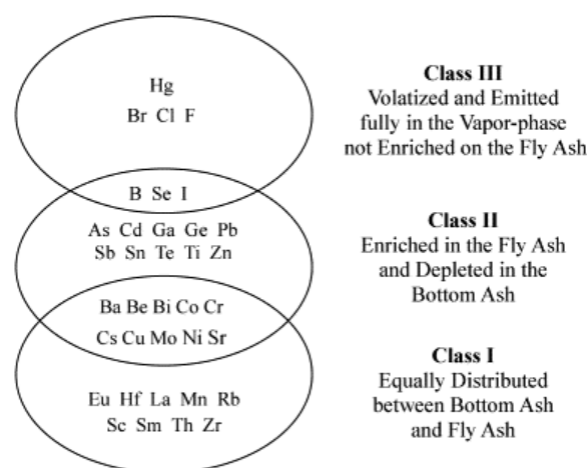


Figure 2.13 Groups of TEs and Other Elements According to Their Volatility

Exposure to volatilised TEs emitted from power plants has negative impacts on human health.¹⁰⁶ According to a study by the United States Environmental Protection Agency (EPA) a couple of decades ago, links had not been convincingly proven between TE exposure and human health;¹⁰⁷ however, more recent evidence has exhibited conflicting findings.^{108,109} Metabolism disturbances in human bodies due to excessive intake of TEs are listed in Table 2.5.

Table 2.5 Health Impacts of Trace Elements

Element	Metabolism Disturbance
Cadmium	Kidney damage, renal lesion, skeletal damage, prostate cancer
Mercury	Lung damage, tremor, restlessness, anxiety, sleep disturbance, depression, kidney damage, contact eczema, oral lichen, myocardial infarction, heart disease
Lead	Headache, irritability, abdominal pain, difficulty in concentration, psychosis, confusion, reduced consciousness, memory deterioration, anaemia, kidney damage, sperm production disturbance
Arsenic	Gastrointestinal symptoms, cardiovascular disturbance, nervous disturbance, bone-marrow depression, haemolysis, hepatomegaly, melanosis, polyneuropathy, encephalopathy, black-foot disease, lung cancer, kidney cancer, skin cancer, hyperkeratosis
Chromium	Nose irritation, asthma, cough, shortness of breath, skin ulcers, skin swelling, liver damage, kidney damage
Nickel	Lung cancer, nose cancer, larynx cancer, prostate cancer, lung embolism, birth defect, asthma, chronic bronchitis, pneumonitis, skin ulcer
Zinc	Metal fume fever, stomach cramps, nausea, vomiting, anaemia, pancreas damage, kidney damage

Copper	Anaemia, reduced number of white blood cells, nausea, vomiting, abdominal pain, liver toxicity, kidney damage, Wilson's disease, delayed bone formation
--------	---

The European Union (EU) has released the Directive 2010/75/EU which sets trace element emission thresholds to limit trace element concentrations in flue gas from waste incineration and to maintain safe atmospheric levels of TEs. The thresholds for TE concentrations in flue gas, along with in drinking water and in the atmosphere, are summarised in Table 2.6.

Table 2.6 *Regulatory Limits for Trace Elements*

Element	Regulatory Limits
Cadmium	5 ppb in drinking water (EPA) 5 ppb in drinking water (FDA) 5 $\mu\text{g m}^{-3}$ in atmosphere for eight hours in working days (OSHA) 0.05 mg m^{-3} including thallium in CHP flue gas at 273.15 K and 1 atm (EU)
Mercury	2 ppb in drinking water (EPA) 1 ppb of methyl mercury in a million parts of seafood (FDA) 0.1 mg m^{-3} of organic mercury in atmosphere for eight hours in working days (OSHA) 0.05 mg m^{-3} of metallic mercury in atmosphere for eight hours in working days (OSHA) 0.05 mg m^{-3} in CHP flue gas at 273.15 K and 1 atm (EU)
Lead	15 ppb in drinking water (EPA) 0.15 $\mu\text{g m}^{-3}$ in atmosphere (EPA) 0.075 mg m^{-3} of tetraethyl lead or tetramethyl lead in atmosphere (OSHA) 0.5 mg m^{-3} including antimony, arsenic, chromium, cobalt, copper, manganese, nickel, and vanadium in CHP flue gas at 273.15 K and 1 atm (EU)
Arsenic	0.1 ppm in drinking water (EPA) 10 $\mu\text{g m}^{-3}$ in atmosphere for eight hours in working days (OSHA) 0.5 mg m^{-3} of organic arsenic in atmosphere (OSHA) 0.5 mg m^{-3} including antimony, lead, chromium, cobalt, copper, manganese, nickel, and vanadium in CHP flue gas at 273.15 K and 1 atm together with thallium (EU)
Chromium	0.1 ppm in drinking water (EPA) 1 mg l^{-1} in drinking water (FDA) 0.0005 to 1 mg m^{-3} in atmosphere for eight hours in working days (OSHA) 0.5 mg m^{-3} of chromium(II) in atmosphere (OSHA)

Nickel	1 mg m ⁻³ of insoluble salt in atmosphere (OSHA)
	0.5 mg m ⁻³ including antimony, arsenic, lead, cobalt, copper, manganese, nickel, and vanadium in CHP flue gas at 273.15 K and 1 atm together with thallium (EU)
	0.000038 µg m ⁻³ in atmosphere (WHO)
	0.02 mg l ⁻¹ in drinking water (WHO)
	0.007 mg m ⁻³ of nickel carbonyl in atmosphere (OSHA)
Zinc	1 mg m ⁻³ of metallic nickel in atmosphere (OSHA)
	0.5 mg m ⁻³ including antimony, arsenic, lead, chromium, cobalt, copper, manganese, and vanadium in CHP flue gas at 273.15 K and 1 atm together with thallium (EU)
	1 µg m ⁻³ of ZnCl aerosol in atmosphere (OSHA)
	5 µg m ⁻³ of ZnO aerosol in atmosphere (OSHA)
Copper	6 mg l ⁻¹ in drinking water (EPA)
	0.1 mg m ⁻³ of copper fume in atmosphere (OSHA)
	1 mg m ⁻³ of copper dust in atmosphere (OSHA)
	0.5 mg m ⁻³ including antimony, arsenic, lead, chromium, cobalt, manganese, nickel, and vanadium in CHP flue gas at 273.15 K and 1 atm together with thallium (EU)

2.4 Modelling Route

The model was developed with increasing modelling scales and complexities as referred to Section 1.3: the single-particle combustion model, the entrained-flow combustion model, and the fate and occurrence model. The single-particle combustion model was used to calculate particle combustion in the entrained-flow combustion model. The fate and occurrence model predicted the fate and occurrence of AFEs and TEs using chemical equilibrium calculations in both particles and bulk, using the intraparticle and bulk temperatures and pressures calculated in the entrained-flow combustion model. To eliminate expensive computation, the last two models were simplified to the simplified entrained-flow combustion model and the simplified fate and occurrence model.

During early development of the solid-fuel combustion model, researchers ignored heat transfer and mass transfer within solid-fuel particles. Baum and Street¹¹⁰ then predicted coal-particle combustion behaviour and kinetic parameters through development of a lumped single-particle combustion model. Similarly, Timothy *et al.*¹¹¹ modelled combustion of pulverised coal particles to understand the characteristics of coal-burning and volatilisation time. Both projects used micron-size particles and showed good validation with experimental results. Agarwal¹¹² has cautioned that dependency of volatilisation time on particle sizes should be treated with care, particularly when relatively large

particle sizes are used. Large particles combust at slower rates than small, due to delayed formation of an ignition flame induced by slower release rates of volatile compounds and the presence of temperature gradients within the particles.^{113,114}

Intra-particle calculations were later developed and incorporated into solid fuel combustion models to improve calculation accuracy. Lu *et al.*¹¹⁵ developed a single-particle combustion model to study the effect of particle sphericity on intra-particle temperature and concentration profiles. Yang *et al.*¹¹⁶ incorporated particle-shape evolution into the single-particle combustion model. Other similar studies were conducted to observe several other aspects, e.g. volatilisation and char oxidation times; the impacts of boundary gas concentrations and rapid heating; the retardation of oxygen heterogeneous reactions due to the presence of fused ash; soot formation; and the fate of inorganic elements.^{117,118,119,120,121,122}

The single-particle combustion model has become an approach used to understand thermal behaviours of large-scale combustion from the perspective of miniaturised combustion. Wurzenberger *et al.*¹²³ used the single-particle combustion model to study the thermal behaviour of particles in a grate-fired boiler combustion. Numerous pieces of work on use of the single-particle combustion model for fluidised-bed boilers were also conducted.^{124,125} The entrained-flow combustion model based on the single-particle combustion model was developed in this thesis, similar to the work conducted by Saastamoinen *et al.*¹²⁶

Entrained-flow combustion has been commonly implemented in numerous power plants around the world. Entrained-flow boilers were the most commercialised combustion facility in the world in 2008. At that time, there were more than 240 operating entrained-flow boilers and another 50 being planned and designed.¹²⁷ One of the main reasons for the wide implementation of entrained-flow combustion is its fuel flexibility. An entrained-flow boiler is capable of combusting a wide range of types of biomass and coal.¹²⁸ An entrained-flow boiler also often generates very high temperatures,¹²⁹ which maximises reaction rates, leading to nearly 100% of solid fuel burnout.¹³⁰ However, entrained-flow boilers were actually designed to combust coal. Industrial applications on biomass combustion in entrained-flow boilers have been only co-combustion with coal. A more detailed explanation on the reason of the development of the entrained-flow combustion of biomass is discussed in Chapter 4.

Numerous research studies have been conducted to develop entrained-flow combustion models. The first development of an entrained-flow combustion model was a decade ago, when Brown *et al.*¹³¹ used CFD to develop a mathematically similar model for coal combustion in an entrained-flow combustion unit. A more simplified approach without CFD was used by Vamvuka *et al.*¹³² to model bituminous coal combustion in an entrained-flow boiler using a one-dimensional model. As use of CFD grew, research that utilised it on the entrained-flow combustion model continued to emerge. Some of the works aimed to obtain accurate predictions of experimental results.^{133,134,135,136,137,138} Others were conducted to evaluate the impact of combustion parameter modifications to certain variables, e.g. the evaluation of the fate and occurrence of AFEs and TEs using chemical equilibrium.

Chemical equilibrium is fundamentally explained using an example of reversible reaction expressed in Reaction 5.1.



A exothermically reacts with *B* to form *C* and release heat. In the reverse reaction, *C* is decomposed into *A* and *B* by absorbing the heat. Reaction 5.1 is considered in a state of equilibrium when the rate of forward reaction of *A* and *B* to form *C* is equal to the rate of backward decomposition of *C* into *A* and *B*.

When the equalised Reaction 5.1 is chemically disturbed, e.g. by addition of more *A*, the change of Reaction 5.1 properties may be explained according to three principles, namely Le Châtelier's principle, the equilibrium law principle, and the reaction rate principle.¹³⁹

According to Le Châtelier's principle, any change of composition that is made to the constituents on the left-hand-side of the equation affects the composition of the constituents on the right-hand-side.

The equilibrium law principle states that the forward reaction rate becomes faster than the backward reaction rate when a quantity of *A* is added to the equilibrated Reaction 5.1 until another equilibrium condition is established. The equilibrium law principle is mathematically expressed as Equation 5.1.

$$K_{eq(p_{eq}, T_{eq})} = \frac{[C]^c}{[A]^a[B]^b} \quad (\text{E5.1})$$

[*A*], [*B*], and [*C*] are concentrations of *A*, *B*, and *C* in mol m⁻³. $K_{eq(p_{eq}, T_{eq})}$ is the equilibrium constant of Equation 5.1 at equilibrium temperature, T_{eq} , and equilibrium pressure, p_{eq} . The addition of *A* means in a mathematical sense that $\frac{[C]^c}{[A]^a[B]^b} < K_{eq(p_{eq}, T_{eq})}$, or the forward reaction rate must increase over the backward reaction rate to re-obtain the condition expressed in Equation 5.1.

According to the reaction rate principle, the concept of the forward reaction rate being superior to the backward reaction rate or vice versa is already established in the two former principles. However, the reaction rate principle expresses a fundamental concept that the equalised forward and backward reaction rate after addition of *A* becomes higher due to the concentration increase.

When the equilibrium calculation incorporates numerous parts and establishes a far more complex case than that of Reaction 5.1, the compounds formed from the chemical rearrangement of these numerous parts are considered in equilibrium when the Gibbs free energy change is at its minimum. The Gibbs free energy change, ΔG , in J mol⁻¹ is calculated by use of Equation 5.2.¹⁴⁰

$$\Delta G = \sum_{i=1}^{n_f} x_{n_i} \left(\frac{\Delta G_i^0}{RT_{eq}} + \ln p_{eq} + \ln \left(\frac{x_{n_i}}{\sum_{i=1}^{n_f} x_{n_i}} \right) \right) \quad (\text{E5.2})$$

n_f is the number of possible formed compounds at T_{eq} and p_{eq} . ΔG^0_i is the standard Gibbs free energy of compound i in J mol^{-1} . To obtain equilibrium composition, x_{n_i} is introduced to Equation 5.2 with values that result in minimum ΔG .

Chemical equilibrium was initially used to estimate the fate of AFEs and TEs during coal combustion. Sandelin and Backman³¹ estimated the occurrence and fate of AFEs and TEs during coal combustion in a simple reactor process of power-plant scale using Chemsage. They extended this work²⁹ to calculate the fate and occurrence of AFEs and TEs in a combustion chamber and clean-up equipment with a similar method. Danihelka *et al.*³² estimated TE fate and occurrence in Czech coal combustion in six power stations.

Numerous studies, particularly on biomass combustion, then applied chemical equilibrium methods. Ljung and Nordin¹⁴¹ conducted AFE and TE fate and occurrence modelling on biomass combustion with Chemsage. Lind *et al.*¹⁴² used HSC Chemistry software to model TE volatilisation in a circulating fluidised-bed boiler that combusted forest residue. Boman *et al.*¹⁴³ studied particulate matter formation from residential biomass combustion with Factsage. A sequential study was conducted by Boman *et al.*¹⁴⁴ to compare AFE and TE occurrence during combustion of two different woody biomass parts, e.g. wood and bark, using FactSage. AFE and TE speciation estimation was later conducted on specific biomass type and species, e.g. orujillo, corn stalk, maize straw, cedar nut shell, wheat straw, etc.^{145,146,30,147}

Chemical equilibrium was further used to estimate AFE and TE fate and occurrence during combustion of mixed solid fuel. Dayton *et al.*²⁸ modelled the occurrence and fate of AFEs during co-firing of coal and biomass, to estimate chlorine and potassium releases. Miller *et al.*¹⁴⁸ used MTDATA to model TE partition during combustion of blends of biomass, coal, and waste in a bench-scale combustor. Several works applied chemical equilibrium methods to herbaceous biomass co-firing with coal. This became an attractive option due to abundant reserves of herbaceous biomass.^{149,150} AFE and TE partition was also evaluated in some studies on co-firing of biomass and coal substitute.^{33,151,152} Moreover, fate and occurrence modelling of AFEs and TEs in combustion of individual solid fuels other than biomass or coal has been conducted.^{153,154,155,156}

The use of chemical equilibrium methods was later extended beyond consideration of AFEs and TEs to the fate and occurrence estimation of other elements,^{157,158,159,160,161,162,163} and to consider the influence of operating conditions and solid-fuel modifications. Chemical equilibrium was used in works on oxy-combustion to analyse the effect of concentrated $\text{O}_{2(g)}$ on AFE and TE partition.^{94,164} Chemical equilibrium was also used to estimate the occurrence and fate of AFEs and TEs in the gasification process.^{165,166,167} Ma *et al.*¹⁶⁸ employed chemical equilibrium to study slag formation during pressurised combustion of wood. The effect of impregnation on AFE and TE release during biomass combustion

was studied using chemical equilibrium.^{169,170,171} Chemical equilibrium was also specifically used to study the problem of agglomeration in fluidised-bed boilers.^{172,173}

The calculations of estimated fate and occurrence might not match data found through experiment since the influence of reaction kinetics is neglected. At temperatures higher than 1500 K, the mismatch may be tolerable due to rapid reaction rates. However, at low temperatures, the poor estimations might be significant due to low reaction rates. Additionally, when multiple phases are involved, e.g. gas and solid aerosols, their reactions are much slower due to mass transfer restrictions.¹⁷⁴ Therefore, fate and occurrence data estimated using chemical equilibrium requires careful interpretation.

Chapter 3

Literature Review: Modelled Solid Fuel and Inorganic Element Origins and Distributions

Table 3.1 presents biomass characterisation data relevant to biomass combustion as discussed in Chapter 2. Four variants of biomass were chosen for modelling based on the aims and objectives discussed in Chapter 1.

Table 3.1 *Characterisation of Modelled Biomass*

Analysis	Component	White Wood	Recycled Wood	Rice Husk	Switchgrass
Proximate Analysis (% a.r. mass)	Moisture	6.69	5.8	6.7	6.7
	Volatile Matter	78.1	73.9	58.59	75.01
	Fixed Carbon	14.51	17.1	17.91	13.53
	Ash	0.7	3.2	16.79	4.76
Ultimate Analysis (% a.r. mass)	C	48.44	51.9	37.63	44
	H	6.34	6	4.66	5.4
	O	37.69	41.7	33.35	38.43
	N	0.15	0.4	0.61	0.62
	S	0.02	0.02	0.06	0.1
	Cl	0.01	0.01	0.1	0.08

AFEs (a.r. mass ppm in fuel)	Na	62.99	335.44	204.86	204.74
	K	547.59	650.62	3281.29	3799.99
	Ca	1260.27	6355.36	1196.59	3465.34
	Mg	216.68	745.53	197.83	1349.05
	Si	415.28	6257.57	76164.95	14703.12
	Al	65.67	925.28	191.83	556.53
	Fe	59.39	1602.47	265.61	452.65
	P	N/A	N/A	406.74	811.89
	Ti	N/A	N/A	20.69	79.85
TEs (a.r. mass ppm in fuel)	As	0.3	3.4	N/A	N/A
	Cd	0.1	0.2	N/A	N/A
	Cr	2.2	10.8	N/A	N/A
	Cu	2.6	19.4	N/A	N/A
	Pb	0.7	12.6	N/A	N/A
	Ni	0.7	2.8	N/A	N/A
	V	0.6	1.3	N/A	N/A
	Zn	10.2	43.9	N/A	N/A
	Hg	0.1	0.1	N/A	N/A

3.1 White Wood

White wood is North American Grade A wood originating from natural forest residue and classified as wood and woody biomass according to Table 2.1.¹⁷⁵ The combustion of white wood and recycled wood, discussed in Section 3.2, was conducted at PACT facility (discussed in Chapter 5) to produce experimental data for validating the developed model in this thesis.

The proximate analysis of white wood is listed in Table 3.1 along with the ultimate and elemental analysis. White wood is composed mainly of volatile matter (78.1%). This is very high in comparison to the abundance of volatile matter in woody biomass which ranges from 30.4 to 79.7%. The rest of white wood is comprised of fixed carbon (14.51%), moisture (6.69%) and ash (0.7%). Typically, woody biomass such as white wood, bark, and poplar has the largest moisture contents with concentrations ranging from 4.7 to 62.9%. The wide range of woody biomass moisture concentrations leads to a high

variability this moisture typically contains water-soluble AFE cations and several anions such as Cl^- , CO_3^{2-} , NO_3^- , OH^- , etc.¹⁷⁶ In contrast, woody biomass has the lowest ash concentrations amongst all biomass types with concentrations ranging from 0.1 to 8.4%. The ash concentration in wood is even lower than in other woody biomass parts, e.g. bark and foliage.³⁴

In the ultimate analysis of white wood, carbon and oxygen are the elements present at the highest mass percentages while the other elements, e.g. oxygen, nitrogen, sulphur, and chlorine, are present at much lower mass percentages. Despite carbon being the most abundant element by mass, the concentration of carbon is still sometimes much lower in woody biomass than in most coals. In some woody biomass, however, carbon concentrations could reach almost 60%. In contrast to coal, woody biomass is richer in oxygen with concentrations ranging from 32 to 45.3%. Hydrogen is also present in woody biomass with concentrations ranging from 3.2 to 9.2%. The presence of hydrogen in woody biomass is due to carbohydrates produced via photosynthesis.¹⁷⁷ Amongst biomass, woody biomass has the lowest nitrogen, sulphur, and chlorine mass percentages ranging from 0.1 to 3.4%, 0.01 to 0.42%, and 0.01 to 0.05%, respectively. Nitrogen is likely present in the form of free amino acids found mainly in parenchyma cells.¹⁷⁸ Sulphur and chlorine concentrations are considered very low and found mainly in bark.^{179,34}

The identified AFEs in white wood as woody biomass in Table 3.1 and also the AFEs in most other types of plants might originate from natural absorption of soil salt solutions as nutrients via the roots during plant growth. The route of this natural absorption is very complex since the absorption rate of each individual element is affected by several ion-related factors, e.g. ion hydration, ion antagonism, ion displacement, etc.¹⁸⁰ Due to lack of data, phosphorus and titanium concentrations are not shown for white wood and recycled wood.

Ion diameters are influenced by their extents of hydration; a less hydrated ion is larger than a more hydrated one. The ions of sodium (Na), potassium (K), magnesium (Mg), and calcium (Ca) in this order are progressively more hydrated. This ranking implies that a potassium ion moves quicker than a sodium ion during absorption. However, ions with low hydration levels and heavy ionic masses might swell the protoplasm and reduce their absorption rates.

Ion antagonism is the term for suppression of the inherent action of an ion due to the presence of another ion with the same charge. For instance, the toxic nature of Na^+ to certain living organisms is suppressed when a certain amount of K^+ or Ca^{2+} is added. Anion antagonism also affects the absorption of ion pairs. For instance, potassium sulphate (K_2SO_4) has a stronger tendency to be absorbed than potassium chloride (KCl), which is more likely to be absorbed than potassium nitrate (KNO_3).

Ion displacement is promoted by acidity and anion uptake. The pH of a salt solution leads to unequivalent proportions of absorbed cations and anions of an individual salt despite the presence of

equal amounts of cations and anions in the original solution. These unequal proportions are probably due to ionic displacement with balanced H^+ and OH^- ions in the protoplasm. During anion uptake, bicarbonate ions that originate from $CO_{2(g)}$ generated during respiration are formed and absorbed at a significant rate. Significant absorption of bicarbonate promotes a greater amount of anion uptake in comparison with the amount of cation uptake.

Each absorbed AFE becomes part of the plant and contributes to plant growth. Phosphorus and sulphur are used as protein-based cell components. Magnesium and iron sustain chlorophyll function. Magnesium, along with calcium, also controls physical fluidic properties of protoplasm and maintains protoplasm pH. Potassium and sodium are responsible for plant metabolism and stress prevention.¹⁸¹ Despite being absorbed from soil, aluminium does not contribute to plant growth due to its poisonous effect. Aluminium availability in the soil depends on the acidity or the level of alkali metal and alkaline earth metal washout from the soil.¹⁸²

The general occurrence of AFEs could be estimated from a previous analysis on spruce, pine, and birch wood since there was no any available quantitative analysis. Unlike coal, wood is not suited for the AFE occurrence analysis with x-ray diffraction (XRD) and scanning electron microscope (SEM) since wood has significantly lower mineral concentrations. The most viable method to characterise the occurrence of AFEs in wood is via chemical fractionation analysis (CFA).¹⁸³

The CFA is conducted by leaching the solid fuel with pure water, buffer, and acid consecutively. The first leaching with water is to separate water-soluble AFE salts, e.g. alkali chlorides and alkali sulphates. The second leaching with buffer is to separate organic-bound AFEs. The last leaching with acid is to separate acid-soluble included minerals, e.g. $CaSO_{4(s)}$. The residual solid contained excluded minerals, e.g. insoluble silicates. Any alkali metals bound to excluded minerals do not promote fouling.¹⁸⁴ The AFE concentrations in the three obtained leachates are measured with inductively-coupled plasma (ICP) equipment. Additionally, the leachates are also analysed to measure the concentrations of dissolved anions, e.g. chloride, sulphates, nitrates, etc. The concentrations of any anions remaining in the solids are measured with methylene blue sorption.

The general AFE occurrence obtained from a CFA analysis on woody biomass is listed in Figure 3.1. Most of AFEs and sulphur form bonds with organic matter. Only aluminium, potassium, and some anions such as phosphates, sulphates, and chlorides are soluble in moisture. $SiO_{2(s)}$ and at around 70% of calcium existing as calcium oxalate are stored as included minerals. The remaining silicon, aluminium, iron, and sodium are found in the excluded minerals, e.g. quartz, feldspar, clays, and alkaline-earth minerals.¹⁸⁵

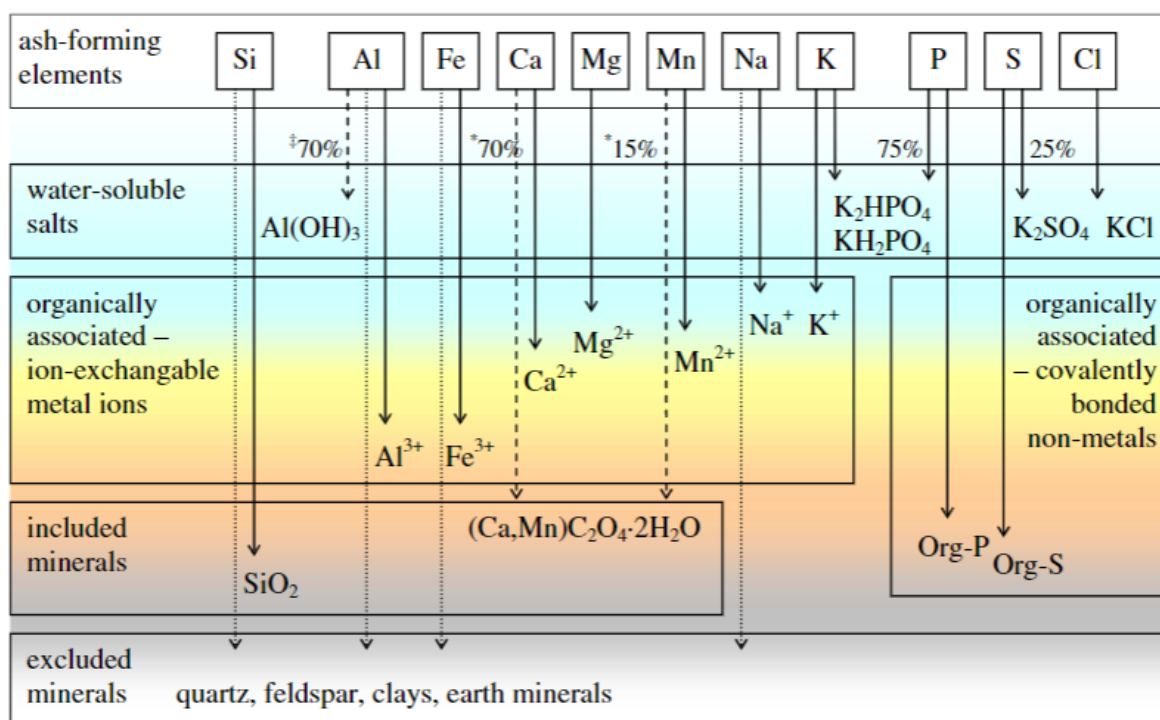


Figure 3.1 The General Occurrence of AFEs in Woody Biomass

The origin of TEs in white wood as a variant of virgin woody biomass is less understood than that of TEs in treated wood, which is explained later in Section 3.2. This is due to no direct influence of anthropogenic activities and being of little consequence since the concentrations are relatively very small. The existence of TEs in virgin woody biomass originates via absorption of TEs in soil during vegetation cycles. The TEs in the soil likely comes from the deposition of atmospheric pollutants.^{186,187}

TE occurrence in virgin woody biomass is not as comprehensively known as the occurrence of AFEs and could be evaluated with CFA. Vassilev *et al.*¹⁸⁸ classified the occurrence of TE in virgin biomass in accordance with the occurrence classification of TEs in coal: TEs covalently or ionically bound to organic matter as organometallic compounds, TEs physically attached to mineral and amorphous compounds, TEs as minerals, and TEs dissolved in moisture as cations.

3.2 Recycled Wood

Recycled wood is treated woody biomass modelled to evaluate the differences of the AFE and TE fate and occurrence of recycled wood from those of white wood. The model evaluates the influence of not only temperatures but also the the initial AFE and TE concentrations on AFE and TE fate and occurrence, which the previous models neglected. Since recycled wood was originally virgin woody biomass, its proximate and ultimate analysis results are identical to white wood, except for ash. Higher

ash concentrations in recycled wood than in white wood is due to higher concentrations of TEs and AFEs as the main constituents of ash. The excess AFEs likely come from anthropogenic treatments as attributes to TE-based additives.

TEs in treated woody biomass originate from various sources. Copper, chromium, and arsenic often originate as copper-chromium-arsenate (CCA) preservatives via impregnation to prevent rot when wood is used as housing or furniture material. Lead and nickel are often present in paints or coatings applied to the wood surface. Cadmium and mercury are produced naturally through volcano eruption, and their concentrations in the atmosphere could increase due to anthropogenic activities, e.g. coal mining and combustion in power stations, etc. It is unclear whether mercury in plants originates due to uptake from soil via roots or due to intake from the atmosphere via leaves. Several studies have proved that both soil uptake and atmospheric intake can account for mercury's presence in plants.^{189,190,191} Ericksen *et al.*¹⁹² conducted a large-scale experiment to replicate the behaviour of mercury in a forest. It was found that intake through foliage was the main route of mercury presence in biomass. It was also shown that mercury accumulated in plants and that less than 3% of the stored mercury exited from trees through rain precipitation.

The distribution of inorganic elements within the wood structure essentially depends on how the elements are introduced to the structure. An element could be distributed almost uniformly within wood structure due to either pressurised impregnation or large wood pore size. On the other hand, an element could be concentrated at the wood surface due to surface application, e.g. painting. The latter distribution may promote non-uniform concentration distribution of inorganic elements in solid fuel. Non-uniform concentration distribution in solid fuel might lead to inconsistent concentrations of emitted inorganic elements upon combustion.

Wood impregnation is conducted essentially by replacing air in wood pores with preservatives. Initially, a wooden block devoid of air is immersed in a chamber of preservative solution. The chamber is then placed under pressure to force preservative solution to flow into the pores of the wooden block. Once the pressure is reduced to atmospheric pressure, the chamber is drained to remove all liquid. The chamber is then placed under vacuum to discard all remaining solvents from within the wood block pores.

Preservative solution undergoes sequential distribution in the wood pores. The sequential distribution depends on the preservative flow behaviour within wood pores, as discussed by Nicholson and Preston.¹⁹³ Preservative solution initially flows within the pores and fills the entire macrostructure including the cell lumens. This process is known as macrodistribution. When the entire macrostructure has been filled, the preservative is fixated by three different fixation methods, namely: the preservative's reaction with wood; the preservative's self-reaction; and preservative deposition after chamber depressurisation. During macrodistribution, preservative solution may flow deeper into the cell wall,

known as microdistribution. Research on microdistribution was uncommon until equipment for scanning electron microscopy – energy dispersion x-ray (SEM-EDXA) became commonly produced.

Wood impregnation does not guarantee that wood will be rot-free. Preservative might be concentrated in macropores only and leave micropores open to fungi. This rotting mechanism is known as soft-rot. However, soft-rot can be due to causes other than preservative absence from micropores. Even when preservative is homogeneously distributed, a certain location within the wood might have higher organic nutrient concentration than other locations. Fungi may continue to live in a rich-nutrient location even when preservative is well fixated.¹⁹⁴

Although coatings and paints are applied to wood surfaces without impregnation, Bulcke *et al.*¹⁹⁵ have shown that they can penetrate to a certain depth within pine sapwood, beech wood, and meranti wood, as illustrated in a microscopic image shown in Figure 3.2. It has also been demonstrated that coatings and paints can penetrate to micropores.

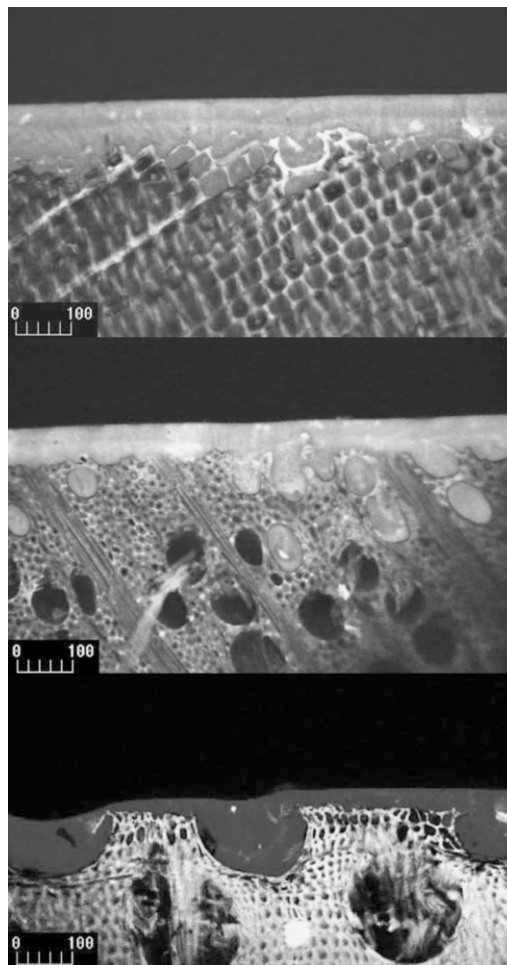


Figure 3.2 Penetration of a Solvent-borne Alkyd Primer into Sapwood Pine (Top), Beech Wood (Centre), and Meranti Wood (Bottom)

Although most paints and coatings currently on the market are not lead-based, many demolished old houses were built during the early 20th century when lead-based paints and coatings were used. A historical record¹⁹⁶ has discussed a case of power sanding renovation work that was carried out on a house built in 1925 in New Orleans without any pre-work discussion regarding lead contaminants. Three children and a pet were living in the house during the renovation. The pet died six weeks after the work was executed. Not long after that, the children fell ill and were taken to a hospital. Analysis of the house structure revealed a lead concentration of around 130,000 $\mu\text{g g}^{-1}$.

Yang *et al.*¹⁹⁷ discovered that foliage could store eight times more mercury than wood could. This discovery was in agreement with earlier work conducted by Ericksen *et al.*¹⁹². However, mercury release is one of the least anticipated problems of woody biomass combustion since wood dominates this biomass content rather than leaves.

Phytoremediation is another common means by which TEs accumulate in plants. Phytoremediation is a process conducted to remove contaminants from soil by sowing contaminated land with plants that absorb and hyperaccumulate the soil contaminants, e.g. heavy metals. Intake pathways of TEs that are exploited in phytoremediation are shown in Figure 3.3.¹⁹⁸

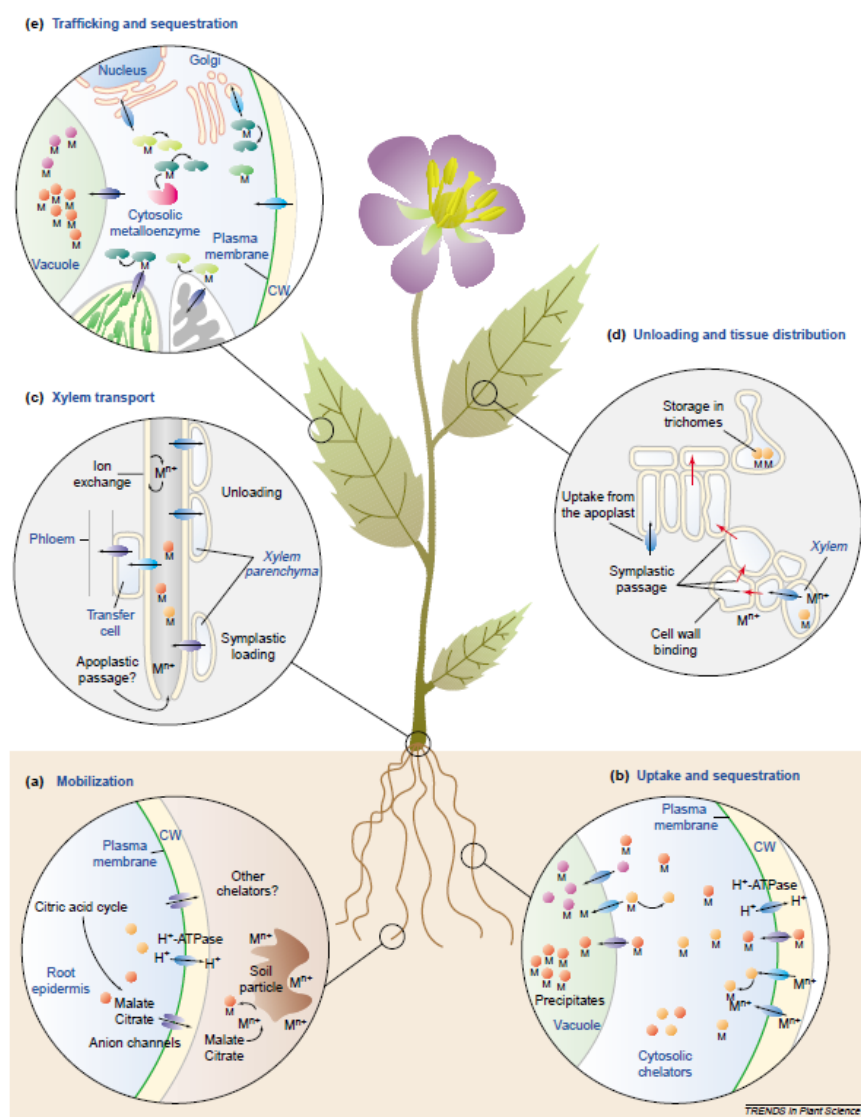


Figure 3.3 TE Intake Pathways in Phytoremediation

Plants treat heavy metal intake differently from animals, including humans. Plants exhibit either avoidance or tolerance mechanisms to manage heavy metal contamination. In the avoidance mechanism, heavy metals are prevented from entering protoplasts and remain in cell walls; or under the tolerance mechanism, heavy metals are internalised via the cell wall membrane and sent to the protoplast via endocytosis.¹⁹⁹ The heavy metals are later neutralised, sequestered from protoplast cytoplasmic compartments, and returned to cell walls and apoplast.²⁰⁰

Plant cell walls have numerous polysaccharides that offer metal binding sites, e.g. $-COOH$, $-OH$, and $-SH$ groups.²⁰¹ Most heavy metals are bound to pectins in cell walls that exhibit some methylesterification.²⁰² Growth of callose²⁰³ offers another defence mechanism. Callose is another polysaccharide that is grown as a temporary cell wall to block heavy metal penetration to the

protoplast.²⁰⁴ Kopittke *et al.*²⁰⁵ conducted microscopic visual analysis (shown in Figure 3.4) on plant cells to observe binding sites of lead that originated from phytoremediation. It is clear from these observations that TEs may be distributed at different binding sites even within the same organ within an individual plant species.

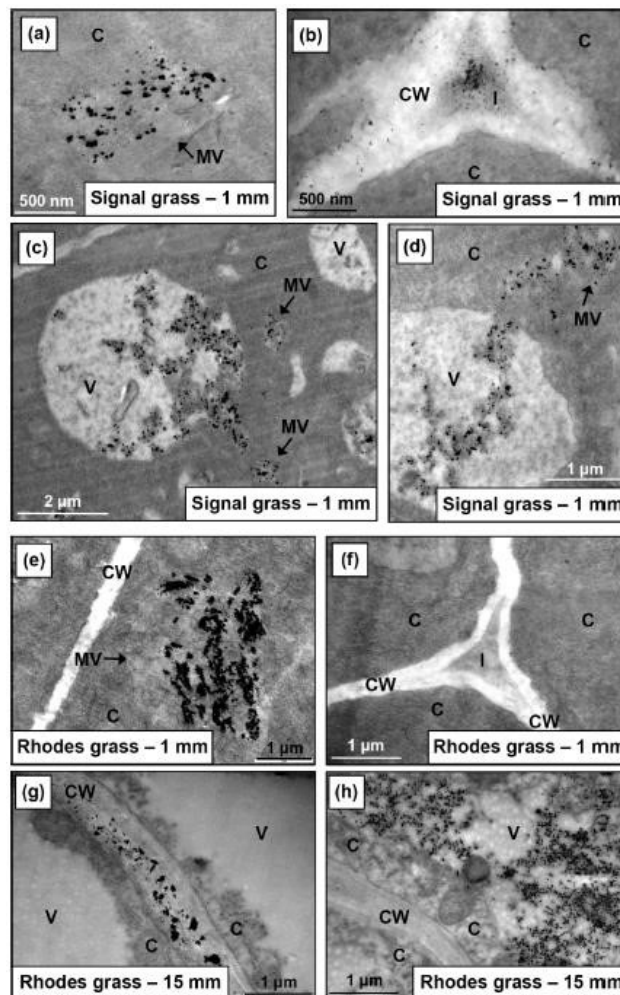


Figure 3.4 Scanning Electron Micrographs of Outer Cortical Cells of Signal Grass and Rhodes Grass Root (V = Vacuole; CW = Cell Wall; C = Cytoplasm; MV = Vesicle)

The occurrence of TEs is not more clearly understood in treated woody biomass than in virgin woody biomass. However, CFA could be as useful as that on virgin woody biomass to determine the occurrence of TEs in treated woody biomass. The results might be similar to the general TE occurrence of virgin woody biomass.

3.3 Rice Husk

The modelling of rice husk and switchgrass, which characterisation is explained in Section 3.4, is to evaluate the fate and occurrence of AFEs in the combustion of herbaceous biomass containing significant quantities of potassium and silicon responsible for slagging and fouling. The rice husk characterisation results used in this the model are from various sources compiled by Vassilev *et al.*²⁰⁶ and listed in Table 3.1. The trace elements are not the focus in this evaluation of herbaceous biomass and their concentrations are, therefore, not incorporated.

The proximate analysis result of rice husk shows almost similar characteristics to that of white wood probably due to their resemblance to virgin plants. However, the ash concentration of rice husk is much higher, at around 16.79%, because herbaceous biomass absorbs a significant amount of nutrients from soil during its lifetime.²⁰⁷ The use of fertiliser may also contribute to the accumulation of ash in herbaceous biomass.²⁰⁸ Data for moisture concentration was not available for rice husk and, additionally, switchgrass and assumed equal to the moisture concentration in white wood.

The ultimate analysis result of rice husk is notably different from that of white wood. The mass percentages of major elements, e.g. carbon, hydrogen, and oxygen, are lower due to larger proportions of ash. The nitrogen concentration, however, is higher in rice husk. Most herbaceous biomass including rice husk, with vascular systems, absorbs significant quantities of soil nitrogen via roots. The absorbed nitrogen promotes rapid growth of herbaceous biomass.²⁰⁹

Table 3.2 CFA Results of Rice Husk

Salt Type	Dissolved Element Concentration (mg (kg of dry fuel) ⁻¹)									
	Si	Al	Fe	Ca	Mg	P	Na	K	S	Cl
Water-soluble Salts	494	4	0	73	100	309	25	2160	212	733
Organically-associated Ion-exchangeable Metal Ions	3058	5	0	624	244	63	27	787	0	0
Included Minerals	2114	7	53	47	11	13	16	4	0	0
Excluded Minerals	81234	113	35	0	0	78	0	108	408	0

The concentrations of AFEs other than calcium in rice husk in Table 3.1 shows significantly higher than those white wood. Apart from the ability of herbaceous biomass to obtain significant quantities of

nutrients via root uptake and fertiliser treatment, harvested herbaceous biomass is often left in fields and exposed to rains containing water-soluble AFEs. This allows an alternating cycle of wetting and drying on the herbaceous biomass. Due to multiple drying cycles, the AFEs accumulate in the herbaceous biomass.²¹⁰ Calcium dominates the composition of woody biomass and is concentrated the most in bark.²¹¹

A CFA result, listed in Table 3.2, by Skrifvars *et al.*²¹¹ is used as a means to understand the general occurrence of AFEs in rice husk since there is no AFE occurrence data of the rice husk in Table 3.2. Silicon and potassium are the main focus of the CFA analysis due to their direct involvement in fouling along with chlorine. Silicon has the highest concentrations in rice husk. Most of the silicon forms excluded minerals. Based on the SEM/EDX observations for rice husk, the excluded minerals form big deposit clusters amorphous $\text{SiO}_{2(s)}$ separated from potassium.²¹² Some silicon also exists as included minerals and organic-bound compounds. A tiny quantity of silicon is dissolved in moisture as $\text{Si}(\text{OH})_{4(aq)}$ formed due to hydration of $\text{SiO}_{2(s)}$. Potassium, often as the second major AFE in rice husk, exists primarily as moisture-soluble salts.²¹³

3.4 Switchgrass

Although the proximate and ultimate analysis results in Table 3.1 shows similar concentrations in white wood and switchgrass, the ash concentration of switchgrass is higher than that of white wood due to the nature of switchgrass as herbaceous biomass. Nevertheless, the ash concentration of switchgrass is significantly lower than that of rice husk. The ash concentrations of switchgrass vary inversely with its maturity.²¹⁴ Switchgrass also has low silicon and chlorine intake rates due to its efficient water consumption during photosynthesis.²¹⁵

Unlike the CFA data of rice husk, the CFA data of switchgrass is not widely available and the AFE occurrence could only be estimated qualitatively. Potassium, sodium, and magnesium are found predominantly as either water-soluble salts or organic-bound compounds.¹⁸³ Most of the calcium is linked to oxalates for forming crystalline calcium oxalate.²¹⁶ The occurrence of phosphorus is not clearly understood. However, majority of phosphorus is probably in the form of water-soluble salts. The reduction of runoff water quality was reported to be due to contamination by significant quantities of phosphorus. This contaminating phosphorus was likely preserved in the switchgrass as the water-soluble phosphorus leached with water from grasses due to the cycle of freezing and thawing during late winter seasons and rain washing during summer.²¹⁷

Chapter 4

Single-particle Combustion Model

The development of the single-particle combustion model in the work described in this thesis has considered several aspects, namely: particle shape, intra-particle transport, and intra-particle chemical reactions. Each aspect along with its assumptions has been discussed thoroughly in this chapter. Particle shape has been assumed to be cylindrical due to the known structure of woody biomass fibre. Intra-particle transport has included heat and mass transfer within particles and at the boundary layer. Intra-particle chemical reactions have comprised homogeneous and heterogeneous reactions within particles.

This chapter discusses the development of the single-particle combustion model as the initial approach to solid fuel combustion. The single-particle combustion model was developed to establish the intra-particle temperature and property profiles as parameters to predict the intra-particle AFE and TE fate and occurrence. In Chapter 5, the single-particle combustion model is used to calculate particle combustion in the entrained-flow combustion model. Section 4.1 explains the mathematical concepts of the single-particle combustion model. The mathematical concepts include calculation of intra-particle concentration and temperature profiles along with their associated thermodynamic parameters, homogeneous and heterogeneous reaction kinetics, and pyrolysis gas mass fractions. In section 4.2, the results of the single-particle combustion model are validated against experimental results available in the literature.

4.1 Mathematical Concept of the Model

The distribution of temperatures and gas concentrations within a particle depends on intra-particle heat transfer, mass transfer, and chemical reactions. Particle temperatures increase due to heat sourced from flowing hot gas that surrounds the particle. Increased intra-particle temperatures pyrolyse the particle into volatile matter and char.²¹⁸ Carbon monoxide, hydrogen and steam in the volatile matter reacts exothermically with $O_{2(g)}$ that diffuses within the particle. The diffusing $O_{2(g)}$ also reacts

heterogeneously with char. The heat of oxidation of both volatile matter and char contributes to increasing particle temperatures. As a particle loses its mass due to pyrolysis and heterogeneous reaction, the sizes of the pores within the particle are enlarged. Both enlarged pore sizes and high particle temperatures promote rapid heat and mass transfer. The dependency of intra-particle temperatures and gas concentrations on heat transfer, mass transfer, and chemical reactions is the fundamental concept of the single-particle combustion model that is considered in this thesis.

Assumptions are applied to the single-particle combustion model to avoid unnecessary complexities. The assumptions are the following:

- The particle is porous solid, e.g. coal or biomass, and consists of wood or coal, tar, char, moisture, and ash at any point in the particle body. Woody biomass is modelled in this chapter.
- Thermal equilibrium is applied to the particle to allow uniform temperatures of all phases at any point in the particle body. This assumption is permitted because of negligible convective heat transfer effect of pore gas due to relatively small pore sizes.
- The particle's geometric dimension is only considered as one dimension (sphere), two dimensions (cylinder), or three dimensions (slab).
- The particle's aspect ratio changes due to particle shrinkage, unless the particle shape is spherical. However, the particle's geometric shape is constant during particle shrinking. For instance, a cylindrical particle continues to have three surfaces, i.e. the upper base, lower base, and a side, until it reaches complete thermal conversion. Nevertheless, this assumption requires careful application on large particles. A mass-loss front propagates towards the centre of the particle with radial symmetry. Constant geometry may overestimate the temperatures at cylindrical particle edges and, subsequently, the intra-particle heat-transfer rates.
- The initial particle porosity is assumed to be uniform within the particle body. This assumption may promote inaccurate prediction on biomass particle combustion since biomass microstructure is widely heterogeneous, even within the very same particle. It was observed that the intra-particle temperature experienced slower increase when the intra-particle microstructure was considered.²¹⁹ However, this assumption is considered reasonable for the single-particle combustion model since the particles are well pulverised with relatively small limitation due to the intra-particle microstructure. In addition, there were no available data provided by PACT for microstructural characterisation, according to Ciesielski *et al.* (2015)²¹⁹.
- Gas in the particle pores behaves as an ideal gas because the gas is under low pressures and high temperatures. Intra-particle gas pressures are considered small and only slightly more or less than atmospheric pressure. Intra-particle gas temperatures could reach as high as 2,000 K, as shown in Figure 4.17.

Biomass particle shapes are commonly irregular. However, for modelling purposes, the shapes are often simplified as regular shapes, e.g. sphere, cylinder, and slab. Previous work has often assumed that biomass particle shapes are spherical and have volumes equal to the volume of the original shapes.^{220,221} However, the spherical shape is not an applicable assumption to particles of diameters larger than 200-300µm.²²² A sieving analysis on milled biomass has shown that biomass particles occur in non-spherical shapes of various aspect ratios.²²³ However, irregular shapes are not considered in this thesis because an irregular shape particle combustion model requires an advance calculation tool, e.g. computational fluid dynamics (CFD), which was not available for this research. In addition, the entrained-flow combustion model integrated with the single-particle combustion model in Chapter 5 calculates primarily micron-size particles, in which the effect of particle shape irregularity is negligible.

For the work described in this thesis, the particles were assumed to be cylindrical. Wood is formed mostly of cellulose fibres and lignin as a skeleton that holds the entire structure. This structure enables the fibres to align in parallel, forming a structure that resembles a cylinder in shape.²²⁴ Comparison between the spherical and cylindrical particle shape has shown that the latter shape produces more accurate predictions of particle burnout time and maximum particle temperatures.²²⁵

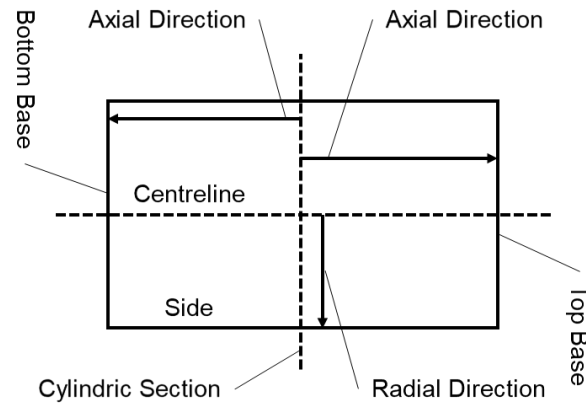


Figure 4.1 The Radial and Axial Directions of a Cylindrical Particle for Intra-particle Numerical Calculations

The rates of heat and mass transfer at the interior of a cylindrical particle are calculated in both radial and axial directions, which are illustrated in Figure 4.1. The radial direction is measured from the centreline to the side. The axial direction is measured from the middle of the cylindrical section to both bases. The interior heat and mass transfer equations are shown as Equations 4.1 and 4.2.

$$\frac{\partial T_p}{\partial t} = \frac{\alpha_p}{r} \frac{\partial}{\partial r} \left(\frac{\partial T_p}{\partial r} \right) + \alpha_p \frac{\partial^2 T_p}{\partial z^2} \quad (\text{E4.1})$$

$$\frac{\partial C_p}{\partial t} = \frac{D_{eff_p}}{r} \frac{\partial}{\partial r} \left(\frac{\partial C_p}{\partial r} \right) + D_{eff_p} \frac{\partial^2 C_p}{\partial z^2} + \frac{1}{r} \frac{\eta_p}{\mu_p} \frac{\partial}{\partial r} \left(r C_p \frac{\partial p_p}{\partial r} \right) + \frac{\eta_p}{\mu_p} \frac{\partial}{\partial z} \left(z C_p \frac{\partial p_p}{\partial z} \right) \quad (\text{E4.2})$$

T_p and C_p are the intra-particle temperature and gas concentration in K and mol m⁻³. α_p is the intra-particle thermal diffusivity in m²s⁻¹ and D_{eff_p} is the effective mass diffusivity of intra-particle gas in m²s⁻¹. Both α_p and D_{eff_p} determine particle heat conduction and mass diffusion driving force. p_p is the intra-particle gas pressure in Pa. η_p is particle permeability in m² and μ_p is the viscosity of intra-particle gas in Pa s. η_p indicates a particle's capability of transmitting gas due to gas pressure difference. r is the radial distance from the centreline and z is the axial distance from the middle cylindrical section, both in m. t is the time in s required to achieve the target T_p and C_p . Equations 4.1 and 4.2 are expanded to Equations 4.3 and 4.4. Both Equations 4.3 and 4.4 are solved numerically.

$$\frac{\partial T_p}{\partial t} = \alpha_p \left(\frac{\partial^2 T_p}{\partial r^2} + \frac{\partial T_p}{r \partial r} + \frac{\partial^2 T_p}{\partial z^2} \right) \quad (E4.3)$$

$$\frac{\partial C_p}{\partial t} = D_{eff_p} \left(\frac{\partial^2 C_p}{\partial r^2} + \frac{\partial C_p}{r \partial r} + \frac{\partial^2 C_p}{\partial z^2} \right) + \frac{\eta_p}{\mu_p} \left(\frac{\partial p_p}{\partial r} \left(\frac{C_p}{r} + \frac{\partial C_p}{\partial r} + C_p \frac{\partial p_p}{\partial r} \right) + \frac{\partial p_p}{\partial z} \left(\frac{\partial C_p}{\partial z} + C_p \frac{\partial p_p}{\partial z} \right) \right) \quad (E4.4)$$

The cylindrical particle is divided into four discrete parts, named as the northwest section (NW), northeast section (NE), southwest section (SW), and southeast section (SE), as illustrated in Figure 4.2. The NE is chosen as the calculation platform. Calculated intra-particle temperature and gas concentration profiles are mirror reflections of the other discrete parts. NW profiles are the symmetrical reflections of the NE profiles. SW and SE profiles are the polar reflections of NW and NE profiles. The green nodes are surface profiles for the side and bases. The blue node is the particle centre. Each node is labelled with a two-row index. The upper row represents a node number counted from the centreline. The lower row represents a node number counted from the middle cylindrical section. The indices m and n are the last node index values.

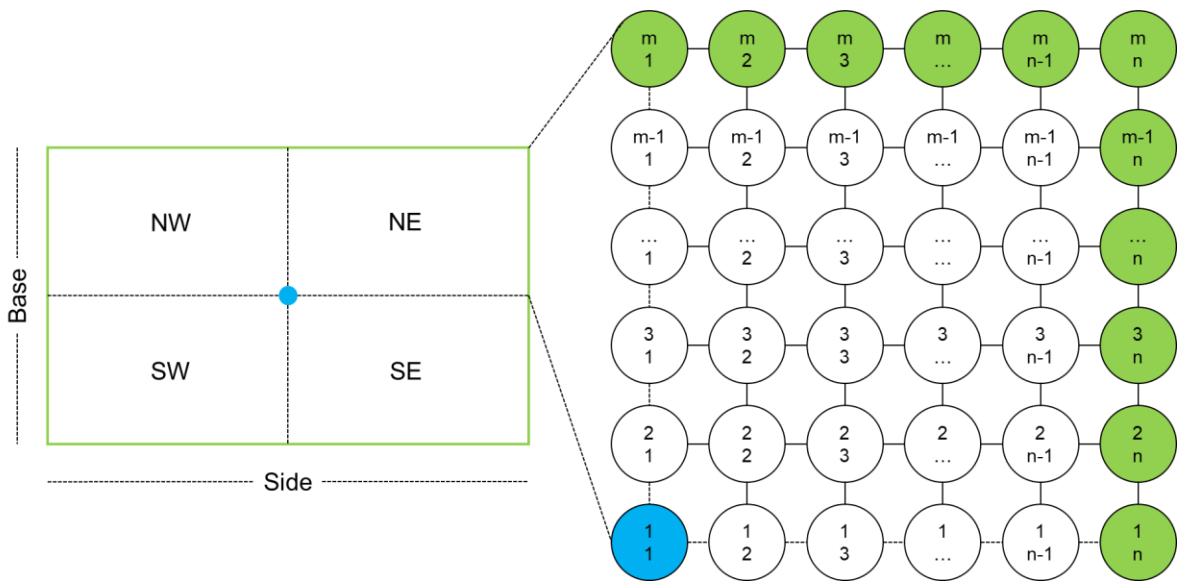


Figure 4.2 The Discrete Intra-particle Parts of a Cylindrical Particle

The reaction rate at any node is not necessarily the same as that at any other nodes due to intra-particle temperature gradients. For instance, the particle surface undergoes pyrolysis whilst the particle centre remains intact. Therefore, a particle reacts and shrinks at various rates within that particle. These variable shrinkage rates establish non-uniform distances between nodes. Non-uniform grid equations shown in Equations 3.5 and 3.6 are used to calculate distances between nodes.

$$\frac{\partial^2 X_p}{\partial l^2} = \frac{X_{p_{l+1}} \Delta l_l + X_{p_{l-1}} \Delta l_{l+1} + X_{p_l} (l_{l+1} - l_{l-1})}{\frac{1}{2} \Delta l_{l+1} \Delta l_l (\Delta l_{l+1} + \Delta l_l)} \quad (\text{E4.5})$$

$$\frac{\partial X_p}{\partial l} = \frac{X_{p_{l+1}} \Delta l_l^2 + X_{p_{l-1}} \Delta l_{l+1}^2 + X_{p_l} (l_{l+1}^2 - l_{l-1}^2)}{\Delta l_{l+1} \Delta l_l (\Delta l_{l+1} + \Delta l_l)} \quad (\text{E4.6})$$

X is the term for T , C , and p . l is the term for r and z . The distances from an evaluated node to its forward neighbour and its backward neighbour are denoted as Δl_{l+1} and Δl_l , respectively.

Heat from gas surrounding the particle increases the particle surface temperatures via heat convection and radiation. The general boundary heat transfer equation for the particle surface is shown as Equation 4.7. The first right-hand side term of Equation 4.7 accounts for heat convection. The second right-hand side term accounts for heat radiation.

$$\frac{\partial T_{p_l}}{\partial l} = h_c (T_{p_l} - T_\infty) + \epsilon_{p_l} \sigma (T_{p_l}^4 - T_\infty^4) \quad (\text{E4.7})$$

T_∞ is the temperature of the gas surrounding the particle, in K. h_c is the convective heat mass transfer coefficient in $\text{W m}^{-1} \text{K}^{-1}$. ϵ_{p_l} is the particle emissivity. σ is the Stefan-Boltzmann constant in $\text{W m}^{-2} \text{K}^{-4}$.

The gases generated during particle drying, pyrolysis, and heterogeneous reactions are released from the particle surface whilst the gas that surrounds the particle diffuses into the particle surface via mass convection. The general boundary mass transfer equation for the particle surface is shown as Equation 4.8.

$$\frac{\partial c_{p_l}}{\partial l} = h_m \left(\frac{c_{p_l}}{\epsilon_{p_l}} - C_\infty \right) \quad (\text{E4.8})$$

C_∞ is the surrounding gas concentration in mol m^{-3} . h_m is the convective mass transfer coefficient in m s^{-1} . ϵ_{p_l} is the particle porosity. ϵ_{p_l} is used to convert particle concentrations from particle-based concentrations to pore-based concentrations.

At the particle centre, there is no change in either temperature or gas concentration. The general boundary equations for the particle centre are shown as Equations 4.9 and 4.10.

$$k_{eff\,p_l} \frac{\partial T_{p_l}}{\partial l} = 0 \quad (E4.9)$$

$$D_{eff\,p_l} \frac{\partial C_{p_l}}{\partial l} = 0 \quad (E4.10)$$

$k_{eff\,p_l}$ is the intra-particle effective thermal conductivity in $\text{W m}^{-2} \text{K}^{-1}$. $D_{eff\,p_l}$ is the intra-particle gas diffusivity coefficient in $\text{m}^2 \text{s}^{-1}$.

Equations 4.7 and 4.8 are rearranged into first-order and second-order differential equations equivalent to Equations 4.5 and 4.6. The rearrangement of Equations 4.7 and 4.8 are given as Equations 4.11 and 4.12 for intra-particle temperatures and Equations 4.13 and 4.14 for intra-particle gas concentrations.

$$\frac{\partial^2 T_{p_l}}{\partial l^2} = \frac{2}{\Delta l^2} \left(\frac{h_c}{k_{eff\,p}} \Delta l_l (T_\infty - T_{p_l}) + \frac{\epsilon_{p_l}}{k_{eff\,p}} \sigma \Delta l_l (T_\infty^4 - T_{p_l}^4) + (T_{p_{l-1}} - T_{p_l}) \right) \quad (E4.11)$$

$$\frac{\partial T_{p_l}}{\partial l} = \frac{1}{\Delta l} \left(2 \frac{h_c}{k_{eff\,p}} \Delta l_l (T_\infty - T_{p_l}) + 2 \frac{\epsilon_{p_l}}{k_{eff\,p}} \sigma \Delta l_l (T_\infty^4 - T_{p_l}^4) + (T_{p_{l-1}} - T_{p_l}) \right) \quad (E4.12)$$

$$\frac{\partial^2 C_{p_l}}{\partial l^2} = \frac{2}{\Delta l^2} \left(\frac{h_m}{D_{eff\,p}} \Delta l_l (C_\infty - C_{p_l}) + (C_{p_{l-1}} - C_{p_l}) \right) \quad (E4.13)$$

$$\frac{\partial C_{p_l}}{\partial l} = \frac{1}{\Delta l} \left(2 \frac{h_m}{D_{eff\,p}} \Delta l_l (C_\infty - C_{p_l}) + (C_{p_{l-1}} - C_{p_l}) \right) \quad (E4.14)$$

A similar rearrangement is applied to Equations 4.9 and 4.10. This rearrangement results in Equations 3.15 and 3.16 for intra-particle temperatures and Equations 4.17 and 4.18 for intra-particle gas concentrations.

$$\frac{\partial^2 T_{p_l}}{\partial l^2} = 2 \frac{(T_{p_{l+1}} - T_{p_l})}{(l_{l+1} - l_l)^2} \quad (E4.15)$$

$$\frac{\partial T_{p_l}}{\partial l} = \frac{T_{p_{l+1}} - T_{p_l}}{l_{l+1} - l_l} \quad (E4.16)$$

$$\frac{\partial^2 C_{p_l}}{\partial l^2} = 2 \frac{(C_{p_{l+1}} - C_{p_l})}{(l_{l+1} - l_l)^2} \quad (E4.17)$$

$$\frac{\partial C_{p_l}}{\partial l} = \frac{C_{p_{l+1}} - C_{p_l}}{l_{l+1} - l_l} \quad (E4.18)$$

α_p is calculated via Equation 3.19.

$$\alpha_p = \frac{k_{eff_p}}{\rho_p c_{Pp}} \quad (E4.19)$$

Each α_p component, i.e. ρ_p , c_{Pp} , and k_{eff_p} , and D_{eff_p} are functions of intra-particle gas concentrations, solid densities, and intra-particle temperatures. ρ_p is the intra-particle density in kg m⁻³. c_{Pp} is the intra-particle heat capacity in J kg⁻¹ K⁻¹. The calculation of c_{Pp} is explained in Appendix B.1. The individual heat capacities of solids, liquid, and gases are listed in Appendix A.1. k_{eff_p} is the sum of the intra-particle conductive thermal conductivities and the intra-particle radiative thermal conductivities. The intra-particle conductive thermal conductivities are of the particle solid phase, $k_{consolid_p}$, and the intra-particle gases, k_{congas_p} , in W m⁻¹ K⁻¹, respectively. The calculations of $k_{consolid_p}$ and k_{congas_p} are explained in Appendix B.2 and B.3. The calculation of the intra-particle radiative thermal conductivities, k_{rad_p} , is explained in Appendix B.4. The individual thermal conductivities of solids and gases are listed in Appendix A.2. D_{eff_p} is a function of the intra-particle Fick diffusivities, D_{Figas_p} , and the intra-particle Knudsen diffusivities, D_{Knigas_p} , and calculated with the parallel pore model in Equation 4.20.

$$D_{eff_{gas_p}} = \frac{1}{\frac{1}{D_{Figas_p}} + \frac{1}{D_{Knigas_p}}} \frac{\varepsilon_p}{\tau_p} \quad (E4.20)$$

$D_{eff_{gas_p}}$ is the intra-particle gas effective diffusivity in m² s⁻¹. D_{Knigas_p} is the intra-particle gas Knudsen diffusivity in m² s⁻¹. D_{Figas_p} is the Fick diffusivity of gas i in m² s⁻¹. τ_p is the tortuosity estimated via Equation 4.21. The calculation of particle porosity, ε_p , is explained in Appendix B.8.

$$\tau_p = \frac{1}{\varepsilon_p} \quad (E4.21)$$

The calculations of D_{Figas_p} and D_{Knigas_p} are explained in Appendix B.6 and B.7, respectively.

The convective heat and mass transfer coefficients are calculated via Equations 4.22 and 4.23.

$$h_c = \frac{Nu_{gas_b} k_{congas_b}}{d_p} \quad (E4.22)$$

$$h_m = \frac{Sh_{gas_b} D_{Figas_b}}{d_p} \quad (E4.23)$$

h_c and h_m are the convective heat and mass transfer coefficients at particle surfaces in W m⁻² K⁻¹ and m s⁻¹. Nu_{gas_b} is the boundary gas dimensionless Nusselt number calculated. Sh_{gas_b} is the boundary gas dimensionless Sherwood number. The calculations of Nu_{gas_b} and Sh_{gas_b} are explained in Appendix B.12

and B.13, respectively. $k_{con_{gas}_b}$ is the boundary gas conductive thermal conductivity in $W\ m^{-2}\ K^{-1}$. The explanation of the calculation of $k_{con_{gas}_b}$ is in Appendix B.3. $D_{Fi_{gas}_b}$ is the boundary gas Fick diffusivity coefficient in $m\ s^{-1}$. d_p is the particle diameter in m. The explanation of the calculation of $D_{Fi_{gas}_b}$ is in Appendix B.6.

Intra-particle moisture evaporation is shown as Reaction 4.1.



The calculations of the rate of Reaction 4.1, $\frac{d\rho_{H_2O_{(l)}}}{dt}_{(R4.1)}$, and the rate of temperature change due to Reaction 4.1, $\frac{dT_p}{dt}_{(R4.1)}$, are explained in Appendix C.1.

Wood is naturally made up of 30-60% cellulose, 20-35% hemicellulose, and 15-30% lignin. Each part of the composition of wood undergoes a very complex conversion pathway. However, simplified conversion pathways that have been widely used in previous pyrolysis models were used in the research for this thesis. These simplified conversion pathways during wood pyrolysis consist of primary and secondary cracking reactions, as illustrated in Figure 4.3. Wood is converted into gas 1, tar, and char via primary cracking. Tar is converted into gas 2 and char via secondary cracking.

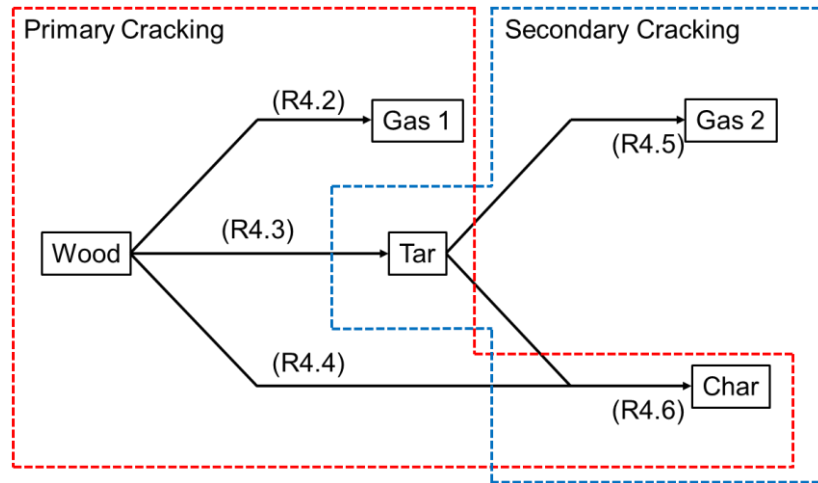


Figure 4.3 Reaction routes during Wood Pyrolysis

The rate of reaction of each conversion route is driven by kinetic parameters. The kinetic parameters are of specific values that depend on the biomass' chemical and physical properties. Previous work has evaluated pyrolysis kinetic parameters of various plants. Thurner and Mann²²⁶ analysed oak wood primary cracking using a tubular pyrolysis reactor. Font *et al.*²²⁷ studied pyrolysis kinetics of almond shells in a fluidised-bed reactor. Wagenaar *et al.*²²⁸ predicted pyrolysis kinetic parameters of pinewood

using a rotating cone reactor. Blasi²²⁹ conducted pyrolysis experiments on beech wood powder using thermogravimetric analysis. Liden *et al.*²³⁰ proposed a tar pyrolysis model to estimate reaction parameters for gas 2 formation, which were validated reasonably well with the available data in the previous literature. The reaction rate for gas 2 formation is often assumed to be forty times quicker than that of the secondary char formation.²³¹

The kinetic equations for Reactions 4.2, 4.3, 4.4, 4.5, and 4.6 are utilised to obtain $\frac{d\rho_{gas}}{dt}$ (R4.2), $\frac{d\rho_{tar}}{dt}$ (R4.3), $\frac{d\rho_{char}}{dt}$ (R4.4), $\frac{d\rho_{gas}}{dt}$ (R4.5), and $\frac{d\rho_{char}}{dt}$ (R4.6) via Equation C.3, C.4, C.5, C.6, and C.7 in Appendix C. The respective rates of temperature changes, e.g. $\frac{dT_p}{dt}$ (R4.2), $\frac{dT_p}{dt}$ (R4.3), $\frac{dT_p}{dt}$ (R4.4), $\frac{dT_p}{dt}$ (R4.5), and $\frac{dT_p}{dt}$ (R4.6), are calculated via Equation C.8, C.9, C.10, C.11, and C.12.

Gas 1 and gas 2 mainly comprise CH_{4(g)}, CO_(g), H_{2O(g)}, CO_{2(g)} and H_{2(g)}, with minor amounts of longer-chain hydrocarbons, e.g. C₂H_{6(g)}, C₂H_{4(g)}.^{232,233} Mass fractions of these compounds in gas 1 and gas 2 have been investigated previously. Kung²³⁴ attempted to analyse transient behaviours during biomass pyrolysis. However, the analysis only achieved measurements of overall gas concentrations. Nunn *et al.*²³⁵ measured gas compositions during pyrolysis of sweet hardwood under pressure of 5 psi of helium gas. However, this work was unable to measure gas compositions from the pyrolysis of H_{2(g)}-rich biomass. Bowersox²³⁶ conducted gas analysis during pyrolysis of populus hybrids. Blasi²³⁷ measured gas compositions during pyrolysis of a wood particle with a thickness of around 0.5cm to 1 cm. Thunmann *et al.*²³⁸ measured gas compositions during pyrolysis of hardwood and softwood using a developed pyrolysis model. Ranzi *et al.*²³⁹ later measured gas compositions and kinetic parameters during pyrolysis of the same biomass. For tar pyrolysis, Morf *et al.*²⁴⁰ measured gas compositions at temperatures within 500-1000 °C in a tubular flow reactor. All gas compositions from the above studies have been compiled and are shown in Table 4.1.

Table 4.1 Wood Pyrolysis Gas Mass Fractions

Biomass	CH _{4(g)}	CO _(g)	CO _{2(g)}	H _{2(g)}	H _{2O(g)}
Wood ²³⁴	0.03	0.16	0.27	0.02	0.52
Hardwood ²³⁵	0.21	0.41	0.19	0.01	0.19
Populus Hybrid ²³⁶	0.08	0.31	0.19	0.01	0.19
Hardwood ¹¹⁵	0.12	0.36	0.19	0.1	0.23
Wood ²³⁷	0.03	0.27	0.39	0.05	0.26
Softwood ²³⁸	0.01	0.25	0.43	0.04	0.27

Hardwood ²³⁸	0.01	0.2	0.51	0.04	0.23
Tar ²³⁹	0.2	0.5	0.3	0	0
Tar ²⁴⁰	0.08	0.46	0.46	0.01	0

Table 4.1 shows that pyrolysis gas compositions are diverse and depend on biomass types. Adoption of a set of compositions as a general biomass composition may lead to mass balance inaccuracies. Therefore, proximate and ultimate analysis results were used in the work performed for this thesis as the sole reference to determine the actual pyrolysis gas compositions. An example of proximate and ultimate analysis results of some biomass is shown in Table 3.1. The molar masses of pyrolysis gases are calculated by solving a set of linear equations shown as Equations 4.24, 4.25, and 4.26.

$$n_{CH_4(g)vm} + n_{CO(g)vm} + n_{CO_2(g)vm} = n_{Cvm} \quad (E4.24)$$

$$4n_{CH_4(g)vm} + 2n_{H_2(g)vm} + 2n_{H_2O(g)vm} = n_{Hvm} \quad (E4.25)$$

$$n_{CO(g)vm} + 2n_{CO_2(g)vm} + n_{H_2O(g)vm} = n_{Ovm} \quad (E4.26)$$

$n_{CH_4(g)vm}$, $n_{CO(g)vm}$, $n_{CO_2(g)vm}$, $n_{H_2(g)vm}$, and $n_{H_2O(g)vm}$ are the molar masses of $CH_4(g)$, $CO(g)$, $CO_2(g)$, $H_2(g)$, and $H_2O(g)$ in volatile matter in mol. n_{Cvm} , n_{Hvm} , and n_{Ovm} are the molar masses of elemental C, H, and O in mol.

Equations 4.24, 4.25, and 4.26 could be solved with the least-square method, since the number of unknown variables is more than the number of equations. However, the least-square method also generates inaccurate results. Therefore, Equations 4.24, 4.25, and 4.26 are simplified by eliminating two compounds that occur in the least significant amounts, i.e. $CO_2(g)$ and $H_2(g)$, to equalise the number of unknown variables and the number of equations. The simplified equations are presented in Equations 4.27, 4.28, and 4.29.

$$n_{CH_4(g)vm} + n_{CO(g)vm} = n_{Cvm} \quad (E4.27)$$

$$4n_{CH_4(g)vm} + 2n_{H_2O(g)vm} = n_{Hvm} \quad (E4.28)$$

$$n_{CO(g)vm} + n_{H_2O(g)vm} = n_{Ovm} \quad (E4.29)$$

At the same time as pyrolysis gases diffuse from the particle centre to the particle surface, they homogeneously react with the $O_{2(g)}$ that is diffusing from the particle surface to the particle centre. The homogeneous gas reactions are shown by Reactions 4.7, 4.8, and 4.9.





The calculations of the kinetic equations for Reactions 4.7, 4.8, and 4.9 to obtain $\frac{d[CH_4(g)]_p}{dt}$ (R4.7), $\frac{d[CO_{(g)}]_p}{dt}$ (R4.8), and $\frac{d[H_{2(g)}]_p}{dt}$ (R4.9) are explained in Appendix C.3. The respective rates of temperature changes, e.g. $\frac{dT_p}{dt}$ (R4.7), $\frac{dT_p}{dt}$ (R4.8), and $\frac{dT_p}{dt}$ (R4.9), are calculated via Equation C.19, C.20, and C.21.

The heterogeneous reactions of char with $O_{2(g)}$, $CO_{2(g)}$, and $H_2O_{(g)}$ are shown by Reactions 3.10, 3.11, and 3.12.



The calculations of the kinetic equations for Reactions 4.10, 4.11, and 4.12 to obtain $\frac{d\rho_{char}}{dt}$ (R4.10), $\frac{d\rho_{char}}{dt}$ (R4.11), and $\frac{d\rho_{char}}{dt}$ (R4.12) are explained in Appendix C.4. The respective rates of temperature changes, e.g. $\frac{dT_p}{dt}$ (R4.11), $\frac{dT_p}{dt}$ (R4.12), and $\frac{dT_p}{dt}$ (R4.12), are calculated via Equation C.26, C.27, and C.28.

The mass of particles decreases due to gas release during pyrolysis and due to char oxidation. Particle mass reduction causes the particle volume to shrink. Particle volume shrinkage could be estimated by Equation 4.30, according to previous researchers.¹¹⁵

$$\begin{aligned} \theta = 1 + (1 - \theta_{H_2O(l)}) \left(\frac{\rho_{H_2O(l)}}{\rho_{H_2O(l)_0}} - 1 \right) \\ + (\theta_{H_2O(l)} - \theta_v) \left(\frac{\rho_{wood}}{\rho_{wood_0}} - 1 \right) + (\theta_v - \theta_c) \left(\frac{\rho_{char}}{\rho_{char_0}} - 1 \right) \end{aligned} \quad (E4.30)$$

$\rho_{H_2O(l)_0}$, ρ_{wood_0} , and ρ_{char_0} are the initial densities of moisture, wood and char in the particle in $kg\ m^{-3}$. θ is the particle shrinkage factor defined as the ratio of particle volume to initial particle volume. $\theta_{H_2O(l)}$ is the moisture shrinkage constant. θ_v is the volatile matter shrinkage constant. θ_c is the char shrinkage constant. θ ranges from 0 to 1. $\theta_{H_2O(l)}$, θ_v , and θ_c are assumed at 0.9, 0.75, and 0. θ_c is 0 since char gasification is controlled by external diffusion and has no effect on particle shrinkage.

However, Equation 4.30 was not used in the work described in this thesis due to several limitations. The estimated values of $\theta_{H_2O(l)}$, θ_v , and θ_c might be compatible only with a very specific type of wood. In addition, $\frac{\rho_{char}}{\rho_{char_0}}$ are undefined since ρ_{char_0} is 0. Equation 4.30 also does not feature the intra-particle ash densities as determinant parameters. Therefore, Equation 4.31 is used to calculate θ with an assumption that the fractional change of particle volumes is equal to the fractional change of particle mass.

$$\theta = 1 + C_\theta \left(\frac{\rho_{wood} + \rho_{tar} + \rho_{char}}{\rho_{wood_0}} - 1 \right) \quad (E4.31)$$

C_θ is the shrinkage constant obtained via Equation 4.31, when θ equal to $\theta_{\rho_{wood} + \rho_{tar} + \rho_{char} = 0}$.

Equation 4.31 cannot be used directly in the single-particle combustion model since Equation 4.31 is based on particle volume shrinkage, considering θ as θ_{3Dp} calculated via Equation 4.32.

$$\theta_{3Dp} = 1 + C_{\theta_{3D}} \left(\frac{\rho_{woodp} + \rho_{tarp} + \rho_{charp}}{\rho_{wood_0}} - 1 \right) \quad (E4.32)$$

θ_{3Dp} is the three-dimensional shrinkage factor. $C_{\theta_{3D}}$ is the three-dimensional shrinkage constant. θ_{3Dp} is converted into the one-dimensional shrinkage factor θ_{1Dp} in Equation 4.33, since the particle shrinkage evaluation is based on length shrinkage or length reduction between neighbouring nodes.

$$\theta_{1Dp} = \sqrt[3]{\theta_{3Dp}} \quad (E4.33)$$

The formula to calculate the one-dimensional shrinkage constant, $C_{\theta_{1D}}$, is shown as Equation 4.34.

$$C_{\theta_{1D}} = \frac{\theta_{1Dp}^{-1}}{\left(\frac{\rho_{woodp} + \rho_{tarp} + \rho_{charp}}{\rho_{wood_0}} - 1 \right)} \quad (E4.34)$$

θ_{1Dp} is defined as the ratio of current lengths between two nodes to their initial lengths. Figure 4.4 shows a visual explanation of θ_{1Dp} .

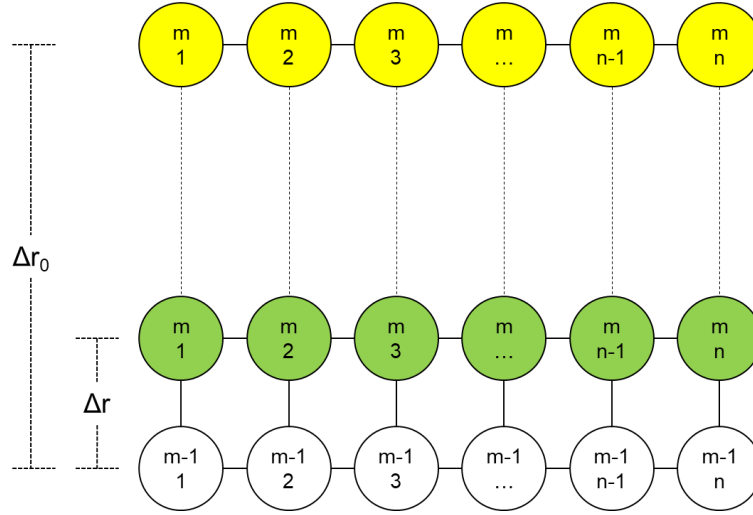


Figure 4.4 Illustration of Nodes of Shrinking Particles

Δr_0 is the initial distance between nodes m and $m-1$. The distances between nodes m and nodes $m-1$ becomes shorter by $\Delta r_0 - \Delta r$ as organic constituents in nodes m are pyrolysed and gasified. Δr_0 and Δr are calculated by Equation 4.35 with θ_{1Dp} .

$$\Delta r = \theta_{1Dp_{exp}} \Delta r_0 \quad (\text{E4.35})$$

Pyrolysis gas released from the particles, reacts with $\text{O}_{2(g)}$ in the particle boundary layer according to Reactions 4.7, 4.8, and 4.9. The reaction of pyrolysis gas with $\text{O}_{2(g)}$ establishes a flame in the boundary layer. The flame increases the boundary layer and particle surface temperatures via heat convection. For modelling purposes, the boundary layer is discretised as a platform to calculate the boundary layer profile. The discretisation is made based on the following assumptions:

- The boundary layer gas is an ideal gas.
- The heat and mass transfer through the boundary layer thickness can be estimated by Equations 4.36 and 4.37, respectively.

$$l_{bl_c} = \frac{d_p}{Nu_{gas_b}} \quad (\text{E4.36})$$

$$l_{bl_m} = \frac{d_p}{Sh_{gas_b}} \quad (\text{E4.37})$$

l_{bl_c} is the heat-transfer boundary layer thickness in m. l_{bl_m} is the mass-transfer boundary layer thickness in m. In the research described in this thesis, l_{bl_m} was used since it was thicker than l_{bl_c} .

- The Peclet number is assumed and the bulk gas motion effect on the particle is neglected. In other words, the flow velocity of the bulk gas is assumed to be low enough that both temperature and concentration fields within the boundary layer are cylindrically -symmetrical.
- The gas velocity at the boundary layer is equal to the gas velocity at the bulk as given by Equation 4.38.

$$v_{bl} = v_{\infty} \quad (E4.38)$$

Here, v_{bl} is the gas velocity at the boundary layer and v_{∞} is the velocity of bulk gas.

Boundary layer discretisation is illustrated in Figures 4.5 and 4.6 for radial and axial boundary layers.

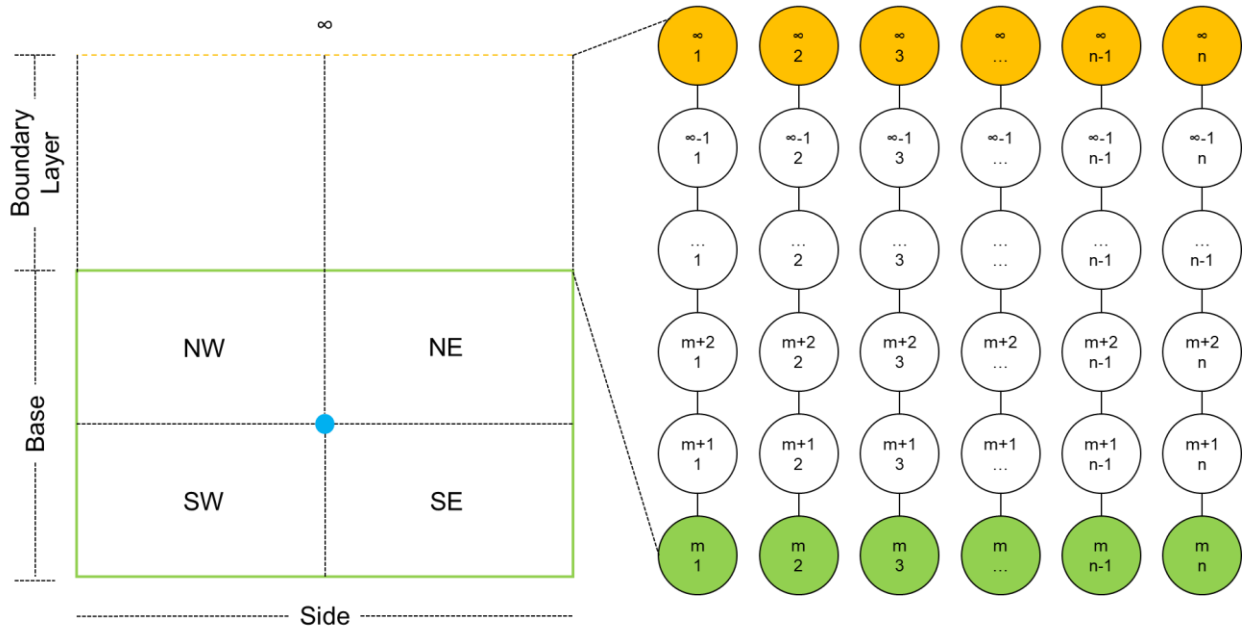


Figure 4.5 Discretisation of the Cylindrical Particle Radial Boundary Layers

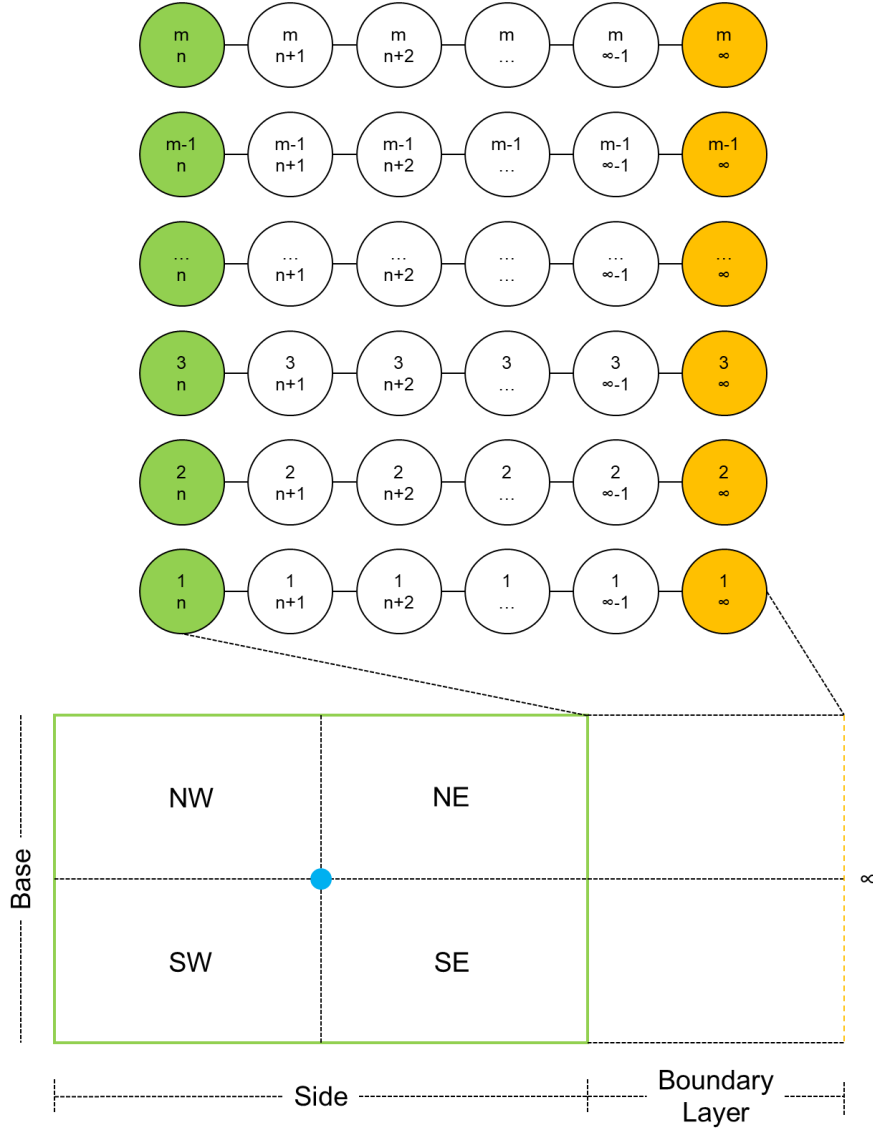


Figure 4.6 Discretisation of the Cylindrical Particle Axial Boundary Layers

The conservation equations for heat and mass transfer within the boundary layer are given as Equations 4.39 and 4.40 for the radial direction and Equations 4.41 and 4.42 for the axial direction.

$$\frac{\partial T_{bl}}{\partial t} = \alpha_{bl} \frac{\partial^2 T_{bl}}{\partial r_{bl}^2} + \left(\frac{\alpha_{bl}}{r_{bl}} - v_{bl} \right) \frac{\partial T_{bl}}{\partial r_{bl}} \quad (\text{E4.39})$$

$$\frac{\partial C_{bl}}{\partial t} = D_{F i g a s_{bl}} \frac{\partial^2 C_{bl}}{\partial r_{bl}^2} + \left(\frac{D_{A B_{bl}}}{r_{bl}} - v_{bl} \right) \frac{\partial C_{bl}}{\partial r_{bl}} \quad (\text{E4.40})$$

$$\frac{\partial T_{bl}}{\partial t} = \alpha_{bl} \frac{\partial^2 T_{bl}}{\partial z_{bl}^2} - v_{bl} \frac{\partial T_{bl}}{\partial z_{bl}} \quad (\text{E4.41})$$

$$\frac{\partial C_{bl}}{\partial t} = D_{F i g a s_{bl}} \frac{\partial^2 C_{bl}}{\partial z_{bl}^2} - v_{bl} \frac{\partial C_{bl}}{\partial z_{bl}} \quad (\text{E4.42})$$

T_{bl} is the boundary-layer temperature in K. C_{bl} is the boundary-layer gas concentration in mol m^{-3} . α_{bl} is the boundary-layer gas thermal diffusivity in $\text{m}^2 \text{s}^{-1}$. r_{bl} and z_{bl} are the distances between boundary-layer nodes to the particle surface in m. v_{bl} is the boundary-layer gas velocity in m s^{-1} . $D_{F i g a s_{bl}}$ is the conductive mass diffusivity coefficient of the boundary-layer in $\text{m}^2 \text{s}^{-1}$.

The boundary layer is assumed to have a uniform grid and is discretised using finite-difference approximation. Central and forward difference is used to solve the second and first derivative term. The numerical solutions for heat and mass transfer are presented in Equations 4.43 and 4.44 for the radial direction and in Equations 4.45 and 4.46 for the axial direction.

$$\frac{\partial T_{blr}}{\partial t} = \alpha_{blr} \frac{T_{blr+2} - 2T_{blr} + T_{blr+1}}{\Delta r_{blr}^2} + \left(\frac{\alpha_{blr}}{r_{blr}} - v_{bl} \right) \frac{T_{blr+1} - T_{blr}}{\Delta r_{blr}} \quad (\text{E4.43})$$

$$\frac{\partial C_{blr}}{\partial t} = D_{F i g a s_{blr}} \frac{C_{blr+2} - 2C_{blr} + C_{blr+1}}{\Delta r_{blr}^2} + \left(\frac{D_{F i g a s_{blr}}}{r_{blr}} - v_{bl} \right) \frac{C_{blr+1} - C_{blr}}{\Delta r_{blr}} \quad (\text{E4.44})$$

$$\frac{\partial T_{bll}}{\partial t} = \alpha_{bll} \frac{T_{bll+2} - 2T_{bll} + T_{bll+1}}{\Delta z_{bll}^2} + v_{bl} \frac{T_{bll+1} - T_{bll}}{\Delta z_{bll}} \quad (\text{E4.45})$$

$$\frac{\partial C_{bll}}{\partial t} = D_{F i g a s_{bll}} \frac{C_{bll+2} - 2C_{bll} + C_{bll+1}}{\Delta z_{bll}^2} + v_{bl} \frac{C_{bll+1} - C_{bll}}{\Delta z_{bll}} \quad (\text{E4.46})$$

T_{blr} and T_{bll} are boundary layer temperatures in radial and axial directions, in K. C_{blr} and C_{bll} are boundary layer temperatures in radial and axial directions in mol m^{-3} . α_{blr} and α_{bll} are boundary layer thermal diffusivities in radial and axial directions in $\text{m}^2 \text{s}$. Δr_{blr} and Δz_{bll} are distances between two neighbouring nodes in radial and axial directions.

4.2 Case Study

The work of Mason *et al.*¹¹⁷ is explained to give an understanding of single-particle combustion from an experimental perspective and to test results of the single-particle combustion model. The explanation comprises biomass properties, experimental setup, experimental results, and tests of the modelled result.

Prior to conducting combustion, biomass particles are prepared and characterised. Biomass particles are prepared to obtain approximately cuboid or cylindrical shapes with diameters varying from 0.5 mm to 4 mm by cutting and removing any bark material. Some portions of biomass are analysed to obtain their chemical composition.

A Méker-type natural gas burner was utilised as the combustion equipment. This burner is designed to produce a stable flame during combustion. The flame was stable at temperatures around 1,823 K. Room temperature was used as the radiative temperature, since biomass particles were combusted in an open atmospheric environment. $O_{2(g)}$ was supplied at 3 m s^{-1} with concentration of 21% of molar percentage at 1 atm. Biomass particles were hung from a fine steel needle during combustion. A video camera was used to record the burning biomass particles for around six seconds at 120 frames per second. The pictures produced were translated into thermal images.

Table 4.2 Numerical Parameters of Mason *et al.*¹¹⁷ Single-Particle Combustion Model

Parameter	Value
Particle Radius Nodes	5
Particle Length Nodes	5
Combustion Time Range	0.1
Relative Tolerance	1e-9
Absolute Tolerance	1e-6

The single-particle combustion model based on the work of Mason *et al.*¹¹⁷ was compiled with use of Matlab 2018a software with a modelling route. It is illustrated in Figure 4.7. The model's numerical parameters are shown in Table 4.2. These parameters were initially set in Matlab Editor of the main file (Mason_et_al_2015.m). The modelled particle section was the NE section with 25 nodes, or 5^2 nodes. Differential equations associated with 25 nodes for both temperature and intra-particle gas concentrations were numerically calculated with the Matlab ordinary-differential-equation (ODE) solver. Initial values required by the Matlab ODE solver were based on the results of the proximate and ultimate analysis. The initial values listed in Table 4.3 were considered to be uniformly distributed in all nodes. The ODE solver was commanded to solve the 25-node differential equations compiled as a function file (Combustion_Function.m). In the function file, functions related to particle thermodynamics and physical properties were set and these are listed in Table 4.4. The ODE solver time span was set from 0 to 6 seconds according to the combustion duration.

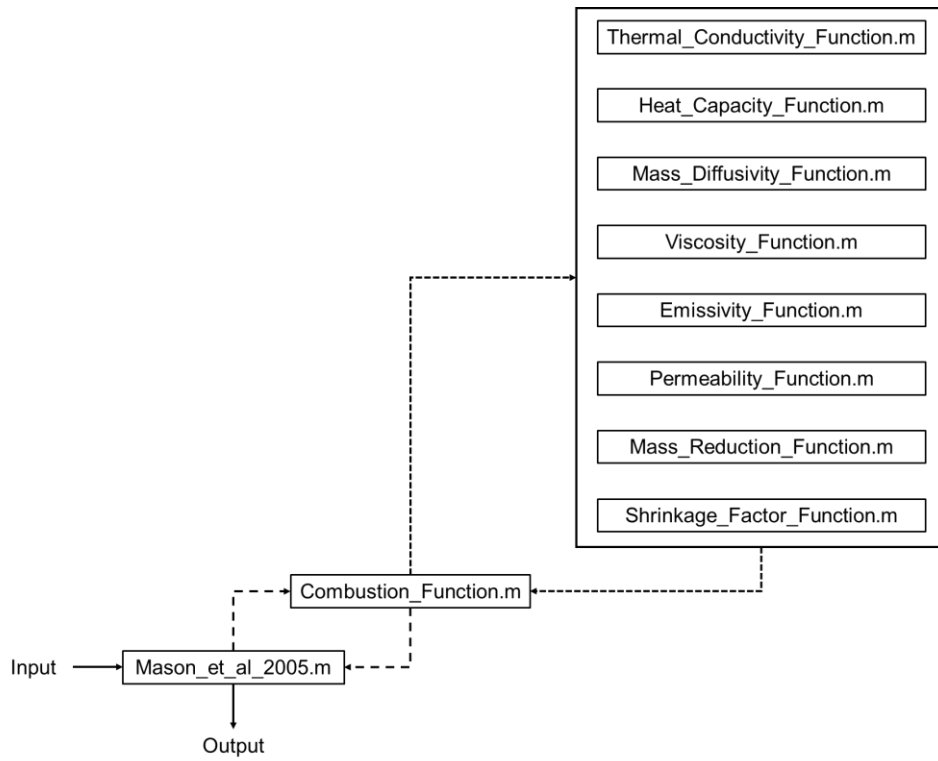


Figure 4.7 Modelling Route of Single-Particle Combustion Model

Table 4.3 Initial Values of Mason et al. 's¹¹⁷ Single-Particle Combustion Model)

Parameter	Value
Particle Temperature (K)	298
Particle Wood Density (kg m ⁻³)	606.45
Particle Tar Density (kg m ⁻³)	0
Particle Char Density (kg m ⁻³)	0
Particle H ₂ O _(l) Density (kg m ⁻³)	39
Particle Gas CH _{4(g)} Concentration (mol m ⁻³)	0
Particle Gas CO _(g) Concentration (mol m ⁻³)	0
Particle Gas CO _{2(g)} Concentration (mol m ⁻³)	0
Particle Gas H _{2(g)} Concentration (mol m ⁻³)	0
Particle Gas H ₂ O _(g) Concentration (mol m ⁻³)	0
Particle Gas O _{2(g)} Concentration (mol m ⁻³)	4.29
Particle Gas N _{2(g)} Concentration (mol m ⁻³)	16.15

Table 4.4 *Property Functions of Single-Particle Combustion Model*

Property	File	Input
Particle Thermal Conductivity	Thermal_Conductivity_Function.m	Particle Temperature Wood Density Tar Density Char Density Ash Density Particle Gas CH _{4(g)} Concentration Particle Gas CO _(g) Concentration Particle Gas CO _{2(g)} Concentration Particle Gas H _{2(g)} Concentration Particle Gas H _{2O(g)} Concentration Particle Gas O _{2(g)} Concentration Particle Gas N _{2(g)} Concentration
Particle Heat Capacity	Heat_Capacity_Function.m	Particle Temperature Wood Density Tar Density Char Density Ash Density Particle Gas CH _{4(g)} Concentration Particle Gas CO _(g) Concentration Particle Gas CO _{2(g)} Concentration Particle Gas H _{2(g)} Concentration Particle Gas H _{2O(g)} Concentration Particle Gas O _{2(g)} Concentration Particle Gas N _{2(g)} Concentration
Particle Mass Diffusivity	Mass_Diffusivity_Function.m	Particle Temperature Particle Gas CH _{4(g)} Concentration Particle Gas CO _(g) Concentration Particle Gas CO _{2(g)} Concentration Particle Gas H _{2(g)} Concentration Particle Gas H _{2O(g)} Concentration Particle Gas O _{2(g)} Concentration Particle Gas N _{2(g)} Concentration
Particle Viscosity	Viscosity_Function.m	Particle Temperature Particle Gas CH _{4(g)} Concentration Particle Gas CO _(g) Concentration Particle Gas CO _{2(g)} Concentration Particle Gas H _{2(g)} Concentration

		Particle Gas H ₂ O _(g) Concentration Particle Gas O _{2(g)} Concentration Particle Gas N _{2(g)} Concentration
Particle Emissivity	Emissivity_Function.m	Wood Density Char Density Ash Density
Particle Permeability	Permability_Function.m	Wood Density Char Density Ash Density
Particle Mass Reduction	Mass_Reduction_Function.m	Wood Density Tar Density Char Density Ash Density
Particle Shrinkage Factor	Shrinkage_Factor_Function.m	Wood Density Tar Density Char Density Ash Density

Attempts were made to run the single-particle combustion model with several ODE solvers as tests to obtain the most efficient ODE solver. Initially, ode45 was used since it is the most versatile ODE solver. This version solves non-stiff differential equations with the medium-order method. However, the run with ode45 became computationally expensive once the run reached transition between drying and volatilisation due to stiff calculations. Therefore, ode15s was chosen to replace ode45. According to the Matlab help file, ode15s is the best choice of stiff ODE solver to use to solve a stiff system. The single-particle combustion model finally ran without any numerical problems.

A single run of the single-particle combustion model generates two forms of results, namely: a node profile and a contour profile. The node profile is essentially an evolution of thermodynamic properties, e.g. temperature, density, and gas concentration, at any node. Thermodynamic property evolution could be used to determine the duration of each combustion stage, i.e. drying, volatilisation, and char-oxidation, at the examined node. On the other hand, the contour profile shows a two-dimensional distribution of thermodynamic properties at all the nodes at a certain time. This thermodynamic property distribution may give information on the quality of heat and mass transfer within the particle.

Unlike spherical particles, cylindrical particles have non-uniform distribution of thermodynamic properties at the particle surfaces. For instance, node $\left(\begin{smallmatrix} m \\ n \end{smallmatrix}\right)$ (particle edge) receives convective heat from the north and east directions. On the other hand, node $\left(\begin{smallmatrix} m \\ 1 \end{smallmatrix}\right)$ (particle middle cylindrical surface) receives convective heat only from the north direction. These conditions cause the temperature of node particle

edge to increase significantly quicker than the temperature of particle middle cylindrical surface. This significant heating rate creates a temperature gradient along the northern surface nodes, e.g. node $\binom{m}{2}$, node $\binom{m}{3}$, node $\binom{m}{4}$, and node $\binom{m}{n-1}$.

However, thermodynamic properties measured at particle temperatures in most previous works have usually been represented by a single value, regardless of the particle shape. This is probably due to the difficulty of measuring the thermodynamic properties of particle surfaces since details of surface area are not sufficiently available for multiple measurements, particularly when the particle shrinks. To obtain a representative value for particle surface thermodynamic properties, an average of thermodynamic properties at the particle surface was used during the work described in this thesis.

Comparison between the particle surface temperature profile obtained from the single-particle combustion model and the particle surface temperature profile taken from the experimental work of Mason *et al.*¹¹⁷ is shown in Figure 4.8. The comparison shows that the particle surface temperature profile obtained through use of the single-particle combustion model is in good agreement with the experimental particle surface temperature profile.

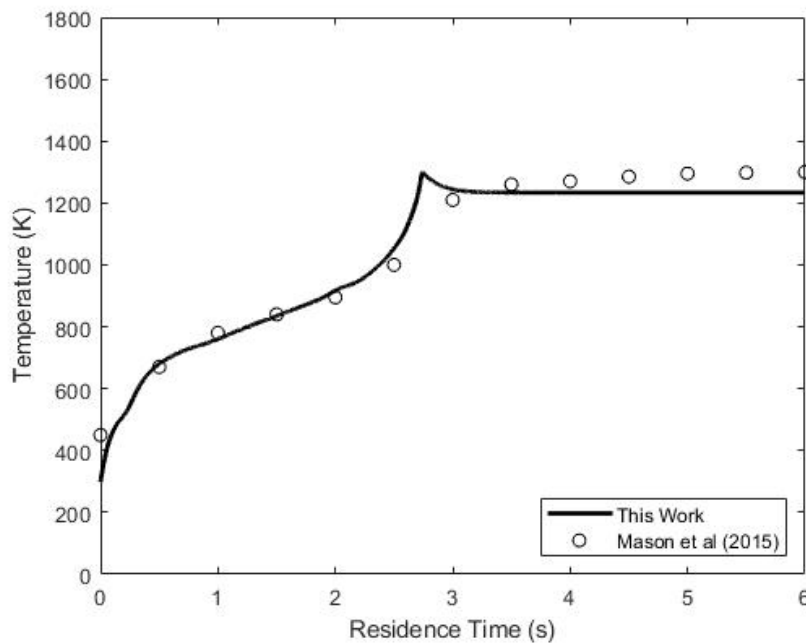


Figure 4.8 Comparison between Particle Surface Temperatures Obtained in This Work and in the Work of Mason *et al.*¹¹⁷

Although the temperature of the particle surface at any timepoint shown in Figure 4.8 is an average for the entire surface, the single-particle combustion model was also extended to provide the actual modelled temperatures at particle surface critical nodes. These critical nodes on the particle surface are

nodes $\binom{m}{n}$ (particle edge), $\binom{m}{1}$ (particle middle cylindrical surface), and $\binom{1}{n}$ (particle base centre). The particle edges are the hottest locations since they are exposed to boundary heat from two different directions. The particle middle cylindrical surfaces and the particle base centres are partially located at the intra-particle boundary line. The temperature evolution of these particle surface critical locations is presented in Figure 4.9 along with that of the particle centre.

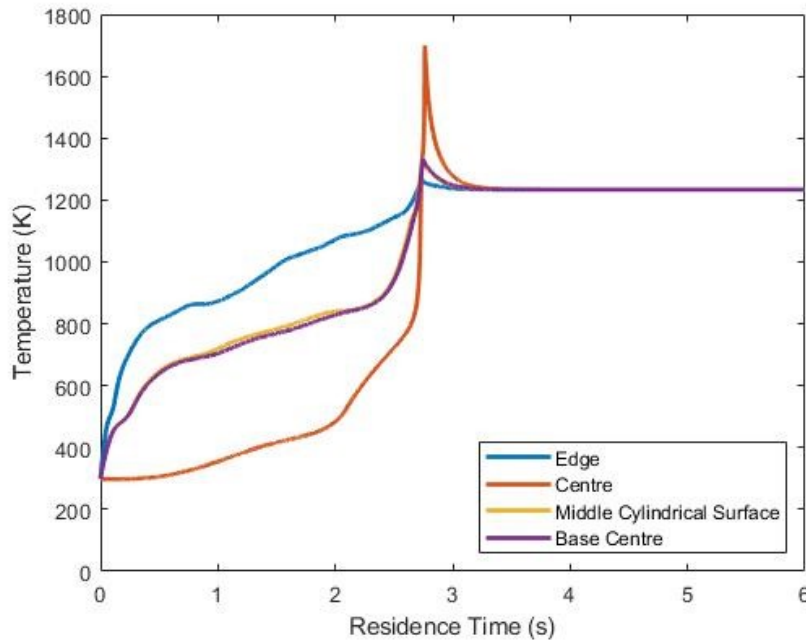


Figure 4.9 Modelled Intra-particle Temperature Profiles at Particle Edge, Particle Centre, Particle Middle Cylindrical Surface, and Particle Base Centre, based on Mason et al.¹¹⁷

At an early stage of combustion, e.g. within 0.5 s, the temperature at the particle edges increases rapidly from 298 K to around 800 K, whilst those at the particle middle cylindrical surfaces and the particle base centres increase from 298 K to around 600 K. The particle edges achieve a higher temperature than the particle middle cylindrical surfaces and the particle base centres since the particle edges receive boundary heat transfer from the north and east directions simultaneously, whilst each of the particle middle cylindrical surface and the particle base centre only receives boundary heat transfer from one direction. The temperature of the particle centre changes slightly until 2 s after the start of combustion, because heat from the surface nodes has not yet reached it.

From around 0.5 s onward, the temperatures at the particle edges, the particle middle cylindrical surfaces, and the particle base centres increase slightly as the heat at these nodes is being used for drying and pyrolysis. As the particle surface becomes very porous due to pyrolysis, pyrolysis gas is released quickly to the boundary layer.²⁴¹ Consequently, the particle surface does not have adequate carbon monoxide and hydrogen to react exothermically with $O_{2(g)}$ at the surface, as seen in Figure 4.11. Due to

lack of heat from oxidation, the particle surface temperature keeps rising gradually. After this the particle surface temperature increases rapidly to around 1,200K to 1,300K, which promotes rapid heat transfer from the particle surface towards the particle centre and consequently raises the temperature at particle centre at a rapid rate.

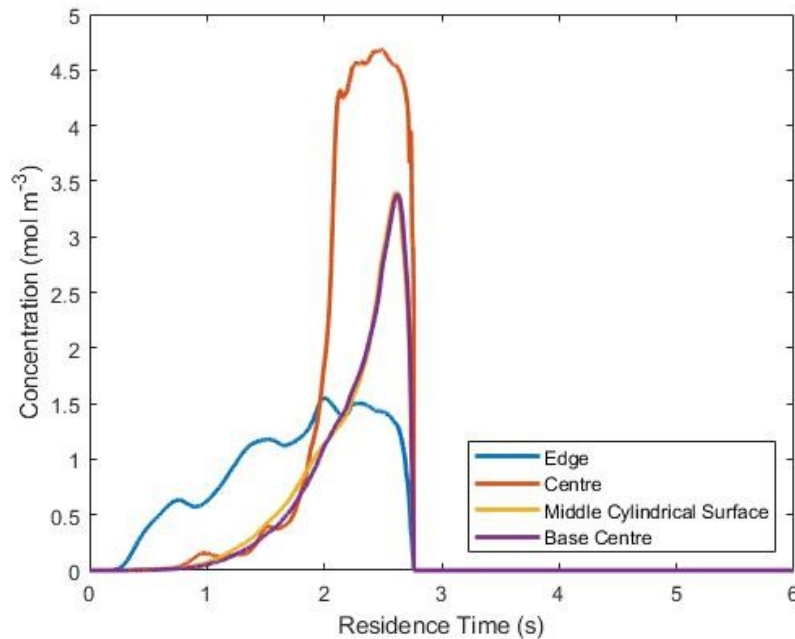


Figure 4.10 Modelled Intra-particle CO(g) Concentration Profile at Particle Edge, Particle Centre, Particle Middle Cylindrical Surface, and Particle Base Centre, based on Mason et al.¹¹⁷

Within 2.5 s to 2.7 s, the particle surface is almost completely combusted due to heterogeneous oxidation by O_{2(g)}. CO_(g) released due to pyrolysis and char oxidation within deep layers of the particle flows towards the particle surface and reacts with O_{2(g)}. At the surface, CO_(g) is at its maximum concentration, as shown in Figure 4.11. A considerable amount of CO_(g) at the particle surface with significant concentration of O_{2(g)} establishes rapid oxidation, as shown in Figure 4.12. This rapid exothermic oxidation increases the particle surface temperature at a rapid rate, as indicated by small temperature spikes at around 2.7 s. At this point, the particle's surface and interior are already more than 50% converted and have very porous pores, whilst the particle centre still contains a significant amount of char, as shown in Figure 4.13. Increased porosity promotes rapid diffusion of O_{2(g)} from the particle surface towards the particle centre. When a significant amount of O_{2(g)} and heat simultaneously arrives at the particle centre, char at the particle centre is oxidised heterogeneously at a very rapid rate. Due to a very rapid exothermic reaction, the temperature the particle centre abruptly climbs to 1700 K. At this point, a very significant temperature gap between the particle surface and the particle centre is observed, as illustrated in Figure 4.14.

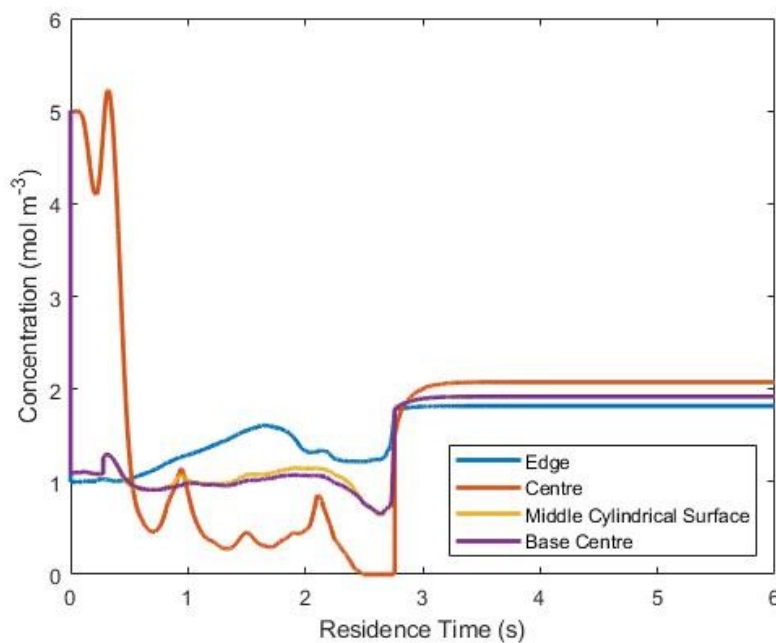


Figure 4.11 Modelled Intra-particle $O_2(g)$ Concentration Profile at Particle Edge, Particle Centre, Particle Middle Cylindrical Surface, and Particle Base Centre, based on Mason et al.¹¹⁷

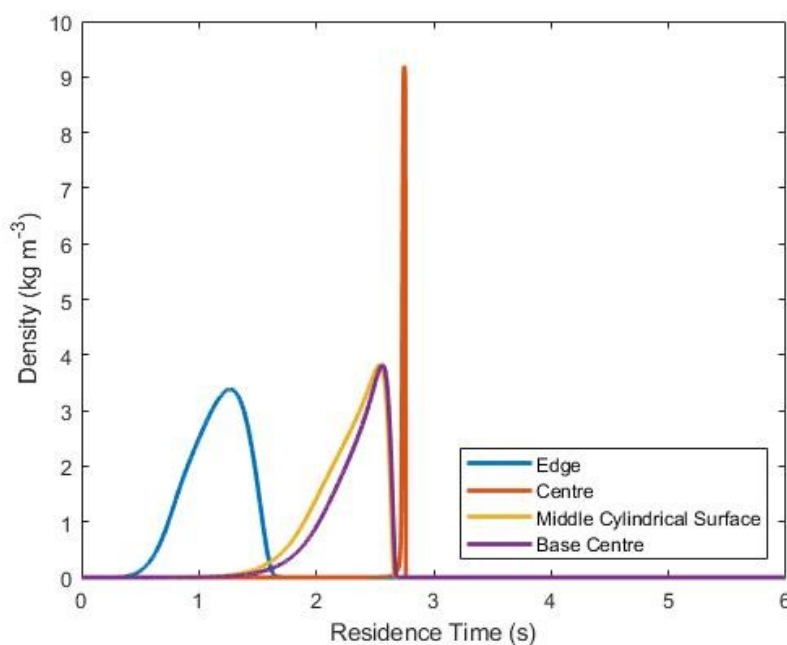


Figure 4.12 Modelled Intra-particle Char Density Profile at Particle Edge, Particle Centre, Particle Middle Cylindrical Surface, and Particle Base Centre, based on Mason et al.¹¹⁷

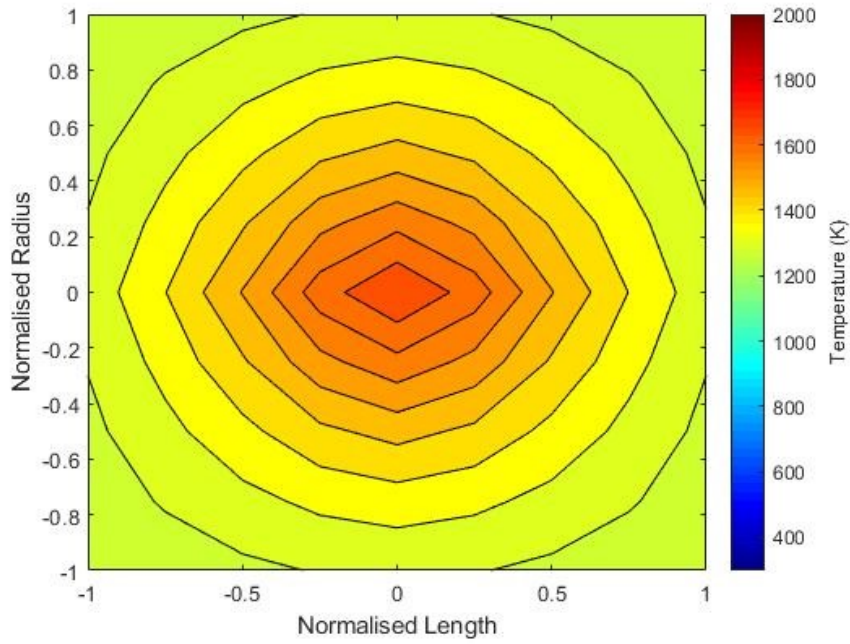


Figure 4.13 Modelled Intra-particle Temperature Contours at 2.763 s, based on Mason et al.¹¹⁷

Shortly after 2.7 s, the temperature at the particle centre plunges dramatically to around 1250 K. This sudden drop in temperature is due to the significant temperature gap between the particle's centre and surface. This gap promotes fast heat transfer from the centre to the surface. By the end of combustion, the temperature within the particle is uniformly distributed, as shown in Figure 4.14.

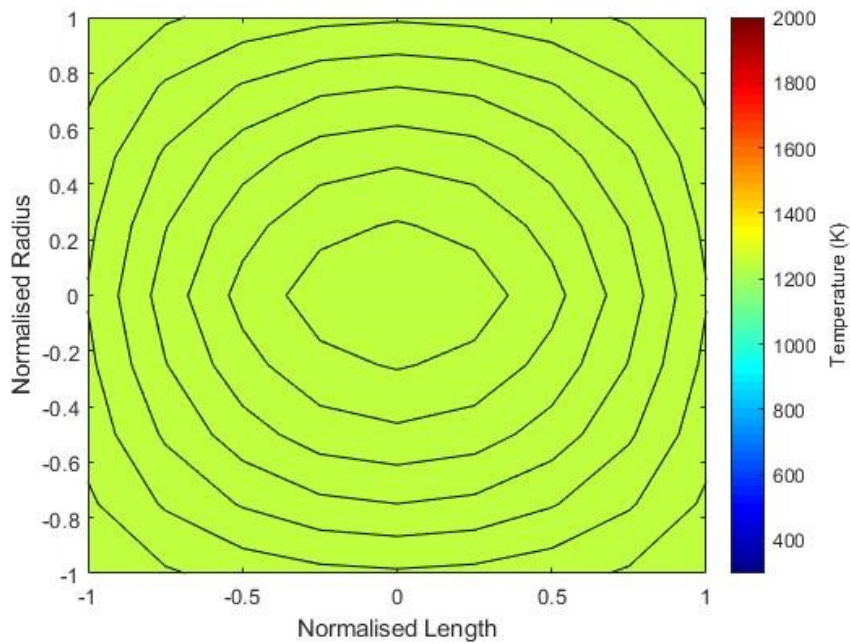


Figure 4.14 Modelled Intra-particle Temperature Contours at 6 s, based on Mason et al.¹¹⁷

The results from the single-particle combustion model are further tested against other experimental results obtained from the work of Lu *et al.*¹¹⁵ and Lewtak and Marek²⁴². Their work aimed to evaluate combustion behaviour of biomass particles in a single-particle combustor. Discussion regarding their research comprises experimental setup, experimental results, and modelled result tests.

In the work of Lu *et al.*¹¹⁵, a cylinder was used as combustion equipment as shown in Figure 4.15. Pre-heated air was introduced from the bottom of the cylinder and it flowed upward to oxidise the particle. The air temperature was controlled through use of a temperature controller with pre-heater temperature adjustment. The particle was hung with a thermocouple type B and connected to a mass balance coupled with a mass data logger. Cylindrical and near-spherical poplar particles were prepared with a diameter of 9.5 mm for this experiment.

Lewtak and Marek²⁴² used a horizontal single-particle combustor as shown in Figure 4.16. In the combustor, a willow particle was hung upward with a thermocouple and initially covered with a cool shield tube that had cooling water flowing within its wall. The cool shield tube was pulled out of the combustor once a steady air flow rate was achieved. The willow particle size was around 1-3 mm. A small hole was drilled to fit an inserted temperature probe for measurement of the temperature of the centre of the particle.

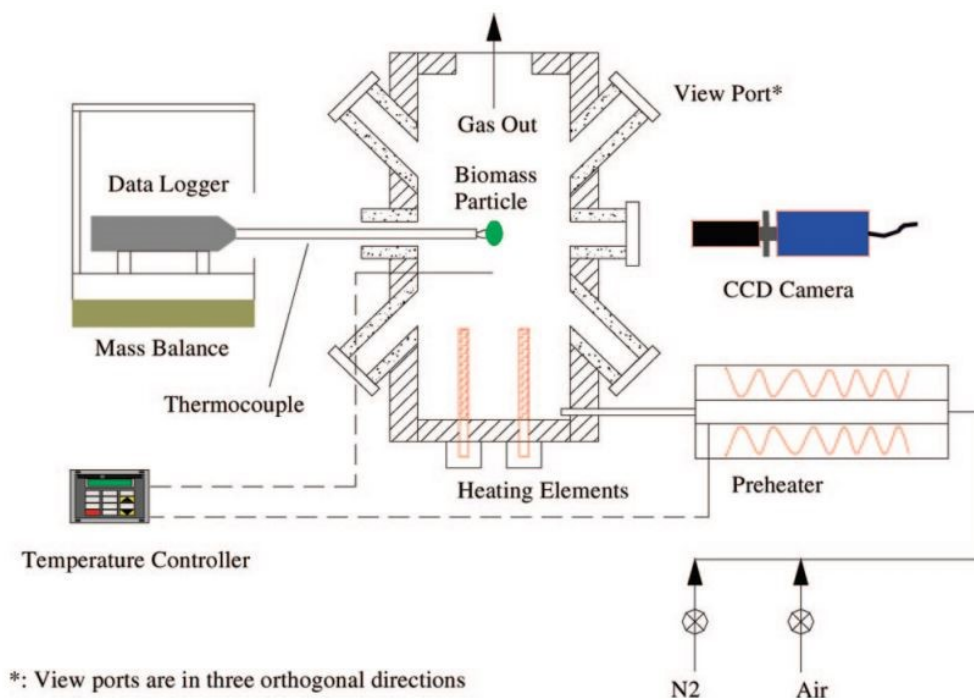


Figure 4.15 Combustion Setup of Lu *et al.*¹¹⁵

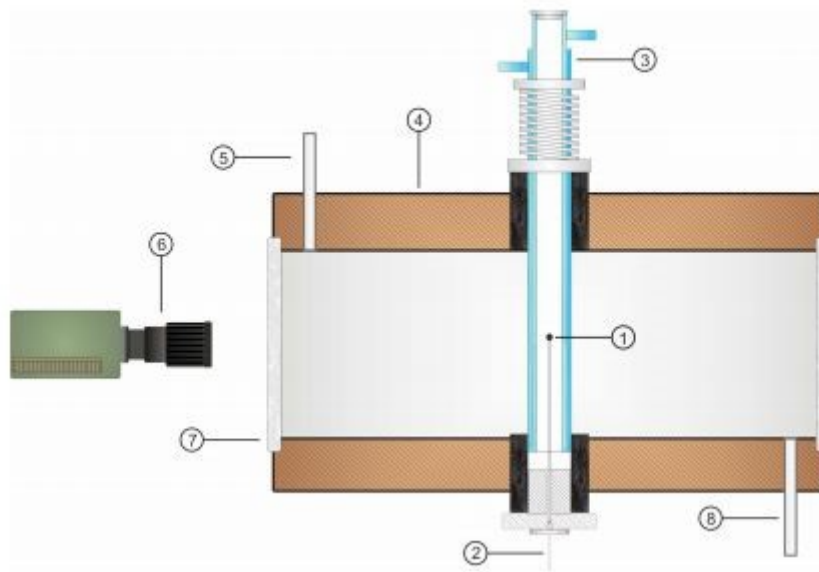


Figure 4.16 Combustion Setup of Lewtak and Marek: 1. Biomass Particle; 2. Thermocouple; 3. Cool Shield Tube; 4. Reactor; 5. Gas Inlet; 6. High Speed Camera; 7. Quartz Window; 8. Gas Outlet

Tests of the particle temperatures based on the work of Lu *et al.*¹¹⁵ is shown in Figure 4.17. The modelled centre temperature is not in good agreement with the centre temperature measured by experiment. The centre temperature according to the model remains relatively constant during drying because heat flowing towards particle centre is allocated to the evaporation of particle moisture at the particle sub-surface. However, the centre temperature was found experimentally to rise by around 300 K due to heat flowing conductively from air outside the particle to its centre via thermocouple B, which pierced the particle. Since the particle is relatively thick, $O_{2(g)}$ requires a longer time to diffuse towards the particle centre in the single-particle combustion model than in the work of Mason *et al.*¹¹⁷. When a significant amount of char in the particle centre is in contact with a large quantity of diffused $O_{2(g)}$, exothermic reaction occurs and raises the centre temperature to around 2300 K. In the experiment, this temperature jump to 2300 K was undetected, probably due to conductive loss of heat from the particle centre to the outside via thermocouple B. After the temperature jump, the temperature at the particle centre quickly decreases from 2300 K to 1250 K in less than 5 s due to rapid heat transfer through the porous particle towards the particle surface. In contrast, in the experiment, the temperature at the particle centre stayed at 1500 K until it dropped to 1250 K after around 50 s. Char oxidation produces a significant amount of $CO_{(g)}$. Reaction of $CO_{(g)}$ with $O_{2(g)}$ at the boundary layer generates heat, which in the experimental situation was transferred to the particle centre and established a constant elevated temperature for approximately 20 s. Conductive heat transferred from air outside the particle to the particle centre via thermocouple B quickly raised the overall temperature of the particle.

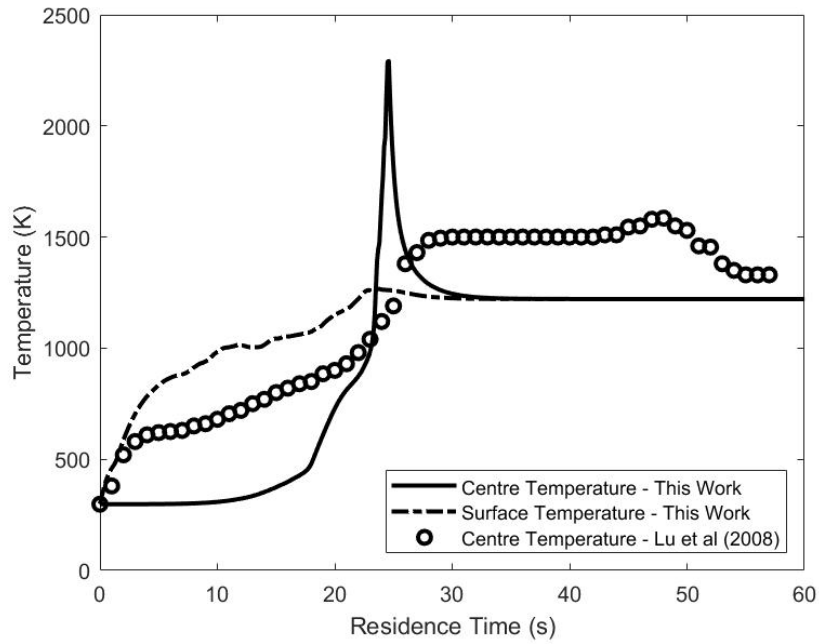


Figure 4.17 Comparison between the Temperature of the Particle Centre and Surface Obtained in This Work and the Temperature of the Particle Centre obtained in the Work of Lu et al.¹¹⁵

A numerical analysis reveals that the thermocouple B is capable of transferring heat conductively from air outside the particle to the particle centre in less than a second. The numerical analysis discretises the thermocouple B and calculates the transient temperature profile along the thermocouple B body. The temperature profile shown in Figure 4.18 exhibits that the temperatures in the thermocouple B become uniform at 1 s and indicates that the thermocouple B has uniform temperatures at all times subsequent.

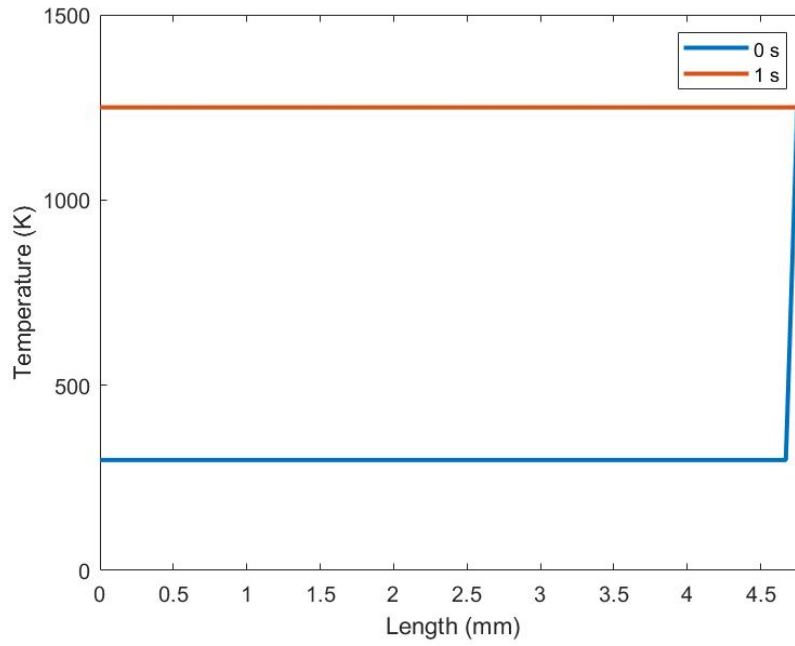


Figure 4.18 Thermocouple Temperature Profile during the Early Combustion Stage with the Surrounding Gas Temperature at 1,250 K

The distortion shown in Figure 4.17 between the experimental and the modelled profiles during drying due to rapid heat transfer within the thermocouple B is analytically evaluated via Equation 4.47.

$$m_T c_{PT} (T_{T_{dry}} - T_{eq_{dry}}) = m_{P_{aff}} c_{PP} (T_{eq_{dry}} - T_{P_{dry}}) \quad (E4.47)$$

m_T is the mass of the thermocouple B pierced in the particle in kg. c_{PT} is the heat capacity of the thermocouple B in $J\ kg^{-1}\ K^{-1}$. c_{PT} is assumed constant at $149.8\ J\ kg^{-1}\ K^{-1}$ for the thermocouple type B consisting of 82% of platinum and 18% of rhodium. $T_{T_{dry}}$ is the thermocouple temperature during drying in K. $T_{T_{dry}}$ is 1,250 K according to Figure 4.17. Since the particle size is relatively thick, the heat originating from the thermocouple type B flows to only a certain distance from the particle centreline. In this evaluation, the geometry of the thermally affected particle body is shown in Figure 4.19.

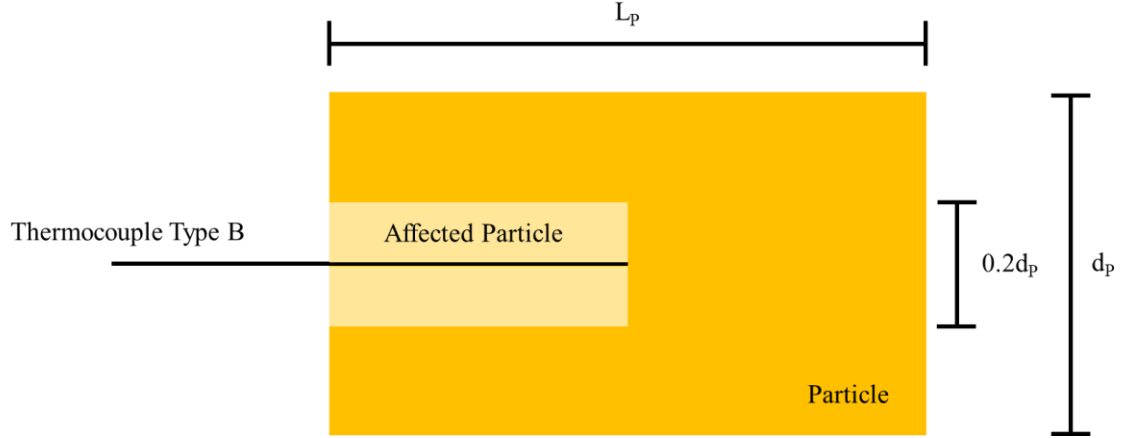


Figure 4.19 The Thermally Affected Particle Body Radially Surrounding the Thermocouple Type B

The diameter of the thermally affected particle body is assumed 0.2 of the diameter of the particle. The volume of the thermally affected particle body, $V_{P_{aff}}$, in m^3 is calculated via Equation 4.48.

$$V_{P_{aff}} = \frac{1}{4}\pi(0.2d_p)^2 \frac{L_p}{2} \quad (E4.48)$$

L_p and d_p are 0.095 m. The mass of the thermally affected particle body, $m_{P_{aff}}$, is calculated via Equation 4.49.

$$m_{P_{aff}} = V_{P_{aff}}\rho_P \quad (E4.49)$$

$T_{P_{dry}}$ is the temperatures of the thermally affected particle body in K, particularly around the particle centre, during drying. $T_{P_{dry}}$ is supposed to be at 298 K. Due to the thermocouple interference, the temperatures of the thermally affected particle body rises to $T_{eq_{dry}}$. $T_{eq_{dry}}$ is the equilibrium temperature during drying in K at around the thermally affected particle body. $T_{eq_{dry}}$ is calculated by rearranging Equation 4.47 into Equation 4.50.

$$T_{eq_{dry}} = \frac{\frac{m_T c_{PT} T_{T_{dry}} + T_{P_{dry}}}{m_{P_{aff}} c_{PP}}}{1 + \frac{m_T c_{PT}}{m_{P_{aff}} c_{PP}}} \quad (E4.50)$$

The calculation via Equation 4.50 generates $T_{eq_{dry}}$ of 712.5 K. Similarly, the thermocouple retards particle burnout by transferring heat from the thermally affected particle body to the surrounding air during char oxidation since the temperatures at the thermally affected particle body are higher than the temperatures at the thermocouple. The combustion retardation is evaluated via Equation 4.51.

$$m_T c_{PT} (T_{eq_{C,ox}} - T_{T_{C,ox}}) = m_{C_{aff}} c_{PC} (T_{C_{C,ox}} - T_{eq_{C,ox}}) \quad (E4.51)$$

m_{caff} is the mass of the thermally affected char body in kg. c_{PC} is the char heat capacities in $\text{J kg}^{-1} \text{K}^{-1}$. $T_{T_{C,ox}}$ is the thermocouple temperature during drying in K. $T_{T_{C,ox}}$ is also 1,250 K. $T_{C_{C,ox}}$ is the temperatures of the affected char body, approximately at around 2,300 K according to Figure 3.18. $T_{eq_{C,ox}}$ is the equilibrium temperatures during char oxidation in K. Equation 4.51 is rearranged into Equation 4.52.

$$T_{eq_{C,ox}} = \frac{\frac{m_T c_{PT} T_{C,ox}}{m_{caff} c_{PC}} + T_{C_{C,ox}}}{1 + \frac{m_T c_{PT}}{m_{caff} c_{PC}}} \quad (\text{E4.52})$$

The calculation via Equation 4.52 generates $T_{eq_{C,ox}}$ of 1,307.6 K, indicating the temperatures drop due to heat loss to the surrounding gas via the thermocouple.

Figure 4.20 illustrates a comparison between the modelled fractional residual particle mass and that obtained in experiments performed by Mehrabian *et al.*²⁴³. This figure shows that the particle lost mass earlier in the experiment than would be expected according to the model, due to a higher overall temperature that promoted more rapid pyrolysis and char oxidation rate than predicted by the model.

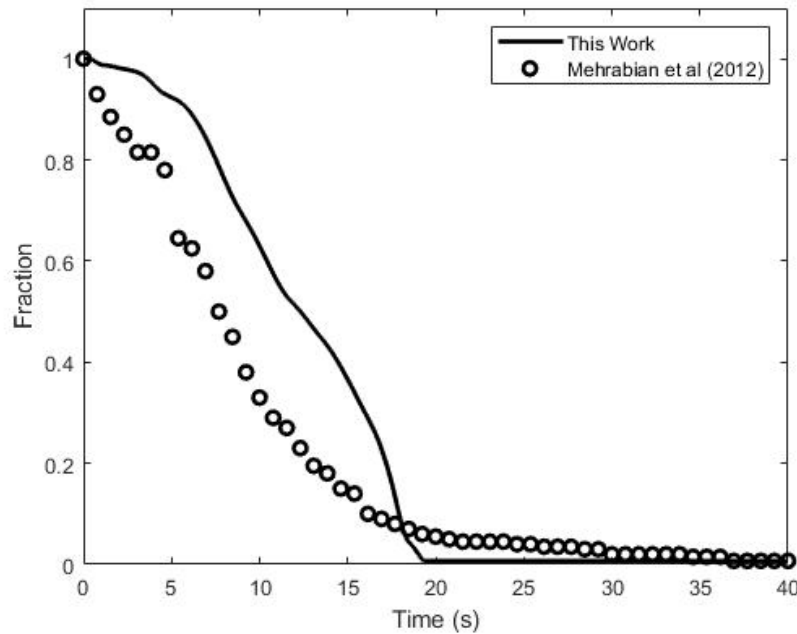


Figure 4.20 Comparison between Fractional Residual Particle Mass Obtained in This Work and in the Work of Mehrabian *et al.*²⁴³

The tests of particle temperatures obtained in this work by comparison with the work of Lewtak and Marek²⁴² is shown in Figure 4.21. The modelled temperature of the particle centre during the drying

stage is in good agreement. The particle size in this experimental case was considerably smaller at about 2 mm than the particle size in the previous case of Lu *et al.*¹¹⁵. This smaller particle size improved the rate of conductive heat transfer towards the particle centre. Thus, the temperature of the particle centre rose at a faster rate than was seen in the work of Lu *et al.*¹¹⁵. Rapid intra-particle heat transfer enhanced the rate of the products of gasification reactions and their release to the particle boundary layer. The homogeneous reaction of these products with $O_{2(g)}$ in the boundary layer may have heated the thermocouple which pierced the particle, allowing the heat to flow conductively to the particle centre. This heated particle centre established a discrepancy between the temperature of the particle centre predicted by the model and the temperature measured at the particle centre in the work of Lewtak and Marek during the volatilisation stage, at around 3 s to 4 s. At around 4.3 s, the temperature at the particle centre calculated by the model reaches its peak due to char oxidation. After 4.3 s, this modelled particle centre temperature plummets to around 930 K. The temperature of the particle centre found by experiment reached a similar peak temperature but subsequently decreased gradually due to the conductive heat that was sourced from the homogeneous reactions of CO and H_2 with $O_{2(g)}$ in the boundary layer.

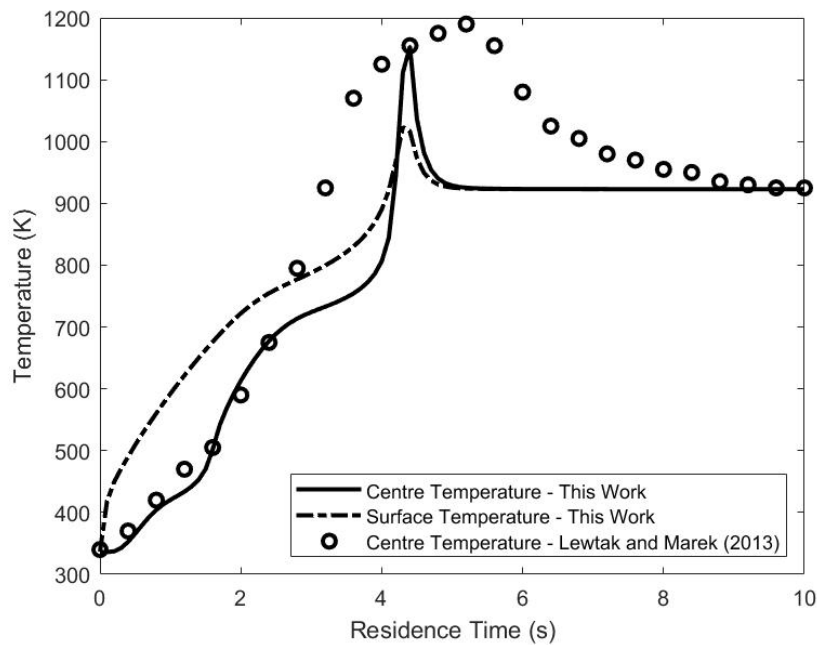


Figure. 4.21 Comparison between Particle Centre Temperature Obtained in This Work and in the Work of Lewtak and Marek²⁴²

4.3 Concluding Remarks

The fundamental concepts of the single-particle combustion model are based on numerous works conducted previously by many researchers. The development of the single-particle combustion model began with pulverised coal combustion that was modelled through use of a lumped particle model. Works published after this attempted to evaluate large particles that were often used in grate-firing and fluidised-bed boilers. It was found that combustion of large particles featured intra-particle temperature and gas concentration gradients that caused non-uniform combustion throughout the particle body. Consequently, extensive works were conducted to evaluate overlapping phenomena of moisture drying, volatilisation, and char oxidation. Later research utilised the single-particle combustion model to develop understanding of solid-fuel combustion in boilers. CFD was later introduced as a platform to obtain more accurate results from the single-particle combustion model. However, the single-particle combustion model explained in this thesis does not feature the latest developments in order to avoid unnecessary complexities and to provide suitability with chemical equilibrium tools. This is further explained in Chapters 5 and 6.

Intra-particle heat and mass transfer rates have been determined with partial differential equations as functions of time, particle length, and particle radius. The partial differential equations have been reduced to ordinary differential equations to reduce numerical complexity. The differential equation reduction has been conducted by discretising the particle into a rectangular area of nodes with size of m -times- n , where m is the number of nodes for the radius and n is the number of nodes for the length. The axial centreline of the particle and the middle of the cylindrical section have been set as internal boundaries.

Intra-particle gas thermodynamic properties, e.g. heat capacity and thermal conductivity, and the particle's physical properties, e.g. porosity and permeability, have been considered essential to the single-particle combustion model. Each property is inherent in solid-fuel biomass combustion and has been mathematically included in the ordinary differential equations as functions of temperature.

The behaviour of the particle surface is not only influenced by intra-particle heat and mass transfer but also by convective heat and mass transfer due to flowing air that surrounds the particle. Convective heat and mass transfer are essentially influenced by combustion operating conditions, e.g. air velocity, air temperature, and air pressure. Convective heat and mass transfer have been mathematically expressed with Nusselt and Sherwood numbers. These numbers are often determined with correlations specific to particle shape.

The boundary layer has also been discretised as a platform to determine temperature and gas concentration profiles in it. The temperature and gas concentration in the boundary layer have also been calculated through use of ordinary differential equations. An attempt to run the single-particle

combustion model equipped with a discretised boundary layer was made. However, the model run was not finished due to expensive computation. From that point onward, the discretised boundary layer was discarded from the single-particle combustion model.

Homogeneous and heterogeneous reactions contribute to gas occurrence and temperature within the particle. Reaction rate equations and their kinetic parameters given for the single-particle combustion model have been based on experimental results obtained from several previous works. The rate equations have been integrated with intra-particle heat and mass transfer equations.

The single-particle combustion model results have been compared with the results from three experimental works, namely: Mason *et al.*¹¹⁷, Lu *et al.*¹¹⁵, and Lewtak and Marek²⁴². The comparisons highlight the following:

- The single-particle combustion model is capable of modelling previous experimental works.
- Particle size affects particle combustion efficiency due to resistance to intra-particle heat and mass transfer as size increases.
- The single-particle combustion model results feature not only particle temperature and gas concentration profiles at the particle's surface and centre, but also contours of temperature and gas concentration distribution.
- Experimental setup can compromise tests of the single-particle combustion model. Thermocouples that pierce the particles during the experiments could potentially transfer heat conductively from air outside the particle to the particle centre or vice versa. This conductive heat could quickly raise the temperature of the particle centre, even during the drying stage. A thermocouple used to measure the temperature at the particle surface could also read false temperatures due to particle shrinkage. A thermal imaging camera may be a viable option for reading the particle surface temperature.

Chapter 5

Entrained-flow Combustion Model

This chapter discusses the development of the entrained-flow combustion model based on the entrained-flow burner at the Pilot-scale Advanced CO₂ Capture Technology (PACT) facility at the University of Sheffield. The entrained-flow combustion model calculates the bulk profiles and the intra-particle profiles of individual particles falling through the entrained-flow burner. The entrained-flow combustion model is integrated with the single-particle combustion model in calculating the intra-particle profiles. All the calculated profiles are later used in Chapter 6 as parameters to predict the fate and occurrence profiles of AFEs and TEs in both particles and bulk.

However, the PACT facility entrained-flow burner is limited in reflecting industrial-scale solid fuel combustion. The burner is unable to provide data on both high- and low-temperature ash deposition due to lack of water wall and intra-burner heat exchanger pipe assembly. The high-temperature ash deposition on the burner wall surface might also not be sufficient to reflect the slagging in industrial scale boilers due to relatively low burner height as later described in Section 5.1. Rather, the burner was designed to explore combustion of different solid fuels. Nevertheless, at the moment, the PACT facility entrained-flow burner is the only pilot combustion equipment available that provides comprehensive online data of the intra-burner temperatures and gas concentrations and the AFE and TE downstream concentrations for model development in this thesis. The developed model could potentially be extended in the future for industrial-scale solid fuel combustion.

Section 5.1 discusses the operating conditions of the PACT facility entrained-flow burner along with associated combustion work. Section 5.2 explains the importance of the mathematical contribution of particle aspect ratios to the entrained-flow combustion model. Section 5.3 explains mathematical concepts of the entrained-flow combustion model. The results from the entrained-flow combustion model are validated with the results from combustion experiments in the PACT facility entrained-flow burner.

5.1 Operating Conditions

The PACT facility entrained-flow burner located in Sheffield, South Yorkshire, has been extensively used to combust a wide range of coals and biomasses. Combustion experiments in the burner are conducted to evaluate several aspects of solid-fuel combustion, e.g. temperature, gas concentrations, flame stability, inorganic emissions, probe ash deposition, and turbine and carbon capture performances. A three-dimensional diagram of the whole combustion unit including the burner is illustrated in Figure 5.1.¹⁷⁵ A flow diagram for this unit is shown in Figure 5.2.

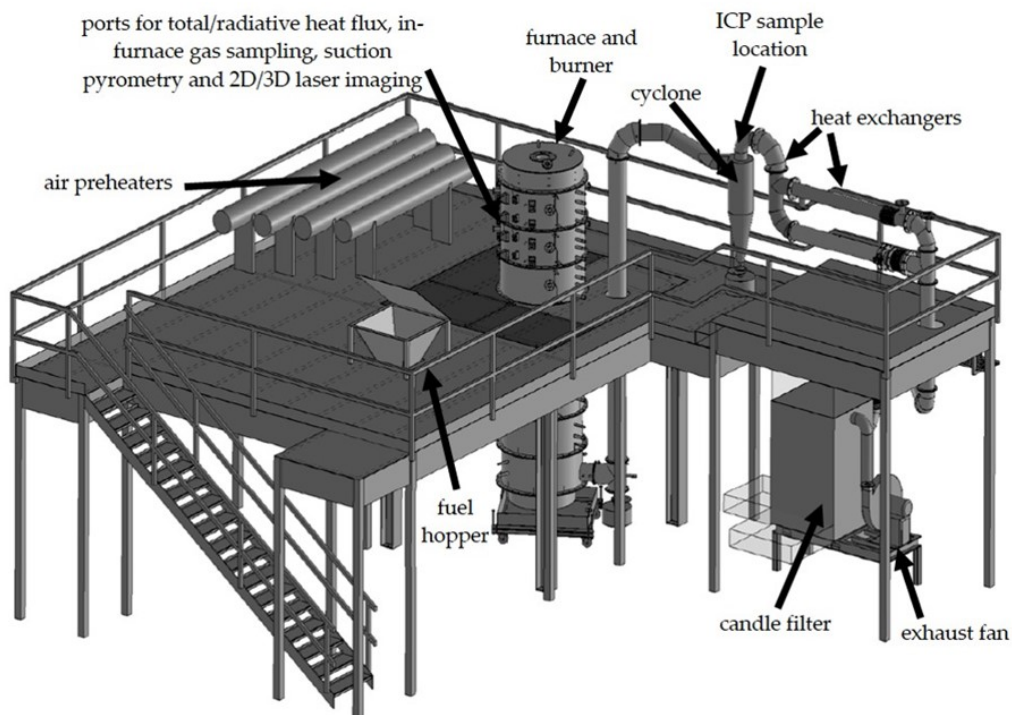


Figure 5.1 Three-dimensional diagram of the PACT Facility 250kW Combustion Unit

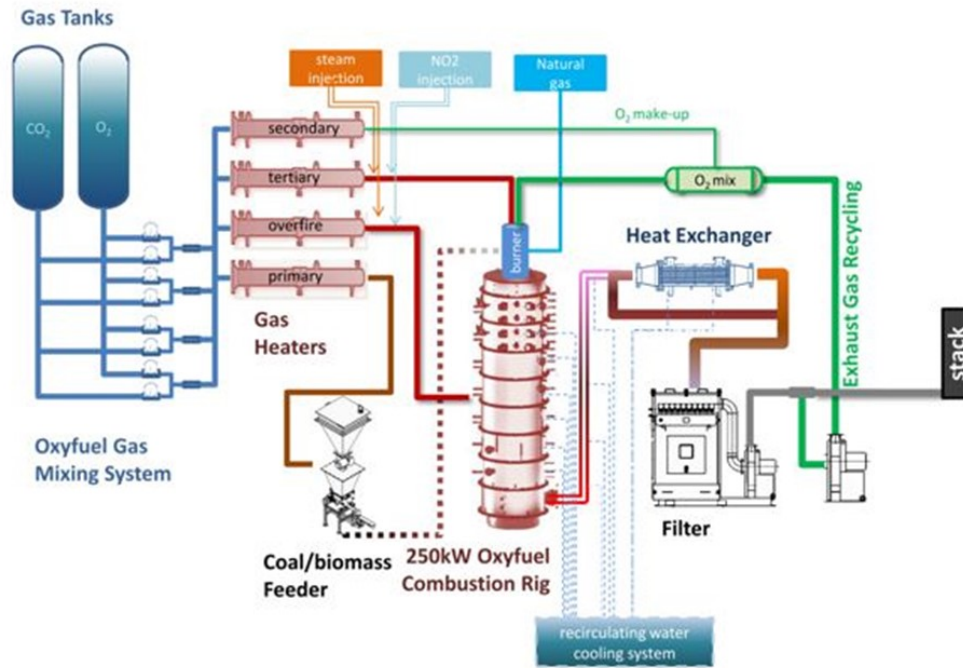


Figure 5.2 Process Flow Diagram for the PACT Facility 250kW Combustion Unit

The combustion unit is made up of three major stages: the upstream, burner and downstream stages. In the upstream stage, combustion gases, e.g. air, $\text{O}_{2(g)}$, and $\text{CO}_{2(g)}$, are stored in designated gas tanks. The combustion gases are pumped from the tanks to the gas pre-heater. The gas pre-heater comprises four identical heat exchangers: primary secondary tertiary and overfire pre-heaters. Gas from the primary pre-heater flows through the bottom of the solid fuel feeder and is mixed with the solid fuel. The mixture flows to the top of the burner and enters the burner through a feed introducer. When air is used as the combustion gas, air from the secondary pre-heater flows to the burner top. On the other hand, in oxy-combustion, $\text{O}_{2(g)}$ flows from the outlet of the secondary pre-heater as supplementary $\text{O}_{2(g)}$ and merges with recycled residual gas that flows from the downstream stage back to the burner. Gas from the tertiary pre-heater flows directly to the top of the burner. In some cases, complete burnout is achieved by addition of extra gas flow from the overfire pre-heater to any middle axial section of the burner.

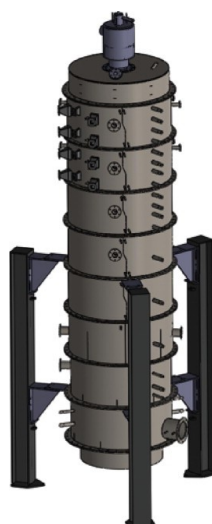


Figure 5.3 *Three-Dimensional Diagram of the PACT Facility 250kW Entrained-flow Burner*

The burner is a 250kW cylindrical furnace provided by Doosan Babcock, as shown in Figure 5.3.²⁴⁴ The cylinder is 4 m in height and 0.9 m in internal diameter. The cylinder consists of eight axial sections separated from each other by 0.1 m thick refractories. The height of each section is 0.5 m. The uppermost section is equipped with a feed introducer through which gas and solids enter the burner. The feed introducer is a cylinder with three concentric annuli as shown in Figure 5.4. Each annulus is connected to each respective pre-heater. Solid fuel and the gas flow vertically to the bottom of the burner. Tools for temperature and gas concentration measurements are installed at various heights to measure changes of temperature and $O_{2(g)}$ molar fraction when the burner is in use. At around 2.8 m from the burner top, a probe is installed to enable ash deposition analysis as part of the ash deposition process. Bottom ash is collected at an ash collector positioned below the lowermost section. Residual gas is released from a small nozzle at the side of the lowermost section.

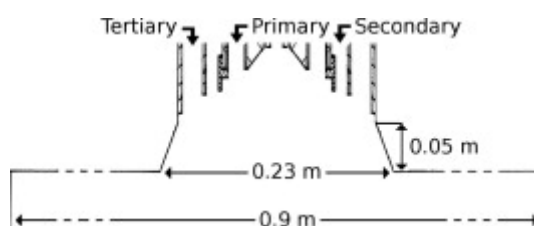


Figure 5.4 *Two-dimensional Diagram of the Feed Introducer in the PACT Facility 250kW Entrained-flow Burner*

In the downstream section, the gas flows to the cyclone, at which light bottom ash entering the downstream section is separated from the gas. After the separation, the exhaust gas goes to the heat exchanger. A small portion of exhaust gas at the cyclone outlet is delivered to the on-line ICP system

for measurement of the concentrations of inorganic elements. The on-line ICP is further explained in Chapter 7. Cooled residual gas from the heat exchanger is delivered to the candle filter. The temperature of residual gas as it enters the candle filter is low enough to form particulate matter (PM). PM is separated from the residual gas at the candle filter. Finally, residual gas is discharged at the stack. For oxy-combustion, the discharged residual gas is sent to a carbon-capture unit.

White wood and recycled wood were combusted in the PACT entrained-flow burner with two combustion gases, air and oxy27 (27% O₂/73% CO₂), which are listed in Table 5.1. Both gas compositions were modelled to evaluate the influence of bulk O_{2(g)} quantities and concentrations on the fate and occurrence of AFEs and TEs of particles and bulk. The integration of the entrained-flow combustion model with both gas compositions and the chemical equilibrium calculation is discussed in depth in Chapter 6 and 7.

The chemical properties and flow rates of both types of wood are shown in Table 3.1. Since both white wood and recycled wood are woody biomass, their chemical compositions are not significantly different. However, recycled wood has an ash concentration that is almost five times higher than that in white wood. Recycled wood is considered to resemble waste wood due to its significant ash content, whilst white wood is regarded as virgin wood. Although different ash contents might not establish distinctive temperature and combustion gas profiles of the two woody biomasses, the occurrence and fate profiles of inorganic elements might exhibit contrasting behaviours. Further explanations of the occurrence and fate of inorganic elements are discussed in Chapters 7 and 8.

Table 5.1 Inlet Gas Operating Conditions at the PACT Entrained-flow Burner

Parameter	Air-combustion	Oxy27-combustion
Inlet Gas Flow Rate (mol s ⁻¹)	2.789	1.913
	CO _{2(g)} (0)	CO _{2(g)} (1.396)
	O _{2(g)} (0.586)	O _{2(g)} (0.517)
	N _{2(g)} (2.203)	N _{2(g)} (0)
Inlet Gas Temperature (K)	480	480
Inlet Gas Composition (% Volume)	CO _{2(g)} (0)	CO _{2(g)} (73)
	O _{2(g)} (21)	O _{2(g)} (27)
	N _{2(g)} (79)	N _{2(g)} (0)

5.2 Particle Aspect Ratio Profile

PSD is one of the most important parameters that affects the performance of the entrained-flow combustion. PSD influences the quality of burnout, ignition delay, and flame stability. A high proportion of fine particle sizes improves combustion efficiency due to improved intra-particle heat and mass transfer. However, production of finely-sized particles requires additional time and energy for milling.

Several studies have been conducted to evaluate optimal particle sizes to establish stable flames. Hein and Bemtgen²⁴⁵ conducted a pulverised-coal combustion experiment and found that coal particles with diameter of 4-8 mm and length of 1-2 cm were of the maximum coal particle geometry to achieve complete burnout in a pilot pulverised-coal boiler. Savoilanen²⁴⁶ suggested that particle micronisation was unnecessary since pulverised solid fuel with 100% of particle size less than 8 mm or 30-40% of particle size less than 1 mm was sufficient to sustain flame stability in a modern boiler. In addition, particle micronisation is not recommended due to high cost, high energy consumption, and health risks associated with dust explosions.

The direction of flow in the boiler system also affects burnout time. An entrained-flow boiler that features upward flow has been shown to exhibit higher combustion efficiency than an entrained-flow boiler with downward flow, owing to greater residence time. In the upward flow design, gas is initially unable to convey particles since the gravitational force on the particle mass dominates over the buoyancy force. Once the particle mass becomes reduced due to combustion, the particles flow upward along with the gas.¹²⁶ For a fluidised-bed boiler, the particle size is typically within 0.5-1.5 mm. Outside this range, smaller particles fly upwards whilst larger particles are dropped to the bottom of the bed.²⁴⁷

To produce a model, a common assumption is made that the solid fuel particle is of a regular geometrical shape.²⁴⁸ However, pulverised biomass particles' size and shapes has been proven to be irregular, as explained in Chapter 4.²⁴⁹ Biomass particles are often assumed to be cylindrical since biomass commonly exhibits a natural, elongated form.²⁵⁰ Cylindrical geometry enables heat and mass transfer not only in the radial direction but also in the axial direction. Therefore, the particle aspect ratio influences particle burnout. Ignoring the aspect ratio by assuming that all particles are spherical may result in production of an inaccurate model. Gera *et al.*²⁵¹ found that the cylindrical shape has 44% more surface area and exhibits a 31% faster burnout rate than a spherical shape of equivalent volume.

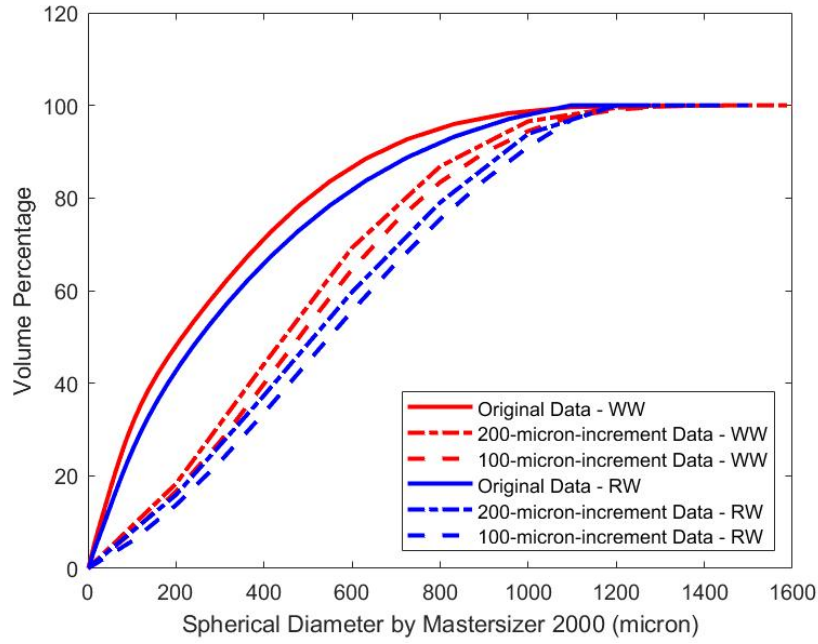


Figure 5.5 Cumulative PSD of White Wood and Recycled Wood

PSD of the white and recycled wood was measured with the Malvern Mastersizer 2000, and is presented in Figure 5.5. The original PSD data generated from the Malvern Mastersizer 2000 is titled as *Original Data – WW* for white wood and *Original Data – RW* for recycled wood. However, more than 20 measurements were made, and incorporation of this amount of data was computationally expensive. Therefore, 100-micron-increment data points were chosen to reduce the number of modelled particle sizes.

The particle sizes measured by the Malvern Mastersizer 2000 and shown in Figure 5.5 were measured as the diameter of particles as if the shape of the particles was near-spherical. These values do not represent the actual particle geometry and need to be converted into cylindrical shapes as expressed in Equation 4.1.

$$\frac{1}{4} \pi \frac{L^3}{A_R^2} = \frac{4}{3} \pi \left(\frac{D_{MS2000}}{2} \right)^3 \quad (E5.1)$$

L is particle length in m. D_{MS2000} is particle diameter in m as given in Figure 5.5. A_R is particle aspect ratio. To obtain A_R , a microscopic analysis was conducted to measure the actual particle aspect ratio. An example of a microscopic image of pulverised biomass particles is illustrated in Figure 5.6. Each observed particle length and diameter was measured visually. According to the analysis of the collected data on particle lengths and diameters based on visual observation, the particle aspect ratio depended

on particle length, as shown in Figure 5.7. The dependency of particle aspect ratio on particle length is formulated in Equation 5.2.

$$A_R = f(L) \quad (E5.2)$$

Equation 5.2 is substituted into Equation 5.1 to calculate L . Particle diameter is calculated via Equation 5.3.

$$D = \frac{L}{A_R} \quad (E5.3)$$

Finally, particle length and radius distributions were obtained and are shown in Figure 5.8. Since 100-increment data points are still considered computationally expensive for the entrained-flow combustion model, 200 micron-increment data points were used with the same method, with particle length and radius distributions shown in Figure 5.9.

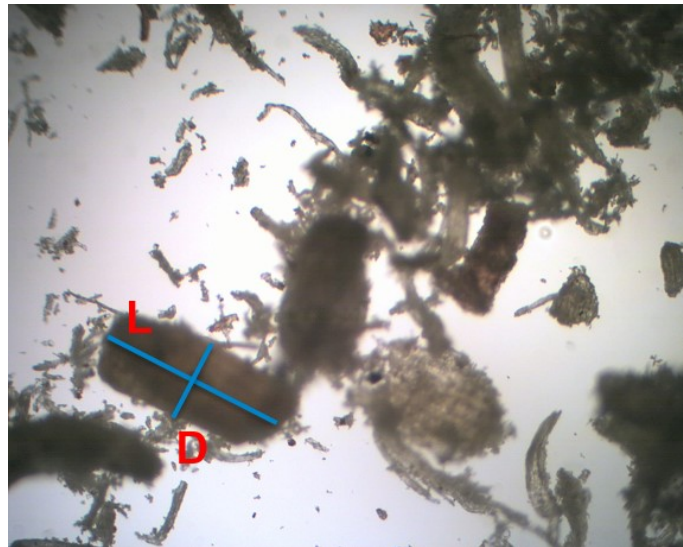


Figure. 5.6 Microscopic Image of White Wood

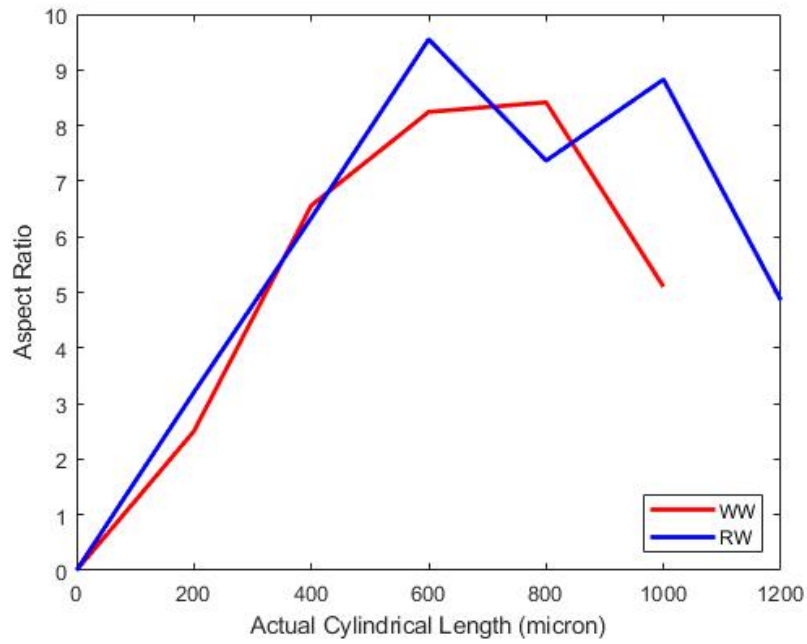


Figure 5.7 Particle Aspect Ratio as a Function of Particle Length

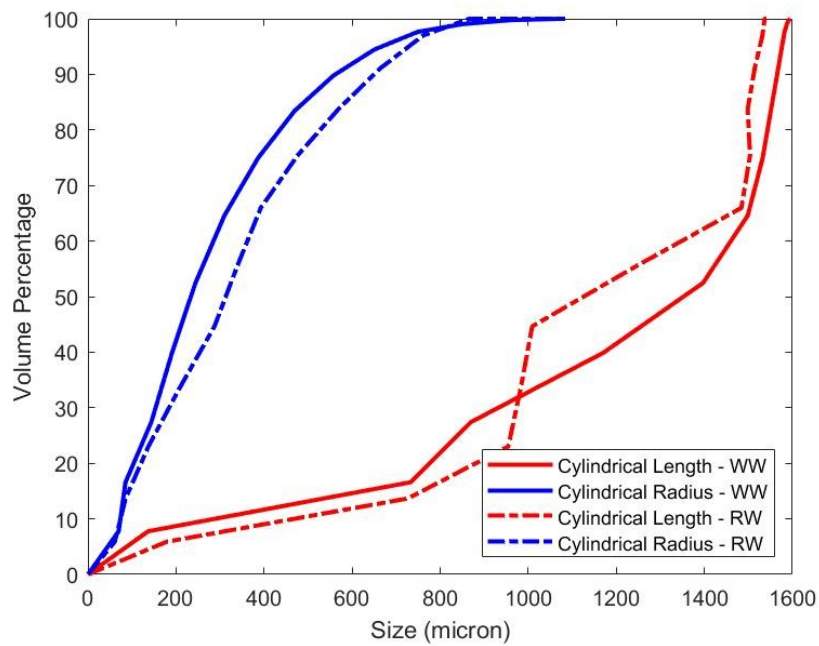


Figure 5.8 Cumulative Particle Length and Radius Distribution with 100-micron-increment Data Points

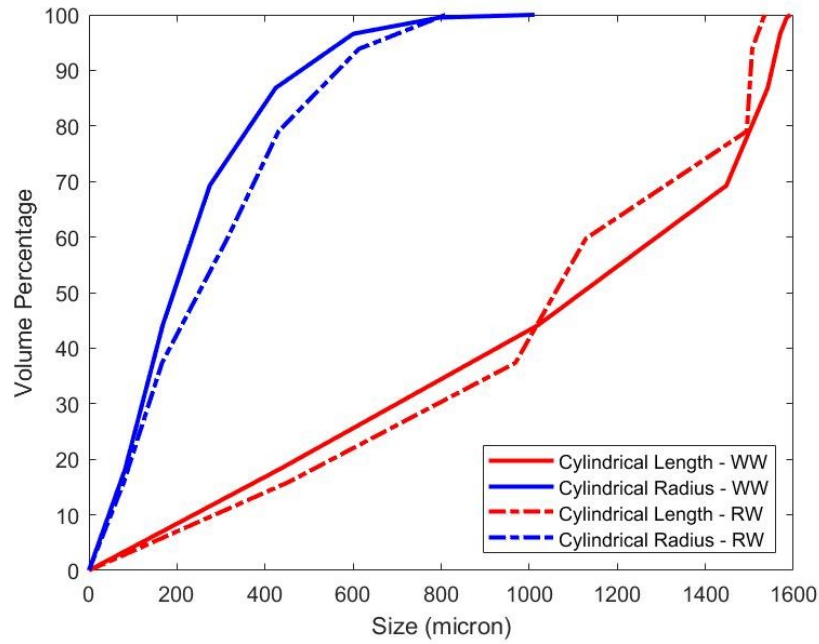


Figure 5.9 Cumulative Particle Length and Radius Distribution with 200-micron-increment Data Points

5.3 Mathematical Concept of the Model

This historical evidence in Chapter 2 shows that CFD has been widely implemented during development of the entrained-flow combustion model. However, the entrained-flow combustion model investigated during the work for this thesis does not utilise CFD as its platform. Rather, a one-dimensional plug-flow calculation is used. The advantages of the one-dimensional plug-flow calculation over CFD are as the followings

- The calculation of both intra-particle profiles of individual particle and burner profiles simultaneously with CFD is computationally expensive and not feasible at this time. However, CFD use may be considered in future works.
- Intra-particle profiles that are generated for use in the entrained-flow combustion model provide a platform for consideration of intra-particle inorganic compound concentrations in Chapter 6. This platform aims to predict liquid formation on particle surfaces, leading to evaluation of particle sticking probability.

In the one-dimensional plug flow model, the PACT facility burner is discretised to provide a platform for consideration of thermodynamic property profiles as a result of combustion. The burner is discretised into numerous numbers of axial sections with a uniform length of thickness for each axial

section, as shown in Figure 5.10. An axial section is called a “thin slice” in this thesis for consistency. Calculation of the processes in a thin slice encompasses intra-particle heat and mass transfer, gas release rates from particles, and homogeneous combustion of bulk gas particles.

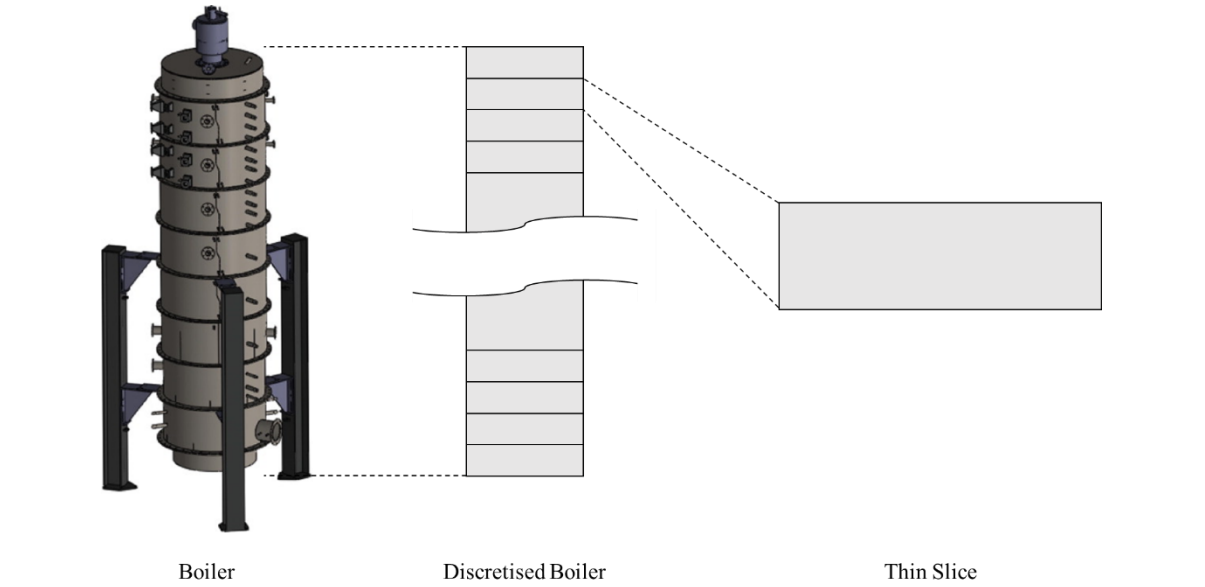


Figure 5.10 Discretisation of the PACT Facility Entrained-flow Burner

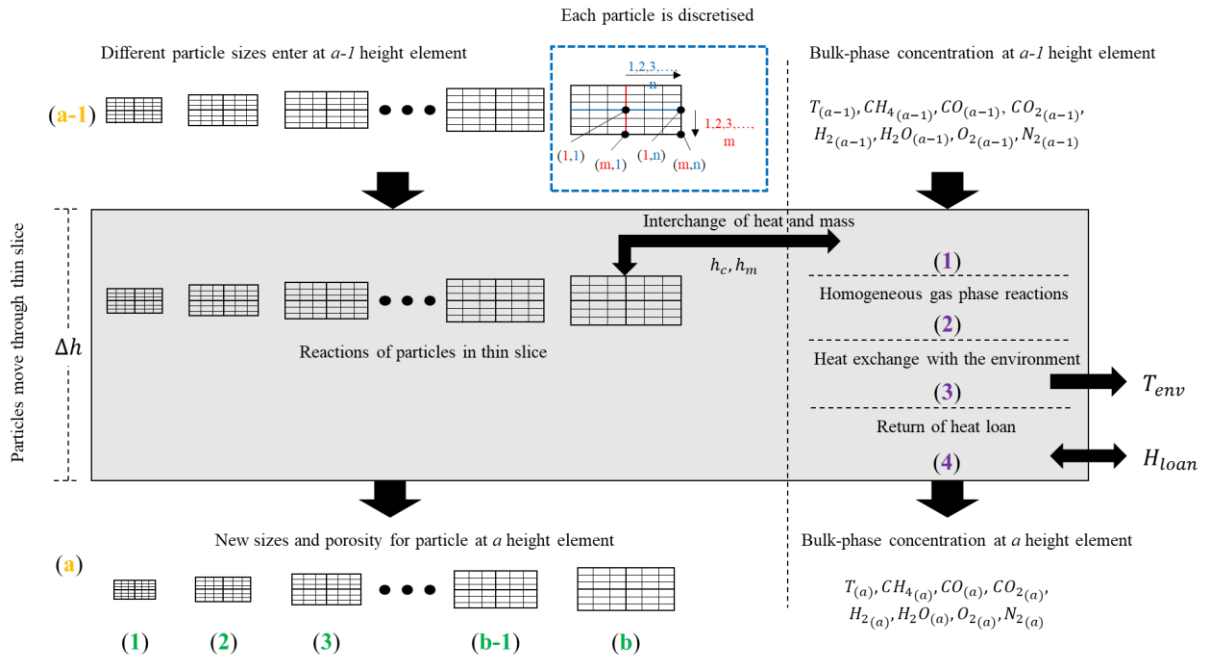


Figure 5.11 Combustion Model Structure of a Thin Slice with Discretised Particles

The route of calculation in a single thin slice is illustrated in Figure 5.11. The thin slice is represented by a grey rectangle with a thickness of Δh . The grey rectangle is divided by a vertical dashed line into the particle phase on the left-hand side and the bulk phase on the right-hand side. The rectangular upper side is of height $a - 1$ and the rectangular lower side is of height a . Particles enter the rectangle at the upper side. Their properties have been generated in another rectangle located above the current rectangle. The particles entering the rectangle are grouped into various size clusters based on Figure 5.9, e.g. from particle size cluster 1 to particle size cluster b . Each particle size is discretised radially and axially according to Figure 4.2.

Particles in the entrained-flow combustion model behave differently from particles in the single-particle combustion model as they are not stationary and they exhibit falling velocities. Whilst particles are falling, bulk gas is also flowing to the burner bottom at a certain velocity. Parameters of convective heat and mass transfer depend on relative velocity, which is defined as the particle falling velocity relative to that of the flowing bulk gas. The falling velocity of particle b , $v_{p(b)}$, is calculated via in Appendix C.

Intra-particle temperature and gas concentration at the particle's interior at height of index a are calculated with the single-particle combustion model explained in Chapter 4. Each differential term is divided by $v_{p(b)}$ to convert the time-based calculation to the height-based calculation.

Particle mass is estimated as the ratio of the current particle density to the initial particle density, as shown in Equation 5.4.

$$m_{p(a,b)} = \left(\frac{\sum_{i=1}^n \sum_{m=1}^{m_s} \sum_{n=1}^{n_s} \rho_{ip(a-1,b,m,n)}}{\sum_{i=1}^n \sum_{m=1}^{m_s} \sum_{n=1}^{n_s} \rho_{ip(a,b,m,n)}} \right) m_{p(a-1,b)} ; i = 1 \text{ for wood, } 2 \text{ for tar, etc.} \quad (\text{E5.4})$$

The indices $(1, b, m, n)$ indicate the initial properties of nodes m and n in particles of size cluster b . The change of particle volume is assumed to correlate linearly with the change of particle mass as shown in Equation 5.5.

$$V_{p(a,b)} = \frac{m_{p(a,b)}}{m_{p(a-1,b)}} V_{p(a-1,b)} \quad (\text{E5.5})$$

The convective mass transfer equation given in Equation 5.6 is used to calculate the gas release rate from or gas penetration to the particle side surface.

$$\dot{F}_{ip(b,m_s,n)} = h_{m(b)} A_{p(b,m_s,n)} \left(\frac{C_{ip(b,m_s,n)}}{\varepsilon_{p(b,m_s,n)}} - C_{i(a-1)} \right) \quad (\text{E5.6})$$

Here, $\dot{F}_{ip(b,m_s,n)}$ is the molar release or penetration rate in mol s⁻¹ of gas i from a single particle at nodes m_s and n in particle size cluster b . $C_{ip(b,m_s,n)}$ is surface pore gas concentration in mol m⁻³ of the single particle at nodes m_s and n in particle size cluster b , with $\varepsilon_{p(b,m_s,n)}$ as porosity at the respective node.

For the particle base surface, Equation 5.7 is used.

$$\dot{F}_{ip(b,m,n_s)} = h_{m(b)} A_{p(b,m,n_s)} \left(\frac{C_{ip(b,m,n_s)}}{\varepsilon_{p(b,m,n_s)}} - C_{i(a-1)} \right) \quad (\text{E5.7})$$

$A_{p(b,m,n)}$ is the radial surface area of the node with coordinates $\binom{m_s}{n}$. $A_{p(b,m,n)}$. Its geometry is wheel-shaped, with width ranging from half the forward distance to half the backward distance, as illustrated in Figure 5.12.

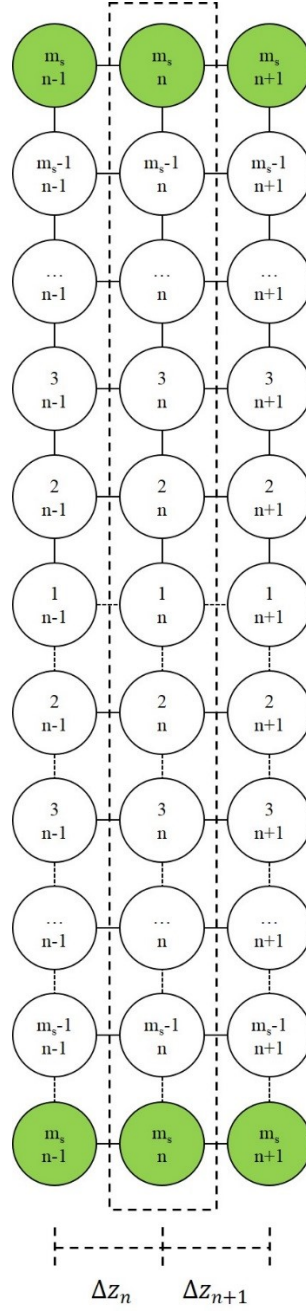


Figure 5.12 Particle Side Surface Area of Node $(m_s)_n$

$A_{p(b,m_s,n)}$ is mathematically described in Equation 5.8. At the particle edge and middle cylindrical section, Equations 5.9 and 5.10 apply.

$$A_{p(b,m_s,n)} = \pi d_{p(b)} (\Delta z_{n+1(b)} + \Delta z_{n(b)}) \quad (\text{E5.8})$$

$$A_{p(b,m_s,n_s)} = \pi d_{p(b)} \Delta z_{n_s-1(b)} \quad (\text{E5.9})$$

$$A_{p(b,m_s,1)} = \pi d_{p(b)} \Delta z_{2(b)} \quad (\text{E5.10})$$

For the particle base, the axial surface area of the node with coordinates $\binom{m}{n_s}$, $A_{p(b,m,n_s)}$, has a geometry of a Saturn ring, as represented in Figure 5.13. The width of the ring ranges from half the forward distance to half the backward distance.

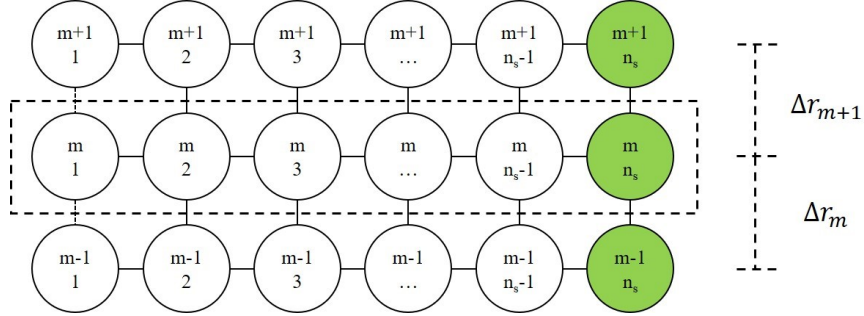


Figure 5.13 Particle Base Surface Area of Node $\binom{m}{n_s}$

$A_{p(b,m,n_s)}$ is calculated via Equation 5.11. Equations 5.12 and 5.13 are used to calculate the base surface area of nodes $\binom{m_s}{n_s}$ and $\binom{1}{n_s}$.

$$A_{p(b,m,n_s)} = 2 \left(\pi \left(r_{m(b)} + \frac{\Delta r_{m+1(b)}}{2} \right)^2 - \pi \left(r_{m-1(b)} + \frac{\Delta r_{m(b)}}{2} \right)^2 \right) \quad (\text{E5.11})$$

$$A_{p(b,m_s,n_s)} = 2 \left(\frac{1}{4} \pi d_{p(b)}^2 - \pi \left(r_{m_s-1(b)} + \frac{\Delta r_{m_s(b)}}{2} \right)^2 \right) \quad (\text{E5.12})$$

$$A_{p(b,1,n_s)} = 2 \pi \Delta r_{2(b)}^2 \quad (\text{E5.13})$$

The total rate of gas released from or penetrating to a single particle, $\dot{F}_{ip(b)}$, is the sum of the gas release molar rate at each surface node, as expressed in Equation 5.14.

$$\dot{F}_{ip(b)} = \sum_{n=1}^{n_s} \dot{F}_{ip(b,m_s,n)} + \sum_{m=1}^{m_s} \dot{F}_{ip(b,m,n_s)} \quad (\text{E5.14})$$

$\dot{F}_{ip(b)}$ is in mol s^{-1} . Equations 5.15 and 5.16 express the gas rate of release from, $\dot{F}_{ip_{rel}(b)}$, and penetration to, $\dot{F}_{ip_{pen}(b)}$, a particle.

$$\dot{F}_{ip_{rel}(b)} = \begin{cases} \dot{F}_{ip(b)}, & \dot{F}_{ip(b)} > 0 \\ 0, & \dot{F}_{ip(b)} \leq 0 \end{cases} \quad (\text{E5.15})$$

$$\dot{F}_{ip_{pen(b)}} = \begin{cases} \dot{F}_{ip(b)}, & \dot{F}_{ip(b)} \leq 0 \\ 0, & \dot{F}_{ip(b)} > 0 \end{cases} \quad (E5.16)$$

The number of particles in a size cluster is determined by use of Equation 5.17.

$$N_{p(b)} = \frac{x_{V(b)} \frac{F_{sf}}{\rho_{sf}}}{\frac{1}{4} \pi d_{p0(b)}^2 l_{p0(b)}} \quad (E5.17)$$

$N_{p(b)}$ is the number of particles with size of cluster b in s^{-1} . F_{sf} and ρ_{sf} are as-received mass flow rate and density of solid fuel in $kg\ s^{-1}$ and $kg\ m^{-3}$. $d_{p0(b)}$ and $l_{p0(b)}$ are the diameter and length in m of a particle of size cluster b . $N_{p(b)}$ is used to calculate size-cluster released and penetrating gas molar rates, $\dot{F}_{ip_{rel(b)}}$ and $\dot{F}_{ip_{pen(b)}}$, as expressed in Equations 5.18 and 5.19.

$$\dot{F}_{ip_{rel(b)}} = N_{p(b)} \int_{h(a)}^{h(a-1)} \frac{\dot{F}_{ip_{rel(b)}}}{v_{p(b)}} dh \quad (E5.18)$$

$$\dot{F}_{ip_{pen(b)}} = N_{p(b)} \int_{h(a)}^{h(a-1)} \frac{\dot{F}_{ip_{pen(b)}}}{v_{p(b)}} dh \quad (E5.19)$$

$\dot{F}_{ip_{rel(b)}}$ and $\dot{F}_{ip_{pen(b)}}$ are in $mol\ s^{-1}$.

According to Figure 5.11, the bulk gas temperature, concentration, and velocity require four stages of calculation:

- Stage 1
Gas released from, and penetrating into, the particle alters bulk gas concentration.
- Stage 2
Due to exothermic oxidation, the bulk gas temperature increases. Increased bulk gas temperature decreases bulk gas concentration and increases bulk gas velocity.
- Stage 3
The burner material enables loss of a certain quantity of heat from the bulk gas. Heat loss reduces the bulk gas temperature and increases the bulk gas concentration.
- Stage 4
During the combustion, introduced gas is heated and pyrolyses the solid fuels near the feed. The bulk gas temperature increases due to reaction of the gasification products released from particles with $O_{2(g)}$. After the reaction, some of the bulk gas is recirculated to the top of the burner and heats another batch of introduced gas. The entrained-flow combustion model

investigated in the research described in this thesis was limited to investigating steady combustion. Bulk gas entering the burner at only 500 K is unable to start fast pyrolysis. To circumvent this issue, a certain amount of heat was loaned to the bulk gas within the upper section of the burner (essentially, allowing ignition). Once solid fuels were completely converted, the heat was taken back from the bulk gas gradually.

Gas i concentration in the gas phase of the thin slice at stage 1 is calculated via Equation 5.20.

$$C_{i_{b_{temp1}}} = \frac{\sum_{b=1}^{b_f} \left(F_{i_{p_{rel(b)}}} - F_{i_{p_{pen(b)}}} \right) \int_0^{\Delta h} \frac{1}{v_{p(b)}} dh}{A_b \Delta h} + C_{i_{b(a-1)}} \quad (5.20)$$

$C_{i_{b_{temp1}}}$ is the temporary bulk gas i concentration at stage 1 in mol m^{-3} . Total temporary bulk gas concentration at stage 1, $C_{b_{temp1}}$, in mol m^{-3} is the sum of $C_{i_{b_{temp1}}}$ as expressed in Equation 5.21.

$$C_{b_{temp1}} = \sum_{i=1}^7 C_{i_{b_{temp1}}} \quad (E5.21)$$

The temporary bulk gas temperature at stage 1, $T_{b_{temp1}}$, in K is calculated using a rearranged ideal gas equation shown in Equation 5.22.

$$T_{b_{temp1}} = \frac{C_{i_{b(a-1)}}}{C_{b_{temp1}}} T_{b(a-1)} \quad (E5.22)$$

The bulk gas velocity at height index $a - 1$ is unchanged and used as temporary bulk gas velocity at stage 1, $v_{b_{temp1}}$, as expressed in Equation 5.23.

$$v_{b_{temp1}} = v_{b(a-1)} \quad (E5.23)$$

$C_{i_{b_{temp1}}}$, $T_{b_{temp1}}$, and $v_{b_{temp1}}$ are used as initial parameters for homogeneous gas reactions of the

bulk gas. The rates of the combustible gas oxidation, e.g. $\frac{d[CH_4(g)]_{b_{temp1}}}{dt} \quad (R4.7)$, $\frac{d[CO(g)]_{b_{temp1}}}{dt} \quad (R4.8)$, and $\frac{d[H_2(g)]_{b_{temp1}}}{dt} \quad (R4.9)$, and the rates of the respective temperature changes, e.g. $\frac{dT_{b_{temp1}}}{dt} \quad (R4.7)$, $\frac{dT_{b_{temp1}}}{dt} \quad (R4.8)$, and $\frac{dT_{b_{temp1}}}{dt} \quad (R4.9)$, are calculated via the kinetic equations in Appendix C.3.

The duration of bulk gas oxidation within a thin slice, t_{homob} , is calculated via Equation 5.24.

$$t_{homob} = \frac{\Delta h}{v_{b_{temp1}}} \quad (E5.24)$$

$C_{ib_{temp1f}}$ and $T_{b_{temp1f}}$ are solutions for the numerical calculations of the bulk homogeneous gas reactions. The bulk homogeneous gas reaction calculations result in temporary variables at stage 2 expressed in Equations 5.25, 5.26, and 5.27.

$$T_{b_{temp2}} = T_{b_{temp1f}} \quad (E5.25)$$

$$C_{ib_{temp2}} = \frac{p_b}{RT_{b_{temp1f}}} \frac{C_{ib_{temp1f}}}{\sum_{i=1}^7 C_{ib_{temp1f}}} \quad (E5.26)$$

$$v_{b_{temp2}} = \frac{T_{b_{temp1f}}}{T_{b(a-1)}} v_{b_{temp1}} \quad (E5.27)$$

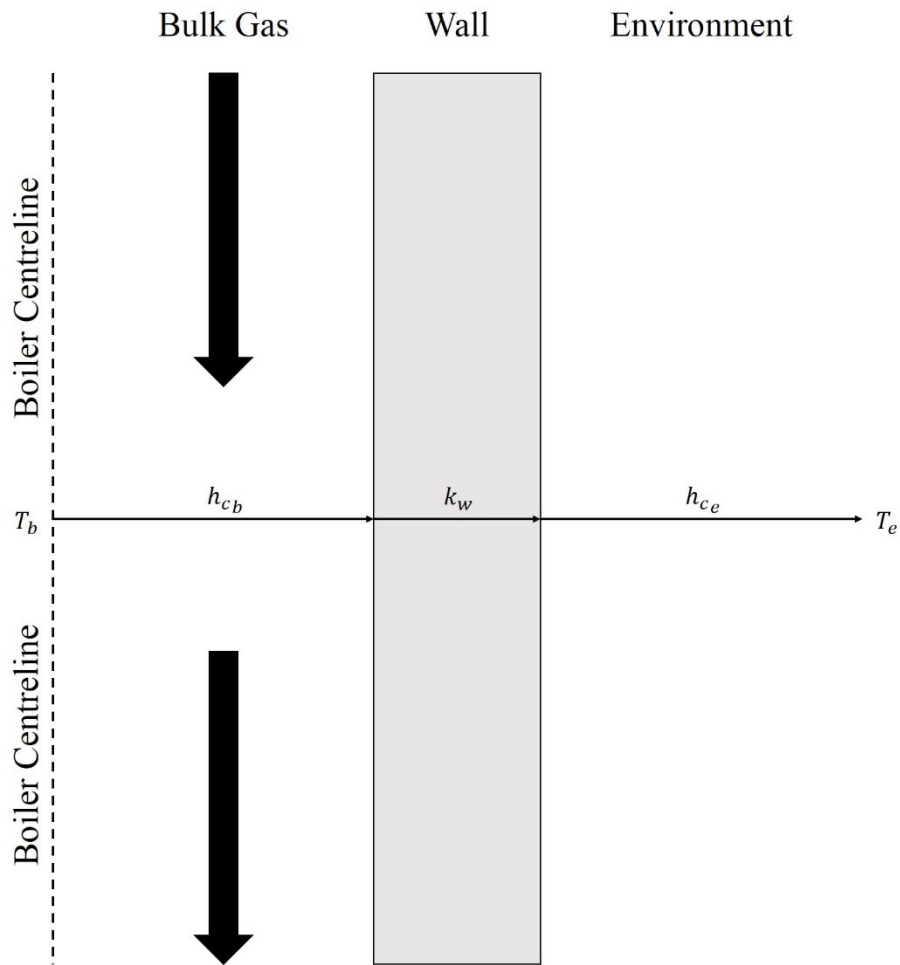


Figure 5.14 Heat Loss through Burner Wall

At stage 3, bulk gas loses heat consecutively through burner bulk gas, the burner wall, and the external environment as illustrated in Figure 5.14. In this figure, h_{cb} is the convective heat transfer coefficient of the bulk gas in $\text{W m}^{-2} \text{K}^{-1}$. k_w is the thermal conductivity of the burner wall in $\text{W m}^{-1} \text{K}^{-1}$. h_{ce} is the convective heat transfer coefficient of the external environment in $\text{W m}^{-2} \text{K}^{-1}$. T_b is the bulk gas

temperature in K. In this case, T_b is equal to T_{btemp2} . T_e is the temperature of the external environment in K. h_{cb} is denoted as $h_{cbtemp2}$ and is calculated through use of Equation 4.31.

$$h_{cbtemp2} = \frac{Nu_{btemp2} k_{conbtemp2}}{d_b} \quad (E5.28)$$

d_b is burner diameter in m. $k_{conbtemp2}$ is the temporary conductive thermal conductivity at stage 2 of the bulk gas and calculated via the equations in Appendix B.3. Nu_{btemp2} is the bulk gas temporary Nusselt number and calculated via the equation in Appendix B.15.

The wall of the entrained-flow burner at the PACT facility is a cylindrical structure without water wall as featured in commercial entrained-flow boiler. The wall is made of polycrystalline, high alumina fibres blended with aluminosilicate fibres and refractory alumina. The alumina to silica ratio is approximately 4:1. The thermal conductivity, k_w , of this alloy in $W m^{-1} K^{-1}$ at the respective thin slice is denoted with k_{wtemp2} and calculated via Equation 5.29.

$$k_{wtemp2} = \frac{10^{-13}}{T_{btemp2}^{-4}} - \frac{6.2 \cdot 10^{-10}}{T_{btemp2}^{-3}} + \frac{1.3 \cdot 10^{-6}}{T_{btemp2}^{-2}} - (9.2 \cdot 10^{-4}) T_{btemp2} + 0.3052 \quad (E5.29)$$

At the external environment, air is assumed to be the only gas present, with temperature, T_e , of 298 K and very low velocity. h_e is assumed to be $10.45 W m^{-2} K^{-1}$. The temporary overall burner heat loss coefficient at stage 2, U_{wtemp2} , is determined through use of Equation 5.30.

$$U_{wtemp2} = \frac{1}{\left(\frac{1}{2\pi d_b \Delta h h_{cbtemp2}} + \frac{\log\left(\frac{d_{bext}}{d_b}\right)}{2\pi \Delta h k_{wtemp2}} + \frac{1}{2\pi d_b \Delta h h_e} \right)} \quad (E5.30)$$

d_{bext} is the external diameter of the burner in m. The bulk gas temporary temperature at stage 3, T_{btemp3} , in K is the temporary temperature at stage 3 due to heat loss. T_{btemp3} is expressed in Equation 5.31.

$$T_{btemp3} = T_{btemp2} - \frac{U_{wtemp2} (T_{btemp2} - T_e)}{c_{pbtemp2} \rho_{btemp2} v_{btemp2} \pi \left(\frac{d_b}{2}\right)^2} \quad (E5.31)$$

The temporary individual gas compound concentration and velocity at stage 3 of the bulk gas, $C_{ibtemp3}$ and v_{btemp3} , are calculated through use of Equations 5.32 and 5.33.

$$C_{ibtemp3} = \frac{p_b}{RT_{btemp3}} \frac{C_{ibtemp2}}{\sum_{i=1}^7 C_{ibtemp2}} \quad (E5.32)$$

$$v_{btemp3} = \frac{T_{btemp3}}{T_{btemp2}} v_{btemp2} \quad (E5.33)$$

The changes in bulk gas temperature, concentration, and velocity at stage 4 are due to loaned and removed heat. Heat is gradually loaned at the early stage of combustion to obtain an elevated temperature sufficient to trigger fast pyrolysis. The heat loan is stopped at an estimated height, e.g. 0.1 m from the top of the burner. When 99% of burnout is achieved or the bulk gas temperature is above 1900 K, the loaned heat is removed gradually. The rate of loaned heat, P_{loan} , is calculated via Equation 5.34.

$$P_{loan} = F_g \sum_{i=1}^7 x_{n_i} \int_{T_g}^{T_{ign}} \frac{c_{P_i}}{\left(\frac{1000}{MW_i}\right)} dT \quad (E4.34)$$

P_{loan} is in W. F_g is the inlet gas molar flow rate in mol s⁻¹. x_{n_i} is the inlet gas compound i molar fraction. T_{ign} is ignition temperature in K or the temperature at which the heat loan stops. T_g is inlet gas temperature in K. c_{P_i} is the heat capacity of gas compound i as listed in Appendix A.1.

At stage 4, P_{loan} is equally divided into the number of thin slices during the heat loan, as presented in Equation 5.35.

$$P_{loan\Delta h} = \frac{P_{loan}}{a_{ign}-1} \quad (E4.35)$$

$P_{loan\Delta h}$ is heat loaned to a thin slice in W. a_{ign} is the height index of the ignition temperature. The addition of $P_{loan\Delta h}$ increases temperature to bulk gas temporary temperature at stage 4, T_{btemp4} . T_{btemp4} is obtained by solving Equation 5.36.

$$P_{loan\Delta h} = v_{btemp3} A_b \sum_{i=1}^7 C_{i_{btemp3}} \int_{T_{btemp3}}^{T_{btemp4}} \frac{c_{P_i}}{\left(\frac{1000}{MW_i}\right)} dT \quad (E5.36)$$

The rate of heat removed from a thin slice, $P_{remove\Delta h}$, is calculated via Equation 5.37.

$$P_{remove\Delta h} = \frac{P_{loan}}{a_{remove_f} - a_{remove_1}} \quad (E5.37)$$

a_{remove_0} and a_{remove_f} are indices of height at which heat removal starts and ends. T_{btemp4} is obtained by solving Equation 5.38.

$$P_{remove\Delta h} = v_{btemp3} A_b \sum_{i=1}^7 C_{i_{btemp3}} \int_{T_{btemp4}}^{T_{btemp3}} \frac{c_{P_i}}{\left(\frac{1000}{MW_i}\right)} dT \quad (E5.38)$$

T_{btemp4} is in K. The temporary concentration 4 of bulk gas compound i and bulk gas temporary velocity at stage 4 are calculated by use of Equations 5.39 and 5.40.

$$C_{ibtemp4} = \frac{p_b}{RT_{btemp4}} \frac{C_{ibtemp3}}{\sum_{i=1}^7 C_{ibtemp3}} \quad (E5.39)$$

$$v_{btemp4} = \frac{T_{btemp4}}{T_{btemp3}} v_{btemp3} \quad (E5.40)$$

T_{btemp4} , $C_{ibtemp4}$, and v_{btemp4} are set as the values at height index a as expressed in Equations 5.41, 5.42, and 5.43.

$$T_{b(a)} = T_{btemp4} \quad (E5.41)$$

$$C_{ib(a)} = C_{ibtemp4} \quad (E5.42)$$

$$v_{b(a)} = v_{btemp4} \quad (E5.43)$$

The calculation of the particle falling velocity at height index a , $v_{p(a,b)}$, is explained in Appendix D.

5.4 Discussion and Validation of the Model Result

The bulk gas temperature profile comprises four consecutive combustion stages, namely: *heat loan*, *simultaneous pyrolysis and char gasification*, *heat removal*, and *heat loss*. This categorisation is proposed based on the most dominant physical and chemical activities that are in process at each stage. The purpose of this stage categorisation is to deliver a clear understanding in the following discussion regarding this topic.

The *heat loan* stage occurs through the deliberate addition of heat gradually to the bulk gas to raise the bulk gas temperature. When this temperature is hot enough to enable rapid particle pyrolysis, heat addition is stopped. The *heat loan* stage essentially aims to replicate solid-fuel rapid pyrolysis that is promoted by self-sustaining high temperature near the feed introducer due to the flow pattern.

Simultaneous pyrolysis and char gasification is the stage at which pyrolysis of solid fuel and gasification of char occur at the same time. The particle sizes used in an entrained-flow burner are very fine. Exposure of fine particles to hot temperature promotes pyrolysis, and char combustion occurs simultaneously due to efficient intra-particle heat and mass transfer. Simultaneous pyrolysis and char combustion release a significant amount of partially combusted gases within a short time. Concentrated CO and H₂ in the bulk gas aids fast exothermic reaction with O_{2(g)}. Fast exothermic reaction quickly raises the bulk gas temperature to its peak temperature.

After achievement of the peak temperature of the bulk gas, the same amount of heat that was given to the bulk gas during the *heat loan* stage is gradually removed. This stage is called *heat removal*. The

bulk gas temperature change during *heat removal* is smaller than that during *heat loan* due to the availability of more gas during the *heat removal* stage.

The *heat loss* stage accounts for heat removed from the bulk gas to the external environment due to the conductivity of the burner wall. Due to heat removal, the bulk gas temperature slowly decreases. Essentially, heat removal to the external environment occurs at any height within the burner. However, its occurrence is distinctive during the *heat loss* stage since there is no other competing thermal activity.

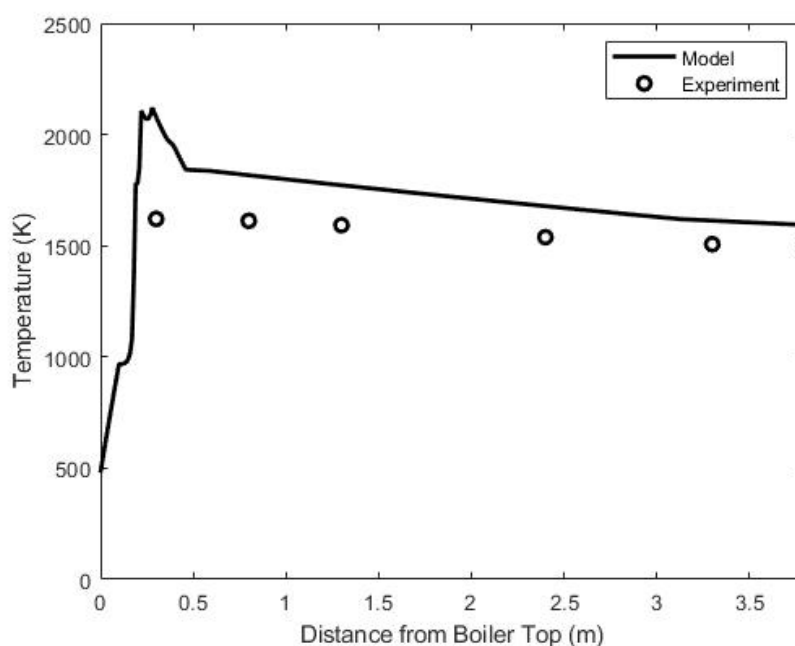


Figure 5.15 Validation of the Modelled Bulk Gas Temperature Profile of White Wood during Air-combustion in the PACT Entrained-flow Burner

Figure 5.15 shows the comparison of the bulk gas temperature profile generated from the entrained-flow combustion model that simulated air-combustion of white wood with experimental results. The comparison shows reasonably good validation of the modelled profile. However, the bulk gas peak temperature was not reached in the experiment. Due to bulk gas recirculation near the feed, close to the burner wall, *simultaneous pyrolysis and char gasification* is likely to establish the peak temperature near the burner wall. However, the temperature probes were installed to measure the centreline temperature. The temperature probes might have missed reading the peak temperature due to their fixed limited position.

Figure 5.16 shows another comparison. In this case, the molar percentage profile of bulk $O_{2(g)}$ generated from the entrained-flow combustion model that simulated air-combustion of white wood is compared with the experimental results. According to the comparison, the modelled profile is poorly validated

within 0.5 m of the burner's upper section. Experimental measurement shows that little $O_{2(g)}$ was present in this section of the burner, whilst the modelled profile shows otherwise. The absence of $O_{2(g)}$ might be due to bulk gas recirculation, which draws $O_{2(g)}$ to flow near the burner wall. As was the case with the temperature probes, the concentration probes are installed to measure the $O_{2(g)}$ molar percentage at the burner centreline. Consequently, the concentration probes were incapable of detecting $O_{2(g)}$ elsewhere.

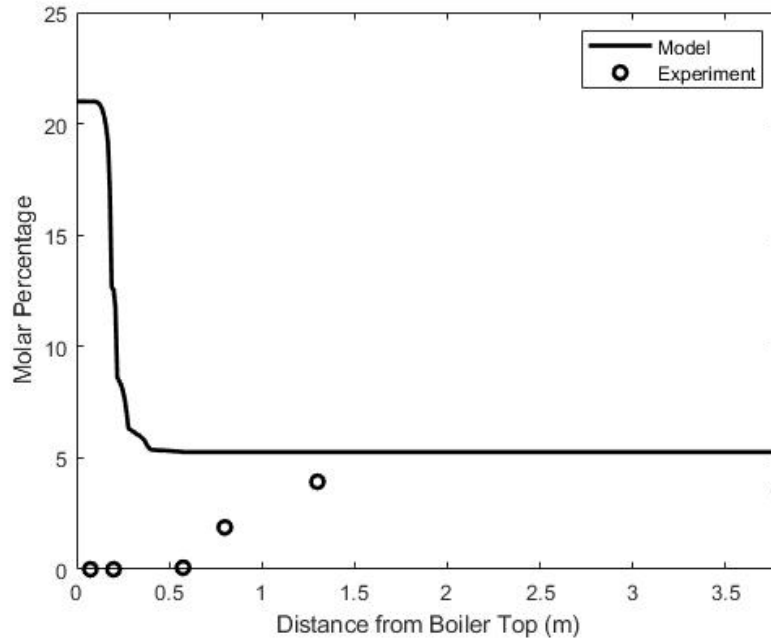


Figure 5.16 Validation of Dry Molar Percentage Profile of the Modelled Bulk $O_{2(g)}$ Gas during Air-combustion of White Wood in the PACT Entrained-flow Burner

The entrained-flow combustion model can also be used to predict particle profiles, e.g. intra-particle temperature, particle falling velocity, and particle residual mass fraction. Particle profiles for three particle sizes, 200 micron, 800 micron, and 1400 micron, were compared. Profiles for 1400-micron particles are discussed exclusively to understand the effect of particle size on the evolution of these profiles.

Intra-particle temperature profiles are shown in Figure 5.17 for particle centre temperature profiles and in Figure 5.18 for particle surface temperature profiles. Both figures show that particle size is directly proportional to the rate of intra-particle temperature increase. The 1400-micron particle was the largest of the three particle sizes investigated, and therefore exhibited the slowest response to heat transfer. Therefore, the surface temperature profile and centre temperature profile of the 1400-micron particle show the longest time lag before reaching their maximum values. The 1400-micron particle also exhibited the quickest falling velocity as it had the heaviest mass, as shown in Figure 5.19. The particle that falls the fastest also shows the shortest residence time and receives the least amount of convective

heat transferred from the bulk gas to the particle surface. The 1400-micron particle also has the longest distance from its surface to its centre, which promotes the greatest resistance to a rise of centre temperature via heat conduction. Consequently, the 1400-micron particle experiences the lowest heating rate and therefore reaches complete burnout at the lowest height inside the burner, at around 1 m. These results are shown in Figure 5.20.

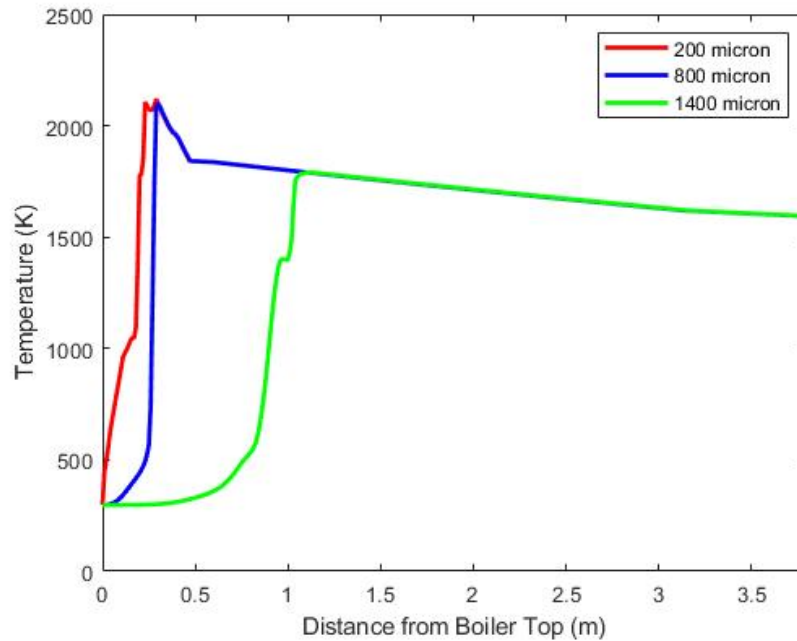


Figure 5.17 Centre Temperature Profiles of Modelled Particles of White Wood during Air-combustion in the PACT Entrained-flow Burner

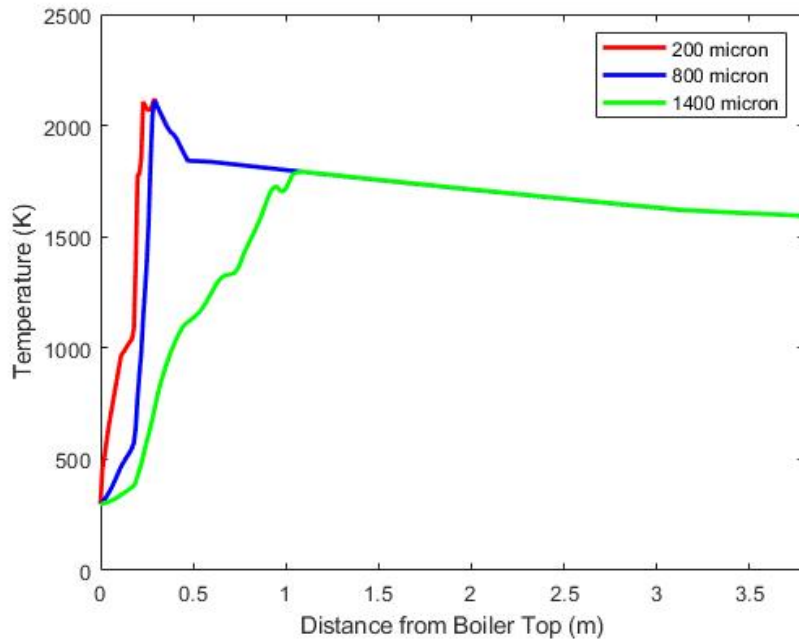


Figure 5.18 Surface Temperature Profiles of Modelled Particles of White Wood during Air-combustion in the PACT Entrained-flow Burner

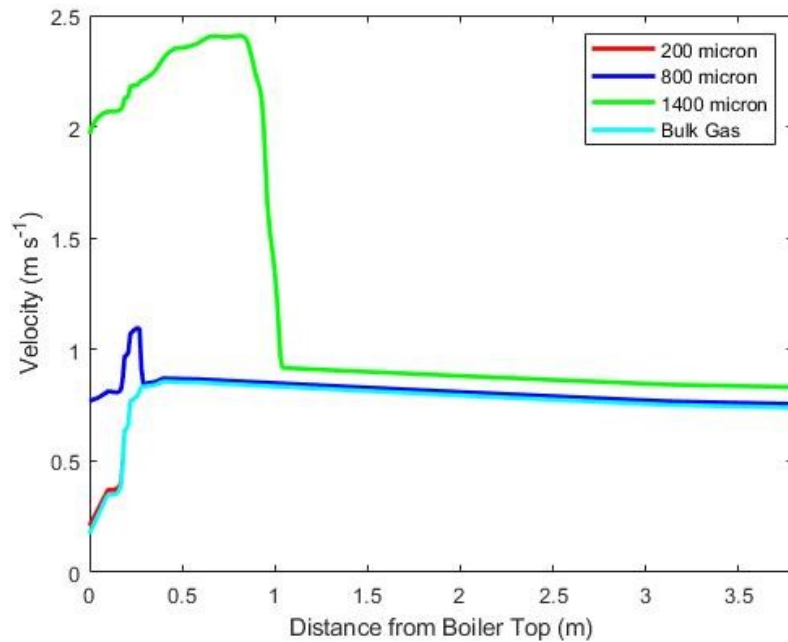


Figure 5.19 Velocity Profiles of Bulk Gas and Modelled Particles of White Wood during Air-combustion in the PACT Entrained-flow Burner

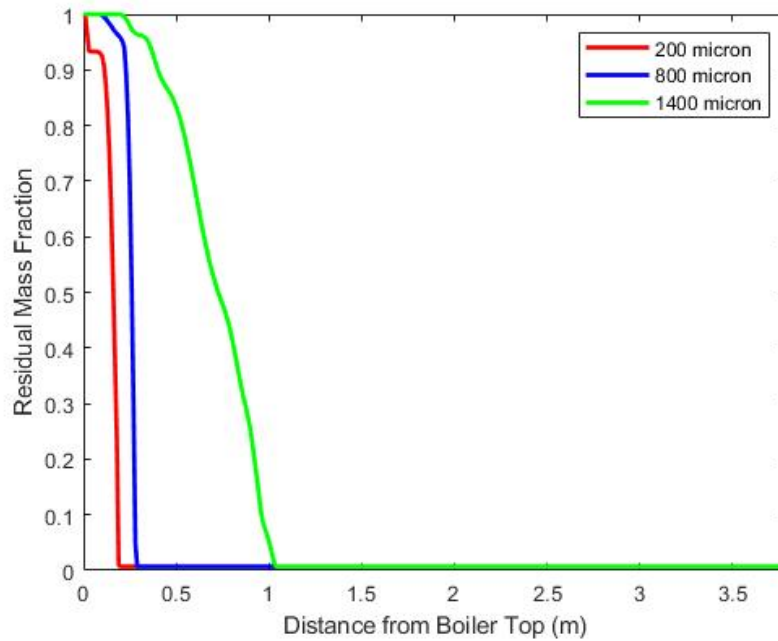


Figure 5.20 Residual Mass Fraction Profiles of Modelled Particles of White Wood during Air-combustion in the PACT Entrained-flow Burner

The comparison between the temperature profiles of the bulk gas measured during experiment and calculated by the entrained-flow combustion model during oxy27-combustion of white wood are shown in Figure 5.21. The comparison shows poor validation, as the modelled bulk gas temperature is higher than that measured by experiment in almost every axial position in the burner. The poor validation might be due to the limited predictive properties of the model regarding the radial temperature distribution of the bulk gas.

Figure 5.22 shows the comparison between the molar percentage profile of the bulk $O_{2(g)}$ generated by the entrained-flow combustion model with that found during experiment. The comparison shows that both profiles exhibit similar trends to those observed during air-combustion of white wood. The modelled molar percentage of $O_{2(g)}$ is lower than the molar percentage of $O_{2(g)}$ observed during experiment at almost every axial position in the burner. A lower modelled $O_{2(g)}$ molar percentage is associated with a reduced quantity of $O_{2(g)}$ in the inlet gas of oxy27-combustion. Nevertheless, the modelled profile predicts that the molar percentage of $O_{2(g)}$ becomes zero when complete conversion is obtained, whilst a stoichiometric calculation expects 1% of $O_{2(g)}$ to remain. The model prediction of 0% $O_{2(g)}$ might originate from numerical error due to rough numerical discretisation.

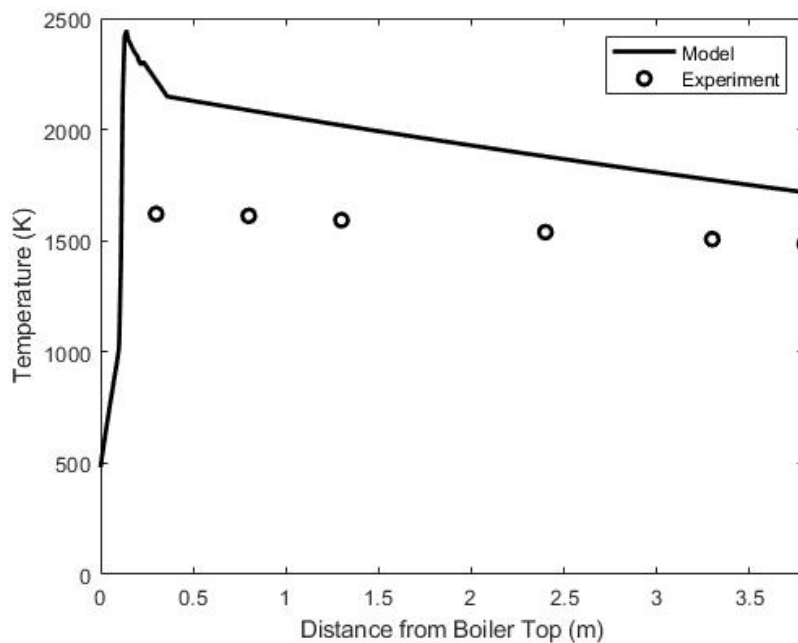


Figure 5.21 Validation of Modelled Bulk Gas Temperature Profile of White Wood during Oxy27-combustion in the PACT Entrained-flow Burner

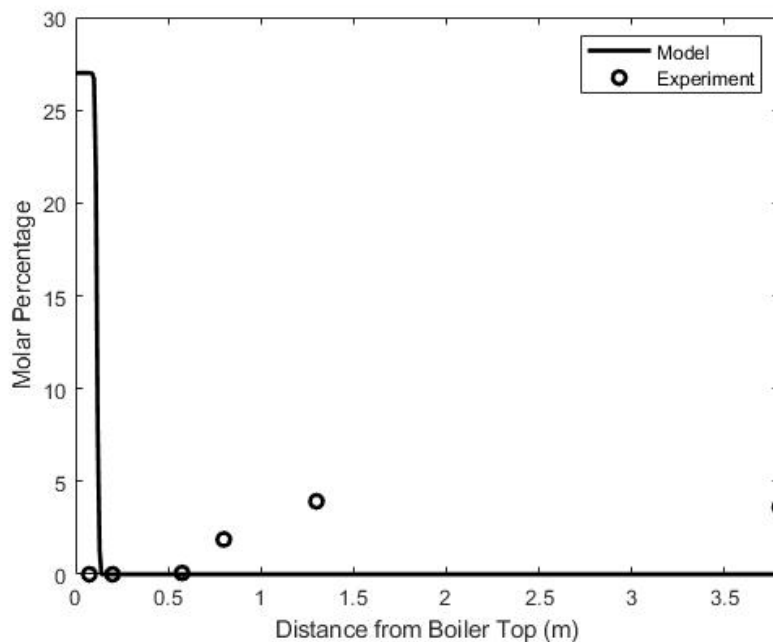


Figure 5.22 Validation of Modelled Dry Molar Percentage Profile of Bulk $O_{2(g)}$ of White Wood during Oxy27-combustion in the PACT Entrained-flow Burner

5.3 Concluding Remarks

The entrained-flow combustion model is a well-developed method for modelling entrained-flow combustion. During the early development of this model, a one-dimensional entrained-flow combustion model was widely used. Many researchers later utilised CFD to obtain more accurate predictions. The results generated from combustion in the entrained-flow burner at the PACT facility in South Yorkshire were used to validate the results generated from the entrained-flow burner combustion model. In the past, several studies were conducted that used CFD to model the PACT-facility combustion. However, CFD has not featured in the work conducted for this thesis to avoid expensive computation.

Prior to development of the entrained-flow combustion model, a certain number of particle sizes was chosen from the PSD. The volume fraction of each particle size was normalised and used as the new volume fraction. However, these particle sizes represented the diameters of spherical shapes, whilst woody biomass particles are of cylindrical shape. Using microscopic analysis, the particle diameter distribution was converted into particle length distribution using a measured aspect ratio. This actual particle length and aspect ratio distribution was used as the particle dimensions in the entrained-flow combustion model.

The entrained-flow combustion model that was produced as part of the work performed for this thesis was developed according to a one-dimensional plug-flow reactor model. A column-shaped burner was discretised from top to bottom into numerous identical axial sections, or so-called “discretised burner sections”. Within each discretised burner section, heat transfer, mass transfer, and chemical reaction kinetics were used to calculate temperatures and gas concentrations in both the particle phase and the bulk phase. In the particle phase, a particle of each size cluster was modelled through use of the single-particle combustion model. Each particle fell from the top to the bottom of the thin slice. Bulk gas properties at the top of the thin slice were used as the boundary conditions. The amount of gas released from the particle phase was determined as functions of particle surface area and mass transfer rate. The released gas was added to the gas entering at the top of the thin slice in the bulk phase. The bulk gas concentration and the temperature at the bottom of the thin slice were calculated by solving reaction kinetic equations for bulk gas.

For white wood combusted in air, the modelled bulk gas temperature and concentration profiles were well-validated with the experimental results. However, the peak temperature predicted in the modelled bulk gas temperature profile was not observed in the experimental temperature profile, since the peak temperature was likely to be established near the wall at 0.5 m from the top of the burner due to the recirculation flow pattern of the bulk gas, whilst the temperature probe installed in the burner only measured temperature at the burner centreline. In the experimental $O_{2(g)}$ molar percentage profile, no $O_{2(g)}$ was detected within 0.5 m of the burner upper section. In contrast, the modelled $O_{2(g)}$ molar

percentage profile predicted the presence of $O_{2(g)}$ in that location. This indicated that $O_{2(g)}$ might have flowed towards the burner wall at 0.5 m from the top of the burner due to recirculation. The undetected $O_{2(g)}$ during combustion could be due to the absence of $O_{2(g)}$ at the centreline at 0.5 m from the burner top.

The modelled bulk gas temperature and concentration profiles were poorly validated by the experimental results in oxy27-combustion of white wood. The modelled bulk gas temperature was found to be higher than the bulk gas temperature measured experimentally, whilst the modelled bulk $O_{2(g)}$ gas molar percentage was lower than the bulk $O_{2(g)}$ molar percentage measured in almost any position in the burner. The poor validation might be due to a limitation of the model in predicting bulk gas temperature and radial distribution of $O_{2(g)}$ concentration in oxy27-combustion.

Chapter 6

Fate and Occurrence Model

This chapter discusses the prediction of the occurrence and fate of AFEs and TEs in the PACT facility entrained-flow burner using the fate and occurrence model, as functions of the intra-particle profiles and bulk profiles obtained in the entrained-flow burner. The intra-particle profiles of temperatures and concentrations of major gases, e.g. $\text{CH}_{4(g)}$, $\text{CO}_{(g)}$, $\text{CO}_{2(g)}$, $\text{H}_{2(g)}$, $\text{H}_2\text{O}_{(g)}$, $\text{O}_{2(g)}$, and $\text{N}_{2(g)}$, were used as the parameters to calculate the intra-particle AFE and TE concentrations. Simultaneously, the bulk temperatures and concentrations of major gases were also used to simulate the bulk AFE concentrations. Both major calculations were conducted with the assistance of a chemical equilibrium tool. Section 6.1 considers the numerical assumptions made for the fate and occurrence model. Section 6.2 explains the mathematical concepts used in the fate and occurrence model that are based on those applied in the entrained-flow combustion model. Section 6.3 discusses the integration of software used to build the fate and occurrence model with the assigned chemical equilibrium tool. The method used here was ultimately unsuccessful, but there is a more successful method in Chapter 6. Of course, it is important to note that chemical equilibrium only gives a guide as to the driving force for reactions to occur; it is not necessarily wholly accurate, but detailed chemical reaction models may contain hundreds of species and thousands of reactions, even for a relatively small number of species, so estimation is necessary.

6.1 Model Assumptions

Inorganic elements, e.g. AFEs and TEs, can be considered relatively homogeneously distributed in wood. However, this might not be entirely the case for wood with a history of painting and coating. When wood is pulverised, the concentrations of paint and coating elements might be different in one pulverised particle compared with another due to their original locations in the wood. Nevertheless, this work assumes that each element is homogeneously distributed throughout a particle body, as mathematically expressed in Equations 6.3 and 6.4.

$$[AFE]_{p(1,b,m_1,n_1)} = [AFE]_{p(1,b,m_2,n_2)}; m_1 \neq m_2; n_1 \neq n_2 \quad (E6.1)$$

$$[TE]_{p(1,b,m_1,n_1)} = [TE]_{p(1,b,m_2,n_2)}; m_1 \neq m_2; n_1 \neq n_2 \quad (E6.2)$$

$[AFE]_p$ and $[TE]_p$ are concentrations of AFEs and TEs in a particle. m_1 , m_2 , n_1 , and n_2 are radial and axial coordinates of arbitrary points in a discretised particle. Although this assumption might not be suitable for paint and coating elements, the effect of this assumption on the fate and occurrence model accuracy is considered insignificant.

The mechanism of AFE and TE release from particles was initially based on the assumption that AFEs and Tes were chemically and physically independent of the particle's organic constituents. A trial model was run with this assumption. The results revealed that complex minerals were suddenly formed and most Tes were released at relatively low temperature, e.g. 298 to 700 K, within the early stage of combustion.

Furthermore, the release mechanism of major elements (MEs), e.g. C, H, O, and N, is explained as an analogy to consider the plausibility of the previous assumption regarding the AFE and TE release mechanism. The majority of wood is composed of C, H, O, and a small amount of N.. Chemical equilibrium calculation of these elements using the previous assumption results in formation of hydrocarbon products unavailable at low temperature in most combustion experiments. This analogy emphasises that MEs, indeed, are available in wood but are bound to the organic constituents and are not ready to react unless a certain temperature for pyrolysis is achieved. Hence, AFE and TE release is assumed to follow this approach.

The units of concentration of biomass AFEs must be converted into ppm in raw fuel since the unit is commonly presented in most literature as percentage in ash, whilst TE concentration is already in ppm. The conversion method is exemplified with K_2O . m_{ash} is mass of ash in kg and set as the basis. $m_{biomass}$ is mass of biomass in kg and calculated via Equation 6.3.

$$m_{biomass} = \frac{1}{x_{m_{ash}}} m_{ash} \quad (E6.3)$$

$x_{m_{ash}}$ is ash mass percentage. m_{K_2O} is mass of K_2O and calculated via Equation 6.4.

$$m_{K_2O} = x_{m_{K_2O_{ash}}} m_{ash} \quad (E6.4)$$

$x_{m_{K_2O_{ash}}}$ is mass percentage of K_2O in ash. m_K is mass of pure potassium in kg and calculated by use of Equation 6.5.

$$m_K = n_{K_{K_2O}} \frac{m_{K_2O}}{MW_{K_2O}} MW_K \quad (E6.5)$$

MW_{K_2O} and MW_K are the molecular weights of K_2O and potassium in $g\ mol^{-1}$. $n_{K_{K_2O}}$ is the elemental number of potassium in K_2O . ppn_K is the concentration of potassium in ppm and calculated by use of Equation 6.6.

$$ppn_K = \frac{m_K}{m_{biomass}} 10^6 \quad (E6.6)$$

AFE and TE release rates during pyrolysis are barely found in the literature. Only a few studies have been conducted to measure AFE and TE release rates during pyrolysis.²⁵² Since pyrolysis rates of inorganic constituents from particles are not available, the mass percentage of inorganic constituents from pyrolysed particles are assumed equal to those of organic constituents from pyrolysed particles as mathematically formulated in Equation 6.7.

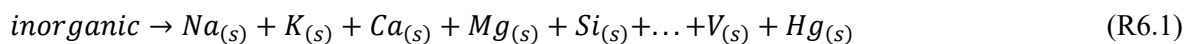
$$\rho_{inorg\ p(a-1,b,m,n)} - \rho_{inorg\ p(a,b,m,n)} = \frac{\rho_{org\ p(a-1,b,m,n)} - \rho_{org\ p(a,b,m,n)}}{\rho_{org\ p(a-1,b,m,n)}} \rho_{inorg\ p(a-1,b,m,n)} \quad (E6.7)$$

The densities of the generated AFEs, $\rho_{AFE\ p_{conv}(a-1,b,m,n)}$, and TEs, $\rho_{TE\ p_{conv}(a-1,b,m,n)}$, in $kg\ m^{-3}$ from pyrolysed inorganic constituents are calculated via Equations 6.8 and 6.9.

$$\rho_{AFE\ p_{conv}(a-1,b,m,n)} = \left(\rho_{inorg\ p(a-1,b,m,n)} - \rho_{inorg\ p(a,b,m,n)} \right) \frac{m_{AFE}}{\sum_{AFE=1}^{10} m_{AFE} + \sum_{TE=1}^{12} m_{TE}} \quad (E6.8)$$

$$\rho_{TE\ p_{conv}(a-1,b,m,n)} = \left(\rho_{inorg\ p(a-1,b,m,n)} - \rho_{inorg\ p(a,b,m,n)} \right) \frac{m_{TE}}{\sum_{AFE=1}^{10} m_{AFE} + \sum_{TE=1}^{12} m_{TE}} \quad (E6.9)$$

Equations 6.8 and 6.9 are based on Reaction 6.1.



However, each AFE and TE is not originally in the form of pure solid elements in particles. Of course, each AFE and TE has its own initial form of occurrence. The initial occurrence of an element may vary, depending on its location within a cell, and its chemical interaction with any other element. Neglecting the initial occurrences does not affect the overall AFE and TE mass balances, but ignores temperature change due to the decomposition heat of initial occurrence.

A calculation was conducted to evaluate the extent of the temperature change of neglecting AFE and TE initial occurrence. Calcium was chosen as the evaluated element since calcium is the most dominant element in woody biomass. $CaC_2O_{4(s)}$ is assumed as the initial calcium occurrence. According to the calculation, neglecting the heat of decomposition of $CaC_2O_{4(s)}$ reduces the particle temperature by around 4.92 K. This value is insignificant in comparison with the increase in particle temperature due

to char oxidation, heat convection, and heat radiation. Therefore, simplification using Reaction 6.1 is reasonable. The details of the calculation are shown in Appendix E.

More than 1,000 formed AFE and TE compounds are assumed to show thermodynamic properties equal to the thermodynamic properties of ME compound mixtures. Most AFE and TE compounds exhibit little known thermodynamic properties. Even if the thermodynamic properties were completely available, their inclusion in the fate and occurrence model would promote extremely expensive computation. The assumptions made are therefore reasonable since a tiny amount of AFE and TE does not significantly affect particle temperature and gas release.

Solid aerosols formed due to AFE and TE compound nucleation are assumed to flow downwards with velocity equal to the bulk gas velocity. This assumption may not be true since solid aerosols are essentially subject to their falling velocities as calculated via Appendix D. Nevertheless, calculation of solid aerosol falling velocities using these equations requires detail of the solid aerosol geometry as parameter.^{253,254} On the other hand, the solid aerosol geometry depends on the surface tension and saturation ratios of the AFE and TE compounds. Moreover, the solid aerosol geometry is likely to change during combustion due to aerosol collisions and condensation. Both surface tension and saturation are barely available for each individual AFE and TE compound. Therefore, use of bulk gas velocity as the solid aerosol falling velocity is considered necessary to avoid complexity. In addition, solid aerosols with small sizes that generate very low Stoke numbers are unlikely to fall independently.

Intra-particle AFE and TE condensation is assumed not to affect the shrinkage factor, $\theta_{(b,m,n)}$. However, this assumption is in disagreement with the investigation results of Biermann and Ondov²⁵⁵. These investigation results suggest that the shrinkage factor, $\theta_{(b,m,n)}$, increases due to inorganic gas condensation. Nevertheless, since the fate and occurrence model is separated from the entrained-flow combustion model, the particle size geometry profile generated in the entrained-flow combustion model is used as a fixed parameter in the fate and occurrence model according to the assumption. This assumption is made to avoid complexity. In addition, the increase of particle size due to AFE and TE condensation is considered insubstantial in biomass combustion.

6.2 Mathematical Concept of the Model

The general fate of ash-forming compounds (AFCs) and trace compounds (TCs) during falling of a particle in the burner is depicted in Figure 6.1. During devolatilization ($h = h_2$), AFCs and TCs are released from the particle as ash-forming gas compounds (AFGCs) and trace gas compounds (TGCs) along with major gas compounds. Simultaneously, the remaining AFGCs and TGCs are condensed and solidified into ash-forming liquid compounds (AFLCs), ash-forming solid compounds (AFSCs), trace liquid compounds (TLCs), and trace solid compounds (TSCs). During heterogeneous reactions ($h =$

h_3), $O_{2(g)}$ diffuses into the particle and reacts with the remaining AFCs and TCs to form high melting-point oxides and silicates. This general fate is dependent on temperatures, intra-particle gas concentrations, and bulk gas concentrations.

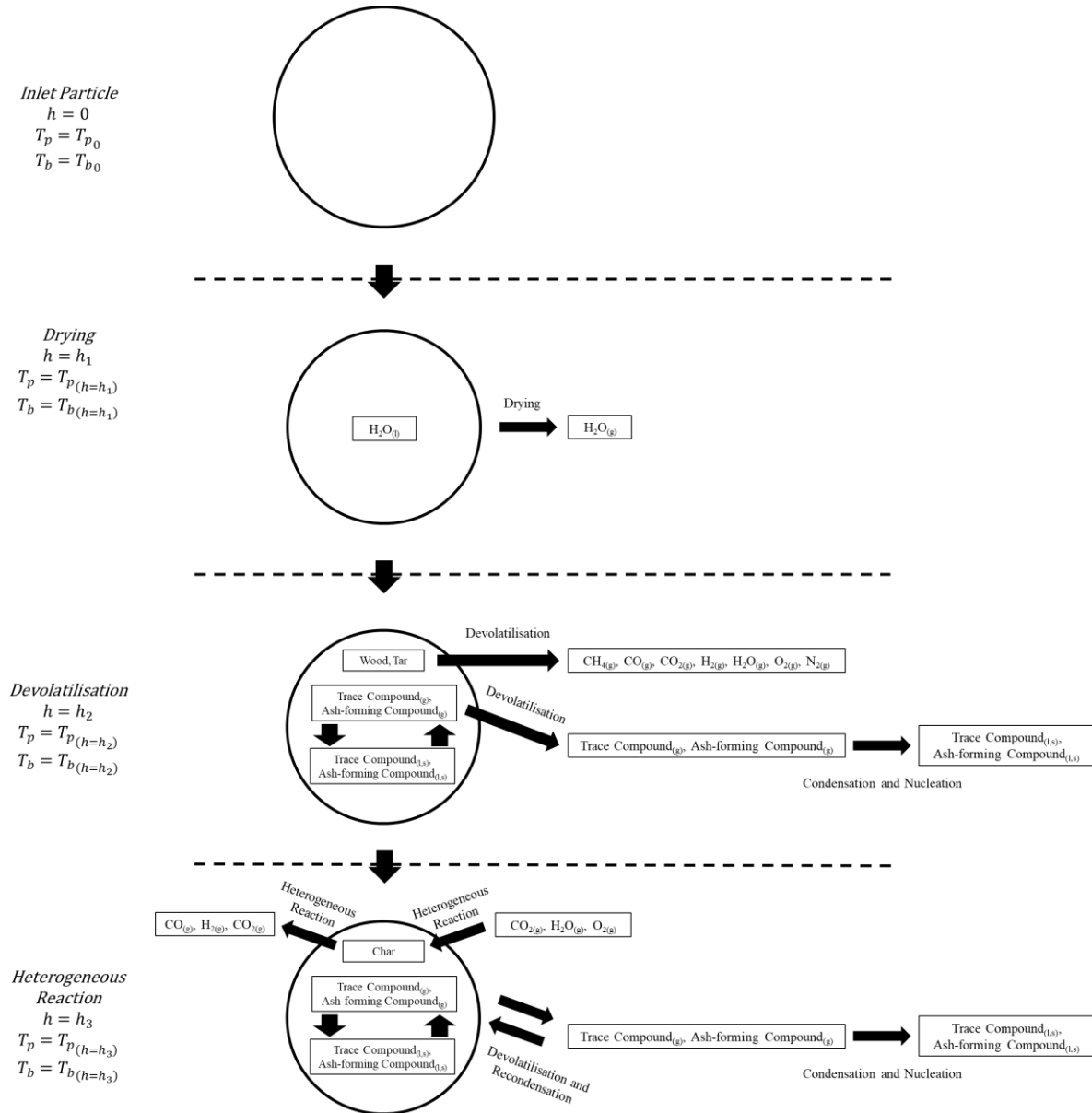


Figure 6.1 General Fate of AFEs and TEs during Falling of Particles in Burner

The route of calculation in a single thin slice for the fate and occurrence model is illustrated in Figure 6.2. A grey rectangle with a thickness of Δh represents the thin slice. The vertical dashed line that crosses the thin slice divides the section into the particle phase shown on the left-hand side and the bulk phase on the right-hand side. Particles grouped into various size clusters are introduced at height $a - 1$ located at the rectangle upper side. Before entering the thin slice, the pure element density of the particle

solid-phase at height $a - 1$, .e.g. $\rho_{Na(s)p(a-1,b,m,n)}$, $\rho_{Mg(s)p(a-1,b,m,n)}$, $\rho_{K(s)p(a-1,b,m,n)}$, etc. is combined with $\rho_{AFEp_{conv(a-1,b,m,n)}}$ and $\rho_{TEp_{conv(a-1,b,m,n)}}$ generated from pyrolysis in the above thin slice. The intra-particle gas calculation consists of two consecutive steps.

The first step is change of intra-particle concentration of AFGCs and TGCs due to mass diffusion and permeation as expressed in Equation 4.4. At the particle boundary, the changes of concentration of AFGCs and TGCs are calculated by use of Equations 4.13 and 4.14 for the particle surface boundary and Equations 4.17 and 4.18 for the inner particle boundary. $D_{effp(b,m,n)}$ is calculated via Equation 4.20. $\mu_{gasp(b,m,n)}$ is calculated via Appendix B.5. $\eta_{p(b,m,n)}$ is calculated by use of Equation B.9.

The second step is the chemical equilibrium calculation on intra-particle concentration at $T_{p(a,b,m,n)}$ and $p_{p(a,b,m,n)}$. The results of the intra-particle chemical equilibrium calculation produces the density of AFCs and TCs at height a , $\rho_{AFCp(a,b,m,n)}$ and $\rho_{TCp(a,b,m,n)}$. AFGC and TGC release rates from, $\dot{F}_{AFGCp_{rel(b)}}$ and $\dot{F}_{TGCp_{rel(b)}}$, and penetration rates to, $\dot{F}_{AFGCp_{pen(b)}}$ and $\dot{F}_{TGCp_{pen(b)}}$, the particle side surface are calculated through use of Equations 5.15 and 5.16. The AFGC and TGC release rates from, $F_{AFGCp_{rel(b)}}$ and $F_{TGCp_{rel(b)}}$, and penetration rates to, $F_{AFGCp_{rel(b)}}$ and $F_{TGCp_{pen(b)}}$, a particle of a particular size cluster are calculated by use of Equations 5.18 and 5.19.

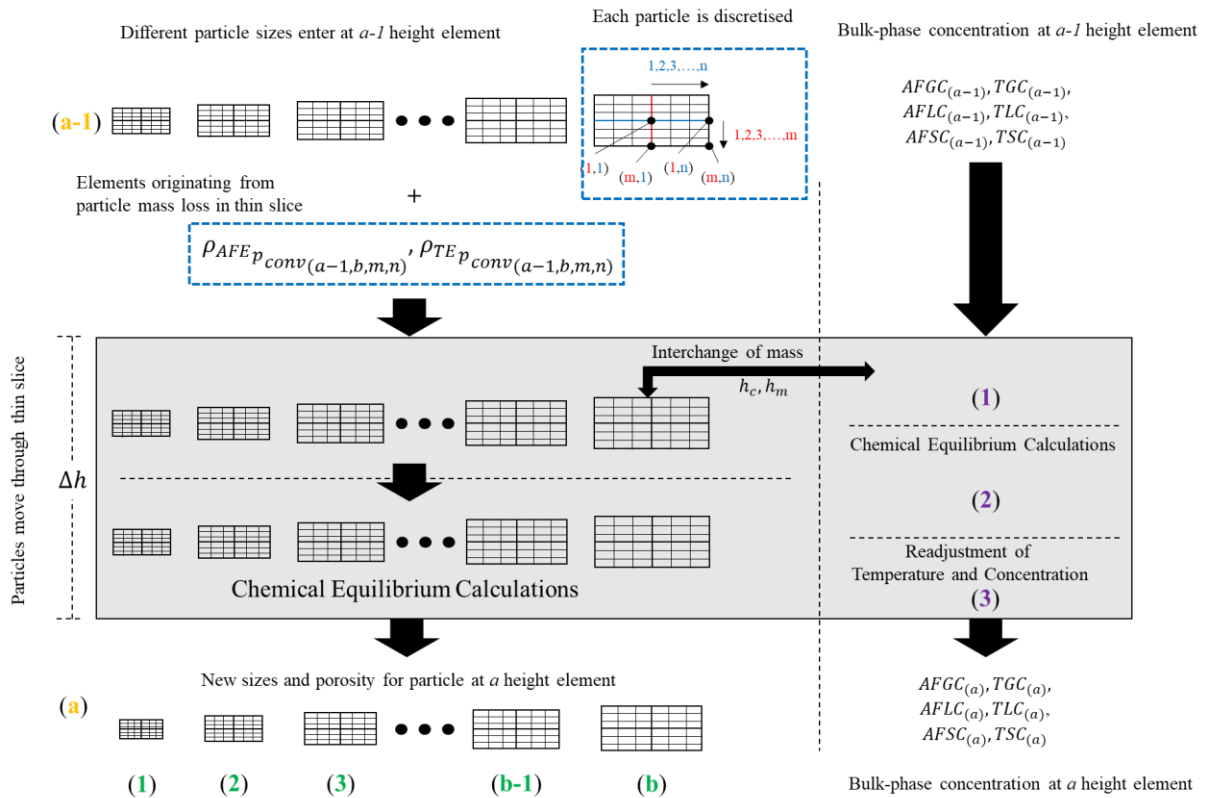


Figure 6.2 AFE and TE Model Structure in Thin Slice with Discretised Particle

Concentrations of AFGCs and TGCs in the bulk gas undergo three stages of change whilst the bulk gas flows through the thin slice.

- Stage 1
Gas that is released from and penetrating to particles changes the bulk gas concentration.
- Stage 2
The concentration of gases and aerosols in the bulk gas change due to chemical equilibrium calculations. $T_{b(a)}$ is used as temperature for the bulk gas chemical equilibrium calculation.
- Stage 3
Altered concentrations of gases and aerosols generated from the chemical equilibrium calculation in stage 2 is readjusted at $T_{b(a)}$.

Concentrations of AFGCs and TGCs at stage 1 are calculated through use of Equations 6.10 and 6.11.

$$C_{AFGCb_{temp1}} = \frac{\sum_{b=1}^{bf} \left(F_{AFGCp_{rel(b)}} - F_{AFGCp_{pen(b)}} \right) \int_0^{\Delta h} \frac{1}{vp(b)} dh}{A_b \Delta h} + C_{AFGCb_{(a-1)}} \quad (E6.10)$$

$$C_{TGCb_{temp1}} = \frac{\sum_{b=1}^{bf} \left(F_{AFGCp_{rel(b)}} - F_{TGCp_{pen(b)}} \right) \int_0^{\Delta h} \frac{1}{vp(b)} dh}{A_b \Delta h} + C_{TGCb_{(a-1)}} \quad (E6.11)$$

$C_{AFGCb_{temp1}}$ and $C_{TGCb_{temp1}}$ are the temporary concentrations at stage 1 of ash-forming gases and trace gas compounds in mol m^{-3} . The temporary concentrations at stage 1 of ash-forming liquid, trace liquid, ash-forming solids, and trace solids are considered equal to $C_{AFLCb_{(a-1)}}$, $C_{TLCb_{(a-1)}}$, $C_{AFSCb_{(a-1)}}$, and $C_{TSCb_{(a-1)}}$ as expressed in Equations 6.12, 6.13, 6.14, and 6.15.

$$C_{AFLCb_{temp1}} = C_{AFLCb_{(a-1)}} \quad (E6.12)$$

$$C_{TLCb_{temp1}} = C_{TLCb_{(a-1)}} \quad (E6.13)$$

$$C_{AFSCb_{temp1}} = C_{AFSCb_{(a-1)}} \quad (E6.14)$$

$$C_{TSCb_{temp1}} = C_{TSCb_{(a-1)}} \quad (E6.15)$$

$C_{AFGCb_{temp1}}$, $C_{TGCb_{temp1}}$, $C_{AFLCb_{temp1}}$, $C_{TLCb_{temp1}}$, $C_{AFSCb_{temp1}}$, and $C_{TSCb_{temp1}}$ are converted into elemental concentrations. The elemental concentrations are used as inputs to the chemical equilibrium calculation at stage 2. The outputs of the chemical equilibrium calculation are the temporary

concentrations at stage 2 of bulk AFE and TE compounds, e.g. $C_{AFGC_{b_{temp2}}}$, $C_{TGC_{b_{temp2}}}$, $C_{AFLC_{b_{temp2}}}$, $C_{TLC_{b_{temp2}}}$, $C_{AFSC_{b_{temp2}}}$, and $C_{TSC_{b_{temp2}}}$. The temporary concentrations at stage 2 of bulk AFE and TE compounds are adjusted at $T_{b(a)}$ to bulk AFE and TE compound temporary concentrations at stage 3, e.g. $C_{AFC_{b_{temp3}}}$ and $C_{TC_{b_{temp3}}}$, in Equations 6.16 and 6.17.

$$C_{AFGC_{b_{temp3}}} = \frac{p_b}{RT_{b(a)}} \frac{C_{AFGC_{b_{temp2}}}}{\sum_{AFC=1}^{AFC_f} C_{AFC_{b_{temp2}}}} \quad (E6.16)$$

$$C_{TGC_{b_{temp3}}} = \frac{p_b}{RT_{b(a)}} \frac{C_{TGC_{b_{temp2}}}}{\sum_{TC=1}^{TC_f} C_{TC_{b_{temp2}}}} \quad (E6.17)$$

$C_{AFC_{b_{temp3}}}$ and $C_{TC_{b_{temp3}}}$ are assigned as the bulk AFE and TE compound concentrations at height a as mathematically expressed in Equation 6.18 and 6.19.

$$C_{AFC_{b(a)}} = C_{AFC_{b_{temp3}}} \quad (E6.18)$$

$$C_{TC_{b(a)}} = C_{TC_{b_{temp3}}} \quad (E6.19)$$

6.3 Chemical Equilibrium Integration and Performance

The most notable and widely used chemical equilibrium software packages at the moment are HSC Chemistry, MTDATA, ChemSage, and FactSage. The working principles of these packages are generally similar. However, preferences regarding which to use are subject to the content of the software's thermodynamic database. HSC Chemistry is a package for thermochemistry developed by Outokumpu Technology. HSC Chemistry aims to assist the mineral and metallurgical industries. However, HSC Chemistry's thermodynamic database cannot be used to solve non-ideal solution phases, e.g. molten slag. MTDATA was developed by the National Physical Laboratory and is used frequently by many researchers. MTDATA is supported by the Scientific Group Thermodata Europe (SGTE) thermodynamic database. However, MTDATA was considered obsolete for the research discussed in this thesis, since the latest update of MTDATA was offered in 2011. On the other hand, Factsage is the most widely used chemical equilibrium tool. It was produced due to a merger of FACT-Win and ChemSage. Hence, FactSage contains both the SGTE and FACT databases. These databases enable the calculation of complex chemical mixtures using FactSage. These mixtures include those produced by metal smelting, molten salt, and slag. Therefore, FactSage was chosen as the sole tool to predict AFE and TE occurrence in the fate and occurrence model.

The first attempt at chemical equilibrium integration with the model environment, as explained in Appendix B, required Matlab to be commanded to automatically open, run, and close FactSage chosen

to conduct the chemical equilibrium calculations for both the particle and bulk phases. However, this first integration attempt was considered impractical due to the following limitations.

- A single run of chemical equilibrium calculation takes around three seconds or more, depending on the number of input and output compounds. The burner height of 3.8 m was discretised into a number of identical 0.001-m thin slices. Each particle was discretised into 3-times-3 resolution. These discretisation settings generate 239,463 calculations. The time required to calculate these calculations was 239,463 times 3 s, equivalent to 8.3 days. This long computation time was not practically feasible.
- A test of the maximum possible number of FactSage automatic runs was conducted. According to the test, FactSage was able to run automatically not more than around 3,400 times. When exceeding 3,400 times, a run-time error window appeared, which notified the user that FactSage had failed to conduct further calculations. Until now, there has not been any official statement from the FactSage developer regarding this limitation.

To eliminate these limitations, a second attempt of integration explained in Appendix C was conducted using Model Development Suite (MoDS), which is a statistical software package developed by CMCL Innovations. Chemical equilibrium calculation results were generated from 3,000 FactSage automatic runs. These generated results were converted into multiple enciphered files stored in a single folder. These files acted as a chemical equilibrium function called by a Matlab Executable (MEX) file provided by CMCL Innovations.

A performance test was conducted on the second integration. The test revealed that the chemical equilibrium calculation time was significantly reduced for a single calculation. However, further observation of compound partition, e.g. $\text{AsO}_{(\text{g})}$, as a function of time exhibits a severely inconsistent trend as shown in Figure 6.3. The molar mass occurrence of $\text{AsO}_{(\text{g})}$ at temperatures above 1800 °C is distributed inconsistently. A quantitative measurement of the degree of deviation of Sobol sequence regression results from FactSage chemical equilibrium calculation results was conducted. The temperature range was set from 500°C to 1500 °C under atmospheric pressure. All element molar masses were set at 1 mol. The molar mass deviations of three common TEs, $\text{AsO}_{(\text{g})}$, $\text{PbO}_{(\text{g})}$, and $\text{Cd}_{(\text{g})}$, in biomass combustion are shown in Figure 6.4. At lower temperature, the deviation is extremely high for both $\text{AsO}_{(\text{g})}$ and $\text{PbO}_{(\text{g})}$. It decreases as temperature rises towards a peak. On the other hand, the $\text{Cd}_{(\text{g})}$ molar mass deviation tends to be only slightly influenced by temperature variation.

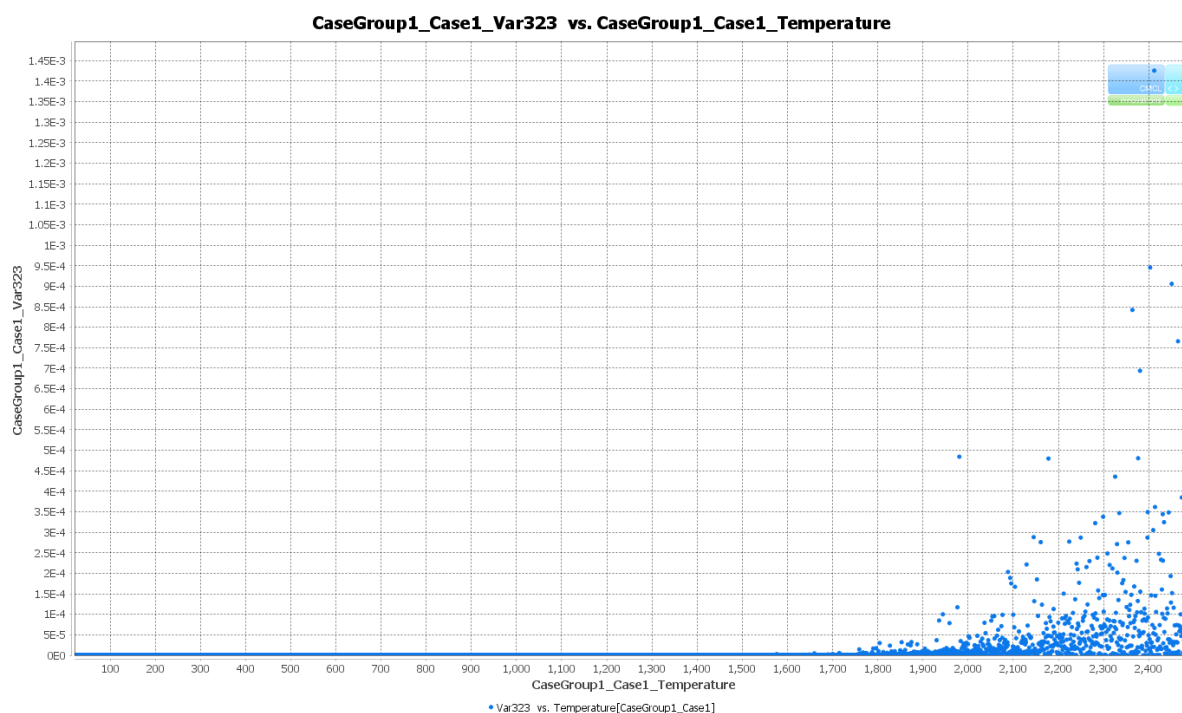


Figure 6.3 Sobol Sequence Data for $\text{AsO}_{(g)}$ Molar Mass (y -axis) vs Temperature (x -axis)

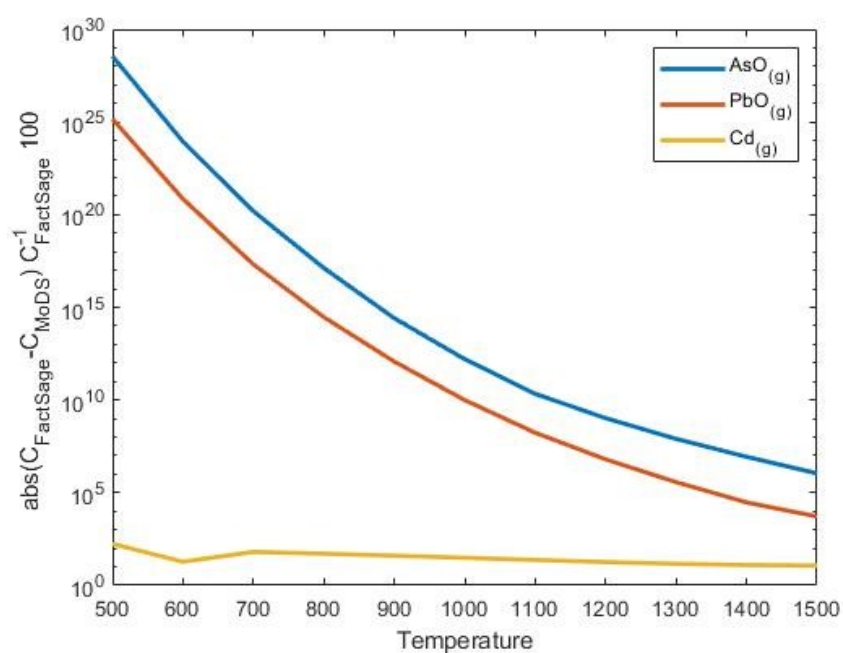


Figure 6.4 Deviations in Chemical Equilibrium Results for $\text{AsO}_{(g)}$, $\text{PbO}_{(g)}$, and $\text{Cd}_{(g)}$

The fate and occurrence model using the second integration was run to observe the effect of deviation in the Sobol sequence regression result on AFE and TE fate and occurrence. The run was initially without problems. However, when relatively significant amounts of intra-particle AFGC and TGC were

present, the model became very computationally expensive. The number of elements was then reduced in an attempt to avoid expensive computation, by including all AFEs but only one TE. This assumption was based on the idea that chemical interaction of one TE with another was very unlikely to occur. However, the fate and occurrence model still did not show any significant improvement. Further investigation revealed that the cause of expensive computation was that the fate and occurrence model was not capable of handling calculations involving the number of gas species that were present.

6.4 Concluding Remarks

Mathematical rendering of chemical equilibrium has been used for years to predict the fate and occurrence of AFEs and TEs in numerous works on coal and biomass combustion. Although the chemical interaction of AFEs and TEs is kinetically limited, use of chemical equilibrium results can generate relatively good predictions. Moreover, chemical equilibrium has also been used to investigate other aspects that affect predictions of AFE and TE fate and occurrence, e.g. inlet gas composition, solid fuel composition, operating condition, etc. Hence, given that chemical equilibrium methods are practical and reliable, the work performed for this thesis employed chemical equilibrium methods to produce a fate and occurrence model. To reduce calculation complexity, the fate and occurrence model was equipped with engineering assumptions.

AFE and TE were considered homogeneously distributed in wood. Homogeneous distribution of TE in wood is mostly realised via pressurised impregnation and soil absorption. Only a few TEs are concentrated at the wood surface, particularly those that originate from paint. Although TE accumulation at the wood surface promotes non-uniform TE concentrations between particles, varying TE concentration may not significantly affect the results of the fate and occurrence model.

The fractional pyrolysed masses of inorganic constituents were assumed equal to the fractional pyrolysed masses of organic constituents. This assumption was made due to a lack of individual AFE and TE pyrolysis rate equations. The pyrolysed inorganic constituents are decomposed into solid pure elements. However, each AFE and TE in wood is in its original form. Assuming that each original AFE and TE in wood occurs as the pure element neglects decomposition heat. However, a calculation suggested that this assumption was plausible since decomposition heat contributes little to temperature change.

Solid aerosols formed via AFE and TE compound nucleation were assumed to flow with the same velocity as the bulk gas, since the size of the solid aerosols was considered to be very small with very low Stoke numbers. Unless parameters such as surface tension and saturation ratio are available, solid aerosol velocity is essentially not calculable. However, most of the required parameters are not available in the literature.

Particle size expansion due to AFE and TE gas condensation within particles at low temperature was assumed negligible. This assumption was made because the fate and occurrence model was separated from the entrained-flow combustion model. Future improvement may discard this assumption by integration of both models.

To integrate the chemical equilibrium software (FactSage) with the model environment (Matlab), two integration methods were attempted, namely: direct command of FactSage with Matlab, and use of a chemical equilibrium function built with MoDS. However, both methods proved inefficient to implement. In Chapter 6, another method in which the fate and occurrence model is simplified is introduced to eliminate this inefficiency. The simplification transforms discretised particles into a single node particle to avoid expensive computation. A single node assumption that considers temperature within the entire particle body to be uniform is plausible, since particle sizes are very small to have an intra-particle temperature gradient. The assumption of uniform temperature was validated by the presence of a very low Biot number for white wood, as shown in Figure 6.5.

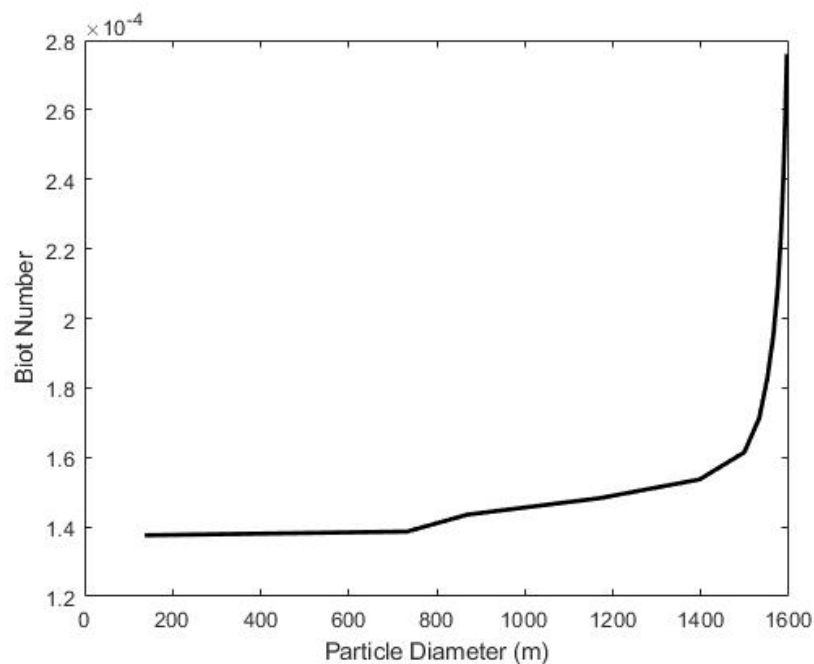


Figure 6.5 White Wood Biot Numbers

Chapter 7

Simplified Entrained-flow Combustion Model and Simplified Fate and Occurrence Model

This chapter discusses the development of the simplified entrained-flow combustion model and the simplified fate and occurrence model. As previously explained in Chapter 6, the incorporation of intra-particle profiles as parameters and platforms for the intra-particle AFE and TE concentrations results in a very computationally expensive calculation. The simplified entrained-flow combustion model reduces the computation cost by eliminating particle temperature and concentration gradients and assuming lumped particle temperatures and concentrations, as justified with low Biot numbers shown in Figure 6.5. for biomass particles. The simplified fate and occurrence model is practically the fate and occurrence model with lumped particle concentrations. Section 7.1 discusses the development of the simplified entrained-flow combustion model with the simplified fate and occurrence model. Section 7.2 introduces ChemApp as the chemical equilibrium software package that was used in the work described in this chapter. Section 6.3 discusses the validation of the results of both models with the respective experimental results.

7.1 Mathematical Concept of the Model

The route of calculation in the simplified entrained-flow combustion model in a single thin slice is illustrated in Figure 7.1. The thin slice is shown in the figure as a grey rectangular area with a thickness of Δh . The thin slice is divided by a vertical dashed line into two areas, namely: the left-hand area for the particle phase and the right-hand area for the bulk phase. Particles enter the upper side of the

rectangle at height $a - 1$ and exit the rectangle's lower side at height a . The thermodynamic and physical properties of the entering particles are generated in the thin slice above the one studied. Similarly to the calculations in Chapter 5, each differential term is divided by the particle falling velocity, $v_{p(b)}$, of a particle of size cluster b , to convert the time-based calculation to the height-based calculation.

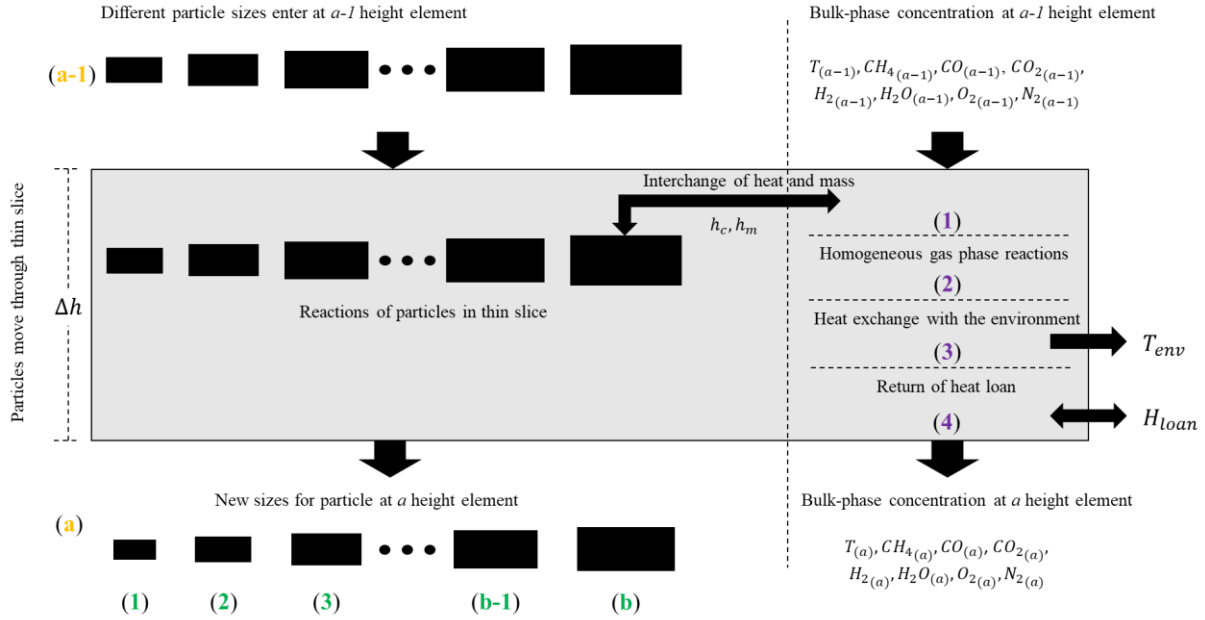


Figure 7.1 Combustion Model Structure of a Thin Slice with Non-discretised Particle

Particle temperature at any height in the thin slice is calculated by use of Equation 7.1.

$$\frac{\partial T_{p(b)}}{\partial h} = \frac{(h_{c(b)}(T_{(a-1)} - T_{p(b)}) + \epsilon_{p(b)} \sigma (T_{(a-1)}^4 - T_{p(b)}^4)) A_{p(b)}}{v_{p(b)} m_{p(b)} c_{p(b)}} \quad (E7.1)$$

$T_{p(b)}$ is the temperature of the particle of size cluster b in K. To simplify the model, all particles are considered to have no intra-particle temperature gradient. This means that $T_{p(b)}$ is a uniform temperature at any location in the body of the particle of size cluster b . This assumption is also applied to all other intra-particle thermodynamic properties. $h_{c(b)}$ is the coefficient of convective heat transfer of a particle of size cluster b in $W m^{-2} K^{-1}$ and calculated by use of Equation 4.73. $\epsilon_{p(b)}$ is the emissivity of a particle of size cluster b . $m_{p(b)}$ is the mass of a particle of size cluster b in kg. $c_{p(b)}$ is the heat capacity of a particle of size cluster b in $J kg^{-1} K^{-1}$ and calculated via Appendix B.1. $A_{p(b)}$ is the surface

area of a particle of size cluster b in m^2 . $v_{p(b)}$ is the falling velocity of a particle of size cluster b in m s^{-1} and calculated via Appendix D. $\epsilon_{p(b)}$ is calculated via Appendix B.10.

The loss rate of moisture mass of a particle of size cluster b , $\frac{dm_{H_2O(l)p}}{dt}_{(R4.1)(b)}$, and the rate of temperature change due to Reaction 4.1, $\frac{dT_p}{dt}_{(R4.1)(b)}$, are calculated via Appendix C.1.

The wood is pyrolysed via Reaction 7.1. This reaction is the simplification of the reactions in Figure 4.3. The purpose of the simplification is to avoid mass balance inaccuracies. The secondary cracking allows the simultaneous generation and decomposition of tar during pyrolysis. A false synergy between the kinetics of tar generation and decomposition forms inaccurate quantities of tar and, eventually, pyrolysis gas. The inaccurate quantities result in either higher or lower quantities of generated pyrolysis gas than the supposed quantities.



x_1 is the ratio of volatile matter mass to dry ash-free wood mass. x_2 is the ratio of fixed carbon to dry ash-free wood mass. Gas and char formation rates of a particle of size cluster b , $\frac{dm_{gas_p}}{dt}_{(R6.1)(b)}$ and $\frac{dm_{char_p}}{dt}_{(R6.1)(b)}$, and the respective rates of temperature change, $\frac{dT_p}{dt}_{(R6.1)(b)}$, are calculated via Appendix C.2.

The calculations of the decomposition rates of heterogeneous char of a particle of size cluster b , e.g. $\frac{dm_{char_p}}{dt}_{(R4.10)(b)}$, $\frac{dm_{char_p}}{dt}_{(R4.11)(b)}$, and $\frac{dm_{char_p}}{dt}_{(R4.12)(b)}$, are explained in Appendix C.5 as functions of the effectiveness factors, e.g. $\eta_{(R4.10)(b)}$, $\eta_{(R4.11)(b)}$, and $\eta_{(R4.12)(b)}$, defined as the ratios of the actual reaction rates to the intrinsic reaction rates. However, the research performed for this thesis assumes that $\eta_{(R4.10)(b)}$, $\eta_{(R4.11)(b)}$, and $\eta_{(R4.12)(b)}$ are equal to 1. The reason behind this assumption is that, in Appendix C.5, most of $m_{char_p(b)}$ has powers of less than unity. These powers are considered to account for $\eta_{(R4.10)(b)}$, $\eta_{(R4.11)(b)}$, and $\eta_{(R4.12)(b)}$ by reducing the value of $m_{char_p(b)}$. In addition, this value reduction may be due to convective bulk gas diffusion resistance. To investigate the influence of the resistance of the bulk gas to diffusion, the *fzero* function in Matlab was used to solve Equation C.45, C.46, and C.47. The investigation revealed that the calculation could not progress after a certain number of steps due to the limitation of the *fzero* function to solve stiff iterations. However, the calculation could progress further when the power was changed from the default values, e.g. 0.49, to higher values, e.g. 1, 2, etc. Therefore, at this stage, the particle surface pressure was set equal to the bulk pressure as

a justified assumption to simplify the calculation of Equation C.45, C.46, and C.47. The rates of the temperature change of the particle of size cluster b is calculated via Equation C.51, C.52, and C.53.

Mass in kg and volume in m^3 of the particle of size cluster b are assumed to be linearly correlated as formulated in Equation 5.5.

The mass fraction of each pyrolysis compound, $x_{m_{i_{vm}}}$, is calculated by use of Equation 7.2 based on ultimate analysis results.

$$x_{m_{i_{vm}}} = \frac{n_{i_{vm}} MW_i}{\sum_{i=1}^5 n_{i_{vm}} MW_i} \quad (\text{E7.2})$$

The release molar mass rate profile of gas compounds in mol s^{-1} are calculated via Equation 7.3 for drying, 7.4 for pyrolysis, 7.5 for char oxidation, 7.6 for gasification with $\text{CO}_{2(g)}$, and 7.7 for gasification $\text{H}_2\text{O}_{(g)}$.

$$\dot{F}_{i_{p(b)}} = x_3 \frac{\frac{dm_{\text{H}_2\text{O}(l)}_p}{dt} (R4.1)(b)}{\left(\frac{MW_i}{1000}\right)}; i = 1 \text{ for } \text{CH}_{4(g)}, 2 \text{ for } \text{CO}_{(g)}, \text{etc} \quad (\text{E7.3})$$

$$\dot{F}_{i_{p(b)}} = x_4 \frac{x_{m_{i_{vm}}} \frac{dm_{\text{gas}}_p}{dt} (R6.1)(b)}{\left(\frac{MW_i}{1000}\right)}; i = 1 \text{ for } \text{CH}_{4(g)}, 2 \text{ for } \text{CO}_{(g)}, \text{etc} \quad (\text{E7.4})$$

$$\dot{F}_{i_{p(b)}} = x_5 \frac{\frac{dm_{\text{char}}_p}{dt} (R4.10)(b)}{\left(\frac{MW_i}{1000}\right)}; i = 1 \text{ for } \text{CH}_{4(g)}, 2 \text{ for } \text{CO}_{(g)}, \text{etc} \quad (\text{E7.5})$$

$$\dot{F}_{i_{p(b)}} = x_6 \frac{\frac{dm_{\text{char}}_p}{dt} (R4.11)(b)}{\left(\frac{MW_i}{1000}\right)}; i = 1 \text{ for } \text{CH}_{4(g)}, 2 \text{ for } \text{CO}_{(g)}, \text{etc} \quad (\text{E7.6})$$

$$\dot{F}_{i_{p(b)}} = x_7 \frac{\frac{dm_{\text{char}}_p}{dt} (R4.12)(b)}{\left(\frac{MW_i}{1000}\right)}; i = 1 \text{ for } \text{CH}_{4(g)}, 2 \text{ for } \text{CO}_{(g)}, \text{etc} \quad (\text{E7.7})$$

The values of x_i of the calculated gas compounds are listed in Table 7.1.

Table 7.1 Combustion Gas Heat Capacity Parameters

x_i	Gas						
	$\text{CH}_{4(g)}$	$\text{CO}_{(g)}$	$\text{CO}_{2(g)}$	$\text{H}_{2(g)}$	$\text{H}_2\text{O}_{(g)}$	$\text{O}_{2(g)}$	$\text{N}_{2(g)}$
x_3	0	0	0	0	1	0	0
x_4	1	1	1	1	1	0	0

x_5	0	1	0	0	0	-0.5	0
x_6	0	2	-1	0	0	0	0
x_7	0	1	0	1	-1	0	0

The total molar mass rate of each individual major compound of the particle of size cluster b , $\dot{F}_{ip(b)}$, is summed as shown in Equations 7.8.

$$\dot{F}_{ip(b)} = \dot{F}_{ip(b)(R4.1)} + \dot{F}_{ip(b)(R7.1)} + \dot{F}_{ip(b)(R4.10)} + \dot{F}_{ip(b)(R4.11)} + \dot{F}_{ip(b)(R4.12)} \quad (E7.8)$$

The total molar mass rate with positive sign indicates gas release to the bulk, whilst total molar mass rate with negative sign indicates gas penetration to the particle. Release and penetration rates of individual major gas compounds, $\dot{F}_{ip_{rel}(b)}$ and $\dot{F}_{ip_{pen}(b)}$, from and to a particle of size cluster b in mol s^{-1} are expressed in Equations 5.15 and 5.16. The total molar rates of release and penetration within a thin slice in mol s^{-1} are calculated using integration and shown in Equations 5.18 and 5.19.

The route of calculation for the simplified fate and occurrence model in a single thin slice is illustrated in Figure 7.2. The thin slice is shown in the figure as a grey rectangular area with a thickness of Δh . The bulk temperature and velocity at height index $a - 1$ and a are generated from the simplified combustion model and used as parameters in the simplified fate and occurrence model.

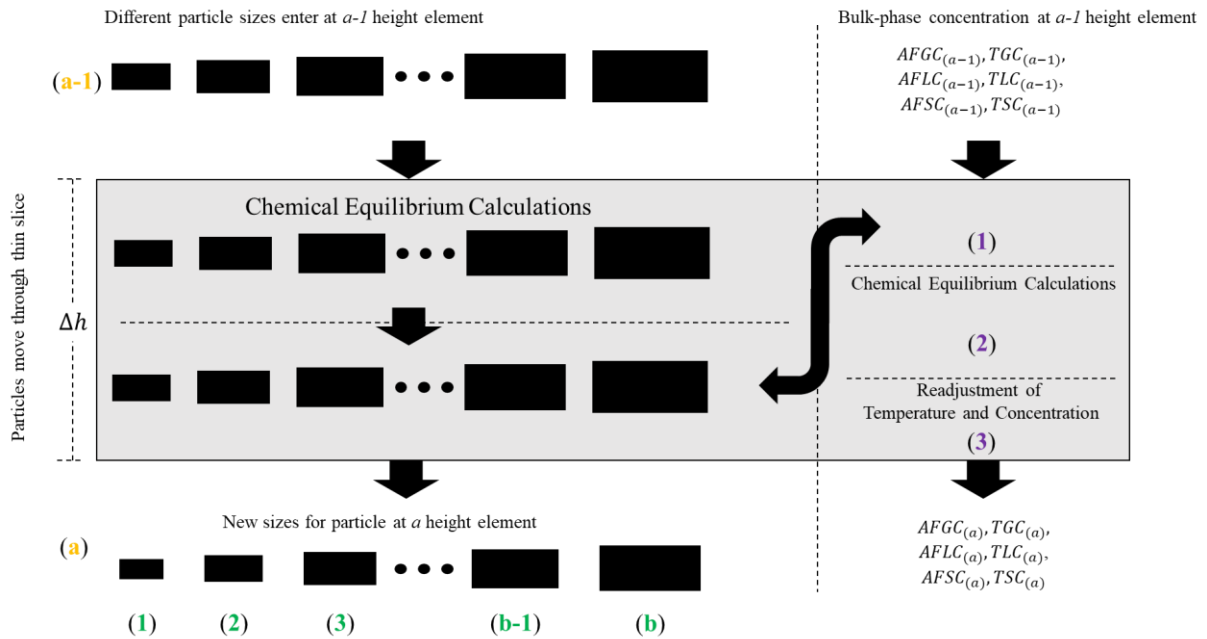


Figure 7.2 AFE and TE Model Structure in a Thin Slice with Non-discretised Particle

The masses of AFEs and TEs generated from pyrolysis are calculated with use of Equation 7.9.

$$m_{inorg p(a-1,b)} - m_{inorg p(a,b)} = \frac{m_{org p(a-1,b)} - m_{org p(a,b)}}{m_{org p(a-1,b)}} m_{inorg p(a-1,b)} \quad (E7.9)$$

$m_{inorg p(a-1,b)}$ and $m_{inorg p(a,b)}$ are inorganic constituent masses at height index $a - 1$ and a of the particle of size cluster b . $m_{org p(a-1,b)}$ and $m_{org p(a,b)}$ are organic constituent masses at height index $a - 1$ and a of a particle of size cluster b . The generated masses of AFEs and TEs, $m_{AFE p_{conv}(a-1,b)}$ and $m_{TE p_{conv}(a-1,b,m,n)}$, are calculated via Equations 7.10 and 7.11.

$$m_{AFE p_{conv}(a-1,b)} = \left(m_{inorg p(a-1,b)} - m_{inorg p(a,b)} \right) \frac{m_{AFE}}{\sum_{AFE=1}^{10} m_{AFE} + \sum_{TE=1}^{12} m_{TE}} \quad (E7.10)$$

$$m_{TE p_{conv}(a-1,b,m,n)} = \left(m_{inorg p(a-1,b)} - m_{inorg p(a,b)} \right) \frac{m_{TE}}{\sum_{AFE=1}^{10} m_{AFE} + \sum_{TE=1}^{12} m_{TE}} \quad (E7.11)$$

In the particle phase, $m_{AFE p_{conv}(a-1,b)}$ and $m_{TE p_{conv}(a-1,b,m,n)}$ are added to the pure elements of AFSCs and TSCs at height index $a - 1$, e.g. $K_{(s)}$, $Ca_{(s)}$, and $Cr_{(s)}$. All inorganic compounds are processed into the chemical equilibrium calculation to obtain the new AFLCs, TLCs, and AFSCs, and TSCs at height index a . The new AFGCs and TGCs are released to the bulk phase and added to the existing $AFGC_{(a-1)}$ and $TGC_{(a-1)}$ in stage 1 of the bulk phase calculation. The bulk-phase chemical equilibrium calculation is applied in stage 2. In stage 3, all AFCs and TCs concentrations are adjusted according to $T_{b(a)}$.

7.2 Chemical Equilibrium Integration

In Section 6.3, it is shown that the first and second integration methods are not practically compatible with the fate and occurrence model. The first integration method requires a considerable amount of time to perform a single chemical equilibrium calculation. The fate and occurrence model consists of thousands of calculation points for each particle at each height position. The second integration method successfully overcomes the incompatibility of the first integration. However, the calculation accuracy is severely sacrificed due to the degree of multidimensionality. To eliminate these problems, the third integration method is proposed by using ChemApp as the chemical equilibrium calculator.

ChemApp is practically FactSage without a user interface. With the absence of a user interface, ChemApp is essentially digital libraries that contain minimum Gibbs free energy equations. These digital libraries work as a chemical equilibrium function called by user-written or commercially available third-party coding software. ChemApp integration with Matlab generates results as accurate as those that would be expected from FactSage but without excessive time consumption.

ChemApp has not been utilised as frequently as FactSage in studies of coal and biomass combustion. However, ChemApp has been used for some studies, such as to predict ash-fusion behaviour,^{256,257} and in a combustion process, ChemApp has been used to predict inorganic element speciation.^{258,259} ChemApp has also been used to investigate the influence of $\text{HCl}_{(\text{g})}$, $\text{SO}_{2(\text{g})}$, and $\text{H}_2\text{O}_{(\text{g})}$ concentrations on AFE and TE fate and occurrence during combustion.^{260,261} Furthermore, the fate and occurrence of individual elements has also been investigated using ChemApp in gasification.^{262,263,264} One study was conducted on alkali metal speciation under the influence of varying gas pressures and solid fuel compositions.²⁶⁵

Matlab and ChemApp are integrated through the following brief procedure, namely: writing up a bridging program, preparing files, and compiling a MEX file. The bridging program is composed of lines of subroutines written in one of four different computational languages, i.e. C/C++, FORTRAN, Delphi, and Visual Basic, to command the library to perform specific actions. For the work described in this thesis, the bridging program was written in C/C++ with Microsoft Visual Studio. By default, ChemApp is written in FORTRAN and is readily compatible with a FORTRAN-written bridging program. An interface file, “cacint.c”, and a header file, “cacint.h”, are provided by GTT Technologies, the developer of ChemApp, to provide translated subroutines compatible with most C/C++ compilers. The utilised subroutines and the bridging program consisting of output assignment, chemical equilibrium calculation, and input assignment are shown in Appendix D. To compile the MEX file, the bridging program, “cacint.c”, “cacint.h”, dynamic library, static library, and a builder program are required. The bridging program is named “chemapp.cpp”. The dynamic and static library, “ca_vc_e_x64.dll” and “ca_vc_e_x64.lib”, are the compilation of minimum Gibbs free energy equations. The builder program, “build.cmd”, is run to compile the MEX file. The MEX file is named “chemapp.mexw64”.

Chemical equilibrium calculations using “chemapp.mexw64” are unable to proceed without thermochemical data files generated manually from FactSage. After setting up all reactants in the “Reactant” window shown in Figure F.2, the “File” button is pressed in the “Menu: last system” window shown in Figure F.3. From the dropdown menu, “File” ► “ChemSage File” ► “Save ChemSage File ...” is chosen to save the thermochemical data file based on the set of reactants. Before saving the file, the file format is set below the “Save ChemSage File ...” button, either as ASCII (.dat) or transparent (.cst) data files. Another format, .e.g. binary data file (.bin), may also be used to accommodate customised data files. For the work performed for this thesis, the thermochemical data files were saved as “all_elements_with_Ar.cst”.

The name “all_elements_with_Ar.cst” accentuates that argon is included in the reactant system. Without the inclusion of argon, the chemical equilibrium calculation may be halted at certain burner height indices. Introduction of all AFEs and TEs as inputs might cause a problem associated with

extreme dimensionality of the chemical system. With X number of elements, the Gibbs free energy minimiser needs to find the $X - 1$ dimensional tangent hyperplane to the most stable compounds and the gas phase that is lowest in Gibbs free energy for the system composition. The minimiser becomes unable to manage this problem whilst all different combinations are being tested. To enhance the robustness of the minimiser, gas phase stability needs to be increased to enable all compound activities to be fixed in the gas phase. Gas phase stability can be increased by the addition of a small amount of noble gas, e.g. argon, helium, neon, krypton, or xenon, as is done here.

7.3 Model Result Discussion and Validation

The modelled bulk gas temperature profile and bulk $O_{2(g)}$ molar percentage profile generated from the simplified entrained-flow combustion model were compared with the experimental profiles. The results are shown in Figures 7.3 and Figure 7.4 for air-combustion. The comparison exhibits reasonable validation of the modelled profiles with the experimental profiles. However, the peak temperature that is shown in the modelled temperature profile is undetected in the experimental temperature profile. This is due to the installed position of the temperature probe to measure the temperature at the burner centreline, whilst the peak temperature was thought to be established near the burner wall. Similarly, the molar percentage of bulk $O_{2(g)}$ gas was undetected within 0.5 m of the burner's uppermost section. $O_{2(g)}$ may have been concentrated near the burner wall and reacted with gasification products to establish the peak temperature. Under these conditions, there is no $O_{2(g)}$ at the burner centreline and hence it is undetected by the $O_{2(g)}$ concentration probe, which, like the temperature probe, is positioned at the burner centreline. The more detailed explanation on this peak temperature deviation is discussed in Section 5.4.

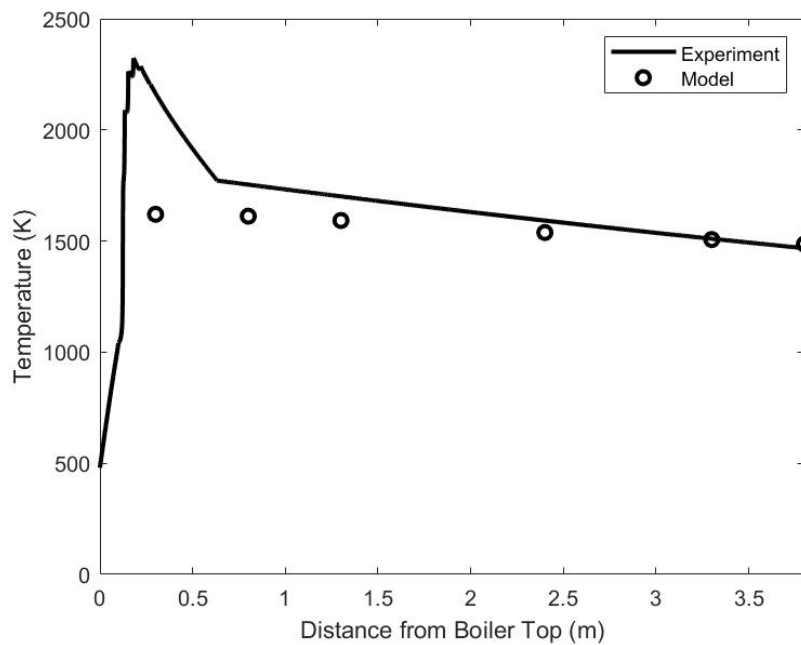


Figure 7.3 Validation of the Modelled Bulk Gas Temperature Profile of White Wood during Air-combustion in the PACT Entrained-flow Burner

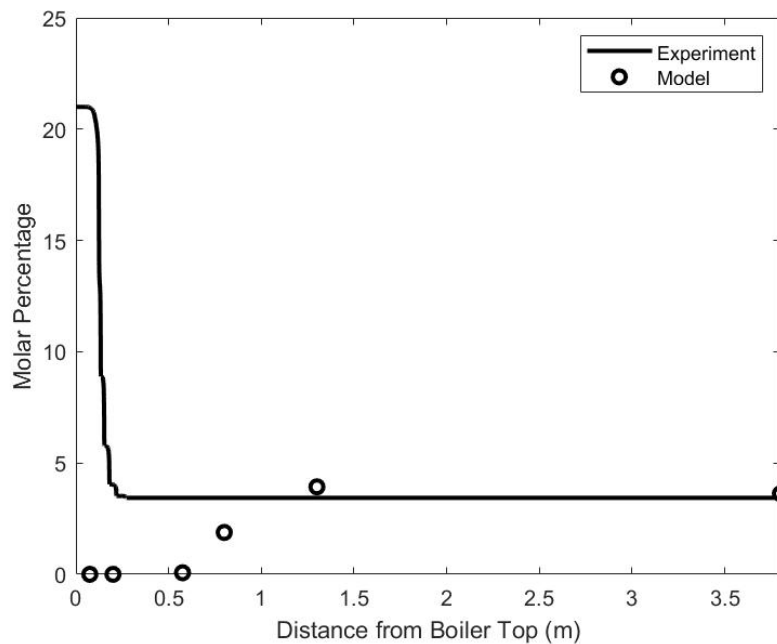


Figure 7.4 Validation of Dry Molar Percentage Profile of the Modelled Bulk $O_{2(g)}$ Gas during Air-combustion of White Wood in the PACT Entrained-flow Burner

For oxy27-combustion, the modelled bulk gas temperature and bulk $O_{2(g)}$ molar percentage profiles generated by the simplified entrained-flow combustion model were compared with the experimental profiles and the results are shown in Figures 7.5 and Figure 7.6, respectively. The comparison shows poor validation of the modelled profiles with the experimental profile. The modelled temperature profile is higher than that found by experiment. On the other hand, the modelled bulk $O_{2(g)}$ profile is lower than that found by experiment. The poor validation might be because of the limitation of the model lacking in incorporating temperature and gas concentration radial distribution. The validation improves as the bulk gas temperature measurement approaches the bottom of the burner. This might indicate that bulk gas temperature becomes more uniformly radially distributed near the bottom of the burner. This distribution pattern of the temperature of the bulk gas also affects the distribution pattern in the bulk $O_{2(g)}$. Nevertheless, stoichiometric calculation shows that the final $O_{2(g)}$ molar percentage once complete burnout is achieved is around 1% as comprehensively explained in Appendix I, which is in agreement with the data shown in Figure 7.6.

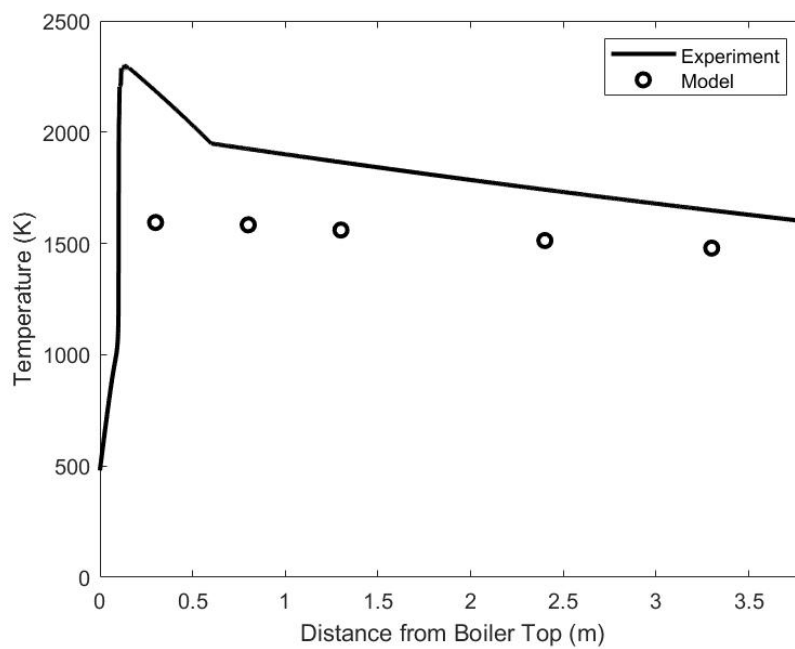


Figure 7.5 Validation of the Modelled Bulk Gas Temperature Profile of White Wood during Oxy27-combustion in the PACT Entrained-flow Burner

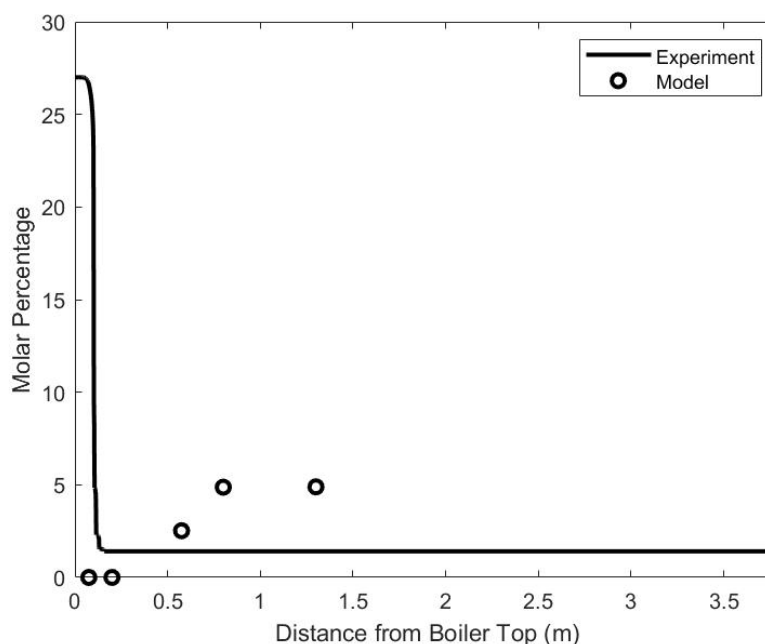


Figure 7.6 Validation of Dry Molar Percentage Profile of the Modelled Bulk $O_{2(g)}$ Gas during Oxy27-combustion of White Wood in the PACT Entrained-flow Burner

Fate and occurrence profiles of each AFE and TE in three combustion cases, that is, white wood during air-combustion, white wood during oxy27-combustion, and recycled wood in air-combustion, were calculated using the fate and occurrence model and compared against each other. The comparison between white wood in air-combustion and in oxy27-combustion aimed to study the influence of the $O_{2(g)}$ molar quantity on the fate and occurrence of AFEs and TEs. The results of combustion of white wood in air were also compared with the results of combustion of recycled wood in air to study the influence of AFE and TE concentrations in the particles on their fate and occurrence. The fate and occurrence profiles of three important AFEs, e.g. potassium, calcium, and silicon, and two TEs, e.g. copper and chromium, are discussed in this section. The discussion of the other AFEs and TEs are compiled in Appendix J.

Potassium

The modelled fate profile of potassium is shown in Figure 7.7 for the Air/Oxy27 comparison and Figure 7.8 for the white/recycled wood comparison. In both figures, it can be seen that potassium shows a similar fate profile to that for sodium. This similarity might be due to the dependency of potassium volatilisation on the sodium content.²⁶⁶

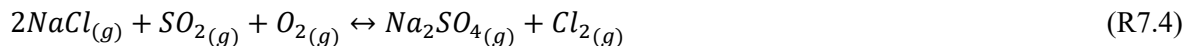
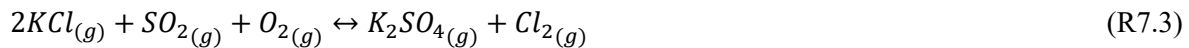
Modelled potassium occurrence profiles for both air-combustion and oxy27-combustion of white wood are shown in Figures 7.9 and 7.10. Before the peak temperatures within the topmost 0.1 m of the burner,

multiple compound transitions occur at low temperatures. These compound transitions are not of concern in this evaluation since the mass of these compounds is considered negligible, as seen in Figures 7.7 and 7.8, and potassium is primarily still concentrated in particles. This trend also occurs in all occurrence evaluations throughout this thesis. A significant proportion of $\text{KOH}_{(g)}$ is formed when the bulk gas temperature is about to reach its peak. Potassium is released from biomass mainly as $\text{KOH}_{(g)}$ and $\text{KCl}_{(g)}$.²⁶⁷ The bulk occurrence of potassium is essentially dictated by Reaction 7.2.²⁶⁸



Above 1050 K, both forward and backward reactions shown in Reaction 6.4 are fast and are considered to be in equilibrium. Since a significant amount of $\text{H}_2\text{O}_{(g)}$ is present, the forward reaction rate dominates the backward reaction rate. This domination of the forward reaction means that $\text{KOH}_{(g)}$ is the major potassium compound formed.

Furthermore, a fraction of sulphur might be volatilised as $\text{SO}_{2(g)}$. $\text{SO}_{2(g)}$ reacts with $\text{KCl}_{(g)}$, and additionally with $\text{NaCl}_{(g)}$, as expressed in Reactions 7.3 and 7.4.



However, $\text{K}_2\text{SO}_{4(g)}$ and $\text{Na}_2\text{SO}_{4(g)}$ are formed in minor amounts. Reactions 6.5 and 6.6 are known to be slow reactions, so sufficient reaction time, e.g. during $\text{KCl}_{(g)}$ and $\text{NaCl}_{(g)}$ deposition on the superheater probe, is required to enable formation of the sulphates.²⁶⁹

The modelled potassium occurrences during air-combustion of recycled wood are shown in Figure 7.11. During the *heat loss* stage, formation of $\text{KAlSi}_2\text{O}_{6(s2)}$, $\text{KAlSi}_2\text{O}_{6(s2)}$ and $\text{NaAlSi}_3\text{O}_{8(s2)}$ might indicate similar potassium and sodium occurrences during combustion. In a boiler with an integrated superheater, refractory material is formed and grows at a certain rate on the superheater surface. Within this refractory material, alkali metal compounds react with silicate compounds. Upon aerosol arrival at the refractory material, it deposits on the superheater surface, after which alkali metal and silicates may react via aerosol collisions.²⁷⁰ Within the refractory material, $\text{KAlSi}_2\text{O}_{6(s2)}$ is commonly found along with other similar compounds, e.g. $\text{KAlSiO}_{4(s)}$, $\text{NaAlSi}_3\text{O}_{8(s2)}$, etc.²⁷¹ The formation is possibly via Reaction 7.5.²⁷²



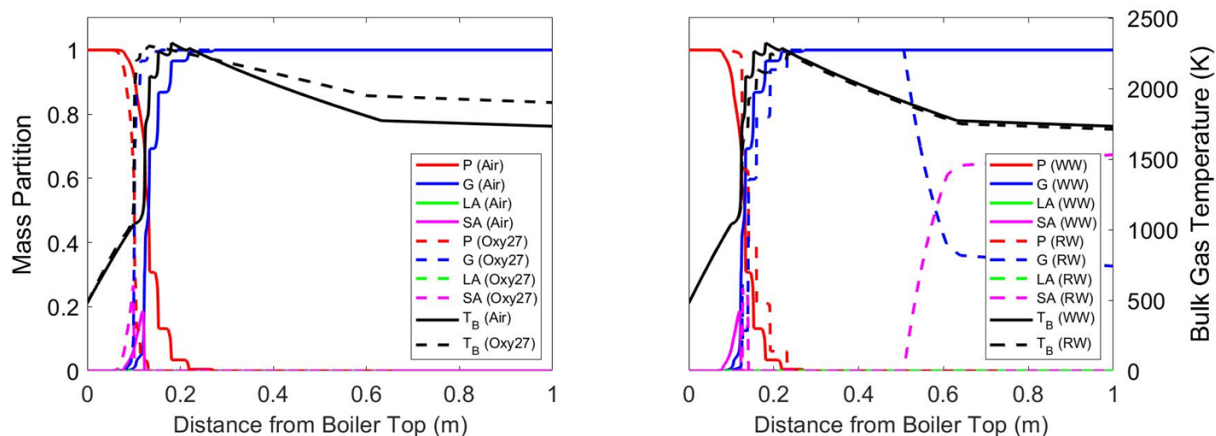


Figure 7.7 (Left) Modelled Potassium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood; **Figure 7.8 (Right)** Modelled Potassium Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

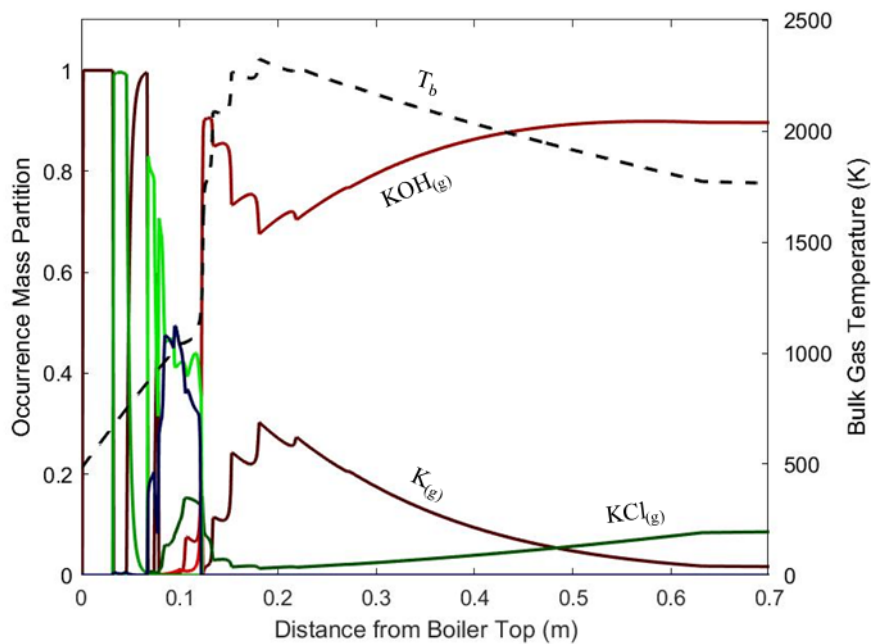


Figure 7.9 Modelled Potassium Bulk Occurrences in Air-combustion of White Wood

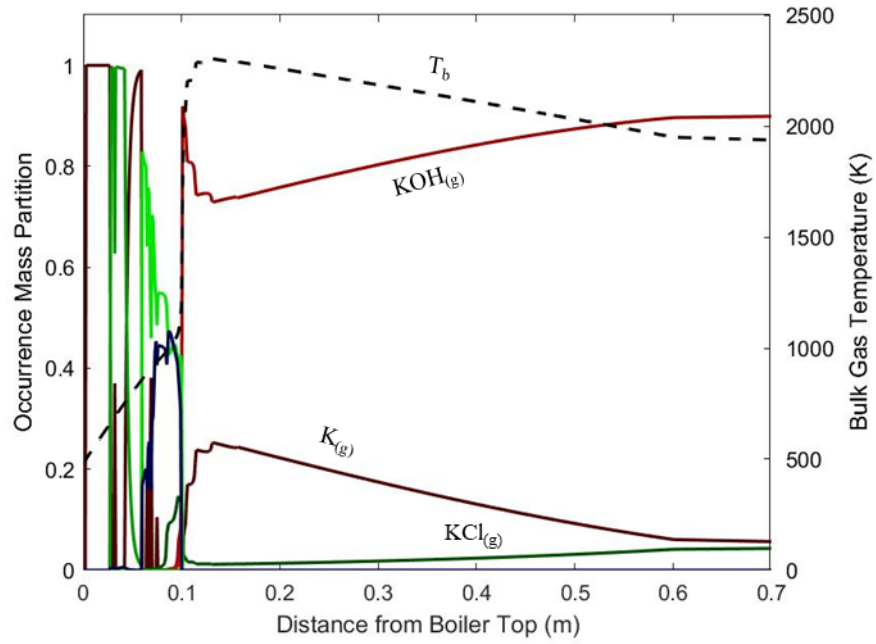


Figure 7.10 Modelled Potassium Bulk Occurrences in Oxy27-combustion of White Wood

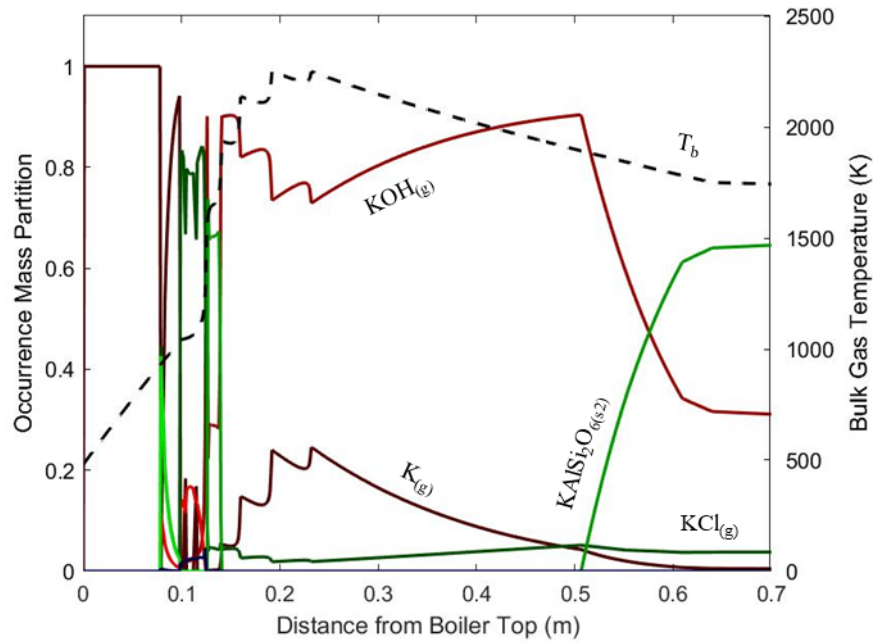


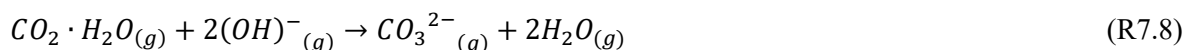
Figure 7.11 Modelled Potassium Bulk Occurrences in Air-combustion of Recycled Wood

Calcium

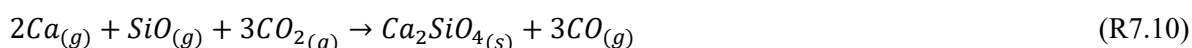
The modelled fate profiles for calcium are shown in Figure 7.12 for the Air/Oxy27 comparison and Figure 7.13 for the white/recycled wood comparison. Figure 7.12 shows that calcium is surprisingly

quite highly volatilised.²⁷³ Most of the released calcium forms solid aerosols. Calcium has a strong tendency to associate with silicate and, to some extent, magnesium.²⁷⁴ In Figure 7.13, air-combustion of recycled wood favours formation of solid calcium aerosols, probably due to the greater calcium content of recycled wood.

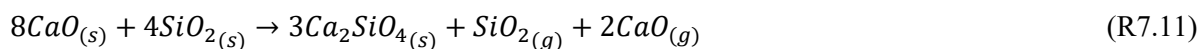
Modelled occurrence profiles of bulk calcium in both air-combustion and oxy27-combustion of white wood are shown in Figures 7.14 and 7.15. A small partition of $\text{Ca(OH)}_{2(g)}$ is formed, as shown in both figures. $\text{CaCO}_{3(g)}$ is likely to form at fast rates at low temperature according to Reactions 7.6, 7.7, 7.8, and 7.9.²⁷⁵



However, these reactions are less likely at high temperature, when calcium occurrence might be shifted from $\text{CaCO}_{3(g)}$ to $\text{Ca(OH)}_{2(g)}$.²⁷⁶ The major bulk calcium compound formed during air-combustion or oxy27-combustion of white wood is $\text{Ca}_2\text{SiO}_{4(s)}$. $\text{Ca}_2\text{SiO}_{4(s)}$ is likely to form due to calcium reaction with $\text{SiO}_{(s)}$ aerosols. Calcium might be released as $\text{Ca}_{(g)}$ and nucleate during reaction with $\text{SiO}_{2(g)}$ at temperatures from 1623K to 1873 K, as in Reaction 7.10.²⁷⁷



At the lower temperature range of 1143 to 1751 K, a different mechanism might promote formation of $\text{Ca}_2\text{SiO}_{4(s)}$ by Reaction 7.11.²⁷⁸



A significant amount of calcium remains in particulate form, mostly as $\text{CaSiO}_{3(s)}$, during air-combustion of recycled wood, as shown in Figure 7.16. According to Table 3.1, the initial concentration of calcium in recycled wood is similar to the initial concentration of silicon in recycled wood. On the other hand, the initial concentration of calcium in white wood is much higher than that of silicon in white wood. According to the CaO-SiO_2 phase diagram, a bulk CaO:SiO_2 ratio of 1 favours $\text{CaSiO}_{3(s)}$ formation, whilst a dominant amount of CaO over SiO_2 promotes $\text{Ca}_2\text{SiO}_{4(s)}$ formation. $\text{CaSiO}_{3(s)}$ might originate from the reaction of $\text{CaCO}_{3(g)}$ with $\text{SiO}_{2(g)}$ as expressed in Reaction 7.12.²⁷⁹



CaSiO_{3(s)} might be formed via Ca(OH)_{2(g)} reaction with SiO_{2(g)}. However, this reaction is unlikely to occur since only a trace proportion of Ca(OH)_{2(g)} is available. CaSiO_{3(s)} could also be formed via Ca₂SiO_{4(s3)} decomposition, as in Reaction 7.13.²⁸⁰



CaMgSi₂O_{6(s)} is also formed at a relatively significant proportion. It is unclear which reaction might lead to CaMgSi₂O_{6(s)} formation. However, evidence shows that CaMgSi₂O_{6(s)} has been found in fly ash created during fir wood combustion.²⁸¹

Calcium occurrence in the bottom ash created during air-combustion or oxy27-combustion of white wood is predicted by the model, as shown in Figures 7.17 and 7.18. Since calcium is the most abundant and one of the least volatile elements present in woody biomass, calcium often remains as one of the main constituents of bottom ash. Calcium tends to form mineral compounds with other AFEs, e.g. magnesium, aluminium, and silica.²⁸² Ca₂SiO_{4(s2)} is the major form of calcium compound found in bottom ash after air-combustion or oxy27-combustion of white wood.²⁸³ During air-combustion of white wood, a small proportion of Ca₂SiO_{4(s)} is also formed that displays different crystal structures. The Ca₂SiO_{4(s2)} partition is higher in oxy27-combustion than in air-combustion, probably due to higher temperatures and the greater oxygen concentration. An X-ray diffraction analysis has shown that the Ca₂SiO_{4(s2)} partition rises with increasing combustion temperature until around 1700 K.²⁸⁴

During air-combustion of recycled wood, more complex calcium silicates associate with magnesium and aluminium, as shown in Figure 7.19. This might be due to higher quantities of ash-forming elements in the particles. Calcium reacts with quartz to form CaSiO_{3(s)} and Ca₂SiO_{4(s)}.²⁸⁵ Due to magnesium and aluminium interference, Ca₂SiO_{4(s)} formation might be inhibited and Ca₃MgSi₂O_{8(s)} and Ca₂Al₂SiO_{7(s)} formation is favoured.^{286,287}

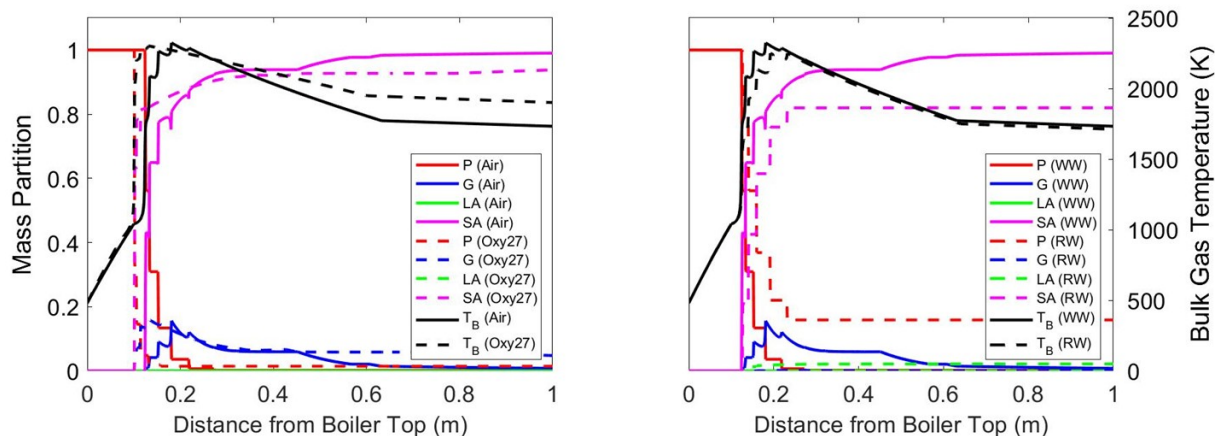


Figure 7.12 (Left) Modelled Calcium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood; **Figure 7.13 (Right)** Modelled Calcium Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_b : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

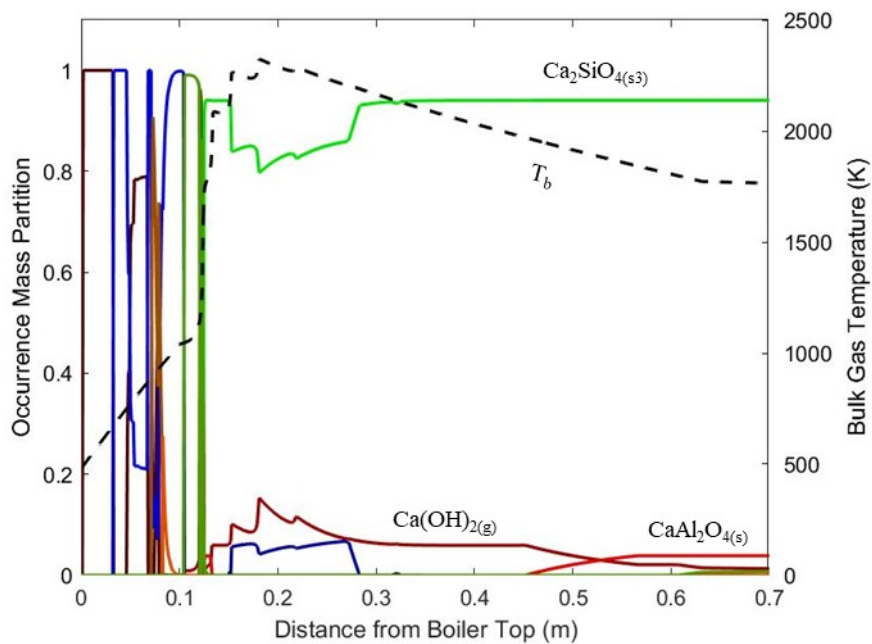


Figure 7.14 Modelled Calcium Bulk Occurrences in Air-combustion of White Wood

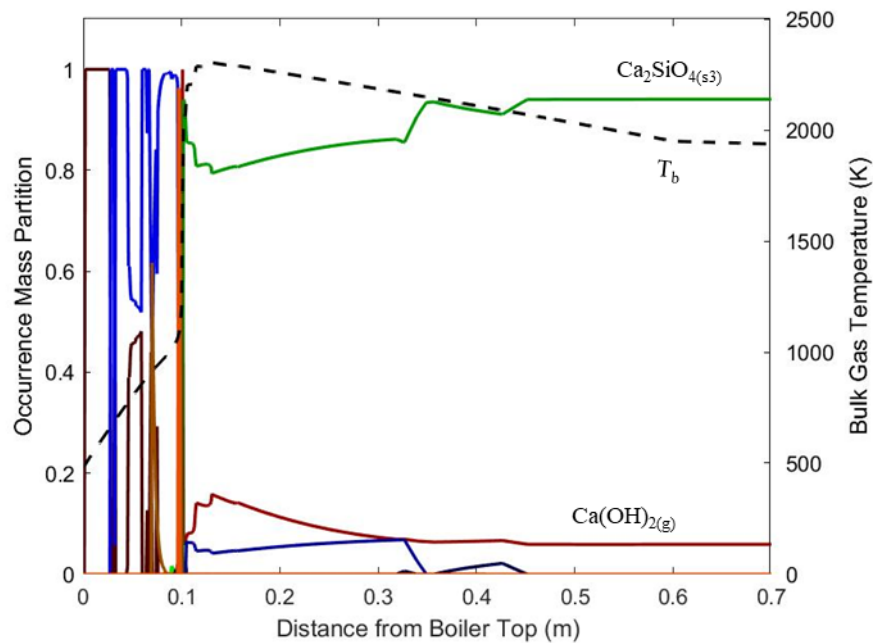


Figure 7.15 Modelled Calcium Bulk Occurrences in Oxy27-combustion of White Wood

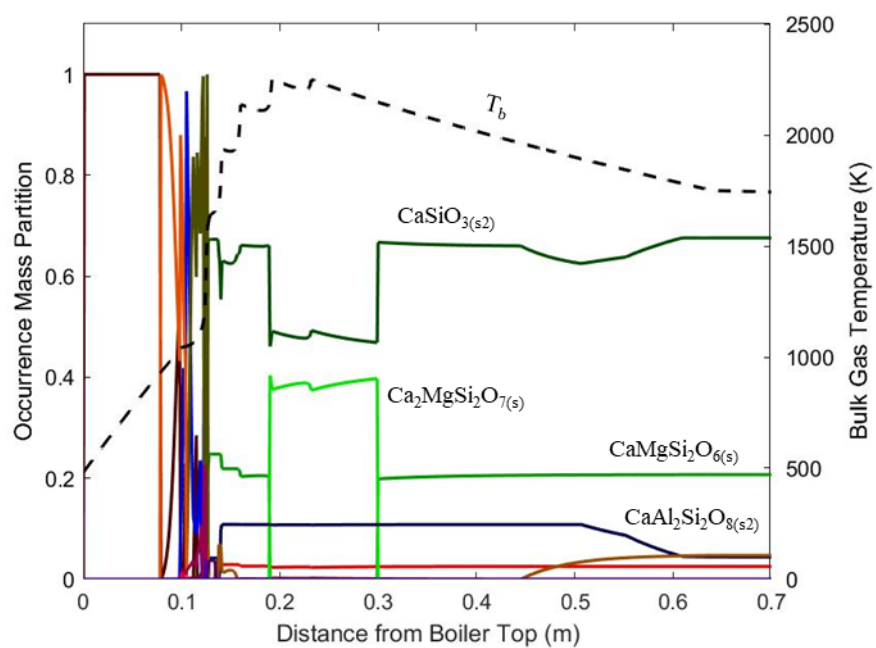


Figure 7.16 Modelled Calcium Bulk Occurrences in Air-combustion of Recycled Wood

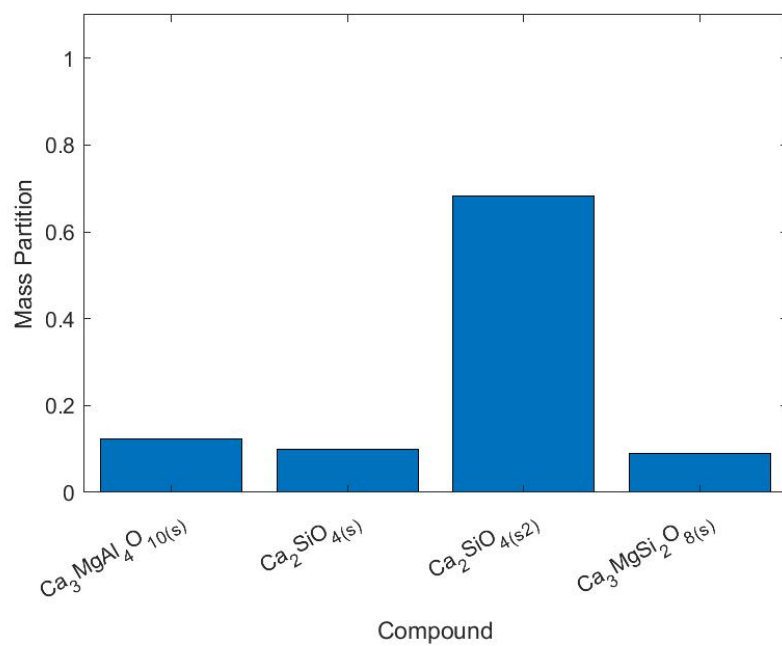


Figure 7.17 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of White Wood

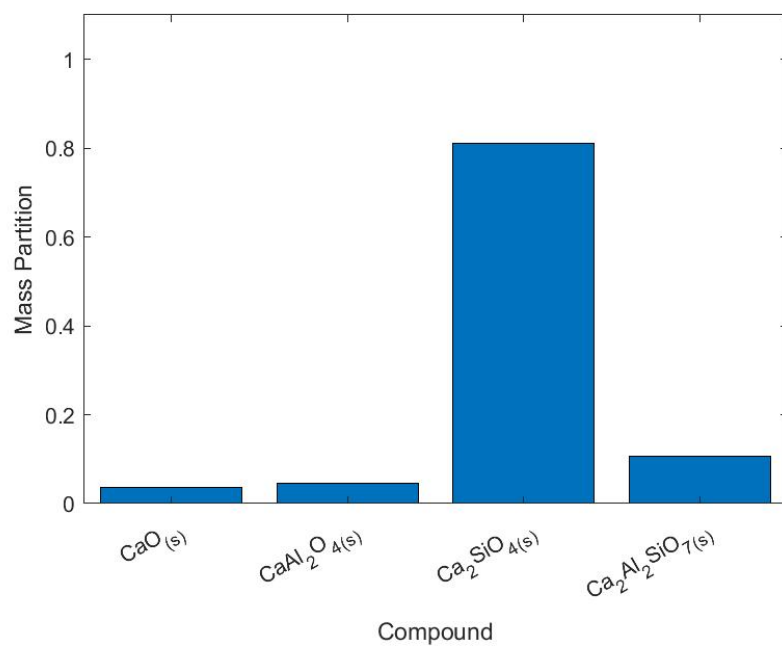


Figure 7.18 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of White Wood

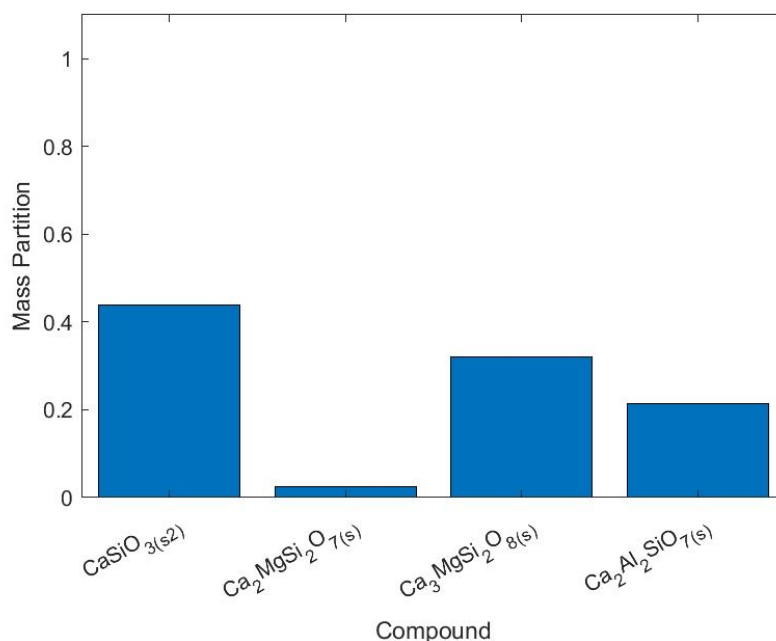


Figure 7.19 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Recycled Wood

Silicon

Modelled silicon fate profiles are shown in Figure 7.20 for the Air/Oxy27 comparison and Figure 7.21 for the white/recycled wood comparison. Silicon fate and occurrence profiles in the Air/Oxy27 comparison show similar behaviour to those of calcium due to silicon's strong affinity with calcium. In the white/recycled wood comparison, the modelled fate profile of silicon predicts a considerable partition of liquid formed during the *heat removal* stage. Subsequently, the liquid partition decreases during the *heat loss* stage.

Due to silicon's strong affinity with calcium, the modelled occurrence of bulk silicon shows similarities to modelled occurrence of bulk calcium. $\text{Ca}_2\text{SiO}_4(\text{s}_3)$ is the primary form of silicon produced by air-combustion and oxy27-combustion of white wood, as shown in Figures 7.22 and 7.23. Similarly, $\text{CaSiO}_3(\text{s}_2)$ is the primary form of silicon that is produced during air-combustion of white wood, as shown in Figure 7.24. At around peak temperature, silicon is condensed as $\text{SiO}_{2(\text{l})}$. Due to the greater concentration of silicon in recycled wood than in white wood, the combustion temperature of recycled wood may not be high enough to vaporise $\text{SiO}_{2(\text{l})}$. McNallan *et al.*²⁸⁸ have described $\text{SiO}_{2(\text{l})}$ formation due to $\text{SiO}_{2(\text{g})}$ supersaturation. Silicon is likely to be released as $\text{SiO}_{(\text{g})}$, which is then oxidised as expressed in Reaction 7.14.



Reaction 7.14 is a rapid reaction. When $\text{SiO}_{2(g)}$ reaches saturation, $\text{SiO}_{2(g)}$ nucleates to form $\text{SiO}_{2(l)}$ as in Reaction 7.15.



On the other hand, heterogeneous nucleation via reaction with $\text{CO}_{2(g)}$ might occur, as expressed in Reaction 7.16.



$\text{SiO}_{2(g)}$ may also react heterogeneously with $\text{CaCO}_{3(s)}$ to form $\text{CaSiO}_{3(s)}$ as expressed in Reaction 6.14. At around 2000 K, no $\text{SiO}_{2(l)}$ is predicted and $\text{CaSiTiO}_{5(l)}$ is the only liquid compound foreseen by the model. $\text{TiO}_{2(s)}$ may be released as aerosols, which react with $\text{CaSiO}_{3(s)}$ to form $\text{CaSiTiO}_{5(l)}$.²⁸⁹

$\text{CaSiO}_{4(s)}$ is the main silicon compound formed in the bottom ash during air- and oxy27-combustion of white wood, as shown in Figure 7.25 and Figure 7.26. On the other hand, $\text{CaSiO}_{3(s)}$ is the main silicon compound formed during air-combustion of recycled wood, as shown in Figure 7.27. Formation of these compounds is in agreement with calcium partition in the bottom ash during air-combustion of recycled wood due to the strong chemical association between silicon and calcium to form calcium silicate compounds.

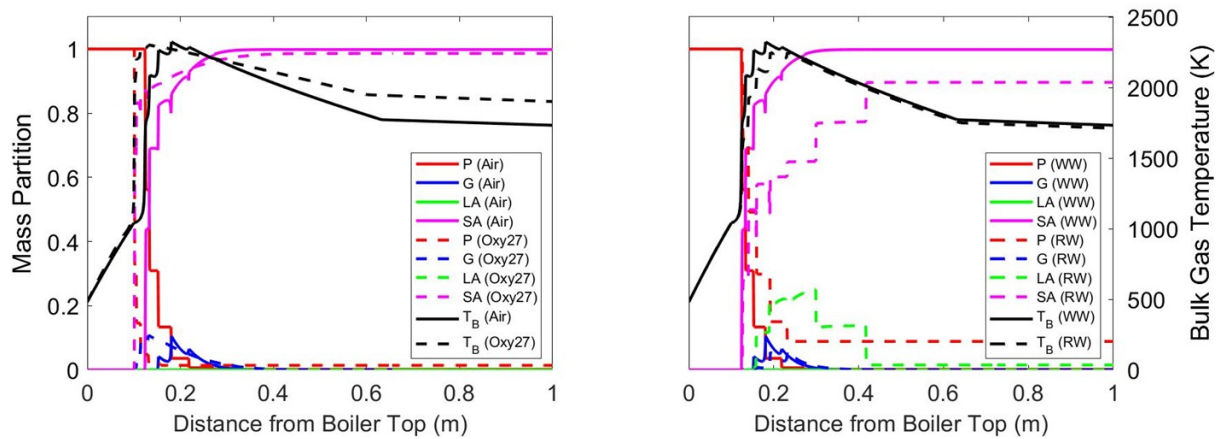


Figure 7.20 (Left) Modelled Silicon Fate Profiles in Air-combustion and Oxy27-combustion of White Wood; **Figure 7.21 (Right)** Modelled Silicon Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

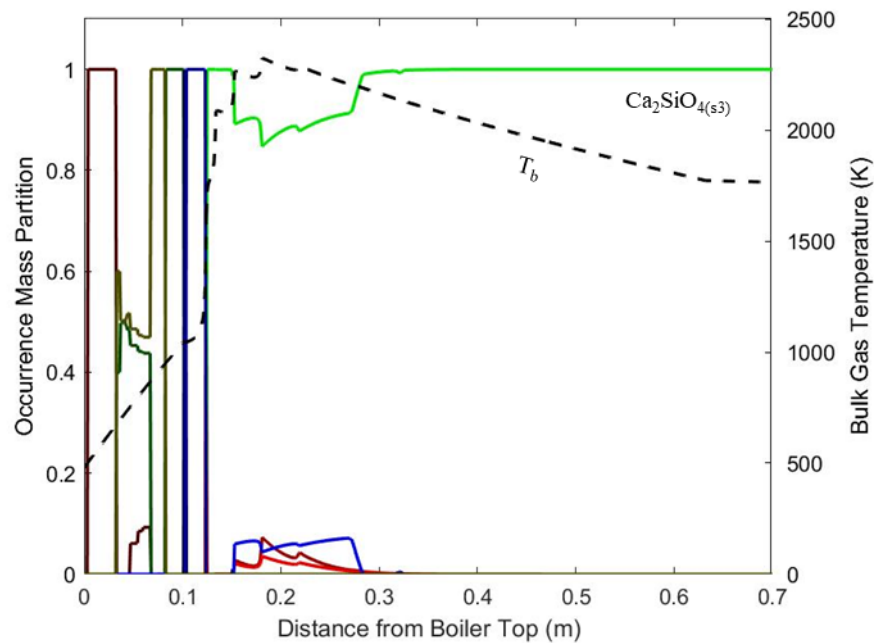


Figure 7.22 Modelled Silicon Bulk Occurrences in Air-combustion of White Wood

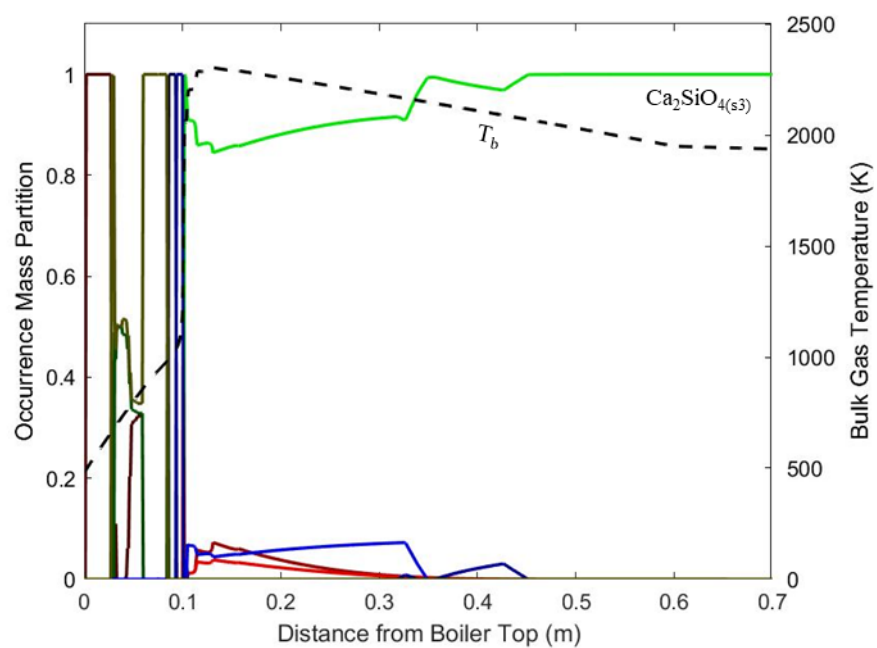


Figure 7.23 Modelled Silicon Bulk Occurrences in Oxy27-combustion of White Wood

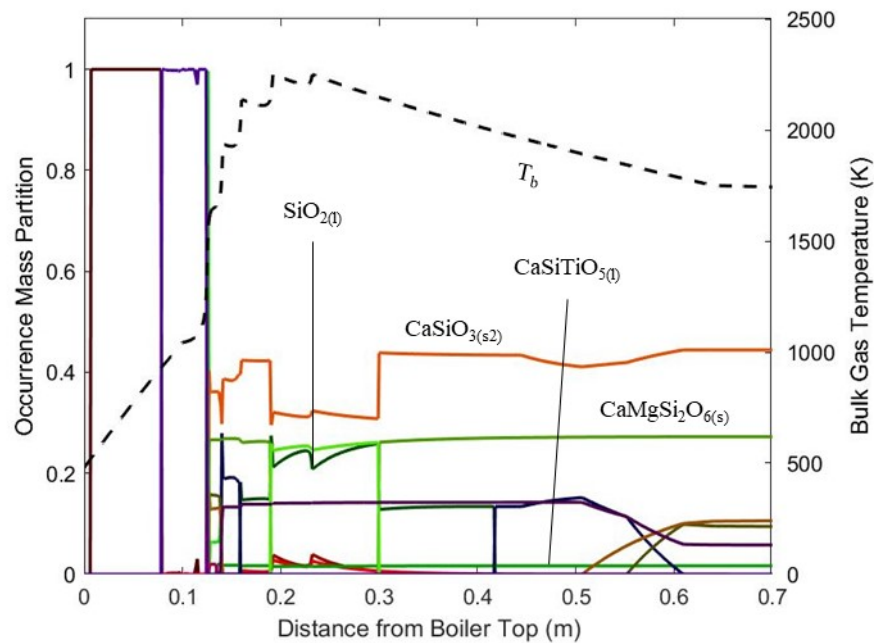


Figure 7.24 Modelled Silicon Bulk Occurrences in Air-combustion of Recycled Wood

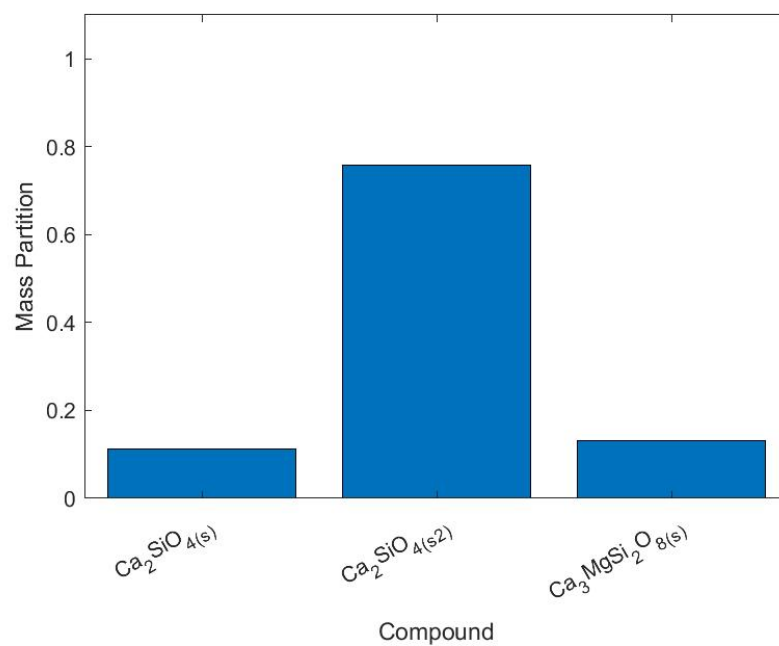


Figure 7.25 Modelled Silicon Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of White Wood

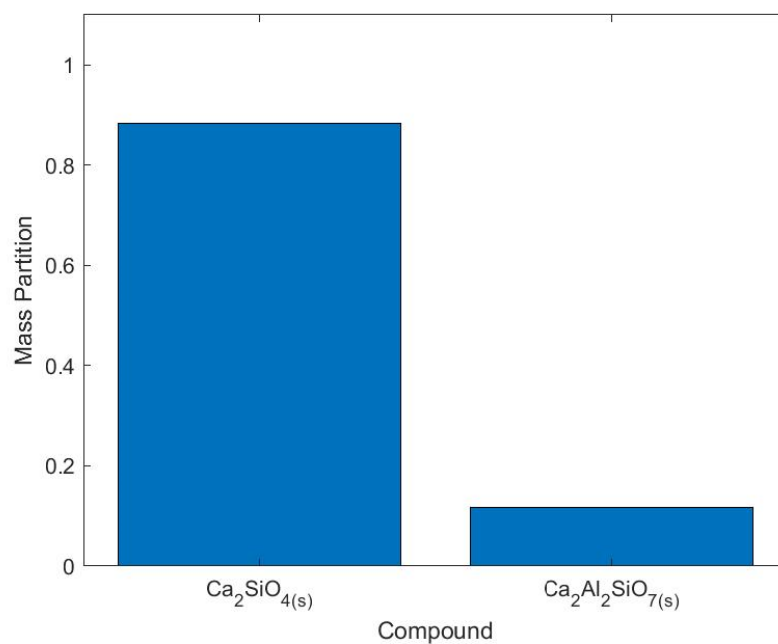


Figure 7.26 Modelled Silicon Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of White Wood

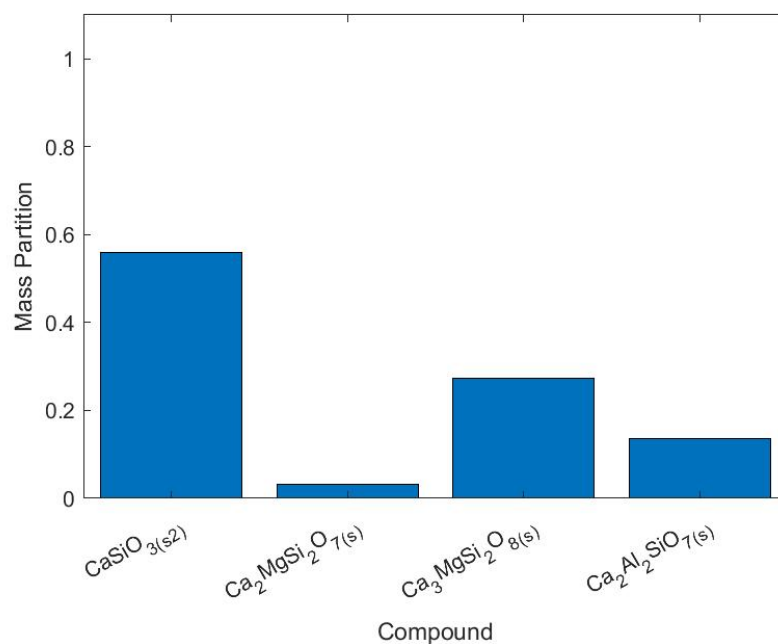


Figure 7.27 Modelled Silicon Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Recycled Wood

Copper

Modelled fate profiles for bulk copper are shown in Figure 7.28 for the Air/Oxy27 comparison and in Figure 7.29 for the white/recycled wood comparison. Both figures show that copper is completely released from particles as gas in all cases. This volatility is similar to that of arsenic and cadmium. Copper is considered to have the same level of volatility as those elements.²⁹⁰

Figures 7.30 and 7.31 show copper occurrence during air-combustion and oxy27-combustion of white wood. Copper is mainly released as $\text{Cu}_{(g)}$. As the temperature decreases during the *heat loss* stage, $\text{Cu}_{(g)}$ is gradually converted to $\text{CuCl}_{(g)}$ due to reaction with chlorine released as $\text{Cl}_{2(g)}$, according to Reaction 7.17.²⁹¹



Reaction 7.17 runs faster at lower temperatures, e.g. 1173 K. The initial gradual conversion rate of $\text{Cu}_{(g)}$ to $\text{CuCl}_{(g)}$ indicates that Reaction 7.17 might run slowly at high temperature. Selectivity towards $\text{CuCl}_{(g)}$ formation is less favoured in oxy27-combustion than in air-combustion of white wood. In air-combustion of recycled wood, selectivity towards $\text{CuCl}_{(g)}$ formation is the most significant among all cases as shown in Figure 7.32. This may be due to greater chlorine release from the particles.

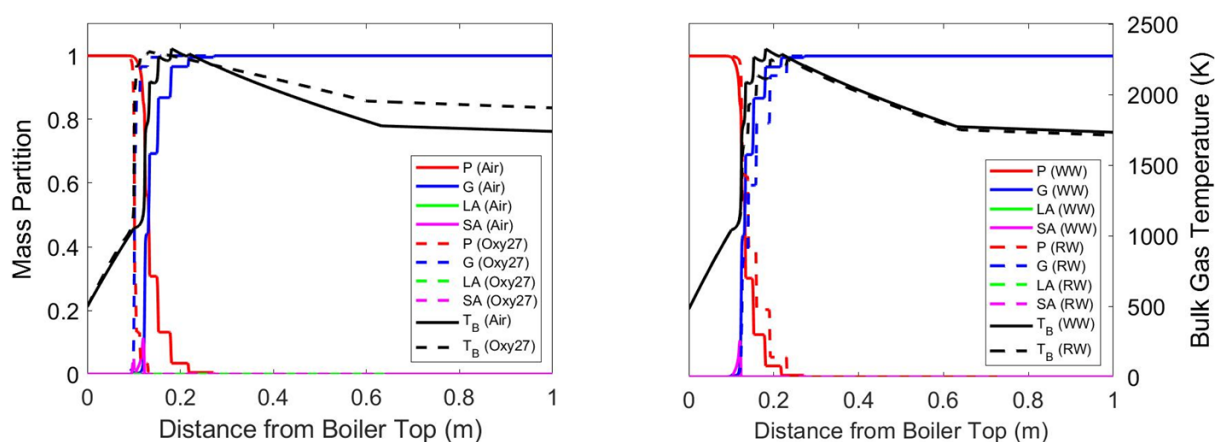


Figure 7.28 (Left) Modelled Copper Fate Profiles in Air-combustion and Oxy27-combustion of White Wood; **Figure 7.29 (Right)** Modelled Copper Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

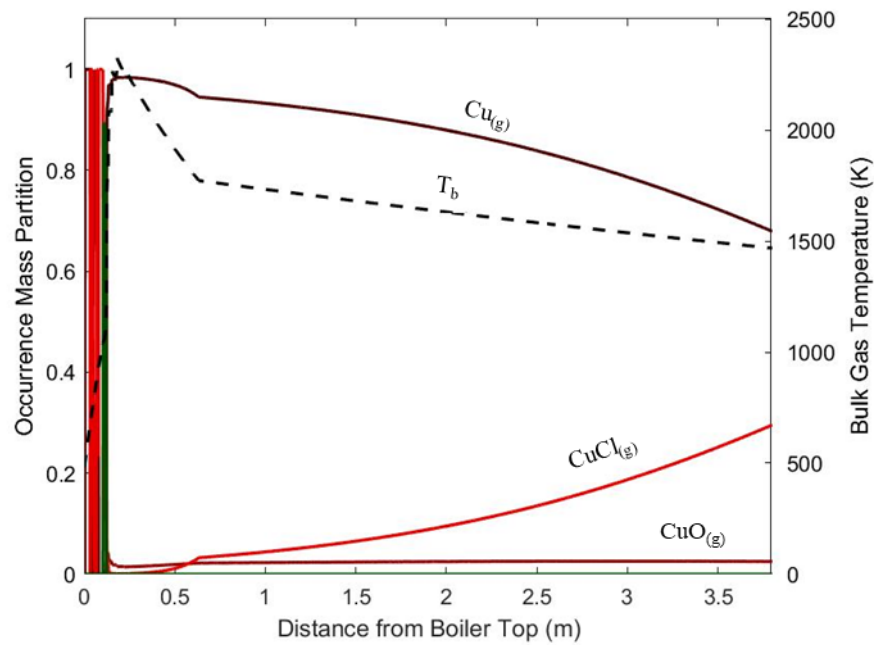


Figure 7.30 Modelled Copper Bulk Occurrences in Air-combustion of White Wood

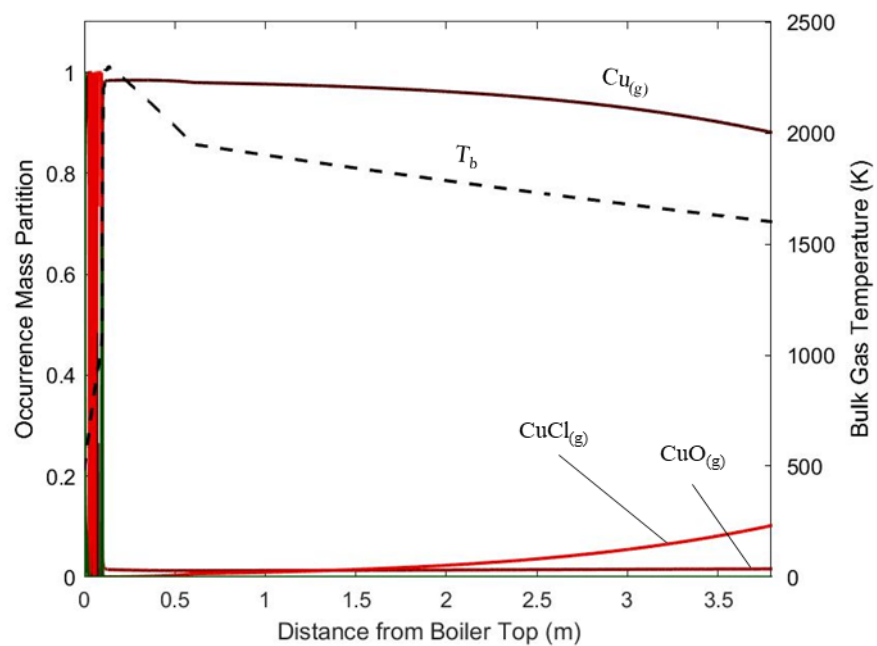


Figure 7.31 Modelled Copper Bulk Occurrences in Oxy27-combustion of White Wood

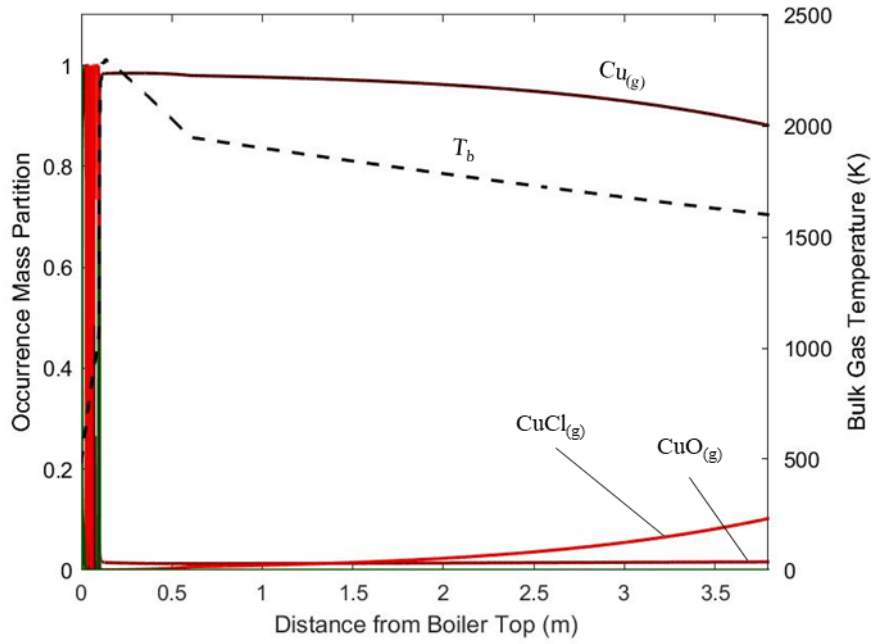
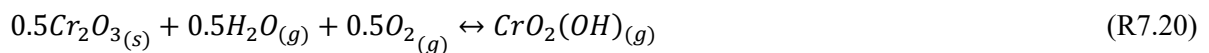
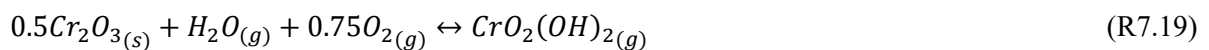


Figure 7.32 Modelled Copper Bulk Occurrences in Air-combustion of Recycled Wood

Chromium

Modelled chromium fate profiles are shown in Figure 7.33 for the Air/Oxy27 comparison and in Figure 7.34 for the white/recycled wood comparison. Both comparisons depict that chromium is entirely volatilised from the particles. Complete chromium volatilisation might be promoted by the stability of gaseous chromium at temperatures above 1673 K.¹⁶⁰

Modelled occurrence profiles of bulk chromium are shown in Figures 7.35, 7.36, and 7.37 for all cases. Chromium is initially released as $\text{CrOOH}_{(g)}$ in all cases. However, there has not been any clear evidence of chromium presence in bulk gas once it has been released from biomass. In the particles, chromium is probably present originally as $\text{CrO}_{2(s)}$, which is converted to $\text{CrOOH}_{(g)}$ in a reducing atmosphere.²⁹² $\text{CrOOH}_{(g)}$ and $\text{CrO}_{2(s)}$ decompose to $\text{Cr}_2\text{O}_{3(s)}$ aerosols at temperatures above 1000 K.²⁹³ According to experimental observation, $\text{CrO}_{3(g)}$, $\text{CrO}_2(\text{OH})_{2(g)}$, and $\text{CrO}_2(\text{OH})_{(g)}$ are the products of $\text{Cr}_2\text{O}_{3(g)}$ oxidation in the presence of $\text{H}_2\text{O}_{(g)}$ as expressed in Reactions 7.18, 7.19, and 7.20.^{294,295,296}



As shown in Figures 7.35, 7.36, and 7.37, selectivity towards $\text{CrO}_2(\text{OH})_{2(\text{g})}$ is favoured at high temperature. This finding is in agreement with a previous thermodynamic calculation result.²⁹⁷ Opila *et al.*²⁹⁸ later confirmed this finding experimentally.

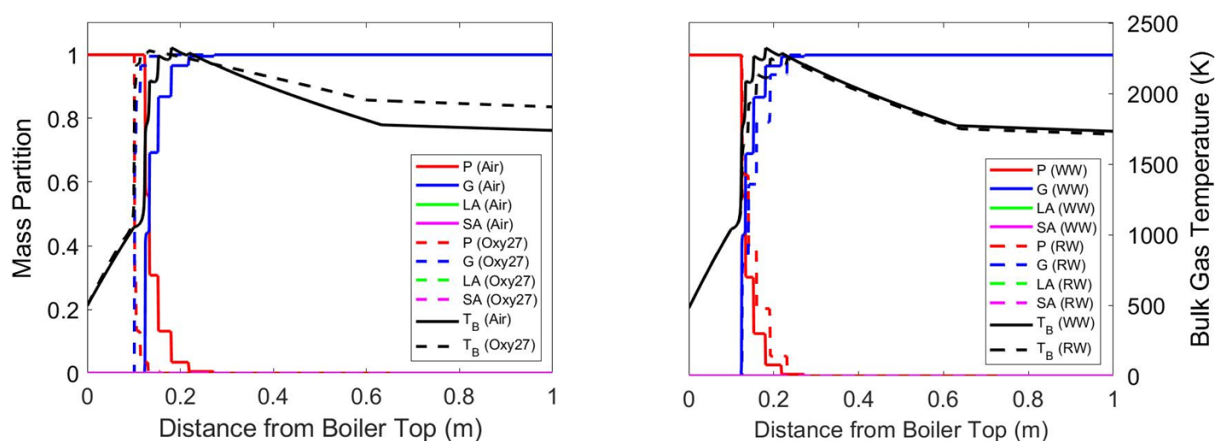


Figure 7.33 (Left) Modelled Chromium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood; **Figure 7.34 (Right)** Modelled Chromium Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

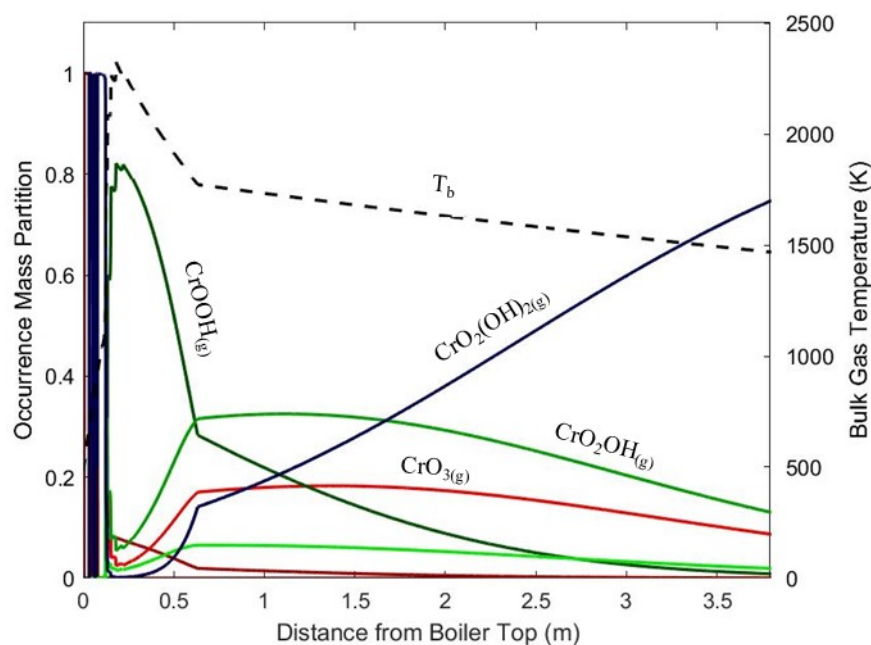


Figure 7.35 Modelled Chromium Bulk Occurrences in Air-combustion of White Wood

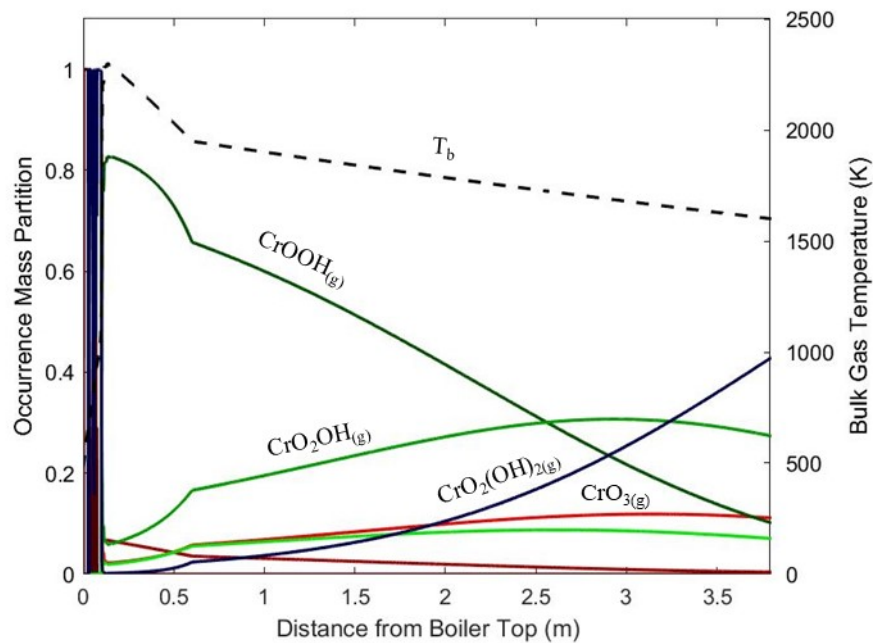


Figure 7.36 Modelled Chromium Bulk Occurrences in Oxy27-combustion of White Wood

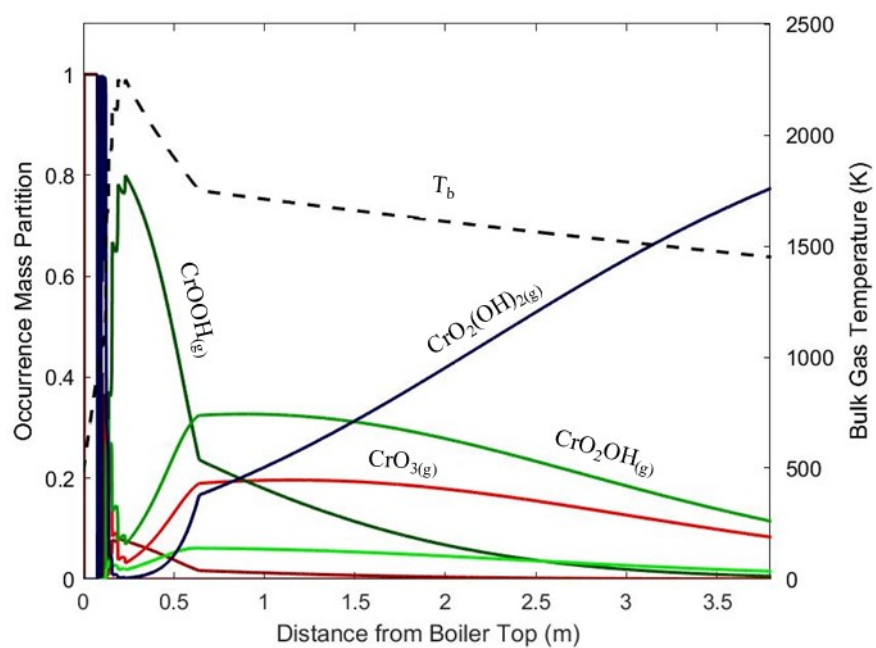


Figure 7.37 Modelled Chromium Bulk Occurrences in Air-combustion of Recycled Wood

7.4 Method of PACT ICP Measurements and Bulk Validation

Combustion products comprise major compounds, e.g. $\text{CO}_{2(g)}$, $\text{H}_2\text{O}_{(g)}$, etc., gaseous AFE compounds, gaseous TE compounds, aerosol AFE compounds, and aerosol TE compounds. They are discharged at temperatures of 800 to 860 K from the burner through a small nozzle at the burner lowermost section and sent to the downstream stage for further analysis. In the downstream stage, the discharged combustion products are initially introduced to a cyclone. The cyclone aims to remove any small residual particles that are mixed with the discharged combustion products. After flowing through the cyclone, a small portion of the stream of discharged combustion products is split from the main stream and flows to the on-line ICP unit for elemental analysis.

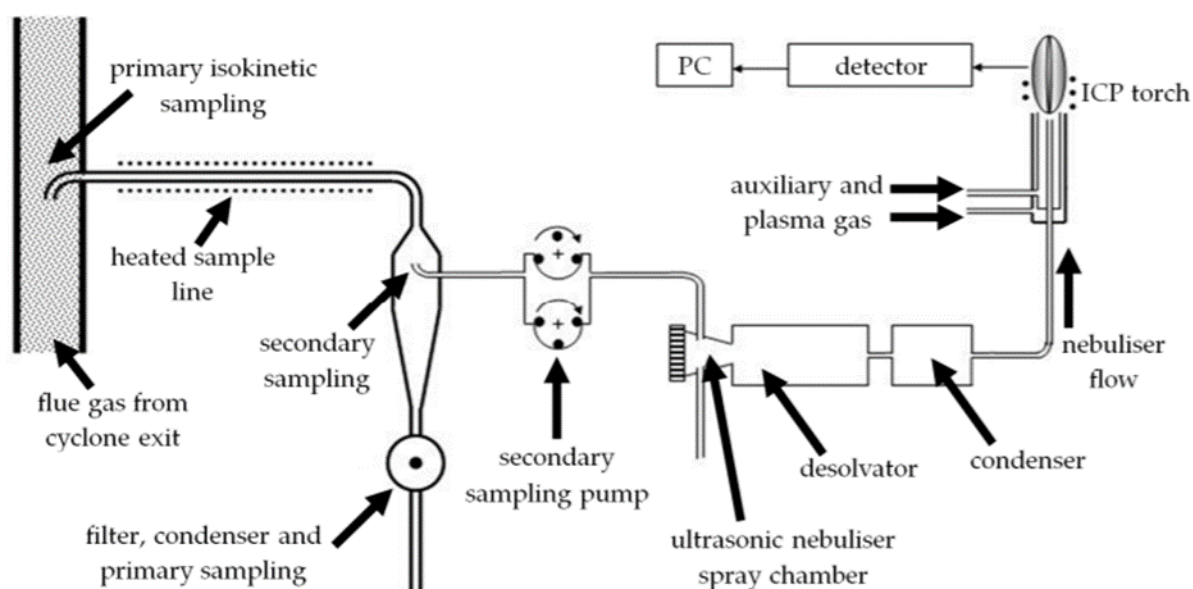


Figure 7.38 Flow Diagram of PACT Online ICP

A detailed process flow diagram of the ICP is shown in Figure 7.38. The ICP feed is pumped to the ICP unit at 200 ml/min with a peristaltic pump and heated in the heated sample line at 453 K to avoid moisture loss. After passing the pump, the feed is cooled down in a desolvator and a condenser at temperatures of 423 and 275 K, respectively, to trap moisture and enable the dry aerosols to flow to the plasma. The formed aerosols are burnt with a plasma flame at 6000 K. At this temperature, all solid and liquid aerosols are expected to vapourise.¹⁷⁵

The main stream of discharged combustion gas released from the cyclone is processed further in the downstream stage. Once released from the cyclone, the main stream flows towards the heat exchanger.

Once the main stream is cooled, it flows to the candle filter where all condensed aerosols are separated from clean gas to ensure that the gas composition is below the administrative limit for trace element emission.²⁹⁹ The online ICP is located prior to the candle filter so that its results can be used to assess the cleanup requirement, based on whether the trace element concentrations exceed their administrative limits. Finally, the clean gas is released to the atmosphere via a gas stack.

The modelled downstream concentrations produced through this work were compared with the ICP measurements. The comparison is presented in Figure 7.39 for air-combustion of white wood and Figure 7.40 for oxy27-combustion of white wood. The comparison shows that the modelled element concentrations in uncooled downstream gas are relatively well validated by the ICP results. However, there is some disagreement possibly due to model limitations.

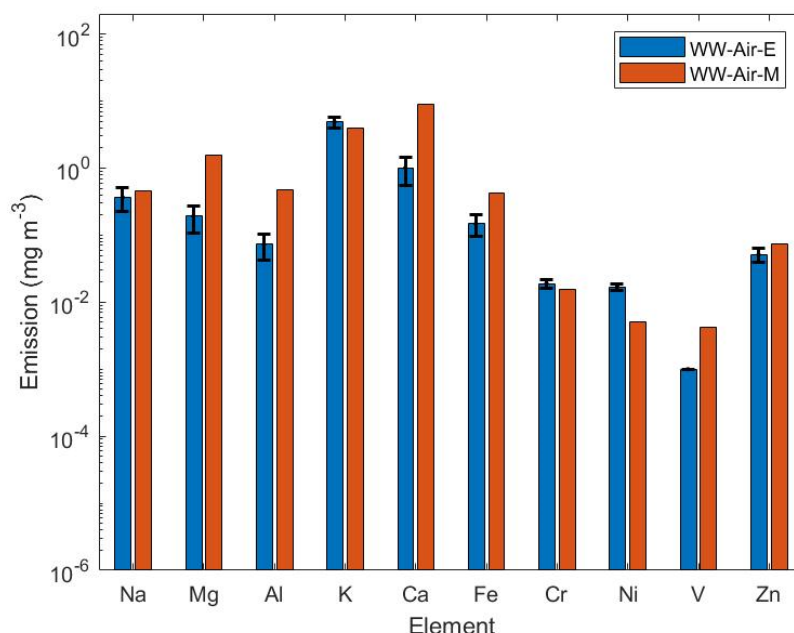


Figure 7.39 Validation of Element Concentrations in Uncooled Downstream Gas during Air-combustion of White Wood (E: Experiment; M: Model; Black Vertical Line: Error Line)

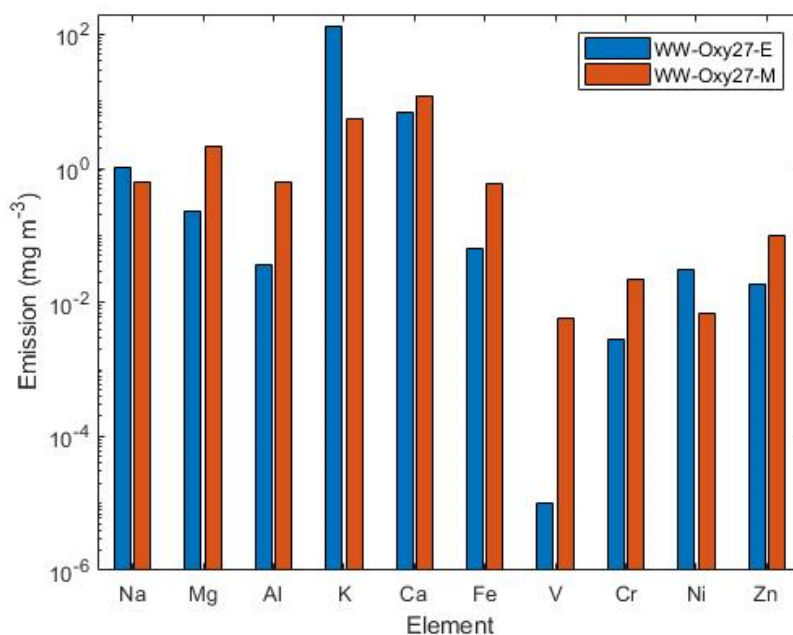


Figure 7.40 Validation of Element Concentrations in Uncooled Downstream Gas during Oxy27-combustion of White Wood (E: Experiment; M: Model)

In both air-combustion and oxy27-combustion, the modelled element concentrations of alkali metals in uncooled downstream gas show relatively good agreement with those of alkali metals in uncooled downstream gas as measured by the ICP, except for potassium in oxy27-combustion. The concentration of potassium in uncooled downstream gas in oxy27-combustion is significantly higher in the experiment than in the model. This may be due to the higher concentration of $O_{2(g)}$ in oxy27-combustion than in air-combustion, which may lead to higher partition of potassium as $KOH_{(g)}$ in the bulk gas. This may be kinetically limited in the model. Further analysis is required to evaluate the influence of other aspects, e.g. candle filter ash analysis, to confirm the validity of this hypothesis. Nevertheless, potassium measurement might have been unconvincing since potassium mass balance, calculated according to Appendix I.1, in both air-combustion and oxy27-combustion of white wood results in an imbalanced mass flow rate possibly due to measurement anomaly. Consequently, potassium partition cannot be presented in the compilation of element partition based on On-line ICP measurement in both air-combustion and oxy27-combustion of white wood, as respectively shown in Figure 7.41 and 7.42. A similar case also occurs for sodium in oxy27-combustion of white wood.

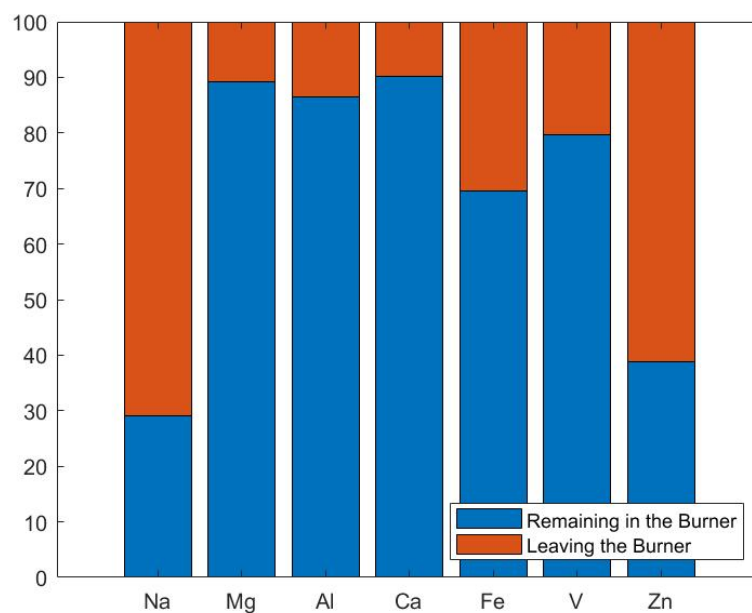


Figure 7.41 Element Partition Based on On-line ICP Measurement in Air-combustion of White Wood

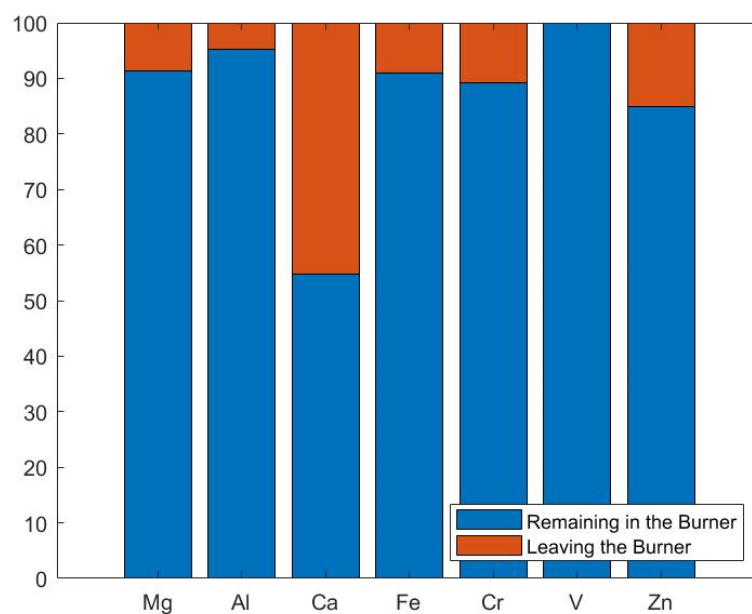


Figure 7.42 Element Partition Based on On-line ICP Measurement in Oxy27-combustion of White Wood

Modelled concentrations of the least volatile AFEs, e.g. calcium, aluminium, magnesium, and iron, are relatively higher than those measured in uncooled downstream gas in both air-combustion and oxy27-

combustion. This might demonstrate that these elements have a strong tendency to remain in the bottom ash. Calcium, aluminium, and magnesium are likely to form silicate compounds, e.g. $\text{CaMgSi}_2\text{O}_6(\text{s})$, $\text{CaSiO}_3(\text{s})$, $\text{Ca}_2\text{SiO}_4(\text{s})$, $\text{CaAl}_2\text{O}_4(\text{s})$, $\text{MgAl}_2\text{O}_4(\text{s})$, due to reaction with silicon at low temperatures during the *heat loss* stage. Similarly, iron is very stable in forming $\text{Fe}_3\text{O}_4(\text{s})$ within the same stage. These compounds are formed via simultaneous reaction and nucleation. For instance, in Reaction 7.10, $\text{Ca}_2\text{SiO}_4(\text{g})$ is initially formed. As $\text{Ca}_2\text{SiO}_4(\text{g})$ becomes more concentrated, it starts to nucleate to form $\text{Ca}_2\text{SiO}_4(\text{s})$ and the reaction is no longer homogeneous. Due to eutectic behaviour, $\text{SiO}_2(\text{g})$ in Reaction 7.11 might condense on the surface of $\text{Ca}_2\text{SiO}_4(\text{s})$ aerosols. This might establish a solid-state reaction as expressed in Reaction 7.21.



Solid-state reactions exhibit slower reaction rates than heterogeneous or homogeneous reactions due to phase restrictions. Hence, a random distribution of minerals may be found within a single aerosol particle. Once nucleated, a single aerosol particle is likely to coagulate with any other aerosol particles and form a larger aerosol particle. Moreover, coagulation is more likely to occur between a single aerosol particle and a fuel particle. This phenomenon may reduce the probability of discharge of heavy AFEs from the burner. Therefore, higher modelled element concentrations than measured element concentrations in uncooled downstream gas would be anticipated, since no aerosol growth calculation was included in the fate and occurrence model.

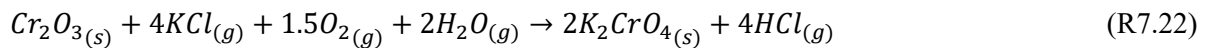
The lack of CFA results might also overestimate the concentrations of the least volatile AFEs in uncooled downstream gas. By neglecting the element initial occurrence in the particles, primarily the included and excluded minerals, e.g. $\text{CaC}_2\text{O}_4(\text{s})$ and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8(\text{s})$) for calcium, the prediction of calcium fate will favour more significant partition of calcium towards flue gas leaving the burner, as shown in Figure 7.12 and 7.13, than the actual measurement, as shown in Figure 7.41 and 7.42. Mineral AFEs might primarily remain in residual particles dropped to the bottom of the burner due to different volatilisation behaviour than the organically-associated AFEs and water-soluble AFEs. Despite exposure to very high temperatures, due to more complex chemical structure than the organically-associated AFEs and water soluble AFEs, the minerals might require longer decomposition time, which the chemical equilibrium calculation does not consider.

Slagging might also promote AFEs partition in the burner according to the slagging mechanism explained in Section 2.2. Ash deposit layers are built due to thermophoresis and inertial impaction of silicate and aluminosilicate aerosols to the burner wall. Once the running slag is formed, the aerosols hitting the slag are liquified and possibly solidified once closer to the bottom of the burner.

The modelled emission concentration of vanadium is higher than the measured emission level of vanadium in both air-combustion and oxy27-combustion. Vanadium forms $(\text{CaO})_3(\text{V}_2\text{O}_5)_2(\text{s})$ according

to Figures J.42 and J.43. $(\text{CaO})_3(\text{V}_2\text{O}_5)_2(\text{s})$ formation might also promote aerosol growth, which was not included in the fate and occurrence model. Less vanadium is discharged from the burner in oxy27-combustion than in air-combustion. According to Figures J.42 and J.43, formation of $(\text{CaO})_3(\text{V}_2\text{O}_5)_2(\text{s})$ starts at a higher position in the burner in air-combustion than in oxy27-combustion. This might enable longer interaction between $(\text{CaO})_3(\text{V}_2\text{O}_5)_2(\text{s})$ and other aerosol particles and eliminate a significant amount of vanadium discharged from the burner.

The modelled chromium concentration compared with the measured chromium emission concentration in uncooled downstream gas shows good validation for air-combustion and poor validation for oxy27-combustion. In oxy27-combustion, the measured concentrations of chromium is less than the modelled equivalent. Again, aerosol growth could be the reason for this discrepancy, and the fate and occurrence model was not designed to take account of aerosol particle growth. Higher $\text{O}_{2(\text{g})}$ concentration during oxy27-combustion than in air-combustion might promote $\text{K}_2\text{CrO}_4(\text{s})$ formation via Reaction 7.22 at lower temperatures. There is evidence from previous published studies that $\text{K}_2\text{CrO}_4(\text{s})$ is deposited in bottom ash.³⁰⁰



However, Reaction 7.22 is unlikely to occur in the work performed for this thesis since chromium occurrence is mostly as $\text{CrO}_2(\text{OH})_2(\text{g})$ at lower temperatures. Another reaction between $\text{CrO}_2(\text{OH})_2(\text{g})$ and $\text{KCl}(\text{g})$ might occur to form $\text{K}_2\text{CrO}_4(\text{s})$.

The modelled zinc concentration is well validated by the measured zinc concentration in uncooled downstream gas for air-combustion but not for oxy27-combustion. In oxy27-combustion, the measured zinc emission concentration is less than the modelled data. This result indicates that zinc is likely to remain in the bottom ash.

In the oxy27-combustion environment with high $\text{O}_{2(\text{g})}$ concentration, $\text{Fe}_3\text{O}_4(\text{s})$ may be oxidised at localised low temperature as expressed in Reaction 7.23.³⁰¹



Simultaneously, $\text{ZnO}(\text{g})$ is formed via backward reaction of Reaction J.14 due to the low temperature. $\text{ZnO}(\text{g})$ subsequently reacts with $\text{Fe}_2\text{O}_3(\text{s})$ to form $\text{ZnFe}_2\text{O}_4(\text{s})$ according to Reaction 7.24.³⁰²



$\text{ZnFe}_2\text{O}_4(\text{s})$ may form as aerosols, and the subsequent aerosol growth would again be numerically excluded from the fate and occurrence model.

Both Figures 7.39 and 7.40 show that the modelled nickel concentration is less than the measured nickel concentration in uncooled downstream gas. However, it is likely that the measured nickel concentration is a measurement anomaly. Since all the nickel is volatilised from the particles, the measured nickel concentration should be less than the modelled nickel concentration, as demonstrated in Appendix I.1. Consequently, it is unable to graphically express nickel partition in both Figure 7.41 and 7.42.

Additionally, bulk liquid aerosols were evaluated to estimate their potential to enhance slagging. According to Figures 7.24 and J.19, three bulk liquid compounds, namely $\text{SiO}_{2(l)}$, $\text{CaSiTiO}_{5(l)}$, and $\text{Fe}_3\text{O}_{4(l)}$, are formed within 0.5 m of the burner's uppermost section in air-combustion of recycled wood. In contrast, bulk liquid compounds are not formed during air-combustion of white wood. The absence of bulk liquid compounds in air-combustion of white wood might be due to the presence of too little AFE to condense. Nevertheless, the bulk liquid:solid ratio profile within the burner was calculated to observe the potential of ash deposition at certain heights within the burner. The bulk liquid:solid ratio profile of recycled wood combustion is shown in Figure 7.43.

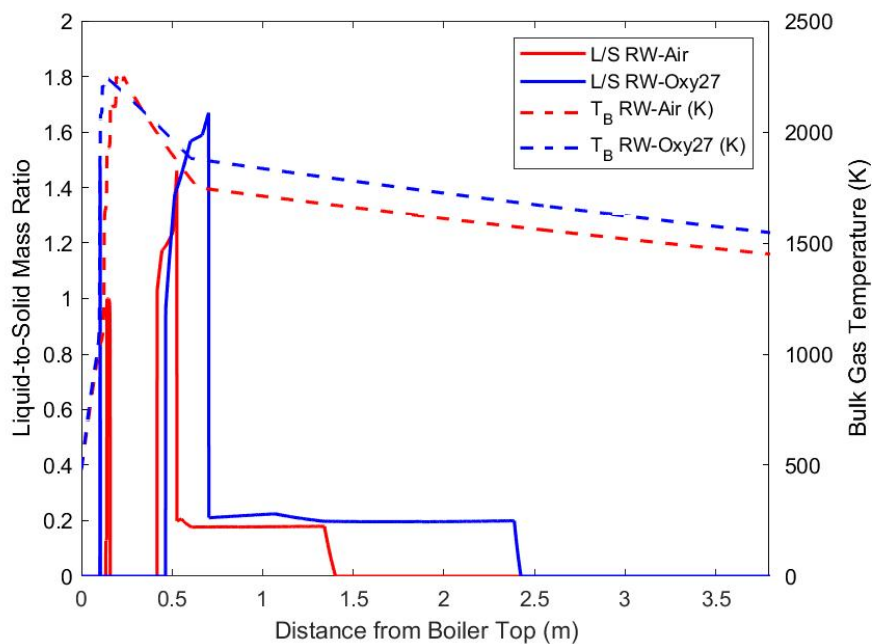


Figure 7.43 Modelled Liquid-to-solid Mass Ratio for Recycled Wood (L: Liquid; S: Solid)

Bulk liquid:solid ratio profiles peak twice in both air-combustion and oxy27-combustion. The first peaks occur shortly before the peak temperature is achieved. Although the first peaks are relatively high, the amount of released inorganic elements is still insignificant. During transition from the *heat removal* stage to the *heat loss* stage, the second peaks occur. The bulk liquid phase is more dominant during the second peak, possibly due to substantial amounts of AFEs and TEs in bulk that then condense into liquid aerosols. After the transition, the bulk liquid:solid ratio profiles step down to around 0.2.

This value remains constant until the bulk temperature profiles are at around 1500 K. Beyond this temperature, there is no bulk liquid present.

Based on the formed liquid compounds, calcium, silicon, and iron play key roles in formation of the aerosol liquid phase. Calcium- and silicon-based liquid compounds are often understood based on ash-fusion characteristics analysis and liquidus isotherms within a K_2O - CaO - SiO_2 ternary diagram. In other types of biomass with significant amounts of potassium, ash is deposited via $KCl_{(l)}$ formation and sulphation. These two mechanisms are explained in Chapter 7 with further discussion of herbaceous biomass with higher silicon and potassium contents.

7.5 Concluding Remarks

ChemApp has successfully integrated chemical equilibrium theory with the simplified entrained-flow combustion model. The integration creates a simplified fate and occurrence model without expensive computation and calculation inaccuracy. The simplified fate and occurrence model was used to model AFE and TE concentrations at the downstream stage and to estimate AFE and TE fates and occurrences in the burner.

The estimation of AFE and TE fates and occurrences in the burner was conducted on three combustion cases, namely: air-combustion of white wood, oxy27-combustion of white wood, and air-combustion of recycled wood. The estimation of air-combustion of white wood and oxy27-combustion of white wood, which taken together were named as the Air/Oxy27 comparison, aimed to study the influence of bulk $O_{2(g)}$ concentration on AFE and TE fates and occurrences. On the other hand, the estimation of air-combustion of white wood and air-combustion of recycled wood, which taken together were named as the white/recycled wood comparison, aimed to study the influence of the initial concentrations of AFEs and TEs in wood on their fates and occurrences.

Regarding fate estimation, the fate of each AFE and TE in all combustion cases were compared. Most AFEs and TEs were volatilised completely in both cases in the Air/Oxy27 comparison. This might be due to low quantities of AFEs and TEs, which led to little attainment of chemical equilibrium to retain the solid phase in the particles. In air-combustion of recycled wood, some elements showed retention in the particles. The least volatile AFE, i.e. calcium, aluminium, magnesium, and silicon, were mostly retained in particles due to their propensity to form silicate compounds. On the other hand, sodium and potassium were volatilised completely from the particles due to their strong volatility. Several TEs, e.g. vanadium, chromium, and nickel, were often found in the bottom ash. However, most TEs were volatilised from the particles.

AFE and TE were primarily modelled to occur either as pure elements, hydroxides, or oxides, once they were released from the particles. At lower temperatures, some of these elements were thought to

condense or associate with other elements to form solid aerosols. Silicate compounds, which are commonly formed by calcium, aluminium, magnesium, and silica, were also predicted to form in bulk mainly as aerosols.

The modelled AFE and TE concentrations were compared with the measured AFE and TE concentrations in uncooled downstream gas. The comparison showed good validation of the modelled concentrations with the measured concentrations. However, some modelled AFE and TE concentrations were poorly validated due to several possible unincorporated factors inhibiting AFEs and TEs to leave the burner, namely: aerosol coagulation, mineral decomposition, and aerosols captured by running slag. An extended comprehensive evaluation on these factors is required to assess how significant each factor contribute to the poor validation.

In addition, bulk liquid:solid ratio was evaluated to investigate the potential of liquid aerosols to initiate deposition. Based on this evaluation, the bulk liquid phase was found to occur at a significant level during the transition from the *heat removal* stage to the *heat loss* stage. This might deliver some insights into ways in which slagging and deposition are initiated in a combustion unit. Further explanation is discussed in Chapter 8 regarding combustion of herbaceous biomass with higher silicon and potassium content.

Chapter 8

Evaluation of Fate and Occurrence of AFEs and TEs in Herbaceous Biomass Combustion with the Simplified Fate and Occurrence Model

The prediction of the fates and occurrences model of AFEs that the AFEs would be the main constituents of ash is of great importance, since certain AFEs, e.g. potassium, sodium, and silicon, have the propensity to initiate ash deposition via formation of sticky liquid aerosols. However, the scope of the fate and occurrence prediction of AFEs discussed in Chapter 7 only covers woody biomass ash mainly composed of calcium. Although the fate and occurrence prediction for AFEs in woody biomass exhibits liquid aerosol formation, the proportion of formed liquid aerosols during combustion of calcium-rich biomass is significantly less than the proportion of formed liquid aerosol in combustion of potassium- or silicon-rich biomass, e.g. herbaceous biomass.

This chapter models the fate and occurrence of AFEs in herbaceous biomass combustion in the PACT facility entrained-flow burner. The fate and occurrence of AFEs are predicted using the simplified entrained-flow combustion model and the simplified fate and occurrence model. Section 7.1 discusses the importance of ternary diagrams on the fate and occurrence evaluation and the model setup. Sections 7.2 and 7.3 discuss the fate and occurrence of AFEs from two herbaceous biomasses.

8.1 CaO-SiO₂-K₂O Ternary Diagram and Model Setup

Liquid aerosol production is one of the main contributors to rapid ash deposition rates in biomass combustion, as explained in Chapter 2. The formation rates of liquid aerosols in both alkali-metal-induced melting and silicate-induced melting are challenging to determine since the kinetics data are not widely available. Kinetics-based calculations were not used in the research described in this thesis to predict liquid aerosol formation due to these limitations. Rather, a more simplified approach, e.g. a ternary diagram, was used to assess the potential of liquid aerosol formation via liquid isotherm lines.

Ternary phase diagrams have been developed since the early 20th century to estimate the mineral phases established at certain independent fractions of three compounds at various temperatures and pressures. Morey *et al.*³⁰³ developed a ternary phase diagram of CaO-SiO₂-K₂O to determine the liquidus isotherm line. Later, ternary phase diagrams of CaO-SiO₂-FeO, CaO-SiO₂-Al₂O₃, and SiO₂-Al₂O₃-FeO were established respectively by Bowen and Schairer³⁰⁴, Rankin and Wright³⁰⁵, and Snow and McCaughey³⁰⁶. Schairer³⁰⁷ later developed a quaternary phase diagram of CaO-SiO₂-Al₂O₃-FeO based on these former works.

Ternary phase diagrams were used extensively in a wide range of work on solid-fuel combustion. Öhman and Nordin³⁰⁸ studied agglomeration during biomass combustion in a fluidised-bed boiler using the ternary phase diagram of CaO-SiO₂-K₂O. Öhman and Nordin³⁰⁹ later studied fluidised-bed boiler agglomeration with kaolin addition as an improvement using the same ternary phase diagram. Lindström *et al.*³¹⁰ used a ternary phase diagram of Ca₂MgSi₂O₇-CaSiO₃-KAlSi₂O₆ to evaluate the influence of kaolin and limestone addition on slag formation. Niu *et al.*³¹¹ further suggested that the ternary phase diagram of K₂O-SiO₂-Al₂O₃ should be used to take account of kaolin addition. Jandačka *et al.*³¹² confirmed by use of the ternary phase diagram of CaO-SiO₂-K₂O that the melting temperature of ash increases by 300 K with kaolin addition.

The CaO-SiO₂-K₂O ternary phase diagram was chosen for use in this thesis since CaO, SiO₂, and K₂O are known to be the major compounds found in biomass ash. FactSage was used to generate the CaO-SiO₂-K₂O ternary phase diagram built at minimum Gibbs free energy, as shown in Figure 7.1. The diagram parameters were configured in Phase Diagram module. The temperature range was set from 200K to 2500 K at 100-K increments to ensure adequate coverage of the bulk temperature. Formation of the liquid phase starts at around 750 K. The liquid constitutes 60% pure K₂O, denoted with a blue line. At higher temperatures from 800K to 1800 K, the liquid phase is seen to be split between the SiO₂-rich region and the K₂O-rich region, possibly as SiO_{2(l)} and K₂SiO_{4(l)}. Within the CaO-rich region, the liquid phase does not form at any temperature since calcium is less likely to promote liquid formation. However, 70% of CaO without the presence of K₂O at 2400 K to 2500 K denoted with red lines is the maximum allowable calcium molar fraction to produce liquid slag, e.g. Ca₂SiO_{4(l)} or CaSiO_{3(l)}. As the

point of the maximum allowable calcium molar fraction is dragged down along the red lines, CaO molar fraction decreases faster than the increase of SiO₂ and K₂O molar fractions.

Nevertheless, the molar fractions of SiO₂, K₂O, and CaO in raw biomass should not be used directly as parameters since these quantities do not imply biomass ash melting characteristics. During combustion, a significant portion of potassium, for instance, is volatilised. Although potassium is initially a major AFE in the solid fuel, liquid phases may not be formed in the combusted residual solid fuel due to lack of potassium. Therefore, the evaluation on the liquid phase formation should be separately conducted on residual particles and gas and aerosols, partition of which depends on combustion parameters.

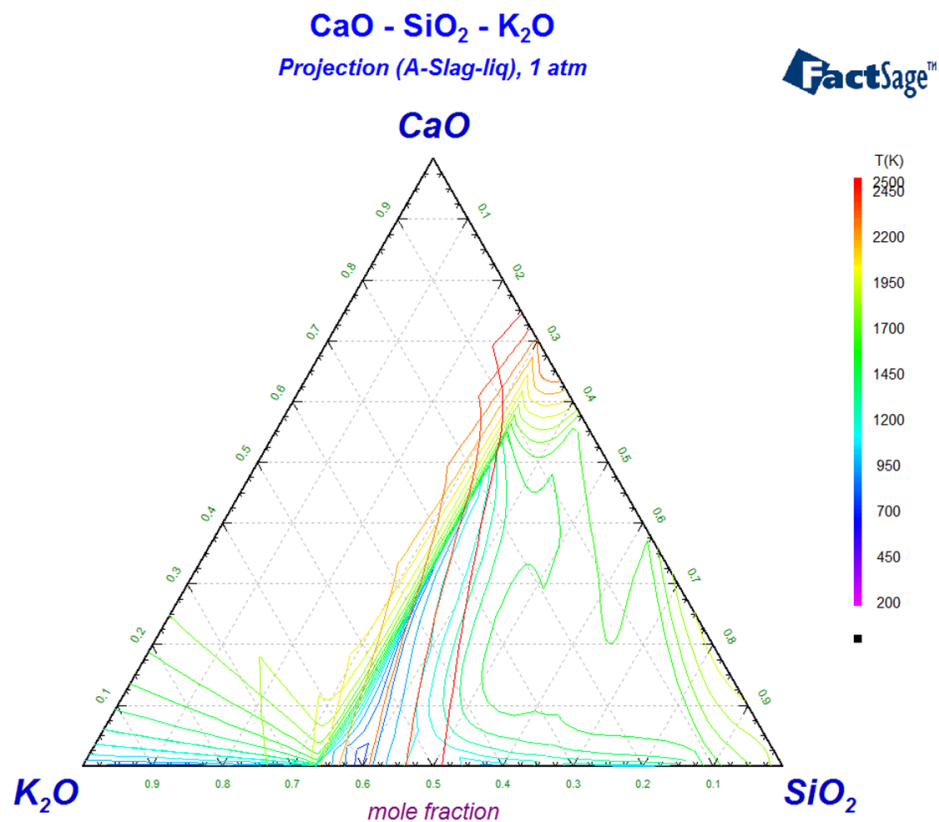


Figure 8.1 Liquidus Isotherm Lines within CaO-SiO₂-K₂O Ternary Phase Diagram

The modelled combustion parameters are mostly based on the results of air-combustion in the PACT facility entrained-flow burner. Combustion operating conditions, e.g. the burner's dimensions, inlet gas properties, and particle size distribution, are considered to be the same as those that were inserted into the model for air-combustion and oxy27-combustion of white wood. The moisture content of herbaceous biomass is assumed to be the same as that of white wood. The flow rate of the inlet air is

reduced from that used during air-combustion to ensure that the outlet bulk $O_{2(g)}$ molar percentage is within 3% to 3.5%.

The calculation routes of the simplified entrained-flow combustion model and the simplified fate and occurrence model used to predict AFE and TE occurrences in herbaceous biomass combustion are the routes according to the model structures shown in Figures 7.1 and 7.2. The only changed parameters from those used in the models for air combustion of white wood are the density of herbaceous biomass and the pyrolysis kinetic equations based on Equations C.13 and C.14. The pyrolysis kinetic parameters are listed in Table 8.1.

Table 8.1 Kinetic Parameters of Pyrolysis of Herbaceous Biomass

Biomass	Reaction	A (s^{-1})	E_A ($J\ mol^{-1}$)	$\Delta H_{Rx,298K}$ ($J\ kg^{-1}$)
Rice Husk	(R7.1)	1.3e9	97.1e3	4.2e5
Switchgrass	(R7.1)	2.84e9	108.7e3	4.2e5

8.2 Discussion of the Model Result: Rice Husk

The modelled temperature profile of the bulk gas and the modelled molar percentage profile of bulk $O_{2(g)}$ gas for rice husk during both air-combustion and oxy27-combustion are shown in Figures 8.2 and 8.3. The bulk gas temperature profile in air-combustion is not significantly distinctive from that seen in oxy27-combustion. However, the bulk $O_{2(g)}$ molar percentage is higher by 3% in oxy27-combustion than in air-combustion at complete burnout. This higher concentration of residual bulk $O_{2(g)}$ in oxy27-combustion than in air-combustion is due to a reduced flow rate of the inlet gas in oxy27-combustion. The fate and occurrence model is executed using these bulk gas temperature profiles, bulk $O_{2(g)}$ molar percentage profiles, and AFE initial concentrations as shown in Table 3.1, as input parameters. The fate and occurrence profiles of potassium, silicon, and calcium are presented in this section. The discussion of the fate and occurrence profiles of the other AFEs are compiled in Appendix K.

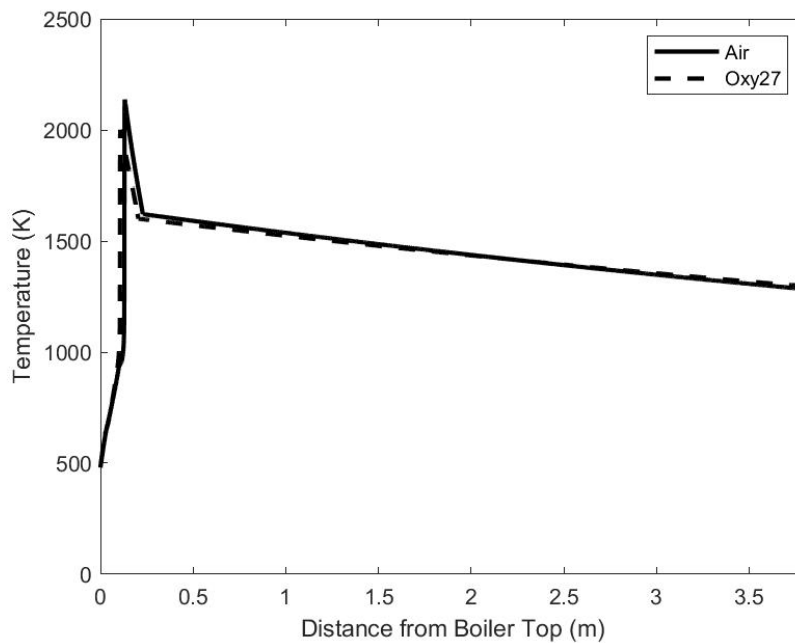


Figure 8.2 Modelled Temperature Profile of Bulk Gas during Rice Husk Combustion in the PACT Entrained-flow Burner

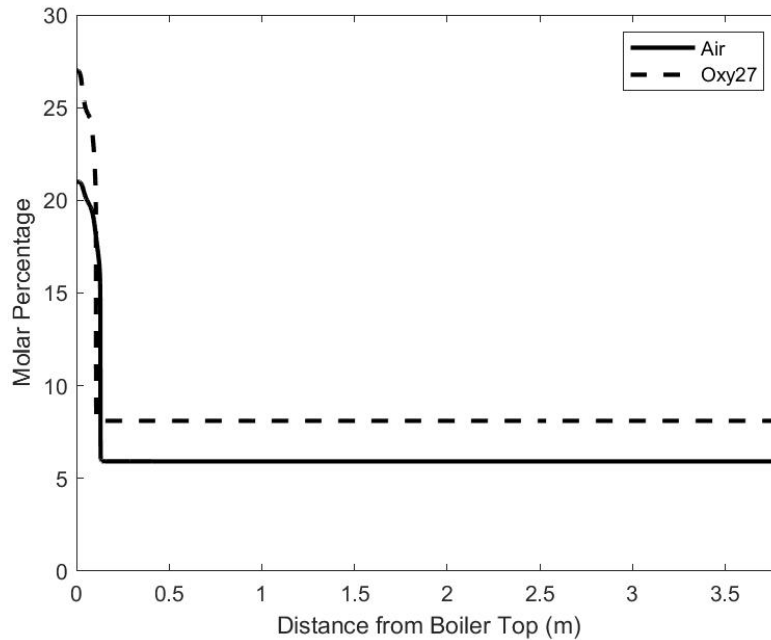


Figure 8.3 Modelled Dry Molar Percentage Profile of Bulk $O_{2(g)}$ Gas during Combustion of Rice Husk in the PACT Entrained-flow Burner

Potassium

The potassium fate profile produced by the model is shown in Figure 8.4. Most potassium is released from the particles as gas. However, in contrast with potassium's strong volatility, a considerable proportion of potassium remains in the particles, probably due to reaction with silicon to form alkali-metal silicates. The significant amount of bulk potassium is transformed during air-combustion into liquid aerosols during the *heat loss* stage. On the other hand, bulk potassium remains as gas during the *heat loss* stage of oxy-27 combustion.

The modelled occurrence profiles of bulk potassium are shown in Figure 8.5 for air-combustion and in Figure 8.6 for oxy27-combustion. In air-combustion, potassium is volatilised at the peak temperature as $\text{KOH}_{(g)}$. During the *heat loss* stage, $\text{KOH}_{(g)}$ is converted into $\text{K}_2\text{Si}_4\text{O}_9(l)$. Anicic *et al.*³¹³ discovered that $\text{K}_2\text{Si}_4\text{O}_9(l)$ was formed via $\text{SiO}_{2(s)}$ reaction with $\text{K}_2\text{CO}_{3(s)}$ by agglomeration in a fluidised-bed boiler, as expressed in Reaction 8.1.



At temperatures above 1,073 K, Reaction 8.1 occurs at a fast rate. However, no presence of $\text{K}_2\text{CO}_{3(s)}$ is shown in Figure 8.5. Rather, a reduced $\text{KOH}_{(g)}$ partition with increased $\text{K}_2\text{Si}_4\text{O}_9(l)$ partition and constant $\text{KCl}_{(g)}$ partition might indicate that Reaction 8.2 occurs, even though there is no clear evidence.



Ma *et al.*³¹⁴ suggested that $\text{K}_2\text{O}_{(s)}$ might react first with $\text{SiO}_{2(s)}$ as expressed in Reaction 8.3. However, Reaction 8.3 is unlikely to occur since $\text{K}_2\text{O}_{(s)}$ is very unstable and is violently reactive with $\text{H}_2\text{O}_{(g)}$.

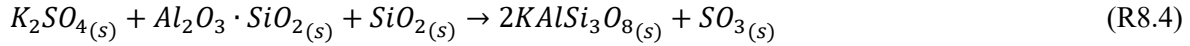


In oxy27-combustion, the partition of $\text{K}_2\text{Si}_4\text{O}_9(l)$ is considered insignificant. Reduced partition of $\text{K}_2\text{Si}_4\text{O}_9(l)$ might be associated with insufficient availability of bulk silicon since silicon is barely volatilised in oxy27-combustion, as shown in Figure 8.13.

The presence of $\text{K}_2\text{Si}_4\text{O}_9(l)$ indicates that a substantial amount of silicon in the bulk might boost fireside fouling in commercial boilers and $R_{S/Cl}$ is no longer the sole parameter to define fouling severity. Although $\text{SiO}_{2(s)}$ melts at around 1,986 K, $\text{SiO}_{2(s)}$ association with potassium forms $\text{K}_2\text{Si}_4\text{O}_9(l)$ at as low as 1,040 K.³¹⁵ It is essential to keep the flue gas temperature below 1,040 K in the vicinity of convective pass in biomass combustion to prevent $\text{K}_2\text{Si}_4\text{O}_9(l)$ formation; e.g. the potential of straw combustion in both Masnedø and Ensted grate-fired boilers to experience frequent fouling due to flue gas temperatures operating at around 1,173 to 1,292 K in the vicinity of convective pass. As shown in Figure 8.7, the intermediate layer of fouling deposit in an Ensted boiler contains a very dense solid mixture of

potassium, chlorine, silicon, and calcium.³¹⁶ The formation of this solid dense mixture is often understood as a result of silicon- and calcium-rich aerosol and residual particle clustering assisted with $KCl_{(l)}$. However, the formation of $K_2Si_4O_9_{(l)}$ might suggest another alternative explanation, that $K_2Si_4O_9_{(l)}$ and $KCl_{(l)}$ are sintered to some degree as the intermediate layer.³¹⁷

Modelled potassium occurrence in bottom ash is shown in Figure 8.8 for air-combustion and Figure 8.9 for oxy27-combustion. In both cases, $KAlSi_3O_8_{(s2)}$ is the major potassium compound formed, with a minor proportion of $K_2Si_2O_5_{(s)}$. $KAlSi_3O_8_{(s2)}$ is probably formed via Reaction 8.4.³¹⁸



$K_2SO_{4(s)}$ is one of the most common compounds found in biomass bottom ash.³¹⁹ $K_2Si_2O_5_{(s)}$ is also common in the bottom ash of biomass that contains excessive silicon content.³²⁰

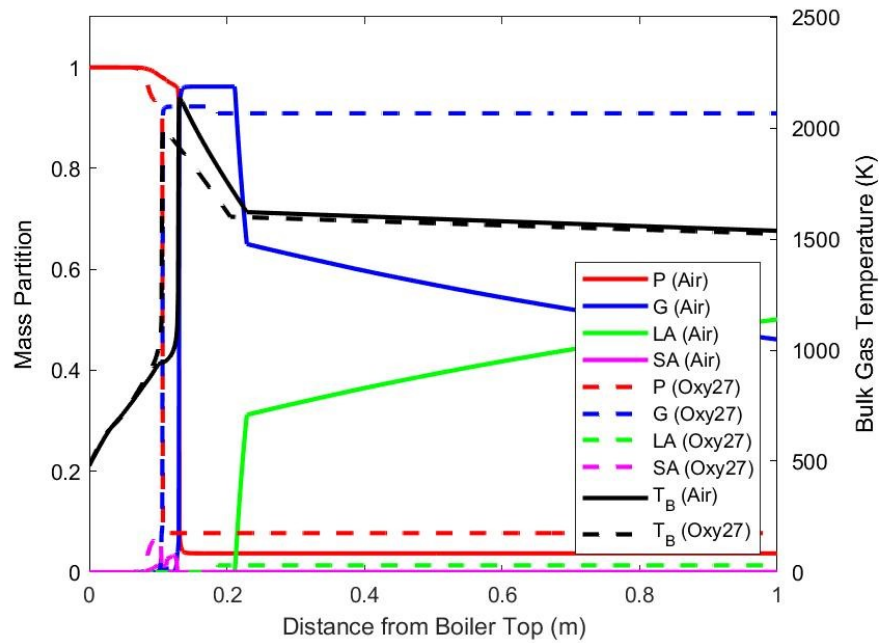


Figure 8.4 Modelled Potassium Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion)

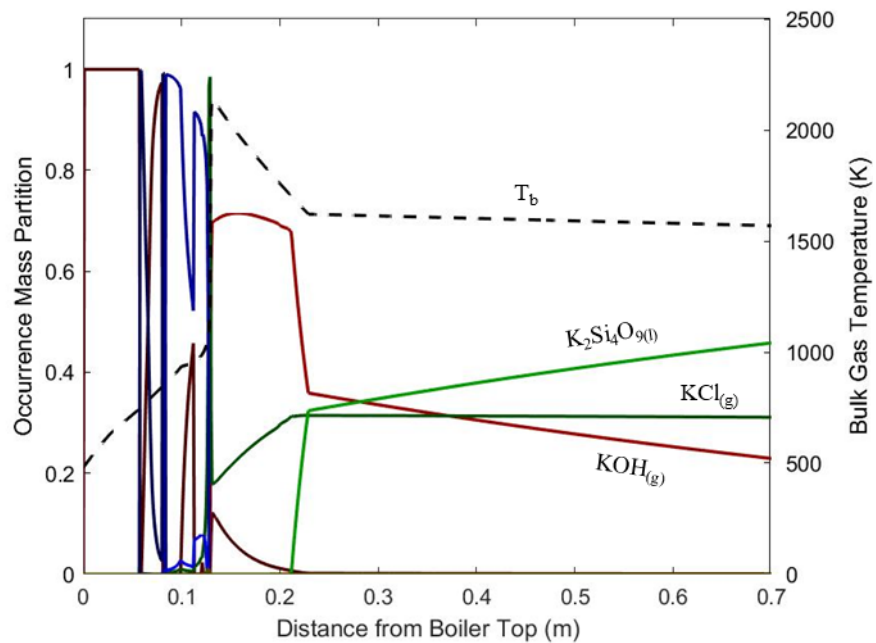


Figure 8.5 Modelled Potassium Bulk Occurrences in Air-combustion of Rice Husk

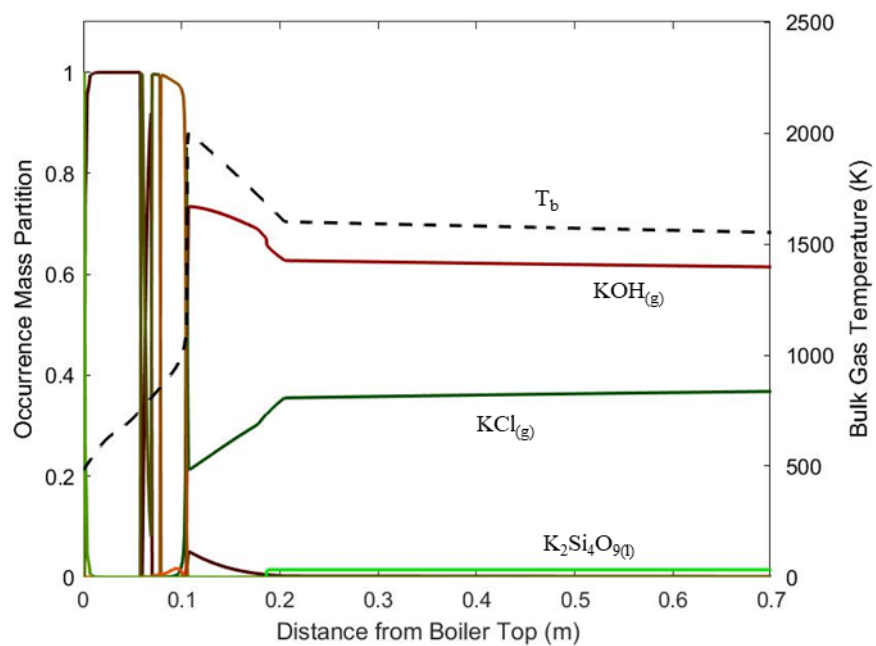


Figure 8.6 Modelled Potassium Bulk Occurrences in Oxy27-combustion of Rice Husk

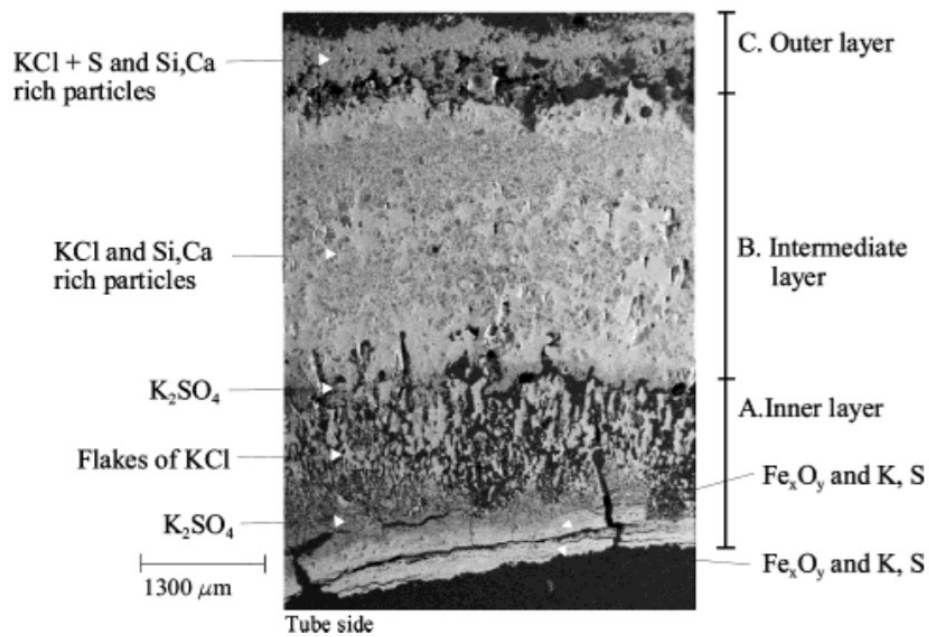


Figure 8.7 SEM Images of Fouling Deposit Layers in Ensted Boiler

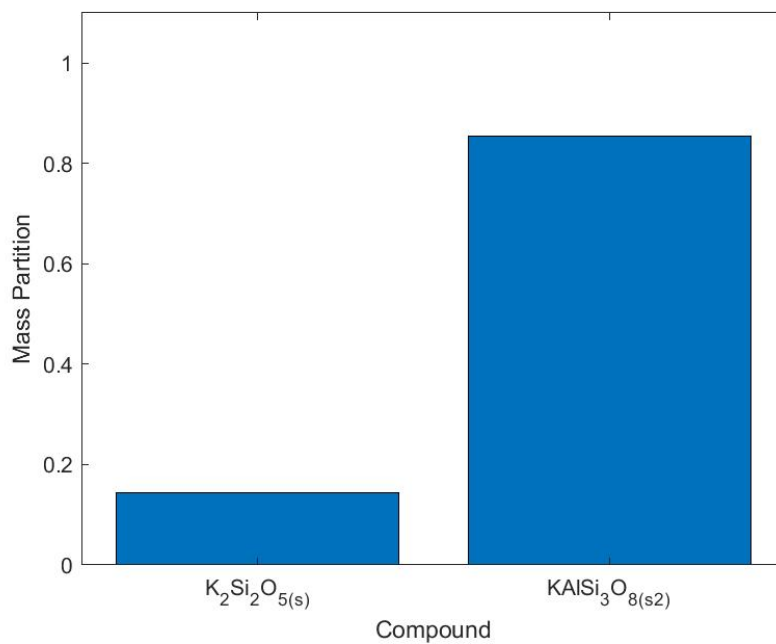


Figure 8.8 Modelled Potassium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Rice Husk

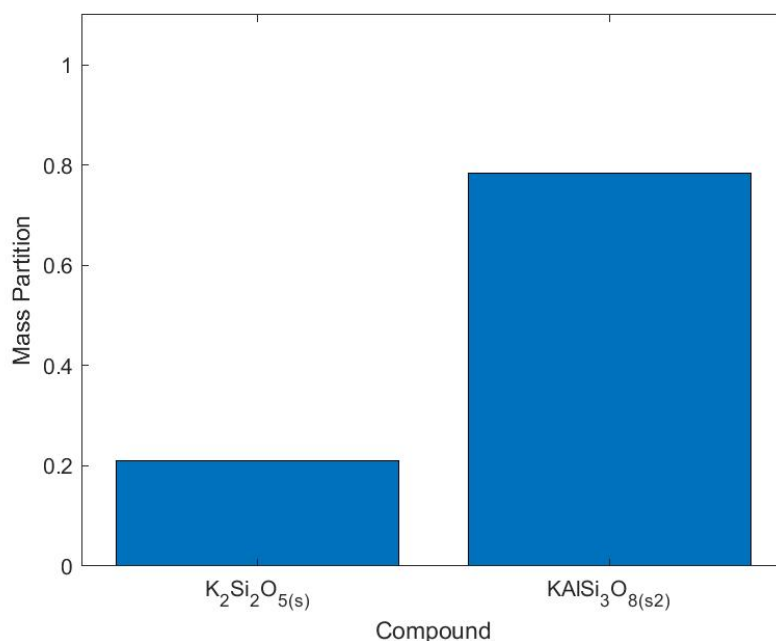


Figure 8.9 Modelled Potassium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Rice Husk

Calcium

Calcium is barely volatilised as seen in the modelled fate profiles for this element shown in Figure 8.10. Since the calcium content of the biomass is significantly lower than that of silicon, selectivity towards formation of $Ca(OH)_{2(g)}$ is not favoured. Rather, calcium reacts with silicon in the particles and is retained in the bottom ash mostly as $CaSiO_{3(s)}$ with a small proportion of $CaMgSi_2O_{6(s)}$ in both air-combustion and oxy27-combustion, as shown in Figure 8.11 and 8.12. $CaSiO_{3(s)}$ is likely to form via Reactions 7.11 and 7.12, consecutively.

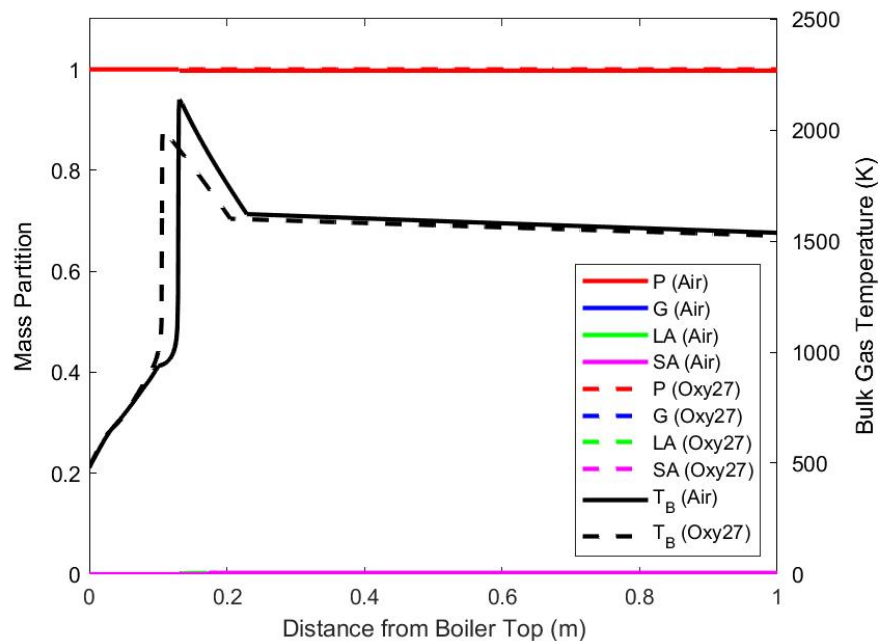


Figure 8.10 Modelled Calcium Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion)

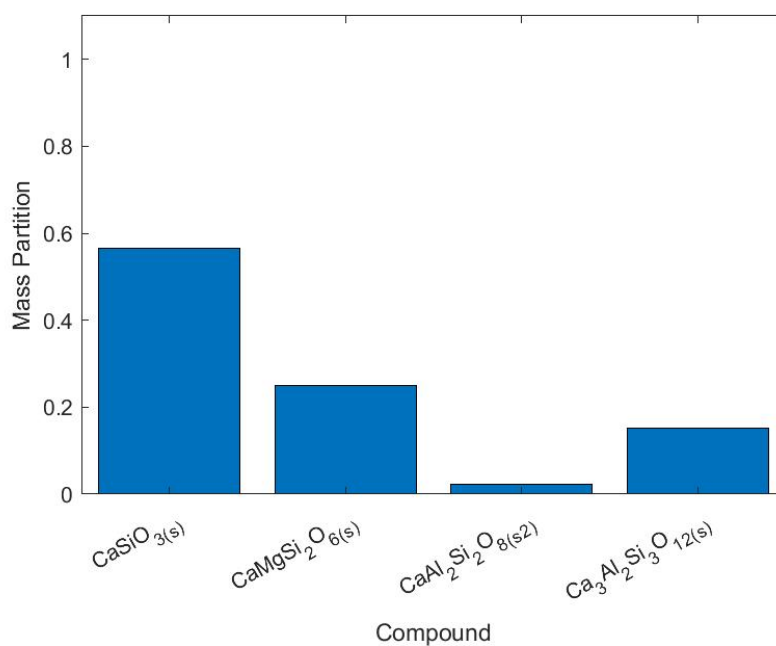


Figure 8.11 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Rice Husk

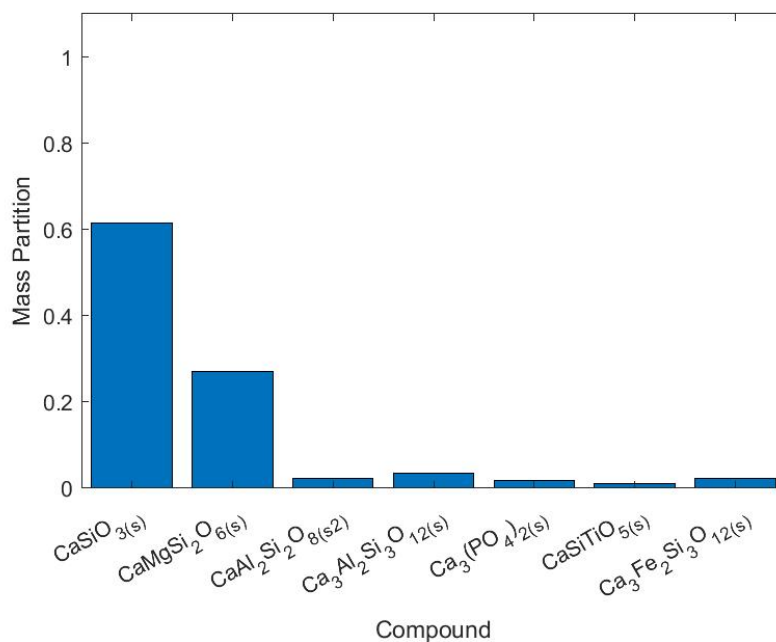


Figure 8.12 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Rice Husk

Silicon

The modelled fate profiles for silicon are shown in Figure 8.13. They show strong retention of silicon in the particles along with calcium and magnesium. This prediction is in agreement with Figures 8.11 and 8.12 that silicon forms silicate compounds associated with calcium and magnesium. A slight proportion of silicon is released from the particles in air-combustion. In oxy27-combustion, almost all silicon remains in the particles.

Modelled occurrence profiles for bulk silicon are shown in Figure 8.14 for air-combustion. Silicon is initially released as $\text{SiO}_{2(\text{l})}$ at peak temperature. As bulk temperature decreases during the *heat removal* stage, $\text{SiO}_{2(\text{l})}$ is solidified into $\text{SiO}_{2(\text{s}6)}$. At the beginning of the *heat loss* stage, $\text{SiO}_{2(\text{s}6)}$ is converted into $\text{SiO}_{2(\text{s}4)}$ and $\text{K}_2\text{Si}_4\text{O}_9(\text{l})$. $\text{K}_2\text{Si}_4\text{O}_9(\text{l})$ is formed possibly via Reaction 8.2 at a temperature of around 1,600 K whilst the proportion of $\text{SiO}_{2(\text{s}4)}$ decreases.

According to the silicon occurrence profile shown in Figure 8.14, $\text{SiO}_{2(\text{l})}$ and $\text{K}_2\text{Si}_4\text{O}_9(\text{l})$ are the only liquid compounds that are produced. They are formed at two different temperatures, at around 2,000 K during the *heat removal* stage for $\text{SiO}_{2(\text{l})}$ and between 1,500 K and 1,600 K during the *heat loss* stage for $\text{K}_2\text{Si}_4\text{O}_9(\text{l})$. In the ternary diagram shown in Figure 8.15, these two liquidus conditions are approximately located within the black box in which the molar fraction of potassium dominates the

molar fraction of silicon. $\text{SiO}_{2(l)}$ and $\text{K}_2\text{Si}_4\text{O}_9(l)$ are respectively represented by yellow lines and green lines.

$\text{SiO}_{2(l)}$ might not contribute to slagging-induced ash deposition in commercial boilers. Slagging is initiated with inertial impaction and thermophoresis of solid aerosols, e.g. $\text{SiO}_{2(s)}$, $\text{Ca}_2\text{SiO}_{4(s)}$, at relatively lower temperatures at water walls than at boiler centreline. Rather, $\text{SiO}_{2(l)}$ could promote agglomeration of the other AFEs into coarse aerosols and increase the proportion of bottom ash over fly ash.³²¹ When the bulk deposit layer is formed with average temperatures closer to bulk gas temperatures, $\text{SiO}_{2(l)}$ might be deposited directly onto the bulk deposit layer and enhance the sintering. A mineral analysis was conducted on a fragment of slagging ash deposit taken from an entrained-flow boiler in the Kardia power plant. The fragment was divided into three zones, namely: zone I for the initial deposit layer, zone II for the bulk deposit layer, and zone III for the running slag layer, as shown in Figure 8.16. According to the mineral analysis, silicon was enriched primarily in zone II in the form of calcium silicates, e.g. $\text{Ca}_2\text{SiO}_{4(s)}$, $\text{CaAl}_2\text{Si}_2\text{O}_8(s)$, $\text{Ca}_2\text{Al}_2\text{SiO}_7(s)$, and $\text{Ca}(\text{Mg},\text{Al})(\text{Si},\text{Al})_2\text{O}_6(s)$.³²² In sulphur-rich solid fuel combustion, $\text{CaSO}_{4(s)}$ was found to be the predominant compound in all zones. Calcium silicates is capable of adsorbing free calcium. The adsorbed free calcium promotes rapid sulphation by attracting sulphates. This mechanism creates a plerospheric structure with $\text{CaSO}_{4(s)}$ as the shell covering calcium silicates as the core.³²¹

Silicon occurs in the bottom ash as $\text{SiO}_{2(s)}$ and as a small partition of $\text{SiO}_{2(s4)}$ in both air-combustion and oxy27-combustion. These results are shown in Figures 8.17 and 8.18. $\text{SiO}_{2(s)}$ is a common compound found in biomass. The mass percentage of $\text{SiO}_{2(s)}$ in bottom ash potentially exceeds 10%.³²³ The estimated location of the $\text{CaO-SiO}_2\text{-K}_2\text{O}$ composition in rice husk particles at complete burnout is in the black box shown in Figure 8.19. The liquid phase in the particles is potentially formed at around 1,400 K to 1,700 K as indicated by green lines that intercept the black box.

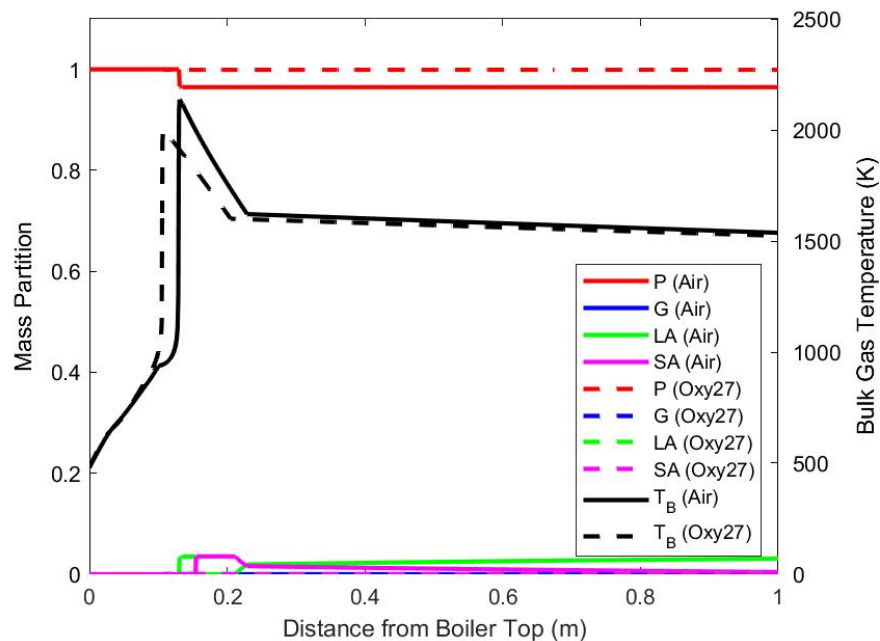


Figure 8.13 Modelled Silicon Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion)

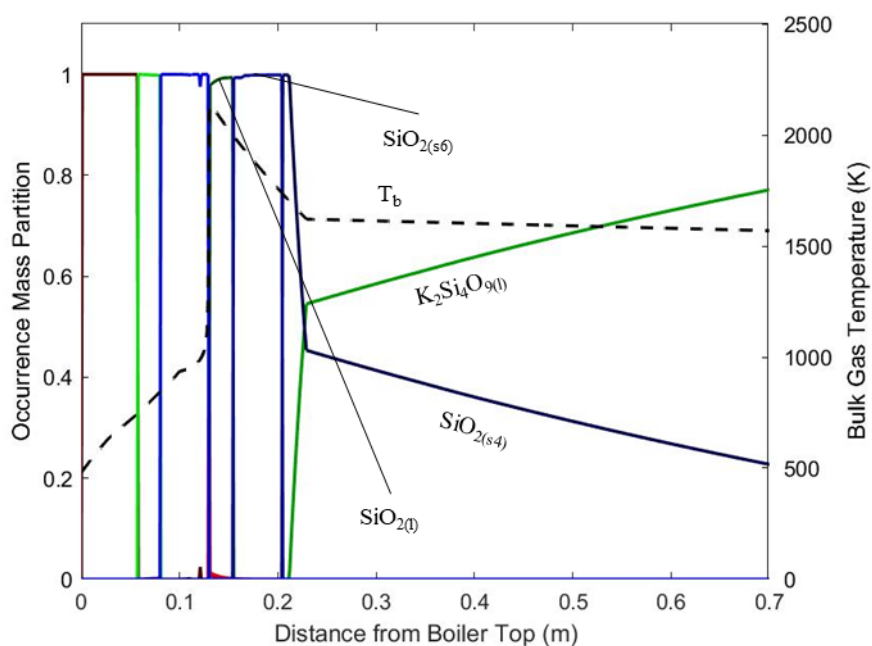


Figure 8.14 Modelled Silicon Bulk Occurrences in Air-combustion of Rice Husk

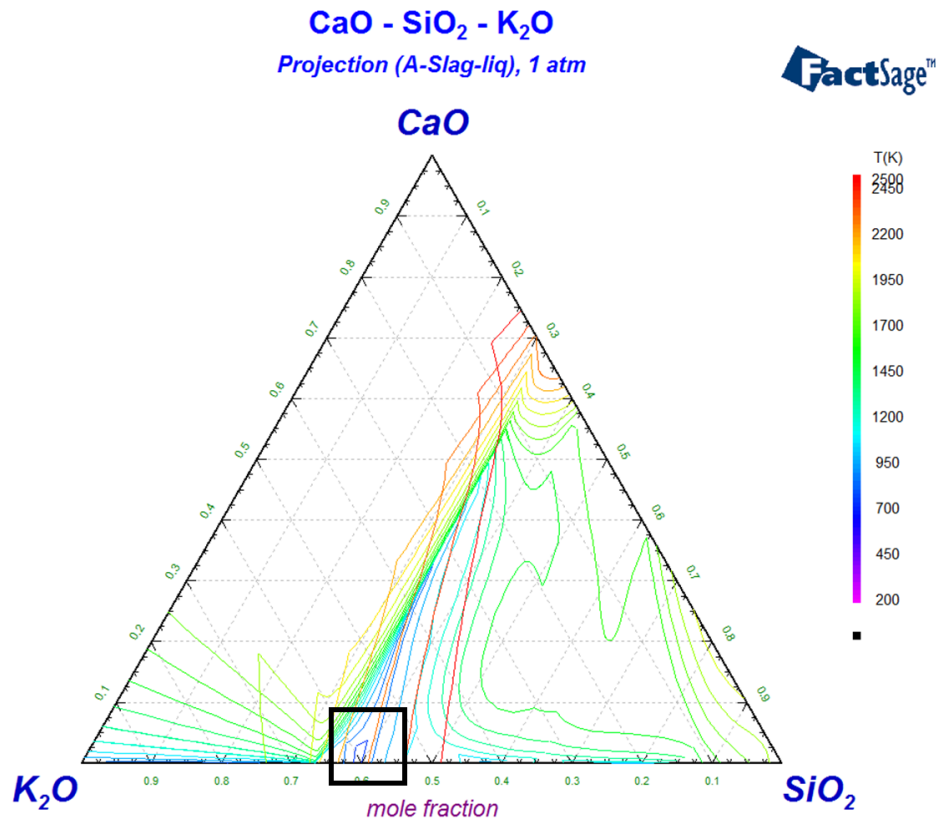


Figure 8.15 Bulk Composition of Rice Husk (Black Box) at Complete Combustion and Liquidus Isotherm Lines within CaO-SiO₂-K₂O Ternary Phase Diagram

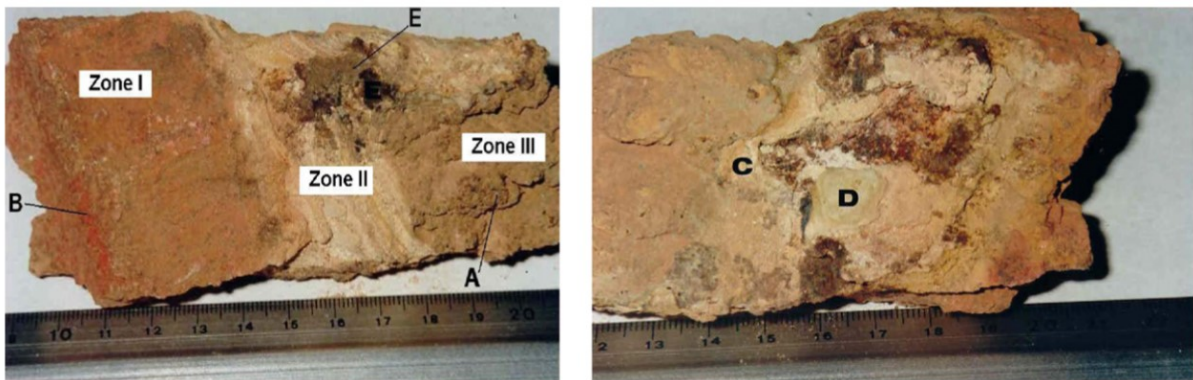


Figure 8.16 A Fragment of Ash Deposit Generated in an Entrained-flow Boiler in Kardia Power Plant

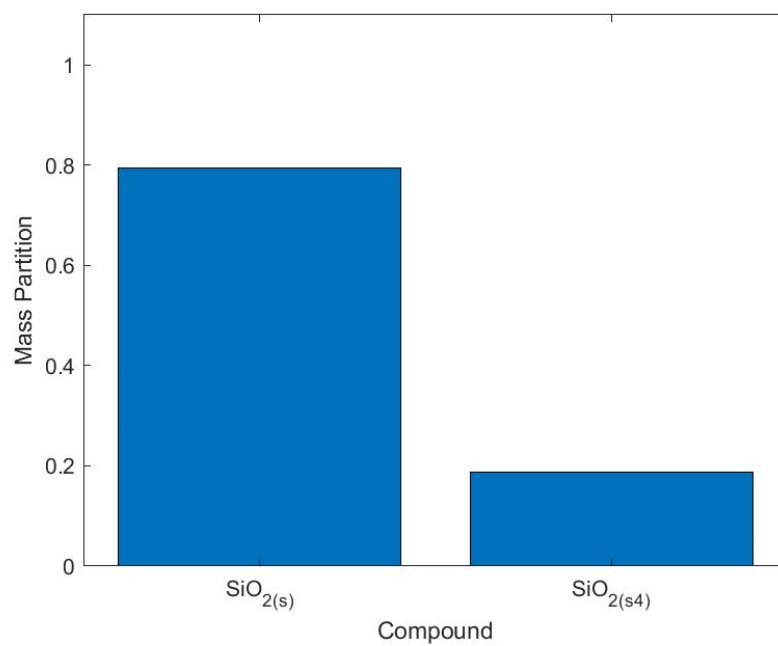


Figure 8.17 Modelled Silicon Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Rice Husk

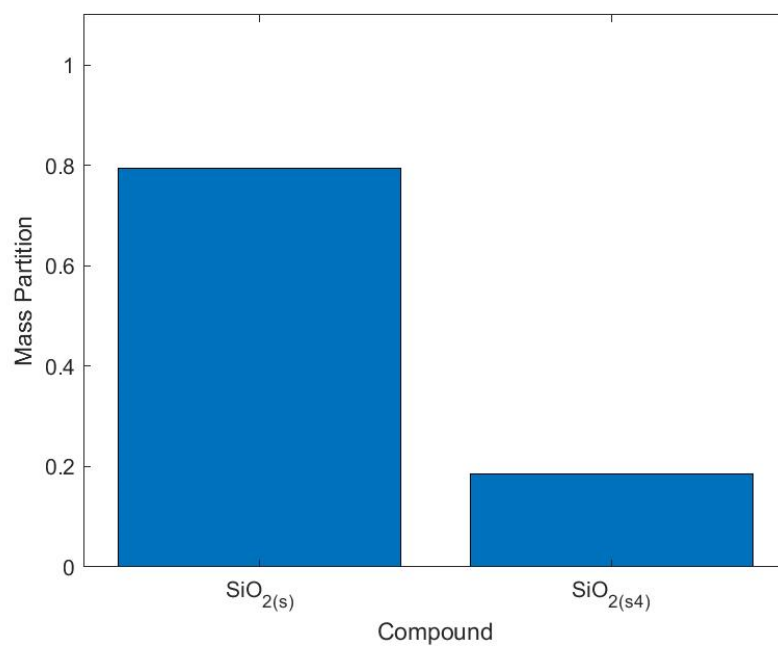


Figure 8.18 Modelled Silicon Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of White Wood

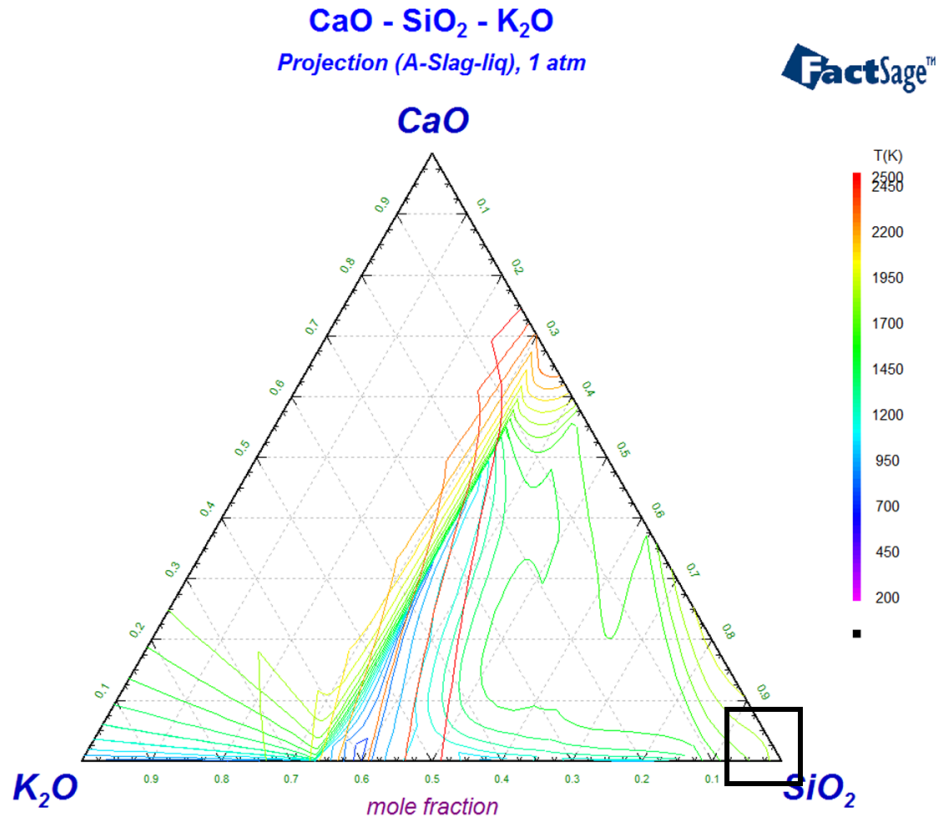


Figure 8.19 Particle Composition of Rice Husk (Black Box) at Complete Combustion and Liquidus Isotherm Lines within CaO-SiO₂-K₂O Ternary Phase Diagram

8.3 Discussion of the Model Result: Switchgrass

The modelled temperature profile of bulk gas and the molar percentage profile of bulk O_{2(g)} gas for switchgrass in both air-combustion and oxy27-combustion are shown in Figures 8.20 and 8.21. In general, the bulk gas profiles illustrated in Figures 8.20 and 8.21 share similar trends with the bulk gas profiles shown for rice husk in Figures 8.2 and 8.3, which would be expected. These bulk gas profiles shown in Figures 8.20 and 8.21 and AFE initial concentrations given in Table 3.1 are used as input parameters for the fate and occurrence model of switchgrass. This section discusses the fate and occurrence profiles of potassium, silicon, and calcium. The discussion of the fate and occurrence profiles of the other AFEs are compiled in Appendix L.

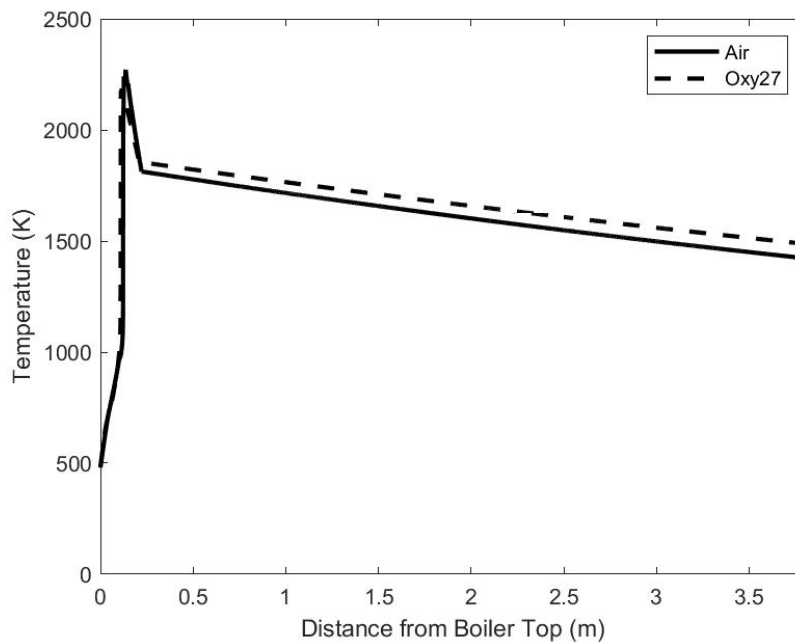


Figure 8.20 Modelled Temperature Profile of Bulk Gas during Switchgrass Combustion in the PACT Entrained-flow Burner

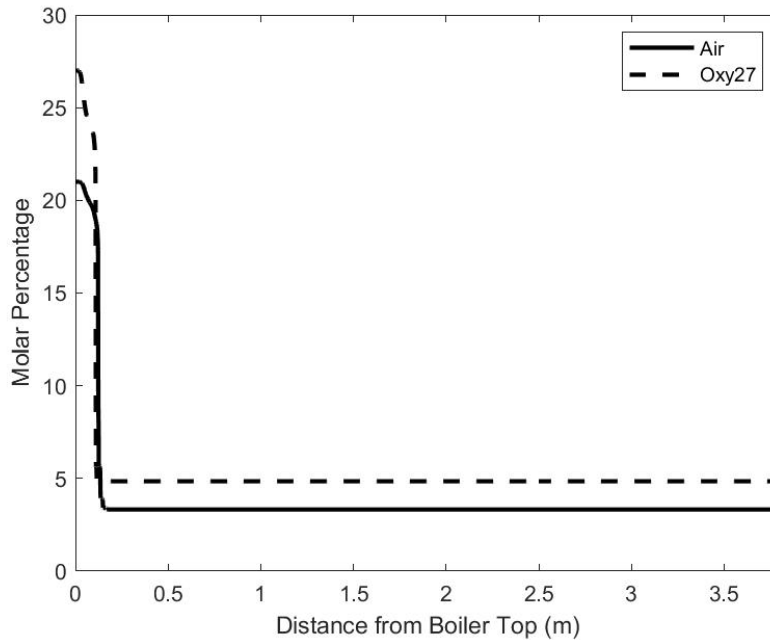


Figure 8.21 Modelled Dry Molar Percentage Profile of Bulk $O_{2(g)}$ during Combustion of Switchgrass in the PACT Entrained-flow Burner

Potassium

The modelled fate profile for potassium is shown in Figure 8.22. Around 20% of the initial potassium remains in the particle in air-combustion whilst all the potassium is volatilised in oxy27-combustion. In oxy27-combustion, the greater quantity of bulk $O_{2(g)}$ retains more silicon in the particles than the lower amount of bulk $O_{2(g)}$ in air-combustion, as shown in Figure 8.31. Greater silicon retention in the particles promotes more potassium release from the particles since the retained silicon forms stable $SiO_{2(s)}$, thereby allocating potassium to form volatile $KOH_{(g)}$.

Modelled bulk potassium occurrence profiles are shown in Figure 8.23 for air-combustion and in Figure 8.24 for oxy27-combustion. In both cases, most of the potassium is released as $KOH_{(g)}$. During the *heat loss* stage, less $KAlSi_2O_{6(s2)}$ is formed in oxy27-combustion due to the release of less silicon to the bulk to react with $KOH_{(g)}$.

$K_2Si_2O_{5(s)}$ and $KAlSi_3O_{8(s2)}$ are the major compounds found in switchgrass bottom ash in air-combustion, as shown in Figure 8.25. $KAlSi_3O_{8(s2)}$ is present in less proportion than $K_2Si_2O_{5(s)}$ in switchgrass bottom ash, whilst an opposite trend occurs in rice husk bottom ash. Since less aluminium is left in the particles after switchgrass combustion, $KAlSi_3O_{8(s2)}$ formation is less favoured.

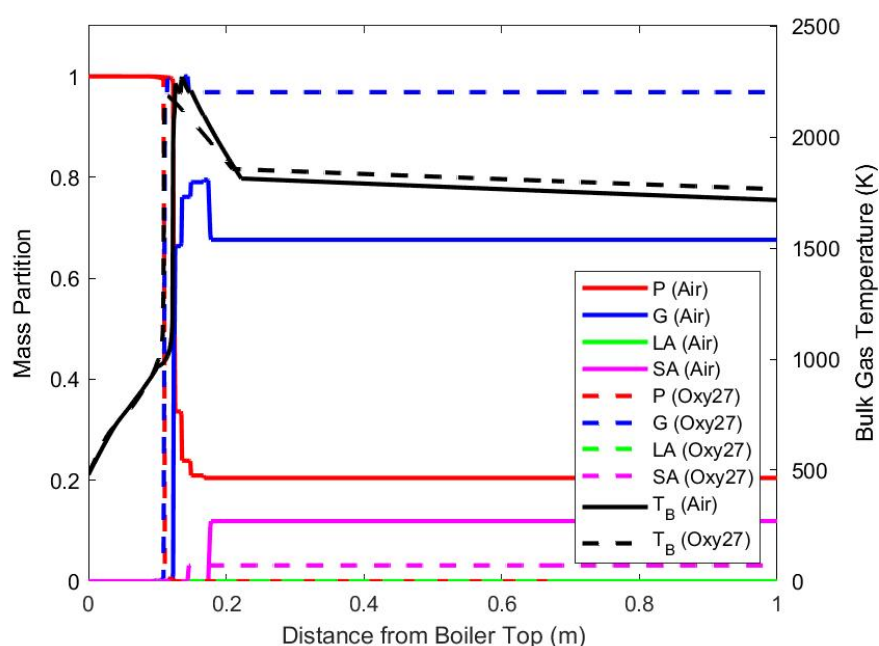


Figure 8.22 Modelled Potassium Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion)

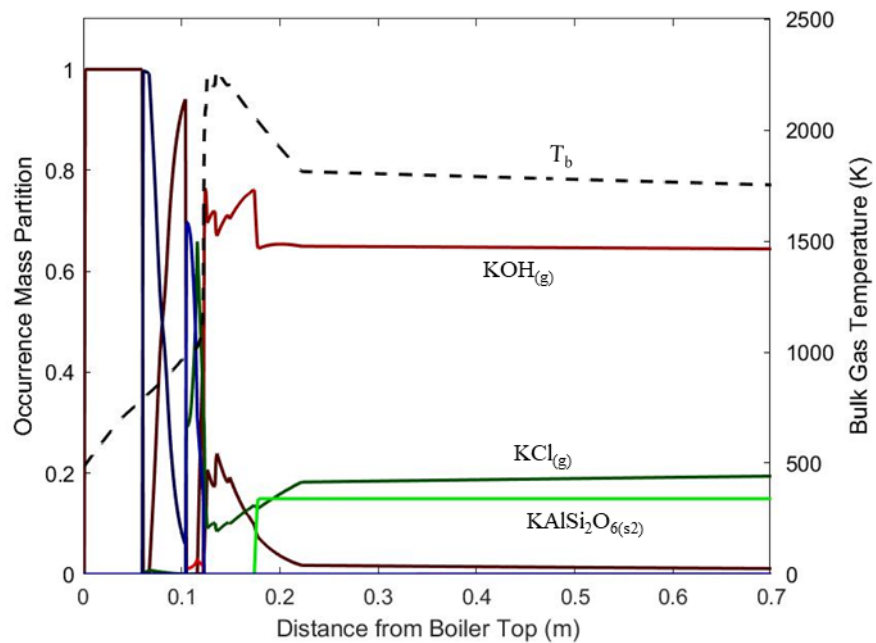


Figure 8.23 Modelled Potassium Bulk Occurrences in Air-combustion of Switchgrass

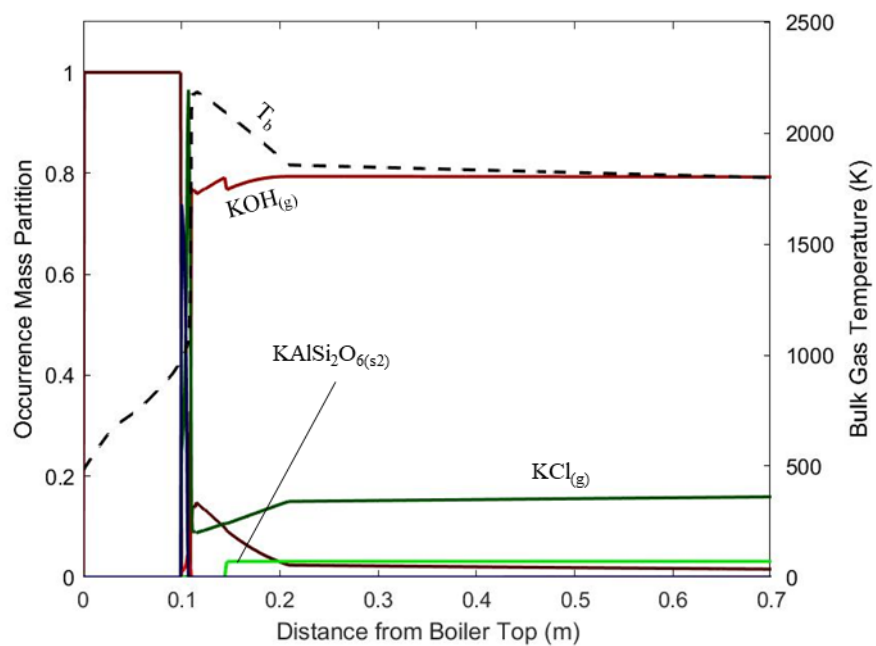


Figure 8.24 Modelled Potassium Bulk Occurrences in Oxy27-combustion of Switchgrass

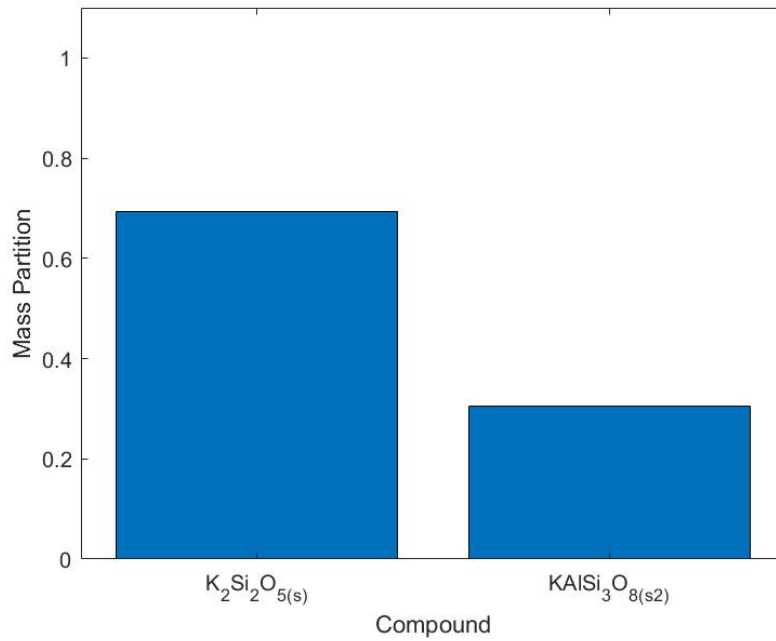


Figure 8.25 Modelled Potassium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Switchgrass

Calcium

Modelled calcium fate profiles are shown in Figure 8.26. During air-combustion, around half of the calcium is volatilised from the particles. On the other hand, less than 10% of the calcium is volatilised from the particles in oxy27-combustion. The release of a significant amount of calcium in air-combustion is probably due to the presence of less silicon in switchgrass than rice husk to form alkaline-earth silicate compounds that are often left in the particles. Oxy27-combustion with higher bulk $O_{2(g)}$ concentration promotes faster $O_{2(g)}$ penetration to the particle to oxidise particle AFEs and to retain more particle silicate compounds.

Modelled occurrence profiles of bulk calcium in air-combustion are shown in Figure 8.27. By the end of the *heat removal* stage, calcium is mainly in the form of $CaSiO_{3(s2)}$. $CaSiO_{3(s2)}$ is formed at high temperature via Reaction 8.5.³²⁴



At the beginning of the *heat loss* stage, $CaSiO_{3(s2)}$ disappears, and $Ca_3(PO_4)_{2(s2)}$ is formed as the major calcium compound during the *heat loss* stage. Due to a considerable quantity of released calcium, phosphorus is more chemically attracted to calcium than sodium in rice husk combustion. Phosphorus is likely to be released from the particles as $PO_{2(g)}$. Due to moisture content in the bulk gas, $PO_{2(g)}$ reacts with moisture to form $H_3PO_{4(g)}$ as expressed in Reaction 8.6.



$H_3PO_{3(g)}$ is decomposed into $H_3PO_{4(g)}$ and $PH_{3(g)}$ at temperatures above 473 K, according to Reaction 8.7.³²⁵



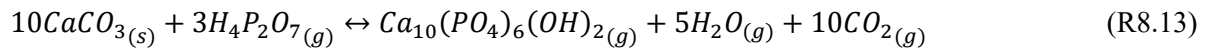
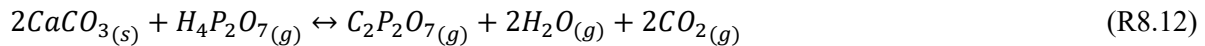
Furthermore, $PH_{3(g)}$ is oxidised as shown in Equation 8.8.



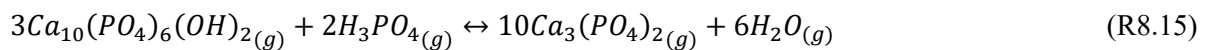
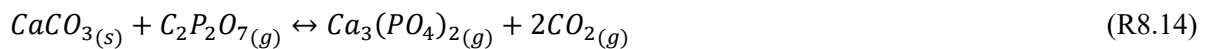
Pan *et al.* have suggested a series of reactions that create a formation mechanism for $Ca_3(PO_4)_2$.³²⁶ According to this mechanism, $H_3PO_{4(g)}$ is further decomposed via a reversible reaction shown in Reaction 8.9.



The $CaSiO_{3(s)}$ might be converted to $CaCO_{3(s)}$. $CaCO_{3(s)}$ might further react with $H_4P_2O_{7(g)}$ at high temperature as shown in Reactions 8.10 and 8.11.



Subsequent proposed reactions are shown in Reactions 8.14 and 8.15.



Modelled bulk occurrence profiles for calcium in oxy27-combustion are shown in Figure 8.28. $Ca_3Mg_4(PO_4)_4(s)$ is the only calcium compound predicted. $Ca_3Mg_4(PO_4)_4(s)$ formation is probably promoted by higher bulk $O_{2(g)}$ concentration. In addition, Sinyaev *et al.*³²⁷ have experimentally discovered $Ca_3Mg_4(PO_4)_4(s)$ in fly ash at a temperature of around 1,273 K.

Modelled calcium occurrence in bottom ash is shown in Figure 8.29 for air-combustion and in Figure 8.30 for oxy27-combustion. $Ca_3(PO_4)_2(s)$ is formed in the bottom ash only in air-combustion since there is no phosphorus available in oxy27-combustion bottom ash to react with calcium to form the compound. $Ca_3(PO_4)_2(s)$ in the bottom ash during air-combustion is possibly produced via Reaction 8.16.³²⁸



In addition to potassium, phosphorus is another important element that needs to be carefully treated due to its potential contribution to fouling in combustion of phosphorus-rich solid fuel, e.g. switchgrass. Evidence exhibits that phosphate was found enriched in ash deposits on superheater in an entrained-flow boiler combusting sub-bituminous coal.³²⁹ Phosphate was also captured in the form of aerosols near an economiser in an entrained-flow boiler co-firing straw and coal.³³⁰ Although these findings were not based on combustion of complete biomass, Kalisz *et al.*³³¹ concludes that high phosphorus content in biomass could contribute to severe fouling.

A significant quantity of calcium in phosphorus-rich biomass is an advantage in combustion. Calcium has high selectivity in reacting with phosphates. Phosphate reaction with calcium may prevent the formation of low-melting-temperature alkali phosphates which is potential to cause fouling. However, the residual alkali metals might induce another problem via reaction with silicates to form low-melting-temperature alkali silicates, as previously discussed in Section 8.2. $\text{CaCO}_{3(s)}$ was reportedly an effective additive to simultaneously prevent the formation of both alkali phosphates and alkali silicates. $\text{CaCO}_{3(s)}$ may coat the existing silicates and remove them from the burner.³³²

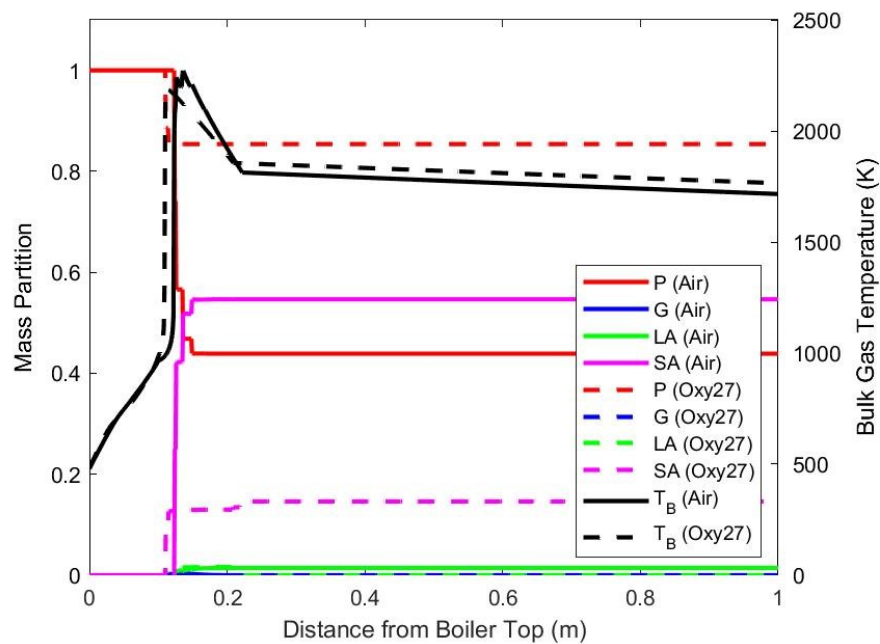


Figure 8.26 Modelled Calcium Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion)

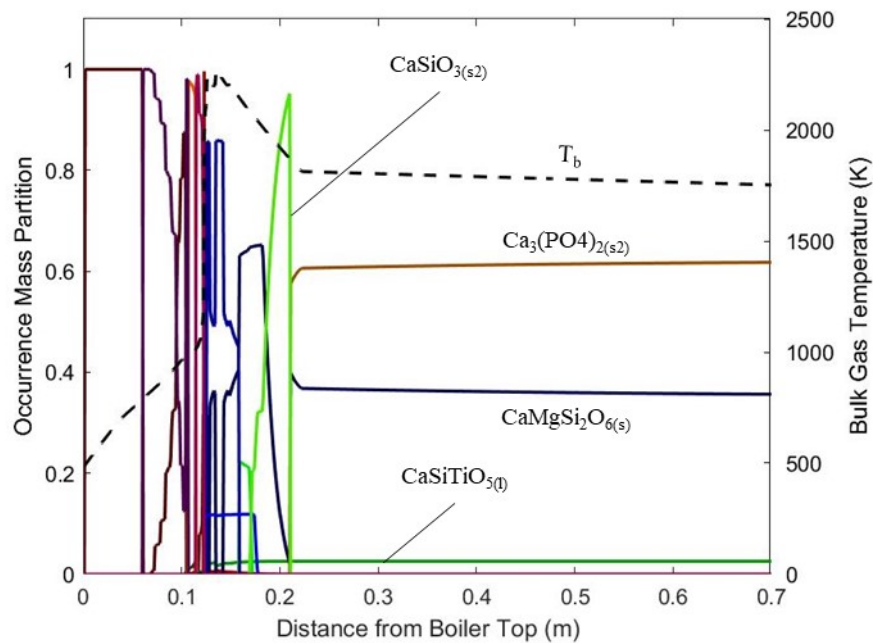


Figure 8.27 Modelled Calcium Bulk Occurrences in Air-combustion of Switchgrass

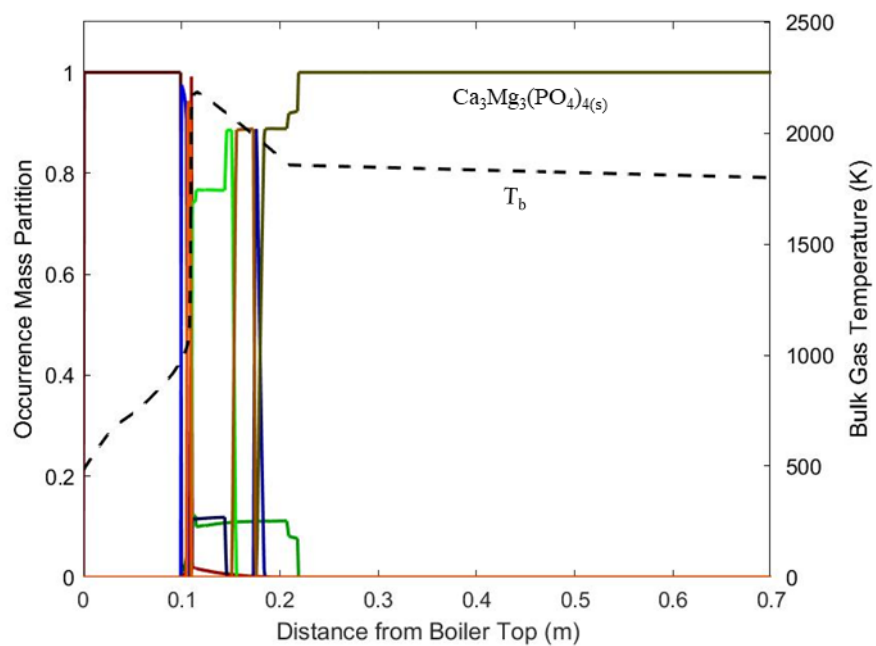


Figure 8.28 Modelled Calcium Bulk Occurrences in Oxy27-combustion of Switchgrass

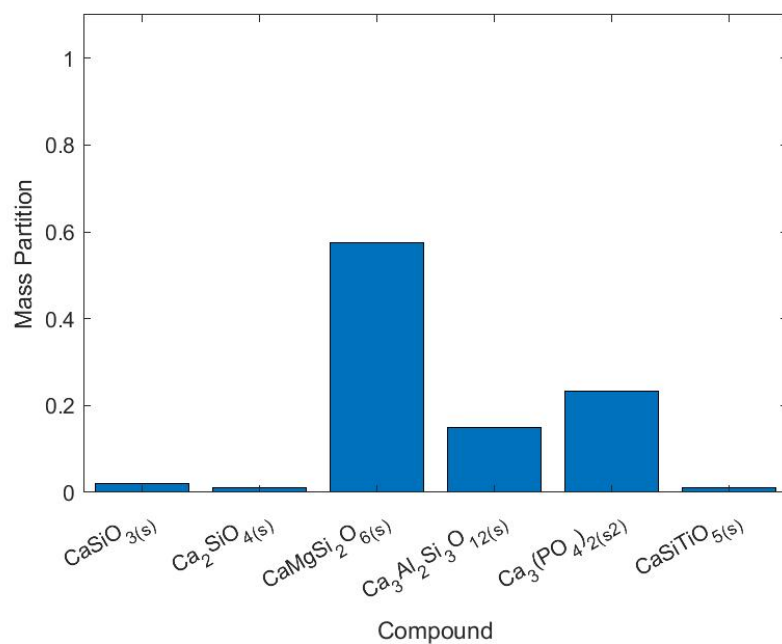


Figure 8.29 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Switchgrass

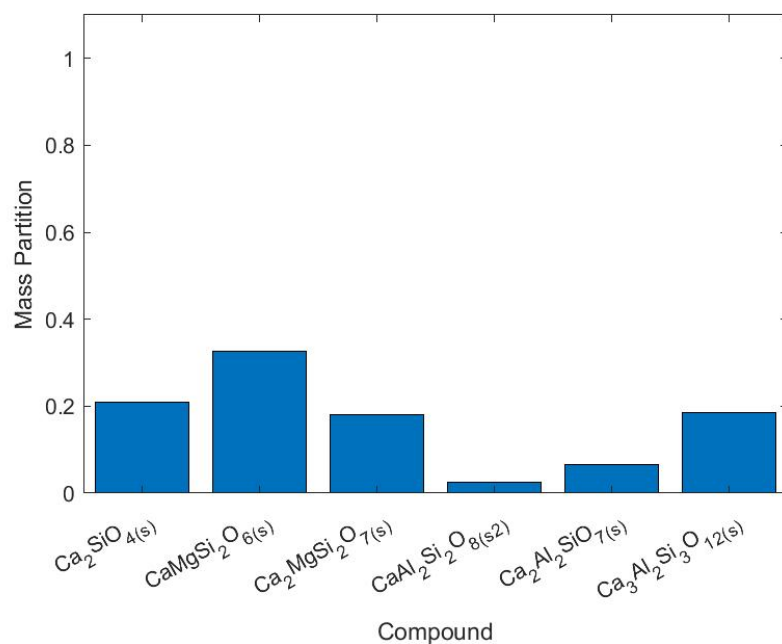


Figure 8.30 Modelled Calcium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Switchgrass

Silicon

Modelled silicon fate profiles are shown in Figure 8.31. The quantity of silicon released from the particles is greater in oxy27-combustion than in air-combustion due to a faster penetration rate of bulk $O_{2(g)}$ in a higher bulk $O_{2(g)}$ concentration. Initially, silicon is released as liquid aerosols at peak temperature. At around 2,000 K during the *heat removal* stage, the liquid aerosols are converted to solid aerosols. However, according to the CaO-SiO₂-K₂O ternary diagram shown in Figure 8.32, SiO_{2(l)} disappears when the temperature is still above the liquidus isotherm temperature at around 1,700 K, located in the black box. This anomaly is probably due to bulk magnesium interference. Switchgrass ash contains 4.2% of magnesium, 40% to 60% of which is released to bulk. This places magnesium as a major AFE with the third largest bulk concentration after silicon and potassium. Another ternary diagram of MgO-SiO₂-K₂O in Figure 8.33 is used for further observation. The black box that locates bulk MgO-SiO₂-K₂O composition has a temperature at around 1,900 K, which is closer to the temperature at which silicon liquid compound disappears. Nevertheless, a quaternary diagram is required to obtain more valid answers.

Selectivity towards SiO₂ crystal formation is favoured when silicon is the major AFE in both particle and bulk phases, as shown in Figures 8.34, 8.35, 8.36, and 8.37. Once silicon is released, SiO_{2(l)} is formed. During *heat loss* stage, SiO_{2(l)} is solidified mostly into SiO_{2(s6)} due to less quantity of potassium in bulk to form K₂Si₄O_{9(l)} in switchgrass than in rice husk. As is found in the bottom ash, partition of SiO₂ crystals dominates.

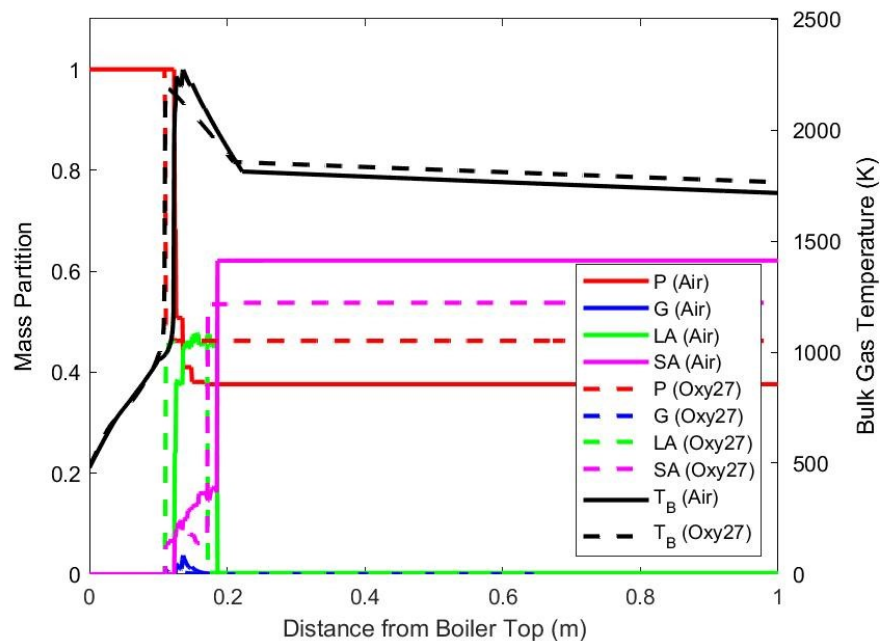


Figure 8.31 Modelled Silicon Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion

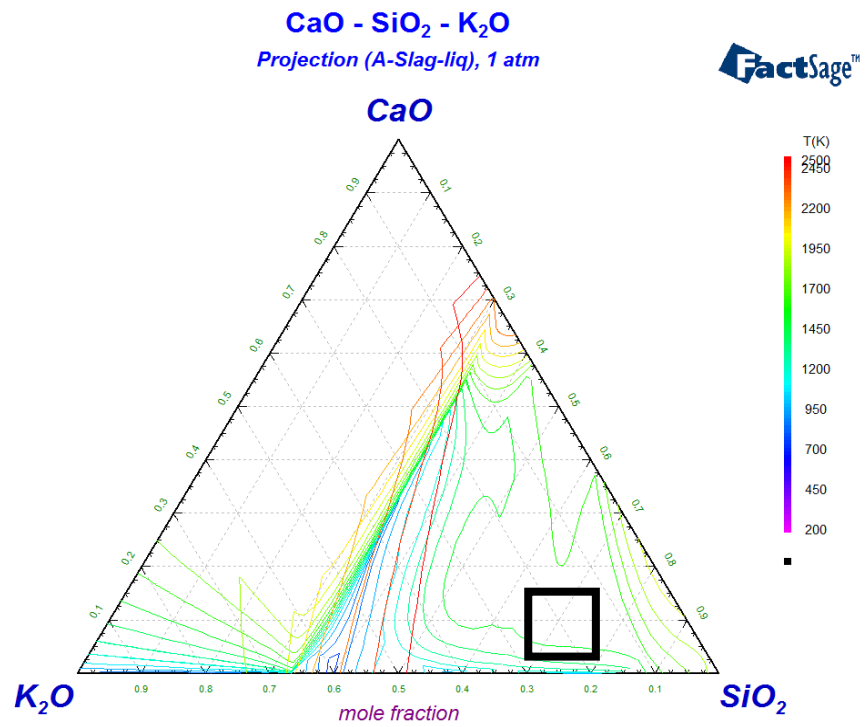


Figure 8.32 Bulk Composition of Switchgrass (Black Box) at Complete Combustion and Liquidus Isotherm Lines within CaO-SiO₂-K₂O Ternary Phase Diagram

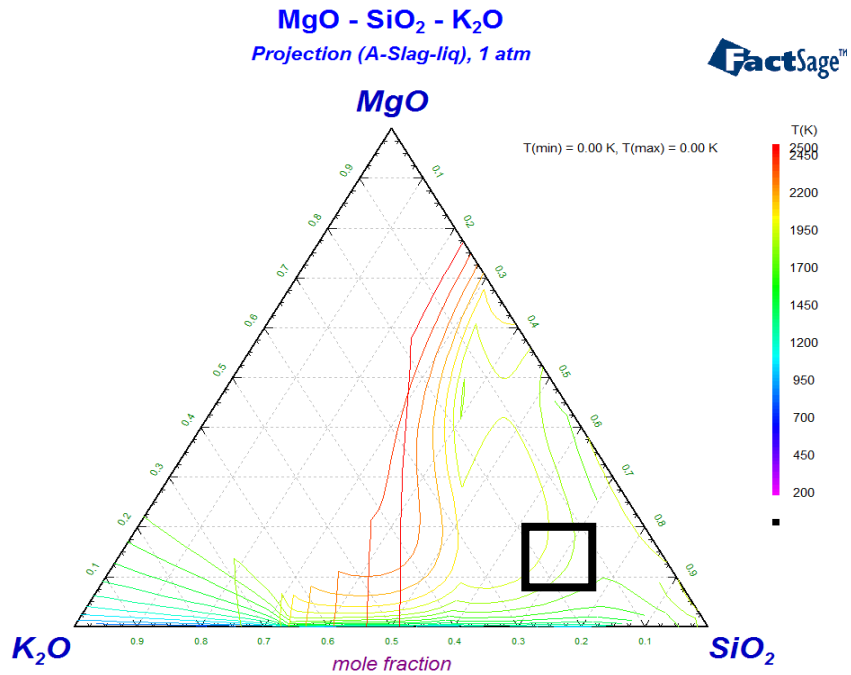


Figure 8.33 Bulk Composition of Switchgrass (Black Box) at Complete Combustion and Liquidus Isotherm Lines within MgO-K₂O-SiO₂ Ternary Phase Diagram

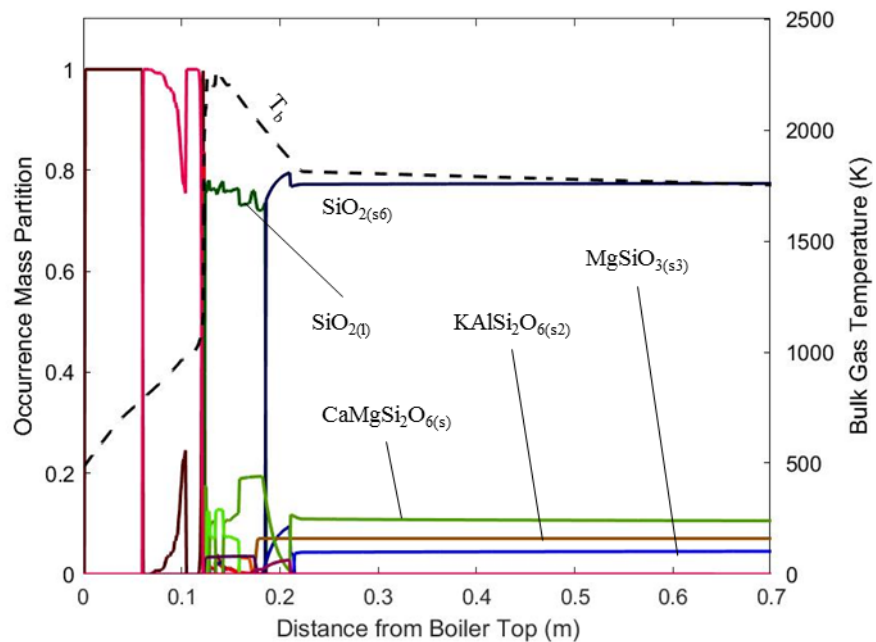


Figure 8.34 Modelled Silicon Bulk Occurrences in Air-combustion of Switchgrass

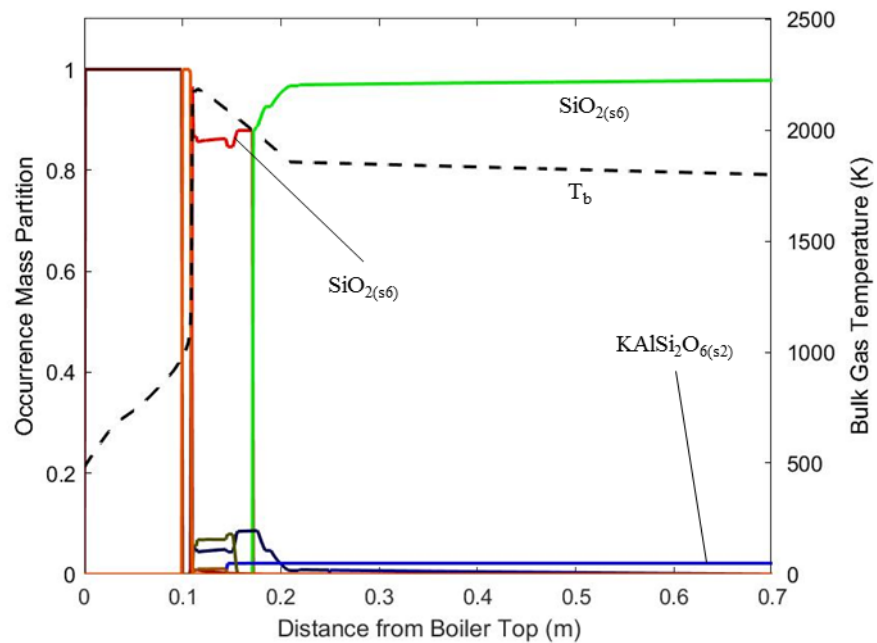


Figure 8.35 Modelled Silicon Bulk Occurrences in Oxy27-combustion of Switchgrass

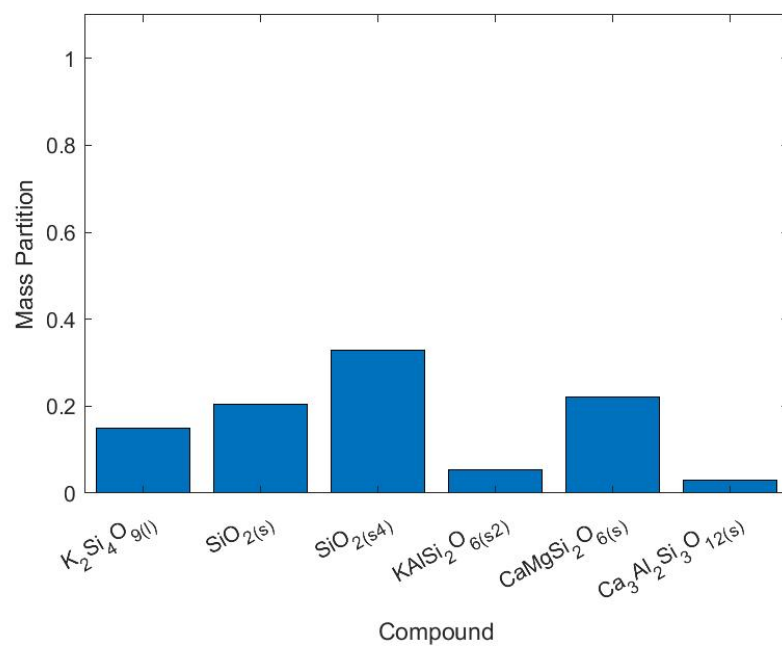


Figure 8.36 Modelled Silicon Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Switchgrass

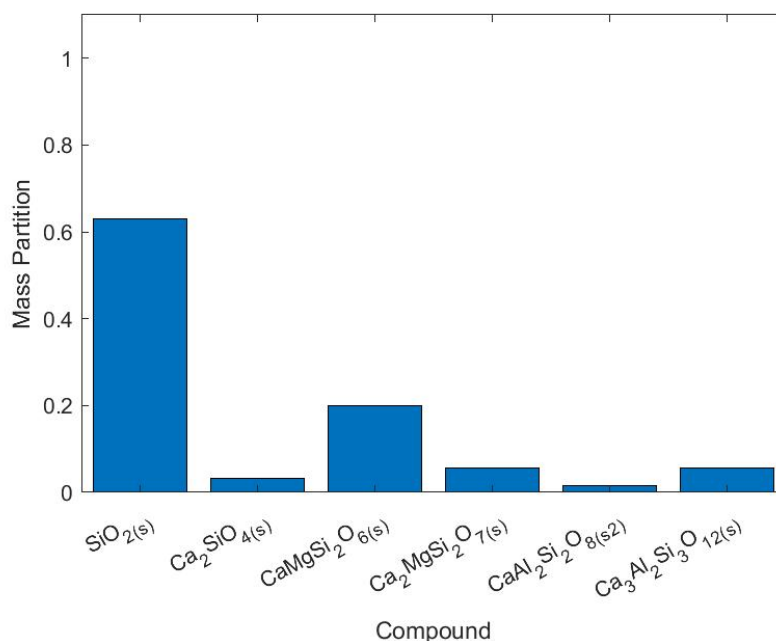


Figure 8.37 Modelled Silicon Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Switchgrass

8.4 Concluding Remarks

Herbaceous biomass has become one of the most promising alternative solid fuels to replace woody biomass since use of woody biomass is not environmentally favourable due to forest preservation. However, herbaceous biomass contains a significant quantity of potassium and silicon, which form liquid aerosols that are responsible for ash deposition. Combustion of herbaceous biomass was modelled in this research and is described in this chapter to predict the potential for liquid aerosol formation.

A ternary diagram of $\text{CaO-SiO}_2\text{-K}_2\text{O}$ was used to evaluate liquid phase formation based on liquidus isotherm temperature lines. Previous research on ternary diagrams has been briefly explained to outline their importance in liquid mineral analysis and study of additives. Due to the limited number of available ternary diagrams in the literature, the required ternary diagram of $\text{CaO-SiO}_2\text{-K}_2\text{O}$ was built for this study using FactSage.

Rice husk and switchgrass were chosen for evaluation due to their potassium and silicon content. The conclusions and highlights regarding mineral composition and its effects on the potential use of rice husk and switchgrass as solid fuels for combustion are listed in the following paragraphs.

- Silicon is present in the largest quantity in both rice husk and switchgrass ash, at around 93% and 68% respectively. Potassium is present in the second largest quantity at around 5% and

25% in rice husk and switchgrass ash, respectively. Fate and occurrence profiles of AFEs and Tes of rice husk and switchgrass were compared to observe the influence of silicon and potassium content on formation of liquid aerosols.

- The molar fraction of calcium was almost five times higher in switchgrass than in rice husk. This potentially promotes more intense slag aerosol production in rice husk than switchgrass. Magnesium and phosphorus concentrations are also higher in switchgrass than in rice husk by four and eight times, respectively. Phosphorus exhibits strong affinity for calcium and magnesium. Phosphorus is thermodynamically proven to form liquid aerosols with magnesium. At lower calcium content, phosphorus is likely to associate with sodium.
- The fate of AFEs depends not only on their concentrations but also on their masses in solid fuel. A solid fuel might produce a larger mass of silicon than another solid fuel if that fuel produces a larger mass of ash, even though the other solid fuel might have higher silicon concentration. Iron and sodium are present at similar molar fractions in both rice husk and switchgrass. Since the mass percentage of dry ash produced by rice husk is 3.5 times higher than that of switchgrass, the actual molar masses of the iron and sodium produced are roughly four times larger in rice husk than in switchgrass.
- Large initial masses of calcium, magnesium, aluminium, and silicon AFEs exhibit strong retention in particles. This suggests that more thermal “effort” is required to volatilise AFEs that are present in large masses in particles.
- Calcium, magnesium, aluminium, and silicon are more likely to be retained in particles in oxy27-combustion than in air-combustion. Bulk $O_{2(g)}$ gains more access in oxy27-combustion than in air-combustion to form higher quantities of calcium, magnesium, and aluminium silicates in the particles due to more rapid particle oxidation. On the other hand, potassium, sodium, iron, and phosphorus are very volatile and are often completely volatilised from the particles in major cases.
- Use of molar fractions of AFEs in raw solid fuel as variables in a ternary diagram to predict liquid aerosol formation is considered inaccurate. In rice-husk combustion, calcium, magnesium, and aluminium are barely volatilised. On the other hand, sodium, potassium, phosphorus and a small partition of silicon are volatilised and become the major bulk inorganic constituents. Bulk sodium reacts with bulk phosphorus to form sodium phosphate compounds. Bulk potassium forms $KCl_{(g)}$, $KOH_{(g)}$, and $K_2Si_4O_9(l)$ as products of bulk potassium reaction with bulk silicon. Partition of $K_2Si_4O_9(l)$ is less than the combined partition of $KCl_{(g)}$ and $KOH_{(g)}$ since only a small quantity of silicon is released to bulk. In switchgrass combustion, a considerable partition of calcium, magnesium, aluminium, and silicon is, however, volatilised to bulk. Bulk sodium no longer forms phosphate compounds and remains in the gas phase since bulk phosphorus is more chemically attracted to bulk calcium and bulk magnesium. Further

observation reveals that calcium is excluded from the list of top three AFEs that exhibit the highest quantity in bulk. These three are silicon, potassium, and magnesium.

- Calcium is thermodynamically capable of reducing the propensity of AFEs to form liquid aerosols. It competes with potassium in reaction with silicon to form calcium and magnesium silicate compounds, e.g. $\text{CaMgSi}_2\text{O}_6(\text{s})$ and $\text{MgSiO}_3(\text{s})$, and, to some extent, prevents formation of potassium liquid aerosol compounds, e.g. $\text{K}_2\text{Si}_4\text{O}_9(\text{l})$. However, the lack of formation of a certain liquid aerosol compound might be an opportunity for any other liquid aerosol compounds to appear. Magnesium's affinity to phosphorus may lead to formation of liquid aerosol compounds, e.g. $\text{Mg}_3\text{P}_2\text{O}_8(\text{l})$. An extended analysis using a ternary diagram of $\text{CaO-P}_2\text{O}_5\text{-MgO}$ reveals that the bulk temperature is within the $\text{Mg}_3\text{P}_2\text{O}_8(\text{l})$ liquidus temperature.
- A ternary diagram has been thermodynamically proven to have certain limitations in determining the liquidus temperature. In switchgrass combustion, $\text{SiO}_2(\text{g})$ formation in bulk was not in agreement with the ternary diagram of $\text{CaO-SiO}_2\text{-K}_2\text{O}$. Rather, $\text{SiO}_2(\text{l})$ formation is expected according to the liquidus temperature line in the ternary diagram of $\text{CaO-SiO}_2\text{-K}_2\text{O}$. A more appropriate liquidus temperature line is obtained when further evaluation is conducted with the ternary diagram of $\text{MgO-SiO}_2\text{-K}_2\text{O}$, since the bulk calcium quantity is less than that of bulk magnesium. Nevertheless, both magnesium and calcium content of the herbaceous biomass may deliver some influence on the establishment of liquidus isotherm lines. The inclusion of both compositions is recommended in a pyramid shape quaternary diagram for more accurate results.
- Bottom ash produced from combustion of both rice husk and switchgrass contains $\text{Fe}_3\text{O}_4(\text{s})$ and various silicate compounds of calcium, magnesium, aluminium, and potassium. These compounds are formed and stable due to $\text{O}_2(\text{g})$ penetration of particles via heterogeneous oxidation during the combustion. The liquid phase might form in the particles as the result of silicate eutectics. Even without the liquid phase, a very small completely burnt particle is able to flow and stick to the superheater surface covered with $\text{KCl}(\text{l})$ and initiate ash deposit growth.

Chapter 9

Conclusions and Future Works

9.1 Conclusions

In the previous chapters, the development of the model to calculate the fate, occurrence, and downstream concentrations of AFEs and TEs has been thoroughly discussed. The initial development of the model was the single-particle combustion model aiming to calculate both intra-particle temperature and gas concentration profiles. The model was later expanded into the entrained-flow combustion model based on PACT entrained-flow burner with particle combustion calculated via the single-particle combustion model, which was validated against experimental work. One interesting finding was that measuring the centreline temperature of a particle by using a thermocouple can lead to significant temperature deviations from the “true” temperature. Due to expensive computation of simultaneous particle and bulk profile calculation, the entrained-flow combustion model was reduced to the simplified entrained-flow combustion model where the intra-particle properties are considered homogeneous. The intra-particle properties and bulk properties were further used as parameters in the simplified fate and occurrence model to calculate the fate and occurrence of AFEs and TEs in both particles and bulk, respectively, via chemical equilibrium.

It has been demonstrated that the developed model is **able to predict the fate, occurrence, and downstream concentrations** of AFEs and TEs in biomass combustion in PACT entrained-flow burner via **the successful integration** of the modelling environment (MATLAB) and the chemical equilibrium calculator (ChemApp) **but that the validation of the results is mixed**. The poor validation is possibly due to several factors, namely: kinetic limitation, initial element association data unavailability, and disregard for aerosol coagulation.

The fate and occurrence of each individual inorganic element is qualitatively predicted in Chapters 7 and 8 with validation with experimental results. Due to the current limitation in the PACT entrained-

flow burner, a quantitative prediction on fate and occurrence of AFEs and TEs could not be produced. Quantitative prediction is required to determine whether the chemical equilibrium is kinetically limited. Nevertheless, the qualitative prediction mostly exhibits good agreement with experimental results.

The lack of use of CFA result data providing element association in raw biomass may reduce the accuracy of prediction of AFE and TE fate and occurrence in the simplified fate and occurrence model in which most AFEs and TEs are released completely. As discussed in Chapter 3, inorganic elements in biomass have multiple chemical associations, e.g. moisture-soluble elements, organic-bound elements, included-mineral elements, and excluded-mineral elements, on which the element volatilisation rates depend. Unlike the three former types of elements possibly volatilised during drying, devolatilisation, and char oxidation, the release mechanisms of the excluded-mineral elements might not simply depend only on temperatures but also on mineral melting behaviour, mineral interactions with the surrounding minerals, and mass diffusion of the elements within the mineral body.

The neglect of aerosol coagulation may overestimate the quantity of elements leaving the burner. Aerosol coagulation allows aerosol particle size growth via the collision and merging of multiple smaller aerosol particles. Once the growing aerosol particle mass is heavy enough to stop flowing along with the flue gas, the growing aerosol particle falls to the bottom of the burner and carries the contained inorganic elements along. Though the model does not include aerosol coagulation, it is important to note that the existence of aerosols is generally ignored entirely in similar work.

Despite poor validation at this stage, **the developed model does exhibit the important effects of bulk $O_{2(g)}$ concentrations and initial inorganic element concentrations in biomass on AFE and TE fate and occurrence during combustion.** High bulk $O_{2(g)}$ concentrations and high initial inorganic element concentrations in biomass individually promote high propensities for the inorganic elements, primarily calcium, magnesium, aluminium, and silicon, to remain in the biomass. Consequently, the formation of a certain compound in either the biomass particle phase or the bulk phase is affected by the availability of the composition of the elements in the respective phase. The importance of element partition on element occurrence may be essential as an improvement of the previous approach, where the element occurrence is simply a function of the inorganic element initial concentrations in biomass without considering element partition.

9.2 Future Work: Model Comparison with the State of the Art and Room for Improvement

After a comprehensive comparison with the previous models and a thorough literature review in this thesis, it is possible to state that the developed model in this thesis is the most advanced AFE and TE

prediction using chemical equilibrium in biomass combustion. The previous models briefly mentioned in Section 1.1 feature much more simplification in terms of chemical equilibrium calculation.

In one of the previous models, Boman *et al.* (2006)³³³ as a comparative example, predicted TE partition and enrichment in a power plant with a grate-fired boiler integrated with a fuel dryer unit, which process flow diagram is shown in Figure 9.1. The methodology implemented by Boman *et al.* (2006)³³³ and many others in fate and occurrence prediction was calculating the fate and occurrence of AFEs and TEs only at certain positions, e.g. grate-fired boiler at 1,000 °C, PM sampling point at 300 °C, direct dryer unit exit at 90 °C, without information and discussion on chemical transformations occurring between those positions. The methodology also neglected element partition in either particle or bulk and, instead, used the initial AFE and TE quantities in biomass fuel as the input for equilibrium.

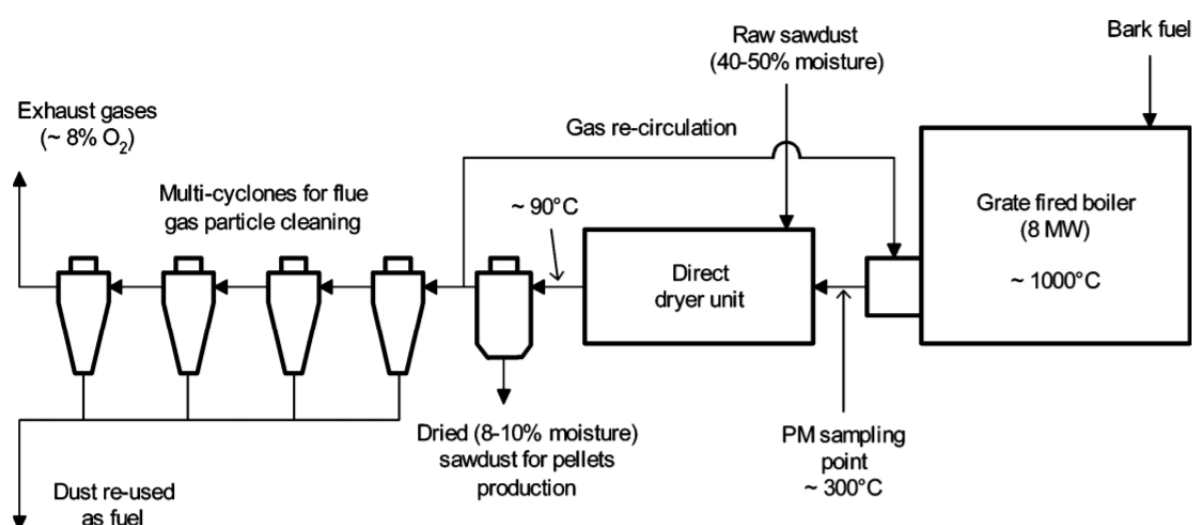


Figure 9.1 A Power Plant with a Bark-combusting Grate-fired Boiler Integrated with a Fuel Dryer Unit in Boman *et al.* (2006)

In comparison to the prediction methodology of the developed model in this thesis, the prediction methodology of the previous models might generate far less accurate results requiring more careful interpretation. The unavailability of AFE and TE fate and occurrence in between the certain positions, e.g. from the bottom to the top to the outlet of the grate-fired boiler via convective pass, does not predict the formation of a number of potential operationally hazardous compounds, e.g. $K_2Si_4O_9(l)$, $KCl(l)$, $SiO_2(l)$, $CaSO_4(s)$. Disregarding element partition in either bulk and particle phase divides the results at a single position into two phases only, a solid phase and a gas phase, whilst the developed model considers the formation of aerosols.

However, the developed model can still be significantly improved, based on another comparison with a more comprehensive model with a similar objective. As an example, James *et al.* (2014)³³⁴ developed

a model of the fate of arsenic, selenium, and antimony in coal combustion in an entrained-flow burner physically similar to that of the PACT facility using CFD. Although their model did not use chemical equilibrium for biomass combustion, it is considered as state-of-the-art research in this field, according to the literature review conducted for this thesis. The main technical differences between the model developed here and the model of James *et al.* (2014)³³⁴ is discussed in the following passages as the baseline for future improvements.

Unlike the developed model, the model of James *et al.* (2014)³³⁴ utilised elemental release mechanisms based on coal CFA result data. As explained in Chapter 3, the inorganic elements in solid fuel are distributed in moisture, organic matrices, included-mineral matrices, and excluded-mineral matrices. The organic-bound elements are released when the element bonds with the organic matrices are broken due to exposure to high temperatures in reducing conditions, which occurs via rapid oxidation of the vicinity carbon. The included-minerals, exposed to similar temperatures and $O_{2(g)}$ concentrations to the organic matrices, melt and vaporise at a considerable amount.³³⁵ On the other hand, the excluded minerals are softened due to exposure to lower temperatures and less reducing conditions. As both minerals are not in solid form, the contained inorganic elements travel from the interior to the surface of the minerals and volatilise to the exterior.³³⁶

The model of James *et al.* (2014)³³⁴ also accounted for the impact of excluded mineral fragmentation on the rate of element release, which is not considered in this thesis. The softened excluded minerals may swell and form hollow structures that might cause fragmentation.³³⁷ The fragmented particles release the inorganic elements at higher rates due to increasing surface area.

The use of CFD in the model of James *et al.* (2014)³³⁴ presents more comprehensive results by providing profiles of both axial and radial directions. With known temperatures and concentrations of each elements in every position within the boiler, those known values may be used as parameters for detailed prediction on ash interactions with every surface within the boiler.

Although adaptation of the methodology of James *et al.* (2014)³³⁴ for future development of the thesis model may improve the accuracy of AFE and TE fate and occurrence prediction in biomass combustion, challenges regarding the adaptation may be required to overcome for methodology optimisation and practicality of conduct.

Implementation of the methodology of James *et al.* (2014)³³⁴ requires an additional comprehensive set of characterisation data other than those of proximate, ultimate, and ash analysis, obtained from various measurement devices, e.g. a SEM and an ICP for chemical association analysis, a PSD analyser, a graphite furnace integrated with atomic absorption spectrometry (GFAAS) to estimate the release activation energy of each elements in each association, and a furnace for ash fusion analysis to

comprehend mineral melting behaviours. Since biomass is considerably more diverse than coal, the use of all these devices for every variant of combusted biomass will be time- and cost-consuming.

The use of chemical reaction instead of chemical equilibrium for the atomic release of the inorganic elements might be sufficient for only three elements in the methodology of James *et al.* (2014).³³⁴ However, when more than 10 elements are involved, the interactions amongst the elements, of which the reactions and the kinetics are hardly available, might become important to allow the release of the elements in the form of compounds rather than atoms. This implies that despite kinetic limitations, the use of chemical equilibrium is useful for the sake of calculation practicality.

Other potential thesis model improvements based on the findings discussed in earlier chapters could also be proposed for future work. The potential improvements may cover numerical calculation accuracy, process scale-up, adaptation to other boiler types (particularly circulating fluidised beds), and ash growth model. The underlying combustion model is particularly suited for translation to other equipment types.

The scale of combustion that was employed in the research for this thesis could be extended to power-plant scale. Modelling of power plants is commonly conducted in process modelling programs, e.g. Aspen Plus. The entrained-flow combustion model could be used as a function to calculate the output of combustion equipment or as a block in the designed process.

Chemical equilibrium methods have the potential to be implemented in boiler types other than entrained-flow boilers. The other common boiler types used in commercial power plants are fluidised-bed boilers and grate-firing boilers. The combustion models for both these types were developed three decades ago. However, studies that have involved comprehensive AFE and TE inclusion in the models of these boilers are still rarely available. Future works on AFE and TE fate and occurrence in fluidised-bed boilers and grate-firing boilers would help to widen emission compliance data to a majority of power plants. Additionally, the fate and occurrence model may also be extended to predict AFE and TE fate and occurrence in clean-up systems. The extended model should not be used to consider whether clean-up systems were required but to optimise clean-up system designs and reduce design costs.

Finally, future work on aerosol coagulation and nucleation could establish a more accurate prediction of the bottom ash PSD and provide comprehensive and accurate input parameters for growth of slagging and fouling ash deposits. However, this work would face many challenges, e.g. heterogeneous nucleation and irregular aerosol shapes, and might require a series of evaluations from aerosol scale to power-plant scale.

Bibliography

1. Kiehl, J. T.; Trenberth, K. E., Earth's annual global mean energy budget. *Bulletin of the American Meteorological Society* **1997**, 78 (2), 197-208.
2. Karl, T. R.; Trenberth, K. E., Modern global climate change. *Science* **2003**, 302 (5651), 1719-1723.
3. Le Quéré, C.; Andrew, R. M.; Canadell, J. G.; Sitch, S.; Korsbakken, J. I.; Peters, G. P.; Manning, A. C.; Boden, T. A.; Tans, P. P.; Houghton, R. A.; Keeling, R. F.; Alin, S.; Andrews, O. D.; Anthoni, P.; Barbero, L.; Bopp, L.; Chevallier, F.; Chini, L. P.; Ciais, P.; Currie, K.; Delire, C.; Doney, S. C.; Friedlingstein, P.; Gkritzalis, T.; Harris, I.; Hauck, J.; Haverd, V.; Hoppema, M.; Klein Goldewijk, K.; Jain, A. K.; Kato, E.; Körtzinger, A.; Landschützer, P.; Lefèvre, N.; Lenton, A.; Lienert, S.; Lombardozzi, D.; Melton, J. R.; Metzl, N.; Millero, F.; Monteiro, P. M. S.; Munro, D. R.; Nabel, J. E. M. S.; Nakaoka, S.-i.; amp; apos; Brien, K.; Olsen, A.; Omar, A. M.; Ono, T.; Pierrot, D.; Poulter, B.; Rödenbeck, C.; Salisbury, J.; Schuster, U.; Schwinger, J.; Séférian, R.; Skjelvan, I.; Stocker, B. D.; Sutton, A. J.; Takahashi, T.; Tian, H.; Tilbrook, B.; van der Laan-Luijkx, I. T.; van der Werf, G. R.; Viovy, N.; Walker, A. P.; Wiltshire, A. J.; Zaehle, S., Global Carbon Budget 2016. *Earth System Science Data* **2016**, 8 (2), 605-649.
4. Schmidt, G.; Ruedy, R.; Persin, A.; Sato, M.; Lo, K. *NASA GISS surface temperature (GISTEMP) analysis*; Environmental System Science Data Infrastructure for a Virtual Ecosystem; Carbon Dioxide Information Analysis Center (CDIAC), Oak Ridge National Laboratory (ORNL), Oak Ridge, TN (United States): United States, 2016.
5. IEA World Energy Outlook 2018. <https://www.iea.org/weo2018/scenarios/>.
6. Bernstein, L.; Bosch, P.; Canziani, O.; Chen, Z.; Christ, R.; Riahi, K., IPCC, 2007: Climate Change 2007: Synthesis Report. 2008.
7. McGlade, C.; Ekins, P., The geographical distribution of fossil fuels unused when limiting global warming to 2 degrees C. *Nature* **2015**, 517 (7533), 187-90.
8. Cuff, M. EU carbon price clears €20 for first time since 2008.
9. Carrington, D. 'Brutal news': global carbon emissions jump to all-time high in 2018.
10. Varol, M.; Atimtay, A. T.; Bay, B.; Olgun, H., Investigation of co-combustion characteristics of low quality lignite coals and biomass with thermogravimetric analysis. *Thermochimica Acta* **2010**, 510 (1-2), 195-201.
11. Vaughn, A. UK government spells out plan to shut down coal plants.
12. Cheah Chee, B., Properties of high calcium wood ash and densified silica fume blended cement. *International Journal of the Physical Sciences* **2011**, 6 (28).
13. Coda, B.; Cieplik, M. K.; Wild, P. J. d.; Kiel, J. H., Slagging behavior of wood ash under entrained-flow gasification conditions. *Energy and Fuels* **2007**, 21 (6), 3644-3652.
14. Udoeyo, F. F.; Dashibil, P. U., Sawdust Ash as Concrete Material. *Journal of Materials in Civil Engineering* **2002**, 14 (2), 173-176.
15. Hennenberg, K.; Böttcher, H.; Fehrenbach, H.; Bischoff, M., Short analysis of the RED 2009, the iLUC Directive 2015 and the 2016 RED proposal regarding implications for nature protection. *Institute for Applied Ecology* **2017**.
16. Searchinger, T. D.; Beringer, T.; Holtsmark, B.; Kammen, D. M.; Lambin, E. F.; Lucht, W.; Raven, P.; van Ypersele, J. P., Europe's renewable energy directive poised to harm global forests. *Nat Commun* **2018**, 9 (1), 3741.
17. Johansson, D. J. A.; Azar, C., A scenario based analysis of land competition between food and bioenergy production in the US. *Climatic Change* **2007**, 82 (3-4), 267-291.
18. Gami, B.; Limbachiya, R.; Parmar, R.; Bhimani, H.; Patel, B., An Evaluation of Different Non-woody and Woody Biomass of Gujarat, India for Preparation of Pellets—A Solid Biofuel. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* **2011**, 33 (22), 2078-2088.

19. Rahman, M. M.; B. Mostafiz, S.; Paatero, J. V.; Lahdelma, R., Extension of energy crops on surplus agricultural lands: A potentially viable option in developing countries while fossil fuel reserves are diminishing. *Renewable and Sustainable Energy Reviews* **2014**, *29*, 108-119.
20. Vainio-Mattila, B.; Ginström, T.; Haaranen, T.; Luomanperä, S.; Lähdetie, P.; Oravuo, M.; Pietola, K.; Suojanen, M.; Virolainen, J.; Knuutila, K.; Ovaska, S. *Peltoviljelyn tulevaisuuden linjaukset Suomessa*; 2005.
21. Nielsen, H. P.; Frandsen, F. J.; Dam-Johansen, K.; Baxter, L. L., The implications of chlorine-associated corrosion on the operation of biomass-fired boilers. *Process in Energy and Combustion Science* **2000**, *26* (3), 283-298.
22. Zeng, T.; Mlonka-Mędrala, A.; Lenz, V.; Nelles, M., Evaluation of bottom ash slagging risk during combustion of herbaceous and woody biomass fuels in a small-scale boiler by principal component analysis. *Biomass Conversion and Biorefinery* **2019**.
23. Bourguignon, D. *Understanding Waste Streams. Treatment of Specific Waste*; European Parliamentary Research Service: 2015.
24. Helsén, L.; Van den Bulck, E., Review of disposal technologies for chromated copper arsenate (CCA) treated wood waste, with detailed analyses of thermochemical conversion processes. *Environ Pollut* **2005**, *134* (2), 301-14.
25. Rose, J., *Trace elements in health: a review of current issues*. Butterworth-Heinemann: 2016.
26. Coudert, L.; Blais, J. F.; Mercier, G.; Cooper, P.; Morris, P.; Gastonguay, L.; Janin, A.; Zaviska, F., Optimization of copper removal from ACQ-, CA-, and MCQ-treated wood using an experimental design methodology. *Journal of Environmental Engineering* **2012**, *193* (4), 576-587.
27. Niu, Y.; Tan, H.; Hui, S. e., Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. *Progress in Energy and Combustion Science* **2016**, *52*, 1-61.
28. Dayton, D. C.; Belle-Oudry, D.; Nordin, A., Effect of Coal Minerals on Chlorine and Alkali Metals Released during Biomass or Coal Cofiring. *Energy Fuels* **1999**, *13* (6), 1203-1211.
29. Sandelin, K.; Backman, R., Trace Elements in Two Pulverized Coal-fired Power Stations. *Environmental Science and Technology* **2001**, *35* (5), 826-834.
30. Jerzak, W., Experimental and Thermodynamic Analyses of Trace Element Speciation during the Combustion of Ground Cedar Nut Shells. *Energy & Fuels* **2017**, *31* (2), 1969-1979.
31. Sandelin, K.; Backman, R., A Simple Two-Reactor Method for Predicting Distribution of Trace Elements in Combustion Systems. *Environmental Science and Technology* **1999**, *33* (24), 4508-4513.
32. Danihelka, P.; Volna, Z.; Jones, J. M.; Williams, A., Emission of trace toxic metals during pulverized fuel combustion of Czech coals. *International Journal of Energy Research* **2003**, *27* (13), 1181-1203.
33. Elled, A.-L.; Åmand, L.-E.; Leckner, B.; Andersson, B.-Å., The fate of trace elements in fluidised bed combustion of sewage sludge and wood. *Fuel* **2007**, *86* (5-6), 843-852.
34. Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vassileva, C. G., An overview of the chemical composition of biomass. *Fuel* **2010**, *89* (5), 913-933.
35. Demirbas, A., Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. *Progress in Energy and Combustion Science* **2005**, *31* (2), 171-192.
36. Someshwar, A. V., Wood and combination wood-fired boiler ash characterization. *Journal of Environmental Quality* **1996**, *25* (5), 962-972.
37. DemİRbaŞ, A., Trace Metal Concentrations in Ashes from Various Types of Biomass Species. *Energy Sources* **2003**, *25* (7), 743-751.
38. McKendry, P., Energy production from biomass (part 1): overview of biomass. *Bioresource Technology* **2002**, *83* (1), 37-46.
39. Obernberger, I.; Brunner, T.; Barnthaler, G., Chemical properties of solid biofuels—significance and impact. *Biomass and Bioenergy* **2006**, *30* (11), 973-982.
40. Sander, B., Properties of Danish biofuels and the requirements for power production. *Biomass and Bioenergy* **1997**, *12* (3), 177-183.
41. Mayoral, M. C.; Izquierdo, M. T.; Andres, J. M.; Rubio, B., Different approaches to proximate analysis by thermogravimetry analysis. *Thermochimica Acta* **2001**, *370* (1-2), 91-97.

42. Nasser, R. A.; Salem, M. Z. M.; Hiziroglu, S.; Al-Mefarrej, H. A.; Mohareb, A. S.; Alam, M.; Aref, I. M., Chemical analysis of different parts of date palm (*Phoenix dactylifera* L.) using ultimate, proximate and thermo-gravimetric techniques for energy production. *Energies* **2016**, *9* (5), 374.
43. ASTM, 7582-12. Standard test methods for proximate analysis of coal and coke by macro thermogravimetric analysis. ASTM International: West Conshohocken, PA, 2013.
44. Sanchez-Silva, L.; Lopez-Gonzalez, D.; Villasenor, J.; Sanchez, P.; Valverde, J. L., Thermogravimetric-mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis. *Bioresour Technol* **2012**, *109*, 163-72.
45. ASTM, 3176-15. Standard test methods for ultimate analysis of coal and coke by macro thermogravimetric analysis. ASTM International: West Conshohocken, 2012.
46. Chiang, K.-Y.; Chien, K.-L.; Lu, C.-H., Characterization and comparison of biomass produced from various sources: Suggestions for selection of pretreatment technologies in biomass-to-energy. *Applied Energy* **2012**, *100*, 164-171.
47. Sheng, C.; Azevedo, J. L. T., Estimating the higher heating value of biomass fuels from basic analysis data. *Biomass and Bioenergy* **2005**, *28* (5), 499-507.
48. Nhuchhen, D. R.; Abdul Salam, P., Estimation of higher heating value of biomass from proximate analysis: A new approach. *Fuel* **2012**, *99*, 55-63.
49. Demirbaş, A., Calculation of higher heating values of biomass fuels. *Fuel* **1997**, *76* (5), 431-434.
50. Yin, C.-Y., Prediction of higher heating values of biomass from proximate and ultimate analyses. *Fuel* **2011**, *90* (3), 1128-1132.
51. Warneke, C.; Roberts, J. M.; Veres, P.; Gilman, J.; Kuster, W. C.; Burling, I.; Yokelson, R.; de Gouw, J. A., VOC identification and inter-comparison from laboratory biomass burning using PTR-MS and PIT-MS. *International Journal of Mass Spectrometry* **2011**, *303* (1), 6-14.
52. Jenkins, B. M.; Jones, A. D.; Turn, S. Q.; Williams, R. B., Particle concentrations, gas-particle partitioning, and species intercorrelations for polycyclic aromatic hydrocarbons (PAH) emitted during biomass burning. *Atmospheric Environment* **1996**, *30* (22), 3825-3835.
53. Mastral, A. M.; Callen, M.; Murillo, R.; Garcia, T., Assessment of PAH emissions as a function of coal combustion variables in fluidised bed. 2. Air excess percentage. *Fuel* **1998**, *77* (13), 1513-1516.
54. Kuehn, S. E., Power for the Industrial Age: A brief history of boilers. *Power Engineering* **1996**, *100* (2), 15-20.
55. Krevelen, V.; Willem, D., *Coal: typology, physics, chemistry, constitution*. Elsevier: Amsterdam, 1993.
56. Elliot, T. C., *Standard handbook of powerplant engineering*. 1989.
57. Loo, S. v.; Koppejan, J., *The Handbook of Biomass Combustion and Co-firing*. Earthscan: London
Sterling, VA, 2008.
58. Walker, P. L.; Rusinko, F.; Austin, L. G., Gas Reactions of Carbon. *Advances in Catalysis* **1959**, *11*, 133-221.
59. Žbogar, A.; Jensen, P. A.; Frandsen, F. J.; Hansen, J.; Glarborg, P., Experimental investigation of ash deposit shedding in a straw-fired boiler. *Energy & fuels* **2006**, *20* (2), 512-519.
60. Yin, C.; Rosendahl, L. A.; Kær, S. K., Grate-firing of biomass for heat and power production. *Progress in Energy and Combustion Science* **2008**, *34* (6), 725-754.
61. Schobert, H. H., *Coal: The energy source of the past and future*. 1987.
62. Anthony, E. J., Fluidized bed combustion of alternative solid fuels; status, successes and problems of the technology. *Progress in Energy and Combustion Science* **1995**, *21* (3), 239-268.
63. Tang, J. T.; Engstrom, F. In *Technical Assessment on the Ahlstrom Pyroflow Circulating and Conventional Bubbling Fluidized Bed Combustion Systems*, 9th International Conference on Fluidized Bed Combustion, Boston, Boston, 1987.
64. Khan, A. A.; Jong, W. d.; Jansens, P. J.; Spliethoff, H., Biomass combustion in fluidized bed boilers: Potential problems and remedies. *Fuel Processing Technology* **2009**, *90* (1), 21-50.

65. Sandberg, J.; Karlsson, C.; Fdhila, R. B., A 7 year long measurement period investigating the correlation of corrosion, deposit and fuel in a biomass fired circulated fluidized bed boiler. *Applied Energy* **2011**, 88 (1), 99-110.
66. Fryda, L. E.; Panopoulos, K. D.; Kakaras, E., Agglomeration in fluidised bed gasification of biomass. *Powder technology* **2008**, 181 (3), 307-320.
67. Miles, T. R.; Miles, T. R.; Baxter, L. L.; Bryers, R. W.; Jenkins, B. M.; Oden, L. L., Boiler deposits from firing biomass fuels. *Biomass and Bioenergy* **1996**, 10 (2-3), 125-138.
68. Nielsen, H. P. Deposition and high temperature corrosion in biomass-fired boilers. Technical University of Denmark, 1998.
69. BEI, *Station Planning and Design*. 3rd ed.; 1991.
70. Bashir, M. S.; Jensen, P. A.; Frandsen, F.; Wedel, S.; Dam-Johansen, K.; Wadenbäck, J.; Pedersen, S. T., Ash transformation and deposit build-up during biomass suspension and grate firing: Full-scale experimental studies. *Fuel processing technology* **2012**, 97, 93-106.
71. Tortosa-Masiá, A. A.; Ahnert, F.; Spliethoff, H.; Loux, C. J.; Hein, K. R. G., Slagging and fouling in biomass co-combustion. *Thermal Science* **2005**, 9 (3), 85-98.
72. Niu, Y.; Tan, H.; Ma, L.; Pourkashanian, M.; Liu, Z.; Liu, Y.; Wang, X.; Liu, H.; Xu, T., Slagging characteristics on the superheaters of a 12 MW biomass-fired boiler. *Energy and Fuels* **2010**, 24 (9), 5222-5227.
73. Li, L.; Yu, C.; Huang, F.; Bai, J.; Fang, M.; Luo, Z., Study on the deposits derived from a biomass circulating fluidized-bed boiler. *Energy & Fuels* **2012**, 26 (9), 6008-6014.
74. Xu, W.; Niu, Y.; Tan, H.; Wang, D.; Du, W.; Hui, S., A new agro/forestry residues co-firing model in a large pulverized coal furnace: Technical and economic assessments. *Energies* **2013**, 6 (9), 4377-4393.
75. Melissari, B., Ash related problems with high alkali biomass and its mitigation experimental evaluation. *Memoria Investigaciones en Ingeniería* **2014**, 12, 31-44.
76. Jia, Y.; Lighty, J. S., Ash particulate formation from pulverized coal under oxy-fuel combustion conditions. *Environmental Science and Technology* **2012**, 46 (9), 5214-5221.
77. Niu, Y.; Zhu, Y.; Tan, H.; Hui, S.; Jing, Z.; Xu, W., Investigations on biomass slagging in utility boiler: Criterion numbers and slagging growth mechanisms. *Fuel Processing Technology* **2014**, 128, 499-508.
78. Dayton, D. C.; Milne, T. A., Laboratory measurements of alkali metal containing vapors released during biomass combustion. In *Applications of advanced technology to ash-related problems in boilers*, Springer: Boston, MA, 1996; pp 161-185.
79. Wei, X.; Schnell, U.; Hein, K. R. G., Behaviour of gaseous chlorine and alkali metals during biomass thermal utilisation. *Fuel* **2005**, 84 (7-8), 841-848.
80. Srinivasachar, S.; Helble, J. J.; Boni, A. A. In *An experimental study of the inertial deposition of ash under coal combustion conditions*, Symposium (International) on Combustion, 1991.
81. Smouse, S. M.; Wagoner, C. L., Deposit initiation via thermophoresis. Part 2—experimental verification of hypothesis using a simulated superheater tube. *Inorganic Transformations and Ash Deposition during Combustion* **1991**, 625-638.
82. Mu, L.; Zhao, L.; Liu, L.; Yin, H., Elemental distribution and mineralogical composition of ash deposits in a large-scale wastewater incineration plant: a case study. *Industrial and Engineering Chemistry Research* **2012**, 51 (25), 8684-8694.
83. Brus, E.; Öhman, M.; Nordin, A., Mechanisms of bed agglomeration during fluidized-bed combustion of biomass fuels. *Energy and Fuels* **2005**, 19 (3), 825-832.
84. Hurley, J. P.; Benson, S. A., Ash deposition at low temperatures in boilers burning high-calcium coals 1. Problem definition. *Energy & fuels* **1995**, 9 (5), 775-781.
85. Su, S.; Pohl, J. H.; Holcombe, D.; Hart, J. A., Slagging Propensities of Blended Coals. *Fuel* **2001**, 80 (9), 1351-1360.
86. Erickson, T. A.; Allan, S. E.; McCollor, D. P.; Hurley, J. P.; Srinivasachar, S.; Kang, S. G.; Baker, J. E.; Morgan, M. E.; Johnson, S. A.; Borio, R., Modelling of Fouling and Slagging in Coal-fired Utility Boilers. *Fuel Processing Technology* **1995**, 44 (1-3), 155-171.
87. Raask, E., *Mineral Impurities in Coal Combustion*. Hemisphere Publishing Corporation: 1985.

88. Srinivasachar, S.; Senior, C. L.; Helble, J. J.; Moore, J. W., A Fundamental Approach to the Prediction of Coal Ash Deposit Formation in Combustion Systems. *Symposium (International) on Combustion* **1992**, 24 (1), 1179-1187.
89. Pronobis, M., Evaluation of the influence of biomass co-combustion on boiler furnace slagging by means of fusibility correlations. *Biomass and Bioenergy* **2005**, 28 (4), 375-383.
90. Lopez, C.; Unterberger, S.; Maier, J.; Hein, K. R. G., Overview of Actual Methods for Characterization of Ash Deposition. In *Heat Exchanger Fouling and Cleaning: Fundamentals and Applications*, Engineering Conferences International: 2003; pp 18-22.
91. Hansen, L. A.; Frandsen, F. J.; Dam-Johansen, K.; Sørensen, H. S., Quantification of fusion in ashes from solid fuel combustion. *Thermochimica Acta* **1999**, 326 (1-2), 105-117.
92. Risnes, H.; Fjellerup, J.; Henriksen, U.; Moilanen, A.; Norby, P.; Papadakis, K.; Posselt, D.; Sørensen, L. H., Calcium addition in straw gasification. *Fuel* **2003**, 82 (6), 641-651.
93. Teixeira, P.; Lopes, H.; Gulyurtlu, I.; Lapa, N.; Abelha, P., Evaluation of slagging and fouling tendency during biomass-co-firing with coal in a fluidized bed. *Biomass and Bioenergy* **2012**, 39, 192-203.
94. Fryda, L.; Sobrino, C.; Cieplik, M.; van de Kamp, W. L., Study on ash deposition under oxyfuel combustion of coal/biomass blends. *Fuel* **2010**, 89 (8), 1889-1902.
95. Grabke, H. J.; Reese, E.; Spiegel, M., The effects of chlorides, hydrogen chloride, and sulfur dioxide in the oxidation of steels below deposits. *Corrosion Science* **1995**, 37 (7), 1023-1043.
96. Salmenoja, K.; Hupa, M.; Backman, R., Laboratory studies on the influence of gaseous HCl on fireside corrosion of superheaters. *Journals of the Institute of Energy* **1999**, 72 (493), 127-133.
97. Veijonen, K.; Vainikka, P.; Järvinen, T.; Alakangas, E., Biomass co-firing—an efficient way to reduce greenhouse gas emissions. VTT Processes: Finland, 2003.
98. Krause, H. H., High temperature corrosion problems in waste incineration systems. *Journal of Materials for Energy Systems* **1986**, 7 (4), 322-332.
99. Ferrer, E.; Aho, M.; Silvennoinen, J.; Nurminen, R.-V., Fluidized bed combustion of refuse-derived fuel in presence of protective coal ash. *Fuel Processing Technology* **2005**, 87 (1), 33-44.
100. Ghosh, D.; Mitra, S. K., High temperature corrosion problem of boiler components in presence of sulfur and alkali based fuels. *High Temperature Materials and Processes* **2011**, 30 (1-2), 81-85.
101. WRAP, PAS 111:2012 Specification for the requirements and test methods for processing waste wood. BSI: 2012.
102. Whitaker, C. *Review of the Quality of Waste Wood Arisings in the UK, Report for SuperGen Bioenergy Hub*; 2016.
103. Gudka, B.; Jones, J. M.; Lea-Langton, A. R.; Williams, A.; Saddawi, A., A review of the mitigation of deposition and emission problems during biomass combustion through washing pre-treatment. *Journal of the Energy Institute* **2016**, 89 (2), 159-171.
104. Swaine, D. J., Trace elements in coal and their dispersal during combustion. *Fuel Processing Technology* **1994**, 39 (1-3), 121-137.
105. Xu, M.; Yan, R.; Zheng, C.; Qiao, Y.; Han, J.; Sheng, C., Status of trace element emission in a coal combustion process: a review. *Fuel Processing Technology* **2004**, 85 (2-3), 215-237.
106. Lind, T.; Hokkinen, J.; Jokiniemi, J. K.; Saarikoski, S.; Hillamo, R., Electrostatic precipitator collection efficiency and trace element emissions from co-combustion of biomass and recovered fuel in fluidized-bed combustion. *Environmental Science and Technology* **2003**, 37 (12), 2842-2846.
107. EPA *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units*; 1996.
108. Finkelman, R. B., Health impacts of coal: facts and fallacies. *AMBIO: A Journal of the Human Environment* **2007**, 36 (1), 103-107.
109. Finkelman, R. B.; Belkin, H. E.; Zheng, B., Health impacts of domestic coal use in China. *Proceedings of the National Academy of Sciences* **1999**, 96 (7), 3427-3431.
110. Baum, M. M.; Street, P. J., Predicting the Combustion Behaviour of Coal Particles. *Combustion Science and Technology* **1971**, 3 (5), 231-243.
111. Timothy, L. D.; Sarofim, A. F.; Beer, J. M., Characteristics of Single Particle Coal Combustion. *Symposium (International) on Combustion* **1982**, 19 (1), 1123-1130.
112. Agarwal, P. K., A Single Particle Model for the Evolution and Combustion of Coal Volatiles. *Fuel* **1986**, 65 (6), 803-810.

113. Ranzi, E.; Pierucci, S.; Aliprandi, P. C.; Stringa, S., Comprehensive and Detailed Kinetic Model of a Traveling Grate Combustor of Biomass. *Energy & Fuels* **2011**, 25 (9), 4195-4205.
114. Ryu, C.; Yang, Y. B.; Khor, A.; Yates, N. E.; Sharifi, V. N.; Swithenbank, J., Effect of fuel properties on biomass combustion: Part I. Experiments—fuel type, equivalence ratio and particle size. *Fuel* **2006**, 85 (7-8), 1039-1046.
115. Lu, H.; Robert, W.; Peirce, G.; Ripa, B.; Baxter, L., Comprehensive Study of Biomass Particle Combustion. *Energy & Fuels* **2008**, 22, 2826-2839.
116. Yang, Y. B.; Sharifi, V. N.; Swithenbank, J.; Ma, L.; Darvell, L. I.; Jones, J. M.; Pourkashanian, M.; Williams, A., Combustion of a Single Particle of Biomass. *Energy Fuels* **2008**, 22 (1), 10.
117. Mason, P. E.; Darvell, L. I.; Jones, J. M.; Pourkashanian, M.; Williams, A., Single particle flame-combustion studies on solid biomass fuels. *Fuel* **2015**, 151, 21-30.
118. Maffei, T.; Khatami, R.; Pierucci, S.; Faravelli, T.; Ranzi, E.; Levendis, Y. A., Experimental and modeling study of single coal particle combustion in O₂/N₂ and Oxy-fuel (O₂/CO₂) atmospheres. *Combustion and Flame* **2013**, 160 (11), 2559-2572.
119. Li, J.; Paul, M. C.; Younger, P. L.; Watson, I.; Hossain, M.; Welch, S., Characterization of biomass combustion at high temperatures based on an upgraded single particle model. *Applied Energy* **2015**, 156, 749-755.
120. Xu, Y.; Zhai, M.; Jin, S.; Zou, X.; Liu, S.; Dong, P., Numerical simulation of high-temperature fusion combustion characteristics for a single biomass particle. *Fuel Processing Technology* **2019**, 183, 27-34.
121. Feng, L.; Wu, Y.; Xu, K.; Zhang, H.; Zhang, Y.; Zhang, M., Coal-Derived Soot Behaviors in O₂/N₂ and O₂/CO₂ Atmospheres, Studied through a 1-D Transient Coal Combustion Model. *Energy & Fuels* **2019**, 33 (4), 3620-3629.
122. Liu, H.; Wang, C.; Zhang, Y.; Zou, C.; Anthony, E., Vaporization model for arsenic during single-particle coal combustion: Model development. *Combustion and Flame* **2019**, 205, 534-546.
123. Wurzenberger, J. C.; Wallner, S.; Raupenstrauch, H., Thermal Conversion of Biomass: Comprehensive Reactor and Particle Modeling. *Environmental and Energy Engineering* **2004**, 48 (10), 13.
124. Thunman, H.; Leckner, B.; Niklasson, F.; Johnsson, F., Combustion of Wood Particles - A Particle Model for Eulerian Calculations. *Combustion and Flame* **2002**, 129 (1-2), 30-46.
125. Winter, F.; Prah, M. E.; Hofbauer, H., Temperatures in a Fuel Particle Burning in a Fluidized Bed: The Effect of Drying Devolatilization and Char Combustion. *Combustion and Flame* **1997**, 108 (3), 302-314.
126. Saastamoinen, J.; Aho, M.; Moilanen, A.; Sørensen, L. H.; Clausen, S.; Berg, M., Burnout of pulverized biomass particles in large scale boiler – Single particle model approach. *Biomass and Bioenergy* **2010**, 34 (5), 728-736.
127. Wagner, N. J., Coal Gasification. *Applied Coal Petrology* **2008**, 114-119.
128. Tremel, A.; Haselsteiner, T.; Nakonz, M.; Spliethoff, H., Coal and char properties in high temperature entrained flow gasification. *Energy* **2012**, 45 (1), 176-182.
129. Hotchkiss, R., Coal Gasification Technologies. *Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy* **2003**, 217 (1), 27-33.
130. Guo, X.; Dai, Z.; Gong, X.; Chen, X.; Liu, H.; Wang, F.; Yu, Z., Performance of an entrained-flow gasification technology of pulverized coal in pilot-scale plant. *Fuel Processing Technology* **2007**, 88 (5), 451-459.
131. Brown, B. W.; Smoot, L. D.; Smith, P. J.; Hedman, P. O., Measurement and Prediction of Entrained-flow Gasification Processes. *AIChE Journal* **1988**, 34 (3), 435-446.
132. Vamvuka, D.; Zografos, D., Predicting the behaviour of ash from agricultural wastes during combustion. *Fuel* **2004**, 83 (14-15), 2051-2057.
133. Fletcher, D. F.; Haynes, B. S.; Christo, F. C.; Joseph, S. D., A CFD-based Combustion Model of an Entrained-flow Biomass Gasifier. *Applied Mathematical Modelling* **2000**, 24 (3), 165-182.
134. Choi, Y. C.; Li, X. Y.; Park, T. J.; Kim, J. H.; Lee, J. G., Numerical Study on the Coal Gasification Characteristics in an Entrained-flow Coal Gasifier. *Fuel* **2001**, 80 (15), 2193-2201.
135. Liu, X. J.; Zhang, W. R.; Park, T. J., Modelling coal gasification in an entrained flow gasifier. *Combustion Theory and Modelling* **2007**, 5 (4), 595-608.

136. Watanabe, H.; Otaka, M., Numerical simulation of coal gasification in entrained flow coal gasifier. *Fuel* **2006**, *85* (12-13), 1935-1943.
137. Silaen, A.; Wang, T. In *Comparison of Instantaneous, Equilibrium, and Finite-rate Gasification Models in an Entrained-flow Coal Gasifier*, 26th International Pittsburgh Coal Conference, Pittsburgh, PA, Pittsburgh, PA, 2009.
138. Halama, S.; Spliethoff, H., Numerical simulation of entrained flow gasification: Reaction kinetics and char structure evolution. *Fuel Processing Technology* **2015**, *138*, 314-324.
139. Louise, T.; David F, T.; Bucat, R. B., The Complexity of teaching and Learning Chemical Equilibrium. *Journal of Chemical Education* **1999**, *76* (4), 554-558.
140. White, W. B.; Johnson, S. M.; Dantzig, G. B., Chemical Equilibrium in Complex Mixtures. *The Journal of Chemical Physics* **1958**, *28* (5), 751-755.
141. Ljung, A.; Nordin, A., Theoretical Feasibility for Ecological Biomass Ash Recirculation: Chemical Equilibrium Behavior of Nutrient Elements and Heavy Metals during Combustion. *Environmental Science Technology* **1997**, *31* (9), 2499-2503.
142. Lind, T.; Valmari, T.; Kauppinen, E. I.; Sfiris, G.; Nilsson, K.; Maenhut, W., Volatilization of the Heavy Metals during Circulating Fluidized Bed Combustion of Forest Residue. *33* **1999**, *3* (496-502).
143. Boman, C.; Nordin, A.; Boström, D.; Öhman, M., Characterization of Inorganic Particulate Matter from Residential Combustion of Pelletized Biomass Fuels. *Energy Fuels* **2004**, *18* (2), 338-348.
144. Boman, C.; Öhman, M.; Nordin, A., Trace Element Enrichment and Behavior in Wood Pellet Production and Combustion Processes. *Energy Fuels* **2006**, *20* (3), 993-1000.
145. Jiménez, S.; Pérez, M.; Ballester, J., Vaporization of Trace Elements and Their Emission with Submicrometer Aerosols in Biomass Combustion. *Energy Fuels* **2008**, *22* (4), 2270-2277.
146. Wang, Q.; Chen, J.; Han, K.; Wang, J.; Lu, C., Influence of BaCO₃ on chlorine fixation, combustion characteristics and KCl conversion during biomass combustion. *Fuel* **2017**, *208*, 82-90.
147. Nutalapati, D.; Gupta, R.; Moghtaderi, B.; Wall, T. F., Assessing slagging and fouling during biomass combustion: A thermodynamic approach allowing for alkali/ash reactions. *Fuel Processing Technology* **2007**, *88* (11-12), 1044-1052.
148. Miller, B. B.; Kandiyoti, R.; Dugwell, D. R., Trace Element Emissions from Co-combustion of Secondary Fuels with Coal: A Comparison of Bench-scale Experimental Data with Predictions of A Thermodynamic Equilibrium Model. *Energy Fuels* **2002**, *16* (4), 956-963.
149. Guo, F.; Zhong, Z.; Xue, H.; Zhong, D., Migration and Distribution of Heavy Metals During Co-combustion of Sedum plumbizincicola and Coal. *Waste and Biomass Valorization* **2017**, *9* (11), 2203-2210.
150. Teixeira, P.; Lopes, H.; Gulyurtlu, I.; Lapa, N.; Abelha, P., Slagging and Fouling during Coal and Biomass Cofiring: Chemical Equilibrium Model Applied to FBC. *Energy & Fuels* **2013**, *28* (1), 697-713.
151. George, A.; Larrion, M.; Dugwell, D.; Fennell, P. S.; Kandiyoti, R., Co-firing of Single, Binary, and Ternary Fuel Blends: Comparing Synergies within Trace Element Partitioning Arrived at by Thermodynamic Equilibrium Modeling and Experimental Measurements. *Energy & Fuels* **2010**, *24* (5), 2918-2923.
152. Miller, B.; Dugwell, D.; Kandiyoti, R., The Fate of Trace Elements during the Co-combustion of Wood Bark with Waste. *Energy Fuels* **2006**, *20* (2), 520-531.
153. Han, J.; Xu, M.; Yao, H.; Furuuchi, M.; Sakano, T.; Kanchanapiya, P.; Kanaoka, C., Partition of Heavy and Alkali Metals during Sewage Sludge Incineration. *Energy and Fuels* **2006**, *20* (2), 583-590.
154. Díaz-Somoano, M.; Unterberger, S.; Hein, K. R. G., Prediction of trace element volatility during co-combustion processes. *Fuel* **2006**, *85* (7-8), 1087-1093.
155. Enestam, S.; Backman, R.; Mäkelä, K.; Hupa, M., Evaluation of the condensation behavior of lead and zinc in BFB combustion of recovered waste wood. *Fuel Processing Technology* **2013**, *105*, 161-169.
156. Vainikka, P.; Lindberg, D.; Moilanen, A.; Ollila, H.; Tiainen, M.; Silvennoinen, J.; Hupa, M., Trace elements found in the fuel and in-furnace fine particles collected from 80MW BFB combusting solid recovered fuel. *Fuel Processing Technology* **2013**, *105*, 202-211.

157. Verhulst, D.; Buekens, A., Thermodynamic Behavior of Metal Chlorides and Sulfates under the Conditions of Incineration Furnaces. *Environmental Science and Technology* **1995**, *30* (1), 50-56.
158. Wei, X.; Lopez, C.; Puttkamer, T. v.; Schnell, U.; Unterberger, S.; Hein, K. R. G., Assessment of Chlorine-Alkali-Mineral Interactions during Co-combustion of Coal and Straw. *Energy Fuels* **2002**, *16* (5), 1095-1108.
159. Diaz-Somoano, M.; Martinez-Tarazona, M. R., Retention of Arsenic and Selenium Compounds Using Limestone in a Coal Gasification Flue Gas. *Environmental Science and Technology* **2004**, *38* (3), 899-903.
160. Stam, A. F.; Meij, R.; Te Winkel, H.; Eijk, R. J.; Huggins, F. E.; Brem, G., Chromium speciation in coal and biomass co-combustion products. *Environ Sci Technol* **2011**, *45* (6), 2450-6.
161. Wu, D.; Wang, Y.; Wang, Y.; Li, S.; Wei, X., Release of alkali metals during co-firing biomass and coal. *Renewable Energy* **2016**, *96*, 91-97.
162. Yang, T.; Kai, X.; Li, R.; Sun, Y.; He, Y., The Behavior of Alkali Metals During the Co-combustion of Straw and Coal. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* **2013**, *36* (1), 15-22.
163. Contreras, M. L.; Arostegui, J. M.; Armesto, L., Arsenic interactions during co-combustion processes based on thermodynamic equilibrium calculations. *Fuel* **2009**, *88* (3), 539-546.
164. Contreras, M. L.; García-Frutos, F. J.; Bahillo, A., Oxy-fuel combustion effects on trace metals behaviour by equilibrium calculations. *Fuel* **2013**, *108*, 474-483.
165. Konttinen, J.; Backman, R.; Hupa, M.; Moilanen, A.; Kurkela, E., Trace element behavior in the fluidized bed gasification of solid recovered fuels – A thermodynamic study. *Fuel* **2013**, *106*, 621-631.
166. Turn, S. Q., Chemical Equilibrium Prediction of Potassium, Sodium, and Chlorine Concentrations in the Product Gas from Biomass Gasification. *Industrial and Engineering Chemistry Research* **2007**, *46* (26), 8928-8937.
167. Reed, G. P.; Dugwell, D. R.; Kandiyoti, R., Control of Trace Elements in a Gasifier Hot Gas Filter - A Comparison with Predictions from a Thermodynamic Equilibrium Model. *Energy Fuels* **2001**, *15* (6), 1480-1487.
168. Ma, C.; Backman, R.; Öhman, M., Thermochemical Equilibrium Study of Slag Formation during Pressurized Entrained-Flow Gasification of Woody Biomass. *Energy & Fuels* **2015**, *29* (7), 4399-4406.
169. Miller, B.; Dugwell, D. R.; Kandiyoti, R., The Influence of Injected HCl and SO₂ on the Behavior of Trace Elements during Wood-Bark Combustion. *Energy Fuels* **2003**, *17* (5), 1382-1391.
170. Miller, B. B.; Kandiyoti, R.; Dugwell, D. R., Trace Element Behavior during Co-combustion of Sewage Sludge with Polish Coal. *Energy Fuels* **2004**, *18* (4), 1093-1103.
171. Lundholm, K.; Bostrom, D.; Nordin, A.; Shchukarev, A., Fate of Cu, Cr, and As during Combustion of Impregnated Wood with and without Peat Additive. *Environmental Science and Technology* **2007**, *41* (18), 6534-6540.
172. Öhman, M.; Pommer, L.; Nordin, A., Bed Agglomeration Characteristics and Mechanisms during Gasification and Combustion of Biomass Fuels. *Energy Fuels* **2005**, *19* (4), 1742-1748.
173. Elled, A. L.; Åmand, L. E.; Steenari, B. M., Composition of agglomerates in fluidized bed reactors for thermochemical conversion of biomass and waste fuels. *Fuel* **2013**, *111*, 696-708.
174. Furimsky, E., Characterization of Trace Element Emissions from Coal Combustion by Equilibrium Calculations. *Fuel processing Technology* **2000**, *63* (1), 29-44.
175. Finney, K. N.; Szuhanski, J.; Darvell, L. I.; Dooley, B.; Milkowski, K.; Jones, J. M.; Pourkashanian, M., Entrained Metal Aerosol Emissions from Air-Fired Biomass and Coal Combustion for Carbon Capture Applications. *Materials (Basel)* **2018**, *11* (10).
176. Werkelin, J.; Skrifvars, B.-J.; Hupa, M., Ash-forming elements in four Scandinavian wood species. Part 1: Summer harvest. *Biomass and Bioenergy* **2005**, *29* (6), 451-466.
177. Jenkins, B. M.; Baxter, L. L.; Miles, T. R.; Miles, T. R., Combustion properties of biomass. *Fuel Processing Technology* **1998**, *54* (1-3), 17-46.
178. Cowling, E. B.; Merrill, W., Nitrogen in wood and its role in wood deterioration. *Canadian Journal of Botany* **1966**, *44* (11), 1539-1554.

179. Oglesby, H. S.; Blosser, R. O., Information on the Sulfur Content of Bark and its Contribution to SO₂ Emissions when Burned as a Fuel. *Journal of the Air Pollution Control Association* **1980**, 30 (7), 769-772.
180. Lundegardh, H., Mineral Nutrition of Plants. *Annual Review of Biochemistry* **1934**, 3 (1), 485-500.
181. Wang, M.; Zheng, Q.; Shen, Q.; Guo, S., The critical role of potassium in plant stress response. *Int J Mol Sci* **2013**, 14 (4), 7370-90.
182. Mossor-Pietraszewska, T., Effect of Aluminium on Plant Growth and Metabolism. *Acta Biochimica Polonica* **2001**, 48 (3), 673-686.
183. Miller, S. F.; Miller, B. G., The occurrence of inorganic elements in various biofuels and its effect on ash chemistry and behavior and use in combustion products. *Fuel Processing Technology* **2007**, 88 (11-12), 1155-1164.
184. Skrifvars, B., Predicting the ash behaviour of different fuels in fluidized bed combustion. *Fuel and Energy Abstracts* **2002**, 4 (43), 252-253.
185. Werkelin, J.; Skrifvars, B.-J.; Zevenhoven, M.; Holmbom, B.; Hupa, M., Chemical forms of ash-forming elements in woody biomass fuels. *Fuel* **2010**, 89 (2), 481-493.
186. Desaulles, A.; Studer, K., NABO-Nationales Bodenbeobachtungsnetz Messresultate 1985-1991. *Schriftenreihe Umwelt* **1993**, 200.
187. Blaser, P.; Zimmermann, S.; Luster, J.; Shotyk, W., Critical examination of trace element enrichments and depletions in soils: As, Cr, Cu, Ni, Pb, and Zn in Swiss forest soils. *Science of the Total Environment* **2000**, 249 (1-3), 257-280.
188. Vassilev, S. V.; Vassileva, C. G.; Baxter, D., Trace element concentrations and associations in some biomass ashes. *Fuel* **2014**, 129, 292-313.
189. Hanson, P. J.; Lindberg, S. E.; Tabberer, T. A.; Owens, J. G.; Kim, K.-H., Foliar Exchange of Mercury Vapor: Evidence for a Compensation Point. *Water, Air, and Soil Pollution* **1995**, 80 (1-4), 373-382.
190. Lindberg, S. E.; Hanson, P. J.; Meyers, T. P.; Kim, K.-H., Air/Surface Exchange of Mercury Vapor over Forests - The need for Reassessment of Continental Biogenic Emissions. *Atmospheric Environment* **1998**, 32 (5), 859-908.
191. Iverfeldt, Å., Mercury in Forest Canopy throughfall Water and Its Relation to Atmospheric Deposition. *Water, Air, and Soil Pollution* **1991**, 56 (1), 553-564.
192. Ericksen, J. A.; Gustin, M. S.; Schorran, D. E.; Johnson, D. W.; Lindberg, S. E.; Coleman, J. S., Accumulation of atmospheric mercury in forest foliage. *Atmospheric Environment* **2003**, 37 (12), 1613-1622.
193. Nicholson, D. D.; Preston, A. F., Interaction of Preservatives with Wood. In *The Chemistry of Solid Wood*, Rowell, R., Ed. American Chemical Society: 1984; Vol. 207, pp 307-320.
194. Hulme, M. A.; Butcher, J. A., Doft-rot Control in Hardwoods Treated with Chromated Copper Arsenate Preservatives. 3. Influence of Wood Substrate and Copper Loadings. *Material Und Organismen* **1977**.
195. Van den Bulcke, J.; Rijckaert, V.; Van Acker, J.; Stevens, M., Quantitative measurement of the penetration of water-borne coatings in wood with confocal lasermicroscopy and image analysis. *Holz als Roh- und Werkstoff* **2003**, 61 (4), 304-310.
196. Pope, J., New Orleans Considers Ban on Sanding Houses. *The Times - Picayune* 17 February 2000, 2000.
197. Yang, Y.; Yanai, R. D.; Montesdeoca, M.; Driscoll, C. T., Measuring mercury in wood: challenging but important. *International Journal of Environmental Analytical Chemistry* **2017**, 97 (5), 456-467.
198. Clemens, S.; Palmgren, M. G.; Kramer, U., A Long Way ahead - Understanding and Engineering Plant Metal Accumulation. *Trends in Plant Science* **2002**, 7 (7), 309-315.
199. Baluska, F.; Hlavacka, A.; Samaj, J.; Palme, K.; Robinson, D. G.; Matoh, T.; McCurdy, D. W.; Menzel, D.; Volkmann, D., F-actin-dependent endocytosis of cell wall pectins in meristematic root cells. Insights from brefeldin A-induced compartments. *Plant Physiol* **2002**, 130 (1), 422-31.
200. Levitt, J., *Response of Plants to Environmental Stresses*. 2nd ed.; Academic Press: New York, 1980; Vol. 2.

201. Dronnet, V. M.; Renard, C. M. G. C.; Axelos, M. A. V.; Thibault, J. F., Heavy Metals Binding by Pectins - Selectivity, Quantification, and Characterisation. *Progress in Biotechnology* **1996**, *14*, 535-540.
202. Krzesłowska, M., The cell wall in plant cell response to trace metals: polysaccharide remodeling and its role in defense strategy. *Acta Physiologiae Plantarum* **2010**, *33* (1), 35-51.
203. Hall, J. L., Cellular Mechanisms for Heavy Metal Detoxification and Tolerance. *Journal of Experimental Botany* **2002**, *53* (366), 1-11.
204. Krzesłowska, M.; Lenartowska, M.; Mellerowicz, E.; Samardakiewicz, S.; Wozny, A., Pectinous cell wall thickenings formation—A response of moss protonemata cells to lead. *Environmental and Experimental Botany* **2009**, *65* (1), 119-131.
205. Kopittke, P. M.; Asher, C. J.; Blamey, F. P. C.; Auchterlonie, G. J.; Guo, Y. N.; Menzies, N. W., Localization and Chemical Speciation of Pb in Roots of Signal Grass (*Brachiaria decumbens*) and Rhodes Grass (*Chloris gayana*). *Environmental Science and Technology* **2008**, *42*, 4595-4599.
206. Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vassileva, C. G.; Morgan, T. J., An overview of the organic and inorganic phase composition of biomass. *Fuel* **2012**, *94*, 1-33.
207. Obernberger, I.; Brunner, T.; Bärnthaler, G., Chemical properties of solid biofuels—significance and impact. *Biomass and Bioenergy* **2006**, *30* (11), 973-982.
208. Paulrud, S.; Nilsson, C., Briquetting and combustion of spring-harvested reed canary-grass: effect of fuel composition. *Biomass and Bioenergy* **2001**, *20* (1), 25-35.
209. Clark, C. M.; Bai, Y.; Bowman, W. D.; Cowles, J. M.; Fenn, M. E.; Gilliam, F. S.; Phoenix, G. K.; Siddique, I.; Stevens, C. J.; Sverdrup, H. U.; Throop, H. L., Nitrogen Deposition and Terrestrial Biodiversity. In *Encyclopedia of Biodiversity*, 2 ed.; Elsevier: 2013; Vol. 5, pp 519-536.
210. Pettersson, A.; Zevenhoven, M.; Steenari, B.-M.; Åmand, L.-E., Application of chemical fractionation methods for characterisation of biofuels, waste derived fuels and CFB co-combustion fly ashes. *Fuel* **2008**, *87* (15-16), 3183-3193.
211. Skrifvars, B.-J.; Yrjas, P.; Kinni, J.; Siefen, P.; Hupa, M., The Fouling Behavior of Rice Husk Ash in Fluidized-Bed Combustion. 1. Fuel Characteristics. *Energy & fuels* **2005**, *19* (4), 1503-1511.
212. Sharma, N. K.; Williams, W. S.; Zangvil, A., Formation and structure of silicon carbide whiskers from rice hulls. *Journal of the American Ceramic Society* **1984**, *67* (11), 715-720.
213. Han, J.; Yu, D.; Yu, X.; Liu, F.; Wu, J.; Zeng, X.; Yu, G.; Xu, M., Effect of the torrefaction on the emission of PM10 from combustion of rice husk and its blends with a lignite. *Proceedings of the Combustion Institute* **2019**, *37* (3), 2733-2740.
214. Sanderson, M. A.; Wolf, D. D., Switchgrass biomass composition during morphological development in diverse environments. *Crop Science* **1995**, *35* (5), 1432-1438.
215. Liu, X.; Bi, X. T., Removal of inorganic constituents from pine barks and switchgrass. *Fuel Processing Technology* **2011**, *92* (7), 1273-1279.
216. Gusman, V. M. Assessment of the Calcium, Phosphorus, and Oxalate Components of Kikuyu Grass Pasture-based Diets in Hawaii and Their Relationship to Calcium, Phosphorus, and Oxalate Intake and Excretion by Horses. University of Hawai'i, 2004.
217. Roberson, T.; Bundy, L. G.; Andraski, T. W., Freezing and drying effects on potential plant contributions to phosphorus in runoff. *Journal of environmental quality* **2007**, *36* (2), 532-539.
218. Wang, S.; Dai, G.; Yang, H.; Luo, Z., Lignocellulosic biomass pyrolysis mechanism: a state-of-the-art review. *Progress in Energy and Combustion Science* **2017**, *62*, 33-86.
219. Ciesielski, P. N.; Crowley, M. F.; Nimlos, M. R.; Sanders, A. W.; Wiggins, G. M.; Robichaud, D.; Donohoe, B. S.; Foust, T. D., Biomass particle models with realistic morphology and resolved microstructure for simulations of intraparticle transport phenomena. *Energy & Fuels* **2015**, *29* (1), 242-254.
220. Backreedy, R. I.; Fletcher, L. M.; Jones, J. M.; Ma, L.; Pourkashanian, M.; Williams, A., Co-firing pulverised coal and biomass: a modeling approach. *Proceedings of the Combustion Institute* **2005**, *30* (2), 2955-2964.
221. Ma, L.; Jones, J. M.; Pourkashanian, M.; Williams, A., Modelling the combustion of pulverized biomass in an industrial combustion test furnace. *Fuel* **2007**, *86* (12-13), 1959-1965.
222. Lu, H.; Ip, E.; Scott, J.; Foster, P.; Vickers, M.; Baxter, L. L., Effects of particle shape and size on devolatilization of biomass particle. *Fuel* **2010**, *89* (5), 1156-1168.

223. Gil, M.; Teruel, E.; Arauzo, I., Analysis of standard sieving method for milled biomass through image processing. Effects of particle shape and size for poplar and corn stover. *Fuel* **2014**, *116*, 328-340.
224. Janse, A. M. C.; Westerhout, R. W. J.; Prins, W., Modelling of Flash Pyrolysis of a Single Wood Particle. *Chemical Engineering and Processing: Process Intensification* **2000**, *39* (3), 13.
225. Yin, C.; Rosendahl, L.; Kær, S.; J. Condra, T., Use of numerical modeling in design for co-firing biomass in wall-fired burners. *Chemical Engineering Science* **2004**, *59* (16), 3281-3292.
226. Thurner, F.; Mann, U., Kinetic Investigation of Wood Pyrolysis. *Industrial and Engineering Chemistry Process Design and Development* **1981**, *20* (3), 482-488.
227. Font, R.; Marcilla, A.; Verdu, E.; Devesa, J., Kinetics of the Pyrolysis of Almond Shells Impregnated with CoCl₂ in a Fluidized Bed Reactor and in a Pyroprobe 100. *Industrial and Engineering Chemistry Research* **1990**, *29*, 10.
228. Wagenaar, B. M.; Prins, W.; Swaaij, W. P. M. v., Flash Pyrolysis Kinetics of Pine Wood. *Fuel Processing Technology* **1993**, *36*, 8.
229. Blasi, C. d., Modelling and Simulation of Combustion Processes of Charring and Non-charring Solid Fuels. *Progress in Energy and Combustion Science* **1993**, *19*, 71-104.
230. Liden, A. G.; Berruti, F.; Scott, D. S., A Kinetic Model for the Production of Liquids from the Flash Pyrolysis of Biomass. *Chemical Engineering Communications* **1988**, *65* (1), 207-221.
231. Blasi, C. D., Analysis of Convection and Secondary Reaction Effects Within Porous Solid Fuels Undergoing Pyrolysis. *Combustion Science and Technology* **1993**, *90* (5), 315-340.
232. Yaman, S., Pyrolysis of biomass to produce fuels and chemical feedstocks. *Energy Conversion and Management* **2004**, *45* (5), 651-671.
233. Kan, T.; Strezov, V.; Evans, T. J., Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renewable and Sustainable Energy Reviews* **2016**, *57*, 1126-1140.
234. Kung, H.-C., A Mathematical Model of Wood Pyrolysis. *Combustion and Flame* **1972**, *18*, 185-195.
235. Nunn, T. R.; Howard, J. B.; Longwell, J. P.; Peters, W. A., Product Compositions and Kinetics in the Rapid Pyrolysis of Sweet Gum Hardwood. *Industrial and Engineering Chemistry Process Design and Development* **1985**, *24*, 836-844.
236. Bowersox, T. W.; Blankenhorn, P. R.; Murphey, W. K., Heat of Combustion, Ash Content, Nutrient Content, and Chemical Content of Populus Hybrids. *Wood Science* **1979**, *11* (4), 257-261.
237. Blasi, C. D., Dynamic Behaviour of Stratified Downdraft Gasifiers. *Chemical Engineering Science* **2000**, *Chemical Engineering Science* (55), 2931-2944.
238. Thunmann, H.; Niklasson, F.; Johnsson, F.; Leckner, B., Composition of volatile gases and thermochemical properties of wood for modeling of fixed or fluidized beds. *Energy & Fuels* **2001**, *15* (6), 1488-1497.
239. Ranzi, E.; Cuoci, A.; Faravelli, T.; Frassoldati, A.; Migliavacca, G.; Pierucci, S.; Sommariva, S., Chemical Kinetics of Biomass Pyrolysis. *Energy & Fuels* **2008**, *22* (6), 4292-4300.
240. Morf, P.; Hasler, P.; Nussbaumer, T., Mechanisms and Kinetics of Homogenous Secondary Reactions of Tar from Continuous Pyrolysis of Wood Chips. *Fuel* **2002**, *81* (7), 10.
241. Guerrero, M.; Ruiz, M. P.; Millera, Á.; Alzueta, M. U.; Bilbao, R., Characterization of biomass chars formed under different devolatilization conditions: differences between rice husk and eucalyptus. *Energy & fuels* **2008**, *22* (2), 1275-1284.
242. Lewtak, R.; Marek, E. In *Numerical and experimental investigations into combustion of a single biomass particle*, 8th US National Combustion Meeting, Salt Lake City, UT, Salt Lake City, UT, 2013; pp 19-22.
243. Mehrabian, R.; Zahirovic, S.; Scharler, R.; Obernberger, I.; Kleditzsch, S.; Wirtz, S.; Scherer, V.; Lu, H.; Baxter, L. L., A CFD model for thermal conversion of thermally thick biomass particles. *Fuel Processing Technology* **2012**, *95*, 96-108.
244. Clements, A. G.; Black, S.; Szuhánszki, J.; Stęchły, K.; Pranzitelli, A.; Nimmo, W.; Pourkashanian, M., LES and RANS of air and oxy-coal combustion in a pilot-scale facility: Predictions of radiative heat transfer. *Fuel* **2015**, *151*, 146-155.
245. Hein, K. R. G.; Bemtgen, J. M., EU Clean Coal Technology - Co-combustion of Coal and Biomass. *Fuel Processing Technology* **1998**, *54* (1-3), 159-169.

246. Savolainen, K., Co-firing of biomass in coal-fired utility boilers. *Applied Energy* **2003**, *74* (3-4), 369-381.
247. Al-Mansour, F.; Zuwala, J., An evaluation of biomass co-firing in Europe. *Biomass and Bioenergy* **2010**, *34* (5), 620-629.
248. Pallarés, J.; Gil, A.; Cortés, C.; Herce, C., Numerical study of co-firing coal and *Cynara cardunculus* in a 350 MWe utility boiler. *Fuel Processing Technology* **2009**, *90* (10), 1207-1213.
249. Gubba, S. R.; Ingham, D. B.; Larsen, K. J.; Ma, L.; Pourkashanian, M.; Tan, H. Z.; Williams, A.; Zhou, H., Numerical modelling of the co-firing of pulverised coal and straw in a 300MWe tangentially fired boiler. *Fuel Processing Technology* **2012**, *104*, 181-188.
250. Molcan, P.; Lu, G.; Bris, T. L.; Yan, Y.; Taupin, B.; Caillat, S., Characterisation of biomass and coal co-firing on a 3MWth Combustion Test Facility using flame imaging and gas/ash sampling techniques. *Fuel* **2009**, *88* (12), 2328-2334.
251. Gera, D.; Mathur, M. P.; Freeman, M. C.; Robinron, A., Effect of Large Aspect Ratio of Biomass Particles on Carbon Burnout in a Utility Boiler. *Energy Fuels* **2002**, *16* (6), 1523-1532.
252. Fatehi, H.; Li, Z. S.; Bai, X. S.; Alden, M., Modeling of alkali metal release during biomass pyrolysis. *Proceedings of the Combustion Institute* **2017**, *36* (2), 2243-2251.
253. Pratsinis, S. E., Simultaneous Nucleation, Condensation, and Coagulation in Aerosol Reactors. *Journal of Colloid and Interface Science* **1988**, *124* (2), 416-427.
254. Warren, D. R.; Seinfeld, J. H., Simulation of Aerosol Size Distribution Evolution in Systems with Simultaneous Nucleation, Condensation, and Coagulation. *Aerosol Science and Technology* **2007**, *4* (1), 31-43.
255. Biermann, A. H.; Ondov, J. M., Application of Surface-deposition Models to Size-fractionated Coal Fly Ash. *Atmospheric Environment* **1980**, *14* (3), 289-295.
256. Tortosa Masiá, A. A.; Buhre, B. J. P.; Gupta, R. P.; Wall, T. F., Characterising ash of biomass and waste. *Fuel Processing Technology* **2007**, *88* (11-12), 1071-1081.
257. Sasi, T.; Mighani, M.; Örs, E.; Tawani, R.; Gräbner, M., Prediction of ash fusion behavior from coal ash composition for entrained-flow gasification. *Fuel Processing Technology* **2018**, *176*, 64-75.
258. Frandsen, F. J.; van Lith, S. C.; Korbee, R.; Yrjas, P.; Backman, R.; Obernberger, I.; Brunner, T.; Jöller, M., Quantification of the release of inorganic elements from biofuels. *Fuel Processing Technology* **2007**, *88* (11-12), 1118-1128.
259. Jiao, F.; Zhang, L.; Dong, Z.; Namioka, T.; Yamada, N.; Ninomiya, Y., Study on the species of heavy metals in MSW incineration fly ash and their leaching behavior. *Fuel Processing Technology* **2016**, *152*, 108-115.
260. Cheng, Y.; Sato, A.; Ninomiya, Y., Effect of HCl/SO₂/H₂O on the Deposition of Heavy Metal Vapors in the Cooling Section of an Incineration Plant. *HJournal of Chemical Engineering of Japan* **2010**, *43* (8), 713-719.
261. Jiao, F.; Zhang, L.; Yamada, N.; Sato, A.; Ninomiya, Y., Effect of HCl, SO₂ and H₂O on the condensation of heavy metal vapors in flue gas cooling section. *Fuel Processing Technology* **2013**, *105*, 181-187.
262. Kramb, J.; Konttinen, J.; Backman, R.; Salo, K.; Roberts, M., Elimination of arsenic-containing emissions from gasification of chromated copper arsenate wood. *Fuel* **2016**, *181*, 319-324.
263. Wan, W.; Engvall, K.; Yang, W., Novel Model for the Release and Condensation of Inorganics for a Pressurized Fluidized-Bed Gasification Process: Effects of Gasification Temperature. *ACS Omega* **2018**, *3* (6), 6321-6329.
264. Wan, W.; Engvall, K.; Yang, W.; Möller, B. F., Experimental and modelling studies on condensation of inorganic species during cooling of product gas from pressurized biomass fluidized bed gasification. *Energy* **2018**, *153*, 35-44.
265. Wan, W.; Engvall, K.; Yang, W., Model investigation of condensation behaviors of alkalis during syngas treatment of pressurized biomass gasification. *Chemical Engineering and Processing - Process Intensification* **2018**, *129*, 28-36.
266. Gallagher, N. B.; Bool, L. E.; Wendt, J. O. L.; Peterson, T. W., Alkali Metal Partitioning in Ash from Pulverized Coal Combustion. *Combustion Science and Technology* **1990**, *74* (1-6), 211-221.
267. Li, B.; Sun, Z.; Li, Z.; Aldén, M.; Jakobsen, J. G.; Hansen, S.; Glarborg, P., Post-flame gas-phase sulfation of potassium chloride. *Combustion and Flame* **2013**, *160* (5), 959-969.

268. Hindiyarti, L.; Frandsen, F.; Livbjerg, H.; Glarborg, P., Influence of potassium chloride on moist CO oxidation under reducing conditions: Experimental and kinetic modeling study. *Fuel* **2006**, *85* (7-8), 978-988.
269. Riedl, R.; Dahl, J.; Obernberger, I.; Narodoslawsky, M. In *Corrosion in fire tube boilers of biomass combustion plants*, The China International Corrosion Control Conference 1999, Beijing, China, Beijing, China, 1999.
270. Kerienè, J. R.; Boris, R.; Antonović, V.; Stonys, R.; Škamat, J., Action of the Products of Biofuel Combustion on the Phase Composition and Structure of Refractory Material. *Glass and Ceramics* **2016**, *72* (9-10), 345-350.
271. Stjernberg, J.; Lindblom, B.; Wikström, J.; Antti, M. L.; Odén, M., Microstructural characterization of alkali metal mediated high temperature reactions in mullite based refractories. *Ceramics International* **2010**, *36* (2), 733-740.
272. Tran, K.-Q.; Iisa, K.; Steenari, B.-M.; Lindqvist, O., A kinetic study of gaseous alkali capture by kaolin in the fixed bed reactor equipped with an alkali detector. *Fuel* **2005**, *84* (2-3), 169-175.
273. Korbee, R.; Shah, K. V.; Cieplik, M. K.; Bertrand, C. I.; Vuthaluru, H. B.; van de Kamp, W. L., First Line Ash Transformations of Coal and Biomass Fuels during PF Combustion. *Energy & Fuels* **2010**, *24* (2), 897-909.
274. Shah, K. V.; Cieplik, M. K.; Bertrand, C. I.; van de Kamp, W. L.; Vuthaluru, H. B., Correlating the effects of ash elements and their association in the fuel matrix with the ash release during pulverized fuel combustion. *Fuel Processing Technology* **2010**, *91* (5), 531-545.
275. Shih, S.-M.; Ho, C. u.-S.; Song, Y.-S.; Lin, J.-P., Kinetics of the reaction of Ca (OH) 2 with CO2 at low temperature. *Industrial and Engineering Chemistry Research* **1999**, *38* (4), 1316-1322.
276. Sheng, C.; Li, Y., Experimental study of ash formation during pulverized coal combustion in O2/CO2 mixtures. *Fuel* **2008**, *87* (7), 1297-1305.
277. Hashimoto, S.; Yamaguchi, A.; Oya, S.-i., Formation of needle-like β -Ca₂SiO₄ crystals by vapor phase reaction. *Journal of Crystal Growth* **1996**, *169* (2), 376-379.
278. Fierens, P.; Picquet, P., Kinetic studies of the thermal synthesis of calcium silicates above 1400° C: I, dynamic thermal synthesis of Ca₂SiO₄. *Journal of the American Ceramic Society* **1975**, *58* (1-2), 50-51.
279. Kotsis, I.; Balogh, A., Synthesis of wollastonite. *Ceramics International* **1989**, *15* (2), 79-85.
280. Kozawa, T.; Yanagisawa, K.; Yoshida, A.; Onda, A.; Suzuki, Y., Preparation of β -CaSiO₃ powder by water vapor-assisted solid-state reaction. *Journal of the Ceramic Society of Japan* **2013**, *121* (1), 103-105.
281. Maschio, S.; Tonello, G.; Piani, L.; Furlani, E., Fly and bottom ashes from biomass combustion as cement replacing components in mortars production: rheological behaviour of the pastes and materials compression strength. *Chemosphere* **2011**, *85* (4), 666-71.
282. Priyanto, D. E.; Ueno, S.; Sato, N.; Kasai, H.; Tanoue, T.; Fukushima, H., Ash transformation by co-firing of coal with high ratios of woody biomass and effect on slagging propensity. *Fuel* **2016**, *174*, 172-179.
283. Etiégni, L.; Campbell, A. G., Physical and Chemical Characteristics of Wood Ash. *Bioresource Technology* **1991**, *37* (2), 173-178.
284. Thy, P.; Jenkins, B.; Grundvig, S.; Shiraki, R.; Leshner, C., High temperature elemental losses and mineralogical changes in common biomass ashes. *Fuel* **2006**, *85* (5-6), 783-795.
285. Matsuya, S.; Yamane, M., Solid State Reaction between CaSO₄ and Quartz. *Gypsum and Lime* **1981**, *174*, 188-193.
286. Laitinen, J.; Koponen, H.; Sippula, O.; Korpjarvi, K.; Jumpponen, M.; Laitinen, S.; Aatamila, M.; Tissari, J.; Karhunen, T.; Ojanen, K.; Jokiniemi, J.; Korpinen, L., Peak exposures to main components of ash and gaseous diesel exhausts in closed and open ash loading stations at biomass-fuelled power plants. *Chemosphere* **2017**, *185*, 183-191.
287. Evic, N.; Brunner, T.; Obernberger, I. In *Prediction of Biomass Ash Melting Behaviour - Correlation between the Data Obtained from Thermodynamic Equilibrium Calculations and Simultaneous Thermal Analysis*, 20th European Biomass Conference and Exhibition, Milan, Italy, Milan, Italy, 2012.

288. McNallan, M. J.; Yurek, G. J.; Elliot, J. F., The formation of inorganic particulates by homogeneous nucleation in gases produced by the combustion of coal. *Combustion and Flame* **1981**, *42*, 45-60.
289. Kunz, M.; Xirouchakis, D.; Lindsley, D. H.; Haeusermann, D., High-pressure phase transition in titanite (CaTiOSiO₄). *American Mineralogist* **1996**, *81* (11-12), 1527-1530.
290. Ruth, L. A., Energy from municipal solid waste: a comparison with coal combustion technology. *Progress in Energy and Combustion Science* **1998**, *24* (6), 545-564.
291. Zhang, J.; Richardson, H. W., Copper Compounds. In *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley: 2000; pp 1-31.
292. Shibasaki, Y., Synthesis of orthorhombic CrOOH and the reaction mechanism. *Materials Research Bulletin* **1972**, *7* (10), 1125-1133.
293. Kohler, K.; Maciejewski, M.; Schneider, H.; Baiker, A., Chromia supported on titania: V. Preparation and characterization of supported CrO₂, CrOOH, and Cr₂O₃. *Journal of Catalysis* **1995**, *157* (2), 301-311.
294. Caplan, D.; Cohen, M., The Volatilization of Chromium Oxide. *Journal of the Electrochemical Society* **1961**, *108* (5), 438-442.
295. Fryburg, G. C.; Miller, R. A.; Kohl, F. J.; Stearns, C. A., Volatile products in the corrosion of Cr, Mo, Ti, and four superalloys exposed to O₂ containing H₂O and gaseous NaCl. *Journal of the Electrochemical Society* **1977**, *124* (11), 1738-1743.
296. Kim, Y. W.; Belton, G. R., The thermodynamics of volatilization of chromic oxide: Part I. the species CrO₃ and CrO₂OH. *Metallurgical Transactions* **1974**, *5* (8), 1811-1816.
297. Ebbinghaus, B. B., Thermodynamics of gas phase chromium species: the chromium oxides, the chromium oxyhydroxides, and volatility calculations in waste incineration processes. *Combustion and Flame* **1993**, *93* (1-2), 119-137.
298. Opila, E. J.; Myers, D. L.; Jacobson, N. S.; Nielsen, I. M. B.; Johnson, D. F.; Olminky, J. K.; Allendorf, M. D., Theoretical and experimental investigation of the thermochemistry of CrO₂(OH)2(g). *The Journal of Physical Chemistry* **2006**, *111* (10), 1971-1980.
299. EU, DIRECTIVE 2010/75/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 24 November 2010 on industrial emissions (integrated pollution prevention and control). Union, E., Ed. Official Journal of the European Union: 2010.
300. Pettersson, J.; Asteman, H.; Svensson, J. E.; Johansson, L. G., KCl Induced Corrosion of a 304-type Austenitic Stainless Steel at 600°C; The Role of Potassium. *Oxidation of Metals* **2005**, *64* (1-2), 23-41.
301. Buxbaum, G., *Industrial Inorganic Pigments*. Second ed.; John Wiley and Sons: 2008.
302. Yang, H.; Zhang, X.; Huang, C.; Yang, W.; Qiu, G., Synthesis of ZnFe₂O₄ nanocrystallites by mechanochemical reaction. *Journal of Physics and Chemistry of Solids* **2004**, *65* (7), 1329-1332.
303. Morey, G. W.; Kracek, F. C.; Bowen, N. L., The ternary system K₂O-CaO-SiO₂. *Society of Glass Technology* **1930**, *14*, 149-187.
304. Bowen, N. L.; Schairer, J. F., The system, FeO-SiO₂. *American Journal of Science* **1932**, *141*, 177-213.
305. Rankin, G. A.; Wright, P. E., The ternary system CaO-Al₂O₃-Fe₂O₃. *American Journal of Science* **1915**, 1-79.
306. Snow, R. B.; McCaughey, W. J., Equilibrium Studies in the System FeO-Al₂O₃-SiO₂. *Journal of the American Ceramic Society* **1942**, *25* (6), 151-160.
307. Schairer, J. F., The system CaO-FeO-Al₂O₃-SiO₂: I, Results of quenching experiments on five joins. *Journal of the American Ceramic Society* **1942**, *25* (10), 241-274.
308. Öhman, M.; Nordin, A.; Skrifvars, B.-J.; Backman, R.; Hupa, M., Bed agglomeration characteristics during fluidized bed combustion of biomass fuels. *Energy and Fuels* **2000**, *14* (1), 169-178.
309. Öhman, M.; Nordin, A., The role of kaolin in prevention of bed agglomeration during fluidized bed combustion of biomass fuels. *Energy and Fuels* **2000**, *14* (3), 618-624.
310. Lindström, E.; Boström, D.; Öhman, M. In *Effect of kaolin and limestone addition on slag formation during combustion of woody biomass pellets*, European Biomass Conference and Exhibition, ETA - Renewable Energies: 2005.

311. Niu, Y.; Wang, Z.; Zhu, Y.; Zhang, X.; Tan, H.; Hui, S. e., Experimental evaluation of additives and K₂O–SiO₂–Al₂O₃ diagrams on high-temperature silicate melt-induced slagging during biomass combustion. *Fuel* **2016**, *179*, 52-59.
312. Jandačka, J.; Malcho, M.; Ochodek, T.; Koloničný, J.; Holubčík, M., The increase of silver grass ash melting temperature using additives. *International Journal of Renewable Energy Research* **2015**, *5* (1), 258-265.
313. Anicic, B.; Lin, W.; Dam-Johansen, K.; Wu, H., Agglomeration mechanism in biomass fluidized bed combustion–reaction between potassium carbonate and silica sand. *Fuel Processing Technology* **2018**, *173*, 182-190.
314. Ma, X.; Ren, T.; Kong, D.; Nie, Y.; Xu, J.; Pang, M.; Xu, G., Effect of Additives on Potassium Distribution during Rice Straw Combustion. In *2011 Asia-Pacific Power and Energy Engineering Conference*, IEEE: 2011.
315. Roth, R. S., *Phase Diagram for Ceramists*. The American Ceramic Society: Westerville, OH, USA, 1995; Vol. 11.
316. Hansen, L. A.; Nielsen, H. P.; Frandsen, F. J.; Dam-Johansen, K.; Hørlyck, S.; Karlsson, A., Influence of deposit formation on corrosion at a straw-fired boiler. *Fuel Processing Technology* **2000**, *64* (1-3), 189-209.
317. Jensen, P. A.; Frandsen, F. J.; Hansen, J.; Dam-Johansen, K.; Henriksen, N.; Hørlyck, S., SEM investigation of superheater deposits from biomass-fired boilers. *Energy & fuels* **2004**, *18* (2), 378-384.
318. Scandrett, L. A. The removal of alkali compounds from gases at high temperatures. University of Cambridge, 1983.
319. Boström, D.; Boström, M.; Lindström, E.; Boman, C.; Backman, R.; Öhman, M.; Grimm, A. In *Ash transformation chemistry during energy conversion of biomass*, Impact of Fuel Quality on Power production and the Environment, 2010.
320. Sonwane, P. B. Speciation of Alkali Metals in Biomass Combustion and Gasification. University of Alabama, 2006.
321. Dai, B.-Q.; Wu, X.; Girolamo, A. D.; Zhang, L., Inhibition of lignite ash slagging and fouling upon the use of a silica-based additive in an industrial pulverised coal-fired boiler. Part 1. Changes on the properties of ash deposits along the furnace. *Fuel* **2015**, *139*, 720-732.
322. Kostakis, G., Mineralogical composition of boiler fouling and slagging deposits and their relation to fly ashes: The case of Kardias power plant. *Journal of hazardous materials* **2011**, *185* (2-3), 1012-1018.
323. Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vassileva, C. G., An overview of the composition and application of biomass ash. Part 1. Phase–mineral and chemical composition and classification. *Fuel* **2013**, *105*, 40-76.
324. Rashid, R. A.; Shamsudin, R.; Hamid, M. A. A.; Jalar, A., Low temperature production of wollastonite from limestone and silica sand through solid-state reaction. *Journal of Asian Ceramic Societies* **2014**, *2* (1), 77-81.
325. Gokhale, S. D.; Jolly, W. L., Phosphine. *Inorganic Syntheses* **1967**, *9*, 56-58.
326. Pan, Y.; Huang, J.-L.; Shao, C. Y., Preparation of β -TCP with high thermal stability by solid reaction route. *Journal of Material Science* **2003**, *38* (5), 1049-1056.
327. Sinyaev, V. A.; Shustikova, E. S.; Levchenko, L. V.; Tokseitova, G. A.; Griggs, D., Nature and thermal behavior of precipitated calcium-magnesium phosphates. *Russian Journal of Applied Chemistry* **2003**, *76* (9), 1375-1378.
328. Castillo, M.; Ayers, R. A.; Zhang, X.; Schowengerdt, F.; Moore, J. J., Combustion synthesis of porous glasses and ceramics for bone repair. *Biomedical Sciences Instrumentation* **2001**, *37*, 469-474.
329. Wee, H. L.; Wu, H.; Zhang, D.-k.; French, D., The effect of combustion conditions on mineral matter transformation and ash deposition in a utility boiler fired with a sub-bituminous coal. *Proceedings of the Combustion Institute* **2005**, *30* (2), 2981-1989.
330. Hansen, P. F. B.; Andersen, K. H.; Wieck-Hansen, K.; Overgaard, P.; Rasmussen, I.; Frandsen, F. J.; Hansen, L. A.; Dam-Johansen, K., Co-firing straw and coal in a 150-MWe utility boiler: in situ measurements. *Fuel Processing Technology* **1998**, *54* (1-3), 207-225.

331. Kalisz, S.; Ciukaj, S.; Tymoszek, M.; Kubiczek, H., Fouling and its mitigation in PC boilers co-firing forestry and agricultural biomass. *Heat Transfer Engineering* **2015**, *36* (7-8), 763-770.
332. Barišić, V.; Åmand, L.-E.; Zabetta, E. C. In *The role of limestone in preventing agglomeration and slagging during CFB combustion of high phosphorus fuels*, World Bioenergy, Jönköping, Sweden, Jönköping, Sweden, 2008.
333. Boman, C.; Öhman, M.; Nordin, A., Trace element enrichment and behavior in wood pellet production and combustion processes. *Energy & fuels* **2006**, *20* (3), 993-1000.
334. James, D. W.; Krishnamoorthy, G.; Benson, S. A.; Seames, W. S., Modeling trace element partitioning during coal combustion. *Fuel processing technology* **2014**, *126*, 284-297.
335. Groves, S. J.; Williamson, J.; Sanyal, A., Decomposition of pyrite during pulverized coal combustion. *Fuel* **1987**, *66* (4), 461-466.
336. Zeng, T.; Sarofim, A. F.; Senior, C. L., Vaporization of arsenic, selenium and antimony during coal combustion. *Combustion and Flame* **2001**, *126* (3), 1714-1724.
337. Seames, W. S., An initial study of the fine fragmentation fly ash particle mode generated during pulverized coal combustion. *Fuel Processing Technology* **2003**, *81* (2), 109-125.
338. Gupta, M.; Yang, J.; Roy, C., Specific Heat and Thermal Conductivity of Softwood Bark and Softwood Char Particles. *Fuel* **2003**, *82* (8), 919-927.
339. Tinaut, F. V.; Melgar, A.; Pérez, J. F.; Horrillo, A., Effect of biomass particle size and air superficial velocity on the gasification process in a downdraft fixed bed gasifier. An experimental and modelling study. *Fuel Processing Technology* **2008**, *89* (11), 1076-1089.
340. M. W. Chase, J., NIST-JANAF Thermochemical Tables. *Journal of Physical and Chemical Reference Data* **1998**.
341. Gurvich, L. V.; Veyts, I. V.; Alcock, C. B., *Thermodynamic Properties of Individual Substances*. Hemisphere: New York, 1989; Vol. 1-2.
342. Ouelhazi, N.; Arnaud, G.; Fohr, J. P., A Two Dimensional Study of Wood Plank Drying. The Effect of Gaseous Pressure below Boiling Point. *Transport in Porous Media* **1992**, *7*, 36-91.
343. Lee, C. K.; Chaiken, R. F.; Singer, J. M., Charring Pyrolysis of Wood in Fires by Laser Simulation. *Symposium (International) on Combustion* **1977**, *16* (1), 1459-1470.
344. Uribe, F. J.; Mason, E. A.; Kestin, J., Thermal Conductivity of Nine Polyatomic Gases at Low Density. *Journal of Physical and Chemical Reference Data* **1990**, *19* (5), 1123-1136.
345. Blais, N. C.; Mann, J. B., Thermal Conductivity of Helium and Hydrogen at High Temperatures. *The Journal of Chemical Physics* **1960**, *32* (5), 1459-1465.
346. Brain, T. J. S., Thermal Conductivity of Steam at Atmospheric Pressure. *Journal of Mechanical Engineering* **1969**, *11* (4), 10.
347. Reid, R. C.; Prausnitz, J. M.; Poling, B. E., *The Properties of Gases and Liquids*. 4th ed.; McGraw-Hill: New York, 1987.
348. Prausnitz, J. M.; Benson, P. R., Effective collision diameters and correlation of some thermodynamic properties of solutions. *AIChE Journal* **1959**, *5* (3), 301-303.
349. Massman, W. J., A Review of the Molecular Diffusivities of H₂O, CO₂, CH₄, CO, O₃, SO₂, NH₃, N₂O, NO, and NO₂, in Air, O₂ and N₂ near STP. *Atmospheric Environment* **1998**, *32* (6), 17.
350. Gronli, M. G., Mathematical Model for Wood Pyrolysis - Comparison of Experimental Measurements with Model Predictions. *Energy & Fuels* **2000**, *14*, 791-800.
351. Wassiljewa, A., Heat Conduction in Gaseous Mixtures. *Physikalische Zeitschrift* **1904**, *5* (22), 737-742.
352. Weber, S., The Heat Conductivity of Gas Mixtures. *Ann. d. Physik* **1917**, *54*, 325.
353. Kennard, E. H., *Kinetic Theory of Gases*. McGraw-Hill Book Co: New York, 1938.
354. Lindsay, A. L.; Bromley, L. A., Thermal Conductivity of Gas Mixtures. *Industrial and Engineering Chemistry* **1950**, *42* (8), 1508-1511.
355. Graham, T., XXVIII On the Motion of Gases. *Philosophical Transactions of the Royal Society of London* **1846**, *136*, 573-631.
356. Fairbanks, D. F.; Wilke, C. R., Diffusion Coefficients in Multicomponent Gas Mixtures. *Industrial and Engineering Chemistry* **1950**, *42* (3), 5.
357. Herning, F.; Zipperer, L., Calculation of the Viscosity of Technical Gas Mixtures from the Viscosity of the Individual Gases. *Gas u. Wasserfach* **1936**, *79*, 69.
358. Brokaw, R. S. *Viscosity of Gas Mixtures*; NASA: Washington D.C., 1968.

359. Yrjölä, J.; Paavilainen, J.; Sillanpää, M., Modelling and experimental studies on heat transfer in the convection section of a biomass boiler. *International Journal of Energy Research* **2006**, 30 (12), 939-953.
360. Ranz, W. E.; W. R. Marshall, J., Evaporation from Drops Part I. *Chemical Engineering Progress* **1952**, 48 (3), 5.
361. Dryer, F. L.; Glassman, I., High-temperature oxidation of CO and CH₄. In *Symposium (International) on combustion*, Elsevier: 1973; Vol. 14, pp 987-1003.
362. Jones, W. P.; Lindstedt, R. P., Global reaction schemes for hydrocarbon combustion. *Combustion and flame* **1988**, 73 (3), 233-249.
363. Di Blasi, C., Combustion and gasification rates of lignocellulosic chars. *Progress in Energy and Combustion Science* **2009**, 35 (2), 121-140.
364. Aarsen, F. G. V. D.; Beenackers, A. A. C. M.; Swaaij, W. P. M. V., *Wood Pyrolysis and Carbon Dioxide Char Gasification Kinetics in a Fluidized Bed*. Springer: Dordrecht, 1985; p 15.
365. Barrio, M.; Hustad, J. E., CO₂ Gasification of Birch Char and the Effect of CO Inhibition on the Calculation of Chemical Kinetics. *Progress in Thermochemical Biomass Conversion* **2008**, 47.
366. Kojima, T.; Assavadakorn, P.; Furusawa, T., Measurement and Evaluation of Gasification Kinetics of Sawdust Char with Steam in an Experimental Fluidized Bed. *Fuel Processing Technology* **1993**, 36 (1-3), 201-207.
367. Janse, A. M. C.; Jonge, H. G. d.; Prins, W.; Swaaij, W. P. M. v., Combustion Kinetics of Char Obtained by Flash Pyrolysis of Pine Wood. *Industrial and Engineering Chemistry Research* **1998**, 37 (10), 10.
368. Neville, M.; Sarofim, A. F., The Fate of Sodium during Pulverized Coal Combustion. *Fuel* **1985**, 64 (3), 384-390.
369. Takata, T.; Yamaguchi, A.; Fukuzawa, K.; Matsubara, K., Numerical Methodology of Sodium-Water Reaction with Multiphase Flow Analysis. *Nuclear Science and Engineering* **2017**, 150 (2), 221-236.
370. Holland, T. J. B., The Reaction Albite = Jadeite + Quartz Determined Experimentally in the Range 600-1200 C. *American Mineralogist* **1980**, 65 (1-2), 129-134.
371. Çelik, Ö.; Damcı, E.; Pişkin, S., Characterization of Fly Ash and Its Effect on the Compressive Strength Properties of Portland Cement. *Indian Journal of Engineering and Material Sciences* **2008**, 15, 433-440.
372. Öhman, M.; Boman, C.; Hedman, H.; Nordin, A.; Boström, D., Slagging tendencies of wood pellet ash during combustion in residential pellet burners. *Biomass and Bioenergy* **2004**, 27 (6), 585-596.
373. Fournier, V.; Marcus, P.; Olefjord, I., Oxidation of magnesium. *Surface and Interface Analysis* **2002**, 34 (1), 494-497.
374. Rotheron, R. N.; Hornsby, P. R., Flame Retardant Effects of Magnesium Hydroxide. *Polymer Degradation and Stability* **1996**, 54 (2-3), 383-385.
375. Anthony, J. W.; Bideaux, R. A.; Bladh, K. W.; Nichols, M. C., *Handbook of Mineralogy*. Mineral Data Publishing: 1995; Vol. 2.
376. French, R. J.; Dayton, D. C.; Milne, T. A. *The Direct Observation of Alkali Vapor Species in Biomass Combustion and Gasification*; National Renewable Energy Lab: Golden, CO, 1994.
377. Steenari, B. M.; Lindqvist, O., High-temperature Reactions of Straw Ash and the Anti-sintering Additives Kaolin and Dolomite. *Biomass and Bioenergy* **1998**, 14 (1), 67-76.
378. Simeone, E.; Nacken, M.; Haag, W.; Heidenreich, S.; de Jong, W., Filtration performance at high temperatures and analysis of ceramic filter elements during biomass gasification. *Biomass and Bioenergy* **2011**, 35, S87-S104.
379. Fagerström, J.; Näzelius, I.-L.; Gilbe, C.; Boström, D.; Öhman, M.; Boman, C., Influence of Peat Ash Composition on Particle Emissions and Slag Formation in Biomass Grate Co-combustion. *Energy & Fuels* **2014**, 28 (5), 3403-3411.
380. Gulyurtlu, I.; Pinto, F.; Lopes, H. M.; Andre, R. N.; Dias, M.; Cabrita, I. In *Prediction of H₂S and HCl Formation during RDF and Co-gasification in Fluidized Bed*, 16th European Biomass Conference and Exhibition, Valencia Spain, Valencia Spain, 2008.
381. Fagerstrom, J.; Rebbling, A.; Olwa, J.; Steinvall, E.; Bostrom, D.; Ohman, M.; Boman, C. In *Control Strategies for Reduction of Alkali Release during Grate Combustion of Biomass - Influence*

of Process Parameters and Fuel Additives in a 40 kW Reactor, Impacts of Fuel Quality, Snowbird, UT, Snowbird, UT, 2014.

382. Farber, M.; Srivastava, R. D., Thermochemical reactions of aluminum and fluorine in hydrogen-oxygen flames. *Combustion and Flame* **1976**, 27, 99-105.

383. Farber, M.; Srivastava, R. D.; Frisch, M. A.; Harris, S. P., Mass spectrometer studies of Al + H₂O reactions in effusion cells and in atmospheric H₂ + O₂ flames. *Faraday Symposia of the Chemical Society* **1973**, 8, 121-130.

384. MgO–MgAl₂O₄, T. s., The system MgO–MgAl₂O₄. *Journal of the American Ceramic Society* **1962**, 45 (6), 263-268.

385. Rivas Mercury, J. M.; De Aza, A. H.; Pena, P., Synthesis of CaAl₂O₄ from powders: Particle size effect. *Journal of the European Ceramic Society* **2005**, 25 (14), 3269-3279.

386. Traoré, K.; Kabré, T. S.; Blanchart, P., Gehlenite and anorthite crystallisation from kaolinite and calcite mix. *Ceramics International* **2003**, 29 (4), 377-383.

387. Belton, G. R.; Richardson, F. D., A Volatile Iron Hydroxide. *Transactions of the Faraday Society* **1962**, 58, 1562-1572.

388. Thompson, M. d. K., The reaction between iron and water in the absence of oxygen. *Transactions of the Electrochemical Society* **1940**, 78 (1), 251-257.

389. Darken, L. S.; Gurry, R. W., The system iron-oxygen. I. The wüstite field and related equilibria. *Journal of the American Chemical Society* **1945**, 67 (8), 1398-1412.

390. Lay, V. The Affect of Ash Chemistry and Deposits from Co-firing Biomass and Coal in Power Plant Systems. Loughborough University, 2016.

391. Masao, K., Conditions for the Formation of Fe₃O₄ by the Air Oxidation of Fe(OH)₂ Suspensions. *Bulletin of the Chemical Society of Japan* **1974**, 47 (7), 1646-1650.

392. Wang, J.; Tomita, A., A Chemistry on the Volatility of Some Trace Elements during Coal Combustion and Pyrolysis. *Energy and Fuels* **2003**, 17 (4), 954-960.

393. Sandelin, K.; Backman, R. *Equilibrium distribution of arsenic, chromium, and copper when burning impregnated wood*; Aabo Akademi: 2000.

394. Wang, C.; Liu, H.; Zhang, Y.; Zou, C.; Anthony, E. J., Review of arsenic behavior during coal combustion: Volatilization, transformation, emission and removal technologies. *Progress in Energy and Combustion Science* **2018**, 68, 1-28.

395. Germani, M. S.; Zoller, W. H., Vapor-phase concentrations of arsenic, selenium, bromine, iodine, and mercury in the stack of a coal-fired power plant. *Environmental Science and Technology* **1988**, 22 (9), 1079-1085.

396. Jadhav, R. A.; Fan, L.-S., Capture of gas-phase arsenic oxide by lime: kinetic and mechanistic studies. *Environmental Science and Technology* **2001**, 35 (4), 747-799.

397. Gluskoter, H. J.; Lindahl, P. C., Cadmium: Mode of Occurrence in Illinois Coals. *Science* **1973**, 181 (4096), 264-266.

398. Ambriz, J. J.; Ducarroir, M.; Sibieude, F., Preparation of cadmium by thermal dissociation of cadmium oxide using solar energy. *International Journal of Hydrogen Energy* **1982**, 7 (2), 143-153.

399. Sen, P.; Hedge, M. S.; Rao, C. N. R., Surface oxidation of cadmium, indium, tin and antimony by photoelectron and Auger spectroscopy. *Applications of Surface Science* **1982**, 10 (1), 63-74.

400. Deng, S.; Shi, Y.; Liu, Y.; Zhang, C.; Wang, X.; Cao, Q.; Li, S.; Zhang, F., Emission characteristics of Cd, Pb and Mn from coal combustion: Field study at coal-fired power plants in China. *Fuel Processing Technology* **2014**, 126, 469-475.

401. Friswell, N. J.; Jenkins, D. R., Identification of lead compounds in flames and determination of the PbO bond energy. *Combustion and Flame* **1972**, 19 (2), 197-201.

402. Galbreath, K. C.; Zygarlicke, C. J., Formation and chemical speciation of arsenic-, chromium-, and nickel-bearing coal combustion PM_{2.5}. *Fuel Processing Technology* **2004**, 85 (6-7), 701-726.

403. Bhangare, R. C.; Ajmal, P. Y.; Sahu, S. K.; Pandit, G. G.; Puranik, V. D., Distribution of trace elements in coal and combustion residues from five thermal power plants in India. *International Journal of Coal Geology* **2011**, 86 (4), 349-356.

404. Pradniak, P., *Handbook of Inorganic Chemicals*. McGraw-Hill Publications: 2002.

405. Foote, H. W.; Smith, E. K., On the Dissociation Pressures of Certain Oxides of Copper, Cobalt, Nickel, and Antimony. *Journal of the American Ceramic Society* **1908**, 30 (9), 1344-1350.

406. Johnston, H. L.; Marshall, A. L., Vapor pressures of nickel and of nickel oxide. *Journal of the American Chemical Society* **1940**, 62 (6), 1382-1390.
407. Belton, G. R., The gaseous hydroxides of cobalt and nickel. *The Journal of Physical Chemistry* **1967**, 71 (12), 4114-4120.
408. Helble, J. J.; Sarofim, A. F., Trace element behavior during coal combustion. *American Chemical Society Division Fuel Chemistry* **1993**, 28, 257-257.
409. Frandsen, F.; Dam-Johansen, K.; Rasmussen, P., Trace Elements from Combustion and Gasification of Coal - An Equilibrium Approach. *Progress in Energy and Combustion Science* **1994**, 20 (2), 115-138.
410. Zhang, J.; Zhang, W.; Zhang, L.; Gu, S., Mechanism of vanadium slag roasting with calcium oxide. *International Journal of Mineral Processing* **2015**, 138, 20-29.
411. Elled, A.-L.; Amand, L.-E.; Eskilsson, D., Fate of zinc during combustion of demolition wood in a fluidized bed boiler. *Energy Fuels* **2008**, 22 (3), 1519-1526.
412. Greenwood, N. N.; Earnshaw, A., *Chemistry of the Elements*. Elsevier: 2012.
413. Linak, W. P.; Wendt, J. O. L., Toxic metal emissions from incineration: mechanisms and control. *Progress in Energy and Combustion Science* **1993**, 19 (2), 145-185.
414. Zhou, J.; Luo, Z.; Hu, C.; Cen, K., Factors impacting gaseous mercury speciation in postcombustion. *Energy Fuels* **2007**, 21 (2), 491-495.
415. Suwarnakar, N. D.; Nemade, S. N.; Thorat, P. V.; Gaikwad, S. G., Synthesis and Characterization of Sodium Tripolyphosphate. *Journal for Research* **2017**, 3 (5), 20-23.
416. Rakotomahanina-Rolaisoa, E.; Averbuch-Pouchot, M.-T.; Durif-Varambon, A., Rakotomahanina-Rolaisoa, Emile, Marie-Thérèse Averbuch-Pouchot, and André Durif-Varambon. "Données cristallographiques sur les triphosphates du type $\text{MIINa}_3\text{P}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$ pour $\text{MII} = \text{Ni, Co, Mn, Mg, Zn et Cd}$. *Bulletin de Minéralogie* **1972**, 95 (4), 516-520.
417. Vrbka, L.; Vondrášek, J.; Jagoda-Cwiklik, B.; Vácha, R.; Jungwirth, P., Quantification and rationalization of the higher affinity of sodium over potassium to protein surfaces. *Proceedings of the National Academy of Sciences* **2006**, 103 (42), 15440-15444.
418. Ust'yantsev, V. M.; Tretnikova, M. G.; Kelareva, E. I.; Mangalova, L. I., Reaction of sodium metaphosphate with magnesium and calcium oxides and their mixtures. *Refractories* **1978**, 19 (5-6), 317-325.
419. Uspensky, A. B.; Ralys, R.; Kremnev, D.; Radin, M.; Slobodov, A., Thermodynamic physico-chemical modelling and calculation for the synthesis process of modern functional materials. *IOP Conference Series: Materials Science and Engineering* **2017**, 175 (1).
420. Shiratsuchi, T.; Okada, S.; Yamaki, J.; Nishida, T., FePO_4 cathode properties for Li and Na secondary cells. *Journal of Power Sources* **2006**, 159 (1), 268-271.
421. Wilhelmy, R. B.; Matijević, E., Preparation and growth kinetics of monodispersed ferric phosphate hydrosols. *Colloids and Surfaces* **1987**, 22 (2), 97-110.
422. Tarr, B. R.; Booth, H. S.; Dolance, A., Anhydrous Iron(III) Chloride. In *Inorganic Syntheses*, Audrieth, L. F., Ed. McGraw-Hill Book Company, Inc: 1950; Vol. 3, pp 191-194.
423. Taylor, B. E.; Liou, J. G., The low-temperature stability of andradite in COH fluids. *American Mineralogist* **1978**, 63 (3-4), 378-393.
424. Jing, N.-j.; Wang, Q.-h.; Yang, Y.-k.; Cheng, L.-m.; Luo, Z.-y.; Cen, K.-f., Influence of ash composition on the sintering behavior during pressurized combustion and gasification process. *Journal of Zhejiang University Science A* **2012**, 13 (3), 230-238.
425. Porbatzki, D.; Stemmler, M.; Müller, M., Release of inorganic trace elements during gasification of wood, straw, and miscanthus. *Biomass and Bioenergy* **2011**, 35, S79-S86.
426. Saxena, S. K.; Chatterjee, N., Thermochemical data on mineral phases: the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. *Journal of Petrology* **1986**, 27 (4), 827-842.
427. Carlson, W. D., Evidence against the stability of orthoenstatite above $\sim 1005^\circ\text{C}$ at atmospheric pressure in CaO-MgO-SiO_2 . *Geophysical Research Letters* **1985**, 12 (7), 409-411.
428. Nagai, T.; Maeda, M., Thermodynamic Measurement of Phosphates by Double Knudsen Cell Mass Spectrometry. *ECS Transactions* **2013**, 46 (1), 313-318.
429. Morris, R. A.; Viggiano, A. A., Chemistry of PO^- , PO^{2-} , and PO^{3-} in the Gas Phase. *The Journal of Chemical Physics* **1998**, 109 (10), 4126-4127.

430. Valley, J. W.; Essene, E. J., Akermanite in the Cascade Slide xenolith and its significance for regional metamorphism in the Adirondacks. *Contribution to Mineralogy and Petrology* **1980**, 74, 143-152.
431. Plane, J. M. C.; Rollason, R. J., Kinetic study of the reactions of CaO with H₂O, CO₂, O₂, and O₃: Implications for calcium chemistry in the mesosphere. *The Journal of Physical Chemistry A* **2001**, 105 (29), 7047-7056.
432. Hirota, K.; Bradt, R. C., Sintering and synthesis of the pseudobrookite oxide (Fe₂TiO₅) by the solid state reaction. *Analytical Sciences* **1991**, 7, 1275-1278.
433. Ku, Y.; Liu, Y.-C.; Chiu, P.-C.; Kuo, Y.-L.; Tseng, Y.-H., Mechanism of Fe₂TiO₅ as oxygen carrier for chemical looping process and evaluation for hydrogen generation. *Ceramics International* **2014**, 40 (3), 4599-4605.
434. Karkhanavala, M. D.; Momin, A. C., Subsolidus Reactions in the System Fe₂O₃-TiO₂. *Journal of the American Ceramic Society* **1959**, 42 (8), 399-402.

Appendix

Appendix A: Individual Property Equations

Appendix A contains the calculations of properties of all solids, moisture, gases incorporated in biomass combustion. The incorporated solids are wood, tar, char, ash. The incorporated gases are $\text{CH}_{4(\text{g})}$, $\text{CO}_{(\text{g})}$, $\text{CO}_{2(\text{g})}$, $\text{H}_{2(\text{g})}$, $\text{H}_2\text{O}_{(\text{g})}$, $\text{O}_{2(\text{g})}$ and $\text{N}_{2(\text{g})}$.

Appendix A.1 Heat Capacities of Solids, Liquids, and Gases

The heat capacities of wood, tar, char, and ash are calculated via Equations A.1, A.2, A.3, and A.4.^{338,339}

$$c_{P_{\text{wood}}} = 2400 - 2500e^{-0.004T} \quad (\text{EA.1})$$

$$c_{P_{\text{tar}}} = 506 + 1.16T - 0.000116T^2 - \frac{0.00000333}{T^2} \quad (\text{EA.2})$$

$$c_{P_{\text{char}}} = 1430 + 0.355T - \frac{0.000000732}{T^2} \quad (\text{EA.3})$$

$$c_{P_{\text{ash}}} = -5e^{-10}T^4 + 3e^{-6}T^3 + 1e^{-10}T^3 - 0.0054T^2 + 4.156T - 173.39 \quad (\text{EA.4})$$

$$c_{P_{\text{H}_2\text{O}_{(\text{l})}}} = (0.0003T^2 - 0.1768T + 104.12)0.018 \quad (\text{EA.5})$$

$c_{P_{\text{wood}}}$, $c_{P_{\text{tar}}}$, $c_{P_{\text{char}}}$, $c_{P_{\text{ash}}}$, and $c_{P_{\text{H}_2\text{O}_{(\text{l})}}}$ are the heat capacities of wood, tar, char, ash and water as moisture in $\text{J kg}^{-1} \text{K}^{-1}$. Ash mainly consists of calcium, silicon, and potassium. Nevertheless, the heat capacity of ash is assumed equal to the heat capacity of $\text{SiO}_{2(\text{s})}$ to avoid needless complexity.³⁴⁰ T is the temperatures of the respective materials in K. The gas heat capacities are calculated via Equation A.6.

$$c_{P_i} = A_{c_{P_i}}T^6 + B_{c_{P_i}}T^5 + C_{c_{P_i}}T^4 + D_{c_{P_i}}T^3 + E_{c_{P_i}}T^2 + F_{c_{P_i}}T + G_{c_{P_i}} \quad (\text{EA.6})$$

i is a gas compound, e.g. $\text{CH}_{4(\text{g})}$, $\text{CO}_{(\text{g})}$, $\text{CO}_{2(\text{g})}$, $\text{H}_{2(\text{g})}$, $\text{H}_2\text{O}_{(\text{g})}$, $\text{O}_{2(\text{g})}$, and $\text{N}_{2(\text{g})}$. c_{P_i} is the heat capacity of gas i in $\text{J kg}^{-1} \text{K}^{-1}$. The values of $A_{c_{P_i}}$, $B_{c_{P_i}}$, $C_{c_{P_i}}$, $D_{c_{P_i}}$, $E_{c_{P_i}}$, $F_{c_{P_i}}$, and $G_{c_{P_i}}$ for each gas i are listed in Table A.1.

Table A.1 Combustion Gas Heat Capacity Parameters

i	$A_{c_{P_i}}$	$B_{c_{P_i}}$	$C_{c_{P_i}}$	$D_{c_{P_i}}$	$E_{c_{P_i}}$	$F_{c_{P_i}}$	$G_{c_{P_i}}$
$\text{CH}_{4(g)}^{341}$	1e-18	-2e-14	1e-10	-7e-8	-0.0014	5.0649	781.64
$\text{CO}_{(g)}^{340}$	3e-19	-5e-15	4e-11	-1e-7	0.0001	0.1814	969.51
$\text{CO}_{2(g)}^{340}$	-5e-19	1e-14	-9e-11	4e-7	-0.001	1.4528	498.41
$\text{H}_{2(g)}^{340}$	2e-18	-5e-14	4e-10	-2e-6	0.0044	-2.6327	14831
$\text{H}_2\text{O}_{(g)}^{340}$	7e-19	-1e-14	1e-10	-4e-7	0.0007	0.2511	1699.6
$\text{O}_{2(g)}^{340}$	-2e-19	6e-15	-5e-11	2e-7	-0.0005	0.7238	719.64
$\text{N}_{2(g)}^{340}$	9e-20	-2e-15	9e-12	-6e-9	-0.0001	0.3948	879.11

Appendix A.2 Thermal Conductivities of Solids and Gases

The thermal conductivities of solids comprise the conductive and radiative thermal conductivities. The conductive thermal conductivities of wood depend on moisture mass fractions as calculated in Equation A.7.

$$x_{m_{\text{H}_2\text{O}_{(l)}}} = \frac{\rho_{\text{H}_2\text{O}_{(l)}}}{\rho_{\text{wood}} + \rho_{\text{tar}} + \rho_{\text{char}} + \rho_{\text{H}_2\text{O}_{(l)}} + \sum_{i=1}^n \rho_i} \quad (\text{EA.7})$$

$x_{m_{\text{H}_2\text{O}_{(l)}}}$ is the $\text{H}_2\text{O}_{(l)}$ mass fraction.

The conductive thermal conductivities of wood are calculated via Equation A.8.³⁴²

$$k_{\text{con}_{\text{wood}}} = \left(0.0932 + 0.0065x_{m_{\text{H}_2\text{O}_{(l)}}}\right) (1 + 0.00365T) \left(0.986 + 2.695x_{m_{\text{H}_2\text{O}_{(l)}}}\right) \quad (\text{EA.8})$$

$k_{\text{con}_{\text{wood}}}$ is the conductive thermal conductivity of wood in $\text{W m}^{-1} \text{K}^{-1}$. The conductive thermal conductivities of char and ash are estimated via Equations A.9 and A.10.³⁴³

$$k_{\text{con}_{\text{char}}} = 0.071 \quad (\text{EA.9})$$

$$k_{\text{con}_{\text{ash}}} = 1.4 \quad (\text{EA.10})$$

$k_{\text{con}_{\text{char}}}$ and $k_{\text{con}_{\text{ash}}}$ are the conductive thermal conductivities of char and ash in $\text{W m}^{-1} \text{K}^{-1}$. $k_{\text{con}_{\text{ash}}}$ is the conductive thermal conductivity of $\text{SiO}_{2(s)}$. The conductive thermal conductivities of gases are calculated via Equations A.11 for $\text{CH}_{4(g)}$, A.12 for $\text{CO}_{(g)}$, A.13 for $\text{CO}_{2(g)}$, A.14 for $\text{H}_{2(g)}$, A.15 for $\text{H}_2\text{O}_{(g)}$, A.16 for $\text{O}_{2(g)}$, and A.17 for $\text{N}_{2(g)}$.^{344,345,346}

$$k_{conCH_4(g)} = \frac{-23.35 + 0.1698T + 0.00001893T^2}{1000} \quad (EA.11)$$

$$k_{conCO(g)} = -7e^{-9}T^2 + 7e^{-5}T + 0.004 \quad (EA.12)$$

$$k_{conCO_2(g)} = (-2.4 + 0.0216T - 0.000003244T^2) \left(\frac{418}{1000} \right) \quad (EA.13)$$

$$k_{conH_2(g)} = (1434 + 1.257(T - 1200)) \left(\frac{418}{1000} \right) \quad (EA.14)$$

$$k_{conH_2O(g)} = 0.0001T - 0.0228 \quad (EA.15)$$

$$k_{conO_2(g)} = 3e^{-5}T + 0.05 \quad (EA.16)$$

$$k_{conN_2(g)} = -3e^{-16}T^4 + 2e^{-12}T^3 - 1e^{-8}T^2 + 0.00007T + 0.0053 \quad (EA.17)$$

$k_{conCH_4(g)}$, $k_{conCO(g)}$, $k_{conCO_2(g)}$, $k_{conH_2(g)}$, $k_{conH_2O(g)}$, $k_{conO_2(g)}$, and $k_{conN_2(g)}$ are the conductive thermal conductivities of CH_{4(g)}, CO_(g), CO_{2(g)}, H_{2(g)}, H_{2O(g)}, O_{2(g)}, and N_{2(g)} in W m⁻¹ K⁻¹.

Appendix A.3 Viscosities of Gases

The viscosities of gases are calculated via Equation A.18.

$$\mu_i = A_{\mu_i}T^2 + B_{\mu_i}T + C_{\mu_i} \quad (EA.18)$$

The values of A_{μ_i} , B_{μ_i} , and C_{μ_i} are listed in Table A.2.

Table A.2 Combustion Gas Viscosity Parameters

i	A_{μ_i}	B_{μ_i}	C_{μ_i}
CH _{4(g)}	0	3e-8	5e-6
CO _(g)	-6e-12	4e-8	8e-6
CO _{2(g)}	-9e-12	5e-8	2e-6
H _{2(g)}	3e-12	2e-8	5e-6
H _{2O(g)}	-4e-12	5e-8	4e-6
O _{2(g)}	-6e-12	5e-8	9e-6
N _{2(g)}	-4e-12	4e-8	8e-6

Appendix A.4 Molecular Collision Diameters of Gases

The molecular collision diameters, r_m , of gases are listed in Table A.3.

Table A.3 Combustion Gas Collision Diameters

i or j	r_m (Å)
CH _{4(g)} ³⁴⁷	3.758
CO _(g) ³⁴⁷	3.690
CO _{2(g)} ³⁴⁷	3.941
H _{2(g)} ³⁴⁸	3.55
H ₂ O _(g) ³⁴⁷	2.641
O _{2(g)} ³⁴⁷	3.467
N _{2(g)} ³⁴⁷	3.798

Appendix A.5 Interaction Energies of Gases

The interaction energies of gases are listed in Table A.4.³⁴⁹

Table A.4 Combustion Gas Interaction Energies

i or j	$\frac{E_{int i}}{k_B}$ or $\frac{E_{int j}}{k_B}$ (K)
CH _{4(g)}	154
CO _(g)	110
CO _{2(g)}	190
H _{2(g)}	38
H ₂ O _(g)	809.1
O _{2(g)}	113
N _{2(g)}	99.8

k_B is the Boltzmann constant with a value of 1.38064852e-23 m² kg s⁻² K⁻¹.

Appendix A.6 Permeabilities of Solids

The permeabilities of solids are listed in Table A.5.

Table A.5 *Permeabilities of Solids*

i	η_i (Å)
Wood ³⁵⁰	1e-14
Char ³⁵⁰	1e-12
Ash	1e-12 (Assumption)

Appendix A.7 Emissivities of Solids

The emissivities of solids are listed in Table A.6.

Table A.6 *Emissivities of Solids*

i	ϵ_i
Wood ¹¹⁵	0.85
Char ¹¹⁵	0.95
Ash	0.95

Appendix B: Total Property Equations

Appendix B contains the calculations of the total value of the individual properties in Appendix A. The calculations include the development of the formulae over time.

Appendix B.1 Heat Capacities of Mixtures for Solids, Liquids, and Gases

The heat capacities, c_P , of the mixture for solids, liquids, and gases are calculated through a weighted average formula, as shown in Equation B.1.

$$c_P = \frac{\sum_{i_{sol}=1}^{n_{sol}} \rho_{i_{sol}} c_{P_{i_{sol}}} + \sum_{i_{liq}=1}^{n_{liq}} \rho_{i_{liq}} c_{P_{i_{liq}}} + \sum_{i_{gas}=1}^{n_{gas}} \rho_{i_{gas}} c_{P_{i_{gas}}}}{\sum_{i_{sol}=1}^{n_{sol}} \rho_{i_{sol}} + \sum_{i_{liq}=1}^{n_{liq}} \rho_{i_{liq}} + \sum_{i_{gas}=1}^{n_{gas}} \rho_{i_{gas}}} \quad (\text{EB.1})$$

$\rho_{i_{sol}}$, $\rho_{i_{liq}}$, and $\rho_{i_{gas}}$ are the densities of i of solids, liquids, and gases in kg m^{-3} . $c_{p_{i_{sol}}}$, $c_{p_{i_{liq}}}$, and $c_{p_{i_{gas}}}$ are the heat capacities of i of solids, liquids, and gases in $\text{J kg}^{-1} \text{K}^{-1}$. n_{sol} , n_{liq} , and n_{gas} are the last species of solids, liquids, and gases.

Appendix B.2 Conductive Thermal Conductivities for Mixtures of Solids and Liquids

The conductive thermal conductivities, k_{con} , of the mixture of the solids and liquids are calculated via Equation B.2 with a weighted-average formula.

$$k_{con} = \frac{\sum_{i_{sol}=1}^{n_{sol}} \rho_{i_{sol}} k_{i_{sol}} + \sum_{i_{liq}=1}^{n_{liq}} \rho_{i_{liq}} k_{i_{liq}}}{\rho_{i_{sol}} + \rho_{i_{liq}}} \quad (\text{EB.2})$$

$\rho_{i_{sol}}$ and $\rho_{i_{liq}}$ are the densities of i of solids and liquids in kg m^{-3} . $k_{i_{sol}}$ and $k_{i_{liq}}$ the thermal conductivities of i of solids and liquids in $\text{W m}^{-1} \text{K}^{-1}$. n_{sol} and n_{liq} are the last species of solids and liquids.

Appendix B.3 Conductive Thermal Conductivities for Mixtures of Gases

Several researchers developed the conductive thermal conductivity equation for gas mixtures. Wassiljewa³⁵¹ proposed a formula based on kinetic theory to calculate the conductive thermal conductivity of a binary mixture of gases A and B , as shown in Equation B.3.

$$k_{con} = \frac{k_{con_A}}{1 + A_{Wassiljewa_{AB}} \left(\frac{x_{n_B}}{x_{n_A}} \right)} + \frac{k_{con_B}}{1 + A_{Wassiljewa_{AB}} \left(\frac{x_{n_A}}{x_{n_B}} \right)} \quad (\text{EB.3})$$

k_{con_A} and k_{con_B} are the conductive thermal conductivities of gases A and B in $\text{W m}^{-1} \text{K}^{-1}$. $A_{Wassiljewa_{AB}}$ is the dimensionless Wassiljewa constant for a binary mixture of gases A and B . x_{n_A} and x_{n_B} are the molar fractions gases A and B . However, Weber³⁵² later proved that Equation B.3 was poorly validated with experimental results. Another conductive thermal conductivity formula for gas mixtures was introduced by Kennard, who proposed a polynomial equation as shown in Equation B.4.³⁵³

$$k_{con_{gas}} = k_{con_A} x_{n_A}^2 + K_{Kennard} x_{n_A} x_{n_B} + k_{con_B} x_{n_B}^2 \quad (\text{EB.4})$$

$K_{Kennard}$ is the Kennard constant, which is determined using the least-square method. However, Equation B.4 also failed to show satisfactory validation when tested against experimental results. Lindsay and Bromley³⁵⁴ later adopted Equation B.2 to develop a more accurate formula that is shown

in Equation B.5. Equation B.5 was used for the work described in this thesis since it had been proven to show good agreement with experimental results.

$$k_{con} = \sum_{i=1}^n \frac{k_{con_i}}{\frac{1}{x_{n_i}} \sum_{j=1, j \neq i}^n A_{Lindsay-Bromley_{ij}} x_{n_j}} \quad (EB.5)$$

k_{con_i} is the gas i thermal conductivity in $W m^{-1} K^{-1}$. x_{n_i} and x_{n_j} are the molar fractions of gases i and j . $A_{Lindsay-Bromley_{ij}}$ is the Lindsay-Bromley constant for a binary mixture of gases i and j , and is calculated via Equation B.6.

$$A_{Lindsay-Bromley_{ij}} = \frac{1}{4} \left(1 + \left(\frac{\mu_i}{\mu_j} \left(\frac{MW_j}{MW_i} \right)^{\frac{3}{4}} \left(\frac{1+S_i}{1+\frac{S_i}{T}} \right)^{\frac{1}{2}} \right)^2 \frac{\left(1+\frac{S_j}{T} \right)}{\left(1+\frac{S_i}{T} \right)} \right) \quad (EB.6)$$

μ_i and μ_j are the viscosities calculated in Appendix B.4 of gases i and j in Pa s. MW_i and MW_j are the molecular weights of gases i and j in $g mol^{-1}$. The Sutherland constants, S_i for gas i and S_j for gas j , are estimated via Equation B.7.

$$S_i = 1.5T_{i_B} \quad (EB.7)$$

T_{i_B} is the boiling temperature of compound i at 1 atm in K. For H_2 , 79 K is used.

Appendix B.4 Radiative Thermal Conductivities for Porous Solid

The radiative thermal conductivities for the mixture of the solids are calculated via Equation B.8.

$$k_{rad} = \frac{\varepsilon \sigma T^3 d_{pore}}{\epsilon} \quad (EB.8)$$

k_{rad} is the radiative thermal conductivities for the solid in $W m^{-1} K^{-1}$. d_{pore} is the solid pore diameter of biomass, assumed constant at $3.2e-6 m$.¹¹⁵ ε is the porosity of the solid. σ is the Stephan-Boltzmann constant or $5.670373e-8 W m^{-2} K^{-4}$. ϵ is the emissivity of the solid.

Appendix B.5 Viscosities for Mixtures of Gases

The viscosity equation for gas mixtures has been developed by previous researchers. Graham³⁵⁵ approximated the gas mixture viscosities using a weighted-average formula that is shown in Equation B.9.

$$\mu = \sum_{i=1}^n x_{n_i} \mu_i \quad (\text{EB.9})$$

μ is the viscosity of the mixture of gases in Pa s. x_{n_i} is the molar fraction of gas i . μ_i is the viscosity of gas i in Pa s. However, Equation B.9 is only accurate for mixtures of gas compounds with similar molecular weights. Fairbanks and Wilke³⁵⁶ later developed multi-component systems with a correlation based on kinetic theory. Their formula is shown in Equation B.10.

$$\mu = \sum_{i=1}^n \frac{x_{n_i} \mu_i}{x_{n_i} + \sum_{j=1, j \neq i}^n x_{n_j} A_{Wilke_{ij}}} \quad (\text{EB.10})$$

$A_{Wilke_{ij}}$ is the Wilke coefficient, which is calculated via Equation B.11. μ_j is the viscosity of gas j in Pa s. MW_i and MW_j are the molecular weights of gases i and j in g mol⁻¹.

$$A_{Wilke_{ij}} = \frac{\left(1 + \left(\frac{\mu_i}{\mu_j}\right)^{\frac{1}{2}} \left(\frac{MW_j}{MW_i}\right)^{\frac{1}{4}}\right)^2}{\frac{4}{\sqrt{2}} \left(1 + \frac{MW_i}{MW_j}\right)^{\frac{1}{2}}} \quad (\text{EB.11})$$

Herning and Zipperer³⁵⁷ had previously developed a more straightforward formula shown in Equation B.12.

$$\mu = \frac{\sum_{i=1}^n \mu_i x_{n_i} \sqrt{MW_i}}{\sum_{i=1}^n x_{n_i} \sqrt{MW_i}} \quad (\text{EB.12})$$

Equation B.12 is accurate for most gases, with an average deviation of 1.5%. However, Equation B.12 gives inadequate validation for H_{2(g)}-rich gases. Brokaw³⁵⁸ later solved the validation problem of H_{2(g)}-rich gases through development of another formula that showed a reduced average deviation of 0.7%. This formula is given in Equation B.13.

$$\mu = \sum_{i=1}^n \frac{x_{n_i} \sqrt{\mu_i}}{\frac{x_{n_i}}{\sqrt{\mu_i}} + \sum_{j=1, j \neq i}^n \frac{S_{Brokaw_{ij}} A_{Brokaw_{ij}} x_{n_i}}{\sqrt{\mu_j}}} \quad (\text{EB.13})$$

$S_{Brokaw_{ij}}$ and $A_{Brokaw_{ij}}$ are the Brokaw constants for binary mixtures of gases i and j . $S_{Brokaw_{ij}}$ and $A_{Brokaw_{ij}}$ are defined in Equations B.14 and B.15.

$$S_{Brokaw_{ij}} = \frac{r_{m_{ij}}^2}{r_{m_i} r_{m_j}} \quad (\text{EB.14})$$

$$A_{Brokaw_{ij}} = MW_{ij} \left(\frac{MW_j}{MW_i}\right)^{\frac{1}{2}} \left(1 + \frac{\frac{MW_i}{MW_j} \left(\frac{MW_i}{MW_j}\right)^{0.45}}{2 \left(1 + \frac{MW_i}{MW_j}\right) + \frac{1 + \left(\frac{MW_i}{MW_j}\right)^{0.45}}{1 + MW_{ij}}} MW_{ij}\right) \quad (\text{EB.15})$$

r_{m_i} and r_{m_j} are the molecular collision diameters of gases i and j in Å. r_m of the combustion gases are listed in Appendix A.4. $r_{m_{ij}}$ is the collision diameter of binary molecules in a mixture of gases i and j in Å. $r_{m_{ij}}$ is calculated via Equation B.16.

$$r_{m_{ij}} = \frac{1}{2}(r_{m_i} + r_{m_j}) \quad (\text{EB.16})$$

MW_{ij} is the combined molecular weight of gases i and j . MW_{ij} is estimated via Equation B.17.

$$MW_{ij} = \left(\frac{4MW_i MW_j}{(MW_i + MW_j)^2} \right)^{\frac{1}{4}} \quad (\text{EB.17})$$

Appendix B.6 Fick Diffusivities for Mixtures of Gases

The Fick diffusivity of mixtures of gases, D_{Fi} , in $\text{m}^2 \text{s}^{-1}$ is calculated in Equation B.18 as a function of individual gas i molar fractions.³⁵⁶

$$D_{Fi} = \frac{1 - x_{n_i}}{\sum_{\substack{j=1 \\ j \neq i}}^n \left(\frac{x_{n_j}}{D_{Fi_{ij}}} \right)} \quad (\text{EB.18})$$

x_{n_i} and x_{n_j} are the molar fractions of gases i and j . $D_{Fi_{ij}}$ is the Fick diffusivity for a binary mixture of gases i and j in $\text{m}^2 \text{s}^{-1}$. $D_{Fi_{ij}}$ is calculated via Equation B.19.

$$D_{Fi_{ij}} = \frac{0.00186T^{\frac{3}{2}}}{pr_{m_{ij}}^2\Omega} \left(\frac{1}{MW_i} + \frac{1}{MW_j} \right)^{\frac{1}{2}} \quad (\text{EB.19})$$

$r_{m_{ij}}$ is the molecular collision diameters of binary mixtures of gases i and j in Å and calculated in Equation B.16. p is the gas pressure in atm. MW_i and MW_j are the molecular weights of gases i and j in g mol^{-1} . Ω is the collision integral estimated visually through use of Figure B.1.

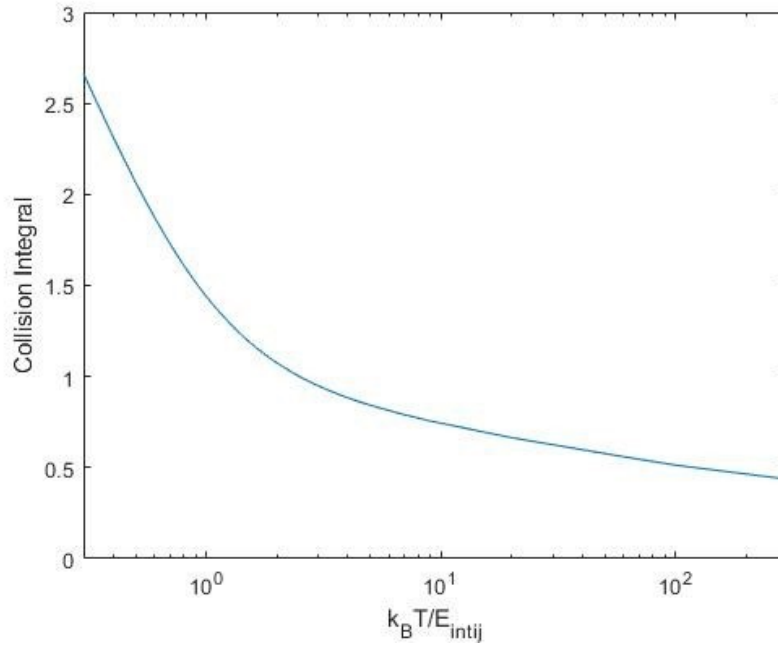


Figure B.1 Collision Integral as a Function of Temperature

On the x-axis, k_B is the Boltzmann constant with a value of $1.38064852 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$. E_{intij} is the interaction energy between gas i and gas j in J. E_{intij} is calculated via Equation B.20.

$$E_{intij} = \sqrt{E_{int_i} E_{int_j}} \quad (\text{EB.20})$$

E_{int_i} and E_{int_j} are the interaction energies of gases i and j in J. E_{int} of the combustion gases is listed in Appendix A.5.

Appendix B.7 Knudsen Diffusivities for Mixtures of Gases

The pore sizes influence the gas diffusivities, since the mean free path of the gas molecules might be within the lengths of pore sizes. The influence of the gas mean free path on gas diffusion is known as Knudsen diffusion. The Knudsen diffusivities for the mixture of gases are estimated via Equation B.21.

$$D_{Kn} = 4850 d_{pore} 100 \sqrt{\frac{T}{MW_i}} \quad (\text{EB.21})$$

D_{Kn} is the particle Knudsen diffusivity in $\text{m}^2 \text{ s}^{-1}$. d_{pore} is the pore size in cm. MW_i is the molecular weight of gas i in g mol^{-1} . T is the temperature of the gas mixtures in K

Appendix B.8 Porosities of Solids

The porosities of solid mixtures, ε , are assumed to show a linear correlation with densities of the solid mixtures, as calculated via Equation B.22.

$$\varepsilon = 1 - \frac{\rho}{\rho_0} (1 - \varepsilon_0) \quad (\text{EB.22})$$

ρ_0 is the initial solid density in kg m^{-3} . ε_0 is the initial solid porosity. ε_0 is assumed to equal 0.4.¹¹⁵

Appendix B.9 Permeabilities of Solids

The permeabilities of solid mixtures, η , are estimated through use of a weighted-average formula as shown in Equation B.23.³⁵⁰

$$\eta = \frac{\sum_{i=1}^n \rho_i \eta_i}{\sum_{i=1}^n \rho_i} \quad (\text{EB.23})$$

ρ_i is the density of solid i in kg m^{-3} . η_i is the permeability of solid i in m^2 .

Appendix B.10 Emissivities of Solids

To calculate the radiative heat transfer and radiative thermal conductivities of the particle surfaces, it is essential to know the emissivities of the particles. The radiative heat transfer at particle surfaces has a more significant impact on increases in particle temperature than the convective heat transfer.³⁵⁹ The emissivities of the particles are estimated with a weighted-average formula that is shown in Equation B.24.

$$\epsilon = \frac{\sum_{i=1}^n \rho_i \epsilon_i}{\rho_i} \quad (\text{EB.24})$$

ρ_i is the density of solid i in kg m^{-3} . ϵ_i is the emissivity of solid i in m^2 .

Appendix B.11 Reynold Number of Flowing Gas Passing a Cylindrical Particle

Reynold number, Re , calculated via Equation B.25 determines gas flow patterns surrounding particles, e.g. laminar flow or turbulent flow.

$$Re = \frac{d_p \rho v}{\mu} \quad (\text{EB.25})$$

d_p is the particle diameter in m. ρ is the gas density in kg m^{-3} . v is the gas velocity in m s^{-1} . μ is the gas viscosity in Pa s .

Appendix B.12 Nusselt Number of Flowing Gas Passing a Cylindrical Particle

Nusselt number, Nu , is defined as how much convective heat transfer is enhanced over conductive heat transfer at particle surfaces due to boundary gas motion. Numerous correlations of Nusselt number have been developed through evaluation of several parameters, e.g. forced convection, natural convection, turbulence, particle geometry, and boiler geometry. In the work described in this thesis, Equation B.26 was used to calculate Nu .³⁶⁰

$$Nu = 2 + 0.6Re^{\frac{1}{2}}Pr^{\frac{1}{3}} \quad (\text{EB.26})$$

Equation B.25 was primarily developed for spherical particles. Previously, the Nu correlation for cylindrical particles with infinite lengths was used in the current research. However, this correlation did not give good agreement with the experimental results. Thus, it was decided to use Equation B.23 for cylindrical particles under the assumption that the cylindrical particle aspect ratios were relatively small so that the particles behaved like spherical particles. Equation B.23 has been used in other research when it satisfies $0 \leq Re < 200$ and $0 \leq Pr < 250$. Re is the boundary gas Reynold number relative to particle positions. Pr is the boundary gas Prandtl number defined as the propensity of gas to flow according to its momentum diffusion or thermal diffusion. Pr is calculated via Equation B.27.

$$Pr = \frac{c_p \mu}{k_{con}} \quad (\text{EB.27})$$

c_p is the gas heat capacity in $\text{J kg}^{-1} \text{K}^{-1}$ and is estimated via Equation B.1. μ is the gas viscosity in Pa s and calculated via Equation B.13. k_{con} is the conductive thermal conductivity of the gas in $\text{W m}^{-1} \text{K}^{-1}$ and calculated via Equation B.5.

Appendix B.13 Sherwood Number of Flowing Gas Passing a Cylindrical Particle

Sherwood number, Sh , is defined as the effectiveness of mass convection at particle surfaces over mass conduction and the mass-transfer equivalent of Nu . Sh is calculated via Equation B.28.³⁶⁰

$$Sh = 2 + 0.6Re^{\frac{1}{2}}Sc^{\frac{1}{3}} \quad (\text{EB.28})$$

Sc is the Schmidt number and the mass-transfer equivalent of Pr . Sc is calculated via Equation B.29.

$$Sc = \frac{\mu}{D_{Fi}\rho} \quad (EB.29)$$

D_{Fi} is the gas Fick diffusivity in $\text{m}^2 \text{s}^{-1}$ and is calculated via Equation B.18. μ is the gas viscosity in Pa s and calculated via Equation B.13. ρ is the gas density in kg m^{-3} .

Appendix B.14 Reynold Number of Flowing Gas in a Column

Reynold number, Re , calculated via Equation B.30 determines gas flow patterns in a column, e.g. laminar flow or turbulent flow.

$$Re = \frac{d_c \rho v}{\mu} \quad (EB.30)$$

d_c is the column diameter in m. ρ is the gas density in kg m^{-3} . v is the gas velocity in m s^{-1} . μ is the gas viscosity in Pa s.

Appendix B.15 Nusselt Number of Flowing Gas in a Column

The Nusselt number, Nu , of gas flowing in a column is calculated via Equation

$$Nu = \begin{cases} 3.66 + \frac{0.065 Re Pr \frac{d_c}{h}}{1 + 0.04 \left(Re Pr \frac{d_c}{h} \right)^{\frac{2}{3}}}, & Re < 2300 \\ \frac{0.125 Re Pr^{\frac{1}{3}}}{(0.79 \log(Re) - 1.64)^2}, & Re \geq 2300 \end{cases} \quad (EB.30)$$

Re is the gas Reynold number calculated via Equation B.30. Pr is the gas Prandtl number calculated via Equation B.27. d_c is the column diameter in m. h is the column height in m.

Appendix C: Reaction Kinetics

Appendix C contains the kinetic equations and parameters of reactions incorporated in biomass combustion. The reactions are homogeneous reactions and heterogeneous reactions.

Appendix C.1 Drying

The kinetic equation for Reaction 4.1 is shown in Equation C.1 and C.2.

$$\frac{d\rho_{H_2O(l)}}{dt}_{(R4.1)} = -A_{(R4.1)} e^{\left(\frac{-E_{A(R4.1)}}{RT}\right)} \rho_{H_2O(l)} \quad (EC.1)$$

$$\frac{dT}{dt}_{(R4.1)} = \frac{d\rho_{H_2O(l)}}{dt}_{(R4.1)} \frac{\Delta H_{Rx,298K(R4.1)} + \int_{298}^T (c_{P_{H_2O(g)}} - c_{P_{H_2O(l)}}) dT}{\rho c_P} \quad (EC.2)$$

$\frac{d\rho_{H_2O(l)}}{dt}_{(R4.1)}$ is the rate of Reaction 4.1 in $\text{kg m}^{-3} \text{ s}^{-1}$. $A_{(R4.1)}$ is the pre-exponential factor of Reaction 4.1. $E_{A(R4.1)}$ is the activation energy of Reaction 4.1. The values of $A_{(R4.1)}$ and $E_{A(R4.1)}$ are $51.3\text{e}9 \text{ s}^{-1}$ and 88 kJ mol^{-1} , respectively. T is the temperature of the respective material in K. $\rho_{H_2O(l)}$ is the density of water in kg m^{-3} . $\frac{dT}{dt}_{(R4.1)}$ is the rate of temperature change due to Reaction 4.1 in K s^{-1} . The heat of Reaction 4.1, $\Delta H_{Rx,298K(R4.1)}$, is $2,440 \text{ kJ kg}^{-1}$. $c_{P_{H_2O(g)}}$ and $c_{P_{H_2O(l)}}$ are the heat capacities of $\text{H}_2\text{O}_{(g)}$ and $\text{H}_2\text{O}_{(l)}$, respectively. $c_{P_{H_2O(g)}}$ and $c_{P_{H_2O(l)}}$ are calculated via Equation A.6 and A.5. ρ and c_P are the density in kg m^{-3} and heat capacity in $\text{J kg}^{-1} \text{ K}^{-1}$ of the respective material.

Appendix C.2 Wood Pyrolysis

The kinetic equations for Reaction 4.2, 4.3, 4.4, 4.5, and 4.6 of wood pyrolysis with secondary cracking are shown in Equation C.3, C.4, C.5, C.6, C.7, C.8, C.9, C.10, C.11, and C.12.

$$\frac{d\rho_{gas}}{dt}_{(R4.2)} = A_{(R4.2)} e^{\left(\frac{-E_{A(R4.2)}}{RT}\right)} \rho_{wood} \quad (EC.3)$$

$$\frac{d\rho_{tar}}{dt}_{(R4.3)} = A_{(R4.3)} e^{\left(\frac{-E_{A(R4.3)}}{RT}\right)} \rho_{wood} \quad (EC.4)$$

$$\frac{d\rho_{char}}{dt}_{(R4.4)} = A_{(R4.4)} e^{\left(\frac{-E_{A(R4.4)}}{RT}\right)} \rho_{wood} \quad (EC.5)$$

$$\frac{d\rho_{gas}}{dt}_{(R4.5)} = -A_{(R4.5)} e^{\left(\frac{-E_{A(R4.5)}}{RT}\right)} \rho_{tar} \quad (EC.6)$$

$$\frac{d\rho_{char}}{dt}_{(R4.6)} = -A_{(R4.6)} e^{\left(\frac{-E_{A(R4.6)}}{RT}\right)} \rho_{tar} \quad (EC.7)$$

$$\frac{dT}{dt}_{(R4.2)} = -\frac{d\rho_{gas}}{dt}_{(R4.2)} \frac{\Delta H_{Rx,298K(R4.2)} + \int_{298}^T (\sum_{i=1}^n x_{m_{iwm}} c_{P_i} - c_{P_{wood}}) dT}{\rho c_P} \quad (EC.8)$$

$$\frac{dT}{dt}_{(R4.3)} = -\frac{d\rho_{tar}}{dt}_{(R4.3)} \frac{\Delta H_{Rx,298K(R4.3)} + \int_{298}^T (c_{P_{tar}} - c_{P_{wood}}) dT}{\rho c_P} \quad (EC.9)$$

$$\frac{dT}{dt}_{(R4.4)} = -\frac{d\rho_{char}}{dt}_{(R4.4)} \frac{\Delta H_{Rx,298K}(R4.4) + \int_{298}^T (c_{P, char} - c_{P, wood})dT}{\rho c_P} \quad (EC.10)$$

$$\frac{dT}{dt}_{(R4.5)} = -\frac{d\rho_{gas}}{dt}_{(R4.5)} \frac{\Delta H_{Rx,298K}(R4.5) + \int_{298}^T (\sum_{i=1}^n c_{P,i} - c_{P, tar})dT}{\rho c_P} \quad (EC.11)$$

$$\frac{dT}{dt}_{(R4.6)} = -\frac{d\rho_{char}}{dt}_{(R4.6)} \frac{\Delta H_{Rx,298K}(R4.6) + \int_{298}^T (c_{P, char} - c_{P, tar})dT}{\rho c_P} \quad (EC.12)$$

$\frac{d\rho_{gas}}{dt}_{(R4.2)}$, $\frac{d\rho_{tar}}{dt}_{(R4.3)}$, $\frac{d\rho_{char}}{dt}_{(R4.4)}$, $\frac{d\rho_{gas}}{dt}_{(R4.5)}$, and $\frac{d\rho_{char}}{dt}_{(R4.6)}$ are the rate of Reaction 4.2, 4.3, 4.4, 4.5, and 4.6 in $\text{kg m}^{-3} \text{s}^{-1}$. $\frac{dT}{dt}_{(R4.2)}$, $\frac{dT}{dt}_{(R4.3)}$, $\frac{dT}{dt}_{(R4.4)}$, $\frac{dT}{dt}_{(R4.5)}$, and $\frac{dT}{dt}_{(R4.6)}$ are the rate of temperature changes due to Reaction 4.2, 4.3, 4.4, 4.5, and 4.6. T is the temperature of the respective material in K. $x_{m_{i_{vm}}}$ is the mass fraction of gas i in the volatile matter. $c_{P, wood}$, $c_{P, tar}$, $c_{P, char}$, and $c_{P,i}$ are the heat capacities of wood, tar, char, and gas i and calculated individually in Appendix A. ρ and c_P are the density in kg m^{-3} and heat capacity in $\text{J kg}^{-1} \text{K}^{-1}$ of the respective material. The values of A , E_A , and $\Delta H_{Rx,298K}$ are listed in Table C.1.

Table C.1 Wood Pyrolysis Kinetic Parameters

Reaction	A (s^{-1})	E_A (J mol^{-1})	$\Delta H_{Rx,298K}$ (J kg^{-1})
(R4.2) ²²⁶	1.44e4	88.6e3	4.2e5
(R4.3) ²²⁶	4.13e6	11.27e4	4.2e5
(R4.4) ²²⁶	7.38e5	106.5e3	4.2e5
(R4.5) ²³⁰	4.28e6	10.75e4	-4e4
(R4.6) ²³¹	1e5	10.75e4	-4e4

The wood pyrolysis reaction is often simplified to Reaction 6.1 by removing tar formation and tar secondary cracking. This simplification mainly aims to improve the accuracy of mass balance. The parameters of Reactions 4.2, 4.3, 4.4, 4.5, and 4.6 might be subject to use of a certain variety of wood grown in a specific location and during a specific season. Any other wood variety might lead to a requirement for different reaction parameters that would be required to be generated from experimental measurement. Use of generalised reaction parameters might lead to inaccurate results. Gas and char formation rates, $\frac{d\rho_{gas}}{dt}_{(R6.1)}$ and $\frac{d\rho_{char}}{dt}_{(R6.1)}$, are calculated via Equations C.13 and C.14.

$$\frac{d\rho_{gas}}{dt}_{(R6.1)} = -x_1 A_{(R6.1)} e^{\left(\frac{-E_{A(R6.1)}}{RT}\right)} \rho_{wood} \quad (EC.13)$$

$$\frac{d\rho_{char}}{dt}_{(R6.1)} = -x_2 A_{(R6.1)} e^{\left(\frac{-E_{A(R6.1)}}{RT}\right)} \rho_{wood} \quad (EC.14)$$

x_1 is the ratio of the initial volatile matter density to the initial dry ash-free wood density. x_2 is the ratio of the initial fixed carbon density to the initial dry ash-free wood density. The temperature change rate due to Reaction 6.1 is calculated via Equation C.15.

$$\frac{dT}{dt}_{(R6.1)} = \frac{d\rho_{woodp}}{dt}_{(R6.1)} \frac{\Delta H_{Rx,298K(R6.1)} + \int_{298}^T (\sum_{i=1}^n c_{P_i} + c_{P_{char}} - c_{P_{wood}}) dT}{\rho c_P} \quad (EC.15)$$

$A_{(R4.2)}$, $E_{A(R4.2)}$, and $\Delta H_{Rx,298K(R4.1)}$ can be used as $A_{(R6.1)}$, $E_{A(R6.1)}$, and $\Delta H_{Rx,298K(R4.1)}$

Appendix C.3 Gas Homogeneous Reactions

The kinetic equations for Reaction 4.7, 4.8, and 4.9 for homogeneous gas reactions are shown in Equation C.16, C.17, C.18, C.19, C.20, and C.21.

$$\frac{d[CH_{4(g)}]}{dt}_{(R4.7)} = -A_{(R4.7)} e^{\left(\frac{-E_{A(R4.7)}}{RT}\right)} [CH_{4(g)}]^{0.7} [O_{2(g)}]^{0.8} \quad (EC.16)$$

$$\frac{d[CO_{(g)}]}{dt}_{(R4.8)} = -A_{(R4.8)} e^{\left(\frac{-E_{A(R4.8)}}{RT}\right)} [CO_{(g)}] [O_{2(g)}]^{0.25} [H_2O_{(g)}]^{0.5} \quad (EC.17)$$

$$\frac{d[H_{2(g)}]}{dt}_{(R4.9)} = -A_{(R4.9)} e^{\left(\frac{-E_{A(R4.9)}}{RT}\right)} [H_{2(g)}]^{0.25} [O_{2(g)}]^{1.5} \quad (EC.18)$$

$$\frac{dT}{dt}_{(R4.7)} = \frac{d[CH_{4(g)}]}{dt}_{(R4.7)} \frac{\Delta H_{Rx,298K(R4.7)} + \int_{298}^T \left(\frac{c_{P_{CO(g)}}}{\left(\frac{1000}{MW_{CO(g)}}\right)} + \frac{2c_{P_{H_2O(g)}}}{\left(\frac{1000}{MW_{H_2O(g)}}\right)} - \frac{c_{P_{CH_4(g)}}}{\left(\frac{1000}{MW_{CH_4(g)}}\right)} - \frac{1.5c_{P_{O_2(g)}}}{\left(\frac{1000}{MW_{O_2(g)}}\right)} \right) dT}{\rho c_P} \quad (EC.19)$$

$$\frac{dT}{dt}_{(R4.8)} = \frac{d[CO_{(g)}]}{dt}_{(R4.8)} \frac{\Delta H_{Rx,298K(R4.8)} + \int_{298}^T \left(\frac{c_{P_{CO_2(g)}}}{\left(\frac{1000}{MW_{CO_2(g)}}\right)} - \frac{c_{P_{CO(g)}}}{\left(\frac{1000}{MW_{CO(g)}}\right)} - \frac{0.5c_{P_{O_2(g)}}}{\left(\frac{1000}{MW_{O_2(g)}}\right)} \right) dT}{\rho c_P} \quad (EC.20)$$

$$\frac{dT}{dt}_{(R4.9)} = \frac{d[H_{2(g)}]}{dt}_{(R4.9)} \frac{\Delta H_{Rx,298K(R4.9)} + \int_{298}^T \left(\frac{c_{P_{H_2O(g)}}}{\left(\frac{1000}{MW_{H_2O(g)}}\right)} - \frac{c_{P_{H_2(g)}}}{\left(\frac{1000}{MW_{H_2(g)}}\right)} - \frac{0.5c_{P_{O_2(g)}}}{\left(\frac{1000}{MW_{O_2(g)}}\right)} \right) dT}{\rho c_P} \quad (EC.21)$$

$\frac{d[CH_{4(g)}]}{dt}_{(R4.7)}$, $\frac{d[CO_{(g)}]}{dt}_{(R4.8)}$, and $\frac{d[H_{2(g)}]}{dt}_{(R4.9)}$ are the rate of Reaction 4.7, 4.8, and 4.9. $\frac{dT}{dt}_{(R4.7)}$, $\frac{dT}{dt}_{(R4.8)}$, and $\frac{dT}{dt}_{(R4.9)}$ are the rate of temperature changes due to Reaction 4.7, 4.8, and 4.9. T is the temperature of the respective material in K. $c_{PCH_{4(g)}}$, $c_{PCO_{(g)}}$, $c_{PCO_{2(g)}}$, $c_{PH_{2(g)}}$, and $c_{PH_2O_{(g)}}$ are the heat capacities of $CH_{4(g)}$, $CO_{(g)}$, $CO_{2(g)}$, $H_{2(g)}$, and $H_2O_{(g)}$, calculated individually in Appendix A. ρ and c_P are the density in $kg\ m^{-3}$ and heat capacity in $J\ kg^{-1}\ K^{-1}$ of the respective material. $MW_{CH_{4(g)}}$, $MW_{CO_{(g)}}$, $MW_{CO_{2(g)}}$, $MW_{H_{2(g)}}$, $MW_{H_2O_{(g)}}$, and $MW_{O_{2(g)}}$ are the molecular weights of $CH_{4(g)}$, $CO_{(g)}$, $CO_{2(g)}$, $H_{2(g)}$, $H_2O_{(g)}$, and $O_{2(g)}$ in $g\ mol^{-1}$. The values of A , E_A , and $\Delta H_{Rx,298K}$ are listed in Table C.2.

Table C.2 Homogeneous Gas Reaction Kinetic Parameters

Reaction	A	E_A ($J\ mol^{-1}$)	$\Delta H_{Rx,298K}$ ($J\ mol^{-1}$)
(R4.7) ³⁶¹	1.58e10	202505.6	-519261
(R4.8) ³⁶¹	1.26e10	179912	-282984
(R4.9) ³⁶²	(3.82e13) T^{-1}	167360	-241818

Appendix C.4 Char Heterogeneous Reactions with Non-homogeneous Intra-particle Profile

The kinetic equations of the heterogeneous reactions of char as deduced in previous works have been compiled by Blasi.³⁶³ One or two of these compiled equations have been chosen for use in this thesis. However, there is no guarantee that the chosen equations are suitable for the single-particle combustion model. The chosen equations are taken from the work of Van den Aarsen *et al.*³⁶⁴ and Barrio and Hustad³⁶⁵ for $CO_{2(g)}$ gasification, Kojima *et al.*³⁶⁶ for $H_2O_{(g)}$ gasification, and Janse *et al.*³⁶⁷ for $O_{2(g)}$ combustion. These equations are used for the following reasons.

- The chemical and physical properties of the gasified biomass that was studied in these researches, i.e. birch wood, beechwood, and sawdust, are of the most common and typical woody biomass.
- The gasification was conducted within a reasonable range of temperature.
- The kinetic equations take into account the temperatures and partial pressures of the intra-particle gases, and the intra-particle char densities. Other kinetic equations are available, but they do not incorporate char density. The absence of intra-particle char densities could lead to misleading results when the molar ratio of available gas to stoichiometrically required gas is larger than unity.

The kinetic equations for Reactions 4.10, 4.11, and 4.12 are given by Equations C.22, C.23 and C.24 respectively of Van den Aarsen *et al.*³⁶⁴ and Barrio and Hustad³⁶⁵, and C.25.

$$\frac{d\rho_{char}}{dt}_{(R4.10)} = -A_{(R4.10)} e^{\left(\frac{-E_{A(R4.10)}}{RT}\right)} p_{O_{2(g)}}^{0.53} \rho_{char}^{0.49} \quad (EC.22)$$

$$\frac{d\rho_{char}}{dt}_{(R4.11)} = -\frac{A_{(R4.11)}}{T^{0.8}} e^{\left(\frac{-E_{A(R4.11)}}{RT}\right)} p_{CO_{2(g)}}^{0.8} \rho_{char}^{\frac{2}{3}} \quad (EC.23)$$

$$\frac{d\rho_{char}}{dt}_{(R4.11)} = -A_{(R4.11)} e^{\left(\frac{-E_{A(R4.11)}}{RT}\right)} p_{CO_{2(g)}}^{0.38} \rho_{char} \quad (EC.24)$$

$$\frac{d\rho_{char}}{dt}_{(R4.12)} = -A_{(R4.12)} e^{\left(\frac{-E_{A(R4.12)}}{RT}\right)} p_{H_2O_{(g)}}^{0.41} \rho_{char} \quad (EC.25)$$

T is the temperature of the entire material, e.g. the particle. $\frac{d\rho_{char}}{dt}_{(R4.10)}$, $\frac{d\rho_{char}}{dt}_{(R4.11)}$, and $\frac{d\rho_{char}}{dt}_{(R4.12)}$ are the rates of Reaction 4.10, 4.11, and 4.12. $p_{O_{2(g)}}$, $p_{CO_{2(g)}}$, and $p_{H_2O_{(g)}}$ are the pressures of $O_{2(g)}$, $CO_{2(g)}$, and $H_2O_{(g)}$ in Pa. ρ_{char} is the density of char in $kg\ m^{-3}$. The values of A , E_A , and $\Delta H_{Rx,298K}$ are listed in Table C.3.

Table C.3 Heterogeneous Gas Reaction Kinetic Parameters

Reaction	A	E_A (J mol ⁻¹)	$\Delta H_{Rx,298K}$ (J kg ⁻¹)
(R4.10) ³⁶⁷	5.3e5	1.25e5	-9.2e6
(R4.11) ³⁶⁴	9.1e6	1.66e5	1.4e7
(R4.11) ³⁶⁵	3.1e6	2.15e5	1.4e7
(R4.12) ³⁶⁶	1.7e3	1.79e5	1.1e7

The temperature change rates of the heterogeneous reactions, e.g. $\frac{dT}{dt}_{(R4.10)}$, $\frac{dT}{dt}_{(R4.11)}$, and $\frac{dT}{dt}_{(R4.12)}$, are calculated via Equations C.26, C.27, and C.27.

$$\frac{dT}{dt}_{(R4.10)} = \frac{d\rho_{char}}{dt}_{(R4.10)} \frac{\Delta H_{Rx,298K}(R4.10) + \frac{\int_{298}^T \left(\frac{c_{P_{CO(g)}}}{\left(\frac{1000}{MW_{CO(g)}}\right)} - \frac{c_{P_{char}}}{\left(\frac{1000}{MW_{char}}\right)} - \frac{0.5c_{P_{O_{2(g)}}}}{\left(\frac{1000}{MW_{O_{2(g)}}}\right)} \right) dT}{\rho c_p}} \quad (EC.26)$$

$$\frac{dT}{dt}_{(R4.11)} = \frac{d\rho_{char}}{dt}_{(R4.11)} \frac{\Delta H_{Rx,298K}(R4.11) + \frac{\int_{298}^T \left(\frac{2c_{PCO(g)}}{\left(\frac{1000}{MW_{CO(g)}}\right)} + \frac{c_{Pchar}}{\left(\frac{1000}{MW_{char}}\right)} - \frac{c_{PCO_2(g)}}{\left(\frac{1000}{MW_{CO_2(g)}}\right)} \right) dT}{\left(\frac{MW_{char}}{1000}\right) \rho c_P} \quad (EC.27)$$

$$\frac{dT}{dt}_{(R4.12)} = \frac{d\rho_{char}}{dt}_{(R4.12)} \frac{\Delta H_{Rx,298K}(R4.12) + \frac{\int_{298}^T \left(\frac{c_{PCO(g)}}{\left(\frac{1000}{MW_{CO(g)}}\right)} + \frac{c_{PH_2(g)}}{\left(\frac{1000}{MW_{H_2(g)}}\right)} + \frac{c_{Pchar}}{\left(\frac{1000}{MW_{char}}\right)} - \frac{c_{PH_2O(g)}}{\left(\frac{1000}{MW_{H_2O(g)}}\right)} \right) dT}{\left(\frac{MW_{char}}{1000}\right) \rho c_P} \quad (EC.28)$$

$c_{PCO(g)}$, $c_{PCO_2(g)}$, $c_{PH_2(g)}$, and $c_{PH_2O(g)}$ are the heat capacities of $CO_{(g)}$, $CO_{2(g)}$, $H_{2(g)}$, and $H_2O_{(g)}$, calculated individually in Appendix A. ρ and c_P are the density in $kg\ m^{-3}$ and heat capacity in $J\ kg^{-1}\ K^{-1}$ of the respective material. $MW_{CO(g)}$, $MW_{CO_2(g)}$, $MW_{H_2(g)}$, $MW_{H_2O(g)}$, and $MW_{O_2(g)}$ are the molecular weights of $CO_{(g)}$, $CO_{2(g)}$, $H_{2(g)}$, $H_2O_{(g)}$, and $O_{2(g)}$ in $g\ mol^{-1}$.

Appendix C.5 Char Heterogeneous Reactions with Lumped Intra-particle Profile

When the particle is not discretised because the intra-particle profiles are homogenously distributed due to relatively small particle sizes, the particle mass is used instead of the particle density, as shown in Equation C.29, C.30, and C.31.

$$\frac{dm_{char}}{dt}_{(R4.10)} = -\eta_{(R4.10)} A_{(R4.10)} e^{\left(\frac{-E_{A(R4.10)}}{RT}\right)} p_{O_2(g)ps}^{0.53} m_{char}^{0.49} \quad (EC.29)$$

$$\frac{dm_{char}}{dt}_{(R4.11)} = -\eta_{(R4.11)} \frac{A_{(R4.11)}}{T^{0.8}} e^{\left(\frac{-E_{A(R4.11)}}{RT}\right)} p_{CO_2(g)ps}^{0.8} m_{char}^{\frac{2}{3}} \quad (EC.30)$$

$$\frac{dm_{char}}{dt}_{(R4.12)} = -\eta_{(R4.12)} A_{(R4.12)} e^{\left(\frac{-E_{A(R4.12)}}{RT}\right)} p_{H_2O(g)ps}^{0.41} m_{char} \quad (EC.31)$$

$p_{O_2(g)ps}$, $p_{CO_2(g)ps}$, and $p_{H_2O(g)ps}$ are the partial pressures of $O_{2(g)}$, $CO_{2(g)}$, and $H_2O_{(g)}$ at the surface of the particle. $\eta_{(R4.10)}$, $\eta_{(R4.11)}$, and $\eta_{(R4.12)}$ are the effectiveness factors of Reactions 4.10, 3.11, and 4.12 and defined as the ratios of the actual reaction rate to the intrinsic reaction rate and calculated via Equations C.32, C.33, and C.34.

$$\eta_{(R4.10)} = \frac{3}{\phi_{(R4.10)}} \left(\frac{1}{\tanh \phi_{(R4.10)}} - \frac{1}{\phi_{(R4.10)}} \right) \quad (EC.32)$$

$$\eta_{(R4.11)} = \frac{3}{\phi_{(R4.11)}} \left(\frac{1}{\tanh \phi_{(R4.11)}} - \frac{1}{\phi_{(R4.11)}} \right) \quad (\text{EC.33})$$

$$\eta_{(R4.12)} = \frac{3}{\phi_{(R4.12)}} \left(\frac{1}{\tanh \phi_{(R4.12)}} - \frac{1}{\phi_{(R4.12)}} \right) \quad (\text{EC.34})$$

$\phi_{(R3.10)}$, $\phi_{(R3.11)}$, and $\phi_{(R3.12)}$ are estimated by use of Equations C.35, C.36, and C.37.

$$\phi_{(R4.10)} = \frac{L_{cp}}{6} \sqrt{\frac{\frac{1.53}{2} A_{(R4.10)} e^{\left(\frac{-E_{A(R4.10)}}{RT}\right)} m_{char}^{0.49} \left(\frac{m_{char}}{MW_{char}}\right)^{RT_{\infty}}}{p_{O_2(g)ps}^{0.47} V D_{eff O_2(g)}}} \quad (\text{EC.35})$$

$$\phi_{(R4.11)} = \frac{L_{cp}}{6} \sqrt{\frac{1.8 A_{(R4.11)} e^{\left(\frac{-E_{A(R4.11)}}{RT}\right)} m_{char}^{\frac{2}{3}} \left(\frac{m_{char}}{MW_{char}}\right)^{RT_{\infty}}}{p_{CO_2(g)ps}^{0.2} V D_{eff CO_2(g)}}} \quad (\text{EC.36})$$

$$\phi_{(R4.12)} = \frac{L_{cp}}{6} \sqrt{\frac{1.41 A_{(R4.12)} e^{\left(\frac{-E_{A(R4.12)}}{RT}\right)} m_{char} \left(\frac{m_{char}}{MW_{char}}\right)^{RT_{\infty}}}{p_{H_2O(g)ps}^{0.2} V D_{eff H_2O(g)}}} \quad (\text{EC.37})$$

T_{∞} is the bulk temperature in K. V is the volume of the particle. in m^3 . $D_{eff O_2(g)}$, $D_{eff CO_2(g)}$, and $D_{eff H_2O(g)}$ are the effective diffusivity coefficients of $O_{2(g)}$, $CO_{2(g)}$, and $H_2O_{(g)}$ and are calculated by use of Equation C.38 where i is a gas compound.

$$D_{eff i} = \frac{1}{\frac{1}{D_{Kn i}} + \frac{1}{D_{Fi i}}} \frac{\varepsilon}{\tau} \quad (\text{EC.38})$$

ε is the porosity of the particle. The tortuosity of the particle, τ , is estimated via Equation C.39.

$$\tau = \frac{1}{\varepsilon} \quad (\text{EC.39})$$

$D_{Fi i}$ is calculated via Equation B.18 as a function of $D_{Fi i j}$. $D_{Fi i j}$ and $D_{Kn i}$ is calculated by use of Equation B.19 and B.21, respectively, at mean temperature of bulk and particle, T_{pb} , calculated via Equation C.40.

$$T_{pb(b)} = \frac{T_{p(b)} + T_{b(a-1)}}{2} \quad (\text{EC.40})$$

Partial pressures of $O_{2(g)}$, $p_{O_2(g)ps}$, $CO_{2(g)}$, $p_{CO_2(g)ps}$, and $H_2O_{(g)}$, $p_{H_2O(g)ps}$, at the particle surface in Pa are calculated by use of Equations C.41, C.42, and C.43.

$$\frac{h_m}{RT_\infty} \left(p_{O_2(g)\infty} - p_{O_2(g)ps} \right) = \frac{0.5 \frac{dm_{char}}{dt} (R4.10)}{MW_{char} A} \quad (EC.41)$$

$$\frac{h_m}{RT_\infty} \left(p_{CO_2(g)\infty} - p_{CO_2(g)ps} \right) = \frac{\frac{dm_{char}}{dt} (R4.11)}{MW_{char} A} \quad (EC.42)$$

$$\frac{h_m}{RT_\infty} \left(p_{H_2O(g)\infty} - p_{H_2O(g)ps} \right) = \frac{\frac{dm_{char}}{dt} (R4.12)}{MW_{char} A} \quad (EC.43)$$

h_m is estimated through the Frössling formula as shown in Equation C.44.

$$h_m = \left(2 + 0.6 Re^{\frac{1}{2}} Sc^{\frac{1}{3}} \right) \frac{D_{Fi}}{L_c} \quad (EC.44)$$

L_c is the characteristic length of the particle in m. Re and Sc are calculated via Equation B.25 and B.29. $p_{O_2(g)ps(b)}$, $p_{CO_2(g)ps(b)}$, and $p_{H_2O(g)ps(b)}$ as shown in Equations C.41, C.42, and C.43 are rearranged and substituted in Equations C.29, C.30, and C.31, respectively. The rearrangements and substitutions generate Equations C.45, C.46, and C.47.

$$\frac{dm_{char}}{dt} (R4.10) = -\eta_{(R4.10)} A_{(R4.10)} e^{\left(\frac{-E_{A(R4.10)}}{RT} \right)} \left(p_{O_2(g)\infty} - \frac{\frac{dm_{char} p}{dt} (R4.10)}{K_{DO_2(g)}} \right)^{0.53} m_{char}^{0.49} \quad (EC.45)$$

$$\frac{dm_{char}}{dt} (R4.11) = -\eta_{(R4.11)} A_{(R4.11)} e^{\left(\frac{-E_{A(R4.11)}}{RT} \right)} \left(p_{CO_2(g)\infty} - \frac{\frac{dm_{char} p}{dt} (R4.11)}{K_{DCO_2(g)}} \right)^{0.8} m_{char}^{\frac{2}{3}} \quad (EC.46)$$

$$\frac{dm_{char}}{dt} (R4.12) = -\eta_{(R4.12)} A_{(R4.12)} e^{\left(\frac{-E_{A(R4.12)}}{RT} \right)} \left(p_{H_2O(g)\infty} - \frac{\frac{dm_{char} p}{dt} (R4.12)}{K_{DH_2O(g)}} \right)^{0.41} m_{char} \quad (EC.47)$$

$K_{DO_2(g)}$, $K_{DCO_2(g)p(b)}$, and $K_{DH_2O(g)p(b)}$ are calculated via Equations C.48, C.49, and C.50.

$$K_{DO_2(g)} = \frac{\left(\frac{MW_{char}}{1000} \right) Ah_m}{0.5 RT} \quad (EC.48)$$

$$K_{DCO_2(g)} = \frac{\left(\frac{MW_{char}}{1000} \right) Ah_m}{RT} \quad (EC.49)$$

$$K_{DH_2O(g)} = \frac{\left(\frac{MW_{char}}{1000} \right) Ah_m}{RT} \quad (EC.50)$$

The rates of temperature changes of the particle due to Reaction 4.10, 4.11, and 4.12 is calculated via Equation C.51 for Reaction 4.10, $\frac{dT}{dt}_{(R4.10)}$, Equation C.52 for Reaction 4.11, $\frac{dT}{dt}_{(R4.11)}$, and Equation C.53 for Reaction 4.12, $\frac{dT}{dt}_{(R4.12)}$.

$$\frac{dT}{dt}_{(R4.10)} = \frac{dm_{char}}{dt}_{(R4.10)} \frac{\Delta H_{Rx,298K}(R4.10) + \int_{298}^T \left(\frac{c_{PCO(g)}}{\left(\frac{1000}{MW_{CO}}\right)} - \frac{c_{Pchar}}{\left(\frac{1000}{MW_{char}}\right)} - \frac{0.5c_{PO_2(g)}}{\left(\frac{1000}{MW_{O_2}}\right)} \right) dT}{m_{CP}\left(\frac{MW_{char}}{1000}\right)} \quad (EC.51)$$

$$\frac{dT}{dt}_{(R4.11)} = \frac{dm_{char}}{dt}_{(R4.11)} \frac{\Delta H_{Rx,298K}(R4.11) + \int_{298}^T \left(\frac{2c_{PCO(g)}}{\left(\frac{1000}{MW_{CO}}\right)} - \frac{c_{Pchar}}{\left(\frac{1000}{MW_{char}}\right)} - \frac{c_{PCO_2(g)}}{\left(\frac{1000}{MW_{O_2}}\right)} \right) dT}{m_{CP}\left(\frac{MW_{char}}{1000}\right)} \quad (EC.52)$$

$$\frac{dT}{dt}_{(R4.12)} = \frac{dm_{char}}{dt}_{(R4.12)} \frac{\Delta H_{Rx,298K}(R4.12) + \int_{298}^T \left(\frac{c_{PCO(g)}}{\left(\frac{1000}{MW_{CO}}\right)} + \frac{c_{PH_2(g)}}{\left(\frac{1000}{MW_{H_2}}\right)} - \frac{c_{Pchar}}{\left(\frac{1000}{MW_{char}}\right)} - \frac{c_{PH_2O(g)}}{\left(\frac{1000}{MW_{H_2O}}\right)} \right) dT}{m_{CP}\left(\frac{MW_{char}}{1000}\right)} \quad (EC.53)$$

Appendix D: Falling Particle Velocity

The velocity, v_p , in $m\ s^{-1}$ of a particle falling co-currently with gas flowing downward in a column is calculated via Equation D.1.

$$v_p = \sqrt[2]{\frac{(m_p - V_p \rho_g)g}{0.5 \rho_g A_{proj_p} C_{Dp}}} + v_g \quad (ED.1)$$

m_p is the particle mass in kg. V_p is the particle volume in m^3 . ρ_g is the gas density in $kg\ m^{-3}$. A_{proj_p} is the particle projected area in m^2 . v_g is the gas velocity in $m\ s^{-1}$. C_{Dp} is the particle drag coefficient calculated in Equation D.2.

$$C_{Dp} = \begin{cases} \frac{24}{Re_p}, Re_p \leq 0.1 \\ \left(2\sqrt{\frac{24}{Re_p}} + 0.5407 \right)^2, 0.1 < Re_p \leq 6000 \\ 0.44, Re_p > 6000 \end{cases} \quad (ED.2)$$

Re_p is the particle Reynold number calculated via Equation D.3

$$Re_p = \frac{L_{cp} \rho_g (v_p - v_g)}{\mu_g} \quad (ED.3)$$

L_{cp} is the particle characteristic length in m. μ_g is the gas viscosity in Pa s. Equations D.1, D.2, and D.3 are solved simultaneously using trial-and-error to obtain v_p .

Appendix E: Particle Temperature Change due to Neglect of Element Initial Occurrence

Mass of 200-micron particle, $m_{p_{200\mu m}}$, of white wood is defined in Equation E.1 with unit of kg.

$$m_{p_{200\mu m}} = 1.09 * 10^{-9} \quad (\text{EE.1})$$

Heat capacity of 200-micron particle is calculated with wood heat capacity formula in Equation E.2 with unit on J kg⁻¹ K⁻¹.

$$c_{p_{p_{200\mu m}}} = 2400 - 2500e^{-0.004T_{p_{200\mu m}}} \quad (\text{EE.2})$$

2300 K as the maximum value of $T_{p_{200\mu m}}$ is used. Nevertheless, since particle temperature evolves during combustion, any temperature within the temperature profile could be used. $c_{p_{p_{200\mu m}}}$ at $T_{p_{200\mu m}}$ equal to 2300 K is 2399.16 J kg⁻¹ K⁻¹. Calcium is chosen as the evaluated element since calcium is the most abundant element in woody biomass. The main occurrence of calcium in woody biomass might be calcium oxalate, CaC₂O₄. The concentration of CaC₂O₄, $ppn_{CaC_2O_4_{p_{200\mu m}}}$, in the particle is 1260 ppm. The mass of CaC₂O₄, $m_{CaC_2O_4_{p_{200\mu m}}}$, in the particle is calculated in Equation E.3 with unit of kg.

$$m_{CaC_2O_4_{p_{200\mu m}}} = \frac{ppn_{CaC_2O_4_{p_{200\mu m}}} m_{p_{200\mu m}}}{10^6} \quad (\text{EE.3})$$

$m_{CaC_2O_4_{p_{200\mu m}}}$ is 1.37e-12 kg. CaC₂O₄ molar mass in mol is calculated in Equation E.4.

$$n_{CaC_2O_4_{p_{200\mu m}}} = \frac{m_{CaC_2O_4_{p_{200\mu m}}} 10^3}{MW_{CaC_2O_4}} \quad (\text{EE.4})$$

$n_{CaC_2O_4_{p_{200\mu m}}}$ is 1.07e-11 mol. The heat of CaC₂O₄ decomposition at 298 K is 1360600 J mol⁻¹. The heat of CaC₂O₄ decomposition at 2300 K or at any other $T_{p_{200\mu m}}$ is calculated in Equation E.5.

$$\Delta H_{F,T_{p_{200\mu m}}_{CaC_2O_4}} = \Delta H_{F,298K}_{CaC_2O_4} + \int_{298K}^{T_{p_{200\mu m}}} C_{p_{CaC_2O_4}}(T) dT \quad (\text{EE.5})$$

$\Delta H_{F,T_{p_{200\mu m}CaC_2O_4}}$ is in J mol⁻¹. $C_{p_{CaC_2O_4}}(T)$ is estimated constant in Equation E.6.

$$C_{p_{CaC_2O_4}}(T) = 152.4 \quad (\text{EE.6})$$

$\Delta H_{F,T_{p_{200\mu m}CaC_2O_4}}$ is 1665704.8 J mol⁻¹. Temperature reduction, $\Delta T_{T_{p_{200\mu m}p}}$, is calculated in Equation E.7.

$$\Delta T_{T_{p_{200\mu m}p}} = \frac{\Delta H_{F,T_{p_{200\mu m}CaC_2O_4}} n_{CaC_2O_4 p_{200\mu m}}}{m_{p_{200\mu m}} c_{p_{p_{200\mu m}}}} \quad (\text{EE.7})$$

$\Delta T_{T_{p_{200\mu m}p}}$ is 6.82 K.

Appendix F: Matlab-FactSage Integration Procedure

The chemical equilibrium calculations in FactSage are accommodated with the Equilib module available on the FactSage main window along with the other module, as shown in Figure F.1. The “Reactant” window shown in Figure F.2 pops up after pressing the Equilib Module button. In the “Reactant” window, six columns, in order from the left-hand side, show the molar mass, species, phase, temperature, pressure, and stream number. If the “Initial Conditions” box at the bottom right of the window is not ticked, it is not necessary to determine the contents of the phase, temperature, and pressure columns. The molar mass, species, and stream columns must be completed. Any additional species is added by pressing “Add a new Reactant”. Once all the reactant data requirements are fulfilled, the “Next” button at the bottom of the window is pressed to bring up the “Menu: last system” window, which is shown in Figure F.3. In the “Menu: last system” window, product phases are determined in the “Compound Species” tab by choosing “gas”, “pure liquids”, or “pure solids”. Equilibrium temperature and pressure is determined in the “Final Conditions” tab. The “Calculate” button at the bottom right of the window is pressed to bring up the “Results” window, which is shown in Figure F.4.

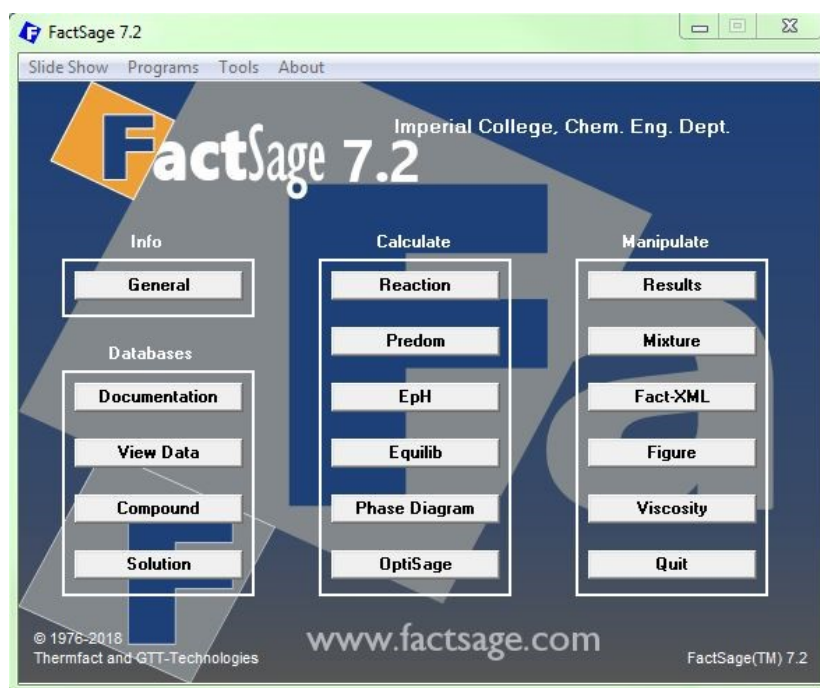


Figure F.1 FactSage Main Window

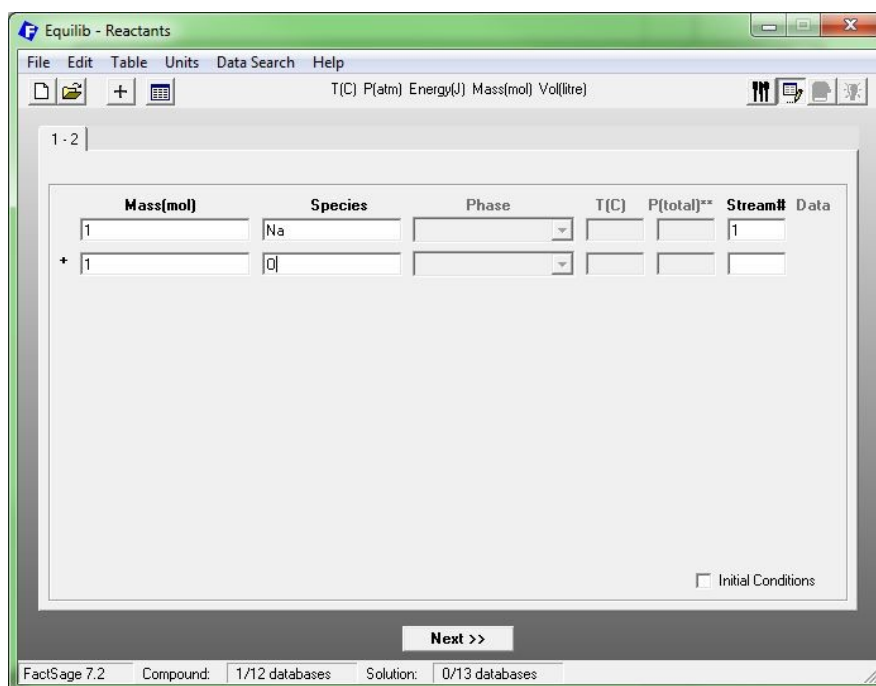


Figure F.2 FactSage Equilib Module “Reactant” Window

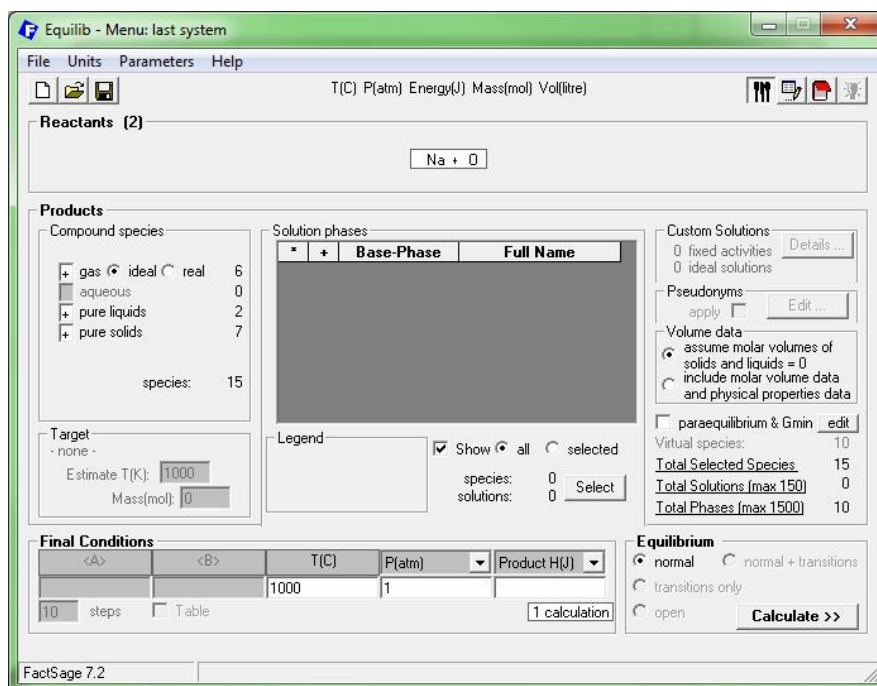


Figure F.3 FactSage Equilib Module “Menu: last system” Window

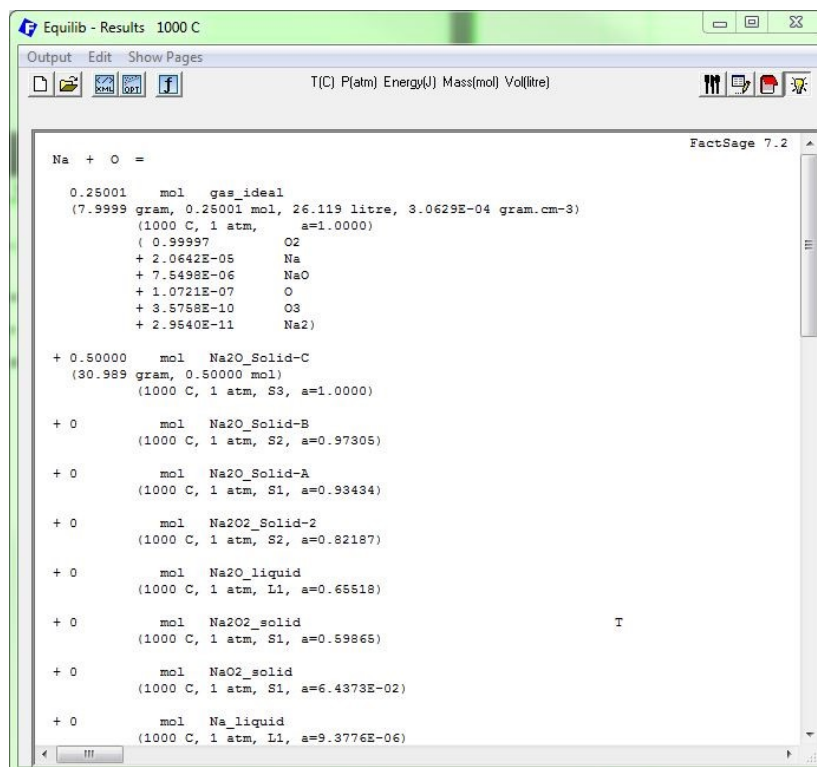


Figure F.4 FactSage Equilib Module “Results” Window

Equilib - List T(C) = 1000, P(atm) = 1 (Page 1/1)

File Edit Help

T(C) P(atm) Energy(J) Mass(mol) Vol(litre)

	Code	Species	Data	Phase	Mole	Fraction	Activity	Range	T	V
+	1	O(g)	FactPS	gas	2.6803E-08	1.0721E-07	1.0721E-07	25 - 5728		
+	2	O2(g)	FactPS	gas	0.2500	1.000	9.9997E-01	25 - 5728		v
+	3	O3(g)	FactPS	gas	8.9397E-11	3.5758E-10	3.5758E-10	25 - 5728		v
+	4	Na(g)	FactPS	gas	5.1607E-06	2.0642E-05	2.0642E-05	25 - 5728		
+	5	Na2(g)	FactPS	gas	7.3852E-12	2.9540E-11	2.9540E-11	25 - 5728		
+	6	NaO(g)	FactPS	gas	1.8875E-06	7.5498E-06	7.5498E-06	25 - 5728		
+	7	Na(liq)	FactPS	liquid			9.3776E-06	25 - 1328		
+	8	Na2O(liq)	FactPS	liquid			6.5518E-01	25 - 1227		
+	9	Na(s)	FactPS	solid			6.0169E-06	25 - 728	T	
+	10	NaO2(s)	FactPS	solid			6.4373E-02	25 - 1728		o
+	11	Na2O(s)	FactPS	Solid-A			9.3434E-01	25 - 1227		
+	12	Na2O(s2)	FactPS	Solid-B			9.7305E-01	25 - 1227		
+	13	Na2O(s3)	FactPS	Solid-C	0.5000		1.0000E+00	25 - 1227		
+	14	Na2O2(s)	FactPS	solid			5.9865E-01	25 - 513	T	
+	15	Na2O2(s2)	FactPS	Solid-2			8.2187E-01	25 - 2227		

Show

Species

☒ gas 6 ☒ duplicate

☒ liquid 2 ☐ selected 15

☐ aqueous 0

☐ solid 7

☐ solution 0 ☒ properties

Format

☒ mole

☐ gram

☐ pound

☐ data

☐ distribution

Post-Calculate

☐ activity

Order

☒ code

☐ amount

☐ fraction

☐ activity

Figure F.5 FactSage Equilib Module “List” Window

The “Results” window shows the occurrence and quantity of chemical equilibrium products. A more organised view of the result is presented in the “List” window by pressing the “List Window” button at the top right of the window. The “List” window is shown in Figure F.5. Automatic FactSage opening is commanded using a batch file executed with codes in a macro file. In Matlab, each line of the code is written in an m-file to imitate the macro file. The *fopen* function is used to create a blank macro file. The *fprintf* function rewrites these codes in the blank macro file. The *system* function reads the batch file to execute the calculation according to the commands in the created macro file. The output of this calculation is stored as an extensible markup language (xml) file. The *xmlread* function is used to translate the xml file characters into a Matlab array to obtain the output of the equilibrium calculation as extractable Matlab variables. An example of an m-file of this integration method is shown below for a system containing carbon, oxygen, and silicon. Each element molar mass is set at 1 mol at 1 atm and 773 K.

```
clear;
clc;

T=500; % unit in deg C
p=1; % unit in atm
n_C=1; % unit in mol
n_O=1; % unit in mol
n_Si=1; % unit in mol

% CREATE MACRO
row_1='VARIABLE %%Element %%Biomass';
row_2='VARIABLE %%Temp1 %%Pres1';
```

```

row_3='VARIABLE %%C1';
row_4='VARIABLE %%O1';
row_5='VARIABLE %%Si1';
row_6='%%Biomass Biomass';
row_7='%%Element ALL';
row_8=['%%Temp1 ',num2str(T)];
row_9=['%%Pres1 ',num2str(p)];
row_10=['%%C1 ',num2str(n_C)];
row_11=['%%O1 ',num2str(n_O)];
row_12=['%%Si1 ',num2str(n_Si)];
row_13='OPEN EquiGeneral.DAT';
row_14='SET REACTANT DEL K';
row_15='SET REACTANT ADD C SOLID #1';
row_16='SET REACTANT C MASS %%C1';
row_17='SET REACTANT ADD O SOLID #1';
row_18='SET REACTANT O MASS %%O1';
row_19='SET REACTANT ADD Si SOLID #1';
row_20='SET REACTANT Si MASS %%Si1';
row_21='SET SELECT GAS + FactPS';
row_22='SET SELECT SOLID + FactPS';
row_23='SET SELECT LIQUID + FactPS';
row_24='SET EQUILIBRIUM NORMAL';
row_25='SET FINAL T %%Temp1';
row_26='SET FINAL P %%Pres1';
row_27='CALC';
row_28='SAVE %%Biomass_%%Element.TXT';
row_29='SAVE Equi%%Biomass_%%Element.RES';
row_30='SAVE %%Biomass_%%Element.XML';
row_31='END';
fid=fopen('Combust4.mac','wt');
factsage_caller=fprintf(fid,[row_1 '\n' row_2 '\n' row_3 '\n' row_4 '\n' row_5 '\n'
row_6 '\n' row_7 '\n' row_8 '\n' row_9 '\n' row_10 '\n' row_11 '\n' row_12 '\n'
row_13 '\n' row_14 '\n' row_15 '\n' row_16 '\n' row_17 '\n' row_18 '\n' row_19 '\n'
row_20 '\n' row_21 '\n' row_22 '\n' row_23 '\n' row_24 '\n' row_25 '\n' row_26 '\n'
row_27 '\n' row_28 '\n' row_29 '\n' row_30 '\n' row_31]);

% RUN FACTSAGE
system('Run_Equilib_Combust4.bat');

% EXTRACT RESULT
xdoc=xmlread('Biomass_ALL.xml');
page=xdoc.getElementsByTagName('page');
child=page.item(0).getElementsByTagName('result');
Si_based_gas_molar_mass=zeros(1,8);
for i=1:1:numel(Si_based_gas_molar_mass)
    Si_based_gas_molar_mass(1,i)=str2double(char(child.item((i-
1)+12).getAttribute('n')));
end
Si_based_liquid_molar_mass=zeros(1,2);
for i=1:1:numel(Si_based_liquid_molar_mass)
    Si_based_liquid_molar_mass(1,i)=str2double(char(child.item((i-
1)+20).getAttribute('n')));
end
Si_based_solid_molar_mass=zeros(1,11);
for i=1:1:numel(Si_based_solid_molar_mass)
    Si_based_solid_molar_mass(1,i)=str2double(char(child.item((i-
1)+24).getAttribute('n')));
end

```

Appendix G: Chemical Equilibrium Function Surrogate

Creation of a chemical equilibrium function using MoDS requires a comprehensive procedure. The MoDS opening window is displayed first as shown in Figure G.1. On the blue background, the “New Project” button is pressed to open the “Create new project” window. Lists of existing projects are shown below the “New Project” button. In the “Create new project” window, shown in Figure G.2, the project name and directory are created. A project description is required to obtain brief project information. By pressing the “OK” button, the MoDS working window pops up as shown in Figure G.3. Model lists are displayed on the left-hand side box. A new model is initiated by pressing the “Add model” button.

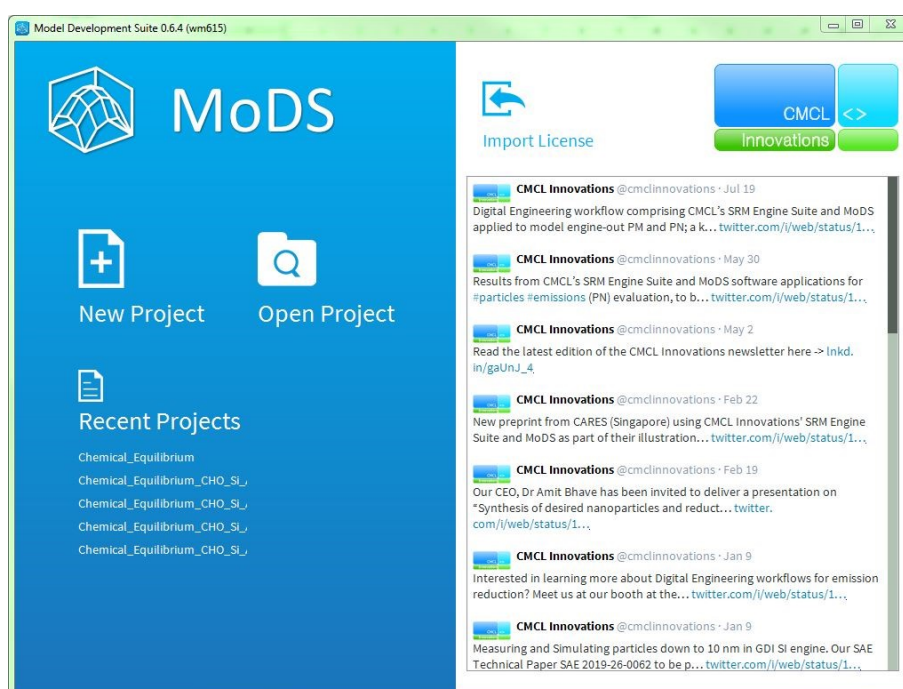


Figure G.1 MoDS Opening Window

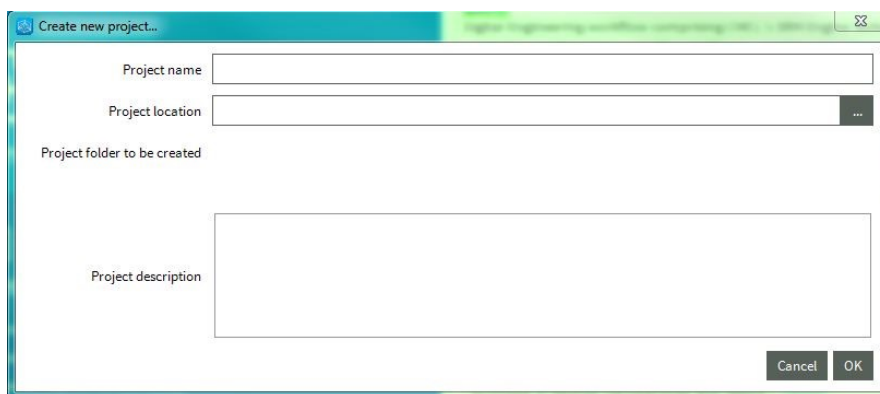


Figure G.2 MoDS “Create new project” Window

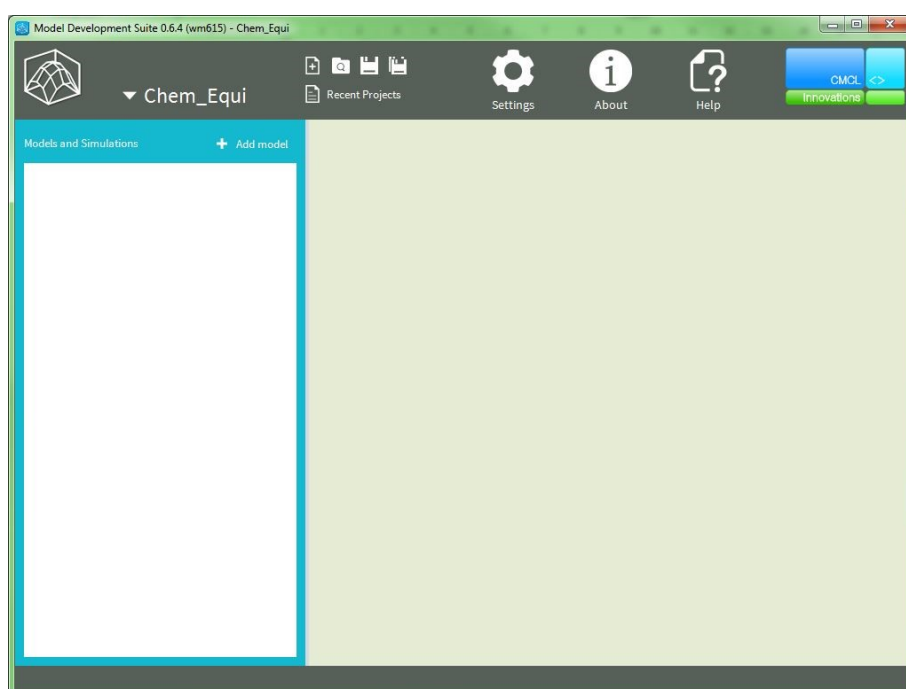


Figure G.3 MoDS Blank Working Window

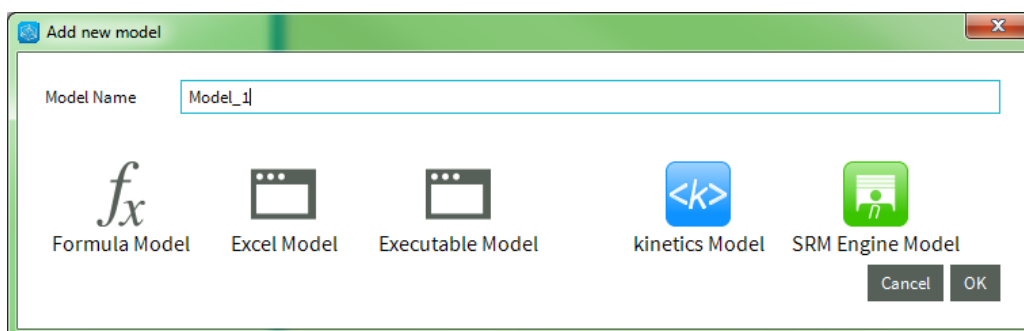


Figure G.4 MoDS “Add new model” Window

The “Add new model” window appears as shown in Figure G.4. “Executable Model” is chosen and named “Model_1”. After pressing the “OK” button, “Model_1” tabs appear on the right-hand side of the MoDS working window as shown in Figure G.5. The tabs are “Files”, “Input Variables”, and “Output Variables”. The “Files” tab contains files required to run FactSage. “Set input directory” is used to open an explorer window and assign the directory in which the files are located as the input directory. As shown in Figure G.6, the files are “Biomass_ALL.xml”, “combust4.mac”, and “Run_Equilib_Combust4.bat”. “Biomass_ALL.xml” is the xml file containing the result of a single FactSage chemical equilibrium calculation of the modelled elements at an arbitrary temperature, pressure, and concentration within the design range. The FactSage automatic run is activated with “Run_Equilib_Combust4.bat”. “Run_Equilib_Combust4.bat” is commanded with text code in “combust4.mac”; “combust4.mac” is based on a modified version of macro code in the first integration attempt to ensure MoDS compatibility with the macro file. “Run_Equilib_Combust4.bat” is chosen as the execution command by pressing “Set as the executable”.

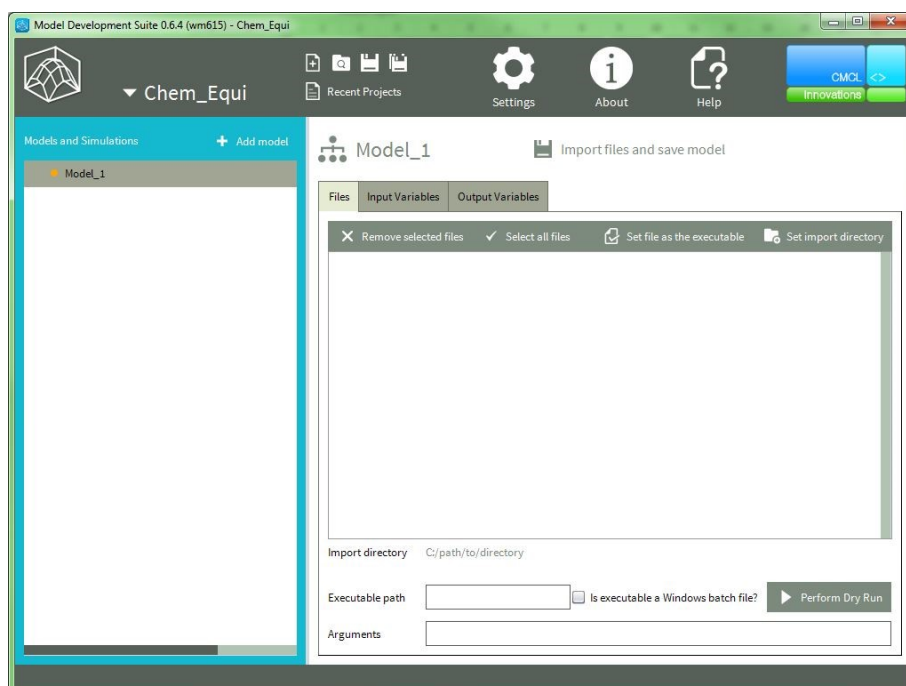


Figure G.5 Blank “Files” Tab of Model 1 MoDS Working Window

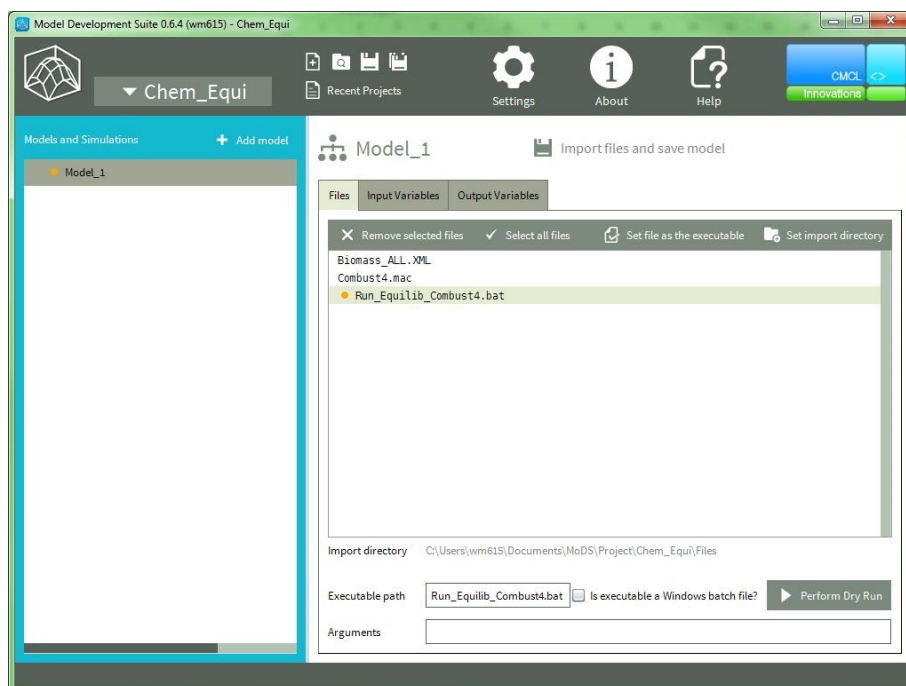


Figure G.6 “Files” Tab of Model 1 MoDS Working Window

“Perform Dry Run” at the bottom right is used to check whether the model runs properly. A successful dry run test is indicated by the notification shown in Figure G.7.

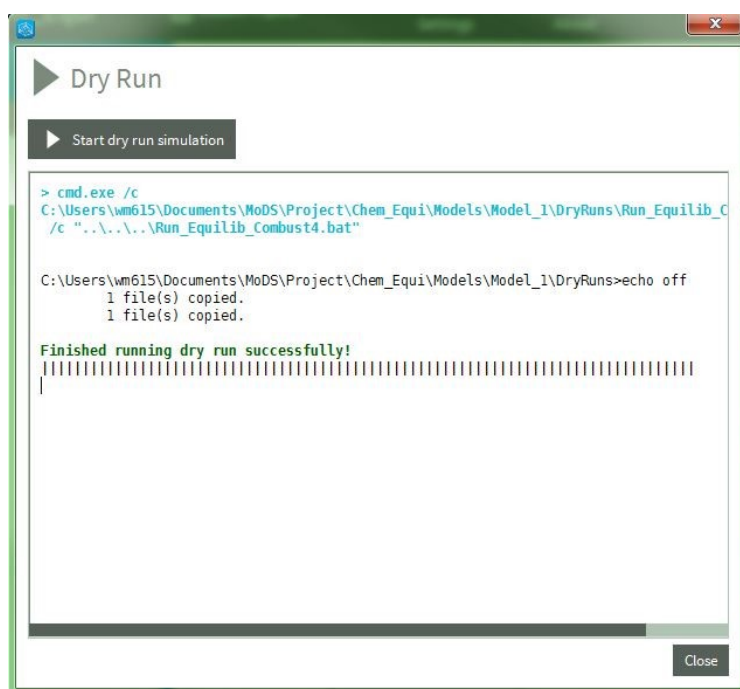


Figure G.7 Successful Dry Run Notification in MoDS Dry Run Window

After conducting a dry run, all input variables are added by pressing “Add from file” in the “Input Variables” tab as shown in Figure G.8.

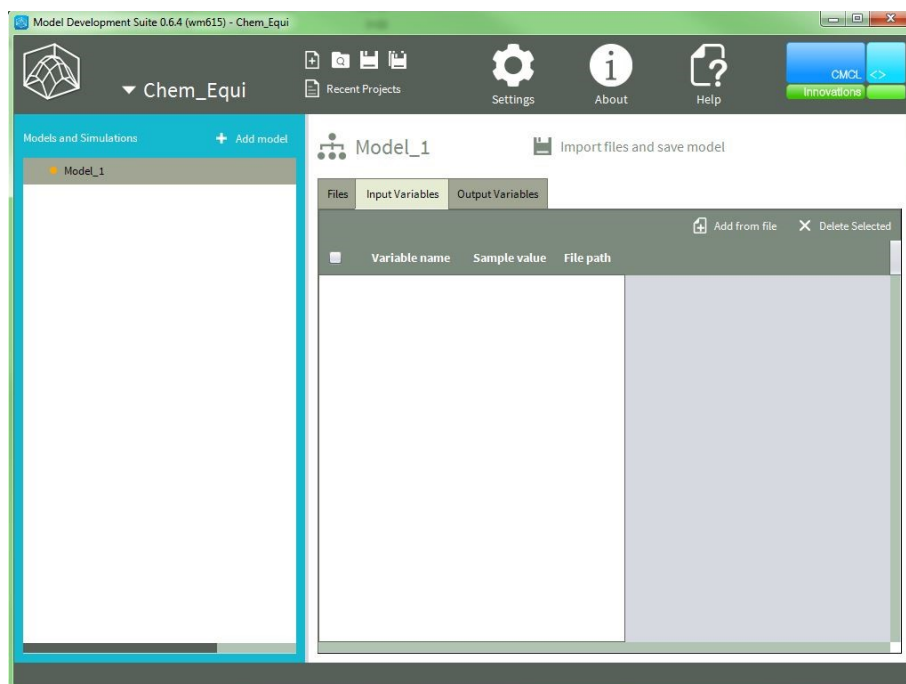


Figure G.8 Blank “Input Variables” Tab of Model 1 MoDS Working Window

The “Choose a file from list” tab in Figure G.9 appears and shows the list of the files. “Combust4.mac” is read as a comma-separated values (CSV) tab character as delimiter.

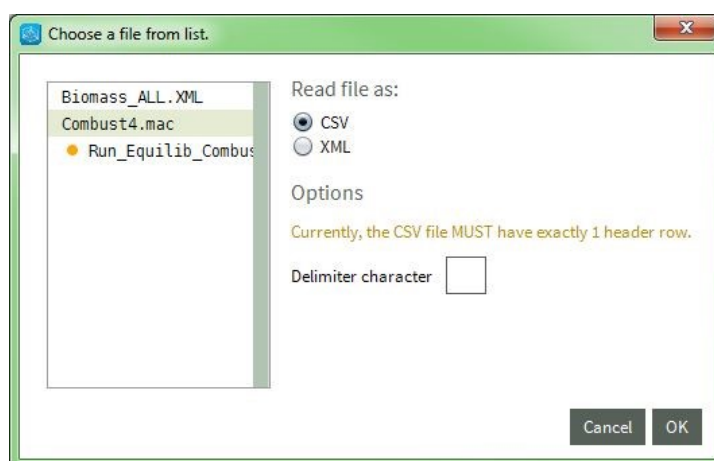


Figure G.9 Selection of “Combust4.mac” in the MoDS “Choose a file from list” Window

The “combust4.mac” code is displayed in the “Variable input file location specifier” window as cells, as shown in Figure G.10. Temperature, pressure, and molar mass are selected with “Single Row Querier” and “Col Query”.

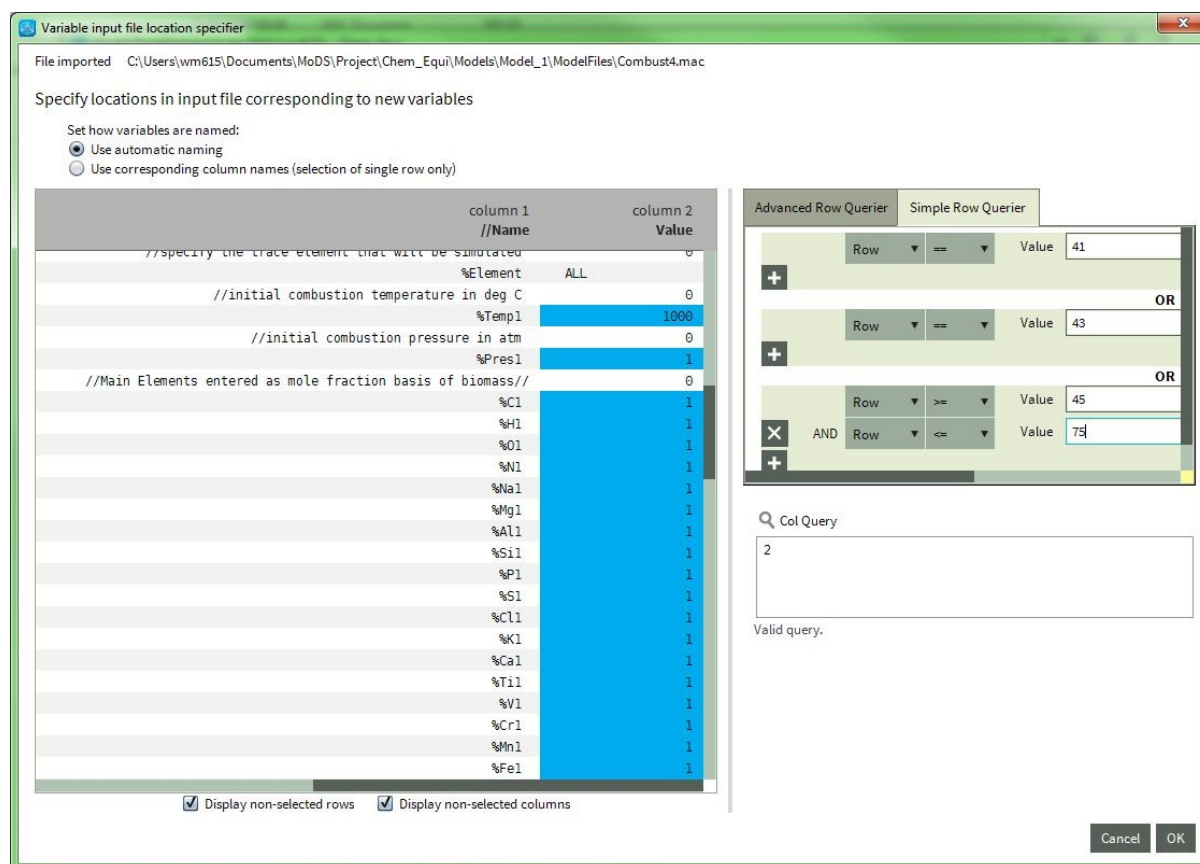


Figure G.10 MoDS “Variable input file location specifier” Window

Once confirmed, all the input variables are listed under the “Input Variables” tab in Figure G.11. In the blank “Output Variables” tab, as shown in Figure G.12, “Add from file” is also chosen to reopen the “Choose a file from list” window. As shown in Figure G.13, “Biomass_ALL.xml” is selected and read as XML.

Model Development Suite 0.6.4 (wm615) - Chem_Equi

Chem_Equi

Models and Simulations + Add model

Model_1

Import files and save model

Files Input Variables Output Variables

Add from file X Delete Selected

Variable name	Sample value	File path	Details
Var1	1000.0	Combust4.mac	Row index: 41 Col name: Value D
Var2	1.0	Combust4.mac	Row index: 43 Col name: Value D
Var3	1.0	Combust4.mac	Row index: 45 Col name: Value D
Var4	1.0	Combust4.mac	Row index: 46 Col name: Value D
Var5	1.0	Combust4.mac	Row index: 47 Col name: Value D
Var6	1.0	Combust4.mac	Row index: 48 Col name: Value D
Var7	1.0	Combust4.mac	Row index: 49 Col name: Value D
Var8	1.0	Combust4.mac	Row index: 50 Col name: Value D
Var9	1.0	Combust4.mac	Row index: 51 Col name: Value D
Var10	1.0	Combust4.mac	Row index: 52 Col name: Value D
Var11	1.0	Combust4.mac	Row index: 53 Col name: Value D
Var12	1.0	Combust4.mac	Row index: 54 Col name: Value D
Var13	1.0	Combust4.mac	Row index: 55 Col name: Value D
Var14	1.0	Combust4.mac	Row index: 56 Col name: Value D
Var15	1.0	Combust4.mac	Row index: 57 Col name: Value D
Var16	1.0	Combust4.mac	Row index: 58 Col name: Value D

Figure G.11 “Input Variables” Tab of Model 1 MoDS Working Window

Model Development Suite 0.6.4 (wm615) - Chem_Equi

Chem_Equi

Models and Simulations + Add model

Model_1

Import files and save model

Files Input Variables Output Variables

Add from file X Delete Selected

Variable name	Sample value	File path
---------------	--------------	-----------

Figure G.12 Blank “Output Variables” Tab of Model 1 MoDS Working Window

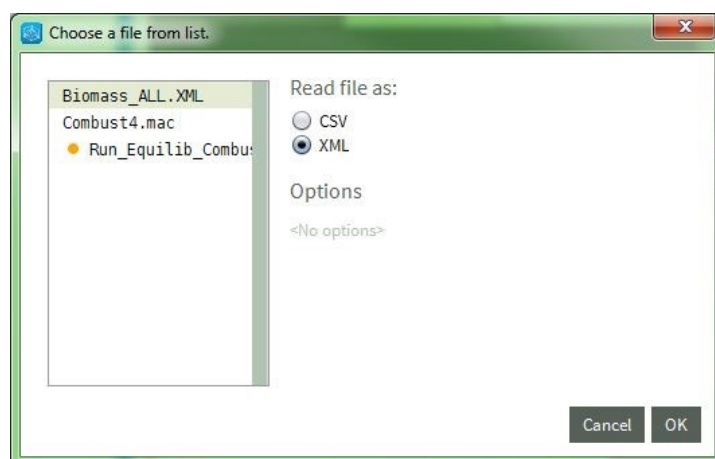


Figure G.13 Selection of “Biomass_ALL.xml” in MoDS “Choose a file from list” Window

The xml import data window is opened as shown in Figure G.14. The xml data branches are shown in the “XML file previewer” box. The output variables are “n” and are located in “result” folders. The “n” is selected in order from each “result” folder and transferred to the “User-chosen xpaths to be submitted” box by pressing the “Copy selected nodes to list” button on the bottom left.

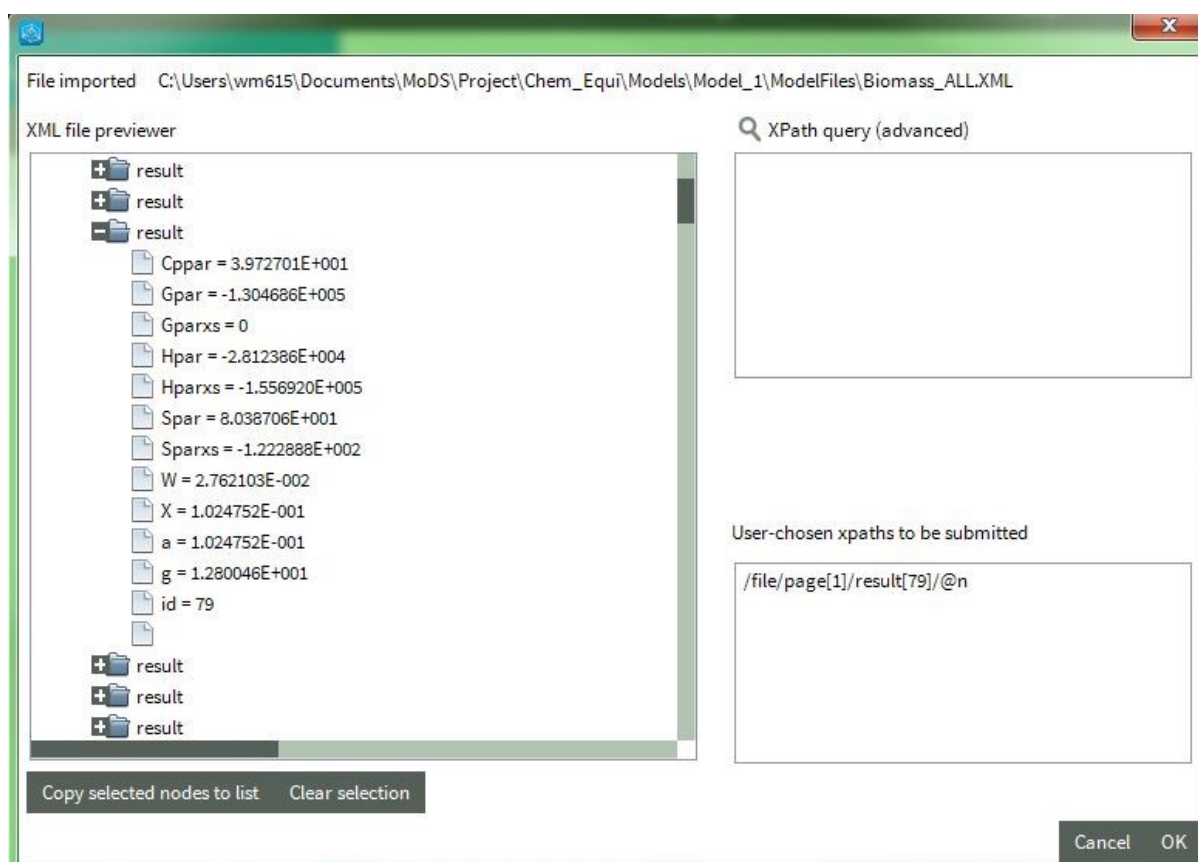


Figure G.14 MoDS xml Data Import Window

Once all variables are set up, “Simulation_1” is created as shown in Figure G.15. “Case1” is assigned as the calculated case in the “Select Cases” tab, as shown in Figure G.16.

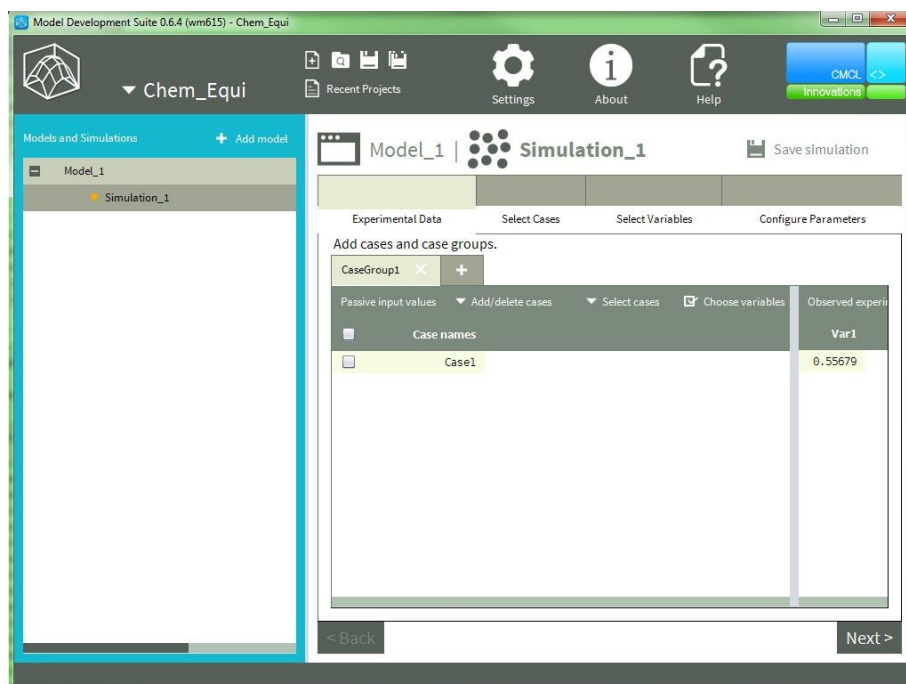


Figure G.15 “Experimental Data” Tab of Simulation 1 MoDS Working Window

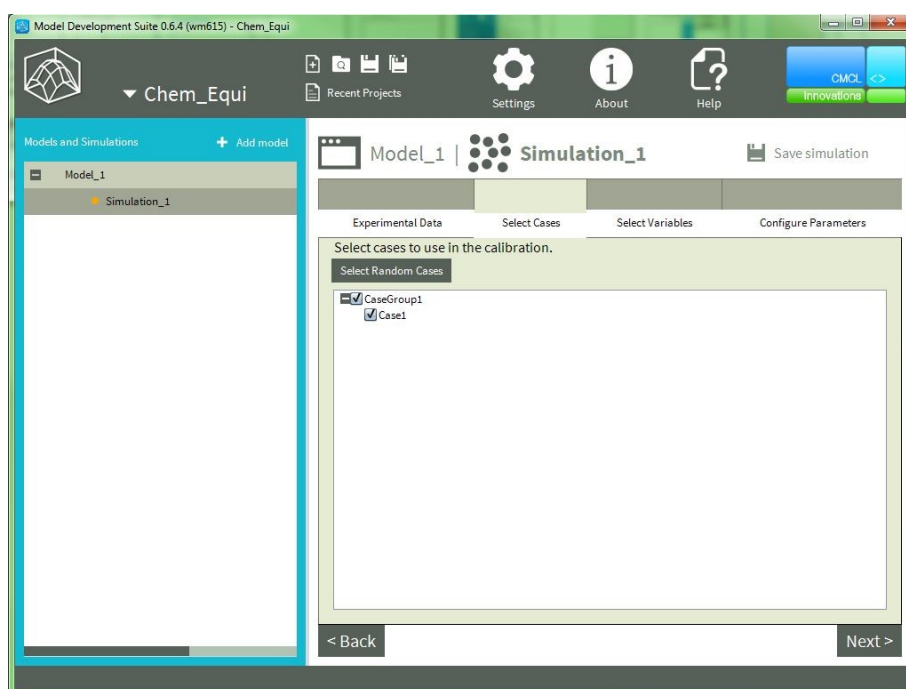


Figure G.16 “Select Cases” Tab of Simulation 1 MoDS Working Window

All variables are ticked in the “Select Variables” tab, as shown in Figure G.17. Figures G.18 and G.19 show how the input and output variable range values are configured in the “Configure Parameters” tab. Since the concentration of an element might be significantly larger or smaller than that of any other element, it is not efficient to use the actual concentration values. The concentration values are set as fractional numbers that range from 0 to 1. Temperature is set within the range of combustion temperature, i.e. 25°C to 2000 °C. Intra-particle pressure can deviate slightly from atmospheric pressure and to accommodate this, a short range of pressure values is allowed, i.e. 0.01atm to 2 atm. The lowest value is chosen to be 0.01 atm to avoid vacuum conditions in the FactSage calculation, selected by “Sobol_Algorithm”.

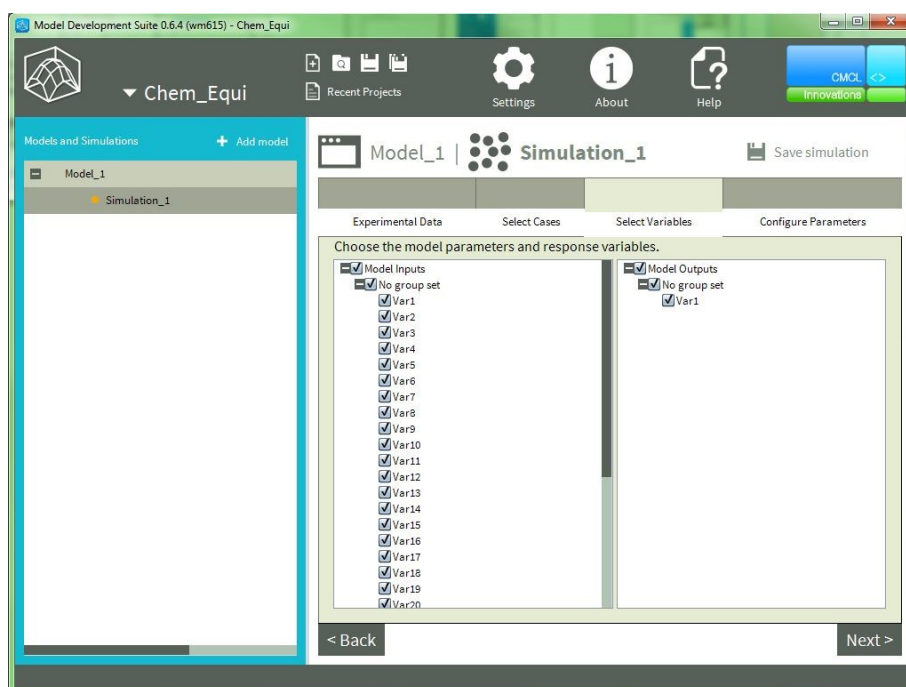


Figure G.17 “Select Variables” Tab of Simulation 1 MoDS Working Window

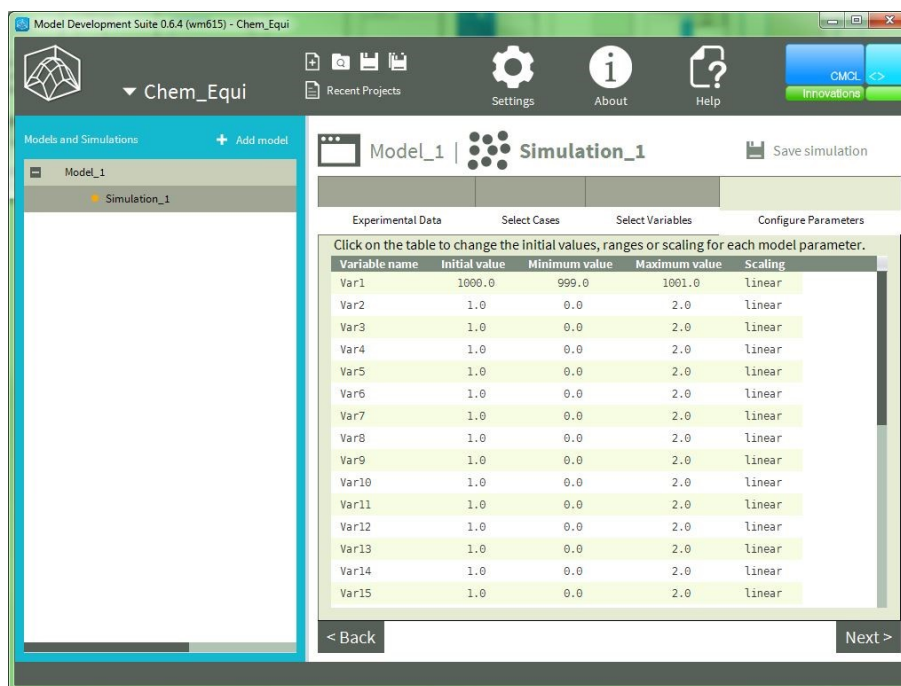


Figure G.18 “Configure Parameters” Tab of Simulation 1 MoDS Working Window

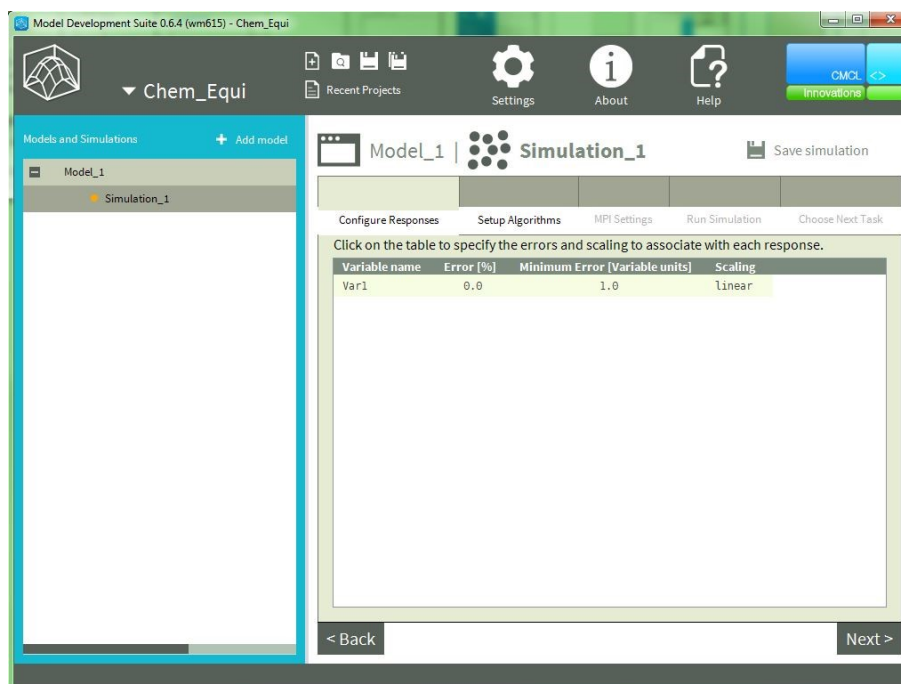


Figure G.19 “Configure Responses” Tab of Simulation 1 MoDS Working Window

FactSage chemical equilibrium calculation inputs are automatically selected based on the Sobol sequence shown in Figure G.20. The number of Sobol points is “n_points” and this is set at 3,000 times the FactSage run.

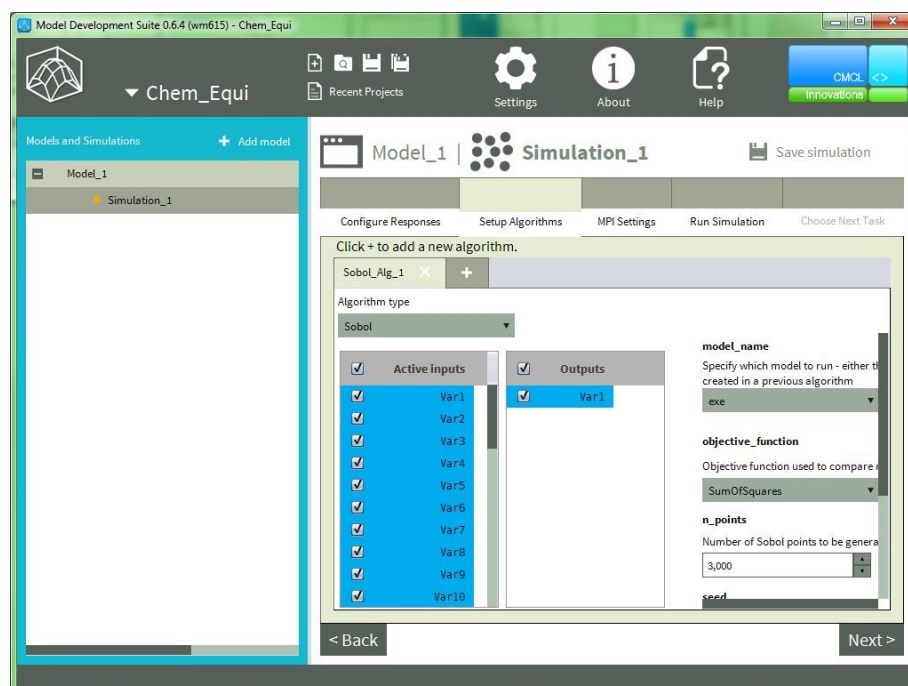


Figure G.20 “Setup Algorithms” Tab of Simulation 1 MoDS Working Window

The local machine is configured in the “MPI Settings” tab, shown in Figure G.21. “Simulation_1” is run in the “Run Simulations” tab, as shown in Figure G.22.

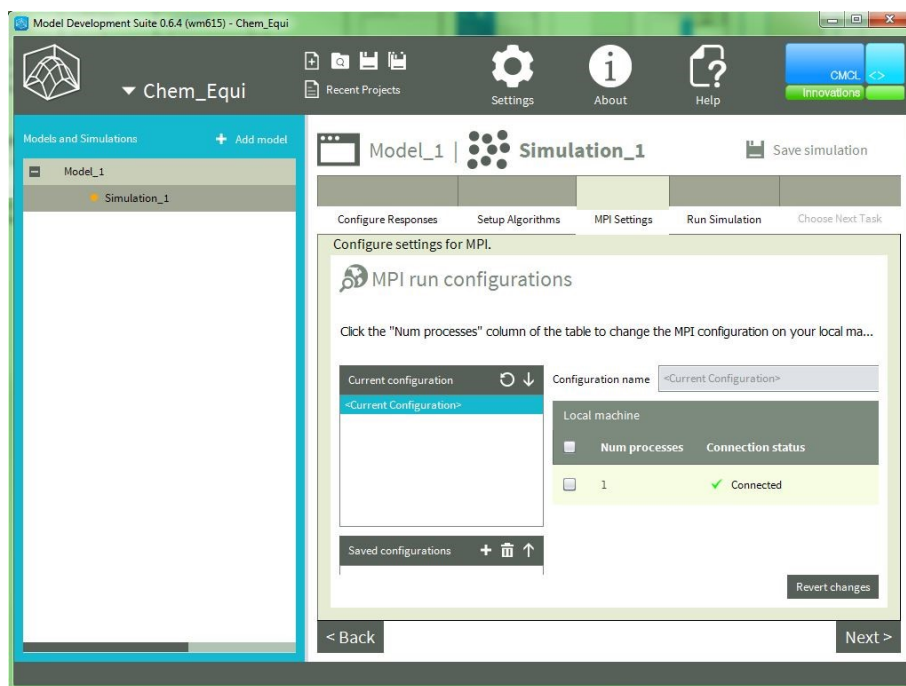


Figure G.21 “MPI Settings” Tab of Simulation 1 MoDS Working Window

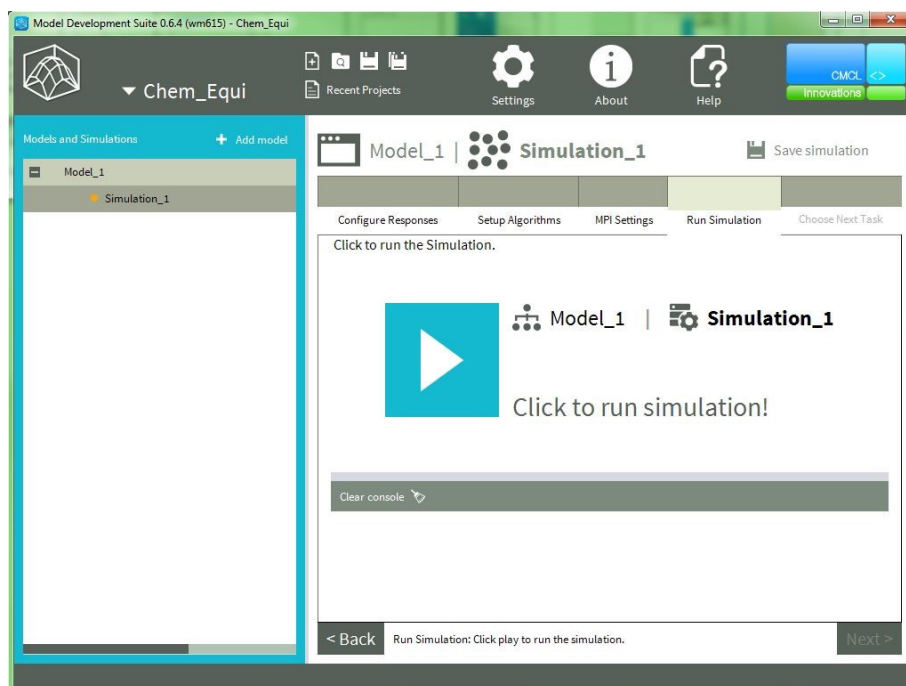


Figure G.22 “Run Simulations” Tab of Simulation 1 MoDS Working Window

“Simulation_2” is created using the same method as “Simulation 1”. It aims to generate a multidimensional function that covers element concentrations, temperature, and pressure based on the

“Sobol_Algl” function. The “Sobol_Algl” function is read by the “Read_previous_Alg_1” in Setup Algorithms tab, as shown in Figure G.23.

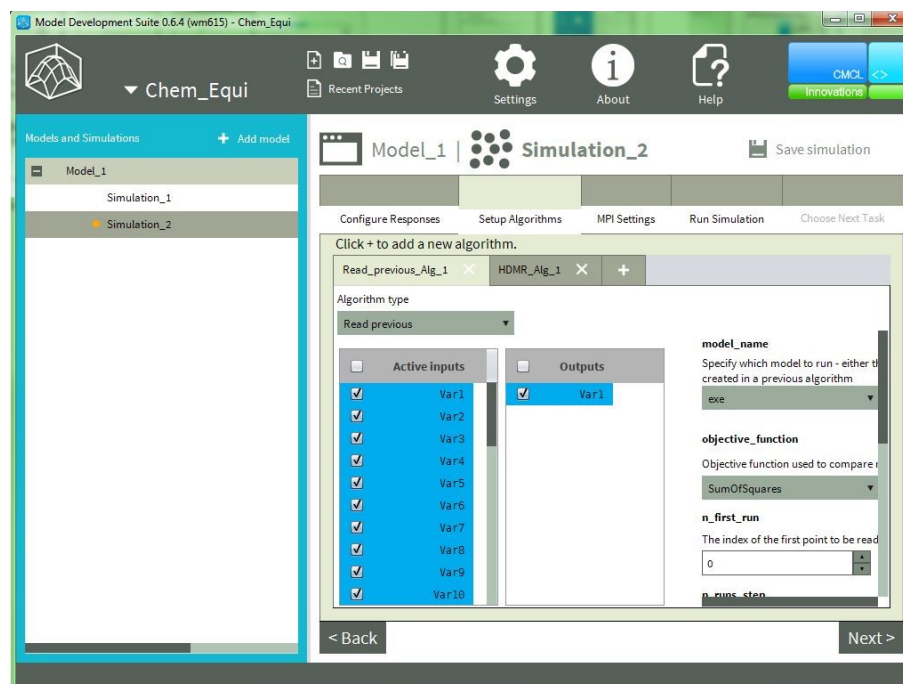


Figure G.23 “Read_previous_Alg_1” in “Setup Algorithms” Tab of Simulation 2 MoDS Working Window

“HDMR_Alg_1” is based on the High-dimensional Model Representation (HDMR) algorithm and is used as a function to read “Read_previous_Alg_1” data. The “HDMR_Alg_1” setup is shown in Figure G.24.

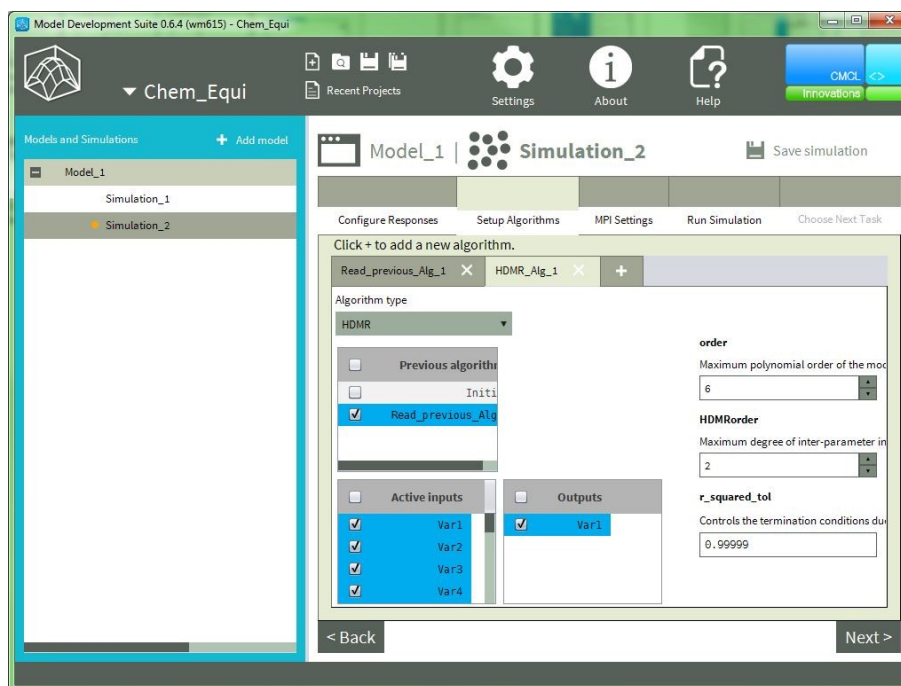


Figure G.24 “HDMR_Alg_1” in “Setup Algorithms” Tab of Simulation 2 MoDS Working Window

Appendix H: Matlab-ChemApp Integration Code

```
#include "cacint.h"
#include "mex.h"
#include "matrix.h"
#include "string.h"

using namespace std;

void assign_result_values(mxArray **result1)
{
    LI nphases, resultCounter, noerr;
    DB amount, chempot, fugoract;
    char name[TQSTRLEN];
    char pname[TQSTRLEN];

    resultCounter = 0;

    /* Get the number of phases */
    tqnop(&nphases, &noerr);

    /* Get the number of expected result*/
    for (LI i = 1; i <= nphases; i++) {

        LI npconTemp;
        tqnopc(i, &npconTemp, &noerr);

        for (LI j = 1; j <= npconTemp; j++) {
            resultCounter++;
        }
    }
}
```

```

*result1 = mxCreateDoubleMatrix((mwSize)resultCounter, 1, mxREAL);
mxDouble *result1Ptr = mxGetDoubles(*result1);

/* Assign result to plhs */
for (LI i = 1; i <= nphases; i++) {

    LI npconTemp;

    tqnopc(i, &npconTemp, &noerr);

    for (LI j = 1; j <= npconTemp; j++) {

        tqgetr("a", i, j, &amount, &noerr);
        //tqgetr("MU", i, j, &chempot, &noerr);
        //tqgetr("AC", i, j, &fugoract, &noerr);

        *result1Ptr = amount;
        result1Ptr++;

    }

}

}

void chemapp(mxDouble Temp, mxDouble Pres,
    mxDouble C, mxDouble H, mxDouble O, mxDouble N, mxDouble Na, mxDouble Mg, mxDouble Al, mxDouble
Si, mxDouble P, mxDouble S, mxDouble Cl, mxDouble K, mxDouble Ca, mxDouble Ti, mxDouble V, mxDouble Cr,
mxDouble Mn, mxDouble Fe, mxDouble Co, mxDouble Ni, mxDouble Cu, mxDouble Zn, mxDouble As, mxDouble Se,
mxDouble Mo, mxDouble Cd, mxDouble Sb, mxDouble Ba, mxDouble Hg, mxDouble Pb, mxDouble Ar)
{

    // Identify variable
    LI noerr;
    LI i_GAS;
    LI i_GAS_PC_C;
    LI i_GAS_PC_H;
    LI i_GAS_PC_O;
    LI i_GAS_PC_N;
    LI i_GAS_PC_Na;
    LI i_GAS_PC_Mg;
    LI i_GAS_PC_Al;
    LI i_GAS_PC_Si;
    LI i_GAS_PC_P;
    LI i_GAS_PC_S;
    LI i_GAS_PC_Cl;
    LI i_GAS_PC_K;
    LI i_GAS_PC_Ca;
    LI i_GAS_PC_Ti;
    LI i_GAS_PC_V;
    LI i_GAS_PC_Cr;
    LI i_GAS_PC_Mn;
    LI i_GAS_PC_Fe;
    LI i_GAS_PC_Co;
    LI i_GAS_PC_Ni;
    LI i_GAS_PC_Cu;
    LI i_GAS_PC_Zn;
    LI i_GAS_PC_As;
    LI i_GAS_PC_Se;
    LI i_GAS_PC_Mo;
    LI i_GAS_PC_Cd;
    LI i_GAS_PC_Sb;
    LI i_GAS_PC_Ba;
    LI i_GAS_PC_Hg;
    LI i_GAS_PC_Pb;
    LI i_GAS_PC_Ar;
    DB TP[2];
    DB vals[2];

```

```

// Initialise ChemApp
tqini(&noerr);

// Open data file for reading
tqopnt("all_elements_with_Ar.cst", 10, &noerr);

// Read data file
tqrcst(&noerr);

// Close data file
tqclos(10, &noerr);

// Set temperature and pressure unit
tqcsu("T ", "C ", &noerr);
tqcsu("P ", "atm ", &noerr);

TP[0] = 100.0; // Input stream temperature unit in degree Celcius
TP[1] = 1.0; // Input stream pressure unit in atmosphere

tqsttp("Stream 1", TP, &noerr); // Stream profile
tqsttp("Stream 2", TP, &noerr); // Stream profile
tqsttp("Stream 3", TP, &noerr); // Stream profile
tqsttp("Stream 4", TP, &noerr); // Stream profile
tqsttp("Stream 5", TP, &noerr); // Stream profile
tqsttp("Stream 6", TP, &noerr); // Stream profile
tqsttp("Stream 7", TP, &noerr); // Stream profile
tqsttp("Stream 8", TP, &noerr); // Stream profile
tqsttp("Stream 9", TP, &noerr); // Stream profile
tqsttp("Stream 10", TP, &noerr); // Stream profile
tqsttp("Stream 11", TP, &noerr); // Stream profile
tqsttp("Stream 12", TP, &noerr); // Stream profile
tqsttp("Stream 13", TP, &noerr); // Stream profile
tqsttp("Stream 14", TP, &noerr); // Stream profile
tqsttp("Stream 15", TP, &noerr); // Stream profile
tqsttp("Stream 16", TP, &noerr); // Stream profile
tqsttp("Stream 17", TP, &noerr); // Stream profile
tqsttp("Stream 18", TP, &noerr); // Stream profile
tqsttp("Stream 19", TP, &noerr); // Stream profile
tqsttp("Stream 20", TP, &noerr); // Stream profile
tqsttp("Stream 21", TP, &noerr); // Stream profile
tqsttp("Stream 22", TP, &noerr); // Stream profile
tqsttp("Stream 23", TP, &noerr); // Stream profile
tqsttp("Stream 24", TP, &noerr); // Stream profile
tqsttp("Stream 25", TP, &noerr); // Stream profile
tqsttp("Stream 26", TP, &noerr); // Stream profile
tqsttp("Stream 27", TP, &noerr); // Stream profile
tqsttp("Stream 28", TP, &noerr); // Stream profile
tqsttp("Stream 29", TP, &noerr); // Stream profile
tqsttp("Stream 30", TP, &noerr); // Stream profile
tqsttp("Stream 31", TP, &noerr); // Stream profile

// Define the content of Stream 1
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 1
tqinpc("C ", i_GAS, &i_GAS_PC_C, &noerr); // Phase constituent of phase of Stream 1
tqstca("Stream 1 ", i_GAS, i_GAS_PC_C, C, &noerr); // Amount of phase constituent of phase of Stream 1

// Define the content of Stream 2
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 2
tqinpc("H ", i_GAS, &i_GAS_PC_H, &noerr); // Phase constituent of phase of Stream 2
tqstca("Stream 2 ", i_GAS, i_GAS_PC_H, H, &noerr); // Amount of phase constituent of phase of Stream 2

// Define the content of Stream 3
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 3
tqinpc("O ", i_GAS, &i_GAS_PC_O, &noerr); // Phase constituent of phase of Stream 3
tqstca("Stream 3 ", i_GAS, i_GAS_PC_O, O, &noerr); // Amount of phase constituent of phase of Stream 3

// Define the content of Stream 4

```

```

tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 4
tqinpc("N ", i_GAS, &i_GAS_PC_N, &noerr); // Phase constituent of phase of Stream 4
tqstca("Stream 4 ", i_GAS, i_GAS_PC_N, N, &noerr); // Amount of phase constituent of phase of Stream 4

// Define the content of Stream 5
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 5
tqinpc("Na ", i_GAS, &i_GAS_PC_Na, &noerr); // Phase constituent of phase of Stream 5
tqstca("Stream 5 ", i_GAS, i_GAS_PC_Na, Na, &noerr); // Amount of phase constituent of phase of Stream 5

// Define the content of Stream 6
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 6
tqinpc("Mg ", i_GAS, &i_GAS_PC_Mg, &noerr); // Phase constituent of phase of Stream 6
tqstca("Stream 6 ", i_GAS, i_GAS_PC_Mg, Mg, &noerr); // Amount of phase constituent of phase of Stream 6

// Define the content of Stream 7
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 7
tqinpc("Al ", i_GAS, &i_GAS_PC_Al, &noerr); // Phase constituent of phase of Stream 7
tqstca("Stream 7 ", i_GAS, i_GAS_PC_Al, Al, &noerr); // Amount of phase constituent of phase of Stream 7

// Define the content of Stream 8
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 8
tqinpc("Si ", i_GAS, &i_GAS_PC_Si, &noerr); // Phase constituent of phase of Stream 8
tqstca("Stream 8 ", i_GAS, i_GAS_PC_Si, Si, &noerr); // Amount of phase constituent of phase of Stream 8

// Define the content of Stream 9
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 9
tqinpc("P ", i_GAS, &i_GAS_PC_P, &noerr); // Phase constituent of phase of Stream 9
tqstca("Stream 9 ", i_GAS, i_GAS_PC_P, P, &noerr); // Amount of phase constituent of phase of Stream 9

// Define the content of Stream 10
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 10
tqinpc("S ", i_GAS, &i_GAS_PC_S, &noerr); // Phase constituent of phase of Stream 10
tqstca("Stream 10 ", i_GAS, i_GAS_PC_S, S, &noerr); // Amount of phase constituent of phase of Stream 10

// Define the content of Stream 11
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 11
tqinpc("Cl ", i_GAS, &i_GAS_PC_Cl, &noerr); // Phase constituent of phase of Stream 11
tqstca("Stream 11 ", i_GAS, i_GAS_PC_Cl, Cl, &noerr); // Amount of phase constituent of phase of Stream 11

// Define the content of Stream 12
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 12
tqinpc("K ", i_GAS, &i_GAS_PC_K, &noerr); // Phase constituent of phase of Stream 12
tqstca("Stream 12 ", i_GAS, i_GAS_PC_K, K, &noerr); // Amount of phase constituent of phase of Stream 12

// Define the content of Stream 13
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 13
tqinpc("Ca ", i_GAS, &i_GAS_PC_Ca, &noerr); // Phase constituent of phase of Stream 13
tqstca("Stream 13 ", i_GAS, i_GAS_PC_Ca, Ca, &noerr); // Amount of phase constituent of phase of Stream 13

// Define the content of Stream 14
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 14
tqinpc("Ti ", i_GAS, &i_GAS_PC_Ti, &noerr); // Phase constituent of phase of Stream 14
tqstca("Stream 14 ", i_GAS, i_GAS_PC_Ti, Ti, &noerr); // Amount of phase constituent of phase of Stream 14

// Define the content of Stream 15
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 15
tqinpc("V ", i_GAS, &i_GAS_PC_V, &noerr); // Phase constituent of phase of Stream 15
tqstca("Stream 15 ", i_GAS, i_GAS_PC_V, V, &noerr); // Amount of phase constituent of phase of Stream 15

// Define the content of Stream 16
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 16
tqinpc("Cr ", i_GAS, &i_GAS_PC_Cr, &noerr); // Phase constituent of phase of Stream 16
tqstca("Stream 16 ", i_GAS, i_GAS_PC_Cr, Cr, &noerr); // Amount of phase constituent of phase of Stream 16

// Define the content of Stream 17
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 17
tqinpc("Mn ", i_GAS, &i_GAS_PC_Mn, &noerr); // Phase constituent of phase of Stream 17

```

```

tqstca("Stream 17 ", i_GAS, i_GAS_PC_Mn, Mn, &noerr); // Amount of phase constituent of phase of Stream 17

// Define the content of Stream 18
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 18
tqinpc("Fe ", i_GAS, &i_GAS_PC_Fe, &noerr); // Phase constituent of phase of Stream 18
tqstca("Stream 18 ", i_GAS, i_GAS_PC_Fe, Fe, &noerr); // Amount of phase constituent of phase of Stream 18

// Define the content of Stream 19
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 19
tqinpc("Co ", i_GAS, &i_GAS_PC_Co, &noerr); // Phase constituent of phase of Stream 19
tqstca("Stream 19 ", i_GAS, i_GAS_PC_Co, Co, &noerr); // Amount of phase constituent of phase of Stream 19

// Define the content of Stream 20
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 20
tqinpc("Ni ", i_GAS, &i_GAS_PC_Ni, &noerr); // Phase constituent of phase of Stream 20
tqstca("Stream 20 ", i_GAS, i_GAS_PC_Ni, Ni, &noerr); // Amount of phase constituent of phase of Stream 20

// Define the content of Stream 21
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 1
tqinpc("Cu ", i_GAS, &i_GAS_PC_Cu, &noerr); // Phase constituent of phase of Stream 21
tqstca("Stream 21 ", i_GAS, i_GAS_PC_Cu, Cu, &noerr); // Amount of phase constituent of phase of Stream 21

// Define the content of Stream 22
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 22
tqinpc("Zn ", i_GAS, &i_GAS_PC_Zn, &noerr); // Phase constituent of phase of Stream 22
tqstca("Stream 22 ", i_GAS, i_GAS_PC_Zn, Zn, &noerr); // Amount of phase constituent of phase of Stream 22

// Define the content of Stream 23
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 23
tqinpc("As ", i_GAS, &i_GAS_PC_As, &noerr); // Phase constituent of phase of Stream 23
tqstca("Stream 23 ", i_GAS, i_GAS_PC_As, As, &noerr); // Amount of phase constituent of phase of Stream 23

// Define the content of Stream 24
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 24
tqinpc("Se ", i_GAS, &i_GAS_PC_Se, &noerr); // Phase constituent of phase of Stream 24
tqstca("Stream 24 ", i_GAS, i_GAS_PC_Se, Se, &noerr); // Amount of phase constituent of phase of Stream 24

// Define the content of Stream 25
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 25
tqinpc("Mo ", i_GAS, &i_GAS_PC_Mo, &noerr); // Phase constituent of phase of Stream 25
tqstca("Stream 25 ", i_GAS, i_GAS_PC_Mo, Mo, &noerr); // Amount of phase constituent of phase of Stream 25

// Define the content of Stream 26
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 26
tqinpc("Cd ", i_GAS, &i_GAS_PC_Cd, &noerr); // Phase constituent of phase of Stream 26
tqstca("Stream 26 ", i_GAS, i_GAS_PC_Cd, Cd, &noerr); // Amount of phase constituent of phase of Stream 26

// Define the content of Stream 27
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 27
tqinpc("Sb ", i_GAS, &i_GAS_PC_Sb, &noerr); // Phase constituent of phase of Stream 27
tqstca("Stream 27 ", i_GAS, i_GAS_PC_Sb, Sb, &noerr); // Amount of phase constituent of phase of Stream 27

// Define the content of Stream 28
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 28
tqinpc("Ba ", i_GAS, &i_GAS_PC_Ba, &noerr); // Phase constituent of phase of Stream 28
tqstca("Stream 28 ", i_GAS, i_GAS_PC_Ba, Ba, &noerr); // Amount of phase constituent of phase of Stream 28

// Define the content of Stream 29
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 29
tqinpc("Hg ", i_GAS, &i_GAS_PC_Hg, &noerr); // Phase constituent of phase of Stream 29
tqstca("Stream 29 ", i_GAS, i_GAS_PC_Hg, Hg, &noerr); // Amount of phase constituent of phase of Stream 29

// Define the content of Stream 30
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 30
tqinpc("Pb ", i_GAS, &i_GAS_PC_Pb, &noerr); // Phase constituent of phase of Stream 30
tqstca("Stream 30 ", i_GAS, i_GAS_PC_Pb, Pb, &noerr); // Amount of phase constituent of phase of Stream 30

```

```

// Define the content of Stream 31
tqinp("gas ", &i_GAS, &noerr); // Phase of Stream 31
tqinpc("Ar ", i_GAS, &i_GAS_PC_Ar, &noerr); // Phase constituent of phase of Stream 31
tqstca("Stream 31 ", i_GAS, i_GAS_PC_Ar, Ar, &noerr); // Amount of phase constituent of phase of Stream 31

// Define output stream temperature and target pressure
tqstec("P ", 0, Pres, &noerr); // Output stream pressure unit in atmosphere
tqstec("T ", 0, Temp, &noerr); // Output stream temperature unit in degree Celcius

// Conduct the equilibrium calculation
tqce(" ", 0, 0, vals, &noerr);
}

/* The gateway function. */
void mexFunction(int nlhs, mxArray* plhs[],
    int nrhs, const mxArray* prhs[])
{
    /* Check for proper number of arguments */
    if (nrhs != 2) {
        mexErrMsgIdAndTxt("MATLAB:mexcpp:nargin",
            "MEXCPP requires 2 input arguments.");
    }

    if (nlhs != 1) {
        mexErrMsgIdAndTxt("MATLAB:mexcpp:nargout",
            "MEXCPP requires 1 output argument.");
    }

    // validate input number
    size_t mrows_1, ncols_1, mrows_2, ncols_2;

    mrows_1 = mxGetM(prhs[0]);
    ncols_1 = mxGetN(prhs[0]);

    mrows_2 = mxGetM(prhs[1]);
    ncols_2 = mxGetN(prhs[1]);

    if (!(mrows_1 == 1 && mrows_2 == 1)) {
        mexErrMsgIdAndTxt("MATLAB:mexcpp:nargin",
            "MEXCPP arguments require one dimensional array.");
    }

    if (!(ncols_1 == 2)) {
        mexErrMsgIdAndTxt("MATLAB:mexcpp:nargin",
            "MEXCPP first input argument require 2 cols array.");
    }

    if (!(ncols_2 == 31)) {
        mexErrMsgIdAndTxt("MATLAB:mexcpp:nargin",
            "MEXCPP second input argument require 31 cols array.");
    }

    // validate input data type
    if (!mxIsDouble(prhs[0]) || !mxIsDouble(prhs[1])) {
        mexErrMsgIdAndTxt("MATLAB:mexcpp:nargin",
            "MEXCPP first input argument should be in double.");
    }

    mxDouble *param1, *param2;
    param1 = mxGetDoubles(prhs[0]);
    param2 = mxGetDoubles(prhs[1]);

    // parse input value
    mxDouble Temp = param1[0];
    mxDouble Pres = param1[1];
    mxDouble C = param2[0];
    mxDouble H = param2[1];

```

```

mxDouble O = param2[2];
mxDouble N = param2[3];
mxDouble Na = param2[4];
mxDouble Mg = param2[5];
mxDouble Al = param2[6];
mxDouble Si = param2[7];
mxDouble P = param2[8];
mxDouble S = param2[9];
mxDouble Cl = param2[10];
mxDouble K = param2[11];
mxDouble Ca = param2[12];
mxDouble Ti = param2[13];
mxDouble V = param2[14];
mxDouble Cr = param2[15];
mxDouble Mn = param2[16];
mxDouble Fe = param2[17];
mxDouble Co = param2[18];
mxDouble Ni = param2[19];
mxDouble Cu = param2[20];
mxDouble Zn = param2[21];
mxDouble As = param2[22];
mxDouble Se = param2[23];
mxDouble Mo = param2[24];
mxDouble Cd = param2[25];
mxDouble Sb = param2[26];
mxDouble Ba = param2[27];
mxDouble Hg = param2[28];
mxDouble Pb = param2[29];
mxDouble Ar = param2[30];

// result length
int phase1Length;
int phase2Length;

chemapp(Temp, Pres, C, H, O, N, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo,
Cd, Sb, Ba, Hg, Pb, Ar);
assign_result_values(&plhs[0]);

}

```

Appendix I: PACT Facility Entrained-flow Burner Elemental Mass Balance

Appendix I.1 Possible ICP Mismeasurements

This calculation reveals the PACT facility ICP mismeasurements of some elements via mass balance calculations. The mass balance of nickel in white wood combustion with air is chosen for this appendix.

White wood enters the burner at mass flow rate, f_{ww} of 0.011 kg s^{-1} . Based on the ultimate analysis result of white wood in Table 3.1, the molar flow rates of C, H, and O are obtained via Equation I.1.

$$F_{i_{ww}} = x_{iUA_{ww}} f_{ww} \frac{1000}{MW_i}; i = 1 \text{ for C, } 2 \text{ for H, } 3 \text{ for O} \quad (\text{EI.1})$$

$F_{i_{ww}}$ is the molar flow rate of element i in mol s^{-1} . $x_{i_{UA_{ww}}}$ is the mass fraction of element i in white wood, according to the ultimate analysis result. MW_i is the molecular weight of element i in g mol^{-1} . The values of $F_{C_{ww}}$, $F_{H_{ww}}$, and $F_{O_{ww}}$ are 0.446, 0.701, and 0.26 mol s^{-1} . $F_{i_{ww}}$ is used to calculate the molar number a , b , and c of the chemical form of white wood, which is $\text{C}_a\text{H}_b\text{O}_c$. The calculation of a , b , and c are shown in Equation I.2, I.3, and I.4.

$$a = \frac{F_{C_{ww}}}{F_{O_{ww}}} \quad (\text{EI.2})$$

$$b = \frac{F_{H_{ww}}}{F_{O_{ww}}} \quad (\text{EI.3})$$

$$c = 1 \quad (\text{EI.4})$$

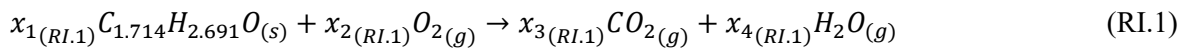
According to Equation I.1, I.2, and I.3, the chemical form of white wood is $\text{C}_{1.714}\text{H}_{2.691}\text{O}$. The molecular weight of white wood, MW_{ww} , is calculated in Equation I.5.

$$MW_{ww} = aMW_C + bMW_H + cMW_O \quad (\text{EI.5})$$

MW_{ww} is 39.255 g mol^{-1} according to Equation I.4. The molar flow rate of white wood is calculated in Equation I.6.

$$F_{ww} = \left(x_{C_{UA_{ww}}} + x_{H_{UA_{ww}}} + x_{O_{UA_{ww}}} \right) f_{ww} \frac{1000}{MW_{ww}} \quad (\text{EI.6})$$

According to Equation I.5, F_{ww} is 0.26 mol s^{-1} . Air enters the burner at molar flow rate, F_{air} , of 2.791 mol s^{-1} . The molar flow rate of $\text{O}_{2(g)}$ and $\text{N}_{2(g)}$ entering the burner is 0.586 mol s^{-1} and 2.205 mol s^{-1} with the $\text{O}_{2(g)}$ - $\text{N}_{2(g)}$ ratio of 0.21:0.79 in air. The combustion of white wood with air is in accordance with Reaction I.1.



The coefficients of Reaction I.1 are defined in Equation I.7, I.8, I.9, and I.10.

$$x_{1(RI.1)} = 1 \quad (\text{EI.7})$$

$$x_{2(RI.1)} = a + \frac{b}{4} - \frac{c}{2} \quad (\text{EI.8})$$

$$x_{3(RI.1)} = a \quad (\text{EI.9})$$

$$x_{4(RI.1)} = \frac{b}{2} \quad (\text{EI.10})$$

According to Equation I.8, I.9, and I.10, the values of $x_{2(RI.1)}$, $x_{3(RI.1)}$, and $x_{4(RI.1)}$ are 1.886, 1.714, and 1.346. At complete combustion conversion, the outlet molar mass rate of each compound, $F_{i,out}$, is calculated stoichiometrically in Table I.1.

Table I.1 Stoichiometry of Reaction I.1 in Air-combustion

	$C_{1.714}H_{2.691}O_{(s)}$	$O_{2(g)}$	$\rightarrow$	$CO_{2(g)}$	$H_2O_{(g)}$
$x_{i(RI.1)}$	1	1.886		1.714	1.314
$F_{i,in}$	0.26	0.586		0	0
Reaction	0.26	0.491		0.446	0.35
$F_{i,out}$	0	0.095		0.446	0.35

The total molar flow rate of the dry flue gas leaving the burner, $F_{dry,out}$, is 2.746 mol and calculated in Equation I.11.

$$F_{dry,out} = F_{O_{2(g)}out} + F_{CO_{2(g)}out} + F_{N_{2(g)}in} = 0.095 + 0.446 + 2.205 = 2.746 \quad (EI.11)$$

The volumetric flow rate of the dry flue gas is calculated in Equation I.12.

$$V_{dry,out} = \frac{F_{dry,out}RT_{out}}{p_{out}} \quad (EI.12)$$

At 1 atm and ICP temperature of 6,000 K to which T_{out} is equal, $V_{dry,out}$ is $1.352 \text{ m}^3 \text{ s}^{-1}$. The mass flow rate of nickel entering the burner, $f_{Ni,in}$, is $7.739\text{e-}9 \text{ kg s}^{-1}$ and calculated in Equation I.13.

$$f_{Ni,in} = \frac{x_{i_{ww}}f_{ww}}{10^6} \quad (EI.13)$$

$x_{i_{ww}}$ is the mass fraction of nickel in white wood at 0.7 mg kg^{-1} . According to the ICP measurement at PACT facility, the flue gas leaving the burner in a dry condition contained nickel with concentration, $c_{Ni,dry,out,ICP}$, of 0.017 mg m^{-3} . The mass flow rate of nickel leaving the burner, $f_{Ni,out,ICP}$, in kg s^{-1} is calculated in Equation I.14.

$$f_{Ni,out,ICP} = \frac{c_{Ni,dry,out,ICP}V_{dry,out}}{10^6} \quad (EI.14)$$

According to Equation I.14, the value of $f_{Ni,out,ICP}$ is $2.299\text{e-}8 \text{ kg s}^{-1}$. The mass balance of nickel would be correct if Equation I.15 was satisfied.

$$f_{Ni,out,ICP} \leq f_{Ni,in} \quad (EI.15)$$

However, this calculation exhibits that Equation I.15 is not satisfied and the ICP measurement of nickel should be revised.

Appendix I.2 Mass Balance of White Wood in Oxy27-combustion

This calculation reveals the PACT facility ICP mismeasurements of some elements via mass balance calculations. The mass balance of nickel in white wood combustion with air is chosen for this appendix.

White wood enters the burner at mass flow rate, f_{ww} of 0.011 kg s^{-1} . Based on the ultimate analysis result of white wood in Table 3.1, the molar flow rates of C, $F_{C_{ww}}$, H, $F_{H_{ww}}$, and O, $F_{O_{ww}}$ are obtained via Equation I.1. The values of $F_{C_{ww}}$, $F_{H_{ww}}$, and $F_{O_{ww}}$ are 0.446, 0.701, and 0.26 mol s^{-1} . $F_{C_{ww}}$, $F_{H_{ww}}$, and $F_{O_{ww}}$ is used to calculate the molar number a, b, and c of the chemical form of white wood, which is $C_aH_bO_c$. The calculation of a, b, and c are shown in Equation I.2, I.3, and I.4. According to Equation I.1, I.2, and I.3, the chemical form of white wood is $C_{1.714}H_{2.691}O$. The molecular weight of white wood, MW_{ww} , is calculated in Equation I.5. MW_{ww} is $39.255 \text{ g mol}^{-1}$ according to Equation I.4. The molar flow rate of white wood is calculated in Equation I.6. According to Equation I.5, F_{ww} is 0.26 mol s^{-1} . A mixture of $O_{2(g)}$ and $CO_{2(g)}$ enters the burner at molar flow rate, F_{air} , of 1.913 mol s^{-1} . The molar flow rate of $O_{2(g)}$ and $CO_{2(g)}$ entering the burner is 0.517 mol s^{-1} and 1.397 mol s^{-1} with the $O_{2(g)}$ - $CO_{2(g)}$ ratio of 0.27:0.73.

The combustion of white wood with the $O_{2(g)}$ is in accordance with Reaction I.1. The coefficients of Reaction I.1 are defined in Equation I.7, I.8, I.9, and I.10. According to Equation I.8, I.9, and I.10, the values of $x_{2(RI.1)}$, $x_{3(RI.1)}$, and $x_{4(RI.1)}$ are 1.886, 1.714, and 1.346. At complete combustion conversion, the outlet molar mass rate of each compound, $F_{i_{out}}$, is calculated stoichiometrically in Table I.2.

Table I.2 Stoichiometry of Reaction I.1 in Oxy27-combustion

	$C_{1.714}H_{2.691}O_{(s)}$	$O_{2(g)}$	$\rightarrow$	$CO_{2(g)}$	$H_2O_{(g)}$
$x_{i(RI.1)}$	1	1.886		1.714	1.314
$F_{i_{in}}$	0.26	0.517		1.397	0
Reaction	0.26	0.491		0.446	0.35
$F_{i_{out}}$	0	0.025		1.843	0.35

The total molar flow rate of the dry flue gas leaving the burner, $F_{dry,out}$, is 1.868 mol and calculated via Equation I.16.

$$F_{dry,out} = F_{O_{2(g)}out} + F_{CO_{2(g)}out} = 0.025 + 1.843 = 1.868 \quad (EI.16)$$

The dry molar fraction of $O_{2(g)}$ leaving the burner, $x_{O_{2(g)}dry,out}$, is 0.0136 as calculated via Equation I.17.

$$x_{O_{2(g)}dry,out} = \frac{F_{O_{2(g)}out}}{F_{dry,out}} = \frac{0.025}{1.868} = 0.0136 \quad (EI.17)$$

Appendix J: AFE and TE Fate and Occurrence Profiles of White Wood and Recycled Wood

This appendix compiles the discussion of the fate and occurrence profiles of the AFEs and TEs other than potassium, calcium, silicon, copper, and chromium in the combustion of white wood and recycled wood in PACT facility entrained-flow boiler.

Sodium

The modelled sodium fate profile is shown in Figure J.1 for the Air/Oxy27 comparison. In Figure J.1, almost all sodium remains intact in the particle during the *heat loan* stage. All the sodium in the particle is volatilised once peak temperature is achieved. Sodium is known as a very volatile element and its volatility is strongly influenced by temperature.³⁶⁸ Due to this characteristic, sodium is converted completely into gas during both air-combustion and oxy27-combustion of white wood (the Air/Oxy27 comparison). The temperature effect on sodium volatility can be seen as there is earlier volatilisation during oxy27-combustion since the peak temperature in this case is located at a higher boiler height than in the case of air combustion.

The modelled profiles of sodium occurrence during air and oxy27 combustion of white wood are shown in Figures J.3 and J.4. Both figures exhibit similar sodium occurrence behaviours. During the *heat loan* stage, it is difficult to observe sodium compounds. In fact, the quantities of sodium are negligible as very little sodium is released from the particles during the *heat loan* stage. Significant amounts of $NaOH_{(g)}$ are formed shortly before peak temperature is reached, due to reaction of the evaporated moisture with $Na_{(g)}$ released from the particles. Takata *et al.*³⁶⁹ suggest that high temperature favours $NaOH_{(g)}$ production from the reaction of $Na_{(g)}$ and $H_2O_{(g)}$, as expressed in Reaction J.1.



During the *heat removal* stage, the occurrence of sodium is shifted from $\text{NaOH}_{(g)}$ to $\text{Na}_{(g)}$. $\text{Na}_{(g)}$ is gradually diminished by the end of the *heat removal stage*. $\text{NaOH}_{(g)}$ is reformed during the *heat loss* stage.

The modelled sodium fate profile is shown in Figure J.2 for the white/recycled wood comparison (combustion in air of white wood compared with recycled wood). This figure indicates that according to the model, gas is converted to solid aerosols during the *heat loss* stage due to the reaction of gaseous sodium with silicon and aluminium to form sodium aluminium silicate ($\text{NaAlSi}_3\text{O}_8(s_2)$). This result is shown in Figure J.5. However, white wood combusted in air does not produce $\text{NaAlSi}_3\text{O}_8(s_2)$. It is found that sodium is completely volatilised in both cases. This difference in occurrence prediction indicates that the high sodium content of recycled wood might be sufficient to form $\text{NaAlSi}_3\text{O}_8(s_2)$. $\text{NaAlSi}_3\text{O}_8(s_2)$ is possibly formed via Reaction J.2, in which sodium and aluminium undergo a series of reactions with $\text{SiO}_{2(g)}$.³⁷⁰



An observation of power-plant fly ash produced during solid-fuel combustion with significant concentrations of sodium revealed that $\text{NaAlSi}_3\text{O}_8(s_2)$ was one of the major constituents.³⁷¹ This finding is in agreement with the predicted sodium behaviour during air-combustion of recycled wood.

In all cases, a small proportion of $\text{NaCl}_{(g)}$ exists during the *heat loss* stage as a residual compound. Based on slag characterisation research, Öhman *et al.*³⁷² suggest that sodium may form $\text{NaCl}_{(g)}$ as a result of reaction with chlorine once sodium is released from the particle. $\text{NaCl}_{(g)}$ subsequently reacts with silicon and $\text{O}_{2(g)}$ to form silicate-associated aerosols.

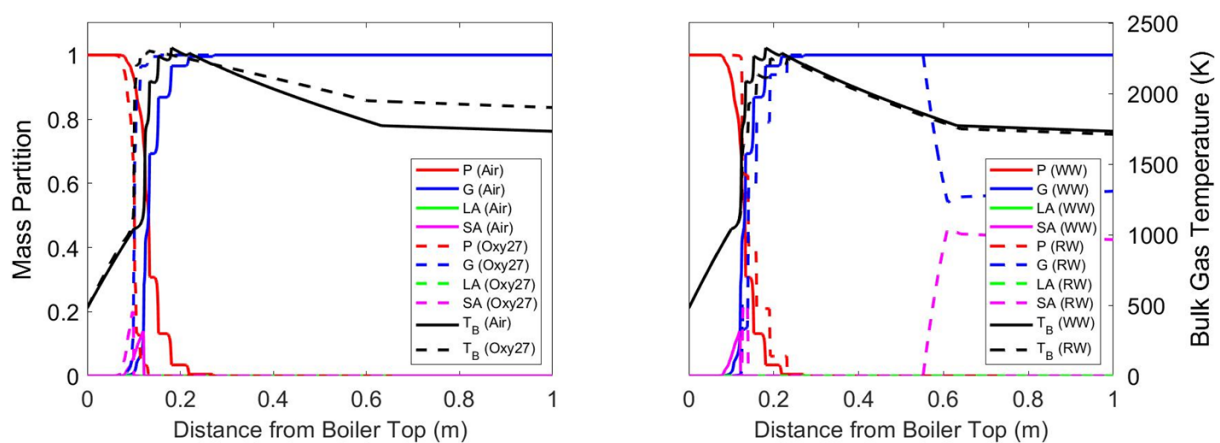


Figure J.1 (Left) Modelled Sodium Fate Profiles in Air-combustion and Oxy27 Combustion of White Wood; **Figure J.2 (Right)** Modelled Sodium Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

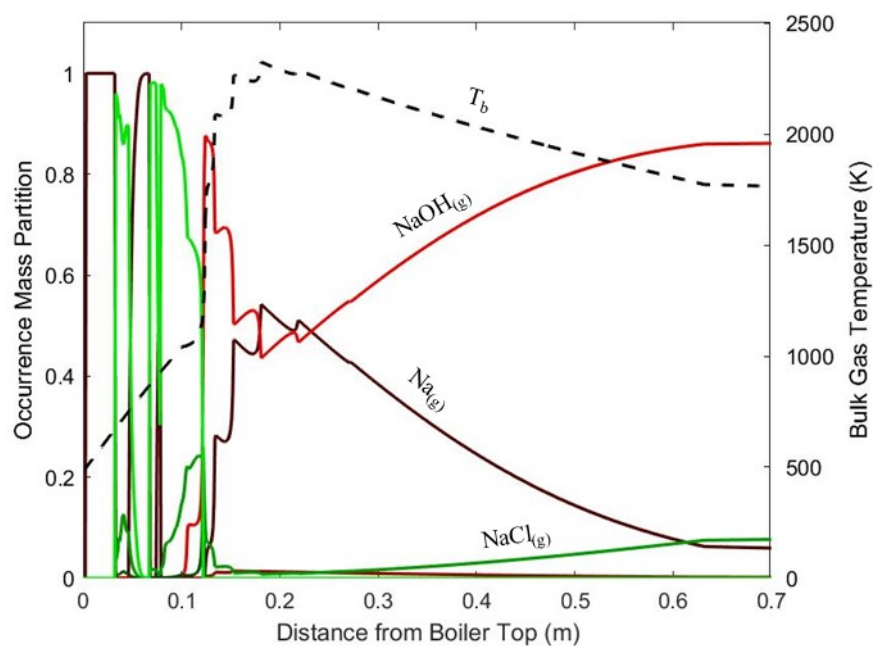


Figure J.3 Modelled Sodium Bulk Occurrences in Air-combustion of White Wood

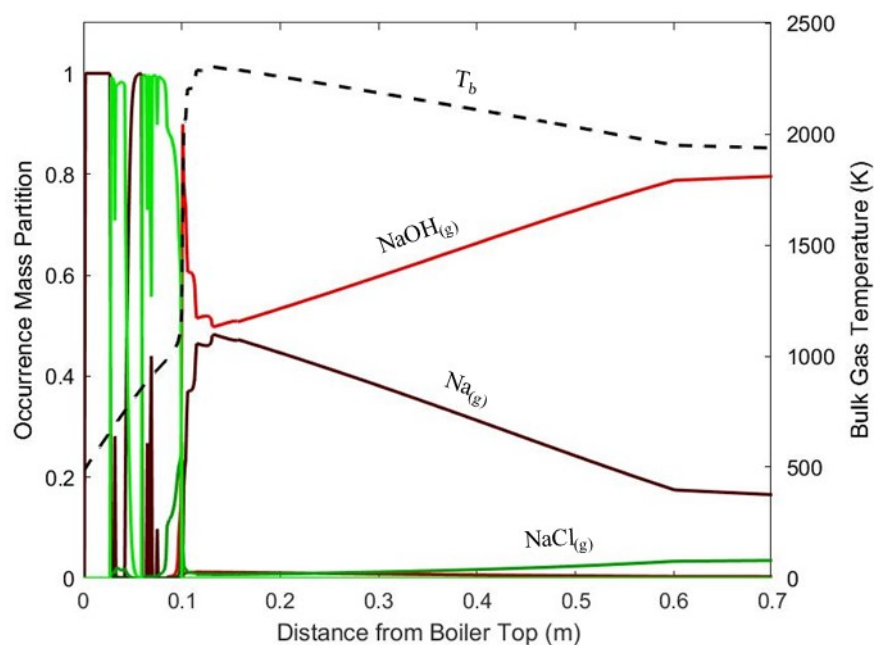


Figure J.4 Modelled Sodium Bulk Occurrences in Oxy27-combustion of White Wood

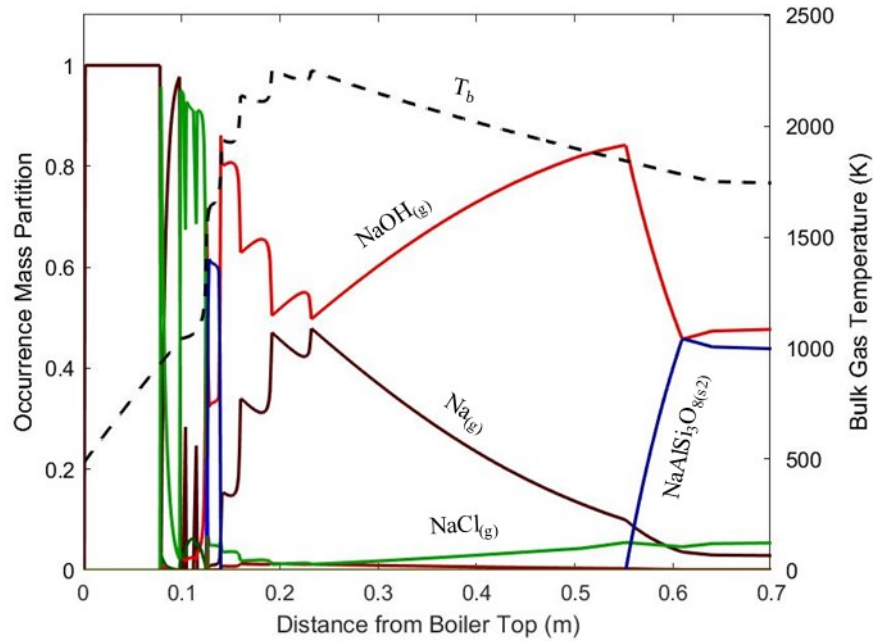


Figure J.5 Modelled Sodium Bulk Occurrences in Air-combustion of Recycled Wood

Magnesium

Modelled magnesium fate profiles are shown in Figures J.6 for the Air/Oxy27 comparison and J.7 for the white/recycled wood comparison. During the air or oxy27 combustion of white wood (the Air/Oxy27 comparison), magnesium is initially released as gas. When the temperature drops during the *heat removal* stage, gaseous magnesium compound is transformed into solid magnesium aerosol compound. In the white/recycled wood comparison, magnesium released from recycled wood is mostly as solid aerosols whilst the rest remains in the particles. Direct solid aerosol formation might be promoted by a high quantity of magnesium being released from recycled wood. In addition, rapid solid magnesium oxide is formed in the presence of $O_{2(g)}$.

The modelled occurrence of bulk magnesium in both air-combustion and oxy27-combustion of white wood is mainly as $Mg(OH)_{2(g)}$, as shown in Figure J.8 and Figure J.9. Magnesium is released primarily as $Mg(OH)_{2(g)}$, while a small portion of $MgOH_{(g)}$ is produced, probably due to magnesium exposure to steam.³⁷³ At lower temperatures during the *heat loss* stage, $Mg(OH)_{2(g)}$ might be decomposed into $MgO_{(g)}$ and $H_2O_{(g)}$, as expressed in Reaction J.3.³⁷⁴



The occurrence profile of bulk magnesium during air-combustion of recycled wood that is predicted by the model is shown in Figure J.10. This indicates that $Mg(OH)_{2(g)}$ formation is suppressed by

formation of Ca-Mg silicates, e.g. $\text{Ca}_2\text{MgSi}_2\text{O}_{7(s)}$ and $\text{CaMgSi}_2\text{O}_{6(s)}$. $\text{Ca}_2\text{MgSi}_2\text{O}_{7(s)}$ is converted to $\text{CaMgSi}_2\text{O}_{6(s)}$ at lower temperatures. $\text{CaMgSi}_2\text{O}_{6(s)}$ is quite stable and is usually formed in a Ca-Mg-rich environment.³⁷⁵ In addition, an experimental observation has discovered various magnesium silicate compounds, e.g. $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2(s)$, formed in aerosols that were captured in a power-plant turbine unit.³⁷⁶ Moreover, magnesium also forms other complex silicate aerosol variants without and with other elements, e.g. Al and Ti.^{377,378} This behaviour suggests that magnesium reaction with calcium, aluminium, and silicon depends on whether the quantity of released magnesium is sufficient to form complex silicate minerals.

Modelled occurrence of magnesium in bottom ash during air-combustion of white wood predicts the formation of $\text{Ca}_3\text{MgAl}_4\text{O}_{10(s)}$, $\text{Ca}_3\text{MgSi}_2\text{O}_{8(s)}$, and a very small portion of $\text{MgO}_{(s)}$, as shown in Figure J.11. In contrast, $\text{MgO}_{(s)}$ was reported in a previous work to be a major compound found in bottom ash.³⁷⁹ The absence of $\text{MgO}_{(s)}$ in the model result might be due to kinetic limitations. Further evaluation is required to investigate the influence of other parameters, e.g. other element concentrations, on formation of $\text{MgO}_{(s)}$.

However, $\text{MgO}_{(s)}$ and $\text{Ca}_3\text{MgAl}_4\text{O}_{10(s)}$ are not predicted to be formed in the bottom ash during air-combustion of recycled wood, as shown in Figure J.12. The absence of $\text{MgO}_{(s)}$ is probably due to the presence of a significant quantity of retained calcium and silica, which react with magnesium in the particles. $\text{Ca}_3\text{MgSi}_2\text{O}_{8(s)}$ formation is consistent in both air-combustion of white wood and air-combustion of recycled wood, and has been proven in previous work.²⁸⁷ Calcium affects the propensity for sodium and potassium release. A higher Ca:C ratio demonstrates an impact on the reduced partition of $\text{NaAlSi}_3\text{O}_8(s)$ and $\text{KAlSi}_2\text{O}_6(s)$ and, as expected, an increased partition of $\text{Ca}_3\text{MgAl}_4\text{O}_{10(s)}$.³⁸⁰ However, combustion of recycled wood, which contains more calcium than white wood, does not generate $\text{Ca}_3\text{MgAl}_4\text{O}_{10(s)}$ partition in bottom ash. According to chemical equilibrium theory, calcium and aluminium in recycled wood has a stronger partition towards $\text{Ca}_2\text{Al}_2\text{SiO}_7(s)$ than $\text{Ca}_3\text{MgAl}_4\text{O}_{10(s)}$. The higher silicon content of recycled wood probably attracts aluminium to react with kaolinite. Kaolinite has previously been considered to have a strong influence only on potassium and sodium partition. However, recent observation has shown that calcium partition is also affected by kaolinite addition.³⁸¹

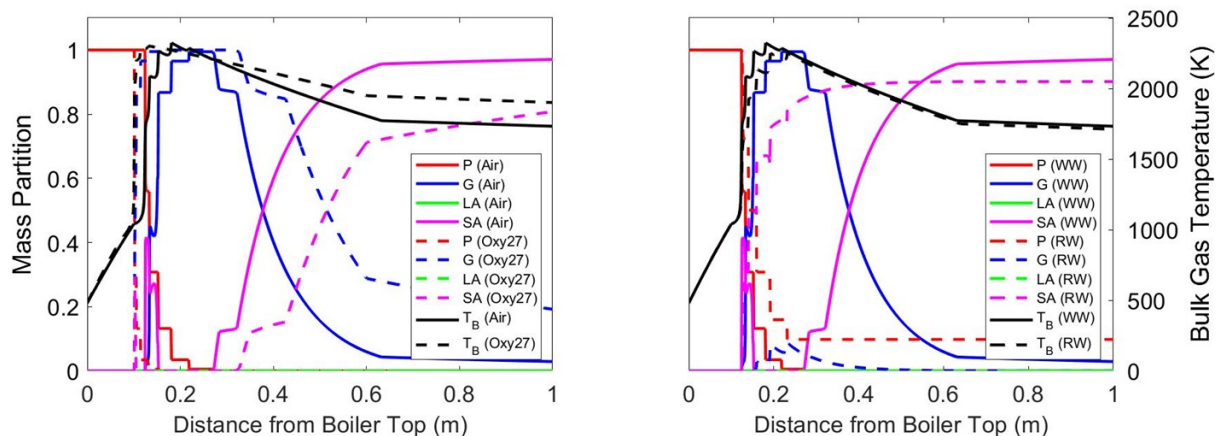


Figure J.6 (Left) Modelled Magnesium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood; **Figure J.7 (Right)** Modelled Magnesium Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

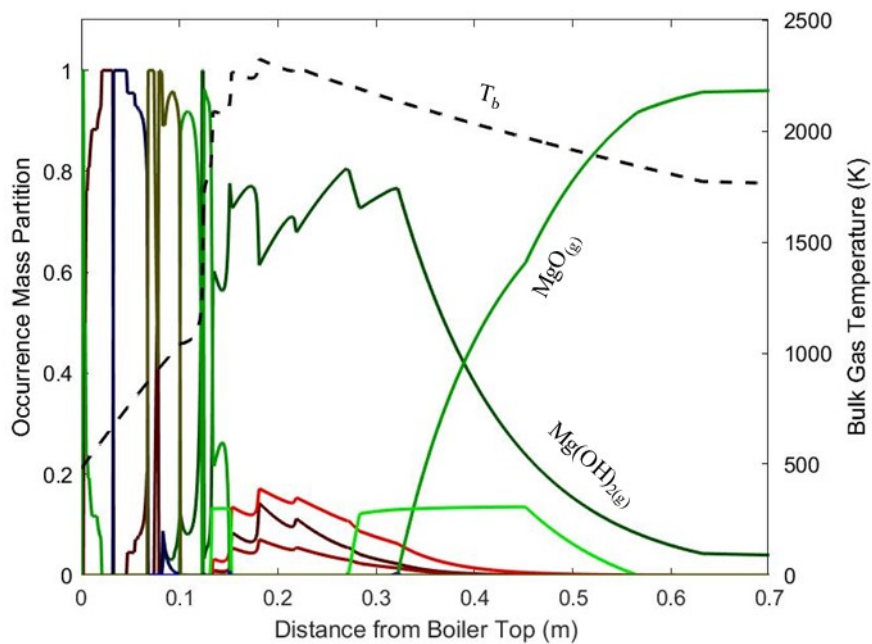


Figure J.8 Modelled Magnesium Bulk Occurrences in Air-combustion of White Wood

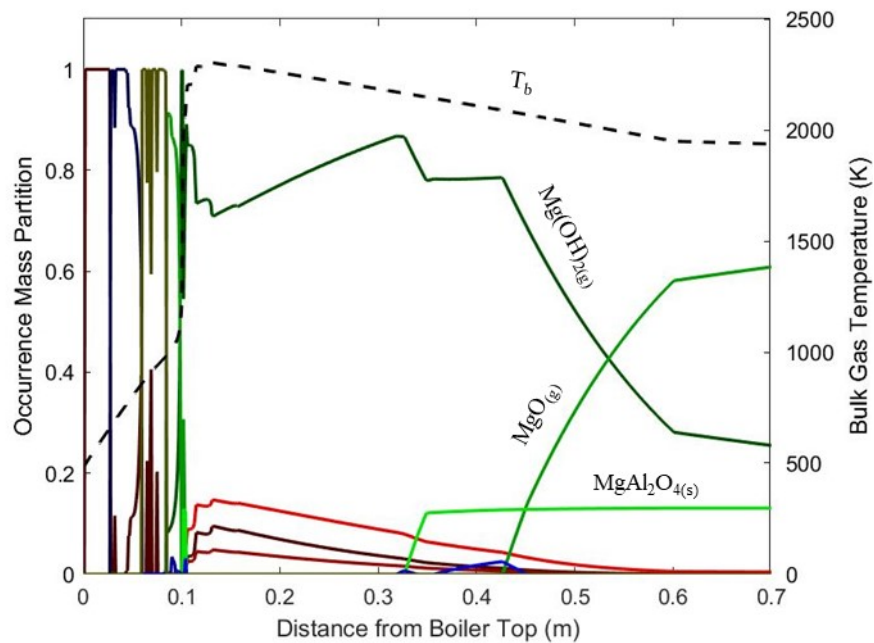


Figure J.9 Modelled Magnesium Bulk Occurrences in Oxy27-combustion of White Wood

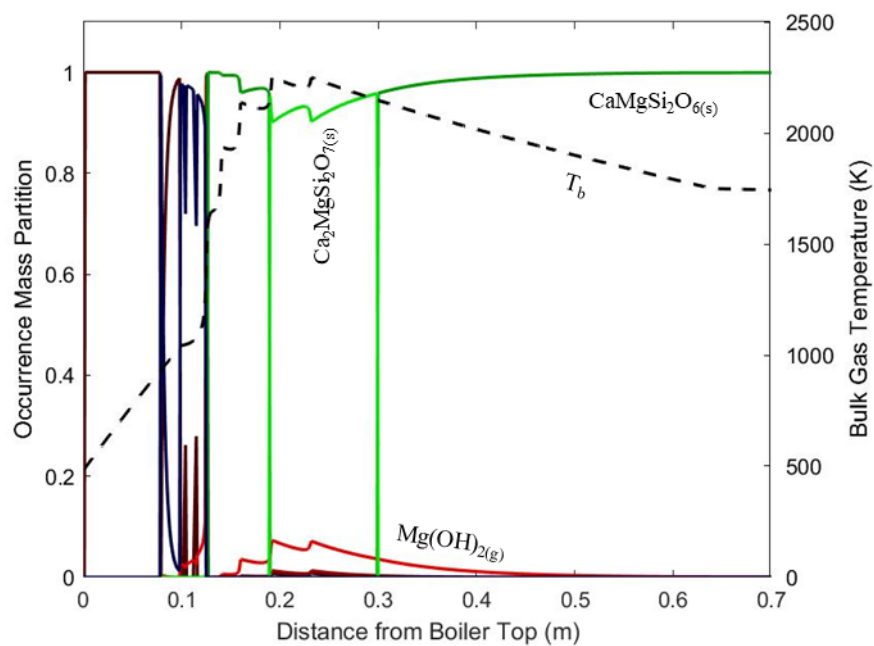


Figure J.10 Modelled Magnesium Bulk Occurrences in Air-combustion of Recycled Wood

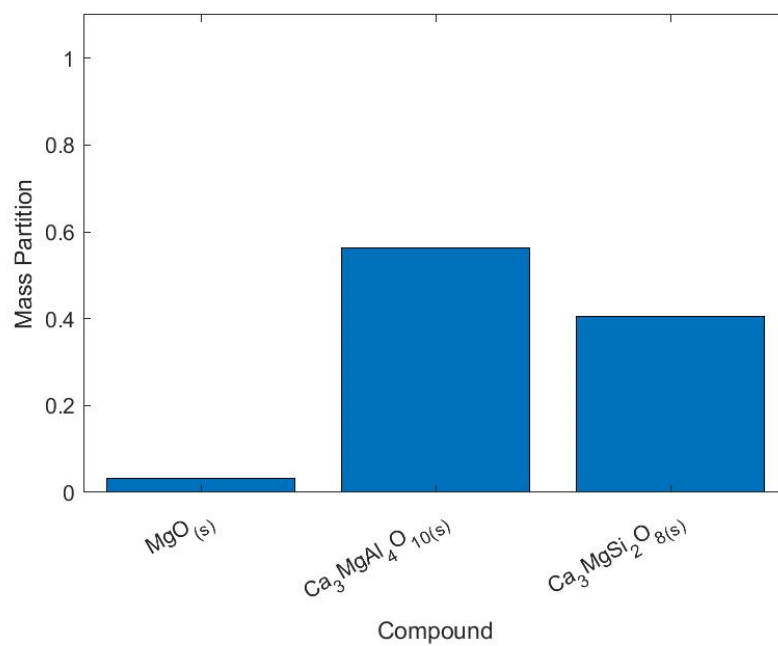


Figure J.11 Modelled Magnesium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of White Wood

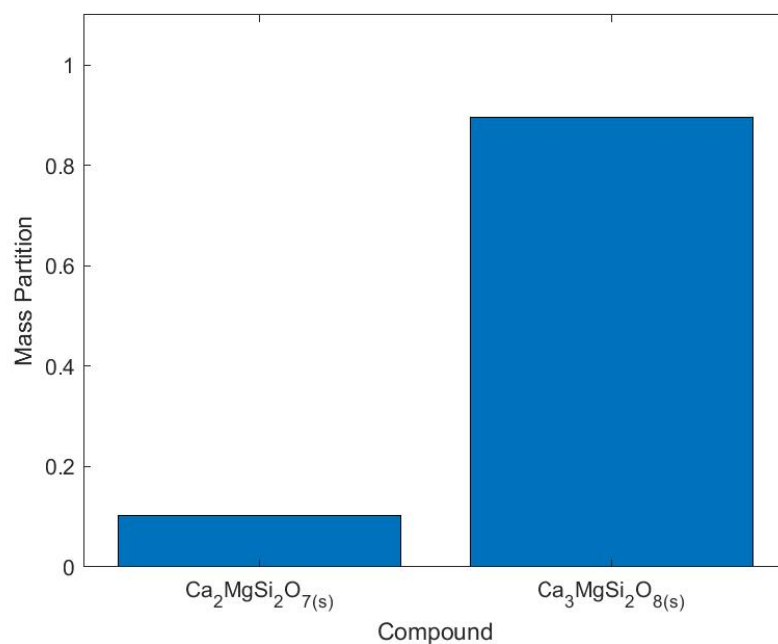


Figure J.12 Modelled Magnesium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Recycled Wood

Aluminium

Figure J.13 shows the modelled fate profile of aluminium in the Air/Oxy27 comparison, which considers the air- and oxy27-combustion of white wood. The model predicts that aluminium is released from the particles in solid and gas forms. Gaseous aluminium is formed initially, but gradually disappears as temperature decreases during the *heat removal* stage. Eventually, all released aluminium takes the form of solid aerosols.

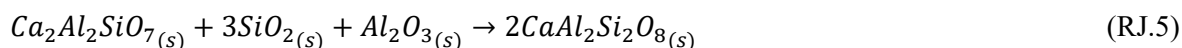
The modelled fate profile of bulk aluminium during air-combustion of recycled wood, shown in Figure J.14, exhibits a similar trend to that during air-combustion of white wood. However, during air-combustion of recycled wood, more aluminium remains in the particles, probably due to the higher aluminium content of recycled wood compared with white wood. In addition, oxy27-combustion of white wood leads to retention of aluminium in the particles. This is probably due to formation of complex silicates as the aluminium is exposed to more concentrated $O_{2(g)}$ in oxy27-combustion.

Modelled occurrence profiles of bulk aluminium in air-combustion of white wood are shown in Figure J.15. Formation and later disappearance of gaseous aluminium compounds might indicate that aluminium is originally released as a gas in the presence of significant amounts of $O_{2(g)}$ and $H_2O_{(g)}$. Farber and Srivastava³⁸² discovered that only gaseous aluminium compounds are produced from aluminium reaction with fluorine in a $H_{2(g)}/O_{2(g)}$ environment. In Figures J.15 and J.16, $OAlOH_{(g)}$ is predicted to form initially and later to diminish. Farber *et al.*³⁸³ observed aluminium occurrence in a flame using mass spectrometry and discovered that $OAlOH_{(g)}$ was produced as one of the major aluminium compounds. $OAlOH_{(g)}$ is possibly formed according to Reaction J.4.



The disappearance of $OAlOH_{(g)}$ simultaneously with formation of $Ca_2Al_2SiO_{7(s)}$ might corroborate the theory that calcium dictates the fates of aluminium, magnesium, and silica. $Ca_2Al_2SiO_{7(s)}$ is replaced by $MgAl_2O_{4(s)}$ at around 0.3 m to 0.4 m from the top of the boiler. Within this height range, $MgO_{(s)}$ is formed, as shown in Figure J.8. $MgAl_2O_{4(s)}$ exists along with $MgO_{(s)}$ and forms a stable solid solution at temperatures above 1773 K.³⁸⁴ $CaAl_2O_{4(s)}$ formation at more than 0.4 m below the boiler top is due to $MgAl_2O_{4(s)}$ decomposition at lower temperatures. Other research has observed that $CaAl_2O_{4(s)}$ formation and nucleation take place at around 1573 K.³⁸⁵

In the modelled occurrence profiles of bulk aluminium in air-combustion of recycled wood, shown in Figure J.17, $CaAlSi_2O_{8(s2)}$ is the main aluminium compound formed. Since the silicon content of recycled wood is higher than that of white wood, excess amounts of silicon and aluminium in the particles might react with $Ca_2Al_2SiO_{7(s)}$ aerosols as in Reaction J.5.³⁸⁶



Further, during the *heat loss* stage, $\text{KAlSi}_2\text{O}_{6(s2)}$ is formed along with $\text{NaAlSi}_3\text{O}_{8(s2)}$ whilst $\text{CaAl}_2\text{Si}_2\text{O}_{8(s)}$ disappears. $\text{KAlSi}_2\text{O}_{6(s2)}$ formation is probably based on Reactions J.1 and 7.4.

Modelled bulk aluminium occurrence in bottom ash is shown in Figures J.18 and J.19. The modelled occurrence in air-combustion of white wood, shown in Figure J.18, predicts $\text{Ca}_3\text{MgAl}_4\text{O}_{10(s)}$ as the major aluminium compound. In oxy27-combustion of white wood, shown in Figure J.19, $\text{CaAl}_2\text{O}_{4(s)}$ and $\text{Ca}_2\text{Al}_2\text{SiO}_{7(s)}$ are the primary products with relatively equal proportions. The high concentration of $\text{O}_{2(g)}$ may lead $\text{Ca}_3\text{MgAl}_4\text{O}_{10(s)}$ to decompose to $\text{CaAl}_2\text{O}_{4(s)}$ further reacting with silicon to form $\text{Ca}_2\text{Al}_2\text{SiO}_{7(s)}$. In air-combustion of recycled wood, $\text{Ca}_2\text{Al}_2\text{SiO}_{7(s)}$ is the only aluminium compound formed. As shown in Figure J.14, a significant proportion of aluminium is left in the particles during air-combustion of recycled wood. Selectivity towards $\text{Ca}_2\text{Al}_2\text{SiO}_{7(s)}$ formation might be enhanced when a considerable quantity of aluminium remains in the particles.

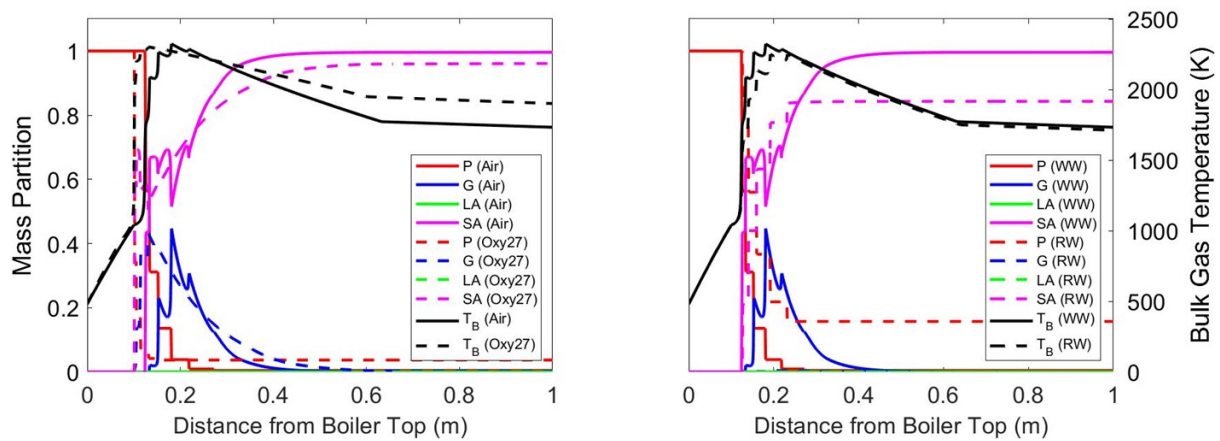


Figure J.13 (Left) Modelled Aluminium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood; **Figure J.14 (Right)** Aluminium Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B: Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

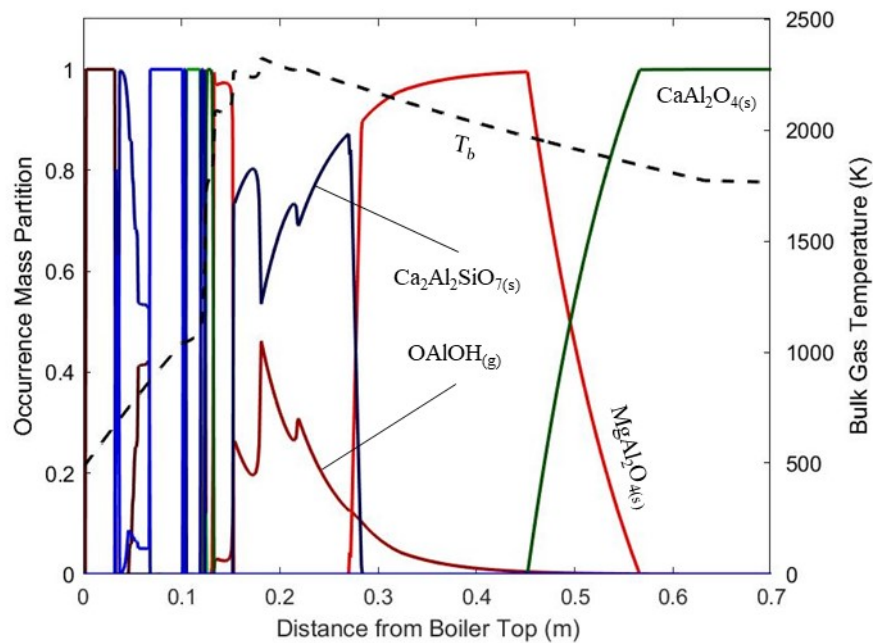


Figure J.15 Modelled Aluminium Bulk Occurrences in Air-combustion of White Wood

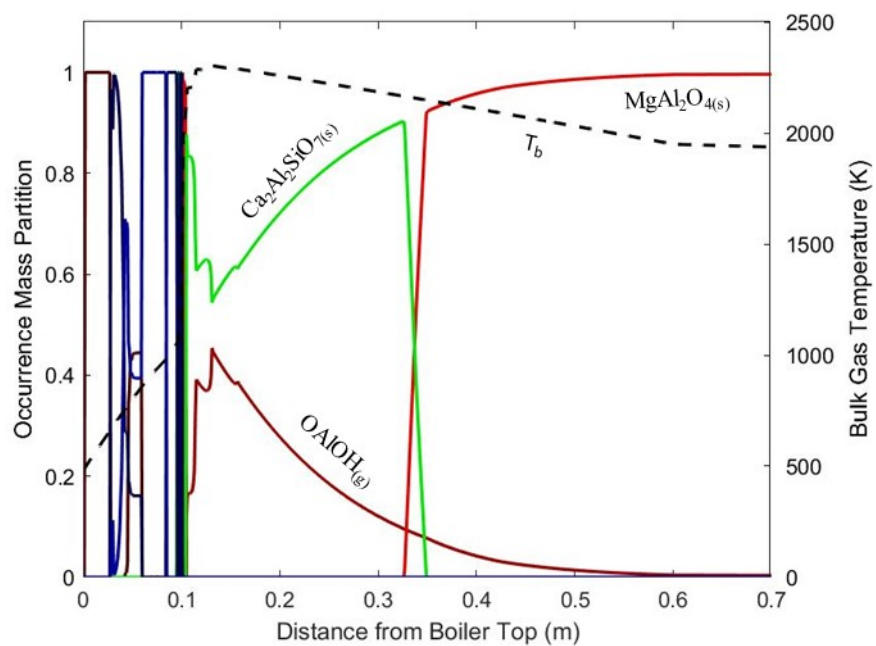


Figure J.16 Modelled Aluminium Bulk Occurrences in Oxy27-combustion of White Wood

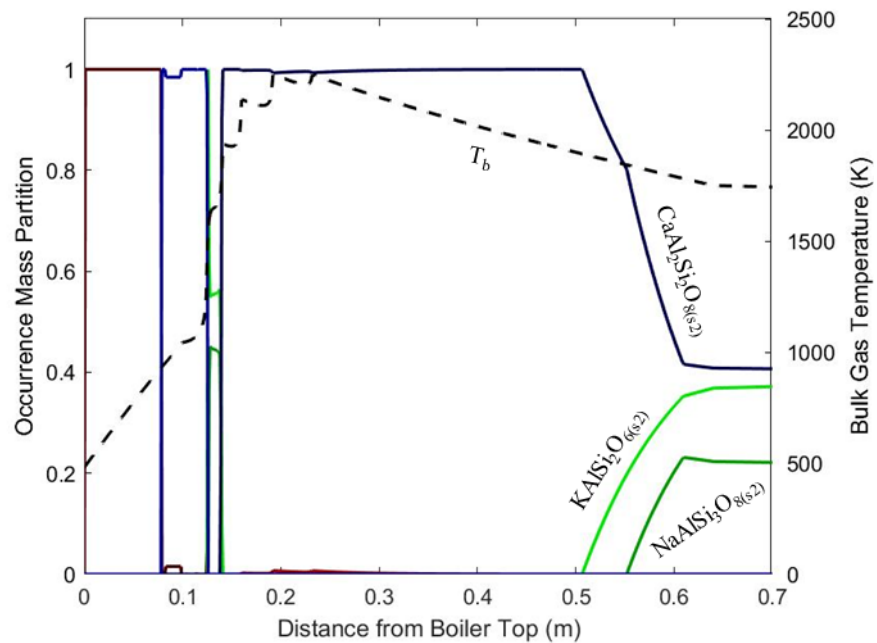


Figure J.17 Modelled Aluminium Bulk Occurrences in Air-combustion of Recycled Wood

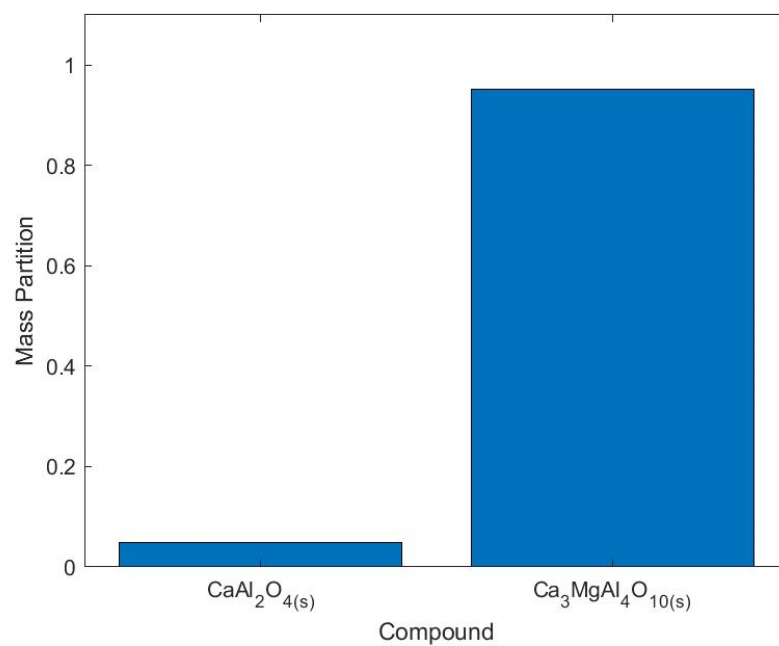


Figure J.18 Modelled Aluminium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of White Wood

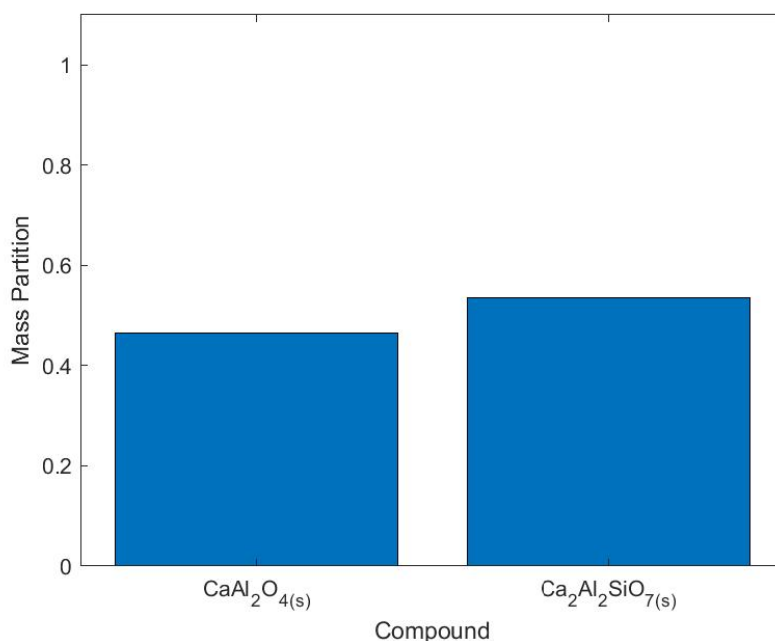


Figure J.19 Modelled Aluminium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of White Wood

Iron

Modelled fate profiles of iron for the Air/Oxy27 comparison and the white/recycled wood comparison are shown in Figure J.20 and Figure J.21. In Figure J.20, iron is modelled to be released as gas in both air-combustion and oxy27-combustion of white wood. During the *heat loss* stage, solid aerosols are formed during air-combustion but not during oxy27-combustion of white wood. In oxy27-combustion of white wood, a reduction of the quantity of $\text{O}_{2(g)}$ does not promote formation of stable solid aerosols. In air-combustion of recycled wood, as shown in Figure J.21, a significant quantity of released iron might promote formation of liquid aerosols that are later transformed into solid aerosols.

Unlike aluminium, iron shows no chemical interaction with calcium for either air-combustion of white wood or of recycled wood. The major formed products in air-combustion of white wood are $\text{Fe}(\text{OH})_{2(g)}$ and lesser amounts of $\text{Fe}_{(g)}$ and $\text{FeO}_{(g)}$, which diminish gradually as shown in Figure J.22. $\text{Fe}(\text{OH})_{2(g)}$ is formed via Reaction J.6.³⁸⁷



$\text{Fe}(\text{OH})_{2(g)}$ might also be formed due to $\text{FeO}_{(g)}$ interaction with steam, although there is no clear evidence that $\text{FeO}_{(g)}$ reacts directly with steam or is reduced first to $\text{Fe}_{(g)}$ which then reacts with steam.

According to modelled occurrence of bulk iron in air-combustion of white wood, shown in Figure J.24, $Fe_3O_{4(l)}$ is formed. A significant quantity of bulk iron at relatively low temperature during the *heat loss* stage promotes conversion of $Fe(OH)_{2(g)}$ to $Fe_3O_{4(l)}$. This reaction is known as the Schikorr reaction and is shown as Reaction J.7.



The Schikorr reaction generally occurs in anaerobic conditions.³⁸⁸ Although $O_{2(g)}$ is present during the *heat loss* stage, its concentration, at 3% to 4% of the volume fraction, is considered low enough for the Schikorr reaction to occur. In addition to $SiO_{2(l)}$, $Fe_3O_{4(l)}$ is a liquid aerosol that is considered to trigger ash deposition.

When the bulk temperature is as low as 1869 K, $Fe_3O_{4(l)}$ is solidified into $Fe_3O_{4(s)}$ as expressed in Reaction J.8.³⁸⁹



In the bottom ash, $Fe_3O_{4(s)}$ is the sole remaining iron compound, and is only present after air-combustion of white wood. $Fe_3O_{4(s)}$ formation in the bottom ash might be dictated by the initial iron concentration. Energy Dispersive X-ray Spectroscopy analysis performed in previous research has shown that a high iron content in solid fuel produces a significant amount of $Fe_3O_{4(s)}$ in bottom ash.³⁹⁰ The formation of $Fe_3O_{4(s)}$ in particles starts with the formation of $Fe_{(s)}$ by reaction with moisture and gasifying $H_2O_{(g)}$. During the *heat loan* stage, $FeOOH_{(s)}$ might be formed at low temperature. $Fe_3O_{4(s)}$ is rapidly formed during the *simultaneous pyrolysis and gasification* stage due to high temperatures and an increased pyrolysis rate. Since most $O_{2(g)}$ has already been utilised for homogeneous and heterogeneous reactions, not enough $O_{2(g)}$ remains to promote the oxidation process to produce $Fe_2O_{3(s)}$.³⁹¹

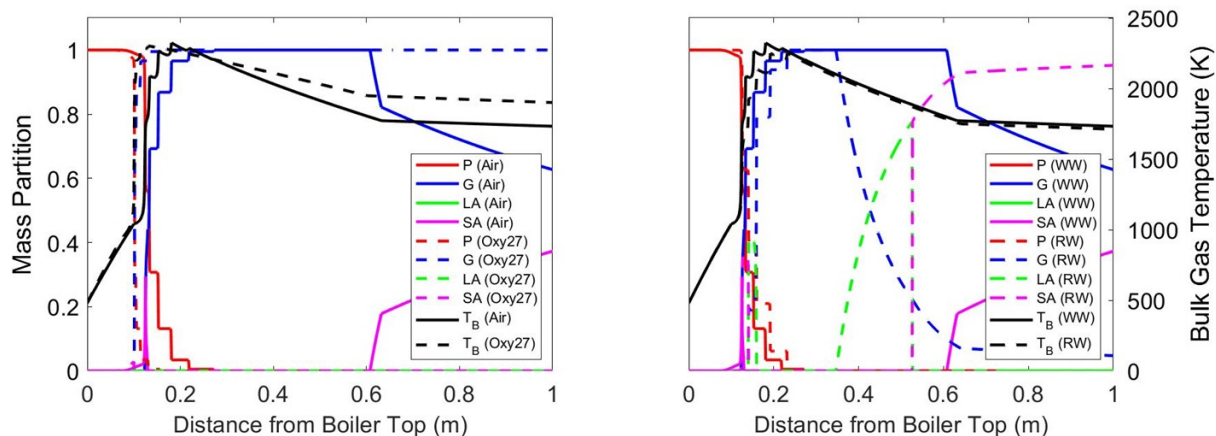


Figure J.20 (Left) Modelled Iron Fate Profile in Air-combustion and Oxy27-combustion of White Wood; **Figure J.21 (Right)** Modelled Iron Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

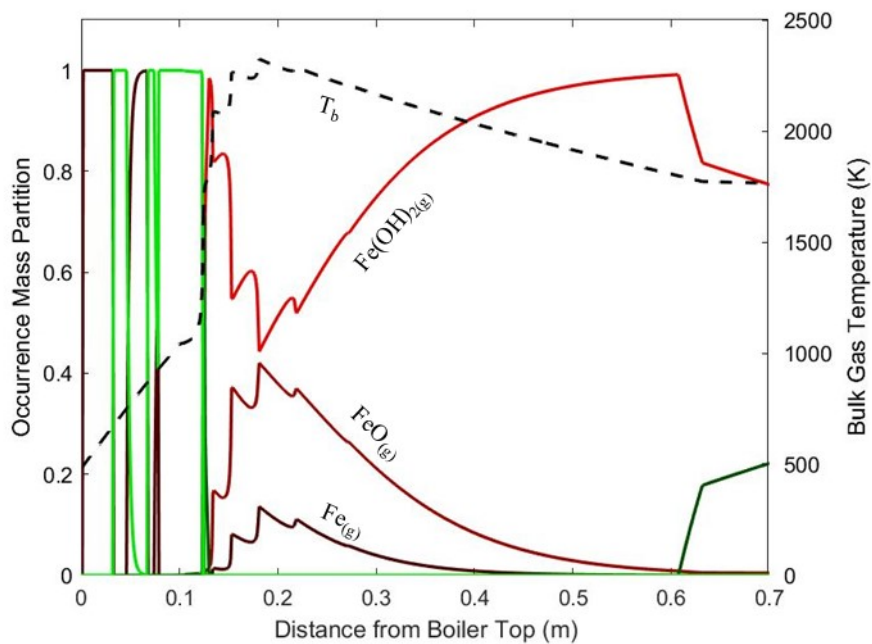


Figure J.22 Modelled Iron Bulk Occurrences in Air-combustion of White Wood

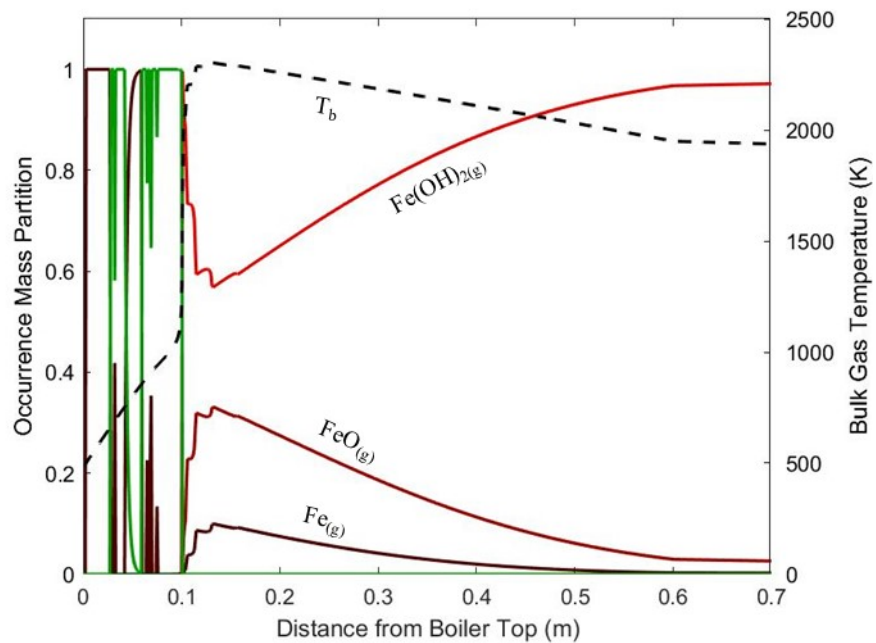


Figure J.23 Modelled Iron Bulk Occurrences in Oxy27-combustion of White Wood

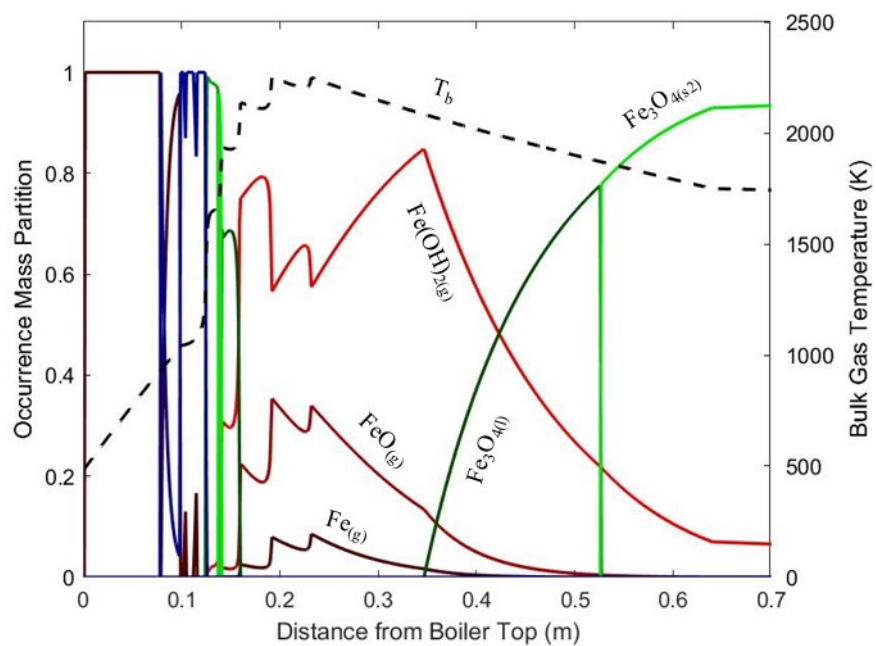


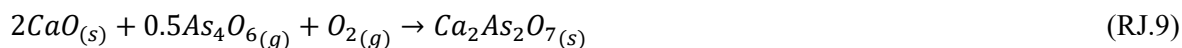
Figure J.24 Modelled Iron Bulk Occurrences in Oxy27-combustion of Recycled Wood

Arsenic

The fate behaviour of arsenic in modelled fate profiles are shown in Figure J.25 for the Air/Oxy27 comparison and in Figure J.26 for the white/recycled wood comparison. They corroborate the theory that arsenic shows high volatility in a high heating-rate combustion environment.³⁹² In both figures, arsenic is predicted to be released entirely as gaseous compounds once peak temperature is achieved, regardless of bulk $O_{2(g)}$ concentration or the original concentration of arsenic in the wood.

$AsO_{(g)}$ is the only formed arsenic compound in all modelled cases, as shown in Figures J.27, J.28, and J.29. $AsO_{(g)}$ is considered stable at high temperature.³⁹³ However, there has not been thorough observation of $AsO_{(g)}$ presence in high-temperature flames. Most works on arsenic occurrence have been conducted at temperatures below 1373 K, whilst the maximum temperature observed in an entrained-flow boiler is more than 2000 K with a heating rate as high as 500 K s^{-1} .³⁹⁴ At low temperatures, the most stable form of arsenic is $As_4O_{6(g)}$.³⁹⁵

$As_4O_{6(s)}$ forms Ca-As compounds during interaction with calcium solid aerosols, according to Reaction J.9.



Due to high temperatures in the fate and occurrence model, all arsenic is volatilised and remains gaseous.³⁹⁶

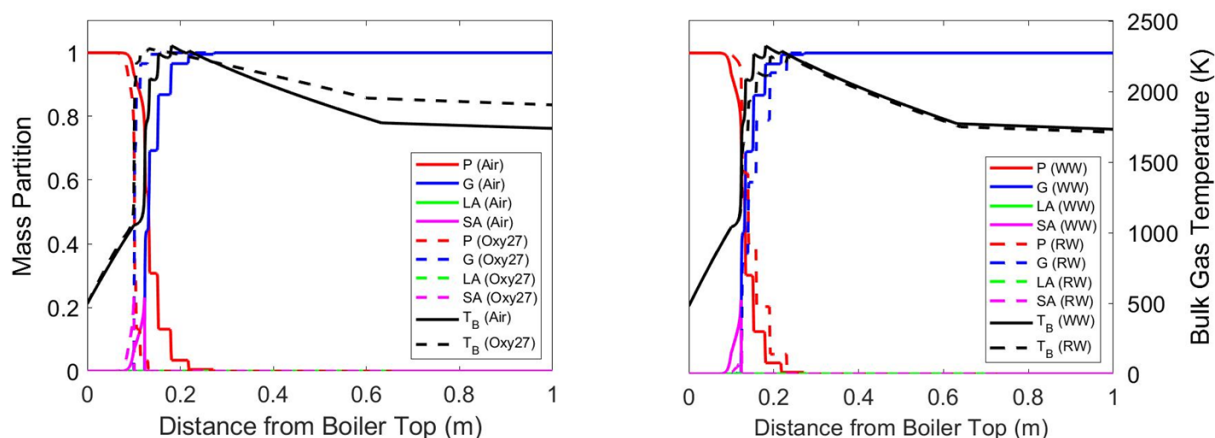


Figure J.25 (Left) Modelled Arsenic Fate Profiles in Air-combustion and Oxy27-combustion of White Wood; **Figure J.26 (Right)** Modelled Arsenic Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

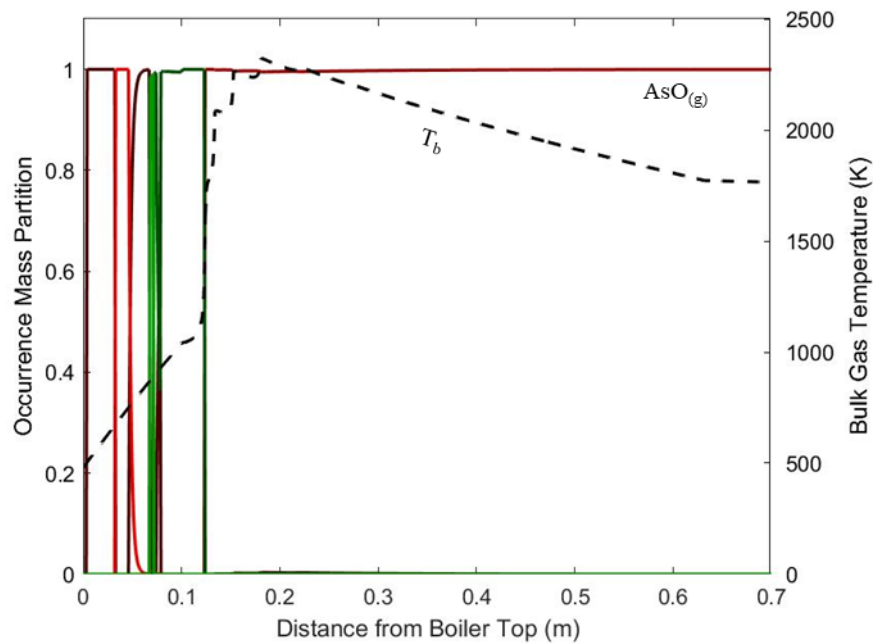


Figure J.27 Modelled Arsenic Bulk Occurrences in Air-combustion of White Wood

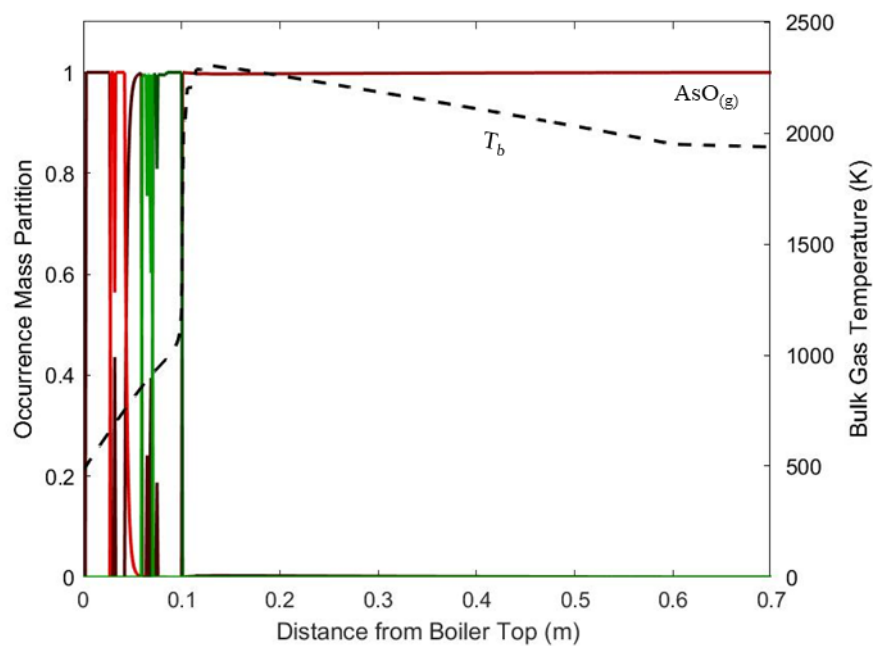


Figure J.28 Modelled Arsenic Bulk Occurrences in Oxy27-combustion of White Wood

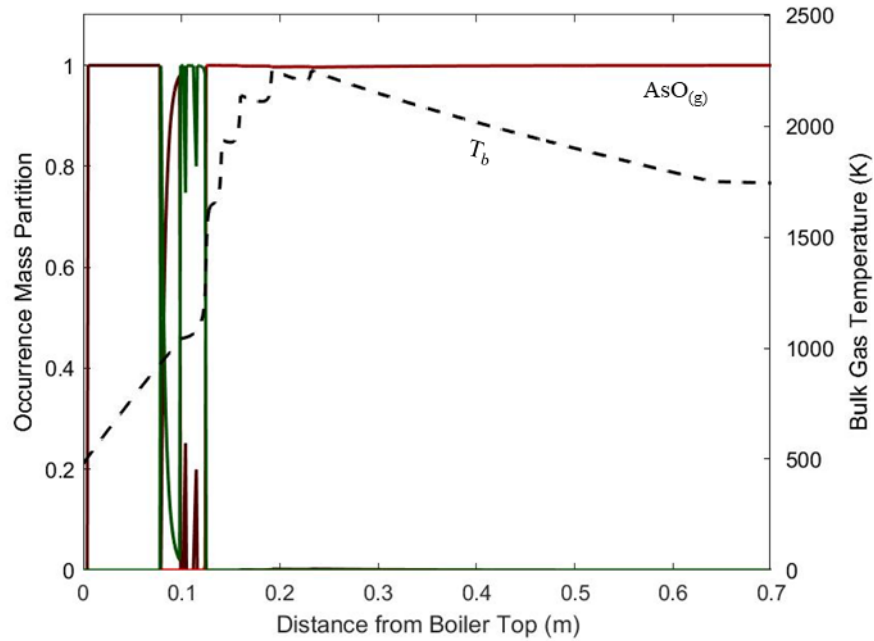


Figure J.29 Modelled Arsenic Bulk Occurrences in Air-combustion of Recycled Wood

Cadmium

Cadmium is known to exhibit strong volatility during solid fuel combustion, as shown in Figure J.30 for the Air/Oxy27 comparison and in Figure J.31 for the white/recycled wood comparison. Both diagrams and Figures J.32, J.33, and J.34 show that cadmium is entirely released as gaseous $\text{Cd}_{(g)}$.³⁹⁷ $\text{Cd}_{(g)}$ is very stable even at low combustion temperatures. A study has been conducted to observe $\text{CdO}_{(g)}$ decomposition within the temperature range 1000K to 1379 K. Within this temperature range, $\text{CdO}_{(g)}$ is decomposed according to Reaction J.10.³⁹⁸



$\text{CdO}_{(g)}$ might be found in ash produced during combustion at operationally low temperatures, e.g. in filter ash.³⁹⁹

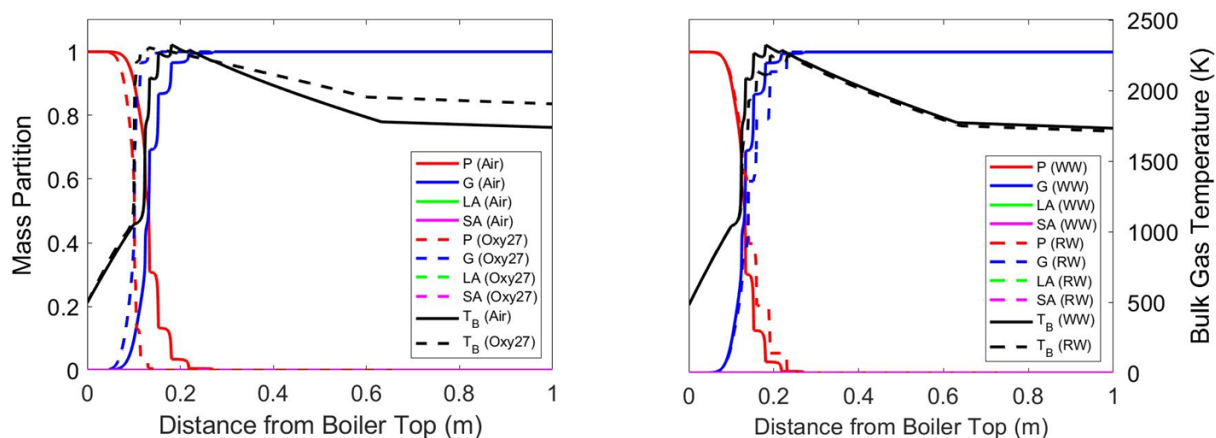


Figure J.30 (Left) Modelled Cadmium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood; **Figure J.31 (Right)** Modelled Cadmium Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

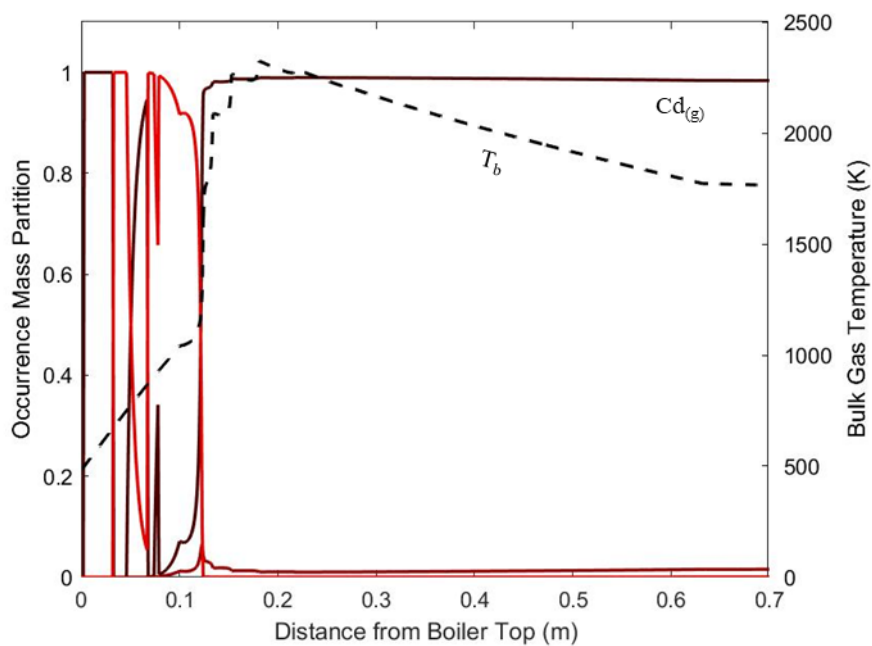


Figure J.32 Modelled Cadmium Bulk Occurrences in Air-combustion of White Wood

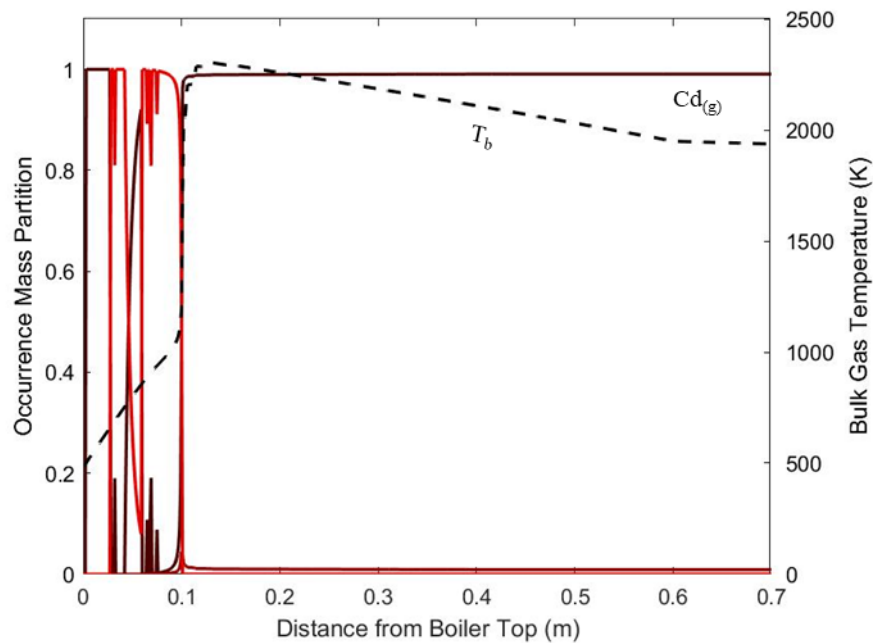


Figure J.33 Modelled Cadmium Bulk Occurrences in Oxy27-combustion of White Wood

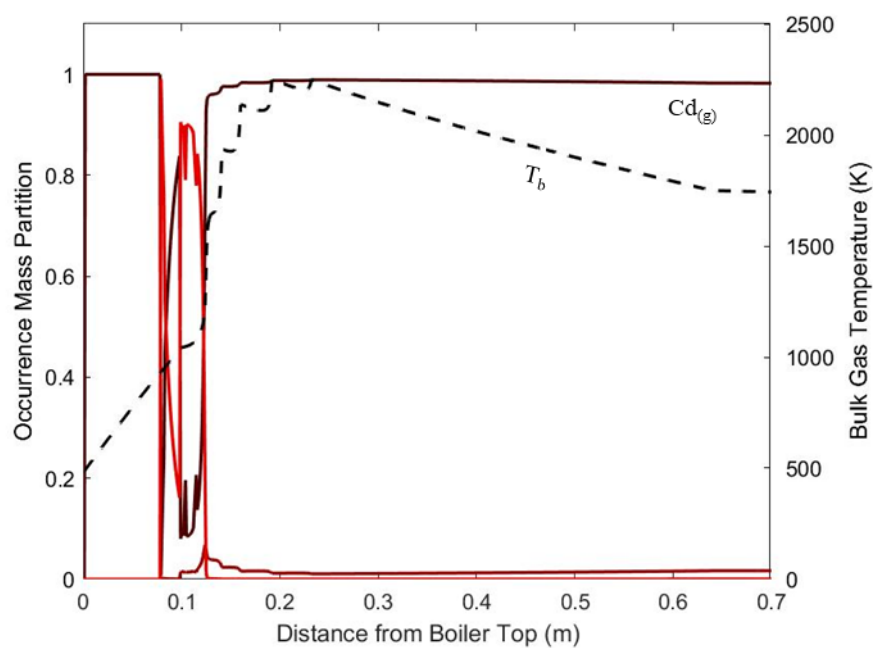


Figure J.34 Modelled Cadmium Bulk Occurrences in Air-combustion of Recycled Wood

Lead

The strong tendency of lead to volatilise has been validated in experiments that observed major lead speciation in fly ash rather than in bottom ash.⁴⁰⁰ As shown in Figure J.35 for the Air/Oxy27 comparison and in Figure J.36 for the white/recycled wood comparison, lead is volatilised completely in all cases according to the model developed in this research.

Modelled occurrence profiles for bulk lead are shown in Figures J.37, J.38, and J.39. $PbO_{(g)}$ and a small proportion of $Pb_{(g)}$ are the major compounds formed in all cases. Friswell and Jenkins⁴⁰¹ discovered experimentally that $Pb_{(g)}$ was stable in a flame environment under fuel-rich conditions. On the other hand, the existence of $PbO_{(g)}$ has been detected in a fuel-lean environment.

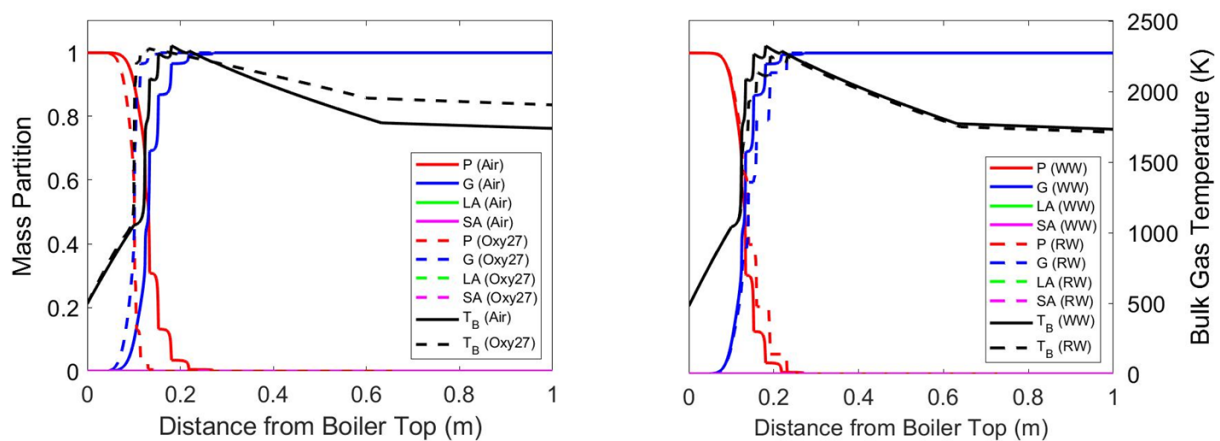


Figure J.35 (Left) Modelled Lead Fate Profiles in Air-combustion and Oxy27-combustion of White Wood; **Figure J.36 (Right)** Modelled Lead Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

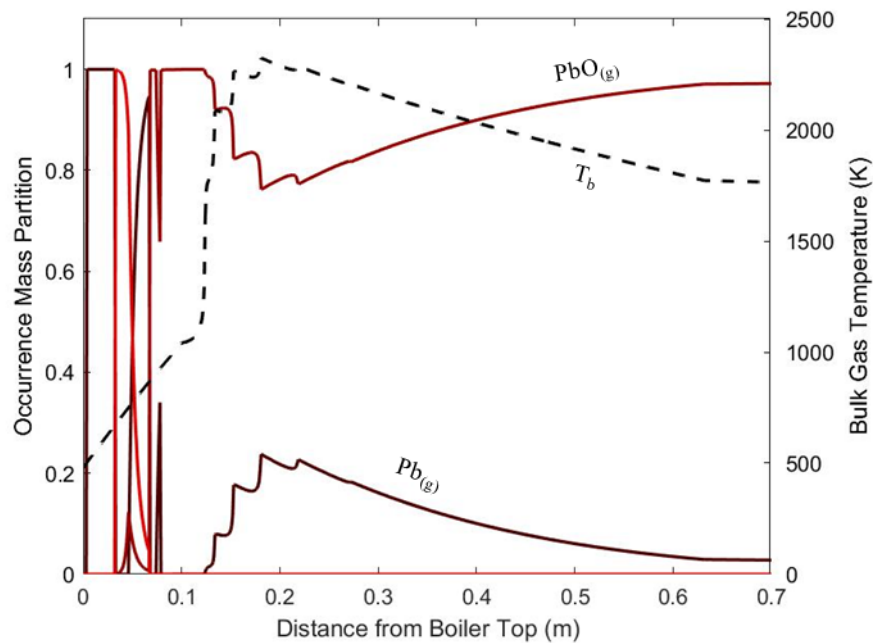


Figure J.37 Modelled Lead Bulk Occurrences in Air-combustion of White Wood

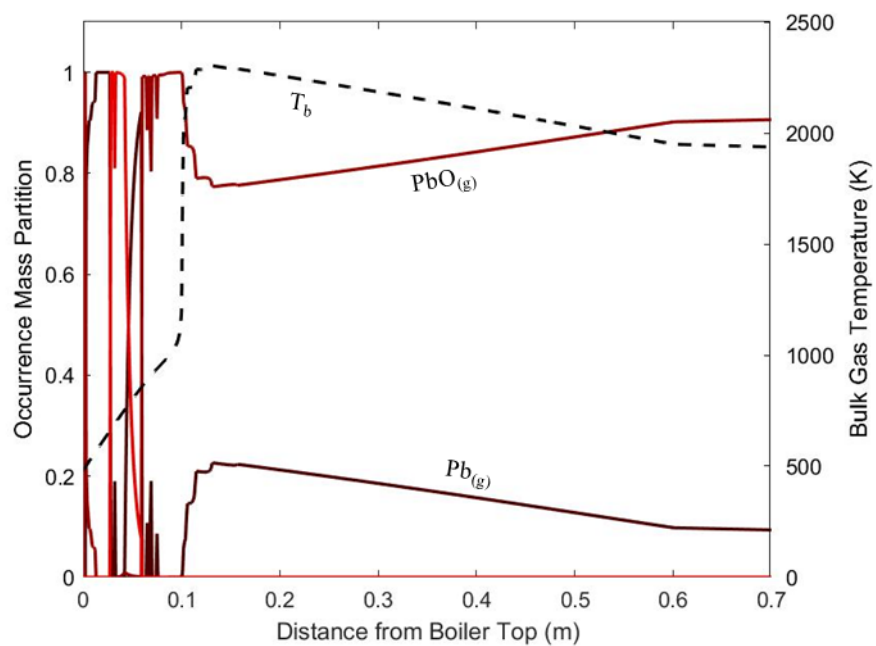


Figure J.38 Modelled Lead Bulk Occurrences in Oxy27-combustion of White Wood

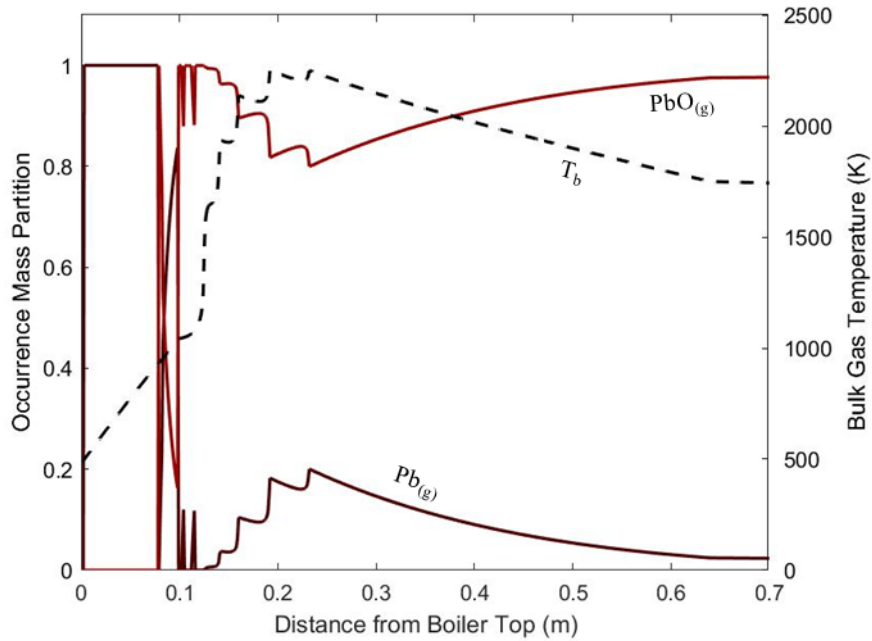


Figure J.39 Modelled Lead Bulk Occurrences in Air-combustion of Recycled Wood

Nickel

Nickel is considered a semivolatile element during solid-fuel combustion.⁴⁰² It has been reported to be distributed in both bottom ash and fly ash, often in similar proportions.⁴⁰³ However, according to the model developed in this research, nickel is entirely volatilised from the particles during the processes considered in the Air/Oxy27 comparison and the white/recycled wood comparison, as shown in Figures J.40 and J.41. This complete volatilisation is probably due to relatively low nickel content of the particles.

Modelled occurrence profiles of bulk nickel are shown in Figures J.42, J.43, and J.44. All figures exhibit relatively similar nickel occurrence. Nickel is likely to be released as $\text{Ni}_{(g)}$. Above 673 K, $\text{Ni}_{(g)}$ reacts with $\text{O}_{2(g)}$ to form $\text{NiO}_{(g)}$ as shown by Reaction J.11.⁴⁰⁴



$\text{NiO}_{(g)}$ is very stable at low temperature.⁴⁰⁵ Johnston and Marshall⁴⁰⁶ discovered that $\text{NiO}_{(g)}$ could be decomposed into $\text{Ni}_{(g)}$ at temperatures above 1,566 K. Since temperature during the *heat loss* stage is far higher than 1700 K, $\text{NiO}_{(g)}$ decomposition into $\text{Ni}_{(g)}$ is favoured. During the *heat loss* stage, $\text{H}_2\text{O}_{(g)}$ has higher partial pressure than $\text{O}_{2(g)}$. $\text{Ni}_{(g)}$ may have a greater tendency to react with $\text{H}_2\text{O}_{(g)}$, as expressed in Reaction J.12.⁴⁰⁷



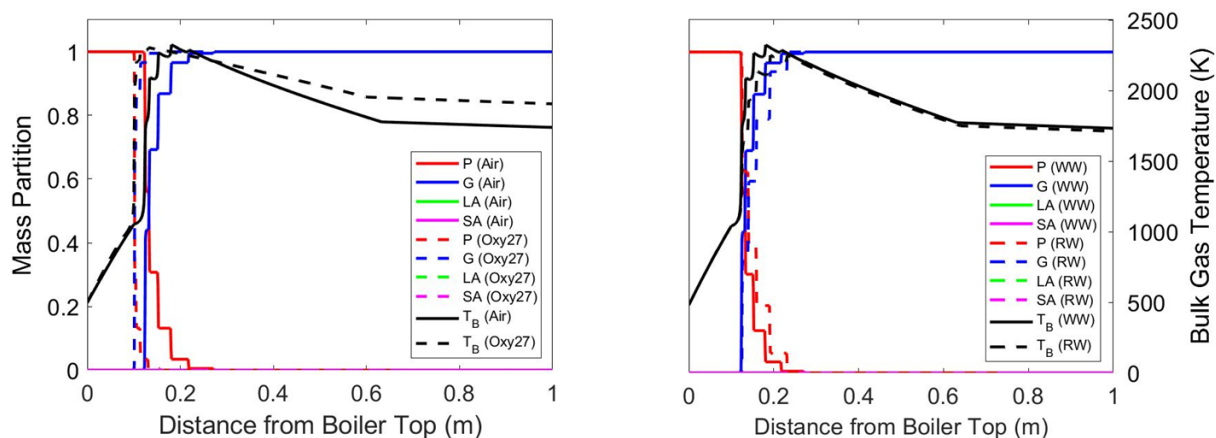


Figure J.40 (Left) Modelled Nickel Fate Profiles in Air-combustion and Oxy27-combustion of White Wood; **Figure J.41 (Right)** Modelled Nickel Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

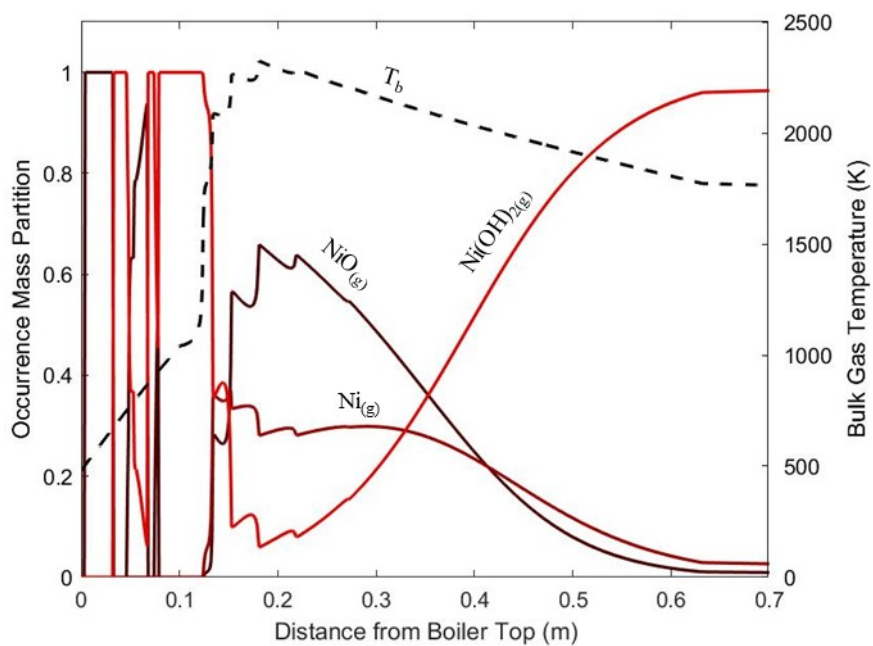


Figure J.42 Modelled Nickel Bulk Occurrences in Air-combustion of White Wood

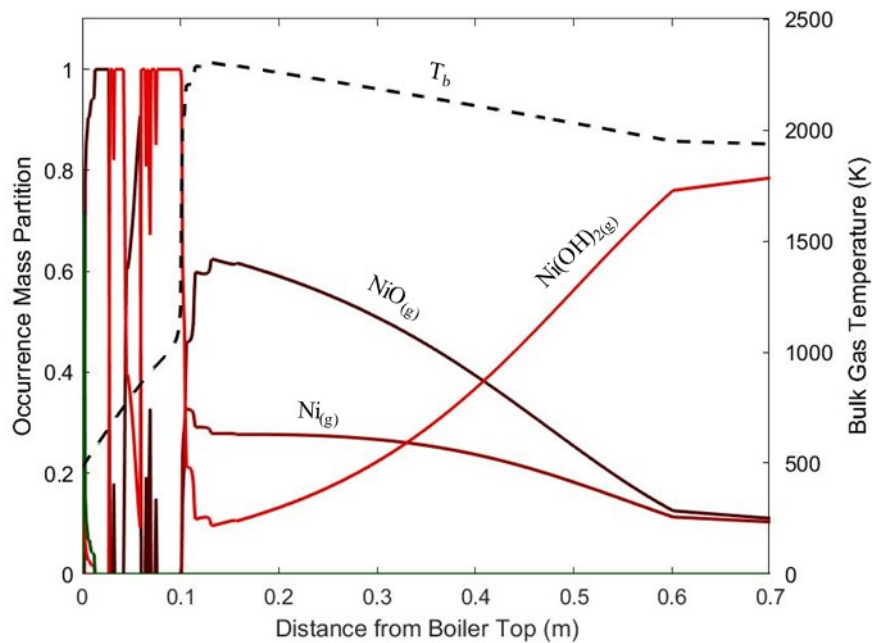


Figure J.43 Modelled Nickel Bulk Occurrences in Oxy27-combustion of White Wood

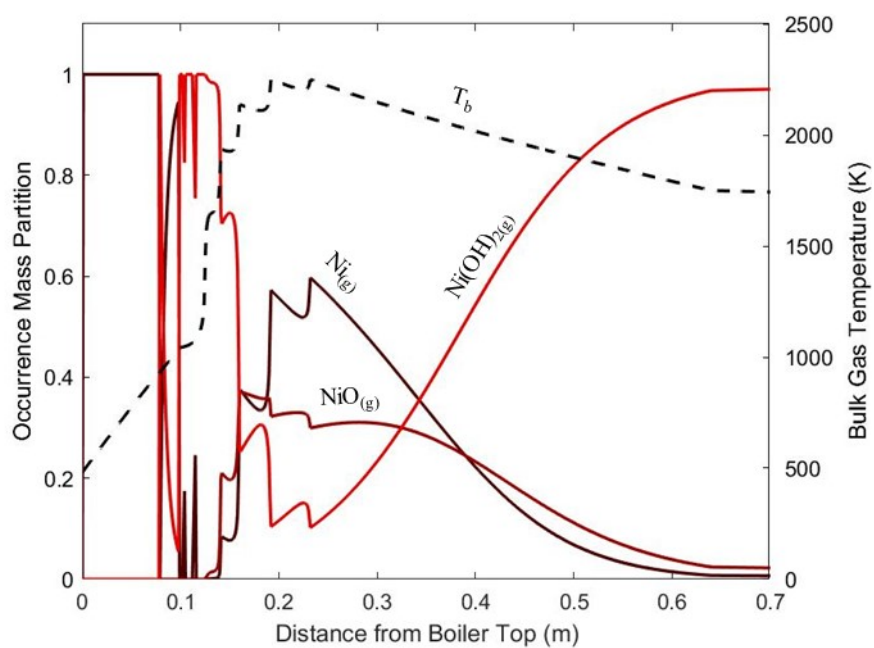


Figure J.44 Modelled Nickel Bulk Occurrences in Air-combustion of Recycled Wood

Vanadium

According to Figure J.45 for the Air/Oxy27 comparison and Figure J.46 for the white/recycled wood comparison, vanadium is completely volatilised as gas in all cases. Gaseous vanadium is converted to solid aerosols when the temperature is at around 1750 K. Vanadium is proven to be relatively non-volatile and is often found in large fly ash.⁴⁰⁸ This might be an indication of vanadium aerosol nucleation and coagulation.

The modelled profiles of vanadium production shown in Figures J.47, J.48, and J.49 indicate that vanadium is released as $\text{VO}_{2(g)}$. $\text{VO}_{2(g)}$ is chemically stable at temperatures above 1640 K.⁴⁰⁹ At lower temperature, $\text{VO}_{2(g)}$ may react with $\text{O}_{2(g)}$ to form $\text{V}_2\text{O}_{5(g)}$ according to Reaction J.13.



However, $\text{V}_2\text{O}_{5(g)}$ may react with calcium compounds at temperatures below 1640 K to form stable vanadates, e.g. $(\text{CaO})_3(\text{V}_2\text{O}_5)_{2(s)}$ and $(\text{CaO})_2(\text{V}_2\text{O}_5)_{2(s)}$.⁴¹⁰

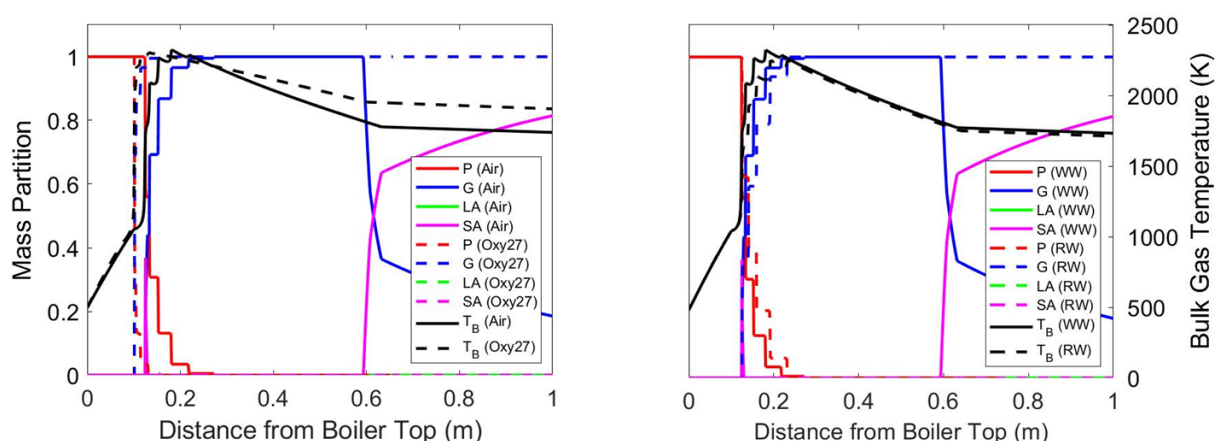


Figure J.45 (Left) Modelled Vanadium Fate Profiles in Air-combustion and Oxy27-combustion of White Wood; **Figure J.46 (Right)** Modelled Vanadium Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

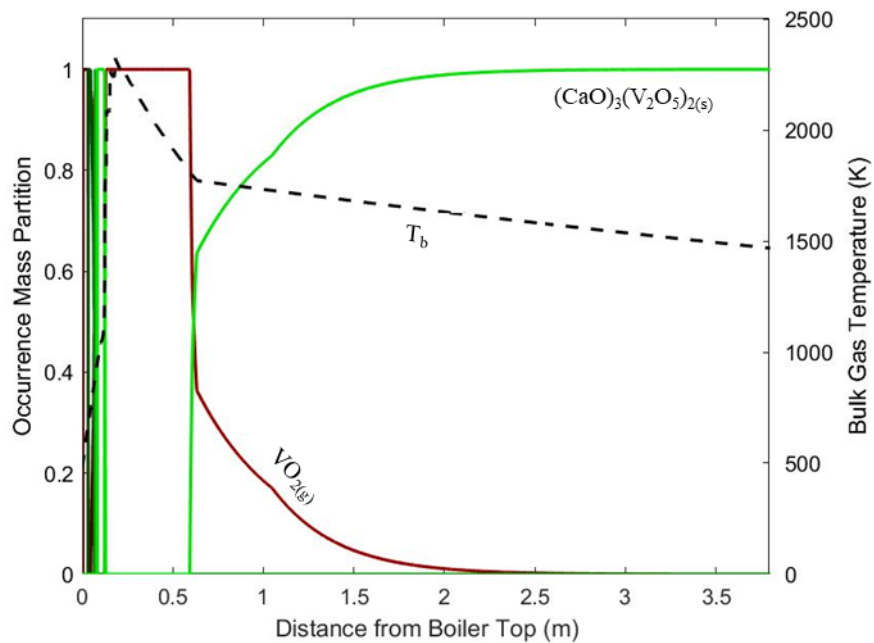


Figure J.47 Modelled Vanadium Bulk Occurrences in Air-combustion of White Wood

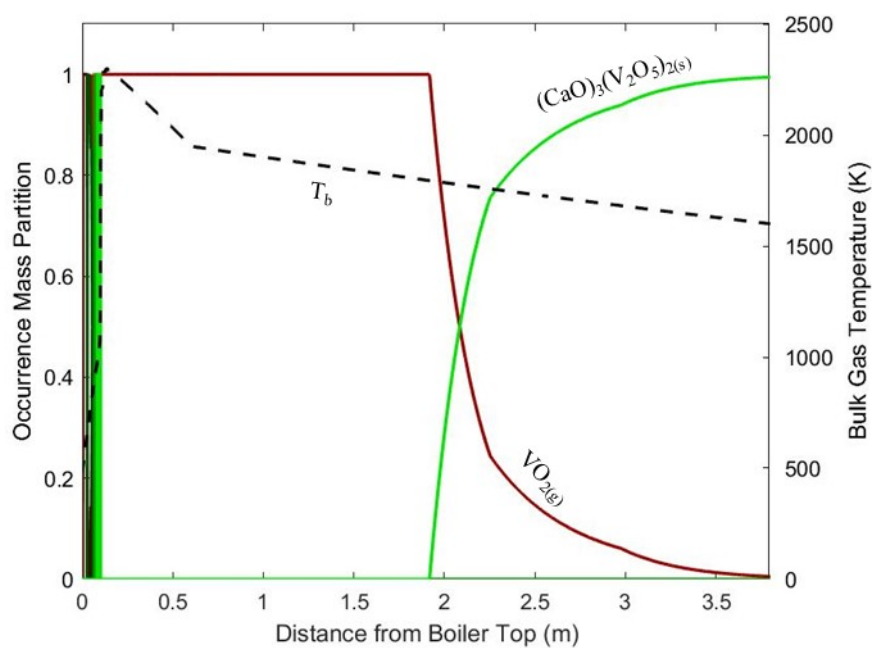


Figure J.48 Modelled Vanadium Bulk Occurrences in Oxy27-combustion of White Wood

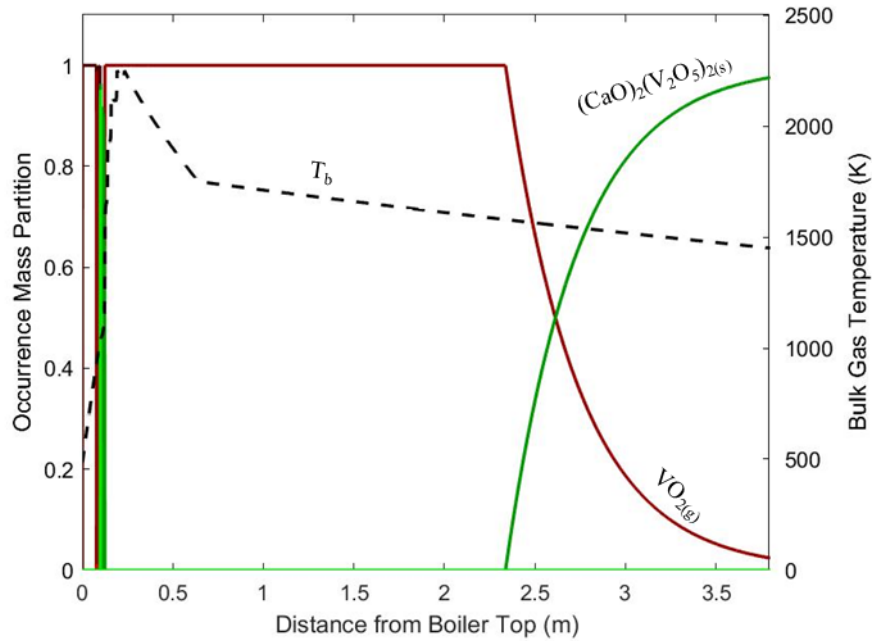


Figure J.49 Modelled Vanadium Bulk Occurrences in Air-combustion of Recycled Wood

Zinc

Zinc is very volatile in a combustion environment with a reducing atmosphere.⁴¹¹ As shown in Figure J.50 for the Air/Oxy27 comparison and in Figure J.51 for the white/recycled wood comparison, zinc is entirely volatilised in all cases. The presence of zinc in all cases is mainly as $Zn_{(g)}$, as shown in Figures J.52, J.53, and J.54. At high temperatures above 1700 K during the *heat removal* and *heat loss* stages, $Zn_{(g)}$ is a very stable compound. An observation of $Zn_{(g)}$ stability at high temperature has been conducted by other researchers, who introduced $ZnO_{(g)}$ into a combustion environment at a temperature of 2,248 K. At high temperature, $ZnO_{(g)}$ is decomposed into $Zn_{(g)}$ and $O_{2(g)}$ according to Reaction J.14.⁴¹²



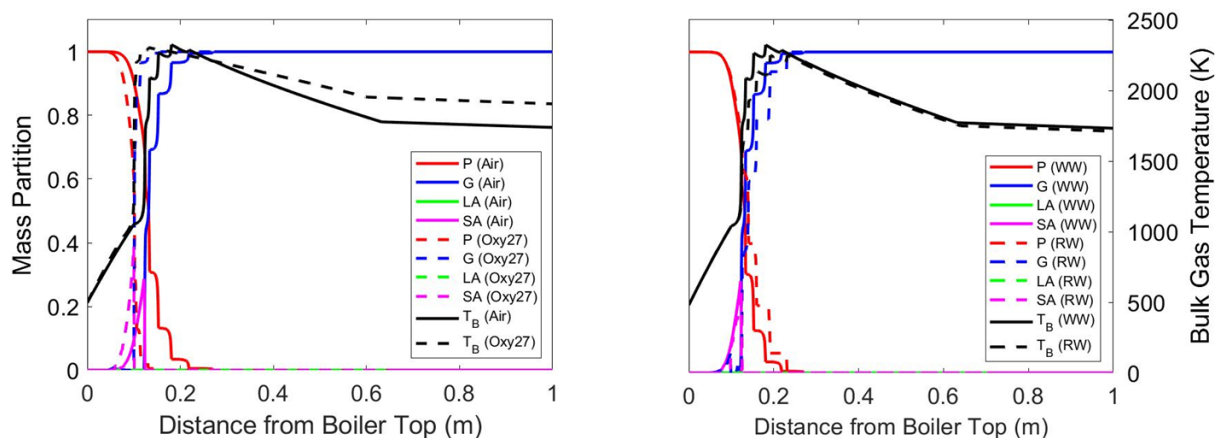


Figure J.50 (Left) Modelled Zinc Fate Profile in Air-combustion and Oxy27-combustion of White Wood; **Figure J.51 (Right)** Modelled Zinc Fate Profile in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B : Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

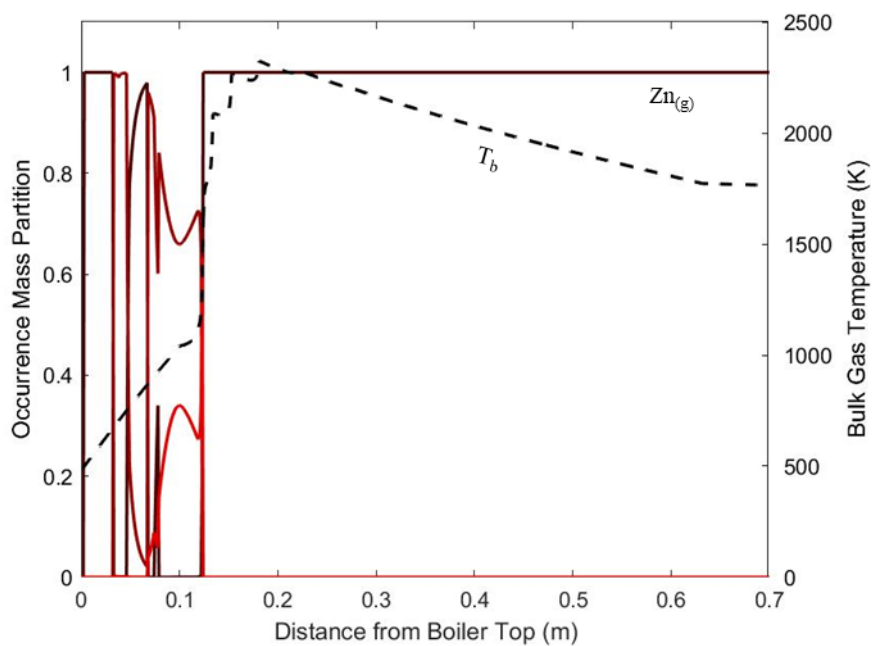


Figure J.52 Modelled Zinc Bulk Occurrences in Air-combustion of White Wood

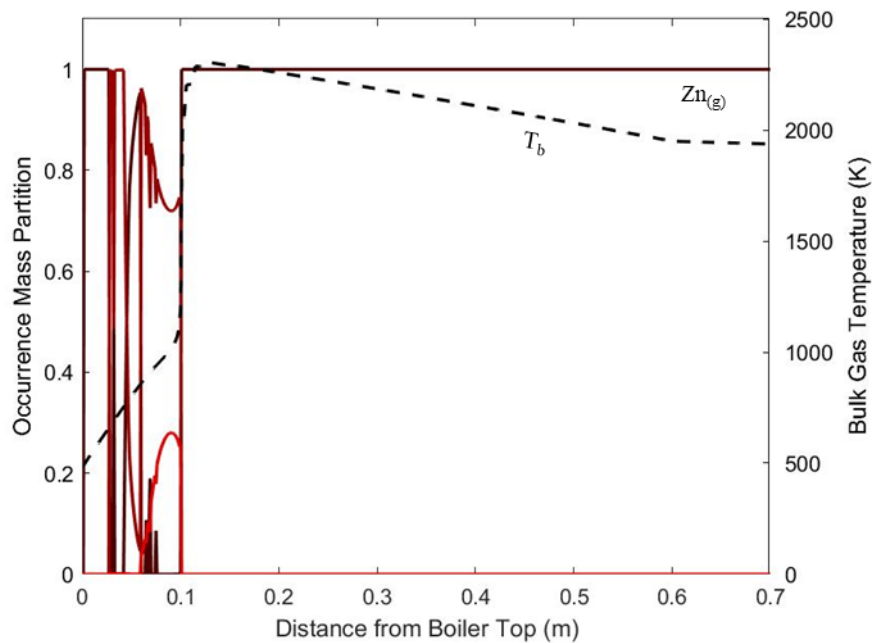


Figure J.53 Modelled Zinc Bulk Occurrences in Oxy27-combustion of White Wood

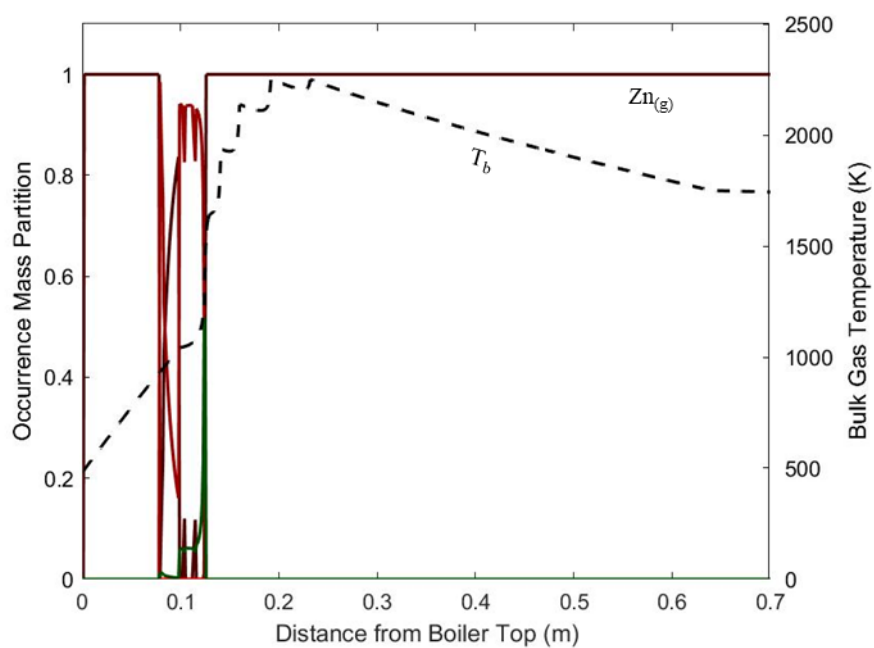


Figure J.54 Modelled Zinc Bulk Occurrences in Air-combustion of Recycled Wood

Mercury

Modelled fate profiles for bulk mercury are shown in Figure J.55 for the Air/Oxy27 and in Figure J.56 for the white/recycled wood comparison. They exhibit that no mercury remains in the particles. Mercury is volatilised mainly as gas due to high vapour pressure.⁴¹³ Mercury is released as $Hg_{(g)}$ in all cases, as shown in Figures J.57, J.58, and J.59. $Hg_{(g)}$ is normally oxidised at temperatures below 500 K, according to Reaction 6.35.



However, at temperatures above 500 K, backward reaction of Reaction J.15 dominates. In an extremely hot environment, $Hg_{(g)}$ is the major compound formed.⁴¹⁴

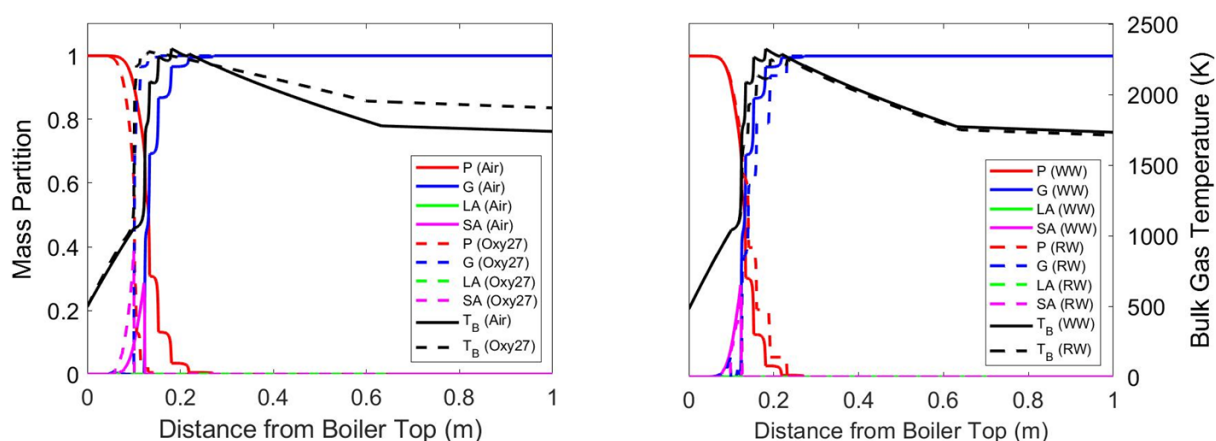


Figure J.55 (Left) Modelled Zinc Fate Profile in Air-combustion and Oxy27-combustion of White Wood; **Figure J.56 (Right)** Modelled Zinc Fate Profiles in Air-combustion of White Wood and Recycled Wood; P: Particle, G: Gas, LA: Liquid Aerosol, SA: Solid Aerosol, T_B: Bulk Temperature, Air: Air-combustion, Oxy27: Oxy27-combustion, WW: White Wood, RW: Recycled Wood

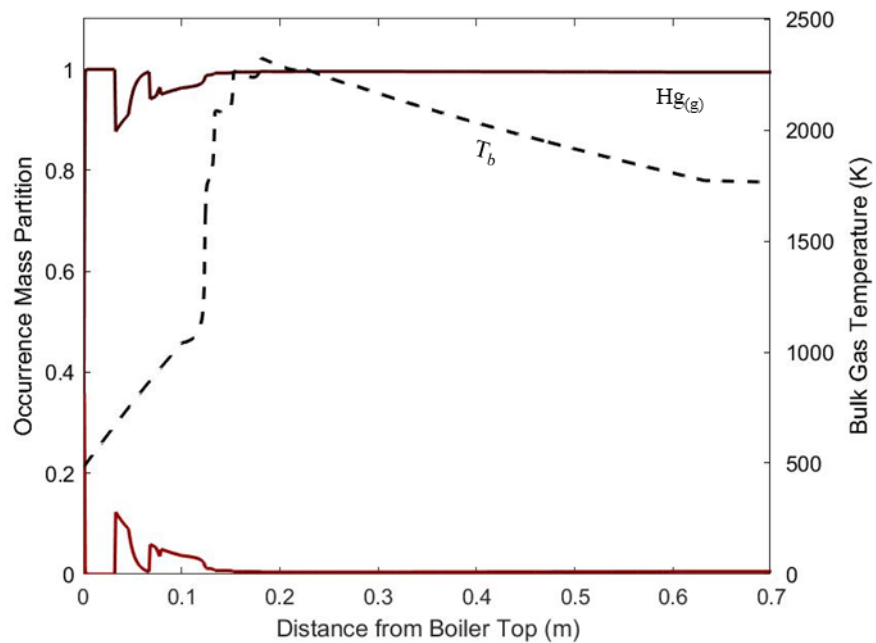


Figure J.57 Modelled Mercury Bulk Occurrences in Air-combustion of White Wood

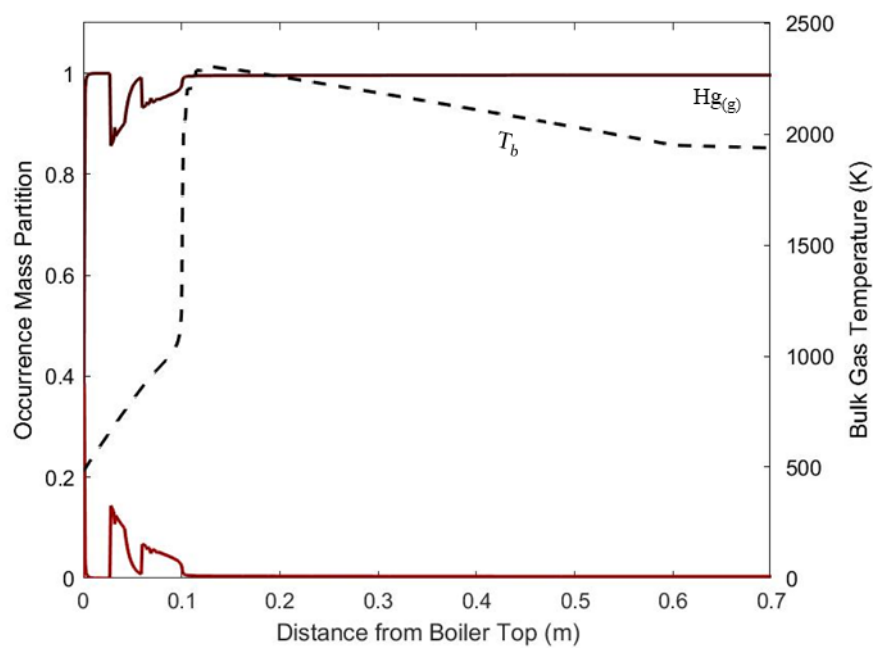


Figure J.58 Modelled Mercury Bulk Occurrences in Oxy27-combustion of White Wood

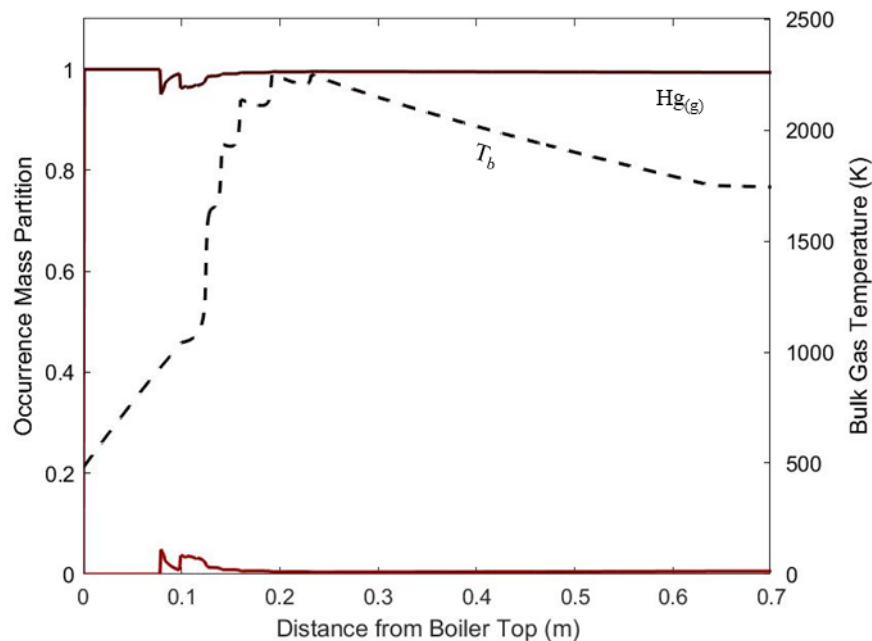


Figure J.59 Modelled Mercury Bulk Occurrences in Air-combustion of Recycled Wood

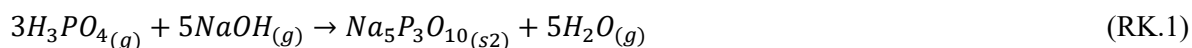
Appendix K: AFE and TE Fate and Occurrence Profiles of Rice Husk

This appendix compiles the discussion of the fate and occurrence profiles of the AFEs and TEs other than potassium, calcium, and silicon in the combustion of rice husk wood in PACT facility entrained-flow boiler.

Sodium

The modelled fate profile of sodium is shown in Figure K.1. At peak temperature, all the sodium is released from the particles as gas. During the *heat loss* stage, the phase of bulk sodium changes from gas to solid aerosols at a significant proportion. This phase change contradicts the previously reported volatile behaviour of sodium shown in Figure J.1, due to the large amount of sodium present in rice husk. This considerable amount is likely to promote chemical association of sodium with the other AFEs to form solid aerosols at relatively high temperatures. Figure K.1 also shows that more concentrated $O_{2(g)}$ in the oxy27-combustion might intensify formation of solid aerosols.

Modelled occurrence profiles of bulk sodium are shown in Figure K.2 for air-combustion and in Figure K.3 for oxy27-combustion. In air-combustion, most of the sodium is initially volatilised as $\text{NaOH}_{(g)}$. This is in agreement with the sodium behaviour reported earlier and shown in Figure J.3. However, $\text{NaOH}_{(g)}$ is converted into $\text{Na}_5\text{P}_3\text{O}_{10(s2)}$ during the *heat loss* stage. $\text{Na}_5\text{P}_3\text{O}_{10(s2)}$ formation might be via Reaction K.1.



Phosphorus is likely to be released as $\text{H}_3\text{PO}_{4(g)}$, which reacts with $\text{NaOH}_{(g)}$. Suwarnakar *et al.*⁴¹⁵ conducted research on $\text{Na}_5\text{P}_3\text{O}_{10(s2)}$ production based on Reaction K.1. Although the production experiment was performed in liquid phase at temperatures below 873 K, Reaction K.1 may occur at temperatures above 1,500 K in gaseous and aerosol phases. Other than $\text{Na}_5\text{P}_3\text{O}_{10(s2)}$, a small proportion of $\text{Na}_{12}\text{Mg}_4\text{P}_{10}\text{O}_{35(s)}$ was formed and this was later transformed into $\text{Na}_3\text{MgP}_3\text{O}_{10(s)}$. $\text{Na}_3\text{MgP}_3\text{O}_{10(s)}$ is possibly produced from $\text{Na}_5\text{P}_3\text{O}_{10(s)}$ reaction with magnesium compounds.⁴¹⁶ On the other hand, $\text{Na}_5\text{P}_3\text{O}_{10(s2)}$ is the only bulk sodium occurrence in oxy27-combustion during the *heat loss* stage, as shown in Figure K.3. The higher $\text{O}_{2(g)}$ concentration in oxy27-combustion might increase selectivity towards $\text{Na}_5\text{P}_3\text{O}_{10(s2)}$ formation. Both Figures K.2 and K.3 show that there is a significant affinity between sodium and phosphorus when they are present at relatively large concentrations. However, despite sharing similar alkaline characteristics, potassium does not exhibit strong association with phosphorus.⁴¹⁷

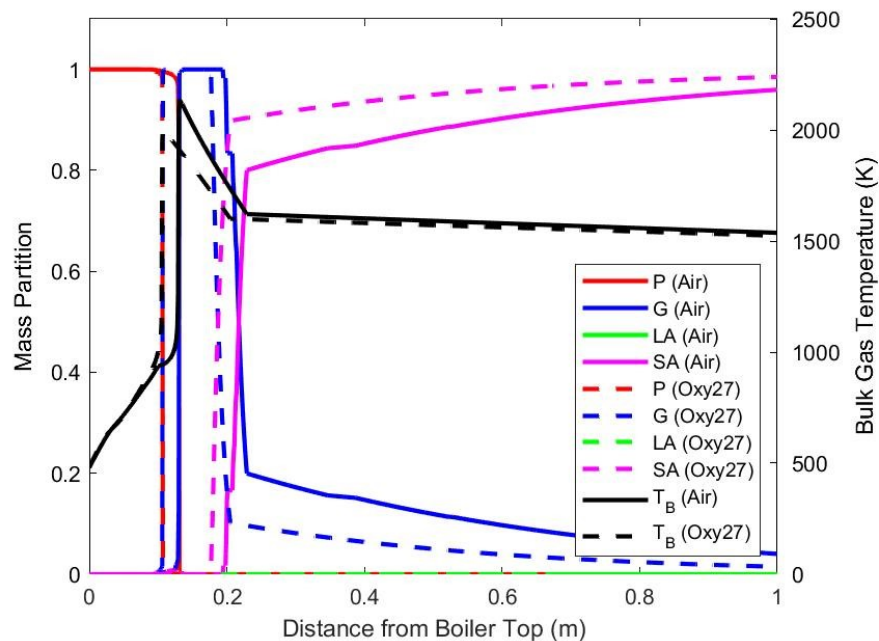


Figure K.1 Modelled Sodium Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion)

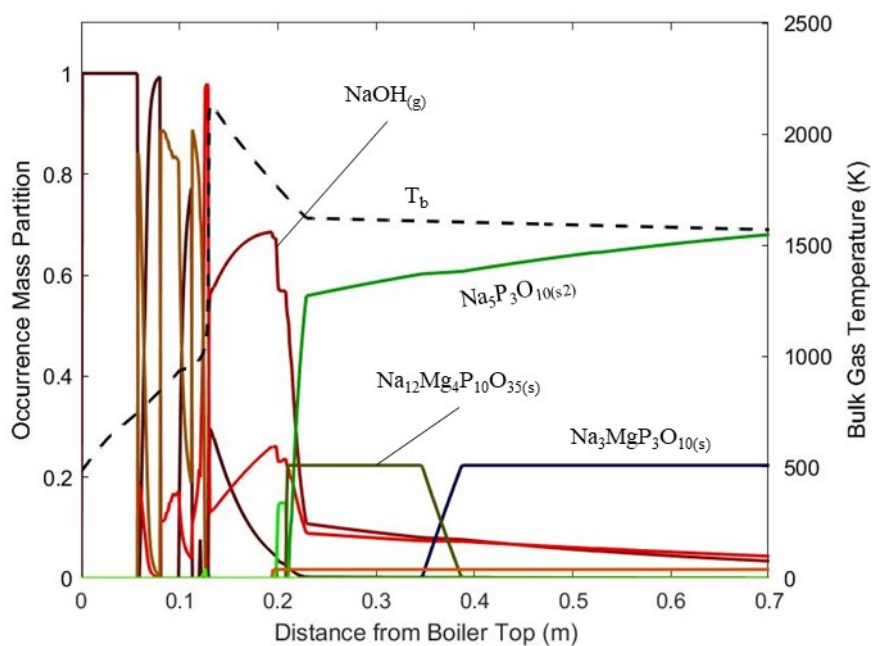


Figure K.2 Modelled Sodium Bulk Occurrences in Air-combustion of Rice Husk

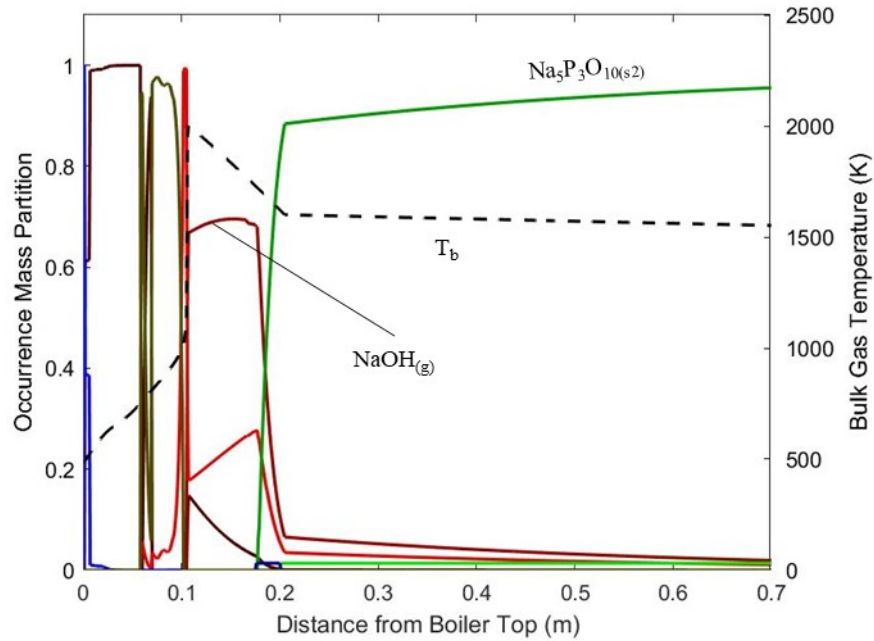


Figure K.3 Modelled Sodium Bulk Occurrences in Oxy27-combustion of Rice Husk

Magnesium

The modelled fate profile of magnesium is shown in Figure K.4. A small partition of magnesium is volatilised from the particles in air-combustion. On the other hand, magnesium completely remains in the particles in oxy27-combustion. In air-combustion, magnesium is released as $\text{Mg}(\text{OH})_{2(\text{g})}$ at peak temperature, as shown in Figure K.5. Magnesium occurrence changes several times during the *heat removal* stage, probably due to reactions with phosphorus and silicon. When the *heat loss* stage begins, $\text{Na}_{12}\text{Mg}_4\text{P}_{10}\text{O}_{35(\text{s})}$ is formed as the major magnesium compound. The quantity of $\text{Na}_{12}\text{Mg}_4\text{P}_{10}\text{O}_{35(\text{s})}$ later diminishes as $\text{Na}_3\text{MgP}_3\text{O}_{10(\text{s})}$ emerges. Unfortunately, the transformation of $\text{Na}_{12}\text{Mg}_4\text{P}_{10}\text{O}_{35(\text{s})}$ into $\text{Na}_3\text{MgP}_3\text{O}_{10(\text{s})}$ has yet to be proven. However, Ust'yantsev *et al.*⁴¹⁸ have confirmed magnesium's affinity to phosphorus by forming $\text{Na}_3\text{MgP}_3\text{O}_{10(\text{s})}$ at high temperature through dissolution of $\text{MgO}_{(\text{s})}$ into $\text{NaPO}_3(\text{aq})$.

Magnesium occur in the bottom ash in air-combustion solely as $\text{CaMgSi}_2\text{O}_6(\text{s})$. Silicon is likely to suppress the departure of magnesium from the particles by reacting with magnesium and calcium to form a silicate compound.

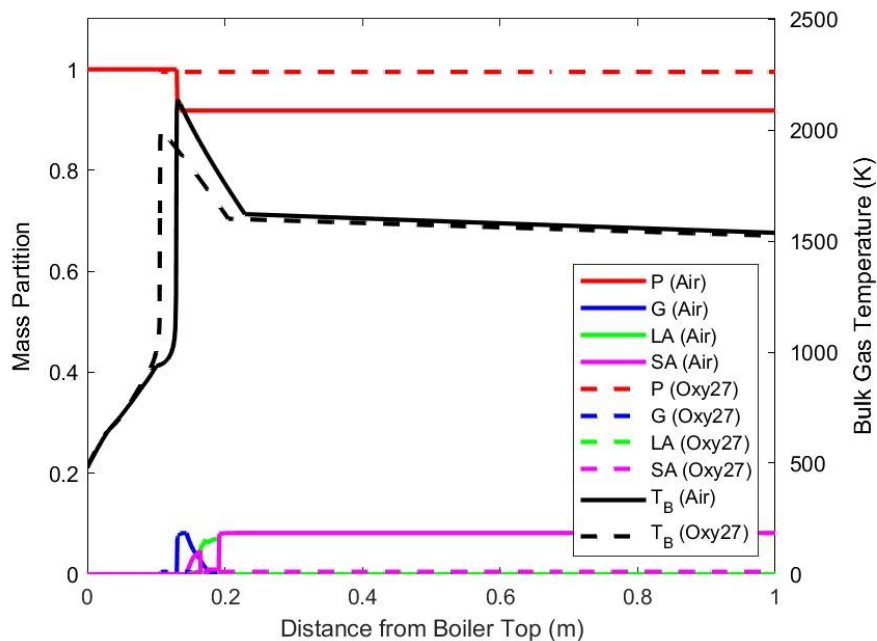


Figure K.4 Modelled Magnesium Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion

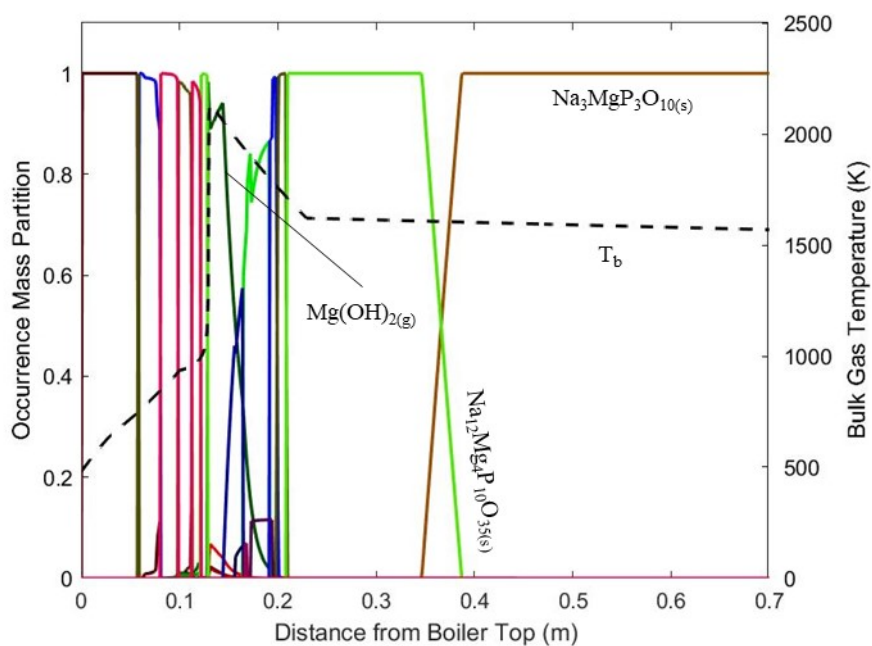
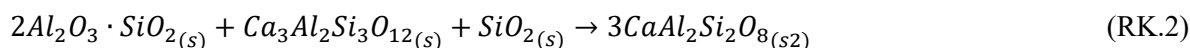


Figure K.5 Modelled Magnesium Bulk Occurrences in Air-combustion of Rice Husk

Aluminium

According to the modelled aluminium fate profile shown in Figure K.6, almost none of the aluminium is released from the particles. As shown in Figures K.7 and K.8, $KaSi_3O_{8(s2)}$, $CaAl_2Si_2O_{8(s2)}$, and $Ca_3Al_2Si_3O_{12(s)}$ are the primary aluminium compounds formed in the bottom ash in both air-combustion and oxy27-combustion. $KaSi_3O_{8(s2)}$ and $CaAl_2Si_2O_{8(s2)}$ are formed via Reactions 8.4 and J.5, respectively. At temperatures below 392 K, $Ca_3Al_2Si_3O_{12(s)}$ is chemically stable. However, $Ca_3Al_2Si_3O_{12(s)}$ might react with $SiO_{2(s)}$ to form $CaAl_2Si_2O_{8(s2)}$ at temperatures above 392 K, according to Reaction K.2.⁴¹⁹



$KaSi_3O_{8(s2)}$ partition dominates over the other compounds predicted to be in bottom ash of oxy27-combustion. This is due to higher potassium retention in oxy27-combustion.

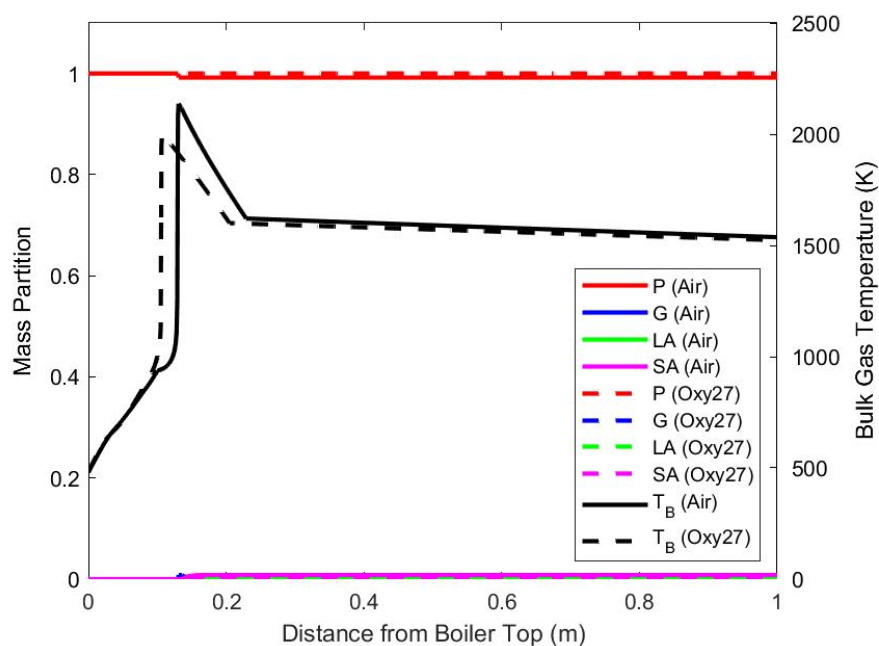


Figure K.6 Modelled Aluminium Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion)

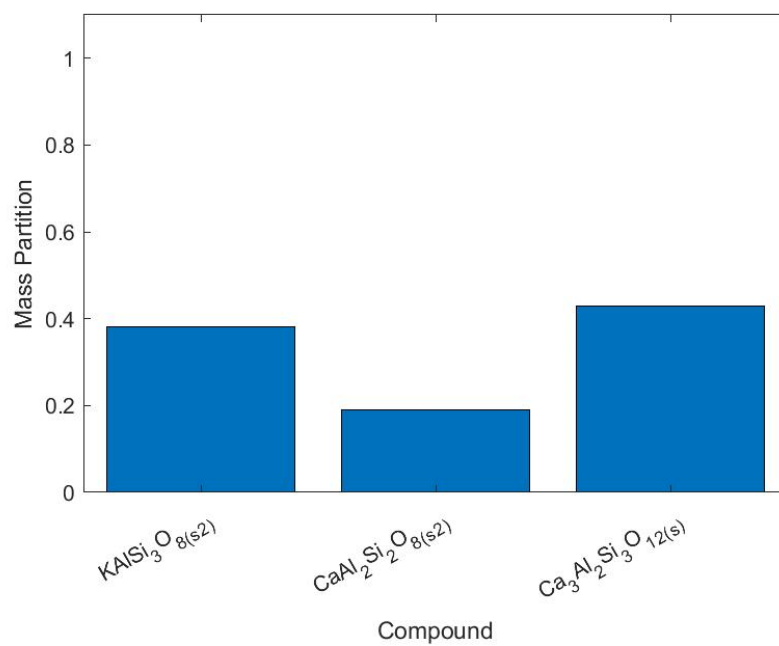


Figure K.7 Modelled Aluminium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Rice Husk

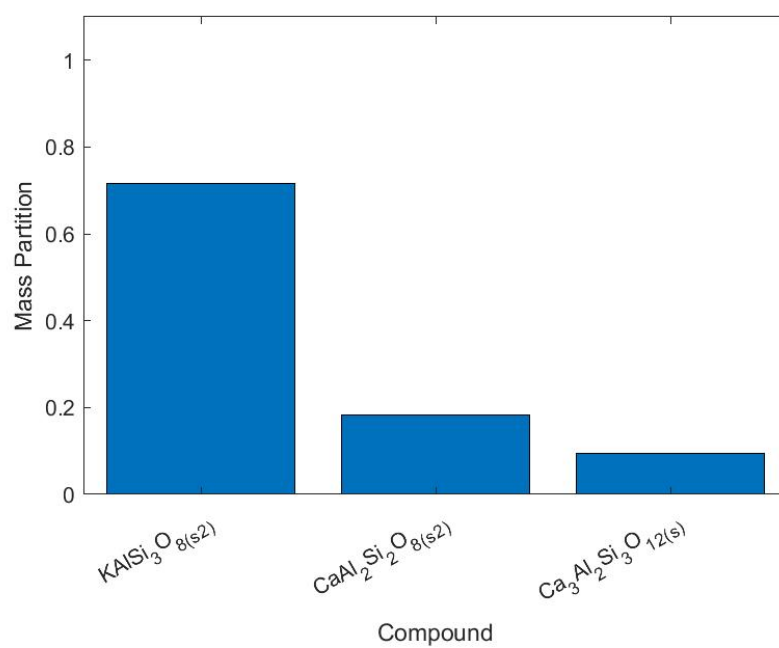
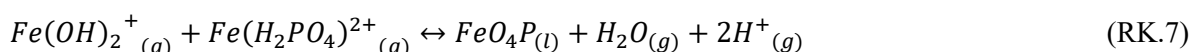
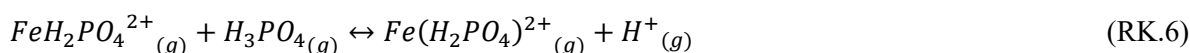
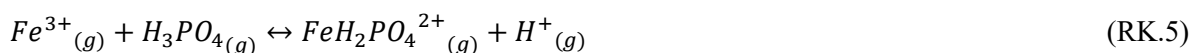
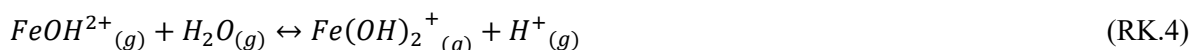


Figure K.8 Modelled Aluminium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Rice Husk

Iron

The modelled fate profile of iron is shown in Figure K.9. Iron is released as gas at peak temperature in both air-combustion and oxy27-combustion. Gaseous iron is converted to solid aerosols during the *heat removal* stage shortly before forming liquid aerosols during the *heat loss* stage. A considerable proportion of iron remains in the particles in oxy27-combustion, whilst all the iron is released from the particles in air-combustion. The remaining iron might form oxides, probably as a result of more intense particle oxidation promoted by the presence of higher quantities of O_{2(g)} in oxy27-combustion.

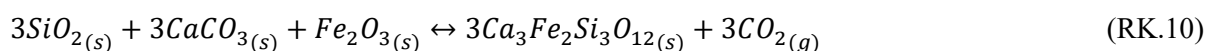
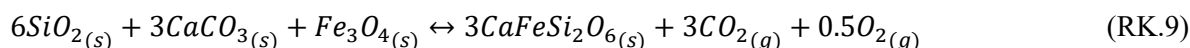
Modelled bulk iron occurrence profiles in air-combustion and oxy27-combustion are shown in Figures K.10 and K.11, respectively. Both profiles show similar iron occurrences. Iron is released from the particles as Fe(OH)_{2(g)}, which is formed via Reaction J.6. Fe(OH)_{2(g)} is transformed into FeO₄P_(l) during the *heat loss* stage. Shiratsuchi *et al.*⁴²⁰ studied iron and phosphorus affinity and found that Fe reacted with P₂O₅ to form FeO₄P. Wilhelmy and Matijevic⁴²¹ suggested the formation of FeO₄P_(l) by the mechanism shown in Reactions K.3, K.4, K.5, K.6, and K.7.



Fe³⁺_(g) in Reaction K.3 might be sourced from FeCl_{3(g)}, which could be instantaneously formed via Reaction K.8.⁴²²



In the bottom ash, iron remains as Ca₃Fe₂Si₃O_{12(s)} and CaFeSi₂O_{6(s)}, as shown in Figure K.12 and K.13. CaFeSi₂O_{6(s)} and Ca₃Fe₂Si₃O_{12(s)} are possibly formed via mineral reactions, as expressed in Reactions K.9 and K.10.⁴²³



However, $\text{CaFeSi}_2\text{O}_6(\text{s})$ and $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}(\text{s})$ are unlikely to form in practice due to kinetic limitations, since Reactions K.9 and K.10 occur at extremely high pressure, e.g. 2000 bar. Jing *et al.*⁴²⁴ discovered $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}(\text{s})$ in coal ash produced from pressurised combustion.

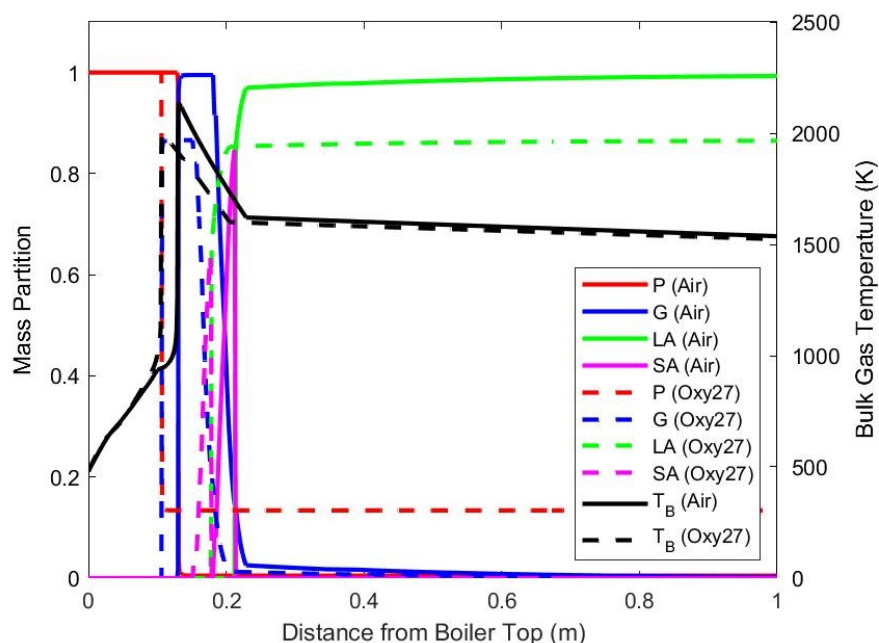


Figure K.9 Modelled Iron Fate Profiles in Air-combustion and Oxy27-combustion of Rice Husk (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion)

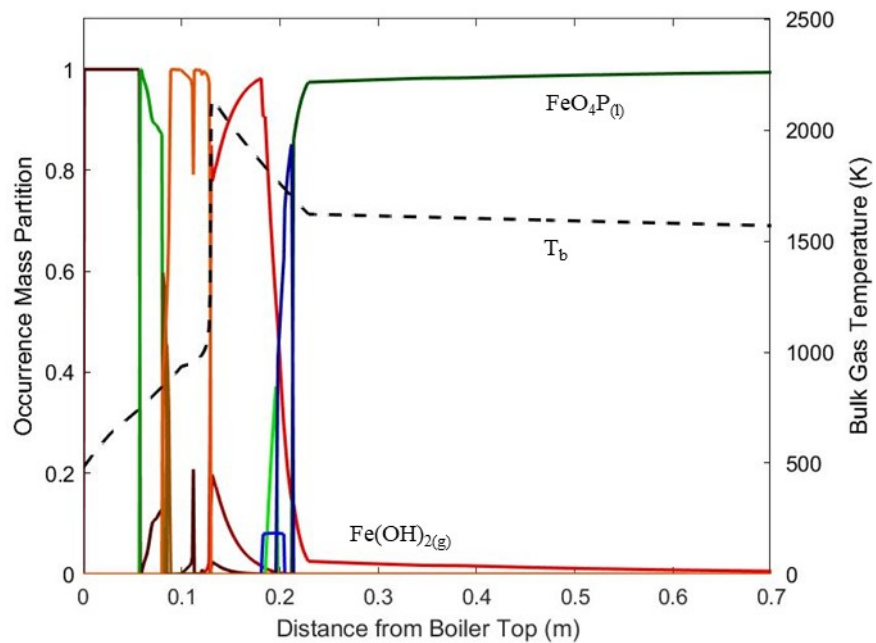


Figure K.10 Modelled Iron Bulk Occurrences in Air-combustion of Rice Husk

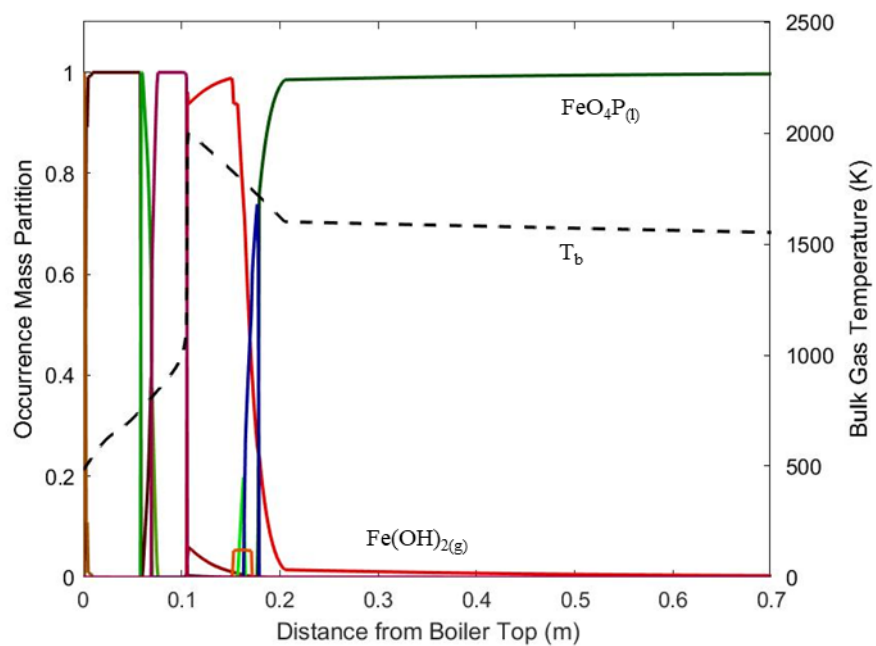


Figure K.11 Modelled Iron Bulk Occurrences in Oxy27-combustion of Rice Husk

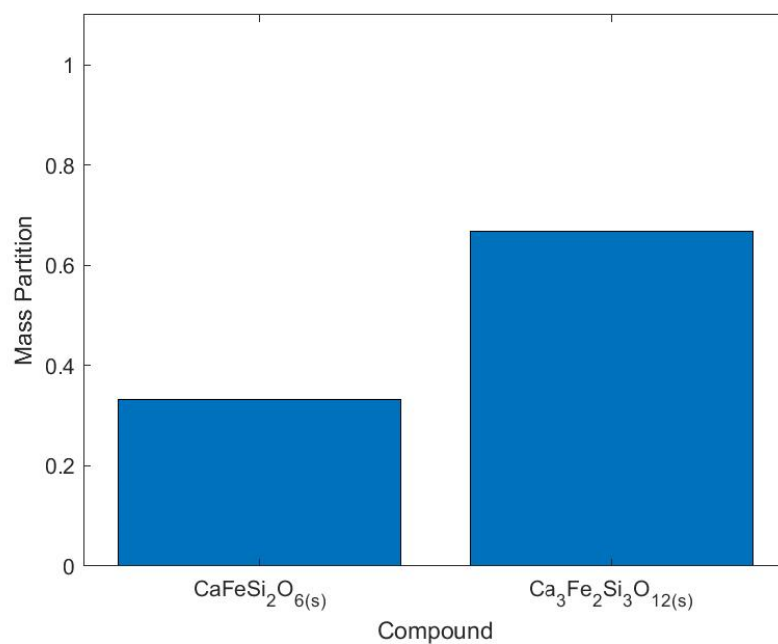


Figure K.12 Modelled Iron Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Rice Husk

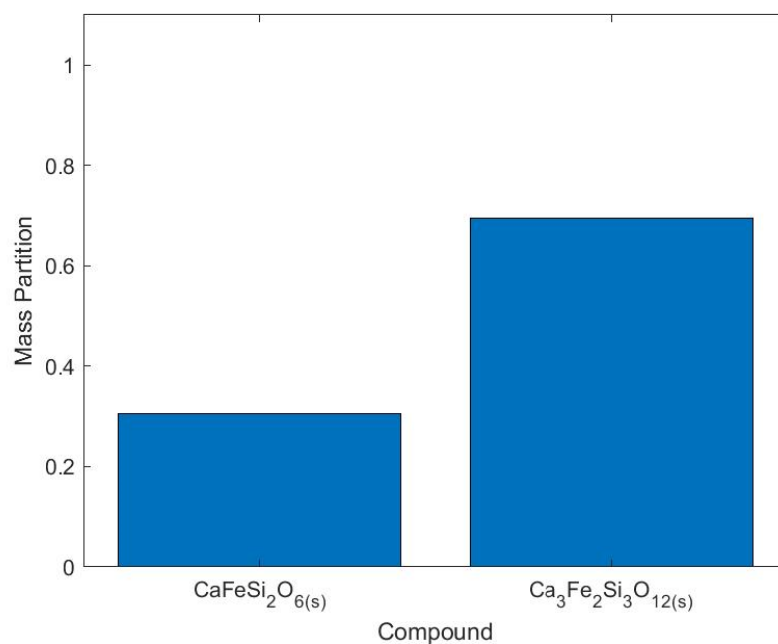


Figure K.13 Modelled Iron Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Rice Husk

Appendix L: AFE and TE Fate and Occurrence Profiles of Switchgrass

This appendix compiles the discussion of the fate and occurrence profiles of the AFEs and TEs other than potassium, calcium, and silicon in the combustion of rice husk wood in PACT facility entrained-flow boiler.

Sodium

The modelled fate profile for sodium in switchgrass is shown in Figure L.1. Sodium is completely volatilised from the particles. In contrast to the modelled fate profile of sodium in rice husk, shown in Figure K.1, sodium remains as gas during the *heat loss* stage during combustion of switchgrass. The absence of solid aerosols of sodium compounds is probably due to the lower quantity of sodium in switchgrass than in rice husk. Also, the released phosphorus might react with other elements, preventing alkali-metal phosphate formation.

In both modelled occurrence profiles for bulk sodium shown in Figures L.2 and L.3, sodium is released as $\text{NaOH}_{(g)}$ and $\text{Na}_{(g)}$ at the peak temperature. $\text{NaOH}_{(g)}$ partition increases whilst $\text{Na}_{(g)}$ partition decreases according to Reaction 6.2. $\text{NaCl}_{(g)}$ partition is at relatively high quantity due to higher chlorine quantity in herbaceous biomass than in woody biomass.⁴²⁵

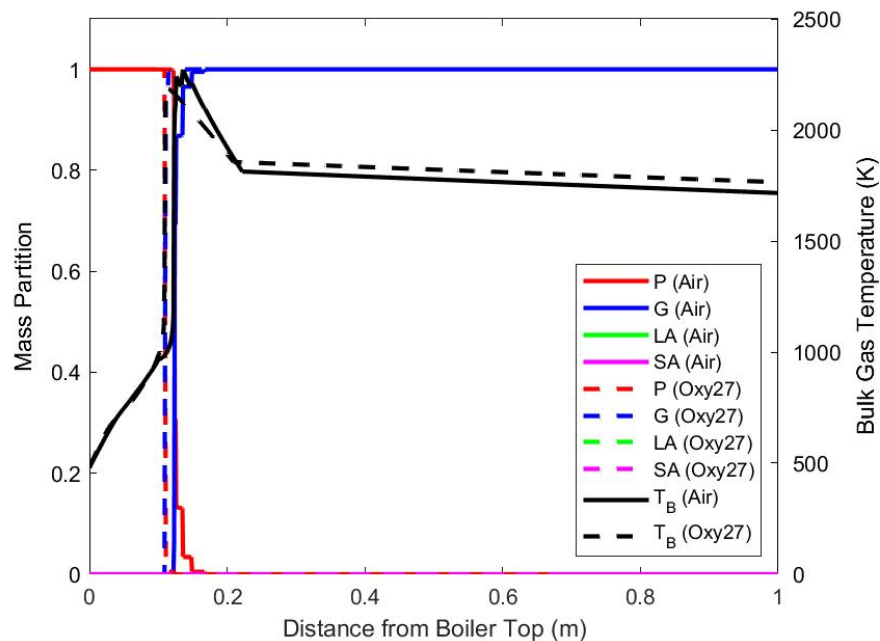


Figure L.1 Modelled Sodium Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion)

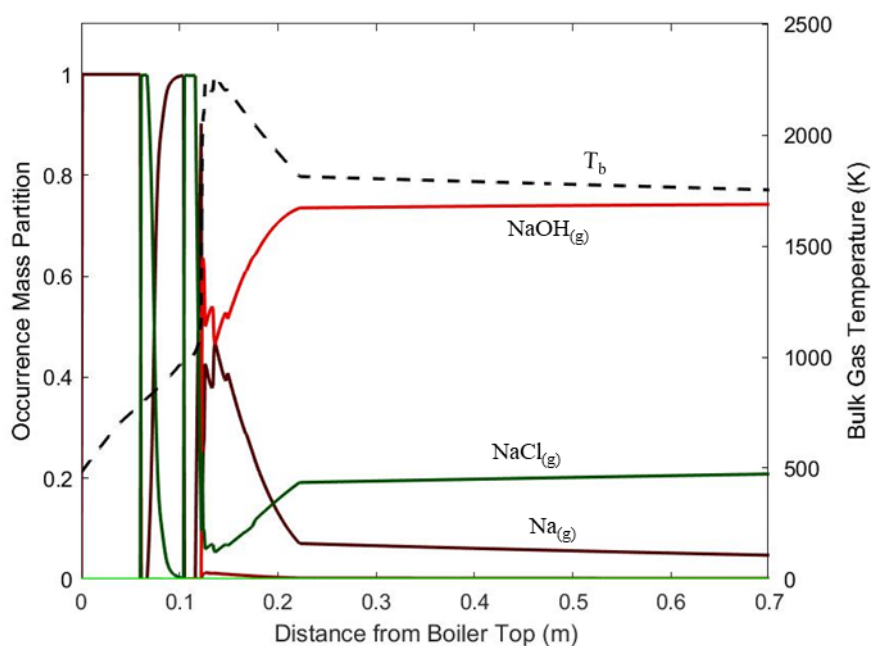


Figure L.2 Modelled Sodium Bulk Occurrences in Air-combustion of Switchgrass

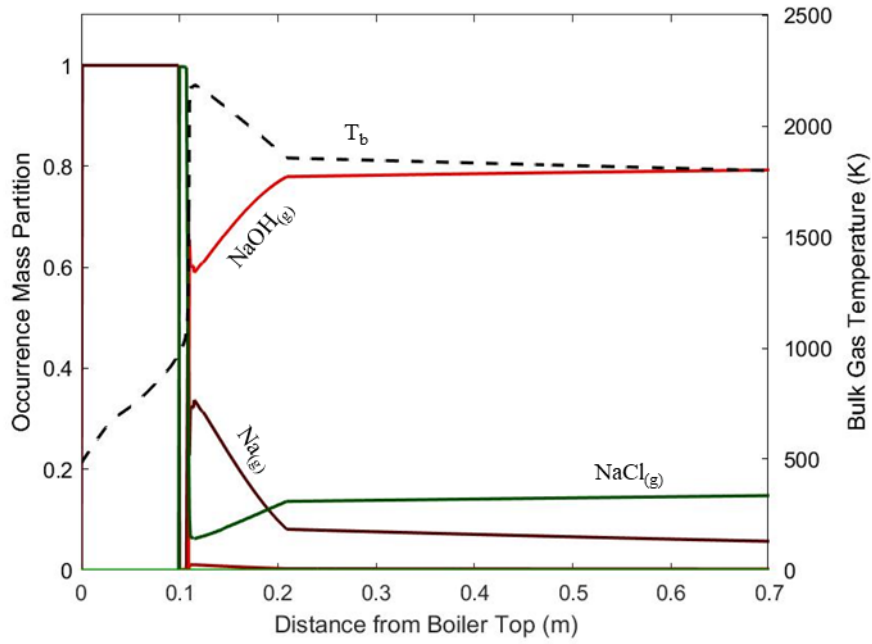


Figure L.3 Modelled Sodium Bulk Occurrences in Oxy27-combustion of Switchgrass

Magnesium

Modelled magnesium fate profiles are shown in Figure L.4. More magnesium remains in the bottom ash in oxy27-combustion than in air-combustion. Higher magnesium retention in oxy27-combustion is due to formation of complex silicates, e.g. pyroxene. Since a considerable amount of magnesium is released in both combustion cases, solid aerosol formation is favoured. In oxy27-combustion, liquid compound is present during the *heat loss* stage due to magnesium association with phosphorus, which is released in larger quantity in oxy27-combustion than in air-combustion.

$MgSiO_{3(s)}$ and $CaMgSi_2O_{6(s)}$ are the major magnesium compounds formed in air-combustion as shown in Figure L.5. Surendra *et al.*⁴²⁶ have suggested a $MgSiO_{3(s)}$ formation mechanism. $MgO_{(s)}$ is supposed to form as shown in Figure J.3. Due to elevated concentration of silicon in the bulk as $SiO_{2(s6)}$, $SiO_{2(s6)}$ reacts with $MgO_{(g)}$, as expressed in Reactions L.1 and L.2.



$Mg_2SiO_{4(s)}$ subsequently reacts with $SiO_{2(s6)}$ to form $MgSiO_{3(s)}$, as expressed in Reaction L.3.



The existence of $\text{CaMgSi}_2\text{O}_{6(s)}$ alongside $\text{MgSiO}_3(s)$ is plausible, although a previous work discovered slightly different co-existing compounds, e.g. $\text{MgSi}_2\text{O}_{6(s)}$ was found to coexist with $\text{CaMgSi}_2\text{O}_{6(s)}$ at around 1,673 K and 1 atm.⁴²⁷

In oxy27-combustion, phosphorus-containing magnesium compounds are formed probably because there is sufficient quantity of released phosphorus to establish those compounds. $\text{Mg}_3\text{P}_2\text{O}_{8(l)}$ is a compound of concern, since it might initiate ash deposition as shown in Figure L.6. $\text{Mg}_3\text{P}_2\text{O}_{8(l)}$ is likely to form via $\text{MgO}_{(g)}$ reaction with $\text{PO}_{2(g)}$ as expressed in Reaction L.4.⁴²⁸

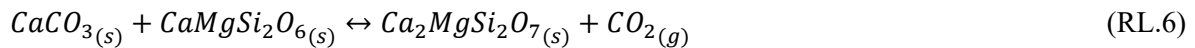


$\text{PO}_{(g)}$ may further react with $\text{CO}_{2(g)}$ to reform $\text{PO}_{2(g)}$ as shown in Reaction L.5.⁴²⁹



Unlike inorganic liquid compounds observed in rice-husk combustion, $\text{Mg}_3\text{P}_2\text{O}_{8(l)}$ is not associated with silicon and potassium. Another ternary diagram shown in Figure L.7 is built to evaluate liquid compound formation based on the $\text{CaO-P}_2\text{O}_5\text{-MgO}$ system. Molar composition is located in the black box. The liquidus isotherm temperature is at around 1,800 K. This is in agreement with the finding that $\text{Mg}_3\text{P}_2\text{O}_{8(l)}$ is stable at this temperature.

Calcium occurs in the bottom ash mostly as $\text{CaMgSi}_2\text{O}_{6(s)}$, as shown in Figure L.8 and L.9. A small proportion of $\text{Ca}_2\text{MgSi}_2\text{O}_{7(s)}$ exists in the bottom ash after oxy27-combustion, possibly via Reaction L.6.⁴³⁰



$\text{Ca}_2\text{MgSi}_2\text{O}_{7(s)}$ is produced due to the presence of sufficient $\text{CaCO}_{3(s)}$. In oxy27-combustion, bulk $\text{O}_{2(g)}$ penetrates the particles faster than in air-combustion. More $\text{CO}_{2(g)}$ is produced, which reacts with $\text{CaO}_{(s)}$ as shown in Reaction L.7.⁴³¹



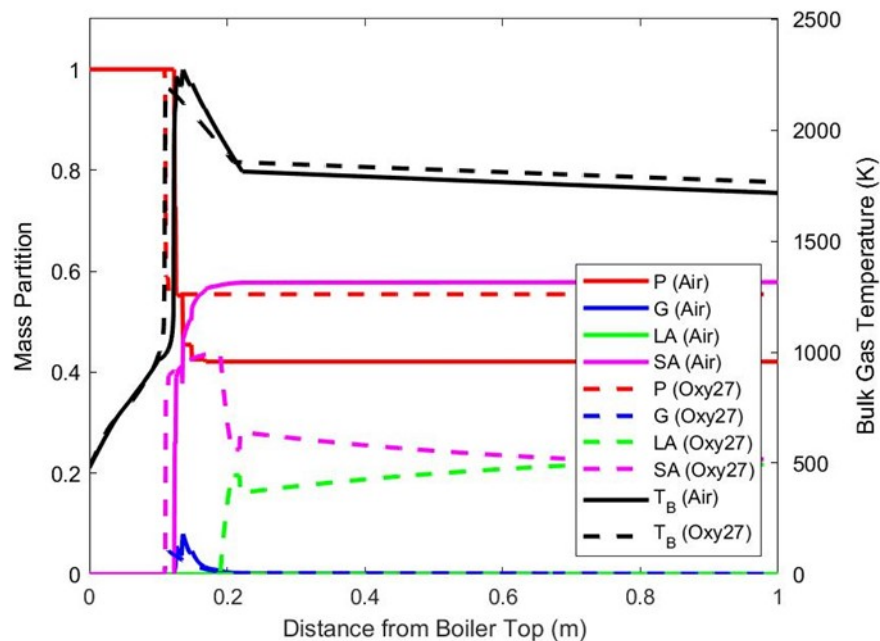


Figure L.4 Modelled Magnesium Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion)

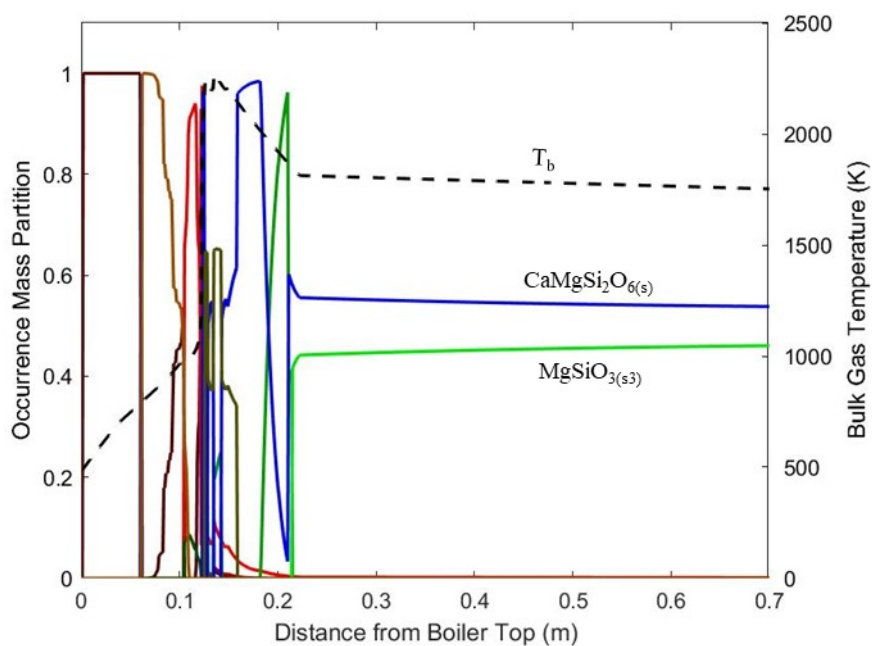


Figure L.5 Modelled Magnesium Bulk Occurrences in Air-combustion of Switchgrass

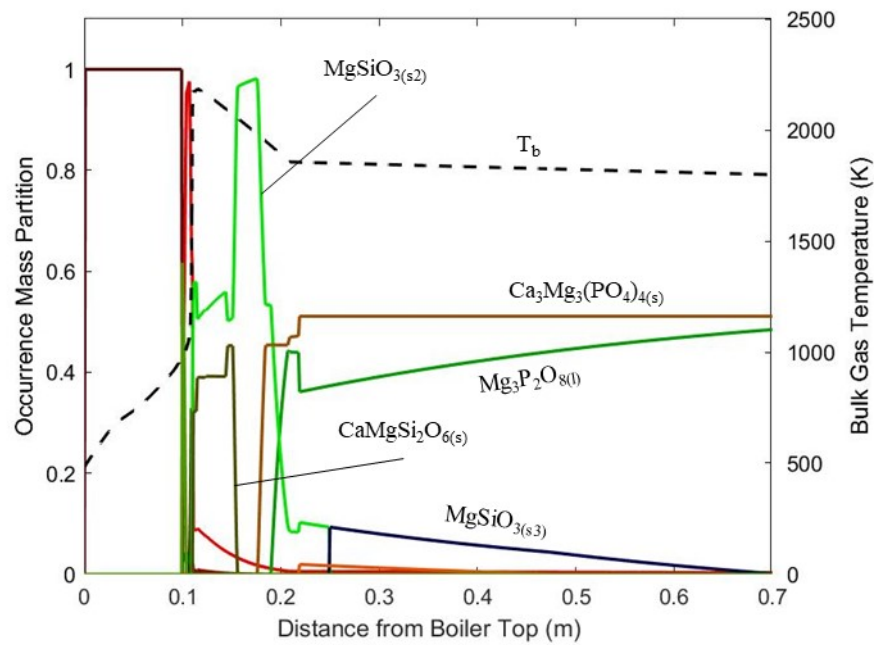


Figure L.6 Modelled Magnesium Bulk Occurrences in Oxy27-combustion of Switchgrass

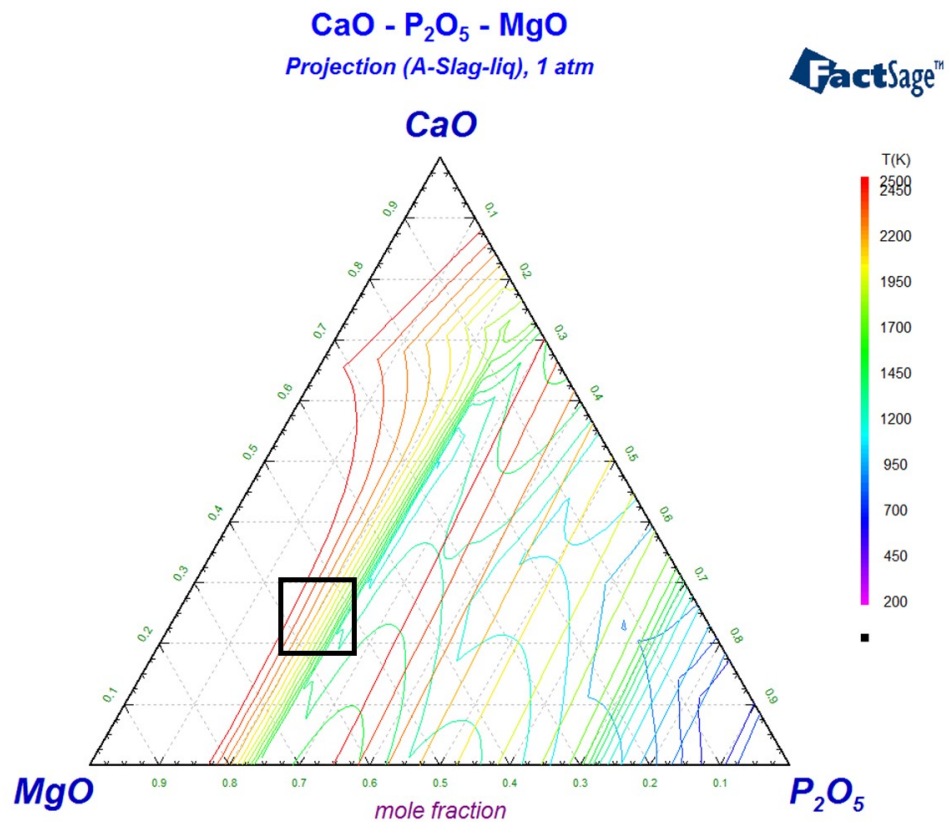


Figure L.7 Bulk Composition of Switchgrass (Black Box) at Complete Combustion and Liquidus Isotherm Lines within CaO-P₂O₅-MgO Ternary Phase Diagram

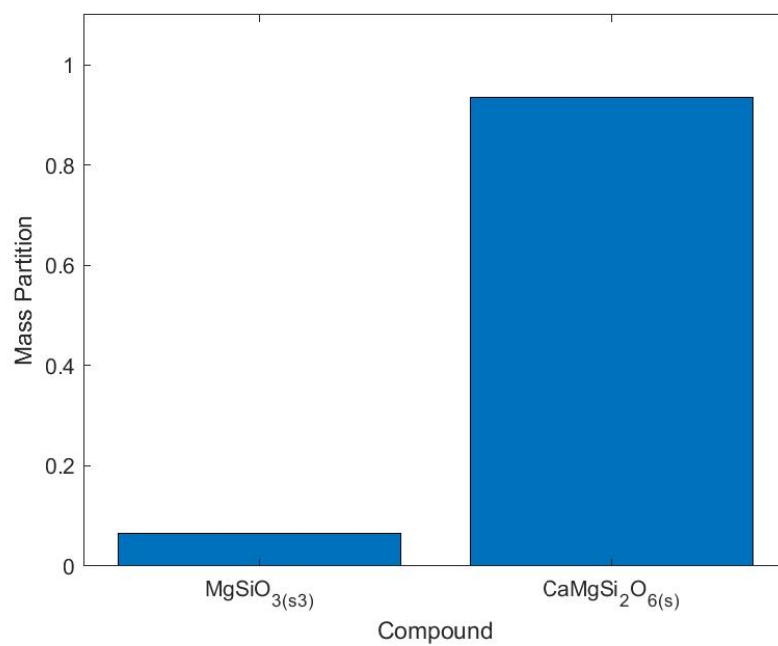


Figure L.8 Modelled Magnesium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Switchgrass

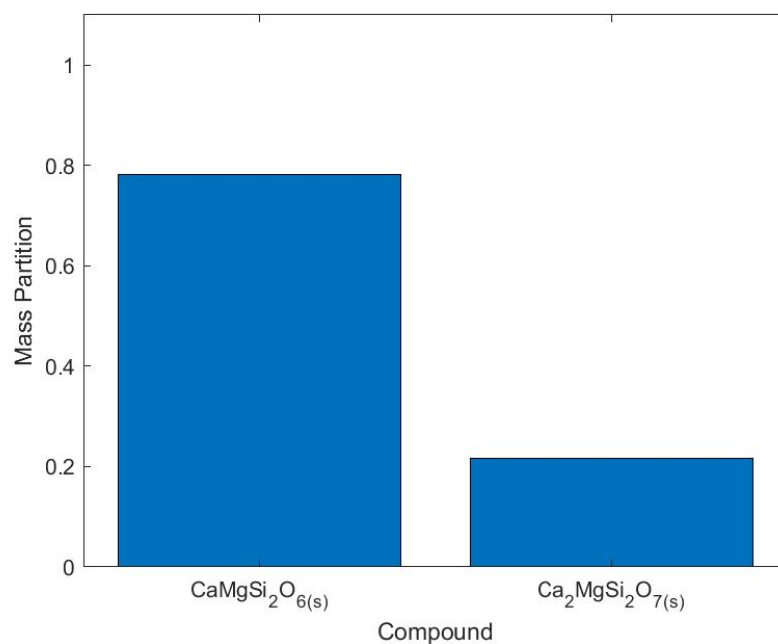


Figure L.9 Modelled Magnesium Occurrence in Bottom Ash at 298 K Obtained from Oxy-fuel combustion of Switchgrass

Aluminium

Modelled aluminium fate profiles are shown in Figure L.10. More aluminium is volatilised in air-combustion than in oxy27-combustion due to formation of aluminosilicate particles promoted by the presence of bulk $O_{2(g)}$. The released aluminium is transformed into solid aerosols. No aluminium gas compound is present.

Modelled occurrence profiles for bulk aluminium are shown in Figure L.11 for air-combustion and in Figure L.12 for oxy27-combustion. Aluminium is likely to be released as $OAlOH_{(g)}$ formed via Reaction J.4. $OAlOH_{(g)}$ subsequently reacts with calcium compound to form $Ca_2Al_2SiO_7_{(s)}$. Further reaction of $Ca_2Al_2SiO_7_{(s)}$ with $SiO_{2(g)}$ produces $CaAl_2Si_2O_8_{(s)}$ during the *heat removal* stage, as expressed in Reaction J.5. $CaAl_2Si_2O_8_{(s)}$ is converted into $KAlSi_2O_6_{(s)}$ shortly before the *heat loss* stage. $KAlSi_2O_6_{(s)}$ is later formed via reaction of aluminosilicate compound with $KCl_{(g)}$, as expressed in Reaction 7.5.

Modelled aluminium occurrence in the bottom ash of air-combustion and oxy27-combustion is shown in Figures L.13 and L.14, respectively. Aluminium occurs in bottom ash after air-combustion as $KAlSi_2O_6_{(s)}$ and $Ca_3Al_2Si_3O_{12(s)}$. These compounds are formed possibly via aluminosilicate reaction with $CaO_{(s)}$ and $K_2O_{(s)}$. In bottom ash after oxy27-combustion, aluminium is only present as calcium aluminosilicate compounds, probably due to the retention of more calcium in the particles.

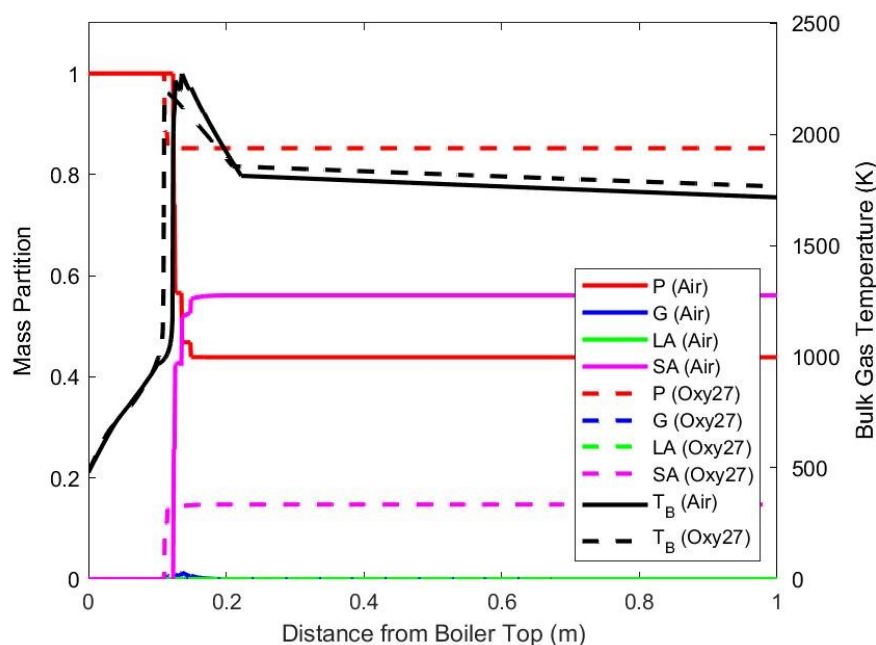


Figure L.10 Modelled Aluminium Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion)

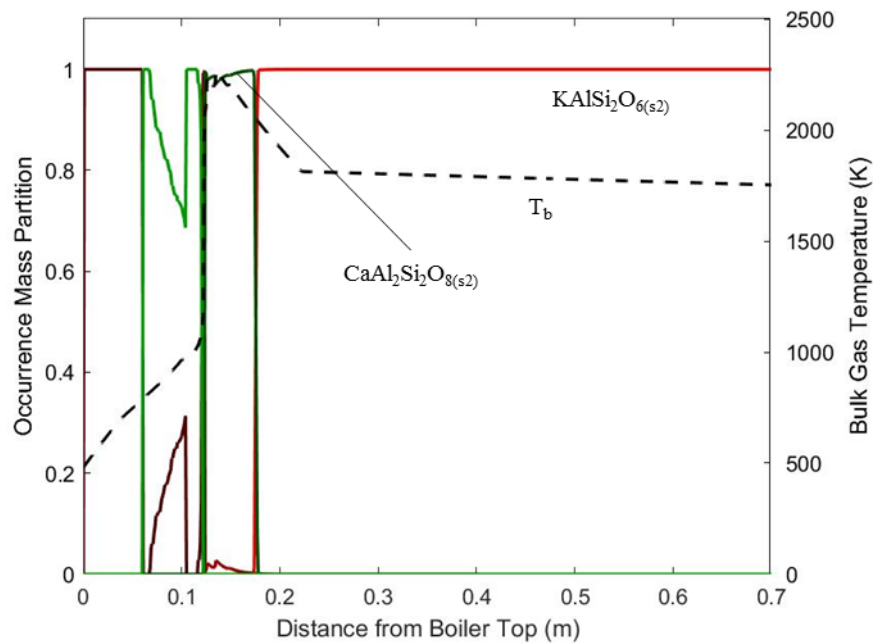


Figure L.11 Modelled Aluminium Bulk Occurrences in Air-combustion of Switchgrass

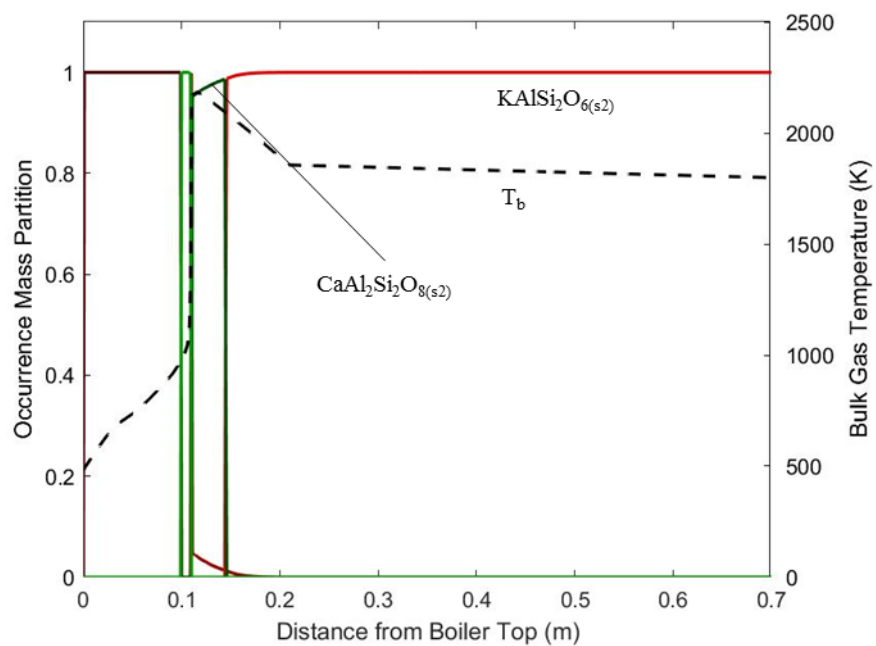


Figure L.12 Modelled Aluminium Bulk Occurrences in Oxy27-combustion of Switchgrass

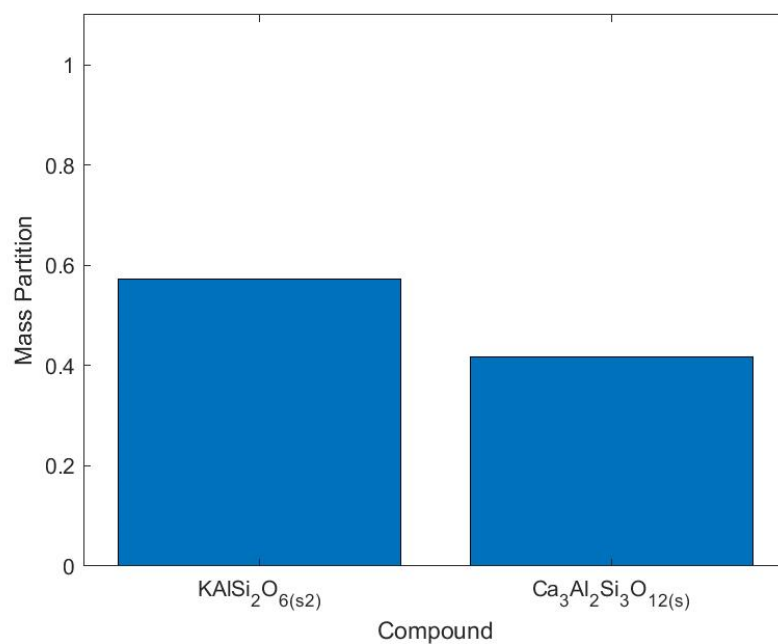


Figure L.13 Modelled Aluminium Occurrence in Bottom Ash at 298 K Obtained from Air-combustion of Switchgrass

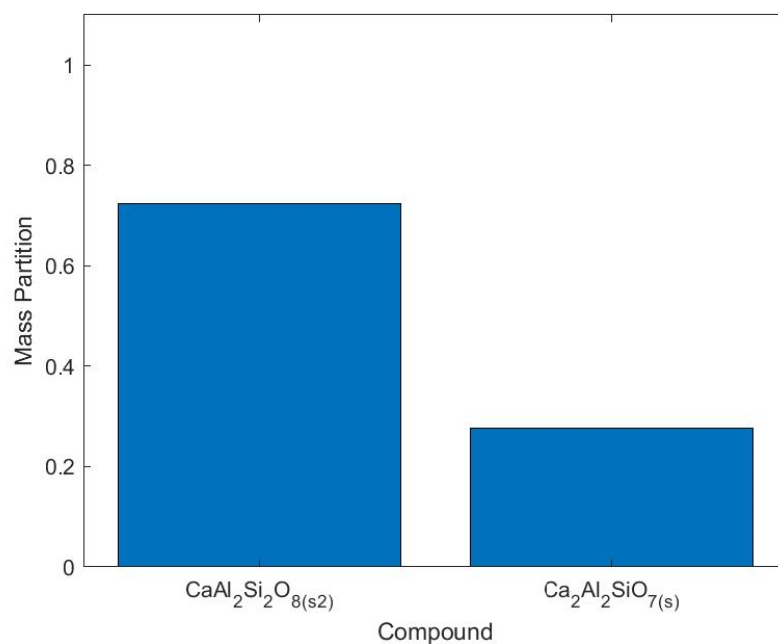


Figure L.14 Modelled Aluminium Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Switchgrass

Iron

Modelled iron fate profiles are shown in Figure L.15. More iron is volatilised in oxy27-combustion than in air-combustion since iron is more volatile at the high bulk temperatures that are achieved during oxy27-combustion. During the *heat loss* stage, solid aerosols are formed in both combustion scenarios since the bulk iron concentration is sufficient to nucleate into solid aerosols.

Modelled bulk iron occurrence profiles are shown in Figure L.16 for air-combustion and in Figure L.17 for oxy27-combustion. In air-combustion, $\text{Fe}(\text{OH})_{2(\text{g})}$ is formed, possibly via Reaction J.6 during the *heat removal* stage. $\text{Fe}(\text{OH})_{2(\text{g})}$ is converted into $\text{Fe}_3\text{O}_{4(\text{s}2)}$ via Reaction J.7 at lower temperatures during the *heat loss* stage. During oxy27-combustion, $\text{Fe}_2\text{O}_5\text{Ti}_{(\text{s})}$ is formed. In contrast to the findings during combustion of rice husk, no phosphorus-containing iron compound is predicted, probably due to the significant amount of magnesium and calcium that is released to bulk and reacts with the phosphorus. Titanium is released as $\text{TiO}_{2(\text{g})}$ at higher quantity in oxy27-combustion than in air-combustion. Hirota and Bradt⁴³² conducted experiments to form $\text{Fe}_2\text{O}_5\text{Ti}_{(\text{s})}$ via $\text{TiO}_{2(\text{g})}$ reaction with $\text{Fe}_2\text{O}_{3(\text{g})}$ at 1373 K, as expressed in Reaction L.8.



$\text{Fe}_2\text{O}_{3(\text{g})}$ is formed via $\text{Fe}_{(\text{g})}$ oxidation as shown in Reaction L.9.⁴³³



Liquid slag might form at around 1,773 K and the liquidus temperature increases as more TiO_2 is added. Further research has discovered that there is no sign of a solid phase at a temperature of around 1,500 K.⁴³⁴

In the switchgrass bottom ash, the majority of iron occurrence is as Fe_3O_4 crystals in both air-combustion and oxy27-combustion. In oxy27-combustion, a small proportion of $\text{CaFeSi}_2\text{O}_{6(\text{s})}$ and $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12(\text{s})}$ exists, as shown in Figure L.18, probably due to significant retention of calcium in the particles.

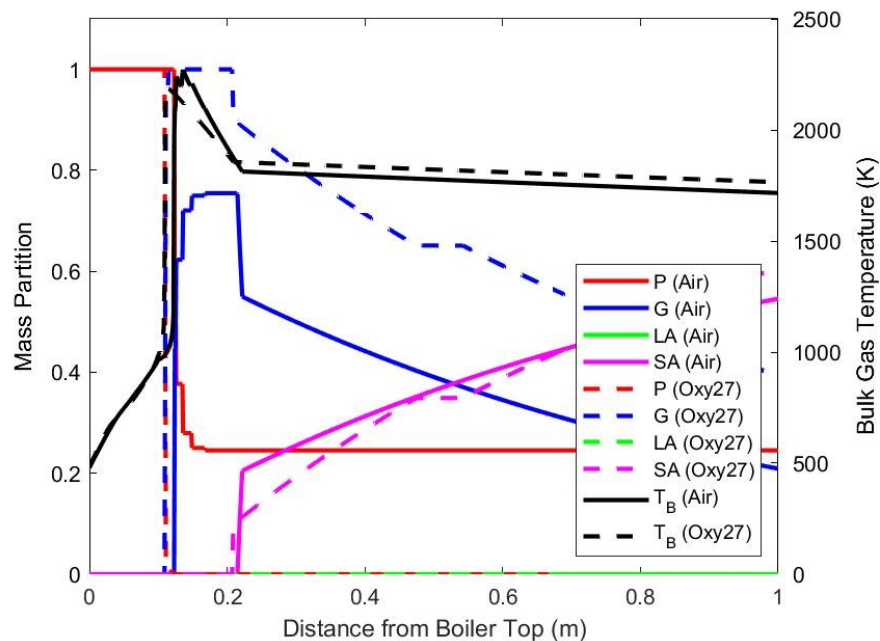


Figure L.15 Modelled Iron Fate Profiles in Air-combustion and Oxy27-combustion of Switchgrass (— P (Air): Particle in Air-combustion; — G (Air): Gas in Air-combustion; — LA (Air): Liquid Aerosol in Air-combustion; — SA (Air): Solid Aerosol in Air-combustion; --- P (Oxy27): Particle in Oxy27-combustion; --- G (Oxy27): Gas in Oxy27-combustion; --- LA (Oxy27): Liquid Aerosol in Oxy27-combustion; --- SA (Oxy27): Solid Aerosol in Oxy27-combustion; — T_B (Air): Bulk Temperature in Air-combustion; --- T_B (Oxy27): Bulk Temperature in Oxy27-combustion

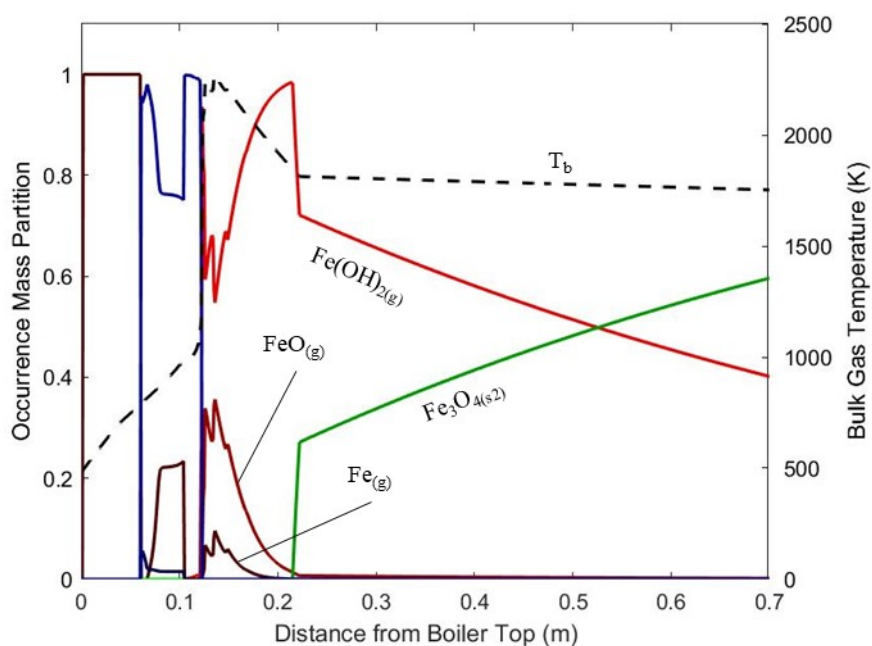


Figure L.16 Modelled Iron Bulk Occurrences in Air-combustion of Switchgrass

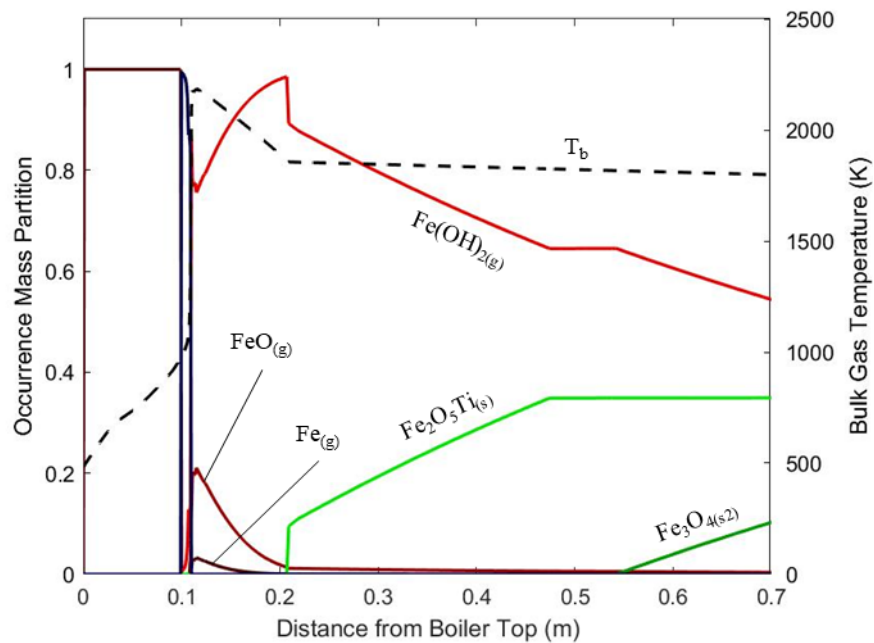


Figure L.17 Modelled Iron Bulk Occurrences in Oxy27-combustion of Switchgrass

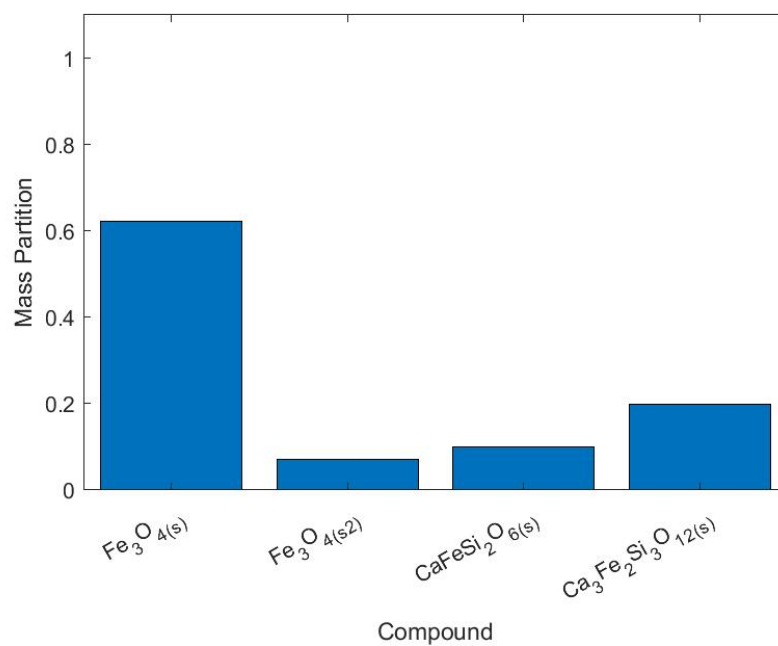


Figure L.18 Modelled Iron Occurrence in Bottom Ash at 298 K Obtained from Oxy27-combustion of Switchgrass

Appendix M: License for Used Figure and Tables

The licenses of figures and/or tables used in this thesis are listed in Table M.1. The license documentations are available upon request to this thesis's author.

Table M.1 *Licenses of Figures and/or Tables Used*

Item	License Number	License Date	License Content Publisher	Publisher Remarks
Figure 2.3	4943991367477	November 7 th 2020	Elsevier	-
Figure 2.4	4944000265556	November 7 th 2020	Elsevier	-
Figure 2.5	4944000438435	November 7 th 2020	Elsevier	-
Figure 2.6	4944000687162	November 7 th 2020	Elsevier	-
Figure 2.7	-	-	National Library of Serbia	Thermal Science is an Open Access Journal. All articles can be downloaded free of charge and used in accordance with the Creative Commons Attribution – Non Commercial – No Derivatives license.
Figure 2.8	-	-	American Chemical Society	One-time permission is granted only for the use specified in the request. No additional uses are granted (such as derivative works or other editions).
Figure 2.9	4944001473616	November 7 th 2020	Elsevier	-
Figure 2.11	4944010159081	November 7 th 2020	Elsevier	-
Figure 2.12	-	-	ETDEWEB	The journal information should be visible in the citation
Figure 2.13	4944011460773	November 7 th 2020	Elsevier	-
Figure 3.1	4944070710028	November 8 th 2020	Elsevier	-
Figure 3.2	4944071020407	November 8 th 2020	Elsevier	-
Figure 3.3	4944071142718	November 8 th 2020	Elsevier	-
Figure 4.15	-	-	American Chemical Society	One-time permission is granted only for the use specified in the request. No additional uses are granted (such as

Figure 5.2	-	-	UKCCS Research Centre	derivative works or other editions). The information contained in the website is for general information purposes only. The information is provided by the University of Sheffield and while the publisher endeavour to keep the information up to date and correct, the publisher makes no representations of warranties of any kind, express or implied, about the completeness, accuracy, reliability, suitability or availability with respect to website or the information, contained on the website for any purpose. Any reliance an information user places on such information is therefore strictly at his/her own risk.
Figure 5.3	4944091402540	November 8 th 2020	Elsevier	-
Figure 5.4	4944091402540	November 8 th 2020	Elsevier	-
Figure 8.7	-	-	American Chemical Society	One-time permission is granted only for the use specified in the request. No additional uses are granted (such as derivative works or other editions).
Figure 8.16	4944190291064	November 8 th 2020	Elsevier	-
Figure 9.1	-	-	American Chemical Society	One-time permission is granted only for the use specified in the request. No additional uses are granted (such as derivative works or other editions).