Oxy-fuel Fluidized Bed Combustion of Victorian Brown Coal

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A thesis submitted in fulfilment of the requirements for the degree of **Doctor of Philosophy**



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DECLARATION

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Bithi Roy August 2014

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ABSTRACT

Coal contributes to almost forty percent of global power generation. As conventional coal-fired power generation technologies result in large CO_2 emission, the pursuit for new technologies focuses on either reducing CO_2 emission or that allows easier capture of the emitted CO_2 from coal-fired power plants. Oxy-fuel fluidized bed (Oxy-FB) combustion is one such technology due to its ability to produce concentrated CO_2 stream in the flue gas. This concentrated CO_2 allows easier capture for subsequent transportation and storage. Other important benefits of this technology are the potential for using any type of fuel, and the ability to control SO_2 and NO_X emissions. Despite its perceived advantages over conventional technologies, very little is known about the applicability of Oxy-FB for brown coal. Brown coal accounts for 91% of Victoria's current electricity needs. Since Victoria has an estimated reserve of over 500 years of brown coal at the current consumption rate, successful application of Oxy-FB can potentially result in environment friendly power generation in Victoria.

This first-ever study investigates the Oxy-FB combustion using Victorian brown coal in a combined experimental and modelling approach. The research involves designing and commissioning of a 10 kW_{th} fluidized bed rig, carrying out experiments in laboratory scale and bench scale equipment, and performing thermodynamic and process modelling.

Laboratory scale experiments using single char particle were conducted to investigate the combustion characteristics of individual and large char particle under Oxy-FB conditions. Particle temperature was observed to be higher compared to bed temperature. Up to 48° C difference was noticed between the char particle temperature and the bed temperature using 15% (v/v) steam in oxy-fuel combustion atmosphere. The temperature of the char particle during Oxy-FB combustion has practical implication for agglomeration.

The bench scale experiments were carried out to evaluate combustion efficiency, agglomeration characteristics, sulphation characteristics, carbonation characteristics, NO_X (NO, NO₂ and N₂O) emission, SO_X (SO₂ and SO₃) emission, and trace elements (Hg, Se, As and Cr) emissions during Oxy-FB combustion of Victorian brown coal. A high level of CO₂ concentration (90-94% in dry flue gas), over 99% combustion efficiency and no bed agglomeration under oxy-fuel combustion conditions including those with the

addition of steam at temperatures between 800°C and 900°C. Moreover, the measured NO_X and SO_X concentration levels in the flue gas are within the permissible limits for coal-fired power plants in Victoria. This implies that additional NO_X and SO_X removal systems may not be required with Oxy-FB combustion of Victorian brown coal. The gaseous mercury concentrations, however, are considerably higher under oxy-fuel combustion compared to air combustion suggesting that mercury removal system may be required to avoid corrosion in the CO_2 separation units if CO_2 capture and transportation is intended. These conventional pollutants and trace elements emission characteristics are of great importance for the design of the gas cleaning systems for CO_2 capture and storage (CCS) purposes. Furthermore, these results also provide information for selecting the optimum operating condition.

Thermodynamic equilibrium modelling was carried out to predict the compounds formed during the combustion of Victorian brown coal under different Oxy-FB combustion conditions. It was predicted that the amount of toxic gaseous Cr^{6+} species was greater for oxy-fuel combustion than for air combustion. The distribution of toxic Se⁴⁺ species, however, remained almost the same in both combustion conditions within the typical temperature range for Oxy-FB combustion (800 - 950°C).

A process model on Oxy-FB combustion using Aspen Plus was also developed to predict combustion performance of any coal during Oxy-FB. It was observed that the concentrations of CO and SO₂ were higher in the lower dense region of the bed. These levels, however, dropped significantly with the introduction of secondary oxygen. The simulation results were consistent with the experimental data.

Overall, this thesis has identified several important issues, for the first time, on Oxy-FB combustion using brown coal. The information generated is useful for academics, industry and policy makers. Future research on Oxy-FB combustion can use the findings of this study while developing Oxy-FB combustion for brown coals.

PUBLICATIONS AND AWARDS

Journal publication(s):

- **B. Roy**, W. L. Choo, and S. Bhattacharya, "Prediction of distribution of trace elements under oxy-fuel combustion condition using Victorian brown coals," *Fuel*, 2013, 114, 135-142.
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- C. Saha, **B. Roy** and S. Bhattacharya, "Chemical looping combustion of Victorian brown coal using NiO oxygen carrier", *International Journal of Hydrogen Energy*, 2011, 36, 3253-3259.
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- **B. Roy**, W. L. Choo, and S. Bhattacharya, "Prediction of selective trace element emissions during Oxy-CFB combustion of Victorian brown coals," *The ICCS&T Conference*, Oviedo, Spain, 2011.
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TABLE OF CONTENTS

DECLAR	ATION II
ACKNOW	VLEDGEMENTSIII
ABSTRA	CT IV
PUBLICA	ATIONS AND AWARDSVI
TABLE O	OF CONTENTS IX
LIST OF	FIGURESXV
LIST OF '	TABLESXXI
LIST OF A	ABBREVIATIONS XXIII
LIST OF S	SYMBOLSXXV
CHAPTE	R 1: INTRODUCTION1
1.1. l	Background2
1.2. (Oxy-fuel fluidized bed combustion5
1.3.	Victorian brown coal and its importance in Oxy-FB6
1.4. I	Motivation7
1.5. l	Research aims7
1.6. l	Research Plan8
1.6.1	1. Single particle combustion experiment
1.6.2	2. Bench scale combustion experiment
1.6.3	3. Thermodynamic equilibrium modelling9
1.6.4	4. Process modelling

1.7. Org	ganization of the thesis9
CHAPTER 2	2: LITERATURE REVIEW
2.1. Int	roduction12
2.2. Sta	tus of oxy-fuel fluidized bed technology12
2.2.1.	Oxy-CFB combustion in the context of Australia17
2.3. Coa	al quality impacts on oxy-fuel fluidized bed combustion17
2.3.1.	Combustion characteristics
2.3.2.	Ash mineral and bed agglomeration21
2.3.3.	Sulphation24
2.3.4.	Recarbonation of fly ash
2.3.5.	Conventional pollutant emissions
2.3.6.	Trace elements emissions
2.4. Mo	delling of Oxy-FB combustion45
2.4.1.	Kinetic modelling on char combustion45
2.4.2.	Computational fluid dynamics modelling47
2.4.3.	Thermodynamic modelling49
2.4.4.	Process modelling
2.5. Su	mmary
CHAPTER 3	3: METHODOLOGY
3.1. Ma	terials53
3.2. Tes	st facilities55
3.2.1.	Quartz reactor facility55
3.2.2.	Stainless steel fluidized bed test facility
3.2.3.	Tubular furnace

3.2	2.4.	Thermogravimetric Analyser	.59
3.3.	Anal	ytical equipment	.60
3.3	8.1.	Elemental analyser	.60
3.3	3.2.	UV spectrophotometer	.61
3.3	3.3.	Moisture analyser	.62
3.3	3.4.	Density measurement	.63
3.3	8.5.	Particle size distribution measurement	.63
3.3	8.6.	X-ray florescence	.64
3.3	8.7.	X-ray diffraction	.65
3.3	3.8.	Scanning electron microscopy and Energy dispersive X-rays	.65
3.4.	Mod	elling	.66
3.4	l.1.	Single char particle modelling	.66
3.4	l.2.	Thermodynamic equilibrium predictions	.68
3.4	4.3.	Process modelling	.69
СНАРТ	'ER 4:	COMBUSTION OF SINGLE CHAR PARTICLES	71
4.1. I	ntrod	uction	.72
4.2. E	Experi	mental section	.73
4.2	2.1. Ma	aterials	.73
4.2	2.2. Ex	perimental procedure	.74
4.2	2.3. Ca	lculation	.76
4.3. F	Result	s and Discussions	.80
4.3	8.1. Pa	rticle temperature	.80
4.3	3.2. Ch	ar combustion tests	.83
4.4. (Conclu	sions	.87

CHAPTER 5: DESIGN AND COMMISSIONING OF A 10 $\ensuremath{KW_{TH}}$ Fluidized bed
RIG
5.1. Introduction90
5.2. Design of experimental rig90
5.3. Experimental setup92
5.3.1. Combustor
5.3.2. Furnace
5.3.3. Gas supply unit94
5.3.4. Coal feeder96
5.3.5. Flue gas processing unit
5.3.6. SO ₃ trap97
5.3.7. Thermocouple and pressure transducer
5.4. Commissioning work98
5.5. Summary101
CHAPTER 6: COMBUSTION EXPERIMENTS IN BENCH SCALE FLUIDIZED BED
COMBUSTORS
6.1. Introduction103
6.2. Experimental section104
6.2.1. Fluidized bed quartz reactor104
6.2.2. 10 kW _{th} fluidized bed combustor105
6.2.3. Analytical measurements111
6.2.4. Thermodynamic equilibrium prediction112
6.3. Results and discussion
6.3.1. Fluidized bed quartz reactor113

6.3.2.	10 kW _{th} fluidized bed combustor122
6.4. Con	clusions
CHAPTER 7	: CARBONATION AND SULPHATION EXPERIMENTS 173
7.1. Intro	oduction174
7.2. Exp	erimental section176
7.2.1.	Materials176
7.2.2.	Experimental procedure
7.2.3.	Analytical measurements
7.3. Res	ults and Discussions
7.3.1.	Carbonation characteristics
7.3.2.	Sulphation characteristics
7.4. Con	clusions
CHAPTER	8: PROCESS SIMULATION ON OXY-FUEL FLUIDIZED BED
CHAPTER COMB	8: PROCESS SIMULATION ON OXY-FUEL FLUIDIZED BED USTION
CHAPTER COMB 8.1. Introc	8: PROCESS SIMULATION ON OXY-FUEL FLUIDIZED BED USTION
CHAPTER COMB 8.1. Introc 8.2. Simul	8: PROCESS SIMULATION ON OXY-FUEL FLUIDIZED BED USTION 195 luction 196 ation of Oxy-FB combustion process 197
CHAPTER COMB 8.1. Introc 8.2. Simul 8.2.1. M	8: PROCESS SIMULATION ON OXY-FUEL FLUIDIZED BED USTION 195 duction 196 ation of Oxy-FB combustion process 197 Iodel description 197
CHAPTER COMB 8.1. Introc 8.2. Simul 8.2.1. M 8.2.2. In	8: PROCESS SIMULATION ON OXY-FUEL FLUIDIZED BED USTION 195 luction 196 ation of Oxy-FB combustion process 197 lodel description 197 uput data 203
CHAPTER COMB 8.1. Introc 8.2. Simul 8.2.1. M 8.2.2. In 8.2.3. A	8: PROCESS SIMULATION ON OXY-FUEL FLUIDIZED BED USTION 195 duction 196 ation of Oxy-FB combustion process 197 Iodel description 197 uput data 203 ssumptions 204
CHAPTER COMB 8.1. Introc 8.2. Simul 8.2.1. M 8.2.2. In 8.2.3. A 8.3. Result	8: PROCESS SIMULATION ON OXY-FUEL FLUIDIZED BED USTION 195 duction 196 ation of Oxy-FB combustion process 197 lodel description 197 uput data 203 ssumptions 204 ts and discussions 204
CHAPTER COMB 8.1. Introc 8.2. Simul 8.2.1. M 8.2.2. In 8.2.3. A 8.3. Result 8.3.1. Si	8: PROCESS SIMULATION ON OXY-FUEL FLUIDIZED BED USTION
CHAPTER COMB 8.1. Introc 8.2. Simul 8.2.1. M 8.2.2. In 8.2.3. A 8.3. Result 8.3.1. Si 8.3.2. M	8: PROCESS SIMULATION ON OXY-FUEL FLUIDIZED BED USTION 195 luction 196 ation of Oxy-FB combustion process. 197 lodel description 197 uput data 203 ssumptions 204 ts and discussions 204 imulation results 205 lodel validation 210
CHAPTER COMB 8.1. Introc 8.2. Simul 8.2.1. M 8.2.2. In 8.2.3. A 8.3. Result 8.3.1. Si 8.3.2. M 8.4. Conclu	8: PROCESS SIMULATION ON OXY-FUEL FLUIDIZED BED USTION

9.1. Conclusions
9.1.1. Single particle combustion experiment
9.1.2. Bench scale combustion experiment
9.1.3. Thermodynamic equilibrium modelling216
9.1.4. Process modelling
9.2. Practical implications of this research216
9.3. Recommendations for Future Research and Development
REFERENCES
APPENDICES
Appendix A: Calculations for the fluidized bed rig design

LIST OF FIGURES

Figure 1.1: The three basic CO ₂ capture technologies (IPCC, 2005)
Figure 1.2: Schematic diagrams of bubbling and circulating fluidized beds (Anthony,
2013)4
Figure 1.3: Thesis structure diagram10
Figure 2.1: Schematic of CanmetENERGY's 0.8 MWth Oxy-CFB combustion pilot
facility (Kuivalainen et al., 2010)14
Figure 2.2: Simplified flow-sheet of CIUDEN's facilities (Álvarez, 2013)15
Figure 2.3: Equilibrium temperature of CaCO ₃ calcination as a function of CO ₂ partial
pressure (Liljedahl et al., 2006)25
Figure 2.4: Sulphur capture efficiency as function of bed temperature and CO ₂
concentration (Wall et al., 2012)
Figure 2.5: Reaction routes of sulphur in a coal combustion system (Belo et al., 2014)34
Figure 2.6: The main reaction paths of fuel-N to NO, N_2O and N_2 (Winter, 2010)38
Figure 2.7: Trace element characterization based on their volatility behaviour (trace
elements in bold represent the hazardous air pollutants) (Bunt and Waanders,
2008)
Figure 2.8: Combustion regimes for coal combustion in air and oxy-fuel combustion
atmospheres (Wall et al., 2009)46
Figure 2.9: Main reaction paths of the 3-D model (Myohanen et al., 2009)48
Figure 3.1: (a) Small scale experimental set-up and (b) Quartz reactor
Figure 3.2: Schematic diagram of the fluidized bed quartz reactor
Figure 3.3: Fluidized bed rig
Figure 3.4: Tubular furnace
Figure 3.5: Thermo-gravimetric analyser60
Figure 3.6: Perkin-Elmer Model 2400 elemental analyser61
Figure 3.7: HACH DR 5000 TM UV-VIS spectrophotometer
Figure 3.8: Moisture analyser62
Figure 3.9: Micromeritics AccuPyc 1330 pycnometer
Figure 3.10: (a) Mastersizer and (b) mechanical vibration sieve shaker
Figure 3.11: Rigaku NEX CG X-Ray fluorescence spectrometer64
Figure 3.12: Rigaku miniflex600 X-Ray diffractor65

Figure 3.13: JEOL 7001F scanning electron microscope
Figure 4.1: (a) Typical char particles and (b) char particle with a thermocouple inserted 74
Figure 4.2: Schematic diagram of the experimental setup of oxy-fuel fluidized bed
combustion75
Figure 4.3: Arrhenius plot of reaction rate constants against temperature
Figure 4.4: Typical temperature profile during oxy-fuel combustion environments [O2:
5% (v/v)]; temperature profile only during steady-state period shown in the inset
Figure 4.5: Peak temperature differences between char particle and bed under different
inlet oxygen concentrations during oxy-fuel combustion
Figure 4.6: Experimental and calculated carbon consumption rates under different inlet
oxygen concentrations [(a) 5% (v/v), (b) 10% (v/v) and (c) 15% (v/v)] during dry
oxy-fuel combustion – steady-state bed temperature 890°C
Figure 4.7: Experimental and calculated carbon consumption rates under different inlet
oxygen concentrations [(a) 5% (v/v), (b) 10% (v/v) and (c) 15% (v/v)] along with
15% (v/v) steam as oxidants – steady-state bed temperature 890°C86
Figure 4.8: Experimental and calculated carbon consumption rates during char
combustion using 10% (v/v) oxygen in feed gas during steady-state period at (a)
890°C and (b) 925°C
Figure 5.1: Schematic diagram of the fluidized bed rig91
Figure 5.2: Photograph of the fluidized bed rig under construction (left) and after
complete construction (right)
Figure 5.3: Fluidized bed reactor with cyclone separators
Figure 5.4: (a) Furnace and (b) Control panel of furnace
Figure 5.5: Steam generator
Figure 5.6: (a) Gas pre-heater and (b) temperature controllers for heating tapes
Figure 5.7: Coal feeder
Figure 5.8: Gas flow meter, gas analyser and data acquisition system
Figure 5.9: Schematic diagram of SO ₃ trap97
Figure 5.10: Coal feeder calibration curve
Figure 5.11: Different samples collected from the bed after first commissioning run 100
Figure 5.12: Auger (a) before and (b) after broken100

Figure 6.1: Schematic diagram of the experimental setup for fluidized bed quartz reactor
104
Figure 6.2: Size distribution of coal, char and quartz sand used in experiments
Figure 6.3: Schematic diagram of the experimental setup for stainless steel fluidized bed
rig
Figure 6.4: Typical (a) temperature and (b) pressure profiles during experiment107
Figure 6.5: Mercury sampling train
Figure 6.6: Concentration profiles of CO ₂ and O ₂ under different combustion environments at 850°C
Figure 6.7: Concentration profiles of CO ₂ and O ₂ at different bed temperatures in oxy-fuel
combustion condition $(30\% \text{ O}_2 + 70\% \text{ CO}_2)$
Figure 6.8: Experimental and predicted levels of chromium in collected ash at various
oxygen concentrations under oxy-fuel combustion conditions at 850°C116
Figure 6.9: Experimental and predicted levels of chromium in collected ash under oxy-
fuel combustion condition ($30\% O_2 + 70\% CO_2$) at different temperatures116
Figure 6.10: Experimental and predicted levels of arsenic in collected ash at various
oxygen concentrations under oxy-fuel combustion condition at 850°C117
Figure 6.11: Experimental and predicted levels of arsenic in collected ash at 850°C with
and without steam under oxy-fuel combustion conditions
Figure 6.12: Experimental and predicted levels of arsenic in collected ash under oxy-fuel
combustion condition (30% O_2 + 70% CO_2) at different temperatures
Figure 6.13: Concentration of selenium in collected ash at various oxygen concentrations
under oxy-fuel combustion conditions at 850°C120
Figure 6.14: Experimental levels of selenium in collected ash under oxy-fuel combustion
condition (30% O_2 + 70% CO_2) at different temperature
Figure 6.15: Concentration profiles of CO ₂ and O ₂ under different oxy-fuel combustion
environments
Figure 6.16: Concentration of generated CO ₂ under different oxy-fuel combustion
environments124
Figure 6.17: Concentration profiles of CO ₂ and O ₂ under different oxy-fuel combustion
environments with and without steam124
Figure 6.18: Concentration of generated CO ₂ under different steam concentration in oxy-
fuel combustion125

Figure 6.19: Concentration profiles of CO ₂ and O ₂ under oxy-fuel combustion condition
at different bed temperatures126
Figure 6.20: Sulphur oxides emissions in (a) ppm and (b) mg/MJ under different
combustion environments127
Figure 6.21: Nitrogen oxides emissions in (a) ppm and (b) mg/MJ under different
combustion environments
Figure 6.22: Effect of bed temperature on nitrogen oxides emissions in (a) ppm and (b)
mg/MJ
Figure 6.23: Combustion efficiency under different combustion environments
Figure 6.24: Combustion efficiency under oxy-fuel combustion condition at different bed
temperatures
Figure 6.25: Particle size distributions of (a) primary cyclone ash, (b) secondary cyclone
ash and (c) bed materials under different combustion
Figure 6.26: SEM images of ash minerals from bed, primary cyclone sample and
secondary cyclone sample after oxy-fuel combustion condition using Loy Yang
coal
Figure 6.27: SEM images of coarse ashes (> 250 μ m) from primary cyclone after oxy-fuel
combustion condition using Loy Yang coal140
Figure 6.28: SEM images of fine ashes (< 20 μ m) from primary cyclone after oxy-fuel
combustion condition using Loy Yang coal141
Figure 6.29: Comparison of (a) primary cyclone ash, (b) secondary cyclone ash and (c)
bed ash under different combustion environments142
Figure 6.30: Comparison of (a) primary cyclone ash, (b) secondary cyclone ash and (c)
bed ash under different oxy-fuel combustion environments144
Figure 6.31: Comparison of (a) primary cyclone ash, (b) secondary cyclone ash and (c)
bed ash under oxy-fuel combustion condition at different bed temperatures145
Figure 6.32: XRD patterns of fly and bed ashes under wet oxy-fuel combustion147
Figure 6.33: Extents of Cr in bed and fly ashes from different combustion environments
Figure 6.34: Extents of Cr in bed and fly ashes under oxy-fuel combustion condition at
different bed temperatures151
Figure 6.35: Equilibrium composition of major toxic Cr species during air and oxy-fuel
combustion (Balance of 100% on the vertical axis are the other Cr-species)152

Figure	6.36: Equilibrium distribution of chromium during oxy-fuel combustion using Loy
	Yang coal
Figure	6.37: Extents of As in bed and fly ashes from different combustion environments
Figure	6.38: Extents of As in bed and fly ashes under oxy-fuel combustion condition at
	different bed temperatures
Figure	6.39: Equilibrium composition of major toxic As species during air and oxy-fuel
	combustion (Balance of 100% on the vertical axis are the other As-species)156
Figure	6.40: Equilibrium distribution of arsenic during oxy-fuel combustion using Loy
	Yang coal
Figure	6.41: Extents of Se in bed and fly ashes from different combustion environments
Figure	6.42: Extents of Se in bed and fly ashes under oxy-fuel combustion condition at
	different bed temperatures
Figure	6.43: Equilibrium composition of major toxic Se species during air and oxy-fuel
	combustion (Balance of 100% on the vertical axis are the other Se-species)159
Figure	6.44: (a) Extents of Hg in bed and fly ashes, and (b) gaseous Hg concentrations
	from different combustion environments160
Figure	6.45: Extents of Hg in bed and fly ashes under oxy-fuel combustion condition at
	different bed temperatures
Figure	6.46: Hg^{2+}/Hg^{total} ratio as functions of (a) NO, (b) NO ₂ and (c) N ₂ O163
Figure	6.47: Hg^{2+}/Hg^{total} ratio as a function of SO_3
Figure	6.48: Equilibrium composition of major toxic Hg species during air and oxy-fuel
	combustion (Balance of 100% on the vertical axis are the other Hg-species)166
Figure	6.49: Equilibrium distribution of mercury under different hydrochloric acid
	concentrations during oxy-fuel combustion (a) without HCl (g), (b) with 0.04
	vol.% HCl (g) and (c) with 0.24 vol.% HCl (g)168
Figure	7.1: SEM images of (A) the original limestone and (B) the ash sample176
Figure	7.2: Effect of flow rate on calcination behaviour of limestone at 1000°C178
Figure	7.3: Crucible used in the tubular furnace
Figure	7.4: Effect of limestone addition on carbonation
Figure	7.5: Effect of CO ₂ concentration on carbonation
Figure	7.6: Effect of steam on carbonation

Figure 7.7: Effect of temperature on carbonation (a) TGA thermograph and (b)
carbonation ratio during isothermal period185
Figure 7.8: Effect of limestone addition on sulphur conversion186
Figure 7.9: Effect of CO_2 concentration on (a) sulphur conversion and (b) limestone
utilization
Figure 7.10: XRD patterns of sulphated samples with the addition of (A) 90% (v/v) CO_2
and (B) 80% (v/v) CO_2 to the flue gas
Figure 7.11: XRD patterns of sulphated samples (A) without and (B) with the addition of
steam to the flue gas
Figure 7.12: XRD patterns of sulphated samples with the addition of (A) 100 ppmv and
(B) 200 ppmv SO ₂ to the flue gas
Figure 7.13: XRD patterns of sulphated samples at (A) 800°C and (B) 850°C191
Figure 7.14: Sulphur capture efficiency as functions of bed temperature and CO ₂
concentration, modified from Wall et al. (2012)192
Figure 8.1: Simplified flowsheet of Oxy-FB combustion process197
Figure 8.2: Steady-state process model for Oxy-FB combustion198
Figure 8.3: Variation of void fraction with bed height (Sotudeh-Gharebaagh et al., 1998)
Figure 8.4: Simulated gas concentration profiles of CO, SO_2 and NO_X along the FB riser
height
Figure 8.5: Simulated gas concentration profiles of CO, SO_2 and NO_X under different
excess oxygen percentages during Oxy-FB combustions
Figure 8.6: Simulated gas concentration profiles of CO, SO_2 and NO_X under different flue
gas recycle ratios during Oxy-FB combustions
Figure 8.7: Comparison between simulated and measured concentrations of SO ₂ and NO
under different Oxy-FB combustion conditions

LIST OF TABLES

Table 1.1: Typical characteristics of Victorian brown coal (DPI, 2010)
Table 2.1: List of major oxy-fuel fluidized bed facilities, modified from Wall et al. (2012)
and Anthony (2013)
Table 2.2: Main features of the 30 MW _{th} Oxy-CFB demonstration plant (Álvarez, 2013)
Table 2.3: Main features of the Callide Oxyfuel Project (Uchida et al., 2013)
Table 2.4: Review of combustion characteristics under oxy-fuel fluidized bed combustion
Table 2.5: Review on ash characteristics under oxy-fuel fluidized bed combustion22
Table 2.6: Review on sulphation characteristics under oxy-fuel fluidized bed combustion
Table 2.7: Review on carbonation characteristics under oxy-fuel fluidized bed
combustion
Table 2.8: Review of SO _X emission under oxy-fuel fluidized bed combustion
Table 2.9: Review of NO _X and N ₂ O emissions under oxy-fuel fluidized bed combustion
Table 3.1: Composition of the Victorian brown coals used in this research
Table 4.1: Composition of the char used in the experiment
Table 4.1: Composition of the char used in the experiment
Table 4.1: Composition of the char used in the experiment
Table 4.1: Composition of the char used in the experiment
Table 4.1: Composition of the char used in the experiment
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 Table 4.1: Composition of the char used in the experiment
 Table 4.1: Composition of the char used in the experiment
Table 4.1: Composition of the char used in the experiment

Table 8.1: Parameters in each block utilized for the simulation of Oxy-FB coal
combustion including reactor dimensions200
Table 8.2: Chemical reactions and kinetic expressions used for the modelling of char
combustion in the fluidized bed
Table 8.3: Properties of coal used in the simulation
Table 8.4: Operating conditions used in the combustion experiments
Table A.1: Design calculation for air combustion 239
Table A.2: Design calculation for Oxy-FB combustion with different gas composition 239
Table A.3: Design calculation for Oxy-FB combustion with different coal feed rates with
0.15 m inner diameter of the combustion240
Table A.4: Design calculation for Oxy-FB combustion with different coal feed rates with
0.1 m inner diameter of the combustion240
Table A.5: Design calculation for Oxy-FB combustion with or without steam241
Table A.6: Design calculation for Oxy-FB combustion with different excess oxygen at
900°C

LIST OF ABBREVIATIONS

AAEM	Alkali and Alkaline Earth Metal
AAS	Atomic Absorption Spectrometry
ASU	Air Separation Unit
BFB	Bubbling Fluidized Bed
CCS	Carbon Capture and Storage
CFB	Circulating Fluidized Bed
CFD	Computational Fluid Dynamics
CPU	Compression and Purification Unit
DPI	Department of Primary Industries
EDX	Energy-Dispersive X-ray
EIA	Energy Information Administration
EPA	Environment Protection Authority
FAAS	Flame Atomic Absorption Spectrometry
FB	Fluidized Bed
FBC	Fluidized Bed Combustion
FGD	Flue Gas Desulfurization
FTIR	Fourier Transform Infrared
HAPs	Hazardous Air Pollutants
ICP-AES	Inductively Coupled Plasma – Atomic Emissions Spectrometry
ICP-MS	Inductivity Coupled Plasma – Mass Spectrometry
ICP-OES	Inductively Coupled Plasma – Optical Emissions Spectrometry
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
Oxy-CFB	Oxy-fuel Circulating Fluidized Bed
Oxy-FB	Oxy-fuel Fluidized Bed
Oxy-PC	Oxy-fuel Combustion with Pulverized Coal
Oxy-PF	Oxy-fuel Combustion with Pulverized Fuel
PC	Pulverized Coal
PF	Pulverized Fuel
RCSTR	Continuous Stirred Tank Reactor
REQUIL	Equilibrium Reactor
RSTOIC	Stoichiometry Reactor
RYIELD	Yield Reactor

SCR	Selective Catalytic Reduction
SEM	Scanning Electron Microscope
SIMS	Secondary Ion Mass Spectrometry
SS	Stainless Steel
TF	Tubular Furnace
TGA	Thermogravimetric Analyser
WHO	World Health Organisation
XANES	X-Ray Absorption Near Edge Structure Spectrometry
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
RFG	Recycle Flue Gas

LIST OF SYMBOLS

Roman symbols

А	Cross-sectional area
С	Concentration
D	Molecular diffusivity
d	Particle diameter
d(t)	Particle diameter as a function of time
Е	Activation energy
g	Gram
h	Hour
Н	Height
\mathbf{k}_0	Pre-exponential factor
kg	Kilogram
kJ	Kilojoule
kV	Kilovolt
kW	Kilowatt
L	Litre
m	Meter
mA	Milliampere
mg	Milligram
min	Minute
MJ	Megajoule
mL	Millilitre
mm	Millimeter
MW	Megawatt
ppb	Parts per billion
ppm	Parts per million
ppmv	Parts per million by volume
ppmw	Parts per million by mass
Re	Reynolds number
S	Second
Sc	Schmidt number
Sh	Sherwood number

t	Time
Т	Temperature
u	Fluidization velocity
UC	Unburnt carbon
vol	Volume
wt	Weight
Х	Conversion

Greek symbols

μm	Micrometer	
μg	Microgram	
3	Bed voidage	
ṁ	Mass flow rate	
ρ	Density	
μ	Viscosity	

Subscripts

c	Conversion
e	Electric
g	Gas
i	Denotes Species
C	\mathbf{M}
mf	Minimum Fluidization velocity
mf p	Particle
mf p s	Particle Solid
mr p s th	Particle Solid Thermal

CHAPTER 1: INTRODUCTION

CHAPTER 1: INTRODUCTION

Globally coal-fired power generation is known to be a major contributor to carbon dioxide (CO₂) emission, which can be reduced with CO₂ capture before its release in the environment. Although oxy-fuel fluidized bed (Oxy-FB) combustion has emerged as a promising technology to capture CO₂ from coal-fired power plants, very little is known about the applicability of Oxy-FB for brown coal. Brown coal accounts for 91% of Victoria's current electricity needs (BP, 2010). Since Victoria has a large reserve of brown coal estimated to be for over 500 years at the current consumption rate, the successful application of Oxy-FB using Victorian brown coal can produce electricity in an environment friendly manner. Hence, this thesis investigates the applicability of Oxy-FB using Victorian brown coal con.

This chapter is organized into seven sections. Section 1.1 provides an overview of the CO_2 emission from energy sector and the different CO_2 capture technologies. Section 1.2 discusses the concept of Oxy-FB technology and its advantages over conventional technologies. Section 1.3 highlights the features of Victorian brown coal. Section 1.4 identifies the research gap and sets the research aims while Section 1.5 presents the research objectives. The research plan and contributions of this thesis are summarized in Section 1.6. This chapter concludes with an outline of the thesis structure in Section 1.7.

1.1. BACKGROUND

Considerable attention has been focused on CO_2 emission due to its impact on climate change. A major portion of CO_2 emission results from combustion of coal. Indeed in 2010, 43% of the CO_2 emission from fuel combustion were due to coal combustion for power generation (IEA, 2012). In the International Energy Outlook 2011 projections, world coal consumption is projected to increase by 1.5 percent per year on average from 2008 to 2035, and it will account for 27 percent of total world energy consumption in 2035 (EIA, 2011). This increased use of coal will increase world CO_2 emission unless carbon capturing technologies are applied.

As shown in Figure 1.1, the three commonly considered technologies for the capture and storage of CO_2 are post-combustion capture, pre-combustion capture and oxy-fuel

combustion capture. In post-combustion capture, CO_2 is captured from flue/exhaust gases by means of chemical absorption process such as scrubbing using a liquid scrubbing agent and amine absorption using amine solvent. The cost of solvent, however, is high. As regards to pre-combustion capture, CO_2 is captured from synthetic gas after conversion of CO into CO_2 , and then H_2 is used as a fuel in a gas turbine combine cycle for applications in industries such as steel making and hydrocarbon manufacture. However, this CO_2 capture technology requires high energy consumption and high capital cost. Oxy-fuel combustion capture, O_2 is separated from N_2 in an air separation unit (ASU), mixed with recycled flue gases, which creates a mixture of mainly O_2 , CO_2 and water vapour used as oxidant in combustion. The resulting flue/exhaust gas consists of essentially CO_2 and water vapour along with some O_2 , N_2 , and trace gases like SO_2 and NO_X . Thus the generated CO_2 can be stored with less downstream processing.



Figure 1.1: The three basic CO₂ capture technologies (IPCC, 2005)

Among these three options, the oxy-fuel combustion has the potential to generate highly concentrated CO_2 stream in the flue gas for easier and cheaper capture and storage of CO_2 (Buhre et al., 2005; Wall et al., 2009; Toftegaard et al., 2010; Edge et al., 2011; Stanger and Wall, 2011; Wall et al., 2011; Wall et al., 2013). While conventional air combustion makes CO_2 capture difficult due to dilution of the CO_2 concentration in the flue gas by nitrogen from the air, oxy-fuel combustion can capture CO_2 without such limitation because of the absence of nitrogen from air. Further advantage of using high oxygen

contents is reduced boiler size (Duan et al., 2011a). It also offers higher efficiency (Czakiert et al., 2006). Moreover, the recycled flue gas controls the flame temperature and makes up the volume of the missing N_2 to ensure enough gas to carry the heat through the boiler. Currently, majority of the development projects on oxy-fuel combustion are based on pulverized coal (PC) fired, which represents the most common form of power generation process as well as the main thrust of research (Wall et al., 2011). It, however, includes the benefits of the fluidized bed combustion as well when the oxy-fuel combustion is introduced into fluidized bed combustion.



Figure 1.2: Schematic diagrams of bubbling and circulating fluidized beds (Anthony, 2013)

Fluidized bed (FB) combustion has already been established as a boiler technology suitable for utility-scale power generation for all types of fuels. As shown in Figure 1.2, there are two forms of fluidized bed: bubbling fluidized bed (BFB) and circulating fluidized bed (CFB). The BFB combustor operates at low velocities (1-2.5 m/s), whereas CFB combustor operates at relatively higher velocities (4-8 m/s) to entrain a large portion of solids which are separated from the flue gas and recycled back to the combustor (Jia et al., 2007; Anthony, 2013). In FB units, bed materials (such as silica sand) are used to burn coal or any solid fuels to generate heat. This hot bed material effectively dries and ignites even demanding fuels with low heating value or high ash content or high moisture content, or various combinations of them. The scrubbing action of the bed material on the fuel particles enhances the combustion process by stripping away the carbon dioxide and char layers that normally form around the fuel particle. Thereby, it allows oxygen to reach

the combustible material much more readily and increases the rate and efficiency of the combustion process. Moreover, strong turbulence and good mixing also result in high combustion efficiency and low emission. Steam, generated in the fluidized bed combustor, can be used for power generation in steam turbines. FB combustion can tolerate varying particle size (from micron size as in pulverized coal-fired units to coarse feed size of around 10 mm), and varying fuel quality (from anthracite to lignite, petroleum coke, biomass and opportunity fuels). Moreover, a sorbent such as limestone may be added to the coal, particularly of high-sulphur coal, to aid in sulphur dioxide removal (Jia et al., 2007; Anthony, 2013).

1.2. Oxy-fuel fluidized bed combustion

Oxy-fuel fluidized bed (Oxy-FB) combustion, a combination of both oxy-fuel and FB technologies, has emerged as a promising technology for reducing CO_2 emission. The major advantages of Oxy-FB combustion include fuel flexibility, good temperature control, low NO_X emission and the possibility of reducing SO₂ emission via addition of sorbents (Jia et al., 2010; Duan et al., 2011a).

Oxy-FB combustion offers several technical, scientific and economic advantages over the oxy-fuel with conventional pulverized fuel (Oxy-PF) combustion. Oxygen concentration in the recycled flue gas can be kept to a low and safe level while additional oxygen can be introduced through oxygen nozzles separate from the burner or the secondary gas inserting points in Oxy-FB. Unlike Oxy-PF, Oxy-FBs thus do not need new burner design. Furthermore, in Oxy-FB the transition from air-mode combustion to oxy-mode combustion is potentially easier compared to Oxy-PF because FB has large amount of inert bed material that also helps in controlling the bed temperature.

Another notable advantage of Oxy-FB combustion over Oxy-PF combustion using brown coal or lignite is the lower furnace temperature. This helps to overcome the problems associated with high alkali ash, and improves combustion efficiency as well as overall plant availability. Since Oxy-FB allows high fuel flexibility and operating flexibility (Wang et al., 1994; Huilin et al., 2000; Jia et al., 2007; Lu et al., 2008; Gungor, 2009; Zhu et al., 2009; Czakiert et al., 2010; Zhou et al., 2011b), the scale-up is also easier in this combustion. More research using a variety of coals including brown coals, therefore, are necessary to develop this technology.

1.3. VICTORIAN BROWN COAL AND ITS IMPORTANCE IN OXY-FB

Victoria, Australia has one of the largest reserves of brown coal in the world. The total estimated reserve of Victorian brown coal is 430 billion tonnes, which is expected to last over 500 years at the rate of current consumption (DPI, 2010).

Victorian brown coal has attained special attention in coal utilization processes due to its low impurities (such as ash, sulphur and heavy metals), abundant pore structure, high oxygen content, the presence of alkali and alkaline earth metallic (AAEM) species and iron, and high moisture content (Li, 2007).

Energy value (net wet)	5.8-11.5 MJ/kg
Energy value (gross dry)	25-29 MJ/kg
Moisture	48-70%
Carbon (dry ash free)	65-70%
Oxygen (dry ash free)	25-30%
Hydrogen (dry ash free)	4.0-5.5%
Nitrogen (dry ash free)	<1%
Sulphur (dry ash free)	<1%
Ash (dry basis)	< 4%

Table 1.1: Typical characteristics of Victorian brown coal (DPI, 2010)

As shown in Table 1.1, Victorian brown coal has many unique physical and chemical properties and structural features. The typical properties of Victorian brown coal are. It has low carbon content accounting for 25-35% (65-70%, dry ash free basis) of raw coal. The oxygen content of Victorian brown coal is very high, whereas the nitrogen, sulphur and ash contents are very low. One of the most important features of this brown coal is high moisture content. Due to this high moisture, Victorian brown coal has low energy content (average 8.6 MJ/kg on net weight basis and 26.6 MJ/kg on dry basis) (DPI, 2010).

The main use of Victorian brown coal is to generate electricity through air-fired pulverized fuel (PF) combustion. It is expected that the brown coal resources will continue to serve as a cheap and secure energy source for the Victorian economy in the foreseeable future. However, the viability of this Victorian brown coal as a future energy source will largely depends on the minimization of the environmental impacts using this coal.

1.4. MOTIVATION

It has been identified that Oxy-FB has become a promising technology for capturing CO₂ in coal-fired power plants. It combines the advantages of both oxy-fuel and fluidized bed technologies. This emerging Oxy-FB technology can be used in power plants to generate electricity in an environment friendly manner using all types of coals. While air-fired FB combustion has been extensively studied, Oxy-FB studies are few and far between. Studies on Oxy-FB combustion using brown coal are non-existent. In terms of Victorian brown coal, this technology has never been investigated. Therefore, to address this research gap, this research is the first to address the issues related to the application of Victorian brown coal in Oxy-FB combustion.

1.5. Research Aims

The broad aim of this research is to develop an understanding, in a combined modelling and experimental approach, of the combustion performance of Victorian brown coal under Oxy-FB combustion conditions necessary for the development of oxy-fuel circulating fluidized bed (Oxy-CFB) as an efficient and CO₂ capturing technology. The specific aims of this research are:

- To investigate the fluidized bed combustion of single coal char particles under simulated oxy-fuel conditions.
- To design and commission a flexible fluidized bed for operation in both oxy-fired and air-fired mode using a variety of coals.
- To conduct the experiments on combustion characteristics of the Victorian brown coal during Oxy-FB conditions.
- To predict the compounds formed and their composition during Oxy-FB combustion conditions by using thermodynamic equilibrium modelling.
- To develop a generic process model for Oxy-FB using Aspen Plus.

1.6. Research Plan

This thesis has four distinct parts – single particle combustion experiment, bench scale combustion experiment, thermodynamic equilibrium modelling, and process modelling.

1.6.1. Single particle combustion experiment

The aim of the combustion experiments using single char particle is to investigate the combustion characteristics of individual and large char particle under Oxy-FB combustion. A thin thermocouple is inserted inside each char particle to monitor the particle temperature during these experiments. Moreover, a kinetic model on char combustion is developed to calculate the carbon consumption rate and the particle diameter as a function of time. The char particle temperature monitored during combustion would help to assess the propensity of agglomeration. Moreover, the single particle model can be used to calculate the burning time of the particle in the oxy-fuel combustion atmosphere consisting of O_2 , CO_2 and H_2O .

1.6.2. Bench scale combustion experiment

This bench scale experiment aims to examine the combustion efficiency, agglomeration characteristics, sulphation characteristics, carbonation characteristics, NO_X (NO, NO₂ and N₂O) emissions, SO_X (SO₂ and SO₃) emissions, and trace elements (Hg, Se, As and Cr) emissions. It involves designing and commissioning of a 10 kW_{th} bench scale fluidized bed rig, carrying out experiments, and analysing the flue gases and solid residues with several analytical techniques. The experimental work is carried out using a wide range of experimental facilities including fluidized bed quartz reactor, bench scale stainless steel fluidized bed rig, tubular furnace and thermo gravimetric analyser. The flue gases are analysed continuously by an on-line gas analyser whereas the solid residues are characterized using different analytical techniques including scanning electron microscopy (SEM), X-Ray diffraction (XRD) and X-ray fluorescence spectroscopy (XRF). Oxy-FB combustion experiments, performed in the laboratory to bench scale fluidized bed unit under different oxy-fuel combustion conditions, provide a basis for the selection of optimum operating condition during scale up. Furthermore, the conventional pollutants and trace elements emission characteristics from experiments would help to design the gas cleaning systems.

1.6.3. Thermodynamic equilibrium modelling

The thermodynamic equilibrium modelling aims to predict the compounds, especially the speciation of trace elements (Hg, Se, As and Cr) and their concentrations, formed during the combustion of Victorian brown coal under different Oxy-FB combustion conditions. It is carried out using FactSage package. The findings would help in setting the parameters for design and operation of Oxy-FB combustion so that the emissions can be controlled within the permissible limits.

1.6.4. Process modelling

A generic steady-state process model for the Oxy-FB combustion can be used for modelling the performance of any coal in Oxy-FB combustion unit. So, the aim is to develop an Oxy-FB process model using Aspen Plus process software. The predicted simulation results are validated with the experimental results from the bench scale Oxy-FB unit. The process simulation model can be utilized for the process optimisation and to predict the combustion performance of Oxy-FB's using different grades of coals.

1.7. Organization of the thesis

This thesis consists of nine chapters. Figure 1.3 shows the structure of the entire thesis. This present chapter is the introductory one. The remainder of the thesis is organized as follows. Chapter 2 reviews the prior literature, chapter 3 covers the experimental set-ups and analytical techniques, chapter 4 discusses the single char particle combustion, chapter 5 describes the design and commissioning of a bench scale 10 kW_{th} fluidized bed rig, chapter 6 analyses the experimental findings on that rig, chapter 7 investigates the sulphation and carbonation characteristics of Victorian brown coal, chapter 8 presents the developed process modelling on Oxy-FB combustion while chapter 9 concludes the thesis with the contributions, practical implications and scope for further research.



Figure 1.3: Thesis structure diagram
CHAPTER 2: LITERATURE REVIEW

CHAPTER 2: LITERATURE REVIEW[†]

2.1. INTRODUCTION

In Chapter 1, the need to investigate the emerging oxy-fuel fluidized bed (Oxy-FB) technology to better use the abundant Victorian brown coals was established. This chapter presents a comprehensive review of the prior research conducted on Oxy-FB technology using different types of coals. The key purpose of this review is to evaluate the prior literature and identify the major issues where more research need to be carried out for the development of oxy-fuel firing circulating fluidized bed (Oxy-CFB) as an efficient CO_2 capturing technology using low-rank coals.

2.2. STATUS OF OXY-FUEL FLUIDIZED BED TECHNOLOGY

Recently Oxy-FB has become a prospective technology for carbon capture and storage (CCS) using variety of fuels, including high-rank and low-rank coals. At present, Foster Wheeler, CIUDEN and to a lesser extent Alstom are the front-runners of this technology. A list of some major oxy-fuel fluidized bed pilot-scale facilities worldwide is given in Table 2.1.

In the beginning, for concept validation Alstom conducted pilot-scale tests in a unit of 3 MW_{th} facility without flue gas recirculation (Liljedahl et al., 2006). In 2004, Foster Wheeler's work (Erikson et al., 2007; Czakiert et al., 2010) involving pilot scale testing (using a small 30-100 kW_{th} CFBC), operated by VTT (technical research centre of Finland), and this work along with CanmetENERGY's work with its own 100 kW_{th} CFBC appeared to be the first unit operated with full flue gas recirculation (Jia et al., 2007; Jia et al., 2010; Wu et al., 2011).

[†] Some of the sections of this chapter have been contributed in the following report:

^{1.} Wall, T.; Liu, Y.; Bhattacharya, S. *A scoping study on Oxy-CFB technology as an alternative carbon capture option for Australian black and brown coals*; Australian National Low Emissions Coal Research and Development (ANLEC R&D), Canberra, Australia: 2012.

Facility location	Capacity	Reactor	Focus of work
Alstom, Windsor, CT, USA	3 MW _{th}	CFB	Feasibility study at O ₂ /CO ₂ atmosphere without recycled flue gas
Foster Wheeler, VTT and Lappeenranta University of Technology, Finland	0.1 MW _{th}	CFB	Provide design and operation data for Oxy-CFB combustion with recycled flue gas
CanmetENERGY, Canada	0.1 and 0.8 MW_{th}	CFB	Provide operation data to support national Canadian program on Oxy-CFB
Czestochowa University of Technology, Poland	0.1 MW _{th}	CFB	Test polish coal and limestone sorbent for Lagisza plant to support Foster Wheeler
Centre of Research for Energy Resources and Consumptions (CIRCE), University of Zaragoza, Spain	0.1 MW _{th}	BFB	Generate fundamental data
Institute de Carboquimica (ICB- CSIC), Spain	3 kW_{th}	BFB	Generate fundamental data
University of Utah , Utah, USA	0.33 MW _{th}	CFB	Generate fundamental data
Metso Power, Finland	4 MW _{th}	CFB	Generate fundamental data performed by Chalmers University, Sweden to develop commercial technology
Southeast University in China	$50 \ kW_{th}$	CFB	Generate fundamental data
Zhejiang University, China	$30 \text{ kW}_{\text{th}}$	BFB	Generate fundamental data
Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart, Germany	150 kW _{th}	CFB	Generate fundamental data
Institute of Engineering Thermophysics (IET), Chinese Academy Sciences (CAS), China	0.1 MW _{th}	CFB	Generate fundamental data

Table 2.1: List of major oxy-fuel fluidized bed facilities, modified from Wall et al. (2012) and

Anthony (2013)

Notes: BFB = Bubbling fluidized bed, CFB = Circulating fluidized bed

Later in 2009, CanmetENERGY conducted pilot plant trials for Foster Wheeler at 0.8 MW_{th} scale in Ottawa, Canada (as shown in Figure 2.1). This facility mainly consisted of a riser (an internal height of 6.6 m and an inner diameter of 0.406 m), hot cyclone, return leg, flue gas cooler, baghouse, and feeders for fuel and sorbent. A flue gas recycle line, including a recycle blower, a flue gas condenser, and pressure control and safety equipment, was also installed to the facility.



Figure 2.1: Schematic of CanmetENERGY's 0.8 MW_{th} Oxy-CFB combustion pilot facility (Kuivalainen et al., 2010)

Recently in September 2011, a 30 MW_{th} scale Oxy-CFB demonstration plant with CCS was commissioned at CIUDEN in Spain. Figure 2.2 shows the simplified schematic of CIUDEN's facilities. In this plant, along with a 30 MW_{th} Oxy-CFB boiler, there are also a 20 MW_{th} Oxy-PC boiler and a 3 MW_{th} bubbling bed biomass gasifier. Along with these boilers, this plant also has fuel preparation system, flue gas cleaning system, CO₂ compression and purification unit (CPU), and CO₂ transport facility. The major equipment in the flue gas cleaning system include cyclones, selective catalytic reduction (SCR) of NO_X, bag filter and flue gas desulfurization (FGD) unit. Moreover, acid gas scrubbing, high performance flue gas dust filtration, low pressure flue gas drying system, flue gas compression, cryogenic CO₂ separation, refrigeration cycle and chilled water production system were also installed to the CO₂ compression and purification unit. Table 2.2 provides the main features of the facility.



Figure 2.2: Simplified flow-sheet of CIUDEN's facilities (Álvarez, 2013)

The experimental results from CIUDEN's 30 MW_{th} Oxy-CFB demonstration plant will be applied to scale up to a 300 MW_e supercritical oxy-combustion power station (OXYCFB300 Compostilla Project) at Compostilla, in Spain. This OXYCFB300 Compostilla Project, intended to demonstrate the CCS facility fully integrated in commercial scale, is targeted to start-up in 2015 (Hotta et al., 2012). Foster Wheeler's Flexi-Burn Oxy-CFB technology up to 800 MW_e is planning to be commercialized by 2020.

CFB boiler	
Furnace dimensions (height, width, depth) (m)	$20 \times 2.9 \times 1.7$
Oxygen consumption (kg/h)	8775
Flue gas flow (kg/h)	28800
Coal consumption (kg/h)	5470
Limestone consumption (kg/h)	720
Feed water temperature (°C)	170
Maximum steam flow (t/h)	47.5
Superheated steam temperature (°C)	250
Superheated steam pressure (bar)	30
Fuel preparation system	
Coal	Anthracite, bituminous and sub-
	bituminous coals, and pet coke
Coal crusher (t/h)	15
Crushed coal silos (m ³)	2×120
Ball mill (t/h)	5
Flue gas cleaning system	
Gases inlet temperature (°C)	350 - 425
DeNO _X in SCR (ppmv NO _X)	< 40
Particulate matter outlet in bag filter (mg/Nm ³)	< 15
DeSO _x efficiency in FGD (%)	> 95
CO ₂ compression and purification unit	
Temperature in CPU inlet (°C)	≈ 200
Temperature in captured CO ₂ stream (°C)	\approx -30
Pressure in CPU inlet (barg)	≈ 1
Pressure in captured CO ₂ stream (barg)	≈ 14
CO ₂ in CPU inlet (% vol. wet basis)	≈ 70
CO ₂ in captured CO ₂ stream (% vol.)	\geq 99
H ₂ O in CPU inlet (% vol.)	15
H ₂ O in captured CO ₂ stream (ppmv)	< 1
SO ₂ in CPU inlet (ppmv)	500
SO ₂ in captured CO ₂ stream (ppmv)	< 1
NO _X in CPU inlet (ppmv)	≈ 50
NO _X in captured CO ₂ stream(ppmv)	< 10
CO ₂ transport facility	
Number of tube coils	10
Total pipe length (m)	3000
Pipe diameter (m)	0.05

Table 2.2: Main features of the 30 $\rm MW_{th}$ Oxy-CFB demonstration plant (Álvarez, 2013)

2.2.1. Oxy-CFB combustion in the context of Australia

Australia is one of major countries in the world generating electricity from coal. Around 75 percent of Australia's electricity was generated from coal in 2007-2008 (ABARE, 2011). In Australia, Callide A Power Station in central Queensland has been recently (2011) retrofitted with Oxy-PF technology with a capacity of 30 MW_e. This Callide Oxyfuel Project, aiming to produce electricity with low emission, is now in the demonstration phase. The main features of this project are given in Table 2.3.

Fuel	Black coal
Power (MW _e)	30
Boiler height (m)	30
Furnace temperature (°C)	1200
Chimney height (m)	76
Exhaust gas temperature (°C)	44
Oxygen production plant capacity (t/d)	660
Oxygen purity	98%
Design CO_2 production rate (t/dy)	75
CO ₂ purity	> 99%
Target CO ₂ geological storage over 3 years (tonnes)	15,000 - 30,000

 Table 2.3: Main features of the Callide Oxyfuel Project (Uchida et al., 2013)

On the other hand, Redbank power station in New South Wales is the only power station in Australia, which has air-fired circulating fluidized bed boiler with a capacity of 150 MW_e . However, there is no oxy-fired circulating fluidized bed development plant in Australia. Therefore, research need to be carried out to develop this technology in Australia using both high-rank and low-rank coals.

2.3. COAL QUALITY IMPACTS ON OXY-FUEL FLUIDIZED BED COMBUSTION

Fuel flexibility is one of the most important advantages of fluidized bed combustion. Power generation using oxy-fuel based fluidized bed combustion is an emerging technology with the major purpose of reducing CO_2 emission, particularly when utilising low-rank coals. In addition to the economic advantage of low-rank coals, the capability of obtaining lower combustion temperature using low calorific value fuels is also an important advantage; thus overcoming the combustion process problems associated with temperature control and heat transfer (Czakiert et al., 2006). However, there are several issues associated with coal quality impacts on Oxy-FB design. Some of these issues are listed below.

2.3.1. Combustion characteristics

Combustion characteristics of coal, such as ignition, burning rate, flame temperature, flame propagation speed, combustion stability and burnout characteristics, are mainly determined by volatile, ash, moisture content and heating value of coal. The volatile content of lignite is twice as bituminous coal, which facilitates to coal burnout (Leng et al., 2010). In coal-fired fluidized bed combustion, combustion efficiency is dependent on several factors, such as coal type, ash content, fluidization velocity, combustion temperature, fluidized bed height, freeboard height, char recirculation, coal particle size and feed gas concentration.

Several experimental studies have been carried out to investigate the combustion performances of various coals under oxy-fuel fluidized bed combustion (Czakiert et al., 2006; Jia et al., 2010; Duan et al., 2011b; Czakiert et al., 2012; Tan et al., 2012; de Diego et al., 2013a; Jia and Tan, 2014; Li et al., 2014; Tan et al., 2014). Table 2.4 provides the summary of prior research work carried out on combustion performances of different types of coals under Oxy-FB combustion.

Using one bituminous coal and one anthracite coal in a 50 kW_{th} circulating fluidized bed combustor under simulated O_2/CO_2 combustion environment, Duan et al. (2011b) studied the effects of oxygen concentration in the combustion atmosphere and oxygen staging on the combustion efficiency. They concluded that oxygen concentration in the atmosphere increased the combustion efficiency, and oxygen staging provided more operation flexibility. Using Czech lignites in a small scale Oxy-CFB combustor, Czakiert et al. (2006) found increased carbon burnout ratio with increase in the oxygen concentration in the gas mixture delivered into the combustion chamber. They did not find any effect of reactor temperature on the carbon burnout ratio. On the other hand, studies by de Diego et al. (2013a) observed lower carbon monoxide at higher combustor temperature.

Reactor	r uei	Fluidizing gas	Major findings
CFB	Brown coal	O ₂ /N ₂ ,	Carbon conversion ratio increased with oxygen concentration in
		O ₂ /CO ₂	oxidant.
CFB	Bituminous and pet coke	Air,	CO concentration decreased with bed temperature;
		O ₂ /RFG	CO concentration was similar for both air and oxy-fuel combustion
			with flue gas recirculation.
CFB	Bituminous and	Air,	CO emission decreased with O ₂ enrichment in the atmosphere;
	anthracite	O ₂ /CO ₂	CO emission was much lower in air combustion than that in oxy-fuel
			combustion.
CFB	Bituminous	O ₂ /CO ₂	Conversion of C to CO was considerable in the bottom zone of
			reactor; while oxidation of C disappeared at the upper part of furnace
			resulting high fraction of unburnt carbon in fly ash.
CFB	Bituminous and	Air,	CO concentration was slightly higher in oxy-fuel than that in air
	petroleum coke	O ₂ /RFG	combustion.
BFB	Anthracite	Air,	CO emission was slightly higher in oxy-fuel than that in air
		O ₂ /CO ₂ ,	combustion;
		O ₂ /CO ₂ /SO ₂ ,	CO concentration increased with SO ₂ recirculation.
		O ₂ /CO ₂ /NO,	
		O ₂ /CO ₂ /H ₂ O	
	CFB CFB CFB CFB CFB BFB	CFBBrown coalCFBBituminous and pet cokeCFBBituminous and anthraciteCFBBituminous and petroleum cokeCFBBituminous and petroleum cokeBFBAnthracite	CFBBrown coalO ₂ /N ₂ , O ₂ /CO ₂ CFBBituminous and pet cokeAir, O ₂ /RFGCFBBituminous and anthraciteAir, O ₂ /CO ₂ CFBBituminous and anthraciteAir, O ₂ /CO ₂ CFBBituminousO ₂ /CO ₂ CFBBituminousO ₂ /CO ₂ CFBBituminous and

Table 2.4: Review of combustion characteristics under oxy-fuel fluidized bed combustion

Authors	Reactor	Fuel	Fluidizing gas	Major findings
Jia and Tan (2014)	TGA	Bituminous, anthracite,	O ₂ /CO ₂	Oxygen concentration had weak effect on ignition;
		lignite and petroleum		Burnout time reduced with oxygen level.
		coke		
Li et al. (2014)	CFB	Low rank bituminous	Air,	CO concentration decreased with excess oxygen in oxy-fuel
			O ₂ /CO ₂ ,	combustion with flue gas recirculation.
			O ₂ /RFG	
Tan et al. (2014)	CFB	Low rank bituminous	O ₂ /CO ₂	Coal burnout was facilitated by secondary flow ratio, thus combustion efficiency increased.

Table 2.4: Review of combustion characteristics under oxy-fuel fluidized bed combustion (Continued)

In a recent study, Jia and Tan (2014) investigated the combustion characteristics of different fuels in a TGA under simulated oxy-CFB atmosphere. They concluded that oxygen concentration, in the range of 25% - 50%, had a very weak effect on the ignition temperature. It was also noticed that gasification reaction between CO₂ and carbon under Oxy-CFB conditions at typical fluidized bed combustion temperature (~ 900°C) could only be significant for low-rank coals (such as lignite), while this reaction could be neglected for high-rank coals (such as anthracite and petroleum coke).

In summary, few studies have been carried out focusing on the combustion characteristics of low-rank coals during Oxy-FB combustion. Therefore, it is essential to investigate the combustion characteristics of brown coals/lignites during Oxy-FB combustion.

2.3.2. Ash mineral and bed agglomeration

In coal-fired fluidized bed combustion, the ash behaviour is also an important consideration as it could affect the design and operation of fluidized bed boilers. Few researchers have studied the characterization of ashes resulting from Oxy-FB combustion using different analytical techniques and using a variety of coals (Wu et al., 2011; Zheng et al., 2013; Wang et al., 2014b). The key findings of prior literature on ash characteristics under Oxy-FB combustion are summarized in Table 2.5. From this table, it can be seen that though several researchers investigated the ash characteristics from oxy-fuel fluidized bed combustor, they used mainly bituminous and anthracite coals. There are no studies on the ash behaviour using brown coal in oxy-fuel fluidized bed combustion.

Furthermore, the issue of agglomeration during coal combustion also has important implications on the operation of Oxy-FB combustors. Agglomeration affects the fluidization characteristics of the bed and generates secondary pollutants such as heavy metals (Pb, Cr, and Cd) (Lin and Wey, 2004; Kuo et al., 2009; Lin et al., 2009; Kuo et al., 2010). If agglomeration remains undetected on time, it may propagate to partial or total defluidization of the bed materials, which in turn may lead to a lengthy and expensive unscheduled shutdown (Lin and Wey, 2004; Bartels et al., 2008; Bie et al., 2009; Lin et al., 2009; Kuo et al., 2010).

Authors	Reactor	Fuel	Fluidizing gas	Major findings
Wu et al. (2011)	CFB	Bituminous and	O ₂ /RFG	Carbon content in fly ash was higher than that in bed ash due to the
		petroleum coke		short residence time in small scale test facility;
				Surface area and pore volume in fly ash were much higher than that in
				bed ash.
Zheng et al. (2013)	FB	Anthracite	Air,	No significant differences were observed in the chemical composition
			O_2/CO_2	of ashes generated under air and oxy-fuel combustion;
				Average particle size and concentration of particulate matter were
				slightly higher in higher oxygen concentration in atmosphere.
Wang et al. (2014b)	FB	Anthracite	Air,	Deposition propensity was higher in air combustion than that in oxy-
			O_2/CO_2	fuel combustion;
				Sulphur content in ash was lower in oxy-fuel than that in air
				combustion.

Table 2.5: Review on ash characteristics under oxy-fuel fluidized bed combustion

Agglomeration is mainly caused by compounds of alkali metals (Na and K), and alkali earth metals (Mg and Ca), sulphur, chlorine, silicon, vanadium, and nickel (Lin and Wey, 2004; Lin et al., 2009). Of these ash forming elements, alkali components play a critical role in bed agglomeration in fluidized bed combustors (Zevenhoven-Onderwater et al., 2001a). Some of these alkali metal compounds have low melting points and sometimes form molten phases in the combustor. These molten phases can react with the bed material, forming a coated layer on the surface. Thereafter, the molten layer forms liquid bridges between bed particles, which facilitate the agglomeration of the particles (Tangsathitkulchai and Tangsathitkulchai, 2001; Zevenhoven-Onderwater et al., 2001a; Lin and Wey, 2004).

Lin and Wey (2004), and Zevenhoven-Onderwater et al. (2001b) studied the species in the liquid bridges and found that Na, Si, K, Mg and Ca were the main elements. These elements combined with the bed material form agglomerates. Bhattacharya and Harttig (2003) performed experiments using a small CFB combustor with high-alkali and high-sulphur lignites. They reported that mainly sulphates of calcium, sodium and magnesium were formed and their interaction with the silica sand bed led to agglomeration. Steenari et al. (1998) found that agglomerates of bed material in a fluidized bed combustor consist of mainly amorphous phases (formed from silicate–alkali interaction) and to a lesser extent crystalline phases (CaSO₄, CaCO₃, SiO₂ and Fe₂O₃).

Moreover, several studies have been conducted to reduce and control the bed agglomeration in the fluidized bed. These include the use of mineral additives, alternative bed materials, large excess of inert ash, pre-treatment of fuels, use of higher fluidization velocity and lower bed temperature (Liljedahl et al., 2006; Bie et al., 2009). In the context of oxy-fuel technology, compared to the oxy-fuel pulverized coal-fired (Oxy-PC) boilers, Oxy-FB boilers have more ways to control the bed temperature, by which agglomeration could be avoided (Zhao et al., 2010). Nsakala et al. (2004) conducted tests in an Oxy-CFB facility to determine the impacts of different fuels (an Eastern US bituminous coal and pet coke) on bed and ash characteristics (agglomeration), and there was no evidence of particle agglomeration in the furnace.

In some low-rank coals, the quantity of the ash forming elements is relatively higher compared to that of high-rank coals. Therefore, the possibility of agglomeration is high in brown coals/lignites and less in black coals. When using high-sodium lignite, however, it

was suggested by Dahlin et al. (2006) that agglomeration could be mitigated by using a nonreactive bed material (e.g., coarse coal ash) instead of sand, operating at slightly reduced temperatures and using additives. Though several studies have been carried out to study the agglomeration characteristics of low-rank coal in air-CFB combustion (Manzoori and Agarwal, 1994; Skrifvars et al., 1994; Vuthaluru et al., 1999; Bhattacharya and Harttig, 2003; Leng et al., 2010), this issue remains unexplored in the context of oxy-fuel combustion. Therefore, it is essential to conduct both experiments and modelling to assess the behaviour of the agglomeration using certain types of low-rank coals during Oxy-FB combustion.

2.3.3. Sulphation

Apart from agglomeration, sulphation has also been considered one of the major operational problems during fluidization that affect the performance of the coal combusting boilers. It produces solid deposits inside the boiler walls, which in turn decreases the fluid flow and the heat transfer.

In fluidized bed combustion (FBC) of high-sulphur fuels, limestone is used to reduce SO_2 emission from the combustion process. Upon injection into the furnace, limestone undergoes calcination, when the calcium carbonate in the limestone is heated to form CaO in fly ash, seen in reaction (R2.1), and then sulphation to achieve 80-90% sulphur retention, when the CaO reacts with SO_2 and oxygen to form solid calcium sulphate, seen in reaction (R2.2). Together, these reactions are termed indirect sulphation (Chen et al., 2009; Stewart et al., 2012).

$$CaCO_{3 (s)} \leftrightarrow CaO_{(s)} + CO_{2 (g)}$$
(R2.1)

$$CaO_{(s)} + SO_{2(g)} + \frac{1}{2}O_{2(g)} \leftrightarrow CaSO_{4}(s)$$
(R2.2)

For an oxy-fuel FBC systems (when CO_2 partial pressure is higher than the equilibrium pressure), the limestone calcinations is normally inhibited due to the excessive partial pressures of CO_2 and the limestone is subject to a direct sulphation, seen in reaction (R2.3) (Liu et al., 2000; Chen et al., 2009).

$$CaCO_{3}(s) + SO_{2}(g) + \frac{1}{2}O_{2}(g) \leftrightarrow CaSO_{4}(s) + CO_{2}(g)$$
 (R2.3)

It is already well known that the calcination temperature of limestone depends on the partial pressure of CO₂, shown in Figure 2.3. At the lower zone of the curve, limestone first calcines to form CaO and undergoes indirect sulphation. However, at the upper zone of the curve, limestone does not decompose and undergoes direct sulphation. In air-fired fluidized bed combustion, where typical CO₂ concentration in flue gas is 15-20%, limestone starts to calcine at around 800°C and SO₂ is captured via indirect sulphation. On the other hand, in oxygen-fired fluidized bed combustion, where the typical CO₂ concentration in flue gas is 70-90%, the combustion temperature of above 875° C is required for calcination. In this case, desulfurization can occur under both mechanisms in typical fluidized bed temperature range (800° C - 950° C). At lower temperature zone, direct sulphation can take place, while at higher temperature zone, indirect sulphation can take place (Zhao et al., 2010).



Figure 2.3: Equilibrium temperature of CaCO₃ calcination as a function of CO₂ partial pressure (Liljedahl et al., 2006)

Figure 2.4 shows the extent and route of sulphur capture under Oxy-CFB combustion. It can be seen that during Oxy-CFB combustion, the sulphur capture efficiency under direct sulphation is observed to be comparatively lower than that in indirect sulphation. It was suggested that the optimum temperature sulphur retention by limestone oxy-fuel fluidized bed boiler is about 925°C - 950°C (Anthony, 2013).



Figure 2.4: Sulphur capture efficiency as function of bed temperature and CO₂ concentration (Wall et al., 2012)

The reaction kinetics and mechanism of sulphation on Oxy-FB combustion have extensively been studied (Jia et al., 2007; Jia et al., 2010; Scala and Salatino, 2010; de Diego et al., 2011; Duan et al., 2011b; Duan et al., 2011c; García-Labiano et al., 2011; Lupiáñez et al., 2011; Takkinen et al., 2011; Wang et al., 2011b; Wang et al., 2011c; Wu et al., 2011; Jia et al., 2012; Stewart et al., 2012; Tan et al., 2012; de Diego et al., 2013b; de las Obras-Loscertales et al., 2013; Rahiala et al., 2013; Tan et al., 2013; Gómez et al., 2014; Li et al., 2014; Tan et al., 2014). Table 2.6 provides the summary of prior research work carried out on sulphation characteristics under Oxy-FB combustion. Although several researchers studied the sulphation characteristics from oxy-fuel fluidized bed combustor, still there are some uncertainties in the sulphation mechanism during Oxy-FB combustion.

It is evident that the rate of sulphation reactions is dependent on several factors, such as temperature, limestone composition (e.g. Ca percentage), limestone microstructure (pore size, surface area etc.), and concentrations of CO₂, SO₂ and O₂. In Oxy-FB combustion, the flue gas also contains a considerable amount of steam which has an important impact on the sulphation mechanism. However, few research have been conducted considering steam in the gas atmosphere to observe the influence of steam on sulphation under Oxy-FB combustion. Moreover, from Table 2.6 it reveals that most of the studies have been done using only limestone. In contrast, limited studies have been carried out using both limestone and ash to produce more realistic boiler conditions.

Authors	Apparatus	Fuel	Sorbent	Gas atmosphere	Major findings
Jia et al. (2007)	CFB	Bituminous and	Limestone	Air,	Sulphur capture efficiency was lower in oxy-fuel
		sub- bituminous		O ₂ /RFG	than that in air combustion.
Jia et al. (2010)	CFB	Bituminous and	Limestone	Air,	Sulphur capture was lower in oxy-fuel than that in
		pet coke		O ₂ /RFG	air combustion.
Scala and Salatino (2010)	BFB	-	Limestone	O ₂ /CO ₂ /SO ₂ /N ₂	Particle sulphation increased with attrition by continuously disclosing unconverted calcium to the sulphur-bearing atmosphere.
de Diego et al. (2011)	FB	-	Limestone	O ₂ /CO ₂ /SO ₂ /N ₂	The rate of direct sulphation increased with
	TGA				temperature, whereas the rate of indirect sulphation decreased.
Duan et al. (2011b)	CFB	Bituminous and	Limestone	Air,	Desulfurization efficiency improved with Ca/S
		anthracite		O ₂ /CO ₂	molar ratio and O_2 concentration in primary gas.
Duan et al. (2011c)	CFB	Bituminous	Limestone	Air,	Desulfurization efficiency of limestone was higher
				O ₂ /CO ₂	in oxy-fuel than that in air combustion.

Table 2.6: Review on sulphation characteristics under oxy-fuel fluidized bed combustion

Authors	Apparatus	Fuel	Sorbent	Gas atmosphere	Major findings
García-Labiano et al. (2011)	TGA	-	Limestone	O ₂ /CO ₂ /SO ₂ /N ₂	Sulphation conversion was much higher under
					indirect sulphation than under direct sulphation;
					Sulphation conversion decreased with sorbent
					particle size.
Lupiáñez et al. (2011)	BFB	-	Limestone	Air,	Primary fragmentation of limestone was
				Air/SO ₂ ,	significantly lower in oxy-fuel than that in air
				CO ₂ ,	combustion.
				CO ₂ /Air,	
				CO ₂ /Air/SO ₂	
Takkinen et al. (2011)	BFB	-	Limestone	N ₂ ,	Maximum sulphur capture efficiency was
				O ₂ /CO ₂ ,	achieved at high temperature and in high CO_2
				O ₂ /SO ₂ /N ₂ ,	concentration via indirect sulphation.
				O ₂ /CO ₂ /SO ₂	
Wang et al. (2011b)	TGA	-	Limestone	O ₂ /CO ₂ /SO ₂ /N ₂ ,	Sulphation reaction of CaO depended on
				O ₂ /CO ₂ /SO ₂ /N ₂ /H ₂ O	temperature, concentrations of CO_2 , SO_2 and H_2O ;
					Water vapour strongly enhanced the sulphation of
					CaO.

Table 2.6: Review on sulphation characteristics under oxy-fuel fluidized bed combustion (Continued)

Authors	Apparatus	Fuel	Sorbent	Gas atmosphere	Major findings
Wang et al. (2011c)	TGA	-	Limestone	O ₂ /CO ₂ /SO ₂ /N ₂ ,	In presence of water vapour, sulphation reaction
				O ₂ /CO ₂ /SO ₂ /N ₂ /H ₂ O	rate was higher at 850°C than that at 800°C;
					Smaller limestone particles showed better calcium
					conversion.
Wu et al. (2011)	CFB	Bituminous and	Limestone	O ₂ /RFG	Under oxy-fuel combustion, desulfurization took
		petroleum coke			place via direct sulphation mode.
Jia et al. (2012)	CFB	Anthracite and	Limestone	Air,	Limestone utilization was lower in oxy-fuel than
		pine bend coke		O ₂ /RFG	that in air combustion.
Stewart et al. (2012)	TGA,	Bituminous and	Limestone	Air,	Addition of steam enhanced direct sulphation
	TF,	pet coke		Air/H ₂ O,	under oxy-fuel combustion;
	CFB			O ₂ /CO ₂ /SO ₂ /N ₂ ,	In presence of steam, direct sulphation was slower
				O ₂ /CO ₂ /SO ₂ /N ₂ /H ₂ O	than the indirect sulphation.
Tan et al. (2012)	CFB	Bituminous and	Limestone	Air,	Sulphur capture rate of limestone increased with
		petroleum coke		O ₂ /RFG	temperature.
de Diego et al. (2013b)	BFB	Anthracite and	Limestone	O ₂ /N ₂ ,	SO ₂ retention was higher in indirect sulphation
		lignite		O ₂ /CO ₂	than under direct sulphation.

Table 2.6: Review on sulphation characteristics under oxy-fuel fluidized bed combustion (Continued)

Authors	Apparatus	Fuel	Sorbent	Gas atmosphere	Major findings
de las Obras-Loscertales et al.	FB	-	Limestone	O ₂ /CO ₂ /SO ₂ /N ₂	The first step of sulphation conversion was
(2013)	TGA				controlled by gas diffusion through the porous
					particle, while the second step was controlled by
					gas diffusion through the $CaSO_4$ product layer.
Rahiala et al. (2013)	BFB	-	Limestone	O ₂ /CO ₂ /SO ₂ /N ₂	Sulphur capture decreased with CO ₂ concentration
					during direct sulphation.
Tan et al. (2013)	CFB	Bituminous,	Limestone	O ₂ /RFG	Higher calcium content in fuel resulted higher
		sub-bituminous			sulphur capture ratio.
		and lignite			
Gómez et al. (2014)	CFB	Anthracite	Limestone	Air,	Sulphur capture efficiency higher in oxy-fuel than
				O ₂ /RFG	that in air combustion;
					Optimum temperature for S capture is 880-890°C.
Li et al. (2014)	CFB	Low rank	Limestone	Air,	Limestone utilization was considerably lower in
		bituminous		O ₂ /CO ₂ ,	oxy-fuel combustion with flue gas recirculation
				O ₂ /RFG	than that in air combustion.
Tan et al. (2014)	CFB	Low rank	-	O ₂ /CO ₂	Lower SO ₂ concentration in the dense zone
		bituminous			inhibited self-desulfurization by the calcium
					content in ash.

Table 2.6: Review on sulphation characteristics under oxy-fuel fluidized bed combustion (Continued)

Since some of the Victorian brown coals have high sulphur content, it is more likely to cause sulphation using these fuels in coal-fired boilers. It is therefore necessary to monitor the sulphation behaviour in the promising technologies, such as oxy-fuel FB combustion, particularly when using high-sulphur Victorian brown coals.

2.3.4. Recarbonation of fly ash

In fluidized bed combustion, the calcination of the limestone occurs to form calcium oxide. In some locations (e.g., cyclone, dipleg, sealpot, external heat exchanger), where the temperature drops below the calcination temperature (800°C in air combustion and 875°C in oxy-fuel combustion), the unreacted calcium oxide is recarbonated to form calcium carbonate, according to the reaction (R2.4), which may cause fouling.

$$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)}$$
(R2.4)

Due to the high CO_2 partial pressure (see Figure 2.4), limestone does not calcine under typical oxy-fuel CFB combustion operating temperature (Wang et al., 2008). However, at 80-85% CO_2 concentration, the limestone calcines, but when the fly ash cools to below the calcination temperature, recarbonation of fly ash takes place. Moreover, the high CO_2 concentration in the flue gas under Oxy-CFB combustion condition facilitates carbonation. It was also suggested that fluidizing the external heat exchanger, sealpot with air or nitrogen rather than recycled flue gas (mostly CO_2) and/or maintaining the sealpot temperature at least as high as the furnace temperature, it was possible to avoid recarbonation (Liljedahl et al., 2006).

Few studies have been conducted to examine the carbonation behaviour in the context of Oxy-FB combustion (Liljedahl et al., 2006; Wang et al., 2008; Wang et al., 2011b; Beisheim et al., 2013; Wang et al., 2014b). Though little studies have been carried out on the recarbonation of fly ash under Oxy-FB combustion (shown in Table 2.7), this phenomena is completely unexplored in low-rank coal context.

Therefore, it is essential to conduct experiments to assess the recarbonation behaviour under Oxy-FB combustion conditions using low-rank coals, particularly having high calcium content.

Authors	Apparatus	Fuel	Sorbent	Gas atmosphere	Major findings
Liljedahl et al. (2006)	CFB	Bituminous and petroleum coke	Limestone	Air, O ₂ /RFG	Recarbonation of calcium in the fly ash was higher in oxy-fuel than that in air combustion.
Wang et al. (2008)	TGA	Anthracite and petroleum coke	Limestone	O ₂ /CO ₂ /N ₂ , O ₂ /CO ₂ /N ₂ /H ₂ O	No carbonation occurred without the presence of water vapour below 400°C, while with the presence of water vapour carbonation was observed even at 250°C.
Wang et al. (2011b)	TGA	-	Limestone	O ₂ /CO ₂ /SO ₂ /N ₂ , O ₂ /CO ₂ /SO ₂ /N ₂ /H ₂ O	Carbonation reaction of CaO depended on temperature, concentrations of CO_2 , SO_2 and H_2O ; Water vapour strongly enhanced the carbonation of CaO.
Beisheim et al. (2013)	BFB	-	Limestone	Air, CO ₂ /H ₂ O/N ₂	Strong recarbonation of calcined particles resulted hard and stable carbonate deposits on cool surfaces.
Wang et al. (2014b)	FB	Anthracite	Limestone	Air, O ₂ /CO ₂	Degree of carbonation increased with molar ratio of Ca/S.

Table 2.7: Review on carbonation characteristics under oxy-fuel fluidized bed combustion

2.3.5. Conventional pollutant emissions

The emission characteristics of conventional pollutants are very important for the operation of oxy-fired fluidized bed combustion using different types of coals. In this section, sulphur oxides and nitrogen oxides emissions are described.

2.3.5.1. SO_X

One of the major advantages of fluidized bed combustion is lower SO₂ emission via addition of sorbents. However, in oxy-fuel combustion it is also important to know the extent of SO₃ formation in flue gas as SO₃ can corrode the air-heater and economizer surfaces (Fleig et al., 2011; Mitsui et al., 2011; Stanger and Wall, 2011). The formation of SO₃ depends on several factors, such as O₂ concentration, sulphur content of coal, temperature, residence time, fly ash composition, presence of catalysts (e.g. Fe₂O₃), and flue gas components (e.g. NO_X and CO) (Fleig et al., 2009; Fleig et al., 2011; Spörl et al., 2013b). Normally at high temperature, most of the organic-S is converted to SO₂. During flue gas cooling a portion of this SO₂ is converted to SO₃, primarily via the oxidation of SO₂ according to reactions (R2.6) and (R2.7) for the temperatures of below 1150 K.(Fleig et al., 2011; Spörl et al., 2013b)

$$SO_2 + O(+M) \rightarrow SO_3(+M)$$
 (R2.5)

$$SO_2 + OH (+M) \rightarrow HOSO_2 (+M)$$
 (R2.6)

$$HOSO_2 + O_2 \rightarrow SO_3 + HO_2 \tag{R2.7}$$

In presence of steam in flue gas, this SO_3 may be subsequently converted to gaseous sulphuric acid (H₂SO₄), according to reaction (R2.8) which can cause corrosion if it is allowed to condense at temperatures between 400°C and 200°C.(Spörl et al., 2013b)

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{R2.8}$$

It is known that the measurement of SO_3 concentration in flue gas is difficult due to the highly reactive nature of SO_3 . Several techniques have been used for the measurement of SO_3 , such as controlled condensation method, isopropanol drop method, isopropanol absorption bottle method, salt method, Pentol SO_3 monitor (using Severn Science Analyser), Fourier transform infrared (FTIR) spectroscopy, and mass spectrometer.(Fleig

et al., 2012b) Another method was developed by Ibanez et al.,(2008) who used calcium oxalate as a reagent which reacts only with SO_3 (not with SO_2) under certain condition to produced a more stable and conveniently measured molecule. The main reaction routes of sulphur during coal combustion were provided by Belo et al. (2014), as shown in Figure 2.5.



Figure 2.5: Reaction routes of sulphur in a coal combustion system (Belo et al., 2014)

In oxy-fuel combustion atmosphere due to the low concentration of air-borne nitrogen and production of water vapour, higher levels of SO₂ (and consequently SO₃) was produced compared to that in air combustion (Ahn et al., 2011; Fleig et al., 2011; Fleig et al., 2012a). Therefore, in oxy-fuel combustion it is very important to know the level of SO₂ as well as SO₃ formation. Though, several researchers investigated the emission of SO₂ under Oxy-FB combustion (Czakiert et al., 2006; Jia et al., 2007; Czakiert et al., 2010; Jia et al., 2010; Xin et al., 2010; Duan et al., 2011b; Duan et al., 2011c; Romeo et al., 2011; Czakiert et al., 2012; Jia et al., 2012; Stewart et al., 2012; Tan et al., 2012; de Diego et al., 2013a; de Diego et al., 2013b; Lupiáñez et al., 2013b; Tan et al., 2013; Duan et al., 2014; Li et al., 2014; Lupiáñez et al., 2014; Tan et al., 2014), only few researchers studied the fate and mechanism of SO₃ formations under Oxy-FB combustion (Czakiert et al., 2012; Tan et al., 2013).

The summary of prior literature regarding SO_X emission under Oxy-FB combustion is provided in Table 2.8. From these prior research work, it is evident that study on the extents of both SO_2 and SO_3 formation using brown coal or lignite in oxy-fuel fluidized bed combustion is still non-existent.

Authors	Reactor	Fuel	Fluidizing gas	Major findings
Czakiert et al. (2006)	CFB	Brown coal	O ₂ /N ₂ ,	Sulphur conversion to SO_2 increased with oxygen concentration in
			O ₂ /CO ₂	feed gas and bed temperature.
Jia et al. (2007)	CFB	Bituminous and sub-	Air,	Sulphur capture efficiency was lower in oxy-fuel than that in air
		bituminous	O ₂ /RFG	combustion.
Czakiert et al. (2010)	CFB	Bituminous	Oxygen-enriched	Sulphur conversion increased under oxygen-enriched conditions; but
			air	decreased with excess oxygen probably due to the oxidation of
				sulphur to SO ₃ .
Jia et al. (2010)	CFB	Bituminous and pet coke	Air,	SO ₂ emission was higher in oxy-fuel than that in air combustion.
			O ₂ /RFG	
Xin et al. (2010)	CFB	Anthracite	Oxygen-enriched	SO ₂ concentration increased with oxygen concentration in fluidizing
			air	gas.
Duan et al. (2011b)	CFB	Bituminous and	Air,	SO ₂ emission increased with O ₂ enrichment in the atmosphere;
		anthracite	O_2/CO_2	Desulfurization efficiency improved with O_2 concentration in primary
				gas.
Duan et al. (2011c)	CFB	Bituminous	Air,	SO ₂ emission was slightly lower in oxy-fuel than that in air
			O ₂ /CO ₂	combustion.

Table 2.8: Review of SO_X emission under oxy-fuel fluidized bed combustion

Authors	Reactor	Fuel	Fluidizing gas	Major findings
Romeo et al. (2011)	BFB	Anthracite	Air,	SO ₂ concentration was similar and almost negligible under both air
			O ₂ /CO ₂	and oxy-fuel combustion.
Czakiert et al. (2012)	CFB	Bituminous	O ₂ /CO ₂	SO ₂ was main S-compound in flue gas;
				SO ₃ was also observed only at lower partial pressures of oxygen.
Jia et al. (2012)	CFB	Anthracite and pine bend	Air,	Sulphur capture was poor in oxy-fuel than that in air combustion.
		coke	O ₂ /RFG	
Stewart et al. (2012)	CFB	Bituminous and pet coke	Air,	SO ₂ emission decreased with H ₂ O.
			Air/H ₂ O,	
			O ₂ /RFG,	
			O ₂ /RFG/H ₂ O	
Tan et al. (2012)	CFB	Bituminous and	Air,	SO ₂ concentration was up to five times higher in oxy-fuel than that in
		petroleum coke	O ₂ /RFG	air combustion.
de Diego et al. (2013a)	BFB	Anthracite	Air,	SO ₂ emission was unaffected by the NO recirculation.
			O ₂ /CO ₂ ,	
			O ₂ /CO ₂ /SO ₂ ,	
			O ₂ /CO ₂ /NO,	
			O ₂ /CO ₂ /H ₂ O	

Table 2.8: Review of SO_X emission under oxy-fuel fluidized bed combustion (Continued)

Authors	Reactor	Fuel	Fluidizing gas	Major findings
de Diego et al. (2013b)	BFB	Anthracite and lignite	O ₂ /N ₂ ,	SO ₂ retention was lower in oxy-fuel than that in air combustion.
			O ₂ /CO ₂	
Lupiáñez et al. (2013b)	BFB	Bituminous and lignite	Air,	Sulphur capture efficiency was improved with bed temperature.
			O_2/CO_2	
Tan et al. (2013)	CFB	Bituminous, sub-	O ₂ /RFG	SO_2 emission was lower in lignite than that in bituminous coal, due to
		bituminous and lignite		the higher Ca content in lignite resulting higher sulphur capture ratio;
				Addition of wood pellets to the coal lowered SO ₂ emission.
Duan et al. (2014)	CFB	Bituminous and	Air,	SO_2 concentration in flue gas was higher, while its emission was
		petroleum coke	O ₂ /RFG	lower in oxy-fuel than that in air combustion.
Li et al. (2014)	CFB	Low rank bituminous	Air,	Sulphur capture efficiency was significantly lower in oxy-fuel
			$O_2/CO_2,$	combustion with flue gas recirculation than that in air combustion.
			O ₂ /RFG	
Lupiáñez et al. (2014)	BFB	Anthracite and lignite	O ₂ /N ₂ ,	Gas-staging increased SO ₂ emission.
			O ₂ /CO ₂	
Tan et al. (2014)	CFB	Low rank bituminous	O ₂ /CO ₂	SO ₂ emission decreased with oxygen concentration in primary flow
				and excess oxygen ratio.

Table 2.8: Review of SO_x emission under oxy-fuel fluidized bed combustion (Continued)

2.3.5.2. NO_X and N₂O

Some of the major advantages of Oxy-FB combustion over Oxy-PF combustion are the lower furnace temperature and lower in-leakage of air, which in turn lower NO_X emission. However, the emission level of N_2O , one of the major greenhouse gases, is also an important consideration due to its ability to destroy the ozone layer in the stratosphere (Winter, 2010). In coal combustion, nitrogen is first released during devolatilization in the form of either HCN or NH₃, which are then further oxidized to NO_X and N₂O during char combustion. The main reaction paths during devolatilization and char combustion of the coal-nitrogen to NO and N₂O were provided by Winter (2010), as shown in Figure 2.6. The main reactions involved in the NO_X chemistry in a fluidized bed reactor were summarized by Lupianez et al. (2013a).



Figure 2.6: The main reaction paths of fuel-N to NO, N₂O and N₂ (Winter, 2010)

A number of experimental studies have been carried out to investigate the NO_X emission characteristics in Oxy-FB combustion (Hosoda et al., 1998; Czakiert et al., 2006; Jia et al., 2007; Czakiert et al., 2010; Jia et al., 2010; Sanchez et al., 2010; Xin et al., 2010; Duan et al., 2011a; Duan et al., 2011b; Romeo et al., 2011; Jia et al., 2012; Stewart et al., 2012; Tan et al., 2012; de Diego et al., 2013a; Lupiáñez et al., 2013a; Lupiáñez et al., 2013b; Tan et al., 2013; Duan et al., 2014; Li et al., 2014; Lupiáñez et al., 2014; Tan et al., 2014). On the other hand, only a few experimental data are available on the N₂O emission during Oxy-FB combustion (Hosoda et al., 1998; Sanchez et al., 2010; de Diego et al., 2013a). Moreover, the limited number of prior studies considered mainly bituminous and anthracite coals. Table 2.9 provides the summary of prior research work on NO_X emission as well as N₂O emission under Oxy-FB combustion.

Authors	Reactor	Fuel	Fluidizing gas	Major findings
Hosoda et al. (1998)	BFB	Bituminous	Air,	NO_{X} concentration decreased with $H_{2}O$ concentration, whereas $N_{2}O$
			$Ar/N_2/O_2$,	concentration increased.
			$CO_2/N_2/O_2,$	
			CO ₂ /H ₂ O/O ₂	
Czakiert et al. (2006)	CFB	Brown coal	O ₂ /N ₂ ,	Significant reduction of fuel-nitrogen conversion to NO_X in oxy-fuel
			O ₂ /CO ₂	compared to air combustion.
Jia et al. (2007)	CFB	Bituminous and sub-	Air,	NO _X concentration was slightly higher in oxy-fuel than that in air
		bituminous	O ₂ /RFG	combustion.
Czakiert et al. (2010)	CFB	Bituminous	Oxygen-enriched	Conversion ratios of fuel-N to NO _X increased under oxygen-enriched
			air	conditions.
Jia et al. (2010)	CFB	Bituminous and pet coke	Air,	NO _x emission was lower in oxy-fuel than that in air combustion, even
			O ₂ /RFG	at higher temperature (950°C).
Sanchez et al. (2010)	FB		O ₂ /Ar,	CO_2 enhanced the formation of NO ₂ , probably due to the oxidation of
			O ₂ /CO ₂	N ₂ O or NO.
Xin et al. (2010)	CFB	Anthracite	Oxygen-enriched	NO _x concentration increased with oxygen concentration in fluidizing
			air	gas and bed temperature.

Table 2.9: Review of NO_X and N_2O emissions under oxy-fuel fluidized bed combustion

Authors	Reactor	Fuel	Fluidizing gas	Major findings
Duan et al. (2011a)	CFB	Bituminous and	Air,	NO emission was lower in oxy-fuel than that in air combustion;
		anthracite	O_2/CO_2	NO emission increased with O_2 concentration, bed temperature and
				oxygen/fuel stoichiometric ratio.
Duan et al. (2011b)	CFB	Bituminous and	Air,	NO emission increased with O ₂ enrichment in the atmosphere;
		anthracite	O ₂ /CO ₂	Oxygen staging helped to reduce NO emission in Oxy-CFB
				combustion.
Romeo et al. (2011)	BFB	Anthracite	Air,	NO _X concentration was higher in oxy-fuel than that in air combustion,
			O_2/CO_2	due to the larger oxygen concentration in the surrounding of particle.
Jia et al. (2012)	CFB	Anthracite and pine bend	Air,	Conversion of fuel-N to NO was extremely low.
		coke	O ₂ /RFG	
Stewart et al. (2012)	CFB	Bituminous and pet coke	Air,	NO _X emission decreased with H ₂ O.
			Air/H ₂ O,	
			O ₂ /RFG,	
			O ₂ /RFG/H ₂ O	
Tan et al. (2012)	CFB	Bituminous and	Air,	NO _x emission rates were very low, but were affected by bed
		petroleum coke	O ₂ /RFG	temperature.
		1	2 -	

Authors	Reactor	Fuel	Fluidizing gas	Major findings
de Diego et al. (2013a)	BFB	Anthracite	Air,	NO emission decreased with H ₂ O, whereas N ₂ O emission increased;
			O ₂ /CO ₂ ,	N_2O emission was unaffected by the SO_2 recirculation.
			O ₂ /CO ₂ /SO ₂ ,	
			O ₂ /CO ₂ /NO,	
			O ₂ /CO ₂ /H ₂ O	
Lupiáñez et al. (2013a)	BFB	Anthracite	Air,	NO emission increased with bed temperature and excess O_2 .
			O_2/CO_2	
Lupiáñez et al. (2013b)	BFB	Bituminous and lignite	Air,	$\ensuremath{\text{NO}_{X}}$ emission was mainly influenced by excess oxygen and type of
			O_2/CO_2	coal rather than the bed temperature.
Tan et al. (2013)	CFB	Bituminous, sub-	O ₂ /RFG	Addition of wood pellets to the coal lowered NO emission.
		bituminous and lignite		
Duan et al. (2014)	CFB	Bituminous and	Air,	NO concentration in flue gas was higher, while its emission was
		petroleum coke	O ₂ /RFG	lower in oxy-fuel than that in air combustion.
Li et al. (2014)	CFB	Low rank bituminous	Air,	Conversion of fuel-N to NO was much lower in oxy-fuel combustion
			O ₂ /CO ₂ ,	with flue gas recirculation than that in air combustion.
			O ₂ /RFG	
Lupiáñez et al. (2014)	BFB	Anthracite and lignite	O ₂ /N ₂ ,	Gas-staging was effective to reduce NO _x emission;
			O ₂ /CO ₂	The extent was larger for lignite compared to anthracite coal.
Tan et al. (2014)	CFB	Low rank bituminous	O ₂ /CO ₂	NO emission decreased with oxygen concentration in primary flow,
				but increased with excess oxygen ratio.

Table 2.9: Review of NO_X and N₂O emissions under oxy-fuel fluidized bed combustion (Continued)

From the above literature, it is clear that the data on both N_2O and NO_X emissions from brown coals during oxy-fuel fluidized bed combustion still does not exist.

The coal containing high sulphur and nitrogen content increases the emission concentrations of SO_X and NO_X respectively under the same combustion atmosphere. Since the SO_X and NO_X emissions depend on the coal characteristics, there is a necessity to conduct targeted experiments to know the emission characteristics using certain types of low-rank coals (e.g. high S and high N) during Oxy-FB combustion.

2.3.6. Trace elements emissions

The issue of trace element emission during coal combustion has also important implication on the operation of Oxy-FB combustors using different types of coals. The fate of trace elements, which are present in coal at very low concentrations of below 100 ppm, (Yan et al., 2000; Yan et al., 2001; Vejahati et al., 2010) are an important consideration as the inclusion of excessive amounts of these elements in the gas beyond the permissible limits is harmful to the health and environment, with additional implications for CO_2 transport and storage (Spörl et al., 2013a). The combustion of coals containing only several parts per million of trace elements could result in the release of several tons of pollutants into the environment per year (Vejahati et al., 2010).

In coal combustion, many trace elements first vaporize and then condense either homogeneously to form submicron ash particles or heterogeneously to adsorb on the surface of fly ash particles (Yan et al., 2000; Vejahati et al., 2010). Significant amounts of several trace elements, however, leave the stack mostly in gaseous forms, resulting in direct emission (Yan et al., 2000). The emission and speciation of trace elements depend on several factors including mineral contents, their distribution in the coal utilized, and the combustor temperature (Vejahati et al., 2010). Moreover different forms and oxidation states of trace elements also determine the ultimate health effects and environmental impacts. For example, As^{3+} form of arsenic is 50 times more toxic than As^{5+} , while Se⁴⁺ is more toxic than Se⁶⁺ and Cr⁶⁺ is more toxic than Cr³⁺. Regarding mercury emission, elemental mercury (Hg⁰) is more toxic than other forms of mercury (Hg^P and Hg²⁺) (Shah et al., 2008; Shah et al., 2012).

At high temperature combustion zone, most of the coal-Hg is converted to Hg^0 . As the combustion flue gas cools at the downstream of the furnace, this Hg^0 can be oxidized by

the flue gas components, (such as HCl, SO_X and NO_X) to form gaseous oxidized mercury (Hg²⁺), according to the reactions (R2.9)-(R2.13) (Spörl et al., 2013a).

$Hg + Cl \leftrightarrow HgCl$	(R2.9)
$Hg + Cl_2 \leftrightarrow HgCl_2$	(R2.10)
$HgCl + Cl \leftrightarrow HgCl_2$	(R2.11)
$HgCl + HCl \leftrightarrow HgCl_2 + H$	(R2.12)
$HgCl + Cl_2 \leftrightarrow HgCl_2 + Cl$	(R2.13)

This Hg^{2+} can react with the particulate in the flue gas to form particulate bound mercury (Hg^{P}) , which is adsorbed onto fly ash (Lee et al., 2006; Wu et al., 2013). Among these forms of mercury, most toxic elemental mercury (Hg^{0}) can stay longer in the environment and disperse long distances from the source of emission. In contrast, gaseous oxidized mercury (Hg^{2+}) is easier to capture due to its high solubility in water. However, it should also be noted that the different modes of occurrence of mercury have specific peculiarities. Elemental mercury is lipid soluble and highly diffusible through the biological membranes, including the blood-brain barrier. In contrast, inorganic mercury is water soluble and less diffusible through the biological membranes (WHO, 2003), but this form of mercury induces protein synthesis rate in metallothionein kidney, being the main binding protein of mercury (Yasutake and Nakamura, 2011).



Figure 2.7: Trace element characterization based on their volatility behaviour (trace elements in bold represent the hazardous air pollutants) (Bunt and Waanders, 2008)

The knowledge of trace element reactions and behaviour during Oxy-FB combustion is important for the control of pollutants and emissions. In order to understand the partitioning behaviour of trace elements during utilization, trace elements are typically divided into three classifications (see Figure 2.7) depending on their volatility and the volatility of their compounds, such as oxides, sulphides and chlorides. The class I elements are classified as the least volatile elements, which remain in the ash. The class II elements are more volatile elements. These elements can be separated between the ash and the gas phases, when condensation of the vaporized species occurs on the surface of the ash particles as the gas cools. The class III elements are highly volatile elements, which show little or no tendency to condense from the vapour phase. Various elements, however, show intermediate behaviour (more than one group), as shown in the Figure 2.12. Furthermore, the trace elements in bold represent the hazardous air pollutants (HAPs) by the 1990 Clean Air Act Amendments (Bunt and Waanders, 2008).

Therefore, it is essential to know the extent of the different forms of trace elements generated during combustion using different types of coals. Many experimental studies have been carried out to study the speciation of trace elements, collected from the bottom ash and fly ash of coal-fired power plants, using different analytical instruments such as inductively coupled plasma - mass spectrometry (ICP-MS), secondary ion mass spectrometry (SIMS), X-ray absorption near edge structure spectrometry (XANES), X-ray fluorescence (XRF), inductively coupled plasma - atomic emissions spectrometry (ICP-AES), inductively coupled plasma - optical emissions spectrometry (ICP-OES), flame atomic absorption spectrometry (FAAS) and atomic absorption spectrometry (AAS) (Shah et al., 2008; Gogebakan and Selçuk, 2009; Skodras et al., 2009; Koukouzas et al., 2011; Shah et al., 2012).

Though few studies have been carried out to study the distribution of trace elements in air-fired fluidized bed combustion (Skodras et al., 2009; Duan et al., 2010; Wang et al., 2010b; Koukouzas et al., 2011), very limited experimental data are available on oxy-fired fluidized bed combustion (Font et al., 2012). Using anthracite coal, Font et al. (2012) studied the fate of trace elements in a 90 kW_{th} bubbling fluidized bed oxy-combustion pilot plant. They concluded that most (82%) of the Hg was present as Hg⁰ in comparison to Hg²⁺, due to the high volatility of Hg⁰. However, using a selective catalytic reactor with TRACTM catalyst, almost all the Hg⁰ was found to be converted into Hg²⁺(Mitsui et al., 2011). In order to avoid corrosion in CO₂ compression units due to the Hg in flue gas,

Hg needs to be removed at the upstream section of CO_2 compressor. It was also reported that due to the re-circulation of flue gas containing Hg, higher concentration of Hg was observed at the outlet of the burner during oxy-fuel combustion compared to that in air combustion (Mitsui et al., 2011; Contreras et al., 2013; Wu et al., 2013). However, prior studies considered mainly bituminous coal and sub-bituminous coal.

During experiment in Oxy-FB combustion using low-rank coal, this behaviour could remain same or different. Therefore, it is essential to have targeted research to know the extent of trace elements (with special emphasis on mercury) emission during Oxy-FB combustion using brown coals/lignites.

2.4. MODELLING OF OXY-FB COMBUSTION

Detail modelling of oxy-fuel fluidized bed technology developed by different methods reported in the literature is discussed in this section.

2.4.1. Kinetic modelling on char combustion

During coal combustion, energy release from coal takes place in several steps. When a coal particle enters into the reactor, initially it causes evaporation of inherent moisture. As this coal particle is heated further, devolatilization occurs with the release of volatile matter from the particle. Then the remaining char particle undergoes combustion at high temperature (Edge et al., 2011). By studying the kinetics of char combustion and by developing models, it is possible to predict the heat transfer or release, char burnout rate (thus the particle temperature) and pollutant formation for the better understanding of the chemical processes.

Char combustion is dependent on several factors, such as coal composition, coal structure (e.g. surface structure, pore size and distribution), operating condition (e.g. temperature, pressure), and gas atmosphere. From Figure 2.8, it can be seen that at low temperature in Regime I, the reaction rates are similar in both air and oxy-fuel combustion. At high temperature, while the reaction rate is higher in oxy-fuel combustion in Regime II, this rate becomes lower in Regime III in the diffusion-controlled zone as the O_2 diffusion is lower in CO_2 than that in N_2 .



Figure 2.8: Combustion regimes for coal combustion in air and oxy-fuel combustion atmospheres (Wall et al., 2009)

In an O_2/CO_2 atmosphere during oxy-fuel combustion of a carbon-containing material, the following reactions are involved during char combustion (Tomita and Ohtsuka, 2004; Scala and Chirone, 2010a).

$$C + O_2 \rightarrow CO_2, \Delta H_{298 K} = -394 \text{ kJ/mol}$$
 (R2.14)

C +
$$\frac{1}{2}$$
O₂ → CO, Δ H_{298 K} = -111 kJ/mol (R2.15)

$$C + CO_2 \rightarrow 2CO, \Delta H_{298 K} = +171 \text{ kJ/mol}$$
 (R2.16)

$$\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2, \ \Delta H_{298 \text{ K}} = -283 \text{ kJ/mol}$$
 (R2.17)

where, reactions (2-14) and (2-15) represent the exothermic carbon combustion reactions, reaction (2-16) represents the endothermic carbon gasification by carbon dioxide, and reaction (2-17) represents the homogeneous carbon monoxide oxidation reaction. It was reported that during oxy-firing fluidized bed combustion condition, the contributions of CO_2 gasification and homogeneous CO oxidation were not negligible at high temperature and low oxygen concentration (Scala and Chirone, 2010a; Scala and Chirone, 2010b; Jia and Tan, 2014).

However, if the combustion environment consists of H_2O along with O_2 and CO_2 , the following reactions are also involved (Tomita and Ohtsuka, 2004).
$C + H_2O \rightarrow CO + H_2$, $\Delta H_{298 \text{ K}} = +130 \text{ kJ/mol}$	(R2.18)
$CO + H_2O \rightarrow CO_2 + H_2, \Delta H_{298 \text{ K}} = -40 \text{ kJ/mol}$	(R2.19)

where, reaction (2-18) represents the endothermic carbon gasification reaction by steam and reaction (2-19) is the exothermic water-gas shift reaction. Since steam is one of the main components in combustor in oxy-fuel combustion, the effect of steam is very important to be considered on char combustion.

While a number of modelling studies are available to predict the combustion characteristics of single char particles in fluidized bed combustor (Sundback et al., 1985; Basu and Halder, 1989; Huang and Scaroni, 1992; Scala, 2009; Scala and Chirone, 2010a; Scala and Chirone, 2010b; Sadhukhan et al., 2011; Scala, 2011), few studies have been done in the context of Oxy-FB combustion (Scala and Chirone, 2010a; Scala and Chirone, 2010b). In addition, some kinetic studies have also been carried out to predict the emission characteristics during Oxy-FB combustion (Krzywanski et al., 2011; Saastamoinen and Tourunen, 2011; Seddighi K et al., 2013a).

However, the effect of steam on char combustion is still not clear. Moreover, prior studies considered mainly bituminous coal. Models using brown coal or lignite in oxy-fuel fluidized bed combustion are very limited.

2.4.2. Computational fluid dynamics modelling

Computational fluid dynamics (CFD) modelling is helpful for the better understanding of the combustion processes and significant for combustor scale-up. CFD is often used as a design tool for coal combustion. It can also be used to improve combustion efficiency, and determine potential reductions in corrosion, slagging, fouling and trace element emission.

Comprehensive reviews of oxygen-fired pulverized coal combustion on CFD modelling were provided by Edge et al. (2011) and Chen et al. (2012c). These reviews mainly focus on the progress and understanding of the specific areas related to CFD modelling, including char combustion, radiation, pollutant formation and removal, and the impact of turbulence. There are also some CFD models of oxygen-fired fluidized bed combustion processes (Myohanen et al., 2009; Pikkarainen et al., 2009; Krzywanski et al., 2010b;

Krzywanski et al., 2010a; Guedea et al., 2011; Krzywanski et al., 2011; Romeo et al., 2011; Takkinen et al., 2011; Wang et al., 2011a; Zhou et al., 2011a; Bolea et al., 2012; Guedea et al., 2013; Rahiala et al., 2013; Seddighi K et al., 2013b; Zhou et al., 2013).

A one-dimensional dynamic model of CFB pilot combustor was developed in order to simulate the combustion under oxy-fuel environment (Pikkarainen et al., 2009). Based on the previous CFD model in air-CFB combustion (Zhou et al., 2011b), a two-dimensional process model was developed to simulate oxygen-enriched combustion in a circulating fluidized bed (Zhou et al., 2011a). The local effects of oxy-fuel combustion on the furnace process were investigated with a three-dimensional CFB furnace model (Myohanen et al., 2009). This model incorporated essential sub-models to describe the complex furnace process, such as the fluid dynamics of solid materials and gases, combustion (drying, devolatilization and char combustion), gaseous reactions, communication of solids, heat transfer, and emission models. The main reaction paths of the three-dimensional model are shown in Figure 2.9. Moreover, a mathematical three-dimensional combustion model in oxygen-enriched CFB environment was developed using a Polish brown coal (Krzywanski et al., 2010b; Krzywanski et al., 2010a; Krzywanski et al., 2011).



Figure 2.9: Main reaction paths of the 3-D model (Myohanen et al., 2009)

In recent years, although CFD approaches have been used to understand the flowfield and combustion processes in oxygen-fired fluidized bed combustion, there are some

uncertainties that need to be resolved to acquire a higher predictive accuracy of combustion characteristics (Chen et al., 2012c).

2.4.3. Thermodynamic modelling

Thermodynamic equilibrium modelling is an easier and useful tool to predict the possible phases formed and the concentrations of the compounds present in the equilibrium state. As experiments are costly to run, a pre-experiment prediction of the possible formation of these compounds may reduce the number of experiments required.

Thus several thermodynamic equilibrium studies have been carried out in air-blown fluidized bed (Skrifvars et al., 1998; Zevenhoven-Onderwater et al., 2000; Zevenhoven-Onderwater et al., 2001a; Zevenhoven-Onderwater et al., 2001b; Bhattacharya and Harttig, 2003; Li et al., 2004; Lin et al., 2005; Kuo et al., 2009; Kuo et al., 2010). In contrast, only few studies have been conducted using thermodynamic equilibrium modelling in the context of oxy-fuel combustion (Zheng and Furimsky, 2003; Yong-chun et al., 2006; Jiao et al., 2011; Zhang et al., 2011a; Zhang et al., 2011b; Contreras et al., 2013; Low and Zhang, 2013).

While a number of thermodynamic equilibrium studies have been carried out on coal combustion, to date no studies have been carried out in the context of Oxy-FB combustion. Therefore, it would be beneficial to have some thermodynamic equilibrium modelling using certain types of coals, including low-rank coals under Oxy-FB combustion conditions.

2.4.4. Process modelling

Since the oxy-fuel fluidized bed combustion technology is still in developing stage, process simulation can help to find out the best process flowsheet and optimum design conditions (Kabir et al., 2013). A number of process simulation packages, such as Aspen Plus, Aspen HYSYS, EBSILON and ThermoFlex, have been used for power plant and CO_2 capture simulation. Using EBSILON simulation package, Günther et al. (2013) and Weng et al. (2013) simulated an integrated overall process of the coal-fired oxy-fuel power plant with circulating fluidized bed combustion.

Among the commercial software packages for process simulation, however, Aspen Plus has successfully been used in steady-state as well as dynamic simulation. Aspen Plus has widely been applied in coal combustion (Sotudeh-Gharebaagh et al., 1998; Hughes et al., 2005; Hong et al., 2009; lloeje et al., 2010; Seltzer et al., 2010; Zhihui et al., 2010; Liu et al., 2011; Yang et al., 2011; Hu and Yan, 2012; Kim et al., 2012; Liu et al., 2012; Pei et al., 2013), coal gasification (Elseviers et al., 1996; Kuchonthara et al., 2005), biomass gasification (Mathieu and Dubuisson, 2002; Tijmensen et al., 2002; De Jong et al., 2003; Prins et al., 2006; Nikoo and Mahinpey, 2008; Doherty et al., 2009) and some other purposes like dimethyl ether production (Kabir et al., 2013). These applications have made Aspen Plus as a reliable and adaptable process simulation technology. Sotudeh-Gharebaagh et al. (1998), Zhihui et al. (2010), Liu et al. (2011), Yang et al. (2011) and Liu et al. (2012) used Aspen Plus to simulate the coal combustion in air-fired circulating fluidized bed reactors. There have also been some attempts to develop the process simulation of coal combustion for oxy-fuel technology (Hong et al., 2009; lloeje et al., 2010; Seltzer et al., 2010; Xiong et al., 2011; Hu and Yan, 2012; Kim et al., 2012; Pei et al., 2013). Process simulation using Aspen Plus in Oxy-FB combustion, however, is almost non-existent. Therefore, it is useful to develop a steady-state process model of oxy-fuel FB combustion used for different grades of coal in Aspen Plus.

2.5. SUMMARY

Oxy-fuel based fluidized bed combustion has become a promising technology for capturing CO₂ emission from all types of coals. It combines the advantages of both oxy-fuel combustion and fluidized bed combustion technologies. The major advantages include fuel flexibility, low emission levels, uniform temperature distribution, and reduced unit size and operating cost. The review of literature reveals that although a number of studies have addressed the Oxy-FB combustion for coals, prior studies considered mainly bituminous and anthracite coals. Studies using brown coal in Oxy-FB combustion are very limited.

Victorian brown coal is an attractive resource with an estimated reserve of 430 billion tonnes. Thus there is a strong incentive for the development of efficient technologies (such as Oxy-FB combustion) for power generation using this coal. The application of Oxy-FB combustion using Victorian brown coal, however, is still unexplored.

Therefore, to address this literature gap it is essential to have targeted research to identify and assess the major issues - combustion performance, conventional pollutants and trace elements emissions, and sulphation, carbonation and agglomeration problems if any during combustion of Victorian brown coal under Oxy-FB environment.

CHAPTER 3: METHODOLOGY

CHAPTER 3: METHODOLOGY

This is the first ever study using Victorian brown coal in oxy-fuel fluidized bed combustion. In this chapter, the different materials used in the experiments, the experimental facilities, different analytical techniques and the processes of the established modelling are discussed.

3.1. MATERIALS

In this research, experiments were carried out with three air-dried Victorian brown coals -Loy Yang, Morwell and Yallourn. All coal samples were crushed and sieved, and the particle size in the desired range was used. The composition of all the coals used in this study is given in Table 3.1.

Some experiments were conducted in fluidized bed quartz reactor with coal particle size of $106 - 152 \mu m$. This pre-dried coal sample was further dried in an oven at 110° C for 10 hours prior to the experiment.

Experiments were also carried out with single char particles prepared from briquetted Victorian brown coal. Initially the single coal particles were shaped into almost spherical of approximately 8 - 10 mm diameter. Then the coal particles were devolatilized in thermo gravimetric analyser (TGA) with N₂ at 600°C for 1.5 hours. The true density of these char particles (5 - 6 mm) were 1682 kg/m³. Finally a hole was drilled to the centre of each char particle and a thin thermocouple was inserted into that hole, and secured carefully. As a bed material, quartz sand of 106 - 150 μ m was also used in that reactor. The particle density of this sand was 2657 kg/m³.

During the experiments in fluidized bed stainless steel reactor, coal particle size in the range of 1- 3 mm was used. Prior to loading in the hopper, the pre-dried coal was additionally dried in an oven at 60°C for about 1.5 hours. As a bed material, silica sand of $350 - 400 \mu m$ was also added into the reactor. In addition, char (77.97% C, 2.42% H, 1.29% N, 0.11% S, 15.77% O and 2.44% ash) of 1 - 3 mm was used during start-up.

	Loy Yang	Morwell	Yallourn	Briquetted Victorian brown coal		
Proximate analysis (wt.% dry basis)						
Volatile matter	49.90	48.10	50.10	49.26		
Fixed carbon	46.40	47.30	47.70	49.54		
Ash	3.70	4.60	2.20	1.20		
Ultimate analysis (wt.% dry basis)						
Carbon	65.00	63.40	64.00	69.60		
Hydrogen	4.60	4.20	4.30	4.80		
Nitrogen	0.72	0.58	0.73	0.64		
Sulphur	0.50	0.93	0.24	0.33		
Oxygen	25.48	26.18	28.45	23.43		
Ash	3.70	4.60	2.20	1.20		
Other elements (wt.% dry b	asis)					
Chlorine	0.11	0.11	0.08	0.11		
Minerals and inorganic (w	t.% ash basis)					
SiO ₂	56.90	13.94	2.10	14.40		
Al_2O_3	20.64	3.64	1.00	10.70		
Fe ₂ O ₃	4.63	15.41	47.60	13.60		
TiO ₂	1.51	0.34	0.10	0.69		
K ₂ O	1.31	0.35	0.20	0.62		
MgO	3.63	9.07	17.20	12.40		
Na ₂ O	4.73	2.53	3.00	6.40		
CaO	1.61	20.46	11.60	11.20		
SO ₃	5.04	24.33	19.60	22.30		
Trace elements (mg/kg dry coal basis)						
Cr	16.00	0.90	0.70	-		
As	0.30	0.10	0.20	-		
Se	1.00	0.70	0.60	-		
Hg	0.06	0.03	0.02	-		

Table 3.1: Composition of the Victorian brown coals used in this research

3.2. TEST FACILITIES

Throughout the research, a wide range of experimental facilities were used. These are described below. Some of these were designed, constructed and commissioned by the author as part of this study.

3.2.1. Quartz reactor facility

The experimental installation consists mainly of a fluidized bed quartz reactor (of around 550 mm high and an inner diameter of 40 mm), electric furnace, different auxiliary systems for gas supply, and flue gas analysis system. Figures 3.1a and 3.1b show the experimental set-up and fluidized bed quartz reactor respectively. The schematic diagram of the reactor is shown in Figure 3.2.

To simulate representative gas composition entering into the reactor under oxy-fuel combustion conditions, all gases (O_2 , CO_2 and N_2) were mixed in a separate vessel before entering into the reactor. O_2 , CO_2 and N_2 were supplied from bottle cylinders, whereas steam was supplied using a HPLC pump. The required gas stream was prepared by mixing the gas components from their cylinders using mass flow controllers. These gases are fed into the reactor through a distributor plate.



Figure 3.1: (a) Small scale experimental set-up and (b) Quartz reactor



Figure 3.2: Schematic diagram of the fluidized bed quartz reactor [All dimensions are in cm, unless mentioned]

The flue gas was first passed through glass fibre filled thimble filters connected to two condensation bottles immersed into ice-water bath to condensate the steam which was produced during combustion. The clean gas was then dried further in a silica gel column, and finally analysed by a gas analyser. One thermocouple was inserted through the side arm of the reactor to monitor the bed temperature during the entire experiment. Temperature and gas composition were continuously recorded by a computer during experiment. After each experiment, the solid residue was collected from the fluidized bed when this cooled down to room temperature, and then preserved for characterization.

3.2.2. Stainless steel fluidized bed test facility

The experimental installation consisted of a $\sim 10 \text{ kW}_{\text{th}}$ fluidized bed combustor, electric furnace, coal feeder, gas supply unit, gas pre-heating system, cyclone separators,

particulate filter, cooler, water condensation unit and gas analyser. Figure 3.3 shows the experimental facility. The combustor consisted of a stainless steel reactor of 0.1 m in diameter and 1.5 m in length, and a freeboard of 0.15 m in diameter and 2 m in length.



Figure 3.3: Fluidized bed rig

To simulate typical gas composition entering into the reactor under oxy-fuel combustion conditions, all gases - O_2 , CO_2 and steam, were mixed before entering into the reactor. O_2 and CO_2 were supplied from cylinders, whereas steam was supplied using a steam generator. The required gas stream was formulated by mixing the gas components using mass flow controllers. Prior to entering the reactor, all reacting gases were pre-heated in a gas heater. To keep the reacting gases hot, high temperature (600°C) heating tapes, insulated with high temperature ceramic wool, were also used along the length from the gas heater to the reactor. An electrically heated furnace was also fitted with the reactor to maintain the riser temperature during combustion, if required. This furnace is 1 m long, with three individually programmed heating sections. The middle section of the reactor was installed inside.

The solids were fed to the reactor using a screw feeder coupled with a variable-speed motor, and located just below the furnace and above the distributor. A small N_2 flow was passed through the screw feeder to aid the flow of coal particles and to prevent back-flow of the flue gas to the hopper. To avoid condensation, the feed line was also heated with heating tape.

Flue gases passed through a primary and a secondary cyclone separator to separate the solids before passing the clean flue gas to the stack. A slip-stream of flue gases was extracted through a particulate filter, cooler and water condensation system, and then analysed continuously by an on-line gas analyser. The outflow of the entire stream of flue gas was metered through a volumetric flow meter and recorded to a computer.

This experimental facility was also fitted with thermocouples and pressure sensors to monitor the temperatures and pressures along the entire installation. Five thermocouples were used to measure the gas temperature of the reactor. One Type-K stainless steel sheathed thermocouple (3.2 mm in diameter) was used along the centreline of the fluidized bed at the position of 0.1 m above the distributor plate, whereas four Type-K ceramic sheathed thermocouples (8 mm in diameter) were used at the sidewall of the freeboard zone sections (1.8 m, 2.2 m, 2.6 m and 3 m above the distributor plate). Four Pressure Transducers were used to provide the pressure signals along the configuration. Pressure signals were monitored using a 4 channel data-logger and logged to a computer. Data acquisition for flue gas composition and temperature was achieved by a LabView system via a FieldPoint instrument interface. General process data (such as total gas flow, gas composition, temperature and pressure) were continuously recorded to a computer during experiment.

3.2.3. Tubular furnace

The sulphation experiments were carried out in a 100 mm diameter and 1000 mm long tubular furnace (Model: LABEC HTHTF80/15, shown in Figure 3.4). To perform these experiments, a mixture of ash and limestone (CaCO₃) was evenly spread over a layer of mesh on a crucible of 90 mm in length, 40 mm in width and 5 mm in thickness. This crucible was specially constructed of perforated stainless steel (SS 316) to allow gas flow through both the top and bottom layer. A mesh was placed over the crucible to continue

allowing gas flow while not losing any of the samples through the holes. The crucible was placed in the centre of the furnace.



Figure 3.4: Tubular furnace

During the heating and cooling periods the furnace was purged with 50 mL/min of CO_2 to avoid calcination, and during the isothermal period the total gas flow rate was increased to 100 mL/min, which is equivalent to an average gas velocity of 0.2 m/s. At the end of each run, the sample was weighed and placed in an airtight container to prevent any unwanted reactions with air to enable further analysis.

3.2.4. Thermogravimetric Analyser

The char reactivity and carbonation experiments were conducted in a NETZSCH 449 F3 Jupiter Thermo-gravimetric analyser (TGA) with steam injection capability. Figure 3.5 shows the experimental set-up for TGA. All the experiments were performed with an alumina crucible of 20 mm in diameter, 10 mm in depth and 1 mm in wall thickness.

Initially the sample was loaded into the crucible and placed that crucible inside the TGA. Then the gas composition appropriate for the experiment being conducted with a total gas (O₂, N₂, CO₂ and steam) flow rate of 100 mL/min, the heating, isothermal and cooling period, and the heating and cooling rate required for the experiments were set. During the entire experiment, the change in mass over the temperature range and time period was recorded by a computer. The temperature of the sample was measured using a type S thermocouple with an accuracy of $\pm 1.5^{\circ}$ C.



Figure 3.5: Thermo-gravimetric analyser

In order to take into account the buoyancy effect for the crucible during experiment, blank (crucible without sample) experiments were also carried out under the same experimental conditions. The mass loss curves from the experiments with samples were then corrected by subtracting the mass loss curves from the blank experiments. Duplicate experiments of each test were also performed to test the reproducibility of the results.

3.3. ANALYTICAL EQUIPMENT

A range of analytical equipment was used in this research to characterize the solid particles. These are illustrated below.

3.3.1. Elemental analyser

A Perkin-Elmer Model 2400 elemental analyser (shown in Figure 3.6) was used to determine the carbon, hydrogen, nitrogen and sulphur concentrations in a given sample. Chlorine was determined according to the standard method AS 1038.8.2. The major inorganics were determined by ICP-AES (inductively coupled plasma – atomic emissions spectrometry) following borate fusion and acid dissolution according to the standard method AS 1038.14.1.



Figure 3.6: Perkin-Elmer Model 2400 elemental analyser

Both trace elements - arsenic and selenium in the solid residue were analysed according to the standard method AS 1038.10.2, chromium was determined according to the standard method AS 1038.10.1, whereas mercury was determined according to the standard method AS 1038.10.5.

3.3.2. UV spectrophotometer

The concentration of gaseous mercury in flue gas was determined by adsorbing this through a series of impingers in ice-water baths. Gaseous oxidized mercury (Hg²⁺) was captured in KCl (1 M) solution containing impingers, whereas gaseous elemental mercury (Hg⁰) was captured in 5% HNO₃ + 10% H₂O₂ and 10% H₂SO₄ + 4% KMnO₄ solutions containing impingers. After experiment, the impinger solutions were well shaked before several 1 ml solutions were taken for analysis. These impinger solutions were analysed for gaseous mercury concentration using HACH DR 5000TM UV-VIS spectrophotometer (shown in Figure 3.7) with 0.03 µg/L Hg sensitivity. This UV spectrophotometer was calibrated before with four concentrations of HgCl₂ standards.



Figure 3.7: HACH DR 5000TM UV-VIS spectrophotometer

3.3.3. Moisture analyser

The moisture content of coal, ash and bed samples was determined by a METTLER TOLEDO HB43-S Halogen moisture analyser (shown in Figure 3.8). This moisture analyser combines outstanding halogen heating technology along with analytical power in a compact arrangement. Here sample (maximum 54 g) is dried in a METTLER TOLEDO aluminium pan at 50°C to 200°C. The repeatability of moisture content with 2 g sample is 0.1%, whereas with 10 g sample the repeatability is 0.015%



Figure 3.8: Moisture analyser

3.3.4. Density measurement

The true density (the ratio of sample mass and occupied sample volume) of a given solid sample was measured by a Micromeritics AccuPyc 1330 pycnometer (shown in Figure 3.9).



Figure 3.9: Micromeritics AccuPyc 1330 pycnometer

Initially the two-thirds of the metal cylindrical sample container were filled with the sample, and the mass of sample, measured by a high quality balance, was entered into the pycnometer software. This pycnometer determines the solid density by measuring their volume very precisely using gas displacement technique. The solid sample volume is calculated indirectly by measuring the amount of displaced gas by observing the pressures upon filling the sample chamber and then discharging it into a second empty chamber. Here the displaced gas is helium because of the small size of gas molecules and the ability to penetrate into the deeper tiniest pores of the sample. Therefore, the true density of the solid sample is provided. This helium pycnometer was calibrated for every second measurement using calibration steel balls. For each measurement, the sample was purged with helium to clean the sample before the density measurement was taken.

3.3.5. Particle size distribution measurement

The size distributions of fine particles (below 1 mm) such as, fly ashes, were analysed by a Malvern Mastersizer 2000, whereas the size distributions of coarse particles (above 1 mm), such as, coal, char and bed samples, were measured by dry mechanical sieves. Figure 3.10 shows the both apparatus for size distribution measurement.



Figure 3.10: (a) Mastersizer and (b) mechanical vibration sieve shaker

In mechanical sieving process, mechanical vibration plays the vital rule for the sample to pass through a nest of sieves of descending aperture size. A sieve shaker (RO-TAP test sieve shakers RX-29 model) was used to mechanically separate the sample according to their size fractions. For each sieving measurement, nine sieves (pan, 150 μ m, 212 μ m, 300 μ m, 355 μ m, 425 μ m, 1 mm, 2 mm and 3 mm) were used, and 50-200 grams of sample was placed on the top sieve. The total vibration period for each measurement was 6 minutes.

3.3.6. X-ray florescence

The elemental compositions of bulk ash samples were quantified with an X-ray fluorescence spectrometer (XRF), using model Rigaku NEX CG (Figure 3.11). To perform the XRF analysis, pelletized samples of 30 mm in diameter and 4 mm in height were required. The pellets were prepared from the fine ash sample mixed with tabletting aid (Hoechst wax C micropowder) in a ratio of 4 using a hydraulic press with 15 tonne of axial force.



Figure 3.11: Rigaku NEX CG X-Ray fluorescence spectrometer

3.3.7. X-ray diffraction

The crystalline mineral phases in ashes are analysed by X-Ray diffraction (XRD), using a Rigaku miniflex600 XRD model (shown in Figure 3.12), at voltage of 40 kV and a current of 15 mA. The XRD patterns are collected at 20 values in the range of $2^{\circ} - 90^{\circ}$ with stepping intervals of 0.02° and a count time per step of 4 s. The qualitative analysis of XRD patterns are conducted using MDI Jade 5.0 software.



Figure 3.12: Rigaku miniflex600 X-Ray diffractor

3.3.8. Scanning electron microscopy and Energy dispersive X-rays

The morphology, porosity and structure of the fine particles can be identified using scanning electron microscope (SEM) by scanning the sample with a high-energy beam of electron. On the other hand, the elemental analysis and chemical characterization can be done using energy dispersive X-rays (EDX). It can identify the elements and the weight percentage of the elements at a particular point of the surface. The SEM-EDX analyses of solids, such as coal, ash and bed samples, were carried out using JEOL 7001F scanning electron microscope equipped with a liquid-nitrogen cooled germanium energy dispersive spectrometer (shown in Figure 3.13). All the samples were coated by platinum before analysis. During analysis, magnification ranges were varied from $50 \times$ to $8000 \times$, depending on the sample. The SEM images were taken under a working distance of 6 mm and an accelerating voltage of 5 kV.



Figure 3.13: JEOL 7001F scanning electron microscope

3.4. MODELLING

3.4.1. Single char particle modelling

The work was aimed at predicting the combustion rate of brown coal char under oxy-fuel fluidized bed combustion conditions. In this modelling, the following assumptions are considered:

- Carbon combustion is completely controlled by boundary-layer oxygen diffusion.
- Carbon consumption takes place only by the reaction of C with O_2 to produce CO_2 .
- The oxygen concentration in the bulk of the bed is equal to the outlet measured oxygen concentration.
- During combustion, solid density is changed linearly with time.
- Homogeneous carbon monoxide oxidation reaction is negligible.
- The particle temperature is close to the bed temperature.

The char particle diameter as a function of time is calculated by shrinking-particle model, as shown in equation (3.1) (Scala and Chirone, 2010b).

$$d(t_1) = \left[\frac{6(m_c^{initial} = \int_0^{t_1} m_c^{consumed}(t) dt)}{\pi \rho_s}\right]^{1/3}$$
(3.1)

where, $m_c^{initial}$ is the initial carbon mass in the particle and ρ_s is the solid density. In a previous study, Scala and Chirone (Scala and Chirone, 2010b) assumed constant particle density during the entire test. In this study, however, initial density as char density and final density as ash density were considered based on the measurement. It was assumed that this density changed linearly with time during combustion.

Moreover, under external diffusion control and under the pseudo-stationary assumption, the carbon consumption rate for a spherical carbon particle due to combustion is calculated by equation (3.2).

$$\dot{m}_{C}^{combustion} = \pi dSh D_{O_2} C_{O_2}^{out}$$
(3.2)

where, *d* is the char particle diameter, D_{O_2} is the molecular diffusivity of oxygen, $C_{O_2}^{out}$ is the O₂ outlet concentration and *Sh* is the particle Sherwood number. The Sherwood number, however, is calculated by equation (3.3) (Fabrizio, 2007).

$$Sh = 2\varepsilon_{mf} + 0.7(Re_{mf}/\varepsilon_{mf})^{1/2}Sc^{1/3}$$
(3.3)

where, ε_{mf} is the bed voidage at minimum fluidization velocity, Re_{mf} is the particle Reynolds number at minimum fluidization velocity and *Sc* is the Schmidt number. The Reynolds number and Schmidt number are calculated by equations (3.4) and (3.5) respectively.

$$Re_{mf} = \rho_g \, u \, d \, / \mu_g \tag{3.4}$$

$$Sc = \mu_g / D_{O_2} \rho_g \tag{3.5}$$

where, ρ_g is the O₂ density, μ_g is the O₂ viscosity, *u* is the fluidization velocity, *d* is the particle diameter and D_{O_2} is the O₂ molecular diffusivity.

The carbon consumption rates due to gasification is calculated by equation (3.6) (Scala and Chirone, 2010a).

$$\dot{m}_{C}^{gasification} = \left(\frac{d(t)}{d_{0}}\right)^{3} m_{C}^{initial} A(X) k_{0} \exp\left(\frac{-E_{a}}{RT}\right)$$
(3.6)

where, d(t) is the particle diameter as a function of time, d_0 is the initial particle diameter, $m_C^{initial}$ is the initial carbon mass in the particle, A(X) is the non-dimensional term accounting for the variation of reactivity with conversion, k_0 is the pre-exponential factor, E_a is the activation energy, and T is the bed temperature.

Hence, the total carbon consumption rate is calculated as the summation of carbon consumption rates due to combustion and gasification, as shown in equation (3.7) (Scala and Chirone, 2010a).

$$\dot{m}_{C}^{consumption} = \dot{m}_{C}^{combustion} + \dot{m}_{C}^{gasification}$$
(3.7)

Finally, this predicted total carbon consumption rates are compared to the experimental carbon consumption rates under different conditions.

3.4.2. Thermodynamic equilibrium predictions

Thermodynamic equilibrium calculations can be used to predict the possible phases formed and the concentrations of the compounds present in the equilibrium state. FactSage is a powerful tool for thermodynamic equilibrium modelling studies. It is the combination of two well-known software packages in the field of computational thermochemistry: F*A*C*T/FACT-Win and ChemSage (Bale et al., 2009). It provides information on the phases and compounds formed in mole or mass and their fractions and thermodynamic properties, the mass fraction of system components in all phases for all compositions, pressures and temperatures.

The FactSage 6.2 software was used to predict the flue gas composition, ash composition, possible agglomerating compounds and the trace element speciation during the combustion of Victorian brown coal under different conditions to compare with the experimental results. Calculations were performed using all components of coal together with air or oxy-fuel gas mixture (containing CO_2 , O_2 , steam and N_2) as input. These inputs were processed under the same operating conditions (i.e. temperature and pressure) used in the experiments. The amounts for each category and the overall amount of gas used as inputs were selected from the FACT53 and FToxid databases inbuilt in FactSage. A key assumption was that all phases were well mixed and reached thermal and chemical equilibrium.

3.4.3. Process modelling

Process simulation is an important tool to identify the best process flow-sheet and optimum design condition. Among several commercial software packages for the process simulation, Aspen Plus has successfully been used in different steady-state processes, including processes containing solids. These applications have made Aspen Plus a reliable and adaptable process simulation software. Aspen Plus TM V7.3 process software was used to develop a steady-state process model of the Oxy-FB combustion unit with Victorian brown coal.

To develop this model, several Aspen Plus unit operation blocks are combined, and appropriate kinetic expressions were used. To simplify the model, the assumptions considered in this study are given bellow:

- The process was steady-state.
- The mixing of solid particles (ash, char and sorbent) was perfect.
- The gas velocity was uniform throughout the bed and constant for each region of the bed.
- The mean voidage in the lower region of the bed was constant for a given superficial gas velocity, while the voidage in the upper region of the bed decreased with the vertical position along the riser.
- Due to the very short time required for volatile combustion, the devolatilization process was considered instantaneous.
- The char distribution throughout the bed was uniform.
- Due to the slower char combustion, it was assumed to occur after burning all the volatile products.
- The temperatures of burning coal particle and gas were considered constant and equal to the bed temperature.
- The effects of fragmentation of coal and char in the overall combustion process were neglected.
- Any size reduction in char particle due to the friction of bed particles and FB riser wall were neglected.
- The conversion of carbon, hydrogen and sulphur in the volatile matter was 100%.

This model helps to identify the major process constraints by predicting the results of Oxy-FB combustion using Victorian brown coal. The predicted results are validated with the experimental results from a bench scale Oxy-FB unit under different combustion conditions.

CHAPTER 4: COMBUSTION OF SINGLE CHAR PARTICLES

CHAPTER 4: COMBUSTION OF SINGLE CHAR PARTICLES

4.1. INTRODUCTION

In this chapter, the combustion performances of single Victorian brown coal char particles during oxy-fuel fluidized bed combustion are investigated.

During oxy-fuel combustion of a carbon-containing species in an O_2/CO_2 atmosphere, the following reactions are involved (Tomita and Ohtsuka, 2004; Scala and Chirone, 2010a).

$$C + O_2 \rightarrow CO_2, \Delta H_{298 K} = -394 \text{ kJ/mol}$$
 (R4.1)

$$C + \frac{1}{2}O_2 \rightarrow CO, \Delta H_{298 K} = -111 \text{ kJ/mol}$$
 (R4.2)

$$C + CO_2 \rightarrow 2CO, \Delta H_{298 K} = +171 \text{ kJ/mol}$$
 (R4.3)

$$CO + \frac{1}{2}O_2 \rightarrow CO_2, \Delta H_{298 \text{ K}} = -283 \text{ kJ/mol}$$
 (R4.4)

where, reactions (R4.1) and (R4.2) represent the exothermic carbon combustion reactions, reaction (R4.3) represents the endothermic carbon gasification by carbon dioxide, and reaction (R4.4) represents the homogeneous carbon monoxide oxidation reaction. It was reported that during oxy-firing fluidized bed combustion conditions, the contributions of CO_2 gasification and homogeneous CO oxidation were not negligible at high temperature and low oxygen concentration (Scala and Chirone, 2010a; Scala and Chirone, 2010b; Jia and Tan, 2014).

However, if the combustion environment consists of H_2O along with O_2 and CO_2 , the following reactions are also involved (Tomita and Ohtsuka, 2004).

 $C + H_2O \rightarrow CO + H_2, \Delta H_{298 K} = +130 \text{ kJ/mol}$ (R4.5)

$$CO + H_2O \rightarrow CO_2 + H_2, \Delta H_{298 K} = -40 \text{ kJ/mol}$$
 (R4.6)

where, reaction (R4.5) represents the endothermic carbon gasification reaction by steam and reaction (R4.6) is the exothermic water-gas shift reaction. Since steam is one of the main components in combustor in oxy-fuel combustion, the effect of steam is very important to be considered on char combustion. Although some studies are available to investigate the combustion characteristics of single char particles in fluidized bed combustor (Sundback et al., 1985; Basu and Halder, 1989; Huang and Scaroni, 1992; Scala, 2009; Scala and Chirone, 2010a; Scala and Chirone, 2010b; Sadhukhan et al., 2011; Scala, 2011), the effect of steam on char particle combustion, however, is still not clear. Moreover, prior studies considered mainly bituminous coal. Studies using brown coal or lignite in oxy-fuel fluidized bed combustion are very limited.

This chapter presents the combustion characteristics of individual and large Victorian brown coal char particles in a small fluidized bed quartz reactor under different oxy-fuel combustion conditions. The effects of oxygen and steam in feed gases in the combustion atmosphere, and bed temperature are considered in this study. Moreover, the particle temperature was also monitored during char combustion to examine the difference between the bed temperature and the char particle temperature.

4.2. EXPERIMENTAL SECTION

4.2.1. Materials

Experiments were carried out with single char particles prepared from briquetted Victorian brown coal. The composition of this char is given in Table 4.1.

Ultimate analysis		Minerals and inorganic			
(wt.% dry basis)		(wt.% a	(wt.% ash basis)		
Carbon	81.96	SiO ₂	14.40		
Hydrogen	2.85	Al_2O_3	10.70		
Nitrogen	0.83	Fe ₂ O ₃	13.60		
Sulphur	0.59	TiO ₂	0.69		
Oxygen	6.99	K_2O	0.62		
Ash	6.78	MgO	12.40		
		Na ₂ O	6.40		
		CaO	11.20		
		SO_3	22.30		

 Table 4.1: Composition of the char used in the experiment

Initially the single coal particles were shaped into almost spherical of approximately 8-10 mm diameter. Then the coal particles were devolatilized in thermo gravimetric analyser (TGA) with N₂ at 600°C for 1.5 hours. The true density of these char particles (5-6 mm) were 1682 kg/m³. Finally a hole was drilled to the centre of each char particle (see Figure 4.1) and a thin Type-K stainless steel sheathed thermocouple (< 0.5 mm in diameter) was inserted into that hole, and secured carefully.



Figure 4.1: (a) Typical char particles and (b) char particle with a thermocouple inserted

As a bed material, quartz sand of 106-150 μ m was used in the reactor. The particle density of this sand was 2657 kg/m³. At minimum fluidization, the bed voidage was 0.48, which is calculated as (Fueyo and Dopazo, 1995):

Bed voidage under minimum fluidization =
$$1 - \left[\frac{M}{L.A.\rho_p}\right]$$
 (4.1)

where, M is the mass of sand in the bed (20 gm), L is the bed height (11.5 mm), A is the cross-sectional area (1256 mm²) and ρ_p is the sand density (2657 kg/m³).

4.2.2. Experimental procedure

Figure 4.2 shows the schematic diagram of the installation which consisted of a small fluidized bed quartz reactor (of around 550 mm high and an inner diameter of 40 mm), electric furnace, systems for gas supply and flue gas analysis system.

To simulate representative gas composition entering into the reactor under oxy-fuel combustion conditions, all gases (O_2 and CO_2) were mixed in a separate vessel before entering into the reactor. O_2 and CO_2 were supplied from bottle cylinders, whereas steam was supplied using a HPLC pump. The required gas stream was prepared by mixing the gas components from their cylinders using mass flow controllers. These gases are fed into the reactor through a distributor plate.



Figure 4.2: Schematic diagram of the experimental setup of oxy-fuel fluidized bed combustion.

Fluidized bed reactor; 2. Electric furnace; 3. Bed material with char particle; 4. Gas mixer; 5 & 6. Gas cylinders; 7 & 8. Mass flow controllers; 9. HPLC pump; 10. Ice water bath for moisture trap; 11. Gas analyser, 12. Data acquisition system; T1. Particle temperature thermocouple; T2. Bed temperature thermocouple

The thermocouples were inserted through the side arm of the reactor to monitor the bed temperature and particle temperature during the entire experiment. At the beginning of experiments, the gas compositions were set to their desired value and the reactor was electrically heated at a rate of 15° C/min to the desired temperature. When the bed temperature reached around 500°C, steam was introduced (in case of experiments with steam). During experiment, the superficial gas velocity was 1.66 m/s at the entrance of the reactor, whilst at the bed the velocity was 0.07 m/s. The start-up period was around 1 hour. During combustion experiment, the steady state temperature was maintained at around 900°C ± 10°C.

The flue gas was first passed through glass fibre filled thimble filters connected to two condensation bottles immersed into ice-water bath to condensate the steam which was produced during combustion. The CO_2 , CO and O_2 concentrations in the dried off gas were then analysed directly and continuously by the gas analyser. Total flue gases were observed through a volumetric flow meter. General process data (temperatures, total gas flow and gas composition) were continuously recorded by a computer during experiment. Experimental conditions are summarized in Table 4.2.

Run	Combustion atmosphere (% Volume)	Bed temperature (°C)	Steady-state period (min)	Average particle diameter (mm)
1	5% O ₂ + 95% CO ₂	890 ± 5	40	5.0
2	10% O ₂ + 90% CO ₂	890 ± 5	30	6.0
3	15% O ₂ + 85% CO ₂	890 ± 5	25	5.5
4	10% O ₂ + 90% CO ₂	925 ± 5	30	6.0
5	5% O ₂ + 75% CO ₂ + 15% H ₂ O	880 ± 10	35	5.0
6	10% O ₂ + 75% CO ₂ + 15% H ₂ O	885 ± 5	30	6.0
7	15% O ₂ + 75% CO ₂ + 15% H ₂ O	890 ± 5	25	5.5

Table 4.2: Operating conditions used in experiments

4.2.3. Calculation

To calculate the carbon consumption rate of a char particle in a combustion environment consisted of oxygen and carbon dioxide, mass balances on oxygen and carbon dioxide were carried out, stated as equations (4.2) and (4.3) respectively (Scala and Chirone, 2010b).

$$\dot{m}_{O_2}^{in} + \frac{32}{44} \dot{m}_{CO_2}^{in} = \dot{m}_{O_2}^{out} (t) + \frac{16}{28} \dot{m}_{CO}^{out} (t) + \frac{32}{44} \dot{m}_{CO_2}^{out} (t)$$
(4.2)

$$\frac{12}{44}\dot{m}_{CO_2}^{in} + \dot{m}_{C}^{consumed}(t) = \frac{12}{28}\dot{m}_{CO}^{out}(t) + \frac{12}{44}\dot{m}_{CO_2}^{out}(t)$$
(4.3)

where, \dot{m}_i^{in} is the mass flow rates (kg/s) of species i that enters and exits the reactor, and $\dot{m}_c^{consumed}$ is the carbon consumption rate (kg/s) by reaction. By combining these two

equations, the carbon consumption rate (kg/s) as a function of time was calculated with equation (4.4).

$$\dot{m}_{C}^{consumed}(t) = \frac{12}{32} \left[\dot{m}_{O_2}^{in} - \dot{m}_{O_2}^{out}(t) \right] + \frac{3}{14} \dot{m}_{CO}^{out}(t)$$
(4.4)

However, to calculate the carbon consumption rate of a char particle in a combustion environment consisting of steam along with oxygen and carbon dioxide, mass balances on oxygen were replaced by equation (4.5).

$$\dot{m}_{O_2}^{in} + \frac{32}{44} \dot{m}_{CO_2}^{in} + \frac{16}{18} \dot{m}_{H_2O}^{in} = \dot{m}_{O_2}^{out}(t) + \frac{16}{28} \dot{m}_{CO}^{out}(t) + \frac{32}{44} \dot{m}_{CO_2}^{out}(t) + \frac{16}{18} \dot{m}_{H_2O}^{out}(t)$$
(4.5)

Then by combining the two equations (4.3) and (4.5), the carbon consumption rate (kg/s) as a function of time was calculated using equation (4.6).

$$\dot{m}_{C}^{consumed}(t) = \frac{12}{32} \left[\dot{m}_{O_{2}}^{in} - \dot{m}_{O_{2}}^{out}(t) \right] + \frac{3}{14} \dot{m}_{CO}^{out}(t) + \frac{6}{18} \left[\dot{m}_{H_{2}O}^{in} - \dot{m}_{H_{2}O}^{out}(t) \right]$$

$$(4.6)$$

By integrating either equation (4.4) or equation (4.6) between time zero and the end of experiment (t_f), the total mass (kg) of carbon consumed by reaction during experiment can be calculated with equation (4.7).

$$m_{\mathcal{C}}^{consumed} = \int_{0}^{t_{f}} \dot{m}_{\mathcal{C}}^{consumed}(t) dt$$
(4.7)

Moreover, the char particle diameter as a function of time can also be calculated by equation (4.8) (Scala and Chirone, 2010b).

$$d(t_1) = \left[\frac{6\left(m_C^{initial} = \int_0^{t_1} m_C^{consumed}(t) dt\right)}{\pi \rho_s}\right]^{1/3}$$
(4.8)

where, $m_C^{initial}$ is the initial carbon mass (kg) in the particle and ρ_s is the density (kg/m³) in the solid particle. In a previous study, Scala and Chirone (2010b) assumed constant particle density during the entire test. In the study, however, initial density as char density (1682 kg/m³) and final density as ash density (2904 kg/m³) were considered based on the measurement. It was assumed that this density changed linearly with time during combustion.

This experimental carbon consumption rate was also compared with the summation of carbon consumption rates due to combustion and gasification, as shown in equation (4.9) (Scala and Chirone, 2010a).

$$\dot{m}_{c}^{consumption} = \dot{m}_{c}^{combustion} + \dot{m}_{c}^{gasification}$$
(4.9)

4.2.3.1. Carbon consumption rate for combustion

In this calculation, it was assumed that carbon combustion was completely controlled by boundary-layer oxygen diffusion (Scala and Chirone, 2010a). Under external diffusion control and under the pseudo-stationary assumption, the carbon consumption rates (kg/s) for a spherical carbon particle due to combustion, $\dot{m}_{c}^{combustion}$, was calculated by equation (4.10).

$$\dot{m}_{c}^{combustion} = \pi dSh D_{O_2} C_{O_2}^{out}$$
(4.10)

where, *d* is the char particle diameter (m), D_{O_2} is the O₂ molecular diffusivity (m²/s), $C_{O_2}^{out}$ is the O₂ outlet concentration (kg/m³) and *Sh* is the particle Sherwood number. The above expression has some additional assumptions which are as follows: (1) carbon consumption takes place only by reaction (R4.1) and (2) the oxygen concentration in the bulk of the bed is equal to the outlet measured oxygen concentration.

The Sherwood number, however, was calculated by equation (4.11) (Fabrizio, 2007).

$$Sh = 2\varepsilon_{mf} + 0.7(Re_{mf}/\varepsilon_{mf})^{1/2}Sc^{1/3}$$
(4.11)

where, ε_{mf} is the bed voidage at minimum fluidization velocity, Re_{mf} is the particle Reynolds number at minimum fluidization velocity and *Sc* is the Schmidt number. The Reynolds number and Schmidt number were calculated by equations (4.12) and (4.13) respectively.

$$Re_{mf} = \rho_g \, u \, d \, / \mu_g \tag{4.12}$$

$$Sc = \mu_g / D_{O_2} \rho_g$$
 (4.13)

where, ρ_g is the O₂ density (kg/m³), μ_g is the O₂ viscosity (kg/m.s), *u* is the fluidization velocity (m/s), *d* is the particle diameter (m) and D_{O_2} is the O₂ molecular diffusivity (m²/s). In calculation, these parameters were used at measured particle temperature.

4.2.3.2. Carbon consumption rate for gasification

The carbon consumption rates (in kg/s) due to gasification, $\dot{m}_c^{gasification}$, is calculated by equation (4.14) (Scala and Chirone, 2010a).

$$\dot{m}_{C}^{gasification} = \left(\frac{d(t)}{d_{0}}\right)^{3} m_{C}^{initial} A(X) k_{0} \exp\left(\frac{-E_{a}}{RT}\right)$$
(4.14)

where, d(t) is the particle diameter (m) as a function of time, d_0 is the initial particle diameter (m), $m_C^{initial}$ is the initial carbon mass (kg) in the particle, A(X) is the nondimensional term accounting for the variation of reactivity with conversion, k_0 is the preexponential factor, E_a is the activation energy, and T is the bed temperature (K). This above expression has some assumptions which are as follows: (1) particle diameter as a function of time is calculated according to the equation (4.8); (2) homogeneous CO oxidation reaction (R4.4) is negligible and (3) particle temperature is close to the bed temperature.



Figure 4.3: Arrhenius plot of reaction rate constants against temperature

In order to find the values of activation energy and pre-exponential factor during gasification, some experiments were also carried out using 45–90 μ m Victorian brown coal char in TGA at three temperatures – 800, 850 and 900°C using 90% (v/v) CO₂ +

10% (v/v) N₂. By taking the reaction rates at 50% conversion for these three temperatures, $E_a = 158.66$ kJ/mol and $k_0 = 18400$ sec⁻¹ are evaluated the Arrhenius analysis. The Arrhenius plot of chemical reaction rate constants at different temperatures is shown in Figure 4.3. The correlation coefficient of linear fitting (R²) is 0.99.

By using these kinetic parameters with the experimental gasification rate using 100% (v/v) CO₂ at 930°C, the following form of A(X) as a function of carbon conversion degree, $X = [1 - (m_c/m_c^{initial})]$, was found.

$$A(X) = -(2 \times 10^{-7}) X^5 + (5 \times 10^{-7}) X^4 - (5 \times 10^{-7}) X^3 + (2 \times 10^{-7}) X^2 - (6 \times 10^{-8}) X^4 + (1 \times 10^{-8})$$
(4.15)

This equation is valid for X > 0.06.

4.3. RESULTS AND DISCUSSIONS

In the following subsections, results are presented first for the peak temperature differences between char particle and bed under different inlet oxygen concentrations. It is followed by the carbon conversion rates under different combustion conditions.

4.3.1. Particle temperature

During the entire experiment, the bed temperature and the char particle temperature profiles were recorded to monitor the difference between these two temperatures. The typical bed and particle temperature profiles during an oxy-fuel combustion experiment, starting from start-up until the end of steady-state operation, are showed in Figure 4.4. In this oxy-fuel experiment, the reacting gas composition consisted of 5% v/v O_2 and 95% v/v CO_2 . It can be seen that during char combustion, the particle temperature is slightly higher than the bed temperature indicating reactions taking place inside the particle. During the steady-state period, the particle temperature is increasing with time. At the end of char combustion, the thermocouple detaches from the particle and shows the same temperature as the bed.



Figure 4.4: Typical temperature profile during oxy-fuel combustion environments [O₂: 5% (v/v)]; temperature profile only during steady-state period shown in the inset



Figure 4.5: Peak temperature differences between char particle and bed under different inlet oxygen concentrations during oxy-fuel combustion

Figure 4.5 shows the maximum temperature differences between these two temperatures during combustion under different inlet oxygen concentrations (balanced by CO_2) during steady-state period. These experiments were conducted at the same bed temperature of 890°C. The experiments showed clearly that this temperature difference increased with the O_2 concentrations in feed gas. This finding is in line with the observation by Scala and Chirone (2010b), who concluded that particle temperature was considerably higher for higher oxygen concentrations in feed gas. The possible mechanism of this behaviour was

explained by Czakiert et al. (2006), who stated that the higher concentration of oxygen leads to increase in particle temperature initially by conducting the reaction of C with O_2 to produce CO, according to the reaction (R4.2). After that due to the facilitated oxygen diffusion, the contact distance between the particle and the combustion zone, where CO reacts with O_2 (according to the reaction R4.4), becomes shorter which leads to further increase in the particle temperature.

Furthermore, it is noticed that these peak temperature differences for the oxygen concentrations considered in this study were little bit smaller compared to the study by Scala and Chirone (2010b). Using the char particles (~6-7 mm) from a bituminous coal (81.3% C dry and ash-free basis), they found 36°C and 68°C temperature differences for 4.5% and 8% inlet oxygen concentrations respectively, whereas in this study using the char particles (~5-6 mm) from briquetted Victorian brown coal (70.45% C dry and ash-free basis), 21°C and 30°C temperature differences were observed using 5% and 10% oxygen concentration in feed gas respectively.

The experimental results also indicate that the addition of steam (even with same 10% v/v oxygen concentration in oxidant) in the combustion environment further increases the peak temperature difference. Around 30°C difference was observed in dry oxy-fuel combustion, while around 48°C difference was found using 15% steam in the oxy-fuel combustion atmosphere.

The higher particle temperature in presence of steam in the oxy-fuel atmosphere is due to the steam gasification to produce CO and H₂ initially, according to the reaction (R4.5) between carbon and steam (Taylor and Neville, 1921; Ahmed and Krumpelt, 2001). Subsequently, in the presence of excess steam in the system, the generated carbon monoxide further undergoes the water-gas shift reaction to produce CO₂ according to the reaction (R4.6). However, it is unlikely that the water-gas shift reaction dominates the steam gasification reaction at this low temperature without any catalyst. At this temperature, on the other hand, the homogeneous CO oxidation reaction (R4.4) is quite fast and favourable to occur. Since the CO oxidation reaction is highly exothermic, elevated particle temperature was observed in presence of steam in the feed gas.

Another experiment was conducted at the bed temperature of 925° C using 10% (v/v) oxygen concentration in feed gas (balanced by CO₂), and up to 39°C difference was
observed, whereas only 30°C difference was observed at 890°C using the same oxygen concentration during char combustion. So, it can be concluded that higher bed temperature increases the temperature difference between the bed and the particle.

4.3.2. Char combustion tests

In this section, the carbon consumption rates are discussed under different experimental conditions to investigate the effects of bed temperature, and oxygen and steam concentrations in the combustor. Since the burning rate of larger particle is controlled by external diffusion, the consumption rates are presented in Figures 4.6 to 4.8 for particle diameter ≥ 1 mm (Scala and Chirone, 2010b).

4.3.2.1. Effect of oxygen concentration in feed gas

Figure 4.6 shows the experimental and calculated carbon consumption rates as a function of particle diameter under different inlet oxygen concentrations, balanced by CO_2 . All these experiments were conducted at the same bed temperature of 890°C. The results indicate that the total calculated carbon consumption rates (summation of carbon consumption rates due to combustion and gasification) were fitted well with the experimental carbon consumption rates, at least for low oxygen concentration. Moreover, it is noticed clearly that carbon combustion dominates the overall conversion, whereas the effect of CO_2 gasification reaction is almost negligible for the oxygen concentration and temperature range considered in this study. Moreover, in real oxy-fuel combustion atmosphere, particularly with steam, the CO_2 gasification effect would be even further lower.



Figure 4.6: Experimental and calculated carbon consumption rates under different inlet oxygen concentrations [(a) 5% (v/v), (b) 10% (v/v) and (c) 15% (v/v)] during dry oxy-fuel combustion – steady-state bed temperature 890°C

With increase in O_2 concentration in the feed gas, carbon consumption rate was observed to increase, supporting the observation by Scala and Chirone (2010b), who reported that carbon combustion rate increases with inlet O_2 concentration. It was also observed that the combustion rate increases almost linearly with the particle diameter (for ≥ 2 mm), indicating that the combustion process is mostly controlled by the diffusion of oxygen through the particle boundary layer (Scala and Chirone, 2010a).

4.3.2.2. Effect of steam in feed gas

Effect of steam in oxidant on carbon consumption rate is shown in Figure 4.7. All these experiments were conducted at almost the same bed temperature, at around 890°C.





Figure 4.7: Experimental and calculated carbon consumption rates under different inlet oxygen concentrations [(a) 5% (v/v), (b) 10% (v/v) and (c) 15% (v/v)] along with 15% (v/v) steam as oxidants – steady-state bed temperature 890°C

Comparing Figures 4.6 and 4.7, it can be noticed that the presence of steam (along with same oxygen concentration) in the feed gases increased the carbon consumption rates. This is due to the higher particle temperature in presence of steam, as discussed in Section 4.3.1.

4.3.2.2. Effect of bed temperature

Figure 4.8 shows the experimental and calculated carbon consumption rates as a function of particle diameter at two different bed temperatures. All these experiments were conducted at the same oxygen concentration (10% v/v and balanced by CO₂) in feed gas.





Figure 4.8: Experimental and calculated carbon consumption rates during char combustion using 10% (v/v) oxygen in feed gas during steady-state period at (a) 890°C and (b) 925°C

As shown in this figure, it can be observed that carbon consumption rate increases with bed temperature. This is in-line with the observation by Scala and Chirone (2010a), who also found higher carbon consumption rate at higher temperature. The explanation of this behaviour is that as the bed temperature increases, the temperature of char particle also increases (as shown in Section 4.3.1) which leads to the increase in carbon combustion rate (Czakiert et al., 2006).

4.4. CONCLUSIONS

The experiments were carried out to investigate the fluidized bed combustion of coal char particle under oxy-fuel conditions using large char particles of different diameters. These char particles were prepared in a thermo gravimetric analyser at 600°C in 100% N_2 atmosphere. The main operating parameters for oxy-fuel combustion experiments are summarized below:

- Reactor: Fluidized bed quartz reactor
- Fuel: Char particles from briquetted Victorian brown coal
- Char particle diameter: Approximately 5-6 mm
- Bed temperature: Around 900°C
- Combustion atmosphere: Combination of O₂, CO₂ and H₂O at different proportions
- Oxygen concentration: 5-15% v/v
- Steam concentration: 0-15% v/v

In these experiments, a thin thermocouple was also inserted inside each char particle to monitor the particle temperature during the experiment. The key results are as follows:

- The addition of steam in combustion atmosphere results in an increase in particle temperature relative to the bed temperature. Up to 48°C difference was noticed between the char particle temperature and the bed temperature using 15% (v/v) steam in oxy-fuel combustion atmosphere.
- Carbon consumption rate is increased by bed temperature as well as by oxygen and steam concentrations in oxidant.
- The CO₂ gasification reaction is almost negligible for the feed gases and temperature considered in this study.

On the whole, the results show that during oxy-fuel fluidized bed combustion using Victorian brown coal char particles, boundary-layer oxygen diffusion controls the carbon combustion rate, and carbon is mostly oxidized to carbon dioxide. The temperature of the char particle monitored during combustion has the practical implication on the possibility of agglomeration.

Focus of the next chapter:

Information generated on the combustion behaviour of Victorian brown coal char particles during oxy-fuel fluidized bed combustion which are useful for combustion of these coals in a large scale rig. Further oxy-fuel experiments are performed in bench-scale fluidized bed combustors using these coals in Oxy-FB combustion. These results will be discussed in details in subsequent chapters. In the next chapter, the design and commissioning of the bench scale fluidized bed combustor will be discussed.

$\begin{array}{c} Chapter 5: Design and \\ Commissioning of a 10 \ kW_{TH} \\ Fluidized Bed Rig \end{array}$

CHAPTER 5: DESIGN AND COMMISSIONING OF A 10 KW_{TH} FLUIDIZED BED RIG

5.1. INTRODUCTION

In this chapter, the design parameters and commissioning procedure of a 10 kW_{th} bench scale fluidized bed rig, used for operation in both air-fired and oxy-fired mode using a variety of coals, are discussed.

5.2. DESIGN OF EXPERIMENTAL RIG

The schematic diagram of the rig is shown in Figure 5.1.

Design Basis:

The major operating parameters are given below:

- Coal feed rate: up to 2 kg/h
- Inner diameter of the main reactor zone: 0.1 m
- Inner diameter of the freeboard zone: 0.15 m
- Height of the main reactor zone: 1.5 m
- Height of the freeboard zone: 2 m
- Material: Stainless Steel 253MA
- Fluidizing velocity: 1-2 m/s
- Fuel: Victorian brown coal
- Bed temperature: 800-900°C
- Base line experiment: Air combustion
- Combustion atmosphere: Combination of oxygen, carbon-dioxide and steam at different proportions
- Flue gas analysis: Online measured during the tests by a gas analyser

Detailed calculations related to the oxy-fuel fluidized bed rig design were conducted. The values include: fluidization velocity, coal feed rate, inner diameter of the main reaction zone of reactor, gas composition, gas flow rates, heat input, heat generation in the reactor and sand particle size at minimum fluidization velocity. The calculations were performed for different combinations of values. Sample calculations are shown in Appendix A.



Figure 5.1: Schematic diagram of the fluidized bed rig

5.3. EXPERIMENTAL SETUP

Figure 5.2 shows the view of constructed fluidized bed rig. In the following sub-sections, the descriptions of the major parts of the rig are given.



Figure 5.2: Photograph of the fluidized bed rig under construction (left) and after complete construction (right)

5.3.1. Combustor

The main combustor (Figure 5.3) consists of two sections: main reaction zone and freeboard zone. The inner diameter of main reactor zone and freeboard zone are 0.1 m and 0.15 m respectively. The overall height of the reactor is 4 m. The main reaction zone

was kept inside the furnace to compensate any heat loss during experiments and to increase the reactor temperature during start-up.



Figure 5.3: Fluidized bed reactor with cyclone separators

5.3.2. Furnace

An electrically heated furnace (shown in Figure 5.4) was fitted with the reactor to keep the riser hot during combustion. This furnace is 1 m long, with three individually programmed heating sections. The middle section of the reactor was installed inside it.



Figure 5.4: (a) Furnace and (b) Control panel of furnace

5.3.3. Gas supply unit

To simulate typical gas composition entering into the reactor under oxy-fuel combustion conditions, all gases - O_2 , CO_2 and/or steam, were mixed before entering into the reactor. O_2 and CO_2 were supplied from cylinders, whereas steam was supplied using a steam generator (Figure 5.5). Steam supply was regulated by using a needle valve from the steam generator. During experiment, the water supply to the steam generator was recorded through a cumulative water flow meter. Composition of the other required gas stream was formulated by mixing the gas components using mass flow controllers.



Figure 5.5: Steam generator

Prior to entering the reactor, all reacting gases were pre-heated in a gas heater (Figure 5.6a). To keep the reacting gases hot, high temperature heating tapes, insulated with high temperature ceramic wool, were also used along the length from gas heater to the reactor.



Figure 5.6: (a) Gas pre-heater and (b) temperature controllers for heating tapes

5.3.4. Coal feeder

The solids (coal and bed material) were fed to the reactor using a screw feeder (Figure 5.7) located just below the furnace and above the distributor plate. The coal feeder was coupled with a variable-speed motor to adjust the feeding rate. A small N_2 flow was passed through the screw feeder to aid the flow of coal particles and to prevent back-flow of flue gases to the hopper. To avoid condensation, the feed line was also heated with heating tape.



Figure 5.7: Coal feeder

5.3.5. Flue gas processing unit

Flue gases passed through a primary and a secondary cyclone separator to separate the solids before passing to the stack. A slip-stream of flue gases was extracted through a particulate filter, cooler and water condensation system, and then analysed continuously by an on-line gas analyser (Infrared Gas Analyser) with inbuilt vacuum pump. CO₂, CO, H₂, CH₄ and O₂ concentrations were measured in that analyser (Figure 5.8). The outflow of the entire stream of flue gas was metered through a volumetric flow meter (Model:

Bios DefinerTM 220 High Flow) and recorded to a computer using the supplied Bios software.



Figure 5.8: Gas flow meter, gas analyser and data acquisition system

5.3.6. SO3 trap

Majority of the generated gases, such as CO_2 , CO, SO_2 , H_2 , CH_4 and O_2 , were monitored continuously using either an on-line gas analyser or a micro gas chromatograph (micro-GC). SO_3 was determined by the method developed by Chen and Bhattacharya (2013). Figure 5.9 shows the schematic diagram of the SO_3 trap.



Figure 5.9: Schematic diagram of SO₃ trap

Calcium oxalate mixed with glass beads was used in this trap, where temperature was controlled in between 300° C - 375° C. At this temperature range, calcium oxalate reacts only with SO₃ to produce additional CO and CO₂, according to the following reaction. SO₃ concentration in the sampling gas was measured indirectly by measuring the CO using the micro-GC.

$$SO_3 + CaC_2O_4 \rightarrow CaSO_4 + CO_2 + CO \tag{R5.1}$$

5.3.7. Thermocouple and pressure transducer

This experimental facility was also furnished with thermocouples and pressure sensors to monitor the temperatures and pressures along the reactor and the entire installation. One Type-K stainless steel sheathed thermocouple (3.2 mm in diameter) was used along the centreline of the fluidized bed at the position of 0.1 m above the distributor plate, whereas four Type-K ceramic sheathed thermocouples (8 mm in diameter) were used at the sidewall of the freeboard sections (1.8 m, 2.2 m, 2.6 m and 3 m above the distributor plate). Four pressure transducers (Setra AccuSenseTM Model ASM) were used to provide the pressure signals along the configuration. Pressure signals were monitored using a 4 channel data-logger (Model: HOBO U12-006) and logged using the HOBOWARE PRO software to a computer.

Data acquisition for flue gas composition and temperature was achieved by a LabView system via a FieldPoint instrument interface. General process data (such as total gas flow, gas composition, temperature and pressure) were continuously recorded in a computer during experiment.

5.4. COMMISSIONING WORK

During cold commissioning of the rig, all mass flow controllers, gas analyser, softwares (such as LabView and Bios), cumulative gas flow meter, water flow meter and the required steam supply through the needle valve were calibrated. Moreover, the feed rate of coal, of different particle sizes, through variable-speed motor connected to hopper was also calibrated. A typical calibration curve for the coal (particle size: 1-3 mm) feed rate as a function of the rotational speed of motor is shown in Figure 5.10. With this curve, it was

able to operate the motor with appropriate speed required for the desired coal feed rate. Calibration of the feeder was carried out at regular intervals.



Figure 5.10: Coal feeder calibration curve

After completing all calibrations, the operating procedure for combustion experiments was established. During hot commissioning, some of the major problems faced and the related technical solutions devised are described below:

• The initial commissioning runs were performed using 2 kg of char as a feed material. The feed rate was around 1.14 kg/hr and gas velocity was 1.36 m/s. No thermocouple was connected to the bottom zone of fluidized bed reactor. The outside wall temperature at the bottom zone was measured which was around 900°C. Samples collected from the primary cyclone, secondary cyclone and bed were 65.813 g, 4.057 g and 51.355 g respectively. However, presence of round shaped high temperature slag, irregular shaped low temperature sintered char and metal flakes, (Figure 5.11) collected from the bed after experiment indicated that the bed temperature inside the reactor exceeded 1000°C.



Figure 5.11: Different samples collected from the bed after first commissioning run

Decision was, therefore, made to measure the bed temperature during experiment. The bottom zone of the reactor was modified and bed temperature was monitored using Type-K stainless steel sheathed thermocouple along the centreline of the bed.

• After few hot commissioning runs, it was observed that the auger inside the screw feeder was broken during experiment. Figure 5.12b shows the broken auger and Figure 5.12a shows the same auger for reference before being broken.



Figure 5.12: Auger (a) before and (b) after broken

By observing the broken auger, it was clear that initially the auger started to twist and then broke due to the over-pressure created by motor. The auger was, therefore, modified with a solid rod inside it, to avoid twisting. The screw feeder with modified auger performed well during the subsequent runs.

These modifications helped to improve the operability of the rig under different conditions. After that a detailed operational procedure, including start-up and shut-down, was prepared to avoid any difficulty in operation during experiment.

5.5. SUMMARY

This chapter describes the design parameters and commissioning procedure of the bench scale fluidized bed reactor used in the experiments. The commissioning runs helped to develop the operating procedure for individual set of experiments.

Focus of the next chapter:

Both air and oxy-fuel experiments were performed in this 10 kW_{th} fluidized bed combustor using Victorian brown coal. The results of these experiments will be discussed in the next chapter. In the next chapter, results from a small fluidized bed quartz reactor will also be discussed.

CHAPTER 6: COMBUSTION EXPERIMENTS IN BENCH SCALE FLUIDIZED BED COMBUSTORS

CHAPTER 6: COMBUSTION EXPERIMENTS IN BENCH SCALE FLUIDIZED BED COMBUSTORS[§]

6.1. INTRODUCTION

To generate fundamental combustion data for Victorian brown coal under Oxy-FB conditions, experiments were undertaken in two sets of experimental facility.

- a) A small scale fluidized bed quartz reactor, described earlier in Section 3.2.1.
 The experiments were aimed to investigate the following:
 - Combustion characteristics of one Victorian brown coal Yallourn under different oxy-fuel combustion conditions.
 - Emission and retention characteristics of trace elements (Se, As and Cr).
- b) A 10 kW_{th} fluidized bed combustor, described earlier in Section 3.2.2 in Chapter 3 and Chapter 5.

The experiments were aimed to investigate the following:

- Combustion characteristics including combustion efficiency of one Victorian brown coal Loy Yang under different oxy-fuel combustion conditions.
- Characteristics of the generated ash and a preliminary assessment of bed agglomeration.
- Emission characteristics of conventional pollutants, such as SO_X (SO₂ and SO_3), and NO_X (NO, NO₂ and N₂O).
- Emission and retention characteristics of trace elements (Hg, Se, As and Cr).

[§] Results from this chapter have been published/submitted for publication in the following journals and peer-reviewed conferences:

^{1.} B. Roy, W. L. Choo and S. Bhattacharya, *Fuel*, 2013, 114, 135-142.

^{2.} B. Roy and S. Bhattacharya, Fuel Processing Technology, 2013, 117, 23-29.

^{3.} B. Roy, L. Chen and S. Bhattacharya, *Environmental Science & Technology*, 2014, Revise resubmit.

^{4.} B. Roy and S. Bhattacharya, *Energy & Fuels*, 2014, Under review.

^{5.} B. Roy, L. Chen, S. Bhattacharya and S. Rajendran, The 35th International Symposium on Combustion, San Francisco, California, USA, 2014.

^{6.} B. Roy, and S. Bhattacharya, The 38th International Technical Conference on Clean Coal & Fuel Systems, Clearwater, Florida, USA, 2013.

^{7.} B. Roy and S. Bhattacharya, The 3rd Oxyfuel Combustion Conference, Ponferrada, Spain, 2013.

^{8.} B. Roy, W. L. Choo and S. Bhattacharya, CHEMECA Conference, Sydney, Australia, 2011.

^{9.} B. Roy, W. L. Choo and S. Bhattacharya, The ICCS&T Conference, Oviedo, Spain, 2011.

The effects of oxygen, carbon dioxide and steam concentrations in feed gas, and reactor temperature are discussed. Moreover, the results from oxy-fuel combustion are also compared to those from air combustion. In addition, prediction of equilibrium levels of trace elements emissions and ash compositions have been made to compare with the experimental data.

6.2. EXPERIMENTAL SECTION

6.2.1. Fluidized bed quartz reactor

6.2.1.1. Materials

Experiments were carried out with an oven-dried Victorian brown coal (Yallourn) of 106-152 μ m of particle size. Coal sample was dried in an oven at 110°C for 10 hours prior to the experiment. The composition of this coal is given in Table 3.1 in Chapter 3.



Figure 6.1: Schematic diagram of the experimental setup for fluidized bed quartz reactor

6.2.1.2. Experimental procedure

Figure 6.1 shows the schematic diagram of the installation which consisted of a small fluidized bed quartz reactor (of around 550 mm high and an inner diameter of 40 mm), electric furnace, coal feeder, systems for gas supply and flue gas analysis system. Detailed description of the facility is given in Section 3.2.1 in Chapter 3.

At the beginning of experiments, the gas compositions were set to their desired value and the reactor was electrically heated at a rate of 15°C/min to the desired temperature without feeding any coal. When the bed temperature reached the set steady value, steam was introduced (in case of experiments with steam) and coal feeding was started continuously into the reactor at an average rate of around 0.15 g/min. Coal was fed continuously from a quartz hopper using a pre-calibrated stopcock. The feed rate was controlled with a pre-set aperture identified during calibration. During experiment, the superficial gas velocity was 0.9 m/s at the entrance of the reactor, whilst at the bed the velocity was 0.04 m/s. The start-up period was around 1 hour. Experiments were run for steady-state period of over 1 hour.

$6.2.2.\ 10\ kW_{th}$ fluidized bed combustor

6.2.2.1. Materials

Experiments were carried out with one air-dried Victorian brown coal - Loy Yang. Coal sample was crushed and sieved, and the particle size in the range of 1- 3 mm was used. Prior to loading in the hopper, the pre-dried coal was additionally dried in an oven at 60°C for about 1.5 hours. The composition of the coal used in these experiments is given in Table 3.1 in Chapter 3.



Figure 6.2: Size distribution of coal, char and quartz sand used in experiments

As bed material, silica sand of $350 - 400 \,\mu\text{m}$ was also added into the reactor. In addition, char (77.97% C, 2.42% H, 1.29% N, 0.11% S, 15.77% O and 2.44% ash) of 1 - 3 mm size was used during start-up. The size distributions of coal, char and sand is given in Figure 6.2.

6.2.2.2. Experimental installation

The experimental installation consisted of a 10 kW_{th} fluidized bed combustor, electric furnace, coal feeder, gas supply unit, gas pre-heating system, cyclone separators, particulate filter, cooler, water condensation unit and gas analyser. Figure 6.3 shows the schematic diagram of the entire installation. The combustor was 0.1 m diameter and 1.5 m length, and the freeboard of 0.15 m diameter and around 2 m length. Detailed description of the facility is given in Section 3.2.2 in Chapter 3.



Figure 6.3: Schematic diagram of the experimental setup for stainless steel fluidized bed rig

6.2.2.3. Experimental procedure

At the beginning of an experiment, the bed was loaded with 2 kg of sand as bed material. Initially hot air was introduced through the gas pre-heating system to heat the bed. When the bed temperature reached around 200°C, the air was replaced by the desired $O_2 + CO_2$ mixture, and char feeding was commenced. Typically, all char was used up during heating up period (after 45 min of char commencement, as evidenced by commissioning run using only char as feedstock). After consuming all char, coal feeding was started. For ignition, additional air was introduced. This air flow was reduced gradually as bed

temperature increased. When the bed temperature reached the desired steady-state value, the additional air flow was completely turned off, and steam was introduced (in cases of wet oxy-fuel experiments). After that the combustor was continued in the desired oxy-fuel mode at constant total gas flow, and the required bed temperature was maintained only by adjusting the coal feed rate. During experiment, the steady state temperature was in the range of 800° C – 900° C, and the gas velocity was in the range of 0.75 - 0.85 m/s. The total start-up period was around 3 h. Experiments were run for steady-state period of up to 8 hrs. At the end of the oxy-fuel test, the oxy-fuel environment was replaced by air before shutdown. Figure 6.4 shows the typical temperature and pressure profiles during an experiment, starting from start-up of the installation until end of the steady-state operation.



Figure 6.4: Typical (a) temperature and (b) pressure profiles during experiment

Combustion atmosphere (% Volume)	Gas velocity (m/s)	Bed temperature (°C)	Steady-state period (h)	Coal feed rate (g/h)				
Measurement of combustion characteristics and trace elements retention								
Air	0.80	840 ± 10	4.50	650				
15% O ₂ + 85% CO ₂	0.80	840 ± 10	3.25	850				
21% O ₂ + 79% CO ₂	0.80	840 ± 10	3.50	850				
30% O ₂ + 70% CO ₂	0.80	845 ± 5	3.75	800				
15% O ₂ + 85% CO ₂	0.75	820 ± 10	3.25	785				
15% O ₂ + 85% CO ₂	0.80	880 ± 10	2.00	855				
14% O ₂ + 82% CO ₂ + 4% H ₂ O	0.80	850 ± 10	2.00	845				
14% O ₂ + 76% CO ₂ + 10% H ₂ O	0.85	850 ± 10	2.00	845				
15% O ₂ + 73% CO ₂ + 12% H ₂ O	0.75	860 ± 10	2.00	840				
Measurement of sulphur oxides								
Air	0.82	850 ± 10	1.65	470-510				
15% O ₂ + 85% CO ₂	0.81	850 ± 10	2.40	600-670				
21% O ₂ + 79% CO ₂	0.81	850 ± 5	1.55	600-735				
30% O ₂ + 70% CO ₂	0.81	850 ± 5	1.40	560-670				
15% O ₂ + 85% CO ₂	0.75	820 ± 10	1.80	530-600				
15% O ₂ + 85% CO ₂	0.79	880 ± 10	1.50	670-770				
15% O ₂ + 73% CO ₂ + 12% H ₂ O	0.75	850 ± 10	1.55	640-670				
Measurement of nitrogen oxides								
Air	0.82	840 ± 10	0.9	450-670				
15% O ₂ + 85% CO ₂	0.76	850 ± 10	0.9	670-750				
21% O ₂ + 79% CO ₂	0.81	845 ± 5	0.9	670-710				
30% O ₂ + 70% CO ₂	0.81	845 ± 10	0.9	600-630				
15% O ₂ + 85% CO ₂	0.75	820 ± 10	1.0	490-670				
15% O ₂ + 85% CO ₂	0.79	880 ± 10	0.9	800-830				
15% O ₂ + 73% CO ₂ + 12% H ₂ O	0.75	850 ± 10	0.9	565-600				
Measurement of gaseous mercury								
Air	0.82	850 ± 10	2.75	515				
15% O ₂ + 85% CO ₂	0.75	850 ± 10	2.50	570				
21% O ₂ + 79% CO ₂	0.81	850 ± 10	2.50	670				
30% O ₂ + 70% CO ₂	0.81	845 ± 10	2.50	600				
$15\% O_2 + 73\% CO_2 + 12\% H_2O$	0.75	850 ± 10	2.25	600				

Table 6.1: Oper	ating conditions used	in combustion exi	neriments using La	v Yang coal
Tuble ofference	uting conditions used	in combustion ex	permitting using Do	j i ung cour

After each experiment, the fly ash and bed material samples were collected and preserved, for characterization and analysis, from two cyclone pots and fluidized bed when these are cooled down to room temperature. Experimental conditions are summarized in Table 6.1.

It was also reported in literature (Chen et al., 2012c) that the typical oxygen concentration in oxy-fuel combustion is 15-30% by volume, therefore this range of O_2 concentration was chosen during these experiments. Moreover, the typical H₂O concentration in the oxidant of oxy-fuel combustion is 4-15% (Lupion, 2009). Therefore, 4-12% H₂O was chosen in these set of experiments.

6.2.2.4. Flue gases measurements

Majority of the flue gases, such as CO₂, O₂, CO, CH₄ and H₂, were monitored continuously by a multi-component gas analyser. A thermal conductivity gas analyser (INZ-TN3ZAF-E) was used for H₂, whereas an infrared analyser (INZ-TN1 ZREc-E) was used for the other four gases. Other major gases, such as SO₂, H₂S, COS and CO were measured using a micro gas chromatograph (Agilent GC 490). NO and NO₂ were observed using another gas analyser (MX6 iBridTM), while N₂O was measured using a gas chromatograph (Agilent GC 7890A).

By using both gas analysers and gas chromatographs, it was able to quantify almost all major gases, except SO₃ and mercury in the flue gas which are described below:

Determination of SO₃

An additional set of experiments were also performed to determine the extents of SO_3 and gaseous mercury in flue gas.

 SO_3 was determined by the method developed by Chen and Bhattacharya (2013). Here calcium oxalate mixed with glass beads was used in the SO_3 trap, where temperature was controlled in between 300°C - 375°C. At this temperature range, calcium oxalate reacts only with SO_3 to produce additional CO and CO_2 , according to the following reaction (R6.1). SO_3 concentration in the sampling gas was measured indirectly by measuring CO using the micro-GC.

$$SO_3 + CaC_2O_4 \rightarrow CaSO_4 + CO_2 + CO \tag{R6.1}$$

Determination of gaseous Hg

The sequential selective extraction method of Hg(g) measurement by Mitsui et al. (2011) was used in this study. A portion of flue gases was extracted through a series of impingers in ice-water baths. Figure 6.5 shows the mercury sampling train.



Figure 6.5: Mercury sampling train

The fractions obtained with corresponding sequential adsorbents were coded as follow: I1 and I2 (KCl, 1M), I3 (5% HNO₃ - 10% H₂O₂), I4 and I5 (10% H₂SO₄ – 4% KMnO₄). Gaseous oxidized mercury (Hg²⁺) was captured in KCl solution containing impingers, whereas gaseous elemental mercury (Hg⁰) was captured in HNO₃ - H₂O₂ and H₂SO₄ – KMnO₄ solutions containing impingers. After experiment, the impinger solutions were well shaked before three batches of 1 ml solutions were taken for analysis. These impinger solutions were analysed for gaseous mercury concentration using HACH DR-5000TM UV VIS spectrophotometer with 0.03 µg/L Hg sensitivity. This UV spectrophotometer was calibrated before with four concentrations of HgCl₂ standards. It is noted that during experiment the temperature at the flue gas sampling point was around 200°C with ± 20°C variation.

6.2.2.5. Analysis of results

To calculate the combustion efficiency, all collected samples from bed and cyclone pots were ashed at 800°C for three hours in a muffle furnace to find out the unburnt carbon contents in the solid samples. The combustion efficiency is calculated as:

Combustion efficiency =
$$\left\{1 - \frac{(UC \text{ in cyclone } 1 + UC \text{ in cyclone } 2 + UC \text{ in bed })}{Total feed carbon}\right\} \times 100 (6.1)$$

where, *UC* represents the unburnt carbon, and cyclone 1 and cyclone 2 are primary cyclone and secondary cyclone respectively.

In case of gaseous conventional pollutants, such as SO_X and NO_X , to compare the emissions under different conditions, results are normalized in mass per unit energy basis (mg/MJ), according to the following formula:

$$Emission (mg/MJ) = \frac{\begin{cases} Concentration(ppm). Molecular weight(\frac{g}{mol}).10^{-6} / 0.0224(\frac{m^3}{mol}) \end{cases}}{\begin{cases} Coal feed rate(\frac{g}{hr}). 10^3 / Flue gas flow(\frac{L}{hr}) \end{cases}} .10^3 \qquad (6.2)$$

Moreover, in some occasion the emissions are corrected to 4% oxygen concentration, which is calculated as:

Corrected concentration @ $4\% O_2 =$

Measured concentration ×
$$\left(\frac{4\% O_2 - Inlet O_2 \text{ concentration}}{Outlet O_2 \text{ concentration} - Inlet O_2 \text{ concentration}}\right)$$
 (6.3)

6.2.3. Analytical measurements

The major inorganics in ashes were determined by ICP-AES (inductively coupled plasma – atomic emissions spectrometry) following borate fusion and acid dissolution according to the standard method AS 1038.14.1.

Both trace elements - arsenic and selenium in the solid residue were analysed according to the standard method AS 1038.10.2, chromium was determined according to the standard method AS 1038.10.1, whereas mercury was determined according to the standard method AS 1038.10.5.

Scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) system in model JEOL 7001F was used to investigate the morphology and structure of fly ash and bed samples. The SEM images were taken under a working distance of 6 mm and an accelerating voltage of 5 kV.

The crystalline mineral phases in ashes are analysed by X-Ray diffraction (XRD), using a Rigaku miniflex600 XRD model, at voltage of 40 kV and a current of 15 mA. The XRD patterns are collected at 2 θ values in the range of 2° – 90° with stepping intervals of 0.02° and a count time per step of 4 s. The qualitative analysis of XRD patterns are conducted using MDI Jade 5.0 software.

6.2.4. Thermodynamic equilibrium prediction

The thermodynamic equilibrium software, FactSage 6.2, was employed to predict theoretically the flue gas composition, ash composition, possible agglomerating compounds and the trace element speciation during combustion of Victorian brown coal under different conditions. To simulate typical gas compositions entering into the reactor in oxy-fuel combustion conditions, a mixed gas containing CO_2 , 2% excess O_2 , steam, N_2 , HCl and SO_2 were used for the calculation. In case of air combustion, 6% excess oxygen assumed to be present in the flue gas. The information of different combustion atmospheres used in this study is given in Table 6.2. All calculations were performed using air/gas mixture and 1 kg of dry coal as input. These inputs were processed over the temperature range 800°C to 1400°C, at 100°C intervals, and at atmospheric pressure.

Atmosphere	O ₂	N_2	CO ₂	H ₂ O	HCl	SO ₂
Air combustion	21	79	-	-	-	-
Oxy-fuel combustion 1	10.23	0.54	74.23	15	-	-
Oxy-fuel combustion 2	10.23	0.4	74.23	15	0.04	0.1
Oxy-fuel combustion 3	10.23	0.2	74.23	15	0.24	0.1

 Table 6.2: Coal combustion atmospheres used for equilibrium calculations (vol.%)

A key assumption in modelling is that in the combustor, all phases are well mixed and reach thermal and chemical equilibrium. The amounts for each category and the overall amount of gas used as inputs were selected from the FACT53 and FToxid databases inbuilt in FactSage.

6.3. **RESULTS AND DISCUSSION**

Here experimental results from the small scale fluidized bed quartz reactor under different combustion conditions are presented first. It is followed by the experimental results from the 10 kW_{th} fluidized bed combustor.

In the following subsections, the combustion performance of Victorian brown coal under oxy-fuel fluidized bed combustion conditions is discussed. These results from oxy-fuel combustion are also compared with that from air combustion.

6.3.1. Fluidized bed quartz reactor

The results from preliminary laboratory scale experiments, carried out using a fluidized bed quartz reactor, are discussed in this section. Results are presented first for an assessment of the influences of oxygen, carbon dioxide and steam concentrations in oxidant, and temperature on the flue gas resulted from combustion. It is followed by an assessment of the effects of oxygen and steam concentrations in the combustor, and temperature on trace elements retention under different combustion conditions.

6.3.1.1. Flue gas analysis

The flue gas characteristics are very important for the operation of Oxy-FB combustion technology using different types of coals. During experiment, the generated gases from combustion were analysed continuously using a micro gas chromatograph (Agilent GC 490).

In this section, the effects of oxygen and steam in feed gas, and temperature on the flue gas CO_2 concentration obtained during the fluidized bed combustion of the considered Victorian brown coal under oxy-fuel combustion conditions are described. It is noted that during these combustion experiments, no CO, H_2 and CH_4 was detected in the gas analyser.



Figure 6.6: Concentration profiles of CO₂ and O₂ under different combustion environments at 850°C

The CO₂ and O₂ concentrations in dry flue gas under different combustion atmospheres are shown in Figure 6.6. These experiments were conducted at the same bed temperature of 850°C. The experiments showed clearly that the CO₂ concentrations in flue gas were much higher in oxy-fuel combustion condition than in air condition, as expected. Around 15% CO₂ was observed in dry flue gas during air combustion, whereas more than 80% CO₂ was found under oxy-fuel combustion condition. The experimental results also indicate that the addition of steam in the combustion environment resulted in high CO₂ concentration in the flue gas. Around 92-94% CO₂ in the dry flue gas was noticed using 21% O₂ + 67% CO₂ + 12% H₂O in oxy-fuel combustion atmosphere. It is evident from the comparison of the air and oxy-condition runs that the contribution from steam addition resulted in an equivalent increase in CO₂ concentration.

Combustion temperature also plays an important role in oxy-fuel combustion. In pilot scale oxy-fuel combustion, the optimum combustion temperature is maintained by mixing oxygen with steam through recycled flue gas. The effect of bed temperature on the CO_2 and O_2 concentrations in the flue gas during oxy-fuel combustion of Victorian brown coal with 30% oxygen concentration in the combustion atmosphere is shown in Figure 6.7. The results indicate that the CO_2 concentration in flue gas increased slightly with the bed temperature for the cases examined. This is due to the higher carbon consumption rate at higher bed temperature, as discussed in Section 4.3.2.2.



Figure 6.7: Concentration profiles of CO₂ and O₂ at different bed temperatures in oxy-fuel combustion condition (30% O₂ + 70% CO₂)

6.3.1.2. Trace elements emissions measurement and prediction

The entire batch of ash samples collected from experiments were analysed to find out the trace elements retention in ash after combustion. In the following subsections, the retention of chromium (Cr), arsenic (As) and selenium (Se) in the ash samples generated from fluidized bed combustion of Yallourn coal under different combustion conditions are presented. The effects of oxygen and steam in the combustion atmosphere, and bed temperature on these trace elements retention are investigated.

FactSage thermodynamic equilibrium modelling was also employed to predict theoretically the trace element distribution during combustion of Victorian brown coal under different conditions to compare with the experimental results. All calculations were performed using air/gas mixture and dry coal as input. These inputs were processed under the same operating conditions (i.e. temperature and pressure) used in the experiments.

6.3.1.2.1. Chromium

Chromium is one of the most important trace elements in coal. Hexavalent chromium (Cr^{6+}) is more toxic than trivalent chromium (Cr^{3+}) . The inhalation exposure to Cr^{6+} can increase the risk of lung cancer (EPA, 2011).



Figure 6.8: Experimental and predicted levels of chromium in collected ash at various oxygen concentrations under oxy-fuel combustion conditions at 850°C

With increase in oxygen concentration in the feed gas, chromium concentration in ash sample was observed to increase, as shown in Figure 6.8. This finding is consistent with the observation by Chen et al. (2012a), who also found higher chromium retention in fine ashes at higher oxygen concentration during oxy-fuel combustion atmosphere. In case of coarse ashes, however, the reverse trend was observed in their study.



Figure 6.9: Experimental and predicted levels of chromium in collected ash under oxy-fuel combustion condition (30% O₂ + 70% CO₂) at different temperatures

Figure 6.9 shows the concentration of Cr retained in ash, as a function of temperature, during the oxy-fuel fluidized bed combustion of Yallourn coal. It can be observed that the measured concentration of chromium in ash residue increased with increase in temperature.

As shown in Figures 6.8 and 6.9, the thermodynamic predictions indicated the same trends of experimental results in case of chromium, and the predicted results in ash content were higher than from the ones measured. According to the prediction, most of the chromium retained in solid phase over the temperature range studied, in-line with the experimental measurements.

The experimental results indicated that a maximum 25% of chromium was emitted into the atmosphere, obtained by difference of what was retained in the ash. This observation is supported by Liu et al. (2006), who found Cr_2O_3 (s) as the dominant Cr-species at temperature below 1000°C. It is thus apparent that within this temperature range, emissions of gaseous Cr-species would be negligible.

6.3.1.2.2. Arsenic

Arsenic is a toxic trace element which affects the gastrointestinal tract, circulatory system, liver, kidney and skin. Inorganic arsenic exposure in human is strongly associated with lung cancer, while ingestion of inorganic arsenic in human can cause skin cancer (EPA, 2011). The toxicity of arsenic is dependent on the oxidation state of the arsenic species present - As^{3+} is significantly more toxic than As^{5+} (Nelson et al., 2010).



Figure 6.10: Experimental and predicted levels of arsenic in collected ash at various oxygen concentrations under oxy-fuel combustion condition at 850°C



Figure 6.11: Experimental and predicted levels of arsenic in collected ash at 850°C with and without steam under oxy-fuel combustion conditions

The experimental results showed that with increase in O_2 concentration in the feed gas, arsenic was observed to increase in ash samples, as shown in Figure 6.10. From Figure 6.11, it can be noticed that steam decreased the extent of arsenic retention in ash. The level of arsenic was lower in the combustion environment in presence of steam than in presence of N_2 while the concentrations of O_2 and CO_2 in combustion atmosphere were held constant. In the thermodynamic calculation, no variation was predicted with increase in oxygen and steam concentrations in case of arsenic, and the predicted results in ash content were higher than from the ones measured. This reveals that As retention is mostly dependent on coal composition.



Figure 6.12: Experimental and predicted levels of arsenic in collected ash under oxy-fuel combustion condition (30% O₂ + 70% CO₂) at different temperatures
As shown in Figure 6.12, it can be noticed that the measured concentration of arsenic in ash residue increased slightly with increase in temperature, as shown in Figure 6.12. This is due to the fact that at higher temperature the mineral matter interactions promoted the arsenic retention in ash, in the formation of calcium arsenate in presence of CaO, according to the following reaction (R6.2).

$$3CaO + As_2O_3 + O_2 \rightarrow Ca_3(AsO_4)_2$$
 (R6.2)

In another experimental study utilizing bituminous coal, Shah et al. (2008) also observed the presence of calcium arsenate as the main arsenic species in fly ash, according to the reactions (R6.3) and (R6.4).

$$3CaO + \frac{1}{2}As_4O_6(g) + O_2 \rightarrow Ca_3(AsO_4)_2$$
 (R6.3)

$$3CaO.SiO_2 + \frac{1}{2} As_4O_{6(g)} + O_2 \rightarrow Ca_3(AsO_4)_2 + 3SiO_2$$
 (R6.4)

Since the Yallourn coal is rich in iron and calcium contents (as shown in Table 3.1), so there is a possibility in the formation of arsenates, such as $FeAsO_4$ and $Ca_3(AsO_4)_2$ due to the interaction with mineral matter within the range of temperature studied.

The thermodynamic calculation also predicted calcium arsenate, $Ca_3(AsO_4)_2$ (s) as the dominant arsenic species in ash. The predictions indicated the same trends of experimental results in case of arsenic, as shown in Figure 6.12. According to the prediction, most of the arsenic retained in solid phase over the temperature range studied. More than 90% of arsenic was predicted to remain in ash, with the rest (approximately 10%) to have been vaporized.

6.3.1.2.3. Selenium

Selenium is considered one of the most volatile trace elements in coal (Yan et al., 2000). The toxicity of selenium compounds depend on its oxidation state (Nelson et al., 2010). Se^{4+} is reported to be more toxic than Se^{6+} . Acute (short-term) exposure to selenium dioxide (SeO₂) causes irritation of the mucous membranes, and severe bronchitis and bronchial pneumonia (EPA, 2011).



Figure 6.13: Concentration of selenium in collected ash at various oxygen concentrations under oxy-fuel combustion conditions at 850°C

Selenium concentration was found to decrease in ash sample with increase in oxygen concentration in the feed gas consisting of O_2/CO_2 mixture, as shown in Figure 6.13. In presence of steam, however, reverse trend was observed. With increase in oxygen concentration in the feed gas consisting of $O_2/CO_2/H_2O$ mixture, selenium was found to increase in ash, and thereby decrease the extent of vaporization.

The addition of steam in to the combustion environment lowered the selenium retention in ash, as is seen in Figure 6.13. The possible reason of this was given by Wang et al. (2014a), who found lower trace elements concentration in particulate matter with the addition of H₂O. They reported that H₂O can increase the evaporation of mineral elements including trace elements. This finding, however, is different from the study by Furimsky (2000), who concluded that the presence of moisture in flue gas containing SeO₂ lowered the degree of vaporization due to the formation of selenious acid (H₂SeO₃). Based on these experimental results, it is evident that the presence of steam in the combustion atmosphere would affect the partitioning behaviour of selenium during Oxy-FB combustion.



Figure 6.14: Experimental levels of selenium in collected ash under oxy-fuel combustion condition (30% O₂ + 70% CO₂) at different temperature

However, no systematic trend was observed in the experimental results of selenium within the measured temperature range, as shown in Figure 6.14. The explanation of this behaviour could be due to the significant interaction between Se and other trace elements (in the formation of selenate or selenide), which could affect the Se partitioning (Yan et al., 2001). Up to 65% of selenium was found to be retained in the solid ash, with the rest (approximately 35%) was estimated to emit into the atmosphere.

Selenium is known to be one of the most volatile trace elements; this element was predicted to release only in the gas phase as SeO_2 (g) during the oxy-fuel combustion of Yallourn coal within the considered temperature range. This finding was also observed by Yashiie et al. (2014) during air combustion using pulverized bituminous coal. However, gaseous selenium dioxide is known to condense below 100°C. Therefore, in a commercial system, this species may condense on the ash particles and captured in the fabric filter.

All these findings have important implication for the selection of optimum operating parameters during scale-up using Victorian brown coal. In addition to the preliminary laboratory scale experiments using the fluidized bed quartz reactor, some bench scale experiments were also carried out in the 10 kW_{th} fluidized bed rig. The results from these set of experiments are discussed in the next section.

$6.3.2.\ 10\ kW_{th}$ fluidized bed combustor

In the following subsections, the combustion performance of Victorian brown coal under oxy-fuel fluidized bed combustion conditions is discussed. These results from oxy-fuel combustion are also compared with that from air combustion.

Results are presented first for evaluation of the effects of oxygen, carbon dioxide and steam concentrations in the combustor, and temperature on flue gas composition. It is followed by an assessment of combustion efficiency and ash characteristics under different combustion conditions, and finally the trace elements emissions are discussed.

In dry oxy-fuel experiment, the reacting gas composition consisted of $21\% \text{ v/v } O_2$ and 79% v/v CO₂, and in wet oxy-fuel experiment, the reacting gas consisted of $12\% \text{ v/v } H_2O$ balanced by O₂ and CO₂ (as shown in Table 6.1) unless it is specified.

6.3.2.1. Flue gas analysis

The flue gas composition depends on several factors, such as oxygen, carbon dioxide and steam concentrations in oxidant, temperature, and coal properties. Therefore, the generated gases were monitored continuously through an on-line gas analyser for different operating conditions. It is noted that in this section all concentrations of gaseous species are expressed on a dry flue gas basis.

6.3.2.1.1. Carbon dioxide

In this section, the effects of oxygen and steam concentration in feed gases, and combustion temperature on the flue gas CO_2 concentration are described. It is noted that no CO, H_2 and CH_4 was detected in the gas analyser during these combustion experiments.

Effect of oxygen concentration

Figure 6.15 shows the concentrations of CO_2 along with excess O_2 in dry flue gas from the oxy-fuel fluidized bed combustion, as a function of oxygen concentration in oxidant. These experiments were conducted at bed temperature of 840°C. As the oxygen concentration in the combustion environment increases, the CO_2 concentration in flue gas was found to increase, as expected.



Figure 6.15: Concentration profiles of CO₂ and O₂ under different oxy-fuel combustion environments

About 6% v/v additional CO₂ (total outlet CO₂ – inlet CO₂) was generated during the oxy-fuel combustion using 15% v/v oxygen in feed gas, whereas 8% and 12% v/v CO₂ was produced using 21% and 30% v/v oxygen in feed gas respectively under oxy-fuel combustion condition (Figure 6.16). This is due to the fact that the carbon burnout ratio to CO₂ and CO increased with increase in oxygen concentration in the feed gas mixture into the combustion chamber, in line with the observation by Czakiert et al. (2006) using a laboratory scale circulating fluidized bed combustor. They concluded that increase in oxygen partial pressure increases combustion rate, and thereby carbon conversion ratio. Similar concentration level of CO₂ was observed in Section 6.3.1.1 with 30% oxygen concentration in the combustion atmosphere during oxy-fuel combustion of Yallourn coal.



Figure 6.16: Concentration of generated CO₂ under different oxy-fuel combustion environments

Effect of steam

In oxy-fuel combustion, steam is an important component in the flue gas as well as in the feed gas. In commercial scale plant, steam will be introduced to the reactor through recycled flue gas. In this study, the oxy-fuel experiments were carried out in a once-through reactor, where the flue gas recirculation is simulated by using CO_2 from cylinder mixed with steam from a steam generator. It can be observed that the CO_2 concentration in flue gas increases with increase in steam concentration in combustion atmosphere, as shown in Figure 6.17. All these experiments were carried out using similar oxygen flow rate and at similar reactor temperature.



Figure 6.17: Concentration profiles of CO₂ and O₂ under different oxy-fuel combustion environments with and without steam

Without steam, around 6% v/v CO_2 (total outlet CO_2 – inlet CO_2) was generated during the dry oxy-fuel combustion, while approximately 11% and 16% v/v CO_2 was produced using 4% and 10% v/v H₂O respectively balanced by O₂ and CO₂ in feed gas (Figure 6.18).



Figure 6.18: Concentration of generated CO₂ under different steam concentration in oxyfuel combustion

The higher amount of CO_2 in presence of H_2O in the oxy-fuel atmosphere can be explained by the steam gasification to produce CO and H_2 initially, according to the following reaction (R6.5) between carbon and steam (Taylor and Neville, 1921; Ahmed and Krumpelt, 2001).

$$C + H_2 O \to CO + H_2 \tag{R6.5}$$

Subsequently, in the presence of excess oxygen and steam in the system, the generated carbon monoxide further undergoes the carbon monoxide oxidation reaction and the water-gas shift reaction to produce CO_2 according to the reactions (R6.6) and (R6.7) respectively.

$$CO + \frac{1}{2}O_2 \to CO_2$$
 (R6.6)

$$\mathrm{CO} + \mathrm{H}_2\mathrm{O} \to \mathrm{CO}_2 + \mathrm{H}_2 \tag{R6.7}$$

The carbon monoxide oxidation reaction is quite fast and favourable at this temperature. In contrast, it is unlikely that the water-gas shift reaction happens at this low temperature without any catalyst. So it can be said that the presence of steam increases the amount of CO which in turns promotes the formation of CO_2 according to CO oxidation reaction.

Another possible reason of higher amount of CO_2 could be the higher particle temperature in presence of steam in the combustion atmosphere which in turns increased the carbon consumption rates, as discussed in Section 4.3. These results have practical implication on choosing the flue gas recirculation options - dry or wet.

Effect of temperature

The effect of bed temperature on the flue gas CO_2 concentration during oxy-fuel combustion is shown in Figure 6.19. In these oxy-fuel experiments, the reacting gas composition consisted of 15% v/v O_2 and 85% v/v CO_2 . The results indicate that at the same oxygen concentration in feed gas into the reactor, bed temperature does not have any significant influence on CO_2 concentration in flue gas, for the cases examined. This finding is also supported by Czakiert et al. (2006), who found no effect on the carbon burnout ratio to CO_2 with the variation in reactor temperature, irrespective of the oxygen concentration in the combustor. However, this observation is different from the previous observation in Section 6.3.1.1 showing higher CO_2 concentration at higher bed temperature, presumably due to the narrow temperature ranges studied in this 10 kW_{th} fluidized bed rig.



Figure 6.19: Concentration profiles of CO₂ and O₂ under oxy-fuel combustion condition at different bed temperatures

6.3.2.1.2. Sulphur oxides

In this section, the effects of feed gas concentrations and combustion temperature on SO_2 as well as SO_3 emissions are discussed. Here in all cases, the first figures are shown in concentration units, whilst the latter figures are shown in normalized emission per energy unit.

Effects of carbon dioxide and steam

The sulphur oxides emissions using Loy Yang coal under different combustion atmospheres are compared in Figure 6.20. All these experiments were conducted at the same bed temperature of 850°C.



Figure 6.20: Sulphur oxides emissions in (a) ppm and (b) mg/MJ under different combustion environments

It can be seen that compared to air combustion, SO_x concentrations are higher (SO_2 by 33% and SO_3 by 7%) in dry oxy-fuel combustion, in common with several literature (Duan et al., 2009; Czakiert et al., 2010; Jia et al., 2010; Ahn et al., 2011; Fleig et al., 2011; Mitsui et al., 2011; Tan et al., 2012; Lupiáñez et al., 2013b). Fleig et al. (2011) concluded that due to the absence of airborne N_2 in oxy-fuel combustion, SO_2 concentration was higher which in turns increased the SO_3 concentration.

The experimental results also indicate that the addition of steam (even with same 15% v/v oxygen concentration in oxidant) in the combustion environment slightly reduces the SO₂ (by 1%) emission. This finding is consistent with the observations by Stewart et al. (2012), who reported that H₂O enhances the direct sulphation reaction under oxy-fuel combustion which in turn reduces the SO₂ emission in gas phase.

On the other hand, steam was found to increase the SO₃ formation by 7%. This increase in SO₃ emission in presence of steam was explained by Fleig et al. (Fleig et al., 2011; 2012a). The presence of steam increases the amount of OH-radicals, according to the reaction (R6.8). Therefore it promotes the formation of HOSO₂, according to reaction (R6.9) and then the formation of SO₃, according to reaction (R6.10).

 $H_2O + O \rightarrow OH + OH \tag{R6.8}$

 $SO_2 + OH (+M) \rightarrow HOSO_2 (+M)$ (R6.9)

$$HOSO_2 + O_2 \rightarrow SO_3 + HO_2 \tag{R6.10}$$

Effect of oxygen concentration

These experiments showed clearly that both sulphur dioxide and sulphur trioxide emissions significantly increased with the oxygen concentrations in feed gas, as shown in Figure 6.20. The SO₂ emission was increased by 72% from 321 mg/MJ to 552 mg/MJ, while the SO₃ emission was increased by 62% from 9 mg/MJ to 14.5 mg/MJ, from 15% (v/v) to 30% (v/v) oxygen concentration in combustion atmosphere. This finding is consistent with the observations on oxy-fuel combustion by many researchers (Czakiert et al., 2006; Duan et al., 2011b; Fleig et al., 2011; Fleig et al., 2012a). Duan et al. (2011b) reported that with increase in oxygen concentration in their experiments, the combustor temperature increased which promoted sulphur release in the gas phase. However, it

should be noted that increase of O_2 concentration does not always mean an increase of the combustor temperature.

Furthermore, it is noted that the measured SO₃ concentration levels in the flue gas were close to the observed SO₃ levels by other researchers (Krishnakumar and Niksa, 2011; Fujimori and Yamada, 2013) with the same coal-S level of 0.5% used in this study (Table 3.1). In this study, around 2 ppm SO₃ was observed using 21% oxygen concentration in the oxy-fuel combustion environment which was very close to the SO₃ concentration level of 3 ppm reported in the study by Krishnakumar and Niksa (2011). Moreover, around 2.5 ppm SO₃ was observed using 30% oxygen concentration in this study which was slightly lower than the SO₃ concentration level of 4 ppm presented in the study by Fujimori and Yamada (2013), presumably due to the highest oxidant level of 35% in their study.

In the present study using Loy Yang coal in oxy-fuel fluidized bed combustion, maximum 125 ppm SO₂ concentration was observed which is much lower than the level from oxy-fuel pulverized fuel combustion. Using Canadian lignite in a 0.3 MW_{th} test facility, Tan et al. (2006) observed 785 ppm SO₂ in oxy-fuel pulverized fuel combustion which was significantly higher than the present study. So, it can be stated that SO₂ emission is lower in oxy-fuel fluidized bed combustion compared to the oxy-fuel pulverized fuel combustion. Maximum 656 mg/m³ @ 4% O₂ concentration of SO₂ was observed in the flue gas, which was well within the permissible SO₂ emission limit of 7200 mg/m³ in coal-fired power plants in Australia (IEA). Therefore, additional SO₂ removal system (such as flue gas desulphurization unit or scrubber) may not need during oxy-fuel fluidized bed combustion using this low-sulphur brown coal.

6.3.2.1.3. Nitrogen oxides

The effects of oxygen and steam concentrations, and bed temperature on N_2O and NO_X (both NO and NO_2) emissions are discussed in this section. Here in all cases, the first figures are shown in concentration units, whilst the latter figures are shown in normalized emission per energy unit.

Effect of steam

The nitrogen oxides emissions using Loy Yang coal under different combustion atmospheres are compared in Figure 6.21. All these experiments were conducted at almost the same bed temperature, at around 850°C.



Figure 6.21: Nitrogen oxides emissions in (a) ppm and (b) mg/MJ under different combustion environments

It can be seen that compared to air combustion NO_X emission are slightly lower (by 4%) in dry oxy-fuel combustion, in common with several literature (Tan et al., 2006; Jia et al., 2010; Yoshiie et al., 2011). This lower amount of NO_X formation in Oxy-FB combustion is for having zero nitrogen in the oxy-fuel combustion atmosphere (Zhao et al., 2010; Lupiáñez et al., 2013a). On the other hand, N₂O formation is higher (by 32%) in oxy-fuel

combustion compared to air combustion, also in-line with the observation by other researchers (Yoshiie et al., 2011). Yoshiie et al. (2011) also reported that by the recirculation of the flue gas, this N_2O concentration was further increased due to the accumulation of additional N_2O resulting from re-circulation.

The experimental results also indicate that the addition of steam (even with same 15% v/v oxygen concentration in oxidant) in the combustion environment promotes NO_X reduction (by 5.5%) and N₂O formation (by 10%). These findings are consistent with the observations by several researchers (Hosoda et al., 1998; Stewart et al., 2012). Steam is known to influence the HCN formation by its reaction with char-N, and simultaneously lowers the NO_X formation by those char-N and O₂ (Hosoda et al., 1998). However, HCN is also known to convert into N₂O, according to the following reactions (R6.11)-(R6.12) (Kilpinen and Hupa, 1991), as a result N₂O formation increases with steam. Maximum 200 ppmv NO_X and 20 ppmv N₂O was observed using 12% v/v steam in oxy-fuel combustion atmosphere.

$$HCN + 0 \rightarrow NCO + H \tag{R6.11}$$

$$NCO + NO \rightarrow N_2O + CO \tag{R6.12}$$

Effect of oxygen concentration

These experiments also showed clearly that the NO_X emission increased with the O₂ concentration in feed gas for both nitric oxide and nitrogen dioxide, as shown in Figure 6.21. The NO_X emission significantly increased by 74% from 350 mg/MJ to 610 mg/MJ, when the oxygen concentration increased from 15% (v/v) to 30% (v/v) in the combustion atmosphere. This finding is consistent with the observations on oxy-fuel fluidized bed combustion by other researchers (Duan et al., 2011a; Lupiáñez et al., 2013a; Lupiáñez et al., 2013b) working with different coals. This is due to the fact that as the oxygen concentration increases, the residence time of the fuel particles in the combustor becomes longer, which promotes the fuel-N to NO_X conversion (Duan et al., 2011a). They also concluded that excess oxygen is the main variable controlling the NO_X formation in both air and oxy-fuel combustion.

In this study, the emission of N_2O was found to increase slightly with the oxygen concentration, as shown in Figure 6.21. The nitrogen dioxide emission increased by 12%

from 59 mg/MJ to 66 mg/MJ, when the oxygen concentration increased from 15% (v/v) to 30% (v/v) in the combustion atmosphere. This increase in N₂O emission with increase in inlet oxygen concentration is due to the higher conversion of volatiles (such as HCN) to N₂O, according to reactions (R6.11)-(R6.12) (de Diego et al., 1996).

Effect of bed temperature

The effect of bed temperature on nitrogen oxides emissions is shown in Figure 6.22. All these experiments were conducted at the same oxygen concentration (15% v/v and balanced by CO_2) in feed gas.



Figure 6.22: Effect of bed temperature on nitrogen oxides emissions in (a) ppm and (b) mg/MJ

In fluidized bed combustion, the NO_X emission is known to increase with bed temperature (de Diego et al., 1996; Duan et al., 2011a; Lupiáñez et al., 2013a). However, a reverse trend was observed for the temperature ranges used in this study. Several studies (Hayhurst and Lawrence, 1996; Lupiáñez et al., 2013b) also did not find any clear trend on NO_X measurement with temperature in fluidized bed combustion attributing this to the fact the NO_X formation is mainly influenced by oxygen partial pressure in the surrounding of the burning particle and type of coal rather than the bed temperature.

 N_2O emission was found to decrease with increase in bed temperature, supporting the observations in previous literature (de Diego et al., 1996; Hayhurst and Lawrence, 1996), which reported that the nitrous oxide emission is mainly influenced by operating temperature.

The N₂O emission decreased by 26% from 82 mg/MJ to 60 mg/MJ, when the bed temperature increased from 820°C to 880°C These lower N₂O emission at higher temperature is due to the decomposition of N₂O, according to the following reactions (R6.13)-(R6.17) (Hayhurst and Lawrence, 1996). An increase in bed temperature increases the rates of these reactions as well as increases the concentrations of H and OH radicals which are important intermediates in the N₂O decomposition.

$$N_2O + H \rightarrow N_2 + OH \tag{R6.13}$$

$$N_2O + OH \rightarrow N_2 + HO_2 \tag{R6.14}$$

$$N_2O + M \to N_2 + O + M$$
 (R6.15)

$$N_2 0 + 0 \rightarrow N_2 + 0_2$$
 (R6.16)

$$N_2 0 + 0 \rightarrow 2N0 \tag{R6.17}$$

In this study using Victorian brown coal in oxy-fuel fluidized bed combustion, maximum 228 ppm NO was observed which is much lower than the level from oxy-fuel pulverized fuel combustion of other lignites. Using Canadian lignite with the coal-N level of 1% in a 0.3 MW_{th} test facility, Tan et al. (2006) observed 555 ppm NO in oxy-fuel pulverized fuel combustion which was considerably higher than in the present study with the coal-N level of 0.72%. Maximum 0.68 g/m³ @ 4% O₂ concentration of NO_X was observed in the flue gas, which was within the allowable NO_X emission limit of 0.78 g/m³ in coal-fired power plants in Victoria, Australia (IEA). Therefore, additional NO_X removal system (such as

selective catalytic reduction or low- NO_X burner) will not be required during oxy-fuel fluidized bed combustion using this coal.

6.3.2.2. Combustion efficiency

After each experiment, the unburned char, ash and bed samples were collected from the two cyclone pots and the fluidized bed when these cooled down to room temperature. All collected samples were then burnt at 800°C for three hours in a muffle furnace to find out the unburnt carbon contents in the solid samples and to calculate the combustion efficiency. During the oxy-fuel combustion runs, no carbon content was observed in the bed ash, whereas in fly ash carbon content ranged from 0.95% to 2.2%. This higher carbon content in fly ash is due to the relatively short residence time for fine coal particles in the small-scale fluidized bed unit (Wu et al., 2011). In this section, the effects of oxygen, carbon dioxide and steam concentration in oxidant, and reactor temperature on combustion efficiency are described.

Effect of oxygen concentration

The combustion efficiencies using Loy Yang coal under different combustion atmospheres are compared in Figure 6.23. All these experiments were conducted at similar combustor temperature. With increase in O_2 concentration in the feed gas, combustion efficiency was observed to increase, supporting the observation by Duan et al. (2011b). This is due to the increased carbon combustion rate by the increase in oxygen partial pressure (Czakiert et al., 2006).





Effects of carbon dioxide and steam

The results also indicate higher combustion efficiency in dry oxy-fuel atmosphere than in air combustion. This finding is in-line with the study by Riaza et al. (2011), who burned a semi-anthracite and a bituminous coal in an entrained flow reactor. They found improved coal burnout under dry oxy-fuel combustion with 30% and 35% oxygen concentrations relative to that in air combustion.

It was also observed that combustion efficiency decreased with the addition of steam in the combustion atmosphere. This finding is also supported by Riaza et al. (2011), who concluded that with the addition of steam in oxy-fuel combustion atmosphere lowered the coal burnout. On the other hand, Hosoda et al. (1998) observed almost same combustion efficiency under both air combustion and oxy-fuel combustion condition with 21% oxygen with the presence of steam through flue gas recirculation. It is noted that they used bituminous coal in their study.

Effect of temperature

Figure 6.24 shows the combustion efficiency as a function of reactor temperature. In these experiments, the reacting gas composition consisted of $15\% \text{ v/v } O_2$ balanced by CO₂. It was observed that higher bed temperature resulted in higher combustion efficiency. This finding is also supported by Duan et al. (2011b), who reported that lower bed temperature resulted in low combustion efficiency.





Some experiments were also conducted to examine the effect of steady-state combustion period on efficiency. It was observed that irrespective of coal type, gas velocity, oxygen concentration and bed temperature in the reactor, the combustion efficiency increases with steady-state period. So it is evident that in commercial scale CFB boilers with char recirculation in long runs, much higher combustion efficiency would be expected.

6.3.2.3. Ash characteristics

After each experiment, the fly ash and bed samples were collected for characterization and analysis, from the two (primary and secondary) cyclone pots, and the fluidized bed respectively. In this section, the characteristics of these generated ashes are discussed.

6.3.2.3.1. Size distribution of fly ash and bed material samples

The size distribution of these bed material and cyclone pot samples is dependent on various factors - coal type, particle size of feed materials and operational parameter like gas velocity and temperature. Figure 6.25 shows the typical particle size distributions of fly ashes and bed materials from the tests under different combustion. In dry oxy-fuel experiment, the reacting gas composition consisted of $21\% \text{ v/v } O_2$ and $85\% \text{ v/v } CO_2$. However, in wet oxy-fuel experiment, the reacting gas consisted of $15\% \text{ v/v } O_2$, $73\% \text{ v/v} CO_2$ and $12\% \text{ v/v } H_2O$. It was observed that the size distribution of the collected samples under oxy-fuel combustion condition is almost similar to that under air combustion. This finding is in line with the previous observations by others (Wall et al., 2009; Yu et al., 2011), who did not find any significant difference in ash particle size distributions from air and oxy-fuel combustion.

No bed agglomeration was observed under oxy-fuel combustion condition during the period of the tests, except the presence of a small quantity (around. 2% of total bed material) of bed materials coated with ash minerals. The particle size of these samples was between 0.5 mm and 3 mm. The mere presence of these did not induce bed agglomeration during the test period.



Figure 6.25: Particle size distributions of (a) primary cyclone ash, (b) secondary cyclone ash and (c) bed materials under different combustion

Some thermodynamic predictions were also performed to predict the amount of total solid ash and molten ash formed during Oxy-FB combustion using Victorian brown coal over a temperature of 800°C to 1000°C at 50°C intervals. The total quantity of ash was predicted to remain almost constant up to 950°C, after that temperature these quantities were predicted to decrease with increase in temperature. Using Loy Yang coal, the solid ash represented 95% of the total mass between 800°C and 950°C, with the rest (approximately 5%) were predicted to have been vaporized. After 950°C, however, small amounts of liquid phases (10%) were predicted to form, which resulted in a small drop in the solid ash content. This prediction was completely supported by the finding of the experimental study.

Therefore, it is expected that agglomeration is unlikely to be a major problem for this Victorian brown coal in oxy-fuel fluidized bed combustion, if the operating temperature is kept below 950°C. However, longer duration experiments are recommended to ascertain the true propensity of agglomeration.

6.3.2.3.2. Scanning Electron Microscopy analysis

The morphology of ash particles depend on mainly combustion temperature and cooling rate (Kutchko and Kim, 2006). Figure 6.26 shows the typical scanning electron microscopy (SEM) images of the ash samples collected from bed, primary and secondary cyclone separators. The images A, C and E are at lower magnification for bed material, primary cyclone sample and secondary cyclone sample respectively, whereas B, D and F are at higher magnification for the same.

The ash mineral from bed does not appear to be disintegrated, whereas the fly ash from cyclone separators appears porous due to the release of trapped volatiles during coal combustion resulting to form hollow cenosphere. Moreover, compared to the secondary cyclone ashes, the primary cyclone ashes were more porous. It can be seen clearly that the fly ash particle size from primary cyclone is much higher than those from secondary cyclone.



Figure 6.26: SEM images of ash minerals from bed, primary cyclone sample and secondary cyclone sample after oxy-fuel combustion condition using Loy Yang coal (Images A, C and E are at lower magnification of 40-50×, and B, D and F are at higher magnification of 500-1500×)

Figures 6.27 and 6.28 show the SEM images of the coarse (>250 μ m) and fine (<20 μ m) fly ashes collected from primary cyclone. The images A are at lower magnification, whereas B, C and D are at higher magnification. In these experiments, the reacting gas composition consisted of 15% v/v O₂, 12% v/v H₂O and balanced by CO₂. The bed temperature was around 860°C.



Figure 6.27: SEM images of coarse ashes (> 250 μm) from primary cyclone after oxy-fuel combustion condition using Loy Yang coal (Images A is at lower magnification of 50×, and B, C and D are at higher magnification of 150-270×)

It can be seen that the coarse particles (Figure 6.27) were mostly in irregular shape. On the other hand, the fine ash particles were irregular (Figure 6.28B) shaped unburnt carbon particles from the upper end of the particle size distribution, aggregate-like (Figure 6.28C) particles due to the inter-particle contact during the fragmentation of burning char particles as well as spherical (Figure 6.28D) shaped particles due to the rapid cooling of condensed particles in the char particle boundary layer (Kutchko and Kim, 2006; Sheng et al., 2007).



Figure 6.28: SEM images of fine ashes (< 20 μm) from primary cyclone after oxy-fuel combustion condition using Loy Yang coal

(Images A is at lower magnification of 300×, and B, C and D are at higher magnification of 2000-8000×)

Overall, majority of the particles were found in irregular shape with a small amount of spherical and aggregate-like particles indicating slightly lower overall combustion temperature (Sheng et al., 2007).

6.3.2.3.3. Analysis of ash samples

For ash analysis, the fly ash samples collected from two cyclone pots were first burnt at 800° C for three hours in a muffle furnace to remove the unburnt carbon. In the bed samples, however, no unburnt carbon was observed. It is noted that in case of bed ashes, the analysis was done on bed coatings. The coated bed materials were separated from uncoated bed materials by careful sieving, and only the large particles in the 1-2 mm range was chosen, and then ground below 200 μ m for analysis.



Figure 6.29: Comparison of (a) primary cyclone ash, (b) secondary cyclone ash and (c) bed ash under different combustion environments

The chemical composition of bed ash and fly ash samples under different combustion atmospheres are compared in Figure 6.29. Loy Yang coal is known to be rich in SiO₂ and Al₂O₃, and so these were found as the dominant species in the sampled materials. However, no significant difference of composition was observed in the sampled bed materials generated during air and oxy-fuel combustion, supporting the observation by Yu et al. (2011), who found similar chemical composition in bulk ashes from air- and oxyfired experiments. It is known that the release of the compounds of Ca, Mg, Fe and S from coal minerals and their physical interaction with bed materials causes bed agglomeration (Bhattacharya and Harttig, 2003). From Figure 6.29, it is evident that majority of these elements were retained in the elutriated fly ashes and so lowered the possibility of bed agglomeration. The results indicate that a maximum 6% and 3.5% of coal-S were retained in the fly ashes under air and oxy-fuel combustion respectively, whereas a small quantity (<1%) of S was retained in bed ashes under both conditions. Compared to air combustion ashes, lower Ca and S were observed in bed ashes generated under oxy-fuel combustion. Retention of lower S-level in the bed ash is due to the production of higher levels of gaseous SO_2 and SO_3 in oxy-fuel combustion (Fleig et al., 2011). As stated later in section 6.3.2.3.4, Ca was mostly emitted as fine particles in the elutriated fly ash. Furthermore, it is known that S-retention in ash is dependent on alkali and alkaline earth metals, particularly on Ca in the ash minerals (Fleig et al., 2009). Therefore, in the bed ash from air combustion, higher S along with higher Ca was observed in the form of $CaSO_4$. It is also noticed that the sulphur concentration in secondary cyclone fly ash is slightly higher in the presence of steam in the oxy-fuel combustion atmosphere, compared to that in the oxy-fuel combustion atmosphere without steam. One possible reason of this could be the entrapped sulphur in wet ash at the relatively cooler temperature zone like cyclone separator, supported by the observation by Croiset and Thambimuthu (2001) who found sulphur to be trapped in the condensed water.



Figure 6.30: Comparison of (a) primary cyclone ash, (b) secondary cyclone ash and (c) bed ash under different oxy-fuel combustion environments

The fly and bed ash compositions are presented in Figure 6.30, as a function of oxygen concentration in feed gas. All these experiments were conducted using Loy Yang brown coal at almost the same bed temperature of 840°C. The results indicate that oxygen

concentration does not have significant impact on ash composition, except for slightly lower S-level in fly ash at higher oxygen concentration.



Figure 6.31: Comparison of (a) primary cyclone ash, (b) secondary cyclone ash and (c) bed ash under oxy-fuel combustion condition at different bed temperatures

Figure 6.31 shows the extents of inorganic elements in the bed and fly ashes, as a function of bed temperature. The reacting gas composition in these oxy-fuel experiments consisted of 15% v/v O_2 and 85% v/v CO_2 . It is also noticed that irrespective of feed gas concentration, reactor temperature does not have any considerable impact on ash composition, except for a small change in S in fly ash. S was found to decrease slightly with combustor temperature. As stated previously, release of coal-S to gaseous SO_2 and SO_3 increases with increase in temperature, consequently resulting in lower S-retention in ash.

6.3.2.3.4. X-Ray diffraction analysis

X-Ray diffraction (XRD) was performed to identify the crystalline species on the collected ash samples under different combustion conditions. It is to be noted that in case of bed ashes XRD was done only on the bed coatings. These bed coatings were separated from the bed material by first sieving to select the coarse particle size in the range of 1-2 mm. These coated bed materials were then carefully ground to dislodge the coatings, which were subjected to XRD analysis. Figure 6.32 presents the XRD spectra for the major crystalline species on bed coatings and fly ashes collected from a wet oxy-fuel combustion using Loy Yang coal. In this wet oxy-fuel experiment, the reacting gas composition consisted of $15\% \text{ v/v }O_2$, $73\% \text{ v/v }CO_2$ and $12\% \text{ H}_2\text{O}$. It is also observed that bed ash is more crystalline than fly ashes due to their longer residence time at higher temperature. This finding is in-line with the observation by other researchers, such as Wu et al. (2011).



Figure 6.32: XRD patterns of fly and bed ashes under wet oxy-fuel combustion

Table 6.3 shows XRD results for both bed coatings and fly ashes collected from different combustion conditions. All these ashes were generated at almost same bed temperature. Similar mineral phases are identified in the ashes from both air and oxy-fuel combustion. However, the relative peak intensities of these phases are varied. Similar results were observed by other researchers using different coals, such as that reported by Sheng et al. (2007), and Sheng and Li (2008) using pulverized coal samples in a drop tube furnace.

It can be seen that due to high SiO_2 content in Loy Yang coal, quartz was the main dominant phase in all ashes. Minor quantities of augite (silicates of Ca, Mg and Fe) were found in bed coatings. In bed coating, thenardite (Na₂SO₄) was also observed which indicates that most of the sodium retained in bed. Another interesting fact noticed from Table 6.3 is the presence of lime (CaO) and anhydrite (CaSO₄) mostly in fly ashes. This finding reveals that most of the calcium was confined in fine ashes, which implies the lower possibility of bed agglomeration (Bhattacharya and Harttig, 2003).

Combustion atmosphere	Sample description	Dominant	Sub-dominant	Minor phase	Trace phase
(% Volume)		phase	phase		
Air	Bed ash	Quartz		Augite	Wustite, Lime and Thenardite
	Primary cyclone ash	Quartz	Augite	Wustite, Lime and Spinel	
	Secondary cyclone ash	Quartz	Augite	Wustite and Lime	
15% O ₂ + 85% CO ₂	Bed ash	Quartz		Augite	Wustite and Lime
	Primary cyclone ash	Quartz		Augite and Lime	Wustite
	Secondary cyclone ash	Quartz		Wustite, Augite, Lime and Spinel	
21% O ₂ + 79% CO ₂	Bed ash	Quartz		Augite	Wustite, Lime and Thenardite
	Primary cyclone ash	Quartz		Wustite, Lime and Spinel	
	Secondary cyclone ash	Quartz	Augite	Wustite, Lime and Anhydrite	
30% O ₂ + 70% CO ₂	Bed ash	Quartz		Wustite, Augite and Thenardite	Lime
	Primary cyclone ash	Quartz		Wustite and Augite	Lime
	Secondary cyclone ash	Quartz	Augite	Wustite, Lime and Anhydrite	
15% O ₂ + 73% CO ₂ + 12% H ₂ O	Bed ash	Quartz		Augite and Lime	Wustite and Thenardite
	Primary cyclone ash	Quartz		Augite and Lime	Wustite
	Secondary cyclone ash	Quartz	Augite	Wustite and Lime	

Table 6.3: XRD analysis of bed and fly ashes under different combustion environments

Notes: Concentration of phases – dominant (>60%), sub-dominant (20-60%), minor (5-20%), and trace (<5%).

Quartz [SiO₂], Augite [(CaMgFe)Si₂O₆], Wustite [FeO], Lime [CaO], Thenardite [Na₂SO₄], Spinel [MgAl₂O₄], and Anhydrite [CaSO₄].

6.3.2.4. Trace elements emissions measurement and prediction

In this section, the trace elements emissions during oxy-fuel fluidized bed combustion using Victorian brown coal are discussed. The trace elements considered in the measurements are chromium (Cr), arsenic (As), selenium (Se) and mercury (Hg), as these are of greatest environmental and health concern (Vejahati et al., 2010). In the following subsections, the retention of Hg, Se, Cr and As in bed ash and fly ashes, and emission of gaseous Hg from the fluidized bed combustion of Loy Yang coal under different combustion conditions are presented. The effects of oxygen, carbon dioxide and steam concentrations in the combustor, and bed temperature on these trace elements emissions are investigated.

After experiments, the fly ash and bed samples were collected from two cyclone pots (primary and secondary), and fluidized bed respectively when these are cooled down to room temperature. For trace elements analysis, the fly ash samples, collected from two cyclone pots, were ashed at 500 °C for three hours in a muffle furnace to remove the unburned carbon. In case of bed samples, however, no unburned carbon was observed. The bed ashes were separated from bed material by sieving. The particle size in the range of 1-2 mm was chosen and then crushed into <200 μ m for analysis.

The extents of Cr, As, Se and Hg retention in collected ash samples from fluidized bed under different combustion atmospheres are compared in Figures 6.33, 6.37, 6.41 and 6.44. All these experiments were conducted at almost the same bed temperature of 840°C. The extents of trace elements in the bed and fly ashes from the oxy-fuel fluidized bed combustion, as a function of bed temperature, are presented in Figures 6.34, 6.38, 6.42 and 6.45. The reacting gas composition in these oxy-fuel experiments consisted of 15% $v/v O_2$ and 85% $v/v CO_2$.

In order to control the trace elements emissions during coal combustion, it is very important to know the species of those trace elements present in the sample. Therefore, thermodynamic predictions were also performed to predict the trace elements (Cr, As, Se and Hg) speciation during oxy-fuel combustion using Victorian brown coal over the temperature range from 800°C to 1400°C at 100°C intervals. The temperature range covers both oxy-fuel based circulating fluidized bed (Oxy-CFB) combustion and pulverized fuel (Oxy-PF) combustion. It is noted that only the species with an important

proportion (more than 1% v/v) of the total species at equilibrium are considered in this study. Based on the thermodynamic equilibrium modelling, the relative quantities of the major toxic trace element species during air and oxy-fuel combustion 1 conditions, and at different temperatures are compared in Figures 6.35, 6.39, 6.43 and 6.48. 100% on the vertical axis in all figures refers to the total amount of Cr/As/Se/Hg in the system.

The predicted possible trace elements species during oxy-fuel CFB combustion of three Victorian brown coals are listed in Table 6.4. For easy understanding, major toxic trace element species are shown in bold font.

Trace element	Species
Cr	$CrO_2(OH)_2$ (g), CrO_3 (g), CrO_2OH (g), $CrO(OH)_4$ (g), $CrO(OH)_3$ (g),
	$CrO(OH)_{2}$ (g), $CrOOH$ (g), $CrOH$ (g), $Cr(OH)_{2}$ (g), $Cr(OH)_{3}$ (g), $Cr(OH)_{4}$ (g),
	Cr(OH)5 (g), Cr(OH)6 (g), CrS (g), CrO2 (g), CrO (g), Cr (g), CrO2Cl2 (g),
	CrO ₂ Cl (g), CrOCl (g), CrOCl ₂ (g), CrOCl ₃ (g), CrOCl ₄ (g), CrCl (g), CrCl ₂
	(g), $CrCl_{3}$ (g), $CrCl_{4}$ (g), $CrCl_{5}$ (g), $CrCl_{6}$ (g), CrN (g), $(MgO)(Cr_{2}O_{3})$ (s).
As	As ₄ O ₆ (g), As ₂ O ₃ (slag), AsSe (g), AsN, AsS (g), As ₂ (g), AsH ₃ (g), As (g),
	$As_{3}(g), As_{4}(g), As_{2}Se_{2}(g), AsCl_{3}(g), As_{4}Se_{3}(g), As_{4}Se_{4}(g), Ca_{3}(AsO_{4})_{2}(s).$
Se	\mathbf{SeO}_{2} (g), \mathbf{H}_{2} Se (g), AsSe (g), SeS (g), Se (g), Se ₂ (g), SeO (g), PbSe (g), HgSe
	(g), As_2Se_2 (g), NSe (g), CSe (g), Se_3 (g), $SeCl_2$ (g), CSe_2 (g), Pb_2Se_2 (g), Se_4
	(g), As ₄ Se ₃ (g), Se ₅ (g), AlSe (g), SiSe (g), As ₄ Se ₄ (g), (g), SiSe ₂ (g), Se ₆ (g),
	TiSe (g), Se ₇ (g), Se ₈ (g), Al ₂ Se (g).
Hg	Hg (g), HgS (g), HgSe (g), HgO (g), HgCl (g), HgH (g), Hg ₂ (g), HgCl ₂ (g),
	$Hg(CH_{3})_{2}(g).$

Table 6.4: List of species containing the four trace elements considered in this work

Notes: g is the gaseous state; s is the solid state; slag is the slag-liquid compound.

6.3.2.4.1. Chromium

From Figure 6.33 it can be seen that compared to air combustion, the extent of Cr retention in the solid ash was lower (by 22%) in oxy-fuel combustion even at the same oxygen concentration (21% v/v). Around 35% of total coal-Cr was observed to retain in the collected ash in air combustion, whereas in oxy-fuel combustion maximum 27% of total coal-Cr was found to adsorb in the collected ash. This finding, however, is different

from the study by Wang et al. (2014a), who observed higher Cr adsorption under oxy-fuel combustion using a Chinese bituminous coal. From this experimental results using Victorian brown coal, it is also evident that steam in the combustion atmosphere did not affect the Cr vaporization. So, it can be said that Cr vaporization is highly dependent on coal composition.



Figure 6.33: Extents of Cr in bed and fly ashes from different combustion environments

With increase in O₂ concentration in the feed gas under oxy-fuel combustion, chromium was observed to decrease slightly in ashes, as shown in Figure 6.33. The Cr retention decreased by 7%, when the oxygen concentration increased from 15% (v/v) to 30% (v/v) in the combustion atmosphere. This finding is consistent with the observations by Chen et al. (2012a) and Wang et al. (2014a). They concluded that rapid oxidation of organic

chromium helped to vaporize the mobile Cr from the char surface.



Figure 6.34: Extents of Cr in bed and fly ashes under oxy-fuel combustion condition at different bed temperatures

Trace elements vaporization is known to be promoted at higher temperature. As shown in Figure 6.34, however, no significant difference was observed in Cr retention (and thereby vaporization) for the temperature ranges used in the experimental study. This finding is consistent with the observation by Chen et al. (2012a), who also found insignificant change in Cr vaporization with temperature above 600°C. This is due to the fact that the volatility of organically bound Cr is independent with temperature during char oxidation/combustion. However, this observation is different from the previous observation in Section 6.3.1.2.1 of increased Cr retention with increasing bed temperature. This difference could be due to the narrow temperature ranges studied in this 10 kW_{th} fluidized bed combustor.

The experimental results indicate that maximum 28% of total coal-Cr was found to retain in the collected ash, while the rest (approximately 72%) was predicted to emit to the atmosphere.



Figure 6.35: Equilibrium composition of major toxic Cr species during air and oxy-fuel combustion (Balance of 100% on the vertical axis are the other Cr-species)

According to the thermodynamic calculation, chromium was also predicted to be present in vapour phase as well as in solid phase over the entire range of temperature studied. Since hexavalent chromium (Cr^{6+}) is more toxic than the other forms of chromium, only the compositions of hexavalent chromium (Cr^{6+}) species are shown in Figure 6.35. The results indicate that the amount of toxic gaseous chromium (Cr^{6+}) species was greater for oxy-fuel combustion than for air combustion up to the temperatures at 1200°C. At higher temperatures, however, these amounts are lower for oxy-fuel combustion. This is due to the stable forms of other chromium species at high temperature.

It can also be seen that the amounts of toxic gaseous chromium oxyhydroxide species, $CrO_2(OH)_2$, is higher in oxy-fuel combustion compared to air combustion in the entire range of considered temperature. The higher amount of these species is due to the presence of water vapour in the oxy-fuel atmosphere, in line with the observations by Opila et al. (2007), who concluded that the water vapour in the atmosphere promoted the formation of volatile $CrO_2(OH)_2$ species, according to the following reaction (R6.18).

$$0.5Cr_2O_{3(s)} + 0.75O_{2(g)} + H_2O_{(g)} = CrO_2(OH)_{2(g)}$$
(R6.18)



Figure 6.36: Equilibrium distribution of chromium during oxy-fuel combustion using Loy Yang coal

In case of Loy Yang coal, the results predict that most of the chromium (around 85%) in the system would exist in the solid phase as (MgO)(Cr_2O_3) up to 1000°C, as shown in Figure 6.36. At temperatures from 1000°C to 1300°C, however, $CrO_2(OH)_2$ (g) is predicted to dominate along with small contributions of $CrO_2(OH)$ (g), $CrO(OH)_2$ (g), CrOOH (g) and CrO_3 (g). At temperatures above 1300°C, however, the volatile $CrO_2(OH)$ is predicted to be a predominant species. This is due to the fact that when a chromium containing material is exposed to oxygen and water vapour environment over a wide range of temperature, the volatile $CrO_2(OH)_2$ species is formed according to the reaction (R6.18) and/or the volatile $CrO_2(OH)$ species is formed according to the reaction (R6.19). The formation of the exact species depends on the partial pressure of water and oxygen. This was also observed by Ebbinghaus (1993).

$$0.5Cr_2O_{3(s)} + 0.5O_{2(g)} + 0.5H_2O_{(g)} = CrO_2(OH)_{(g)}$$
(R6.19)

As most of the gaseous chromium exists in the form of a toxic Cr^{6+} compound, gas cleanup system will be required. Since the low volatile Cr is mostly captured in fly ash, it should be keep in mind that the recovery of Cr in fly ash could be attributed to the erosion of the alloyed steel or stainless steel gas sampling probes in the combustor (Selçuk et al., 2006).

6.3.2.4.2. Arsenic

The experimental results showed that compared to air combustion, arsenic (As) adsorption in ash was significantly higher (by 82%) in oxy-fuel combustion at the same oxygen concentration of 21% (v/v), in common with the literature (Wang et al., 2014a). This could be attributed to the lower As vaporization due to the lower flame temperature under oxy-fuel atmosphere (21% $O_2/79\%$ CO₂) associated with relatively higher heat capacity of CO₂ compared to N₂ (Molina and Shaddix, 2007).



Figure 6.37: Extents of As in bed and fly ashes from different combustion environments

Moreover, the addition of steam (even with same 15% v/v oxygen concentration in oxidant) in the combustion environment was found to enhance (by 11.5%) the arsenic retention. This finding is in-line with the observations by Wang et al. (2014a), who also observed higher extent of total As in particulate matter due to the enhancement in the formation of particulate matter by H₂O. This observation, however, is different from the previous observation in Section 6.3.1.2.2.
The experimental results also showed that with increase in oxygen concentration in feed gas, the total As adsorption in ash was found to slightly decrease (by 13%), as indicated in Figure 6.37. This finding is supported by other researchers (Wang et al., 2014a), who also observed lower As concentration in fine ashes at higher oxygen concentration under oxy-fuel combustion. This observation is also different from the previous observation in Section 6.3.1.2.2 in small scale fluidized bed quartz reactor experiments using Yallourn coal. So, it can be said that arsenic retention is highly dependent on coal composition.



Figure 6.38: Extents of As in bed and fly ashes under oxy-fuel combustion condition at different bed temperatures

However, no systematic trend was observed for the temperature ranges used in the experimental study, as shown in Figure 6.38. So it is evident that bed temperature does not have any considerable effect on As volatilization, for the temperature range studied. From the experimental results, maximum 83% of arsenic was found to remain in ash, with the rest (approximately 17%) to have been vaporized. However, further experiments are recommended to identify the proportion of water leachable arsenic in ash sample in order to dispose these ash samples.



Figure 6.39: Equilibrium composition of major toxic As species during air and oxy-fuel combustion (Balance of 100% on the vertical axis are the other As-species)

Among the two major arsenic species, since As^{3+} is more toxic than As^{5+} , so only the compositions of As^{3+} species are shown in Figure 6.39. It can be observed that at low temperature (up to 900°C) the toxic arsenic (As^{3+}) species are predicted in gas phase for both air and oxy-fuel combustion. However, almost all of the As-species will be confined in the solid slag phase at temperature above 1000°C.



Figure 6.40: Equilibrium distribution of arsenic during oxy-fuel combustion using Loy Yang coal

The results indicate that almost all of the As was found to present as As_2O_3 (slag), $Ca_3(AsO_4)_2$ (s) and As_4O_6 (g) under oxy-fuel combustion. As shown in Figure 6.40, it can be observed that at high temperature (above 1000°C), the solubility of this species increase, which results in the corresponding increase in As_2O_3 (slag) species. In addition,

it is noted that the amounts of As_2O_3 (slag) represent almost 100% of total arsenic at higher temperature (above 1100°C) for Loy Yang coal. It is thus apparent that beyond 1000°C temperature, emissions of the gaseous As-species will be negligible.

6.3.2.4.3. Selenium

From Figure 6.41 it can be seen that compared to air combustion, one of the most volatile trace elements - selenium retention in the solid ash was significantly lower (by 60%) in oxy-fuel combustion at the same oxygen concentration. Around 17% of total coal-Se was observed to retain in the collected ash in air combustion, whereas in oxy-fuel combustion only 7% of total coal-Se was found to adsorb in the collected ash. This finding is supported by the observation by Contreras et al. (2013), who found elevated vaporization of selenium under oxy-fuel atmosphere.



Figure 6.41: Extents of Se in bed and fly ashes from different combustion environments

Moreover, it was noticed that the addition of steam in to the combustion environment lowered (by 15%) the selenium retention in ash. This finding is in line with the previous observation in Section 6.3.1.2.3, and the possible reason of lower Se retention in presence of steam is discussed in that section. Based on these experimental results, it is confirmed that the presence of steam would affect the partitioning behaviour of Se during oxy-fuel combustion.

With the variation of oxygen concentration in feed gas, however, no systematic trend was observed in the experimental results, as shown in Figure 6.41. This finding is consistent

with the observation by Contreras et al. (2013) using sub-bituminous coal, who also did not find any differences in percentages of Se volatilization with increase in oxygen concentration in O_2/CO_2 mixture. They concluded that in oxy-fuel combustion, the trace elements behaviour was highly dependent on the fuel composition.



Figure 6.42: Extents of Se in bed and fly ashes under oxy-fuel combustion condition at different bed temperatures

Moreover, with increasing temperature in the reactor, the retention of selenium in ash was observed to be unchanged, shown in Figure 6.42. Similar observation was also found in Section 6.3.1.2.3 in earlier set of experiments using Yallourn coal in fluidized bed quartz reactor. The experimental results indicate that maximum 7% of total coal-Se was found to adsorb in the collected ash, with the rest (approximately 93%) was estimated to emit to the atmosphere. According to the thermodynamic equilibrium calculation, however, almost 100% of total Se was predicted to be in the gas phase. It should keep in mind that thermodynamic calculations make equilibrium predictions, and do not consider the reaction time. Moreover, it is important to understand that the equilibrium predictions consider the total steady-state period on a batch mode and does not give any transient results, whereas experiments were performed on a continuous mode.



Figure 6.43: Equilibrium composition of major toxic Se species during air and oxy-fuel combustion (Balance of 100% on the vertical axis are the other Se-species)

As regards the gaseous Se species, SeO_2 (g) is considered as one of the most toxic selenium (Se⁴⁺) species. The prediction results, shown in Figure 6.43, indicate that the distribution of this compound remains almost same in both air and oxy-fuel combustion, particularly at low temperatures (up to 1000°C). It is also noted that the amounts of these species represent almost 100% of the total arsenic between 800°C and 1000°C in both cases. At temperatures above 1000°C, however, these gaseous emissions are predicted to decrease due to the corresponding increase in the less toxic gaseous SeO compound.

This is due to the fact that due to its high volatility during combustion almost all of the Se presents in the gas phase mainly as SeO_2 at temperature up to $1000^{\circ}C$, in-line with the literature studies using thermodynamic equilibrium approaches (Frandsen et al., 1994; Yan et al., 2001; Shah et al., 2008). However, gaseous selenium dioxide is known to condense below 100C. Therefore, in a commercial system, this will condense on the ash particles and captured in the fabric filter. Its presence could necessitate downstream gas treatment.

6.3.2.4.4. Mercury

Mercury is also one of the most volatile trace elements in coal and is considered to be a highly toxic pollutant. Most of the Hg in the atmosphere is elemental Hg vapour, which circulates in the atmosphere for up to a year, thereby can be widely dispersed and transported thousands of miles from likely sources of emissions (EPA, 2011). Discharge of mercury in the gaseous effluent creates problem for both health and environment. Even

when utilising coals with low mercury content, capture and removal of mercury by air pollution control systems is problematic (Yan et al., 2000). Australian coals generally contain lower level of mercury compared to the overseas coals. The mercury concentration in Loy Yang coal, used in this study, is 0.06 ppm. Thus the mercury emission using this coal is expected to be lower than the over-seas coals.

To investigate the mercury emission using this coal in oxy-fuel fluidized bed combustion, along with the determination of mercury retention in ash particles, the concentration of gaseous mercury species (Hg^0 and Hg^{2+}) were also measured. Here, the extent of particulate Hg adsorbed in the collected ash samples are shown in the first figures, whilst the gaseous Hg^0 and Hg^{2+} emissions are shown in the latter figures.



Figure 6.44: (a) Extents of Hg in bed and fly ashes, and (b) gaseous Hg concentrations from different combustion environments

In all cases, it was observed that mercury adsorption was higher in fly ashes, compared to the bed ashes, due to the higher carbon content in fly ash. This observation was supported by Wang et al. (2010b) and Duan et al. (2010), who reported that the presence of carbon-oxygen radicals favoured the oxidation and adsorption of Hg. Moreover, the porous structure and large surface area of unburned carbon promoted the Hg adsorption in fly ash.

The experimental results showed that compared to air combustion, Hg^0 emission was higher (by 28%) in oxy-fuel combustion with similar oxygen (21% v/v) concentration in feed gas, in common with the literature (Contreras et al., 2013; Spörl et al., 2013a; Wu et al., 2013). In this experiment, the total gaseous mercury concentration level of 20 µg/m³N was observed in air combustion, whereas 26 µg/m³N was observed in oxy-fuel combustion. About 69% of gaseous mercury was observed to emit as Hg⁰ in air combustion, while 73% of gaseous mercury emitted as Hg⁰ in oxy-fuel combustion. This is due to the lower NO_X formation for having zero nitrogen in the oxy-fuel combustion atmosphere, since NO_X is known to promote Hg⁰ oxidation (Contreras et al., 2013).

The addition of steam (even with same 15% v/v oxygen concentration in oxidant) in the combustion environment was found to promote (by 32.6%) the Hg⁰ emission. This finding is consistent with the observations by Niksa et al. (2001), who reported that H₂O strongly inhibited the mercury oxidation. The higher amount of Hg⁰ in presence of H₂O is due to the production of HgO at higher temperature (> 450°C) initially, according to the following reaction (R6.20) between the dominant mercury species at low temperature (<450°C), HgCl₂ and H₂O. However, HgO gradually decomposes to Hg⁰, according to reaction (R6.21) (Galbreath and Zygarlicke, 1996).

$$HgCl_{2} + H_{2}O \rightarrow HgO + 2HCl$$
(R6.20)
$$HgO \rightarrow Hg^{0} + \frac{1}{2}O_{2}$$
(R6.21)

These experiments also showed clearly that with increase in the O_2 concentration in oxidant, the total solid mercury in ash decreased and subsequently the total released mercury in gas phase increased (by 54%), as indicated in Figure 6.44. The Hg⁰ emission increased from 13 µg/m³N to 19 µg/m³N, when the oxygen concentration was increased from 15% to 30% (v/v) in the combustion atmosphere. This finding is in line with the observations by other researchers (Suriyawong et al., 2006; Acuña-Caro et al., 2009). A

possible reason is that as the oxygen concentration increases, the temperature in the vicinity of the burning particle also increases which promotes the vaporization of mercury inherent with coal particle (Suriyawong et al., 2006). Moreover, Acuna-Caro et al. (2009) concluded that high level of oxygen could decrease the mercury oxidation, particularly when high concentration of Cl⁻ were not present in the system.



Figure 6.45: Extents of Hg in bed and fly ashes under oxy-fuel combustion condition at different bed temperatures

As shown in Figure 6.45, with increase in temperature, the mercury retention in fly ash was found to increase significantly (by 75%). It is noted that during experiment temperature at the cyclone separators was below 300°C. At this temperature range, HgSO4(s) and HgO(s) were supposed to be the thermodynamically stable species (Zhuang et al., 2007). Regarding mercury in bed ash, however, results showed an opposite trend. With increase in temperature, the mercury retention in bed ash was found to decrease (by 46%), demonstrating higher Hg emission at higher temperature due to the longer residence time at the higher temperature zone. This finding in good agreement with the other researchers, such as Wilcox et al. (2012).



Figure 6.46: $Hg^{2\ast}/Hg^{total}$ ratio as functions of (a) NO, (b) NO_2 and (c) N_2O



Figure 6.47: Hg²⁺/Hg^{total} ratio as a function of SO₃

From the above discussion on the emission characteristics under different oxygen concentration it was possible to correlate the effects of other flue gas components, such as NO, NO₂, N₂O and SO₃ on mercury oxidation. The degree of Hg oxidation was observed to increase with increase in NO_X and N₂O (as shown in Figure 6.46), and SO₃ (as shown in Figure 6.47) in the flue gas. The correlations were found to be significant for all flue gas components, except for NO₂ using Loy Yang coal.

The overall mass balances (out/in) of mercury on the basis of coal stream under different combustion condition are summarized in Table 6.5. It can be seen that the mass balances were between 71% and 85%, somewhat in line with the mass balance closures between 70% and 130% reported by others (Lee et al., 2006).

Combustion atmosphere (% volume)	Input (mg/h)	Output (mg/h)				Balance (%)			
	Coal	Hg ⁰	Hg ²⁺				Hg ^P	Total	
				Bed ash	Primary cyclone ash	Secondary cyclone ash			
Air	0.0281	0.0136	0.0061	0.00006	0.00009	0.00007	0.0002	0.0199	70.89
15% O ₂ + 85% CO ₂	0.0308	0.0162	0.0061	0.00031	0.00032	0.00010	0.0007	0.0231	74.78
21% O ₂ + 79% CO ₂	0.0363	0.0219	0.0083	0.00021	0.00026	0.00013	0.0006	0.0308	84.88
30% O ₂ + 70% CO ₂	0.0329	0.0177	0.0075	0.00010	0.00023	0.00006	0.0004	0.0256	78.01
15% O ₂ + 73% CO ₂ + 12% H ₂ O	0.0320	0.0212	0.0043	0.00009	0.00067	0.00007	0.0008	0.0263	82.25

Table 6.5: Hg mass balance under different combustion conditions

In the experiment results using Loy Yang coal in oxy-fuel fluidized bed combustion, maximum 3% of total coal-Hg was found to adsorb in the collected ash, with the rest (approximately 97%) being estimated to emit to the atmosphere. As regards the gaseous mercury, most of the mercury (83%) was released as Hg^0 , while the rest (only 17%) of total gaseous mercury was emitted as Hg^{2+} . These percentages of released elemental mercury and oxidized mercury in the exhaust gas were close to the observed percentages by other researchers (Suriyawong et al., 2006; Font et al., 2012). Around 82.6% elemental mercury and 17.4% oxidized mercury were observed using 25% O₂/75% CO₂ in the oxy-fuel combustion environment studied by Suriyawong et al. (2006). In another study, 82% elemental mercury and 18% oxidized mercury were reported to emit using 30% O₂/70% CO₂ in the oxy-fuel fluidized bed combustion environment studied by Font et al. (2012).



Figure 6.48: Equilibrium composition of major toxic Hg species during air and oxy-fuel combustion (Balance of 100% on the vertical axis are the other Hg-species)

However, according to the equilibrium calculation, 100% of the total Hg was predicted in the gas phase. Since the elemental mercury (Hg^0) is more toxic than other forms of mercury, only the compositions of gaseous Hg^0 are shown in Figure 6.48. It can be seen that the predicted mercury emission is relatively unchanged regardless of atmospheres or temperatures. In all cases, greater than 98.5% of mercury leaves in the gas phase as elemental mercury (Hg^0) . So, based on the modelling it can be concluded that the mercury emission is marginally greater for oxy-fuel combustion than that for air combustion. In an earlier study Mitsui et al. (2011) reported that due to the recirculation of flue gas containing Hg, mercury concentrations are higher in oxy-fuel combustion than that in air

combustion. It is expected that mercury concentration in actual oxy-fuel unit might be higher than these predicted values. Since this mercury in the flue gas may result in corrosion in the CO_2 purification and compression unit, effluent gas treatment is necessary to eliminate this mercury during oxy-fuel combustion.

Chlorine is regarded as one of the important elements influencing the partitioning behaviour of mercury during coal combustion. To study the effect of chlorine on mercury distribution, different concentrations of hydrogen chloride were also considered in the oxy-fuel combustion atmospheres, as shown in Table 6.2. The equilibrium distribution of mercury as a function of HCl (g) concentrations during the oxy-fuel combustion of Loy Yang coal is presented in Figure 6.49.





Figure 6.49: Equilibrium distribution of mercury under different hydrochloric acid concentrations during oxy-fuel combustion (a) without HCl (g), (b) with 0.04 vol.% HCl (g) and (c) with 0.24 vol.% HCl (g)

The results indicate that no HgCl₂ (g) was formed over the entire temperature range when there was no HCl (g) in the combustion atmosphere (Figure 6.49a), whereas up to 1 vol.% of HgCl₂ (g) is observed at 800°C when the combustion gas atmosphere contains 0.24 vol.% HCl (g) (Figure 6.49c). At higher temperature (above 1100°C), however, no HgCl₂ (g) was predicted to form. This is due to the fact that at low temperature hydrogen chloride promotes the conversion of elemental mercury (Hg⁰) to oxidized mercury (Hg²⁺), according to the following reactions (Shah et al., 2008).

$$Hg^{0}_{(g)} + 2HCl_{(g)} = HgCl_{2(g)} + H_{2(g)}$$
(R6.22)

$$2Hg^{0}_{(g)} + 4HCl_{(g)} + O_{2(g)} = 2HgCl_{2(g)} + 2H_{2}O_{(g)}$$
(R6.23)

It is thus evident that higher chlorine content in combustion atmosphere, particularly at low temperature, produces more oxidized mercury (Hg^{2+}) making removal of mercury easier in coal-fired oxy-fuel combustion processes.

To control this harmful Hg^0 , mercury removal system, such as particulate control unit (e.g. electrostatic precipitator) or selective catalytic reduction unit, will need to be considered to avoid the corrosion in the boiler and in the CO_2 separation units during oxyfuel fluidized-bed combustion using this coal. However, while investigating mercury emission characteristics by pulverized-coal and circulating fluidized bed boilers equipped with electrostatic precipitators, Wang et al. (2010b) concluded that compared to the PC boiler the mercury removal rate was much higher in CFB boiler due to the circulating materials having higher carbon content. The average mercury removal efficiency was 99.6% in CFB boiler, whereas in PC boiler it was only 33.56%. Therefore it is probable that higher levels of mercury capture will occur during oxy-fuel circulating fluidized bed combustion.

6.4. CONCLUSIONS

The chapter presents the results of combustion performance of Victorian brown coal by performing experiments under oxy-fuel combustion conditions in two sets of bench scale experimental facility - a small scale fluidized bed quartz reactor and a 10 kW_{th} fluidized bed combustor. The key results from these two sets of experimental facility are stated below.

Small scale fluidized bed quartz reactor

- ✤ Around 15% CO₂ was observed in dry flue gas during air combustion, whereas more than 80% CO₂ was found under oxy-fuel combustion condition. Using 12% steam delivered in to the oxy-fuel combustion atmosphere, around 92% CO₂ in dry flue gas was observed.
- Higher temperature and oxygen concentration in feed gas resulted in higher chromium retention in ash. Up to 25% of chromium was estimated to emit into the gas phase within the considered temperature range.
- In case of selenium, 100% of this element was predicted to be in the gas phase as toxic selenium dioxide; however, up to 63% of this element was found to be in the collected ash under oxy-fuel combustion condition using Yallourn coal in the temperature range studied (800-900°C).
- As regards to arsenic, higher temperature resulted in higher arsenic level in the ash residue. Around 30% of this element was estimated to be retained in ash at 900°C. This might be due to the formation of arsenates during the combustion of high iron and calcium rich Yallourn coal under the operating condition studied.

With the addition of steam in the combustion environment, the trace elements levels in ash were found to be lower, which could affect their partitioning behaviour.

$10 \ kW_{th} \ fluidized \ bed \ combustor$

- ✤ The experimental results indicate that the addition of steam in the combustion environment results in high CO₂ concentration in the flue gas (90-94% CO₂ in the dry flue gas). Over 99% combustion efficiency was achievable under oxy-fuel fluidized bed combustion condition. The addition of steam in the mixed gas resulted in an increase in CO₂ concentration.
- The particle size distribution of fly and bed ashes under oxy-fuel combustion condition was almost similar to that under air combustion. The results show that bed ash composition was independent of the reactor temperature and reacting gas concentration in combustion atmosphere. During experiments below 900°C, this study found no bed agglomeration under oxy-fuel combustion condition for the duration of the tests. So it can be concluded that agglomeration is unlikely to be a major problem during oxy-fuel fluidized bed combustion of Loy Yang coal, if the operating temperature was kept around 900°C. However, longer duration experiments are recommended to ascertain the true propensity of agglomeration.
- ✤ It was also observed that the addition of steam in the combustion environment enhanced the NO_X reduction and N₂O formation. Up to 200 ppmv NO_X and 20 ppmv N₂O in the dry flue gas were observed using steam in oxy-fuel combustion atmosphere. Therefore, selection of the appropriate level of flue gas re-circulation is also important in order to control the nitrogen oxides emissions within permissible limits. Furthermore, the obtained NO level in oxy-fuel fluidized bed combustion was much lower than the level in oxy-fuel pulverized fuel combustion.
- Using Loy Yang coal, maximum 125 ppm SO₂ concentration and 3 ppm SO₃ concentration were observed. The emission of SO₃ which could cause corrosion in the boiler and in the CO₂ separation units was higher under the oxy-fuel conditions compared with those in air combustion. However, the obtained SO₂

concentration level in oxy-fuel fluidized bed combustion was much lower than the level from oxy-fuel pulverized fuel combustion.

- The NO_X and SO_X concentration levels in the flue gas were within the permissible limit in coal-fired power plants in Victoria. Therefore, additional NO_X removal system (such as selective catalytic reduction or low-NO_X burner) and SO_X removal system (such as flue gas desulphurization unit or scrubber) will not be required during oxy-fuel fluidized bed combustion using this coal.
- However, the emission of gaseous mercury, especially the harmful Hg⁰, was considerably higher under oxy-fuel combustion compared to air combustion. This experimental result indicates that maximum 3% of total coal-Hg was adsorbed in the collected ash, with the rest (approximately 97%) was estimated to emit to the atmosphere. As regards the gaseous mercury, most of the mercury (83%) was released as Hg⁰, while only 17% of total gaseous mercury was emitted as Hg²⁺. Therefore, to control this significant level of harmful Hg⁰, mercury removal system, such as particulate control unit (e.g. electrostatic precipitator) or selective catalytic reduction unit may need to be considered to avoid the corrosion in the boiler and in the CO₂ separation units during oxy-fuel fluidized-bed combustion using this coal.
- ✤ In terms of the speciation of trace elements, it was predicted by thermodynamic prediction that the amount of toxic gaseous Cr⁶⁺ species was greater for oxy-fuel combustion than for air combustion. The distribution of toxic Se⁴⁺ species, however, remained almost the same in both combustion conditions within the typical temperature range for Oxy-FB combustion (800 950°C). At 900°C, the toxic arsenic (As³⁺) species are predicted only in the gas phase for both air and oxy-fuel combustion conditions.

Focus of the next chapter:

This chapter investigates the combustion efficiency, conventional pollutants (SO_X and NO_X) emissions, trace elements (Hg, Se, As and Cr) emissions and agglomeration characteristics of Victorian brown coal in two bench scale combustors - a small scale fluidized bed quartz reactor and a 10 kW_{th} fluidized bed combustor under different oxy-

fuel combustion conditions. These results provide a guideline to choose the optimum operating conditions for the further application of the Victorian brown coal in a pilot scale rig. Moreover, the conventional and trace elements emission characteristics are of great importance to the design of the gas cleaning systems.

Additional experiments were also performed using the fly ash generated in this combustor to investigate the extents of sulphation and carbonation characteristics using a moderately high sulphur Victorian brown coal (Morwell) during Oxy-FB combustion. These results will be discussed in the next chapter.

CHAPTER 7: CARBONATION AND SULPHATION EXPERIMENTS

CHAPTER 7: CARBONATION AND SULPHATION EXPERIMENTS

7.1. INTRODUCTION

In fluidized bed combustion (FBC) utilizing high-sulphur coals, limestone is used as a sorbent to reduce the SO_2 emission. It has been identified in Section 2.3 that during coal combustion limestone sulphation can occur via two different routes - indirect sulphation and direct sulphation.

Upon injection into the bed, limestone undergoes calcination, when the calcium carbonate in the limestone decomposes to form CaO in fly ash, seen in reaction (R7.1). It then undergoes sulphation to achieve 80-90% sulphur retention, when the CaO reacts with SO_2 and oxygen to form solid calcium sulphate, seen in reaction (R7.2). Together, these reactions are termed indirect sulphation (Chen et al., 2009; Stewart et al., 2012).

$$CaCO_{3 (s)} \leftrightarrow CaO_{(s)} + CO_{2 (g)}$$
(R7.1)

$$CaO_{(s)} + SO_{2(g)} + \frac{1}{2}O_{2(g)} \leftrightarrow CaSO_{4(s)}$$
 (R7.2)

For an oxy-fuel FBC system the limestone calcination is normally inhibited due to the high partial pressure of CO_2 and the limestone is subject to a direct sulphation, seen in reaction (R7.3) (Liu et al., 2000; Chen et al., 2009).

$$CaCO_{3 (s)} + SO_{2 (g)} + \frac{1}{2} O_{2 (g)} \leftrightarrow CaSO_{4 (s)} + CO_{2 (g)}$$
(R7.3)

In air-fired fluidized bed combustion, where typical CO_2 concentration in flue gas is 15-20%, limestone starts to calcine around 800°C and SO_2 is captured via indirect sulphation. On the other hand, in oxygen-fired fluidized bed combustion, where the typical CO_2 concentration in flue gas is 70-90%, above 875°C is required for calcination. In this case, desulfurization can occur under both mechanisms in typical fluidized bed temperature range (800°C - 950°C). At lower temperature zone, direct sulphation can take place, while at higher temperature zone, indirect sulphation can take place (Zhao et al., 2010).

The rate of sulphation reaction is dependent on several factors, such as temperature, limestone composition (e.g. Ca percentage), limestone microstructure (pore size, surface area etc.), and concentrations of CO_2 , SO_2 , O_2 and H_2O . Though the reaction kinetics and

mechanism of sulphation have extensively been studied on Oxy-FB combustion (Jia et al., 2007; Jia et al., 2010; Scala and Salatino, 2010; de Diego et al., 2011; Duan et al., 2011b; Duan et al., 2011c; García-Labiano et al., 2011; Lupiáñez et al., 2011; Takkinen et al., 2011; Wang et al., 2011b; Wang et al., 2011c; Wu et al., 2011; Jia et al., 2012; Stewart et al., 2012; Tan et al., 2012; de Diego et al., 2013b; de las Obras-Loscertales et al., 2013; Rahiala et al., 2013; Tan et al., 2013; Li et al., 2014; Tan et al., 2014), most of the studies have been performed using only limestone. In contrast, limited studies have been carried out using both limestone and ash to mimic realistic boiler conditions.

Furthermore, in some locations (e.g., cyclone, dipleg, sealpot, external heat exchanger), where the temperature drops below the calcination temperature (800°C in air combustion and 875°C in oxy-fuel combustion), the unreacted calcium oxide is recarbonated to form calcium carbonate, according to the reaction (R7.4), which may cause fouling.

$$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)}$$
(R7.4)

Several studies have been carried out on the recarbonation of fly ash under Oxy-FB combustion (Liljedahl et al., 2006; Wang et al., 2008; Wang et al., 2011b; Beisheim et al., 2013; Wang et al., 2014b). This carbonation characteristic, however, is relatively unexplored in the low-rank coal context and completely unexplored for Victorian brown coal.

Since some of the Victorian brown coals have moderate sulphur and high calcium contents, it is more likely to cause sulphation as well as carbonation using these fuels in coal-fired boilers. Therefore, it is essential to assess the sulphation and carbonation behaviour under Oxy-FB combustion conditions using these coals.

In this chapter, the sulphation and carbonation characteristics of a Victorian brown coal are investigated using a tubular reactor and a thermo-gravimetric analyser respectively. The effects of limestone, concentrations of CO_2 , SO_2 and H_2O , and temperature are examined on the extent of sulphation and carbonation under different combustion conditions.

7.2. EXPERIMENTAL SECTION

7.2.1. Materials

The carbonation and sulphation experiments were conducted using a mixture of commercial reagent-grade limestone (CaCO₃) having mean particle size of 14 μ m and fly ash having mean particle size of 60 μ m. Figure 7.1 shows the typical scanning electron microscopy (SEM) images of the limestone and ash sample.



Figure 7.1: SEM images of (A) the original limestone and (B) the ash sample

Prior to mixing, the limestone was preheated in an oven at 105° C for 1 hour, in order to remove any excess moisture. The fly ash sample was collected from the primary cyclone of the 10 kW_{th} oxy-fuel fluidized bed reactor using Morwell coal. Detailed description of the experimental installation and procedure is provided in Chapter 6. The operating conditions of the combustion experiment are given in Table 7.1.

Table 7.1: Fuel used and operating conditions of the oxy-fuel combustion experiment in
bench scale FB rig

Coal	Morwell
Combustion atmosphere (% volume)	16% O ₂ + 75% CO ₂ + 9% H ₂ O
Gas velocity (m/s)	0.75
Bed temperature (°C)	870 ± 10
Steady-state period (h)	2.25
Coal feed rate (g/h)	830

This fly ash was then heated in a muffle furnace at 800° C for 3 hours to remove the unburnt carbon. The ash (having lower particle size of 20-180 μ m) was then separated

from the sand (having larger particle size of $180-250 \,\mu\text{m}$) by careful sieving, and only the particles of less than $180 \,\mu\text{m}$ were considered in the study. Table 7.2 shows the composition of the used fly ash.

Minerals and in (wt.% ash ba	organic asis)
SiO ₂	72.59
Al ₂ O ₃	3.75
Fe ₂ O ₃	5.26
TiO ₂	0.40
K ₂ O	0.25
MgO	5.16
Na ₂ O	0.63
CaO	8.20
SO ₃	3.76

Table 7.2: Composition of the fly ash used in experiments

7.2.2. Experimental procedure

7.2.2.1. Carbonation experiments

A mixture of fly ash and limestone was used to carry out the calcination and carbonation experiments in a thermo-gravimetric analyser (TGA). A known amount of sample was loaded into a round alumina crucible (20 mm diameter, 10 mm depth and 1 mm wall thickness) which was placed inside the TGA. This sample was heated from room temperature to the desired calcination temperature of 900°C under desired gas atmosphere (containing CO₂, O₂, H₂O and N₂), and maintained at that temperature for 15 min, following which it was cooled down to a carbonation temperature range of 800-300°C, and maintained at that temperature for 6 h. The heating and cooling rate was set at 10 K/min.

To assess the influence of the total gas flow rate on calcination, two different flow rates (50 ml/min and 100 ml/min) of air ($21\% O_2 + 79\% N_2$) were examined using 100% limestone. Under these conditions, the limestone sample mass decreased by about 44% on heating to 1000°C, as shown in Figure 7.2. The mass loss was due to the loss of carbon

dioxide from the calcium carbonate. It was found that the flow rate had no effect on mass loss, so on calcination, as shown in Figure 7.2. Therefore, in all following experiments the total gas flow rate of 100 ml/min was used.



Figure 7.2: Effect of flow rate on calcination behaviour of limestone at 1000°C

Table 7.3 shows the experimental conditions for these set of experiments. During the entire experiment, the change in mass over the temperature range and time period was recorded. All experiments were performed in duplicate.

	Table 7.3	: Experimental	conditions for	carbonation	experiments
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Condition	Range
Calcination temperature	900°C
Carbonation temperature	300°C, 400°C, 500°C, 600°C, 700°C, 800°C
O_2 concentration (v/v)	4%
CO ₂ concentration (v/v)	15%, 80%
H ₂ O concentration (v/v)	0%, 15%
N_2 concentration (v/v)	Balance

The conversion ratio of carbonation was calculated using the following formula.

$$Conversion ratio = \frac{\Delta W_{Carbonation}}{\Delta W_{Calcination}}$$
(7.1)

where, $\Delta W_{Calcination}$ is the weight loss of the sample due to calcination and $\Delta W_{Carbonation}$ is the weight gain of the sample due to carbonation.

7.2.2.2. Sulphation experiments

To perform the sulphation experiments, a mixture of ash and limestone was evenly spread over a layer of mesh (aperture ~ 10 μ m) on a crucible (90 mm in length, 40 mm in width and 5 mm in thickness), as shown in Figure 7.3. This crucible was constructed of perforated stainless steel (SS 316) to allow gas flow through both the top and bottom layer. A mesh was placed over the breathable crucible to continue allowing gas flow while not losing any of the samples through the holes. The crucible was placed in the centre of a 100 mm diameter and 1,000 mm long tubular furnace (TF).



Figure 7.3: Crucible used in the tubular furnace

During the heating and cooling periods, the furnace was purged with 50 mL/min of CO_2 to avoid calcination, and during the isothermal period the total gas flow rate was increased to 100 mL/min, which is equivalent to an average gas velocity of 0.2 m/s. The experimental conditions are summarized in Table 7.4. During the oxy-fuel combustion experiments using Morwell coal in the bench scale fluidized bed combustor, the SO_2 concentration level of 100-200 ppmv was observed, therefore, this range was chosen for the sulphation experiments.

Range		
800°C, 850°C		
6 hrs		
4%		
80%, 85%, 90%		
0%, 15%		
100 ppm, 200 ppm		
Balance		

Table 7.4: Experimental conditions for sulphation experiments

Some experiments were also conducted separately with only ash or limestone to establish a baseline. At the end of each run, the sample was weighed and placed in an airtight container for further analysis later.

The degree of sulphur conversion was calculated by the difference between total sulphur in bulk ash samples after sulphation and before sulphation over the additional sulphur passed through SO_2 during the experiments. When limestone is mixed with ash, the percentage of limestone used for sulphation is calculated as (Chen et al., 2012b):

% of limestone sulphated =

 $\frac{\left\{ \left(Y_{Sulphated sample} \times S_{Sulphated sample}\right) - \left(Y_{Raw sample} \times S_{Raw sample}\right) \times \frac{40}{32}\right\}}{M_{Limestone} \times \frac{40}{100}} \times 100$ (7.2)

where, Y and S represent the yield and sulphur percentage in ash sample respectively, while M denotes the mass percentage of limestone added to the sample.

7.2.3. Analytical measurements

The elemental compositions of bulk ash samples were quantified with an X-ray fluorescence spectrometer (XRF).

Scanning electron microscope (SEM) was used to investigate the morphology of the fly ash samples. The SEM images were taken under a working distance of 6 mm and an accelerating voltage of 5 kV.

The crystalline mineral phases in ashes were analysed by X-Ray diffraction (XRD), using a Rigaku miniflex600 XRD model, at voltage of 40 kV and a current of 15 mA. The XRD patterns are collected at 2 θ values in the range of 2° – 90° with stepping intervals of 0.02° and a count time per step of 4 s. The qualitative analysis of XRD patterns are conducted using MDI Jade 5.0 software.

7.3. **RESULTS AND DISCUSSIONS**

In the following subsections, results are presented first for the assessment of the carbonation characteristics during oxy-FB combustion using Victorian brown coal. It is followed by an evaluation of the extent of sulphation under different combustion conditions.

7.3.1. Carbonation characteristics

During oxy-fuel combustion, the carbonation reaction takes place due to the calcination of CaCO₃ forming CaO during heating, with in turn reacts with CO₂ forming CaCO₃ upon cooling. The weight loss during heating represents calcination, while the weight gain during cooling represents carbonation. This calcination and carbonation behaviour is influenced by several factors, such as limestone quantity, gas environment (presence of CO₂ and H₂O), and carbonation temperature. The impacts of these factors are described in the following sub-sections.

7.3.1.1. Effect of limestone addition

The degree of carbonation of pure ash, pure limestone and 8% limestone mixed with ash is discussed in this section. By performing the TGA experiments at 900°C with the gas atmosphere consisting of 4% O_2 with 80% CO_2 balanced by N_2 , it was found that as the limestone quantity increased, more calcination as well as more recarbonation occurred, as expected. In case of pure ash, the contribution of carbonation reaction was observed to be very small and even almost negligible, indicating that the inherent calcium in ash (~20% CaO in raw coal ash, as shown in Table 3.1) did not have any effect on carbonation. However, using 8% limestone mixed with ash carbonation conversion of 38% with 2.1% weight gain was observed, whilst using pure limestone about 57% carbonation conversion was observed with weight gain of about 25%, as shown in Figure 7.4.



Figure 7.4: Effect of limestone addition on carbonation

It is also evident that at the initial stage of cooling, the rate of recarbonation was quite fast and then the rate gradually reduced as the reaction proceeded. This could be because of the formation $CaCO_3$ product layer which inhibited the direct contact between CaO and CO_2 (Wang et al., 2008).

7.3.1.2. Effect of CO₂ concentration

The CO₂ concentration in the wet flue gas from air combustion is around 15%; from oxyfuel combustion it is around 80%. To study the effect of CO₂ concentration on carbonation conversion, TGA experiments were conducted at 15% and 80% CO₂ with 4% O₂ balanced by N₂ in the gas atmosphere using the mixture of fly ash and limestone.



Figure 7.5: Effect of CO₂ concentration on carbonation

It can be seen from Figure 7.5 that as the concentration of CO_2 in the flue gas stream increased from 15% to 80%, the temperature required for calcination to occur also increased from 770°C to 840°C. This is due to the fact that that limestone decomposition was slower under oxy-fuel condition due to higher partial pressure of CO_2 , consistent with the results of Chen et al. (2012b). This means that under oxy-fuel combustion condition higher temperature is required for calcination. It was also found that under oxyfuel condition, recarbonation occurred at approximately 860°C with the weight gain of about 2.2%. The carbonation conversion of 38.5% was observed during oxy-fuel combustion condition. In case of air combustion, however, recarbonation occurred at approximately 730°C with the weight gain of only 1% due to the low concentration of CO_2 in the atmosphere. About 18.5% carbonation conversion ratio was observed during air combustion. The higher conversion of carbonation at higher CO_2 concentration is inline with the observation by other researchers (Wang et al., 2011b).

7.3.1.3. Effect of steam

To assess the effect of steam on the carbonation conversion, TGA experiments were conducted using 4% O_2 and 80% CO_2 with and without 15% H_2O , balanced by N_2 in the gas atmosphere using the mixture of fly ash and limestone.



Figure 7.6: Effect of steam on carbonation

It can be observed from Figure 7.6 that at certain CO_2 concentration with or without steam, recarbonation started to occur at the same temperature of approximately 840°C. During further cooling to 670°C, the amount of carbonation conversion was 37.7% without steam in the gas atmosphere while in presence of 15% steam in the gas atmosphere the carbonation conversion was 38.1% at this temperature.

The higher amount of carbonation in presence of steam can be explained by the formation of $Ca(OH)_2$ initially, according to the reaction (R7.5). Then $Ca(OH)_2$ reacts with CO_2 to form $CaCO_3$, according to the reaction (R7.6). Since the carbonation of $Ca(OH)_2$ is much faster than the carbonation of CaO, the rate of carbonation increased in presence of steam during the initial stage of cooling (Wang et al., 2008).

$$CaO + H_2O = Ca(OH)_2$$
 (R7.5)

 $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$ (R7.6)

However, it is noted that the unstable $Ca(OH)_2$ can quickly calcine to CaO, which is evident during the further cooling period. During cooling from 670°C to 150°C, the ratio of carbonation conversion was observed to decrease by 21.5% in presence of steam in the atmosphere.

Thus, it was found that with the addition of steam in the gas atmosphere lowered the amount of carbonation during oxy-fuel combustion.

7.3.1.4. Effect of temperature

To investigate the effects of temperature on recarbonation, some experiments were carried out with the gas atmosphere consisting of 4% O₂ with 80% CO₂ balanced by N₂. In these experiments, the mixture of fly ash and limestone was heated from room temperature to 900°C, and cooled to various temperatures ranging between 300°C and 800°C. Once the sample reached the set temperature, it was kept for an isothermal period of 6 hours and then cooled down to room temperature. The TGA isotherm and carbonation conversion ratio during isothermal period are shown in Figure 7.7.





Figure 7.7: Effect of temperature on carbonation (a) TGA thermograph and (b) carbonation ratio during isothermal period

It can be seen that over 6 hours isothermal period the carbonation conversion increased with the carbonation temperature. At the initial stage of cooling, the sample partially carbonated and the carbonation conversion gradually increased with time, supported by the findings of prior study (Wang et al., 2008).

However, at the lowest recarbonation temperature used in this study (at 300°C), recarbonation conversion was observed to be higher at the initial stage of cooling. The conversion gradually reduced as the time proceeded.

It is also interesting to note that highest carbonation conversion was observed at 700°C over the isothermal period of 6 hours, as shown in Figure 7.11b. The finding of increased recarbonation conversion at 700°C is also in-line with the observation by other researchers (Wang et al., 2011b). The possible reason of this could be due to that formation of product layer encouraging the carbonation of CaO at 700°C compared to that at other temperatures (Wang et al., 2011b). All these results have practical implications for the extent of carbonation as a function of time at different downstream locations where the temperature drops below 800°C.

7.3.2. Sulphation characteristics

The degree of sulphation is influenced by several factors. In the following sub-sections, the effects of some of these factors – limestone quantity, concentrations of CO_2 , SO_2 and H_2O , and temperature are discussed.

7.3.2.1. Effect of limestone addition

Figure 7.8 shows the degree of sulphation of pure ash, pure limestone and 8% limestone mixed with ash. These experiments were performed at 800°C for 6 hrs with the gas atmosphere consisting of 4% O_2 and 80% CO_2 with 100 ppm SO₂ balanced by N₂.



Figure 7.8: Effect of limestone addition on sulphur conversion

It can be seen that the sulphur conversion increased with limestone quantity, as expected. In case of pure ash, 32% conversion was observed due to self-desulphurization by the inherent calcium content in ash. However, up to 47% conversion was observed using 100% limestone, while using 8% limestone mixed with ash about 41.5% sulphur conversion was observed, as shown in Figure 7.8. This finding is in-line with the prior literature that sulphur capture was improved with Ca/S molar ratio (Duan et al., 2011b; Chen et al., 2012b).

7.3.2.2. Effect of CO₂ concentration

Typical CO₂ concentration in flue gas in oxygen-fired fluidized bed combustion is around 80-90%. 80% CO₂ was chosen to study sulphur conversion in majority of experiments.

To study the influence of CO_2 concentration on sulphation reaction, experiments were also conducted at 85% and 90% CO_2 with 4% O_2 and 100 ppm SO_2 balanced by N_2 in the gas atmosphere at 800°C using the mixture of fly ash and limestone.



Figure 7.9: Effect of CO₂ concentration on (a) sulphur conversion and (b) limestone utilization

Figure 7.9 shows the sulphur conversion and the effectiveness of limestone utilization as a function of CO_2 concentration in the flue gas stream. It can be seen that as the concentration of CO_2 in the flue gas increased, the degree of sulphation decreased. As stated in Section 7.3.1.2, CO_2 concentration increased the carbonation conversion. Since the carbonation reaction is faster than the sulphation reaction (Wang et al., 2011b), CO_2 concentration lowered the sulphur capture efficiency. This finding is consistent with the observations on oxy-fuel fluidized bed combustion by other researchers (de Diego et al., 2011; Wang et al., 2011b). This is due to the fact that the limestone sulphation conversion decreased with CO_2 concentration in case of direct sulphation. In case of indirect sulphation, however, the limestone sulphation conversion increased with CO_2 concentration due to the higher porosity of CaO which allowed better access of the SO_2 towards inner part of the particle before plugging of the external pores (de Diego et al., 2011). From Figure 7.9(b), it can be observed that regardless of Ca/S ratio, the efficiency of utilization of added limestone also decreased with CO_2 concentration. Maximum 53.5% limestone utilization efficiency was observed at 80% CO_2 , whereas only 15.5% limestone utilization efficiency was observed at 90% CO_2 in flue gas.



Figure 7.10: XRD patterns of sulphated samples with the addition of (A) 90% (v/v) CO₂ and (B) 80% (v/v) CO₂ to the flue gas

XRD characterization was also conducted to quantify the extents of calcium species qualitatively in the sulphated samples, especially $CaSO_4$. It can be seen that anhydrite ($CaSO_4$) was the main Ca-species in all samples. Minor quantities of calcite ($CaCO_3$) and lime (CaO) were also found in the ash samples. These XRD patterns also confirmed the obtained sulphation trends in different cases, as shown in Figure 7.10.

7.3.2.3. Effect of steam

The effect of steam on sulphation is an important consideration, particularly during direct sulphation. This is because in presence of steam, direct sulphation is slower and less effective than indirect sulphation (Stewart et al., 2012). Figure 7.11 presents the XRD spectra identifying the major crystalline species in the sulphated samples generated under gas atmosphere consisting of 4% O_2 , 80% CO₂ and 100 ppm SO₂ with and without 15% H₂O, balanced by N₂ at 800°C using ash-limestone mixture. It was found that addition of steam in the gas atmosphere increased the intensity of CaSO₄. This is consistent with the results by other researchers (Stewart et al., 2010; Wang et al., 2010a; Wang et al., 2011b; Wang et al., 2011c; Stewart et al., 2012), who also found higher degree of sulphation in presence of steam.



Figure 7.11: XRD patterns of sulphated samples (A) without and (B) with the addition of steam to the flue gas

This higher amount of $CaSO_4$ through sulphation reaction in presence of steam can be explained by the initial formation of $Ca(OH)_2$, according to the reaction (R7.5). At typical Oxy-FB combustion temperature, the unstable $Ca(OH)_2$ then undergoes sulphation reaction, according to the reaction (R7.7). Since the sulphation of $Ca(OH)_2$ is much faster

than the sulphation of $CaCO_3/CaO$, therefore improved sulphation was observed in presence of steam in the gas atmosphere (Wang et al., 2010a; Wang et al., 2011c).

$$Ca(OH)_2 + SO_2 + \frac{1}{2}O_2 = CaSO_4 + H_2O$$
(R7.7)

7.3.2.3. Effect of SO₂ concentration

In all previous cases, 100 ppm SO₂ was chosen to study the sulphur conversion. To study the influence of SO₂ concentration on sulphation reaction, experiments were also carried out at 200 ppm SO₂ with 4% O₂ and 90% CO₂ balanced by N₂ in the gas atmosphere at 800°C using the mixture of fly ash and limestone. Using Morwell coal in the bench scale fluidized bed combustor during oxy-fuel combustion, the SO₂ concentration level of 100-200 ppm was observed, therefore, this range was used in this set of sulphation experiments.



Figure 7.12: XRD patterns of sulphated samples with the addition of (A) 100 ppmv and (B) 200 ppmv SO₂ to the flue gas

The sulphation conversion was observed to increase with increase in SO_2 concentration in the flue gas, as shown in Figure 7.12, in-line with the observations by other studies
(Wang et al., 2011b). At higher SO_2 concentration, the higher peak intensities of $CaSO_4$ and CaO indicate that at this condition indirect sulphation was also happening under these test conditions.

7.3.2.4. Effect of temperature

Figure 7.13 presents the XRD spectra for the major crystalline species on the sulphated samples with the gas atmosphere consisting of 4% O_2 , 90% CO_2 and 200 ppm SO_2 balanced by N_2 using ash-limestone mixture at two different temperatures of 800°C and 850°C. It was found that higher temperature significantly increased the intensity of CaSO₄ and thereby the sulphur conversion through direct sulphation. This is consistent with the observations during oxy-fuel combustion by other researchers (Liu et al., 2000; Wang et al., 2011b). However in air combustion having 15% CO_2 (without H₂O) in the atmosphere, reverse trend was observed (Wang et al., 2010a) indicating that during indirect sulphation, higher temperature inhibits the degree of sulphation.



Figure 7.13: XRD patterns of sulphated samples at (A) 800°C and (B) 850°C

In this study using ash-limestone mixture, the direct sulphation reaction was clearly observed at higher temperature with high SO₂ concentration in the Oxy-FB combustion

atmosphere. However, the indirect sulphation was observed to be dependent on the concentrations of H_2O and SO_2 in the oxy-fuel gas atmosphere.



Figure 7.14: Sulphur capture efficiency as functions of bed temperature and CO₂ concentration, modified from Wall et al. (2012)

Figure 7.14, modified from Figure 2.4 in Section 2.3.3, shows the sulphur capture efficiency under different combustion conditions using a variety of coals including Victorian brown coal. From the above results using Morwell coal in case of 8% limestone mixed with ash, maximum 54% sulphur capture efficiency was observed. In terms of sulphur conversion, maximum 42% conversion was observed, while the rest (58%) of total sulphur was emitted as SO₂. To improve the desulphurization efficiency, it may need to increase the Ca/S molar ratio or the residence time. Therefore, further experiments are recommended in fluidized bed reactor, by achieving a good contact between sample with SO₂, using the mixture of limestone and coal with different levels of Ca/S molar ratio to mimic realistic boiler conditions.

7.4. CONCLUSIONS

This chapter investigates the carbonation and sulphation characteristics of one Victorian brown coal (Morwell) by performing experiments under different Oxy-FB combustion conditions. The effects of limestone, concentrations of CO_2 , SO_2 and H_2O , and temperature are considered in this study to examine the extent of carbonation and sulphation under different combustion conditions. The salient results of this study are as follows:

- In case of pure ash, the extent of carbonation reaction was almost negligible, while 32% sulphur conversion was observed due to the self-desulphurization by the inherent calcium content in ash.
- ✤ In case of 8% limestone mixed with ash, maximum 42% sulphur conversion was observed at 80% CO₂ concentration in flue gas with 4% O₂ and 100 ppm SO₂ balanced by N₂ in the gas atmosphere at 800°C using the mixture of fly ash and limestone, while the rest (58%) of total organic sulphur was estimated to emit as SO₂. Therefore, to improve the desulphurization efficiency, it may need to increase the Ca/S molar ratio or the residence time.
- By performing experiments over 6 hours isothermal period at different carbonation temperatures (300°C - 800°C), highest (up to 70%) carbonation conversion was observed at 700°C. However, at the lowest recarbonation temperature used in this study (at 300°C), recarbonation conversion was observed to be higher at the initial cooling stage and the conversion gradually reduced as the time proceeded, which indicates that residence time is also important for carbonation conversion which is kinetics controlled.
- ✤ As the concentration of CO₂ in the flue gas stream increased, the temperature required for calcination to occur also increased. Therefore, under oxy-fuel combustion higher temperature was required for calcination.
- ✤ Higher carbonation conversion was observed at higher CO₂ concentration, whereas sulphur conversion was found to decrease with CO₂ concentration.
- The direct sulphation reaction was clearly observed at higher temperature with high SO₂ concentration in the atmosphere using ash-limestone mixture in the Oxy-FB combustion environment. However, the indirect sulphation was observed to be dependent on the concentrations of SO₂ and H₂O in the gas atmosphere.
- The addition of steam in the gas atmosphere lowered the amount of carbonation during oxy-fuel combustion. In contrast, steam was observed to improve the limestone sulphation reaction.

It can be concluded that in Oxy-FB combustion of Victorian brown coal, the sulphation performance can be enhanced by maintaining the concentration level of water vapour at 15% in the flue gas. Therefore, this will have implications for the extent of drying of the

Victorian brown coal prior to its utilization. However, it should be kept in mind that the higher level of water vapour will also have adverse effect on the surface corrosion which can affect the operation and life of the boiler.

Focus of the next chapter:

In the previous chapters, experimental findings obtained from bench-scale fluidized bed combustor under oxy-fuel combustion conditions using Victorian brown coals, were discussed. The next chapter will focus on the process model of this bench-scale fluidized bed combustor during oxy-fuel combustion with flue gas recirculation which can be used to predict the combustion performance of different grades of coals.

CHAPTER 8: PROCESS SIMULATION OF OXY-FUEL FLUIDIZED BED COMBUSTION

CHAPTER 8: PROCESS SIMULATION OF OXY-FUEL FLUIDIZED BED COMBUSTION

8.1. INTRODUCTION

Since Oxy-FB combustion technology is still in developing stage, process simulation can help to find out the best process flowsheet and optimum design conditions (Kabir et al., 2013). Among the commercial software packages for the process simulation, Aspen Plus has successfully been used in steady-state processes, including processes containing solids. Aspen Plus has widely been applied in coal combustion (Sotudeh-Gharebaagh et al., 1998; Hughes et al., 2005; Hong et al., 2009; Iloeje et al., 2010; Seltzer et al., 2010; Liu et al., 2011; Yang et al., 2011; Hu and Yan, 2012; Kim et al., 2012; Liu et al., 2012; Pei et al., 2013), coal gasification (Elseviers et al., 1996; Kuchonthara et al., 2005), biomass gasification (Mathieu and Dubuisson, 2002; Tijmensen et al., 2009) and some other purposes like dimethyl ether production (Kabir et al., 2013). All these applications have made Aspen Plus a reliable and adaptable process simulation software.

Several researchers have used Aspen Plus to simulate the coal combustion in air-fired circulating fluidized bed reactors (Sotudeh-Gharebaagh et al., 1998; Liu et al., 2011; Yang et al., 2011; Liu et al., 2012). There have also been some attempts to develop the process simulation of oxy-fuel pulverized coal combustion technology (Hong et al., 2009; lloeje et al., 2010; Seltzer et al., 2010; Xiong et al., 2011; Hu and Yan, 2012; Kim et al., 2012; Pei et al., 2013). The process simulation using Aspen Plus in Oxy-FB combustion, however, is non-existent.

In this chapter, the process model of Oxy-FB combustion developed for Victorian brown coal (Loy Yang) using Aspen Plus TM V7.3 process software is described. This developed model mainly focuses on the emission characteristics of CO, SO_2 and NO_X . The predicted simulation results are also validated with the experimental results from the bench scale Oxy-FB unit described in Chapter 6.

8.2. SIMULATION OF OXY-FB COMBUSTION PROCESS

The simplified schematic of the Oxy-FB combustion process is shown in Figure 8.1.



Figure 8.1: Simplified flowsheet of Oxy-FB combustion process

8.2.1. Model description

The flowsheet of the steady state process model for Oxy-FB combustion in Aspen Plus is shown in Figure 8.2. In this model, the entire fluidized bed combustor (FBC) was divided into two regions: a lower region/dense bed and an upper region/dilute bed. To illustrate these two regions in a FBC unit, the upper region was divided into two sections - a fully developed zone and an acceleration zone. Since the height of the acceleration zone is relatively higher with a considerable solid fraction variation, this zone was also divided into two sections.

Coal decomposition, volatile combustion, char combustion, NO_X formation and SO_2 capture took place in the lower region. Assuming the decomposition and volatile combustion to took place completely in the dense region, only char combustion, NO_X formation and SO_2 capture were considered to occur in each three sections of the upper region (Sotudeh-Gharebaagh et al., 1998). Figure 8.3 shows the variation of void fraction in a FBC unit with the bed height.

CHAPTER 8: PROCESS SIMULATION OF OXY-FUEL FLUIDIZED BED COMBUSTION



Figure 8.2: Steady-state process model for Oxy-FB combustion



Figure 8.3: Variation of void fraction with bed height (Sotudeh-Gharebaagh et al., 1998)

In order to demonstrate the combustion phenomena in a FBC unit, four Aspen Plus reactor blocks (RYIELD, RSTOICH, RCSTR and REQUIL) were utilized (Sotudeh-Gharebaagh et al., 1998). To develop this model, several Aspen Plus unit operation blocks were combined and some kinetic expressions were developed, where necessary. The summary of the blocks and their parameters used for this process model is expressed in Table 8.1.

When coal is fed to the FB reactor, it decomposes into volatile matter and char. The decomposition process, when coal is converted into its constituent elements (carbon, hydrogen, oxygen, sulphur, nitrogen, chlorine and ash) based on the ultimate analysis of coal, was modelled using a yield reactor (RYIELD).

To model the volatile matter combustion step, a stoichiometry reactor (RSTOIC) was used as this block allows for chemical reactions and the conversion to be specified. The volatile matter in the coal consists of carbon, hydrogen and sulphur. All the hydrogen and sulphur present in the coal was assumed to be present in the volatile matter and therefore entirely converted to water vapour and sulphur dioxide respectively. During the volatile combustion process, the volatile carbon formed carbon monoxide due to the depletion of oxygen in the lower region of the riser (Sotudeh-Gharebaagh et al., 1998).

Phenomena	Reactor block	Block parameters	Description
Decomposition	RYIELD	P = 1 bar, T = 850°C	Converts the coal into its constituent elements.
			$C_x H_y O_z S_\alpha N_\beta ClASH$
			$\rightarrow xC + \frac{1}{2}yH_2$
			$+\frac{1}{2}zO_2+\alpha S$
			$+\frac{1}{2}\beta N_2$
			$+\frac{1}{2}\gamma Cl_2$
			+ ASH
Volatile combustion	RSTOIC	P =1 bar, T = 850°C, $X_{C} = 0.473551$, $X_{S} = 1$, $X_{H}=1$	Combustion of volatile matter in the coal.
			$C + \frac{1}{2}O_2 \to CO$
			$S + O_2 \rightarrow SO_2$
			$H_2 + \frac{1}{2}O_2 \to H_2O$
Char combustion	RCSTR	P =1bar, T = 850°C, D ₁ = 0.1 m, D _{2,3,4} = 0.15 m, H ₁ = 1.5 m, H ₂ = 0.4 m, H _{3,4} = 0.8 m	Combustion of char particle in the bed.
			$C + \frac{1}{2}O_2 \to CO$
			$CO + \frac{1}{2}O_2 \to CO_2$
			$C + CO_2 \rightarrow 2CO$
NO_X formation	REQUIL	P =1bar, T = 850°C	NO_X formation in CFB combustion.
			$\frac{1}{2}N_2 + O_2 \rightarrow NO_2$
			$N_2 + \frac{1}{2}O_2 \rightarrow N_2O$
			$N_2 + O_2 \rightarrow 2NO$
SO ₂ adsorption	RSTOIC	P =1bar, T = 850°C, $X_{CaCO3} = 1$, $X_{SO2} = 0.6$	SO_2 absorption by limestone in CFB combustion.
			$CaCO_3 \rightarrow CaO + CO_2$
			$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4$

Table 8.1: Parameters in each block utilized for the simulation of Oxy-FB coal combustion including reactor dimensions

Phenomena	Reactor block	Block parameters	Description
Cyclone separator	CYCLONE	D = 0.3 m	Separates unburned char particle and ash from flue gas.
Cooler	HEATER	P = 1 bar, T = 300°C	Cools the flue gas.
Recycle flue gas	FSPLIT	Flue gas recycle ratio = 0.7	Specifies flue gas recycle ratio.
Fan	COMPR	P = 1.1bar	Increases the pressure.
Feed gas mixer	MIXER	Mix components	Mixes oxygen with recycle flue gas.
Oxygen mixer	MIXER	Mix components	Mixes oxygen with flue gas.
Notes: D = Diameter, H = Height, P = Pressure, T = Temperature, X = Conversion, Superscripts 1, 2, 3 and 4 denote the reactor numbers according to Figure 8.3			

Table 8.1: Parameters in each block utilized for the simulation of Oxy-FB coal combustion (Continued)

The char particle in the bed consists of the fixed or non-volatile carbon and the ash. Char combustion is a slow burning process to produce a mixture of carbon monoxide and carbon dioxide. The heat generated in the system exited at this reactor. During char combustion, three main reactions are involved, as shown in Table 8.1. The first and second reactions are exothermic carbon combustion reactions, while the third reaction is the endothermic carbon gasification reaction by carbon dioxide. It was reported that during Oxy-FB combustion, the contribution of CO₂ gasification at typical fluidized bed combustion temperature was not negligible for low-rank coals (Jia and Tan, 2014); so this reaction was also considered in this model. The process was modelled using a continuous stirred tank reactor (RCSTR), in which some reaction kinetic expressions were used. The data used in these kinetic data were taken from the literature. For the third reaction, however, the kinetic data was taken from the experiments performed in TGA at three temperatures - 800, 850 and 900°C using Victorian brown coal char in 90% (v/v) CO₂ + 10% (v/v) N₂ gas atmosphere. The detailed description of the experiments was provided in Chapter 4.

Reaction no.	Chemical reaction	Reaction rate constant	Reference
(1)	$C + \frac{1}{2}O_2 \to CO$	$k_1 = 1.55 \times 10^7 \exp(\frac{-1.5 \times 10^4}{T})$	Gordon and Amundson (1976).
(2)	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	$k_2 = 1.3 \times 10^8 \exp(\frac{-1.51 \times 10^4}{T})$	Howard et al. (1973).
(3)	$C + CO_2 \rightarrow 2CO$	$k_3 = 1.84 \times 10^4 \exp(\frac{-1.91 \times 10^4}{T})$	

 Table 8.2: Chemical reactions and kinetic expressions used for the modelling of char

 combustion in the fluidized bed

The NO_X formation in the fluidized bed combustion is modelled using an equilibrium reactor (REQUIL). This block predicts the amount of NO_X (NO and NO_2), and N_2O using simultaneous phase chemical equilibrium by solving the stoichiometric chemical and phase equilibrium reactions.

To model the SO_2 adsorption in the FBC reactor using limestone, a stoichiometry reactor (RSTOIC) was used. The limestone (mainly calcium carbonate) is unstable in the FBC conditions, so the calcination process is assumed to occur instantaneously and completely. The calcium oxide then absorbs the sulphur dioxide by forming calcium sulphate. The limestone is added in the char combustion block which is prior to the SO_2 capture reactor, because the limestone needs to heat up to the reactor temperature as this the ideal thermodynamic temperature for the limestone to absorb the SO_2 . Although the considered Loy Yang coal is a low sulphur coal, this SO_2 adsorption process was included so that this model can also be adapted to any high sulphur coal.

A cyclone separator (CYCLONE) was used to separate the unburned char particle and ash from the flue gas. To control the reactor temperature with an oxy-fuel technology, it is necessary to cool the flue gas prior to recirculation using a cooler. In industry, the flue gas could be cooled using water which would generate steam. This steam could then be used to dry the coal prior to entering the reactor or in the steam cycle. In this developed model, a cooler (HEATER) was used to cool the flue gas. The cooled gas was then entered to a splitter (FSPLIT), where a proportion of the flue gas was recycled back to the reactor. This recycled flue gas was then passed through a fan (COMPR) which increased the pressure to drive the flue gas into the FBC reactor. Prior to entering the reactor, the recycled flue gas was mixed with pure oxygen in a mixer (MIXER) to produce the oxidant during oxy-fuel combustion. To achieve the convergence of the simulation streams, oxygen was entered at the bottom of the bed as well as at three secondary oxygen injection ports (MIXER). The secondary oxygen was introduced to the FB riser at three different locations (1.5 m, 1.9 m and 2.7 m above the distributor plate). A calculator block named "YIELD" was used to calculate the yields of constituent elements based on the ultimate analysis of the coal. So, the model can be used later for different types of coals.

8.2.2. Input data

For this model, Loy Yang coal was used. The properties of this coal are given in Table 8.3. This model was simulated under the coal and lime feed rates of 1 kg/hr and 0.014 kg/hr respectively. All the feed streams were entered to the system at 25°C and 1 bar. In the base cases, 0.7 was chosen for the flue gas recycle ratio and the recycled flue gas temperature was set at 300°C (shown in Table 8.1).

Proximate analysis	
Volatile matter (wt.% dry basis)	49.90
Fixed carbon (wt.% dry basis)	46.40
Ash (wt.% dry basis)	3.7
Moisture (wt.% as received)	12.5
Ultimate analysis (wt.% dry basis)	
Carbon	65.00
Hydrogen	4.60
Nitrogen	0.72
Sulphur	0.50
Oxygen	25.37
Chlorine	0.11
Ash	3.7
Heating value (MJ/kg)	26.30

Table 8.3: Properties of coal used in the simulation

8.2.3. Assumptions

To simplify the model, some assumptions were considered which are given below (Sotudeh-Gharebaagh et al., 1998; Liu et al., 2011; Yang et al., 2011; Liu et al., 2012):

- The process was steady-state.
- The mixing of solid particles (ash, char and sorbent) was perfect.
- The gas velocity was uniform throughout the bed and constant for each region of the bed.
- The mean voidage in the lower region of the bed was constant for a given superficial gas velocity, while the voidage in the upper region of the bed decreased with the vertical position along the riser.
- Due to the very short time required for volatile combustion, the devolatilization process was considered instantaneous.
- The char distribution throughout the bed was uniform.
- Due to the slower char combustion, it was assumed to occur after burning all the volatile products.
- The temperatures of burning coal particle and gas were considered constant and equal to the bed temperature.
- The effects of fragmentation of coal and char in the overall combustion process were neglected.
- Any size reduction in char particle due to the friction of bed particles and FB riser wall were neglected.
- The conversion of carbon, hydrogen and sulphur in the volatile matter was 100%.

8.3. RESULTS AND DISCUSSIONS

In the following subsections, simulation results are presented first for the concentration profiles of CO, SO_2 and NO_X along the height of the fluidized bed. It is followed by the evaluation of emission characteristics under different excess oxygen percentages and different recycle flue gas ratios during Oxy-FB combustion. The predicted simulation results are also verified with the experimental results from the bench scale Oxy-FB unit.

8.3.1. Simulation results

8.3.1.1. Concentration profiles along the FB riser height

From the developed process simulation model, it was possible to know the gas components concentration profiles along the height of the fluidized bed. The concentration profiles of CO, SO_2 and NO_X along the bed height during Oxy-FB combustion are shown in Figure 8.4. In this simulation, the oxygen was fed to the combustor considering at 4% excess oxygen in the flue gas.





Figure 8.4: Simulated gas concentration profiles of CO, SO₂ and NO_x along the FB riser height

It can be observed that the CO concentration was quite high in the lower dense region due to the lower oxygen concentration in this zone. After injecting the secondary oxygen in the upper dilute region, however, there was a sharp decrease of CO concentration from 205 ppb to 8 ppb. This is due to the further combustion reactions of char particles along the riser height to generate CO_2 and simultaneously lowered the CO formation. As for SO_2 , the concentration was also observed to decrease with the FB riser height. The SO_2 concentration dropped from 68 ppm to 4 ppm. On the other hand, the concentrations of both NO and NO_2 were observed to increase due to the introduction of secondary oxygen along the bed height. The NO concentration increased from 5 ppm to 200 ppm, while NO_2 concentration increased from 1 ppb to 90 ppb.

8.3.1.2. Effect of excess oxygen on the concentration profiles

In coal combustion, the amount of excess oxygen has significant effect on the concentration profiles of the flue gas components. The predicted concentrations of CO, SO_2 and NO_X with changing the excess oxygen percentages from 2% to 4% are shown in Figure 8.5.



Figure 8.5: Simulated gas concentration profiles of CO, SO₂ and NO_x under different excess oxygen percentages during Oxy-FB combustions

The results indicate that with increase in excess oxygen, the concentration of CO sharply decreased from 55 ppm to 8 ppm, whereas the concentrations of SO₂ remained unchanged. This lower amount of CO with increasing oxygen concentration was caused by the complete combustion to form CO₂. In contrast, increasing oxygen concentration lead to an increase in the concentrations of NO and NO₂, from 175 ppm to 200 ppm and from 66 ppb to 87 ppb respectively. This is due to the fact that as the oxygen concentration increases, the residence time of the coal particles in the combustor becomes longer, which promotes the coal-N to NO_X conversion (Duan et al., 2011a). Moreover, due to the lower number of char particles and small amount of CO in presence of higher excess oxygen, the reduction of NO on the char particle surface through the following reactions is inhibited. Therefore, more NO was generated at higher excess oxygen during fluidized bed combustion (Liu et al., 2012).

$$NO + C \rightarrow CO + \frac{1}{2} N_2$$
 (R8.1)

$$NO + CO \rightarrow CO_2 + \frac{1}{2} N_2$$
 (R8.2)

8.3.1.3. Effect of flue gas recycle ratio on the concentration profiles

In oxy-fuel combustion, the amount of recycle flue gas is one of the important parameters for the system operation, which can affect the combustion characteristics in the furnace and the flue gas composition (Xiong et al., 2011). Though the flue gas recycle ratio of 0.7 was chosen in the base cases, in this section the recycle ratio was varied from 0.6 to 0.7 to study the effect of flue gas recycle ratio on the concentration profiles of the flue gas components. For this simulation, oxygen was fed to the combustor ensuring 4% excess oxygen in the flue gas.

From Figure 8.6, it can be observed that regardless of excess oxygen, as the recycle ratio increases, the concentration of CO increases, whereas the concentrations of both SO_2 and NO_X decrease slightly. The small decrease in SO_2 and NO_X concentrations could be due to the relatively higher H₂O concentration observed in the flue gases with increasing recycle ratio. Since H₂O has an important effect on SO_2 and NO_X reduction (Stewart et al., 2012), lower SO_2 and NO_X were generated at higher flue gas recycle ratio during Oxy-FB combustion.



Figure 8.6: Simulated gas concentration profiles of CO, SO₂ and NO_X under different flue gas recycle ratios during Oxy-FB combustions

8.3.2. Model validation

The process simulation model was also validated with limited experimental data from the bench-scale 10 kW_{th} fluidized bed unit under oxy-fuel combustion conditions. In order to validate this model, several sets of operating data were used. The operating conditions are summarized in Table 8.4. Detailed description of the experimental installation and procedure is provided in Chapter 6.

Run	Bed temperature (°C)	Coal feed rate (kg/h)	Lime feed rate (kg/h)	Oxygen feed rate (kg/h)
1	850	1	0	2.618
2	850	1	0	2.716
3	850	1	0	2.838
4	820	1	0	2.618
5	880	1	0	2.618

Table 8.4: Operating conditions used in the combustion experiments

It is also noted that no SO_2 sorbent was used during experiment, so during this validation the feed rate of lime was also set to zero. Since the flue gas composition was measured in dry basis during experiment, the predicted results obtained from simulation were also converted to dry basis.





Figure 8.7: Comparison between simulated and measured concentrations of SO₂ and NO under different Oxy-FB combustion conditions

The CO concentration levels predicted by the model ranged from 10 to 15 ppb, while no CO was detected during the combustion experiments. In the gas analyser used during experiments, the sensitivity of CO was up to 100 ppb. So it can be expected that due to these low concentration levels, it was not possible to measure any CO during experiment.

Figure 8.7 shows the comparison between the predicted and experimental concentration levels of SO_2 and NO. The predicted SO_2 concentration levels ranged from 200 to 205 ppm, whereas the measured SO_2 concentration levels ranged from 65 to 125 ppm. The model was found to consistently over-predict the SO_2 concentration. This is because Aspen Plus simulation did not consider the ash mineral interaction with the coal-S, and therefore the possibility of self-desulfurization by the calcium content in ash. Due to this limitation, the model overestimated the SO_2 concentration in the flue gas.

Regarding NO emission, however, Figure 8.7 (b) shows good agreement between the predicted and experimental concentration levels of NO in the flue gas. The predicted concentration levels of NO ranged from 150 to 250 ppm, whereas the measured concentration levels ranged from 180 to 230 ppm. This good agreement made this Oxy-FB combustion model reliable to predict the pollutant emissions in a fluidized bed combustor.

8.4. CONCLUSIONS

The aim of this study is to develop a generic steady-state process model for the oxy-fuel fluidized bed combustor (used in this study for bench scale experiments) using a commercial package Aspen Plus. The model can then be used for modelling the performance of Oxy-FB's using different grades of coals.

To develop this model, several Aspen Plus unit operation blocks were combined and some kinetic expressions were used. This model was used to predict the combustion performance of the considered Victorian brown coal (Loy Yang coal) in terms of the emission characteristics. The results obtained in this simulation work allowed us to predict the emission behaviour along the height of a fluidized bed combustor during real oxy-fuel environment with flue gas recirculation. It was observed that the concentrations of CO and SO₂ were quite high in the lower dense region of the bed. With the introduction of secondary oxygen, these levels were observed to drop significantly. However, increase in excess oxygen percentage lead to an increase in the concentration of NO_X. When the recycle flue gas ratio was increased from 0.6 to 0.7 for a given excess oxygen percentage, the concentration of CO was found to increase, while the concentrations of SO₂ and NO_X were observed to decrease marginally. Therefore, the selection of optimum recycle ratio and excess oxygen level would be crucial for the best utilization of the process.

These predictions from this model were also verified with limited experimental data performed in a bench-scale fluidized bed unit under simulated oxy-fuel combustion conditions. The simulated results were in good agreement with the measured results. This good agreement show that this Oxy-FB combustion model based on Aspen Plus can successfully be used to describe the combustion characteristics of any coal in an Oxy-FB combustor.

Focus of the next chapter:

The experimental and process simulation work performed on Oxy-FB combustion using Victorian brown coal are discussed until this chapter. In the next chapter, the summary of the entire research work and recommendations for future work will be described.

CHAPTER 9: CONCLUSIONS AND RECOMMENDATIONS

CHAPTER 9: CONCLUSIONS AND RECOMMENDATIONS

9.1. CONCLUSIONS

This is a first-ever study, in a combined experimental and modelling approach, on the oxy-fuel fluidized-bed (Oxy-FB) combustion using Victorian brown coal. The study involves targeted experiments in laboratory scale and bench scale equipment including a 10 kW_{th} fluidized bed rig designed and commissioned for this study. Laboratory scale experiments using single char particle were conducted to investigate the combustion characteristics of individual large char particle under Oxy-FB condition. The objectives of bench scale experiment include assessment of combustion efficiency, agglomeration characteristics, sulphation characteristics, carbonation characteristics, NO_X (NO, NO₂ and N₂O) emission, SO_X (SO₂ and SO₃) emission, and trace elements (Hg, Se, As and Cr) emissions during Oxy-FB combustion of Victorian brown coal. Moreover, thermodynamic equilibrium modelling was carried out to predict the gaseous compounds formed in particular trace elements emissions and their concentrations. A process model on Oxy-FB combustion was also developed to predict combustion performance of any coal during Oxy-FB.

The research has four distinct parts – single particle combustion experiment, bench scale combustion experiment, thermodynamic equilibrium modelling and process modelling. The key findings from each part are stated below.

9.1.1. Single particle combustion experiment

In single particle combustion experiments, particle temperature was observed to be higher compared to the bed temperature. Up to 48°C difference was noticed between the char particle temperature and the bed temperature using 15% (v/v) steam in oxy-fuel combustion atmosphere. The temperature of the char particle monitored during combustion has practical implication for the assessment of agglomeration. It was evident that boundary-layer oxygen diffusion controlled the carbon combustion rate during oxy-fuel fluidized bed combustion using Victorian brown coal char particles. The CO₂ gasification reactions were almost negligible for the feed gases and temperature range applicable for Oxy-FB combustion.

9.1.2. Bench scale combustion experiment

The experimental results show a high level of CO_2 concentration (90-94% v/v in dry flue gas), over 99% combustion efficiency and no bed agglomeration under oxy-fuel combustion conditions even with the addition of steam at temperatures between 800°C and 900°C.

With respect to emission, up to 200 ppmv NO_X and 20 ppmv N₂O in the dry flue gas were observed using steam in oxy-fuel combustion atmosphere. The obtained NO_X level in oxy-fuel fluidized bed combustion was much lower than the level in oxy-fuel pulverized fuel combustion of coals with similar nitrogen level and within the permissible limit in coal-fired power plants in Victoria. A maximum of 125 ppm SO₂ concentration and 3 ppm SO₃ concentration were observed. The SO₂ level in oxy-fuel fluidized bed combustion of coals with similar nitrogen level and within the permissible limit of coals with similar not be required fuel combustion was much lower than the level in oxy-fuel fluidized bed combustion was much lower than the level in oxy-fuel pulverized fuel combustion of coals with similar sulphur level. This is also within the permissible limit for coal-fired power plants in Victoria. As the NO_X and SO_X emission levels are within the allowable limit, additional NO_X removal system and SO_X removal system will not be required during oxy-fuel fluidized bed combustion using Loy Yang coal.

Most of the mercury (83%) was released as toxic elemental mercury (Hg⁰), while only 17% of total gaseous mercury was emitted as oxidized mercury (Hg²⁺). This level of Hg⁰ emission, however, was higher under oxy-fuel combustion compared to air combustion. So, mercury removal system may be needed to control Hg⁰ and avoid in the CO₂ separation units if CO₂ capture is intended during oxy-fuel fluidized-bed combustion of this coal.

Direct sulphation was observed at 850°C with a SO₂ concentration level of 200 ppm using ash-limestone mixture in the Oxy-FB combustion environment. Up to 42% of sulphur conversion with 54% limestone utilization efficiency was achieved using 8% limestone mixed with ash at 800°C with 80% CO₂ and 100 ppm SO₂ in the gas atmosphere. In case of pure ash, 32% sulphur conversion was observed due to the self-desulphurization by the inherent calcium content in ash, while the extent of carbonation reaction was almost negligible. Using 8% limestone mixed with ash, up to 70% of carbonation conversion was observed over a 6 hours isothermal period at 700°C. Carbonation conversion, however, was lower when 15% steam was added to the environment.

9.1.3. Thermodynamic equilibrium modelling

Thermodynamic equilibrium modelling using FactSage suggested that higher chlorine content in combustion atmosphere, particularly at low temperature, produced more Hg^{2+} making removal of mercury easier in coal-fired oxy-fuel combustion processes. In terms of the speciation of trace elements emissions, it was predicted that the amount of toxic gaseous Cr^{6+} species was greater for oxy-fuel combustion than for air combustion. The distribution of toxic Se⁴⁺ species, however, remained almost the same in both combustion conditions within the typical temperature range for Oxy-FB combustion (800 - 950°C). At 900°C, the toxic arsenic (As³⁺) species are predicted only in the gas phase for both air and oxy-fuel combustion conditions.

9.1.4. Process modelling

Process simulation was carried out using the Aspen Plus software. It was observed that the concentrations of CO and SO₂ were higher in the lower dense region of the bed. These levels were observed to drop significantly with the introduction of secondary oxygen. However, increase in excess oxygen percentage lead to an increase in the concentration of NO_X. When the recycle flue gas ratio was increased from 0.6 to 0.7 for a given excess oxygen percentage, the concentration of CO was found to increase, while the concentrations of SO₂ and NO_X were observed to decrease marginally. Therefore, the selection of optimum recycle ratio and excess oxygen level would be crucial for the best utilization of the process. The simulated results of gaseous emission were consistent with the limited experimental data.

9.2. PRACTICAL IMPLICATIONS OF THIS RESEARCH

This thesis has identified several important issues, for the first time, on Oxy-FB combustion as a prospective process for utilization of Victorian brown coal. Some of these are as follows:

During the combustion experiments in 10 kW_{th} fluidized bed rig, combustion efficiency in excess of 99% was obtained. In addition, no bed agglomeration was observed at temperatures between 800°C and 900°C. Therefore, it is expected that agglomeration is unlikely to be a major problem for the Victorian brown coal in

oxy-fuel fluidized bed combustion, if the operating temperature is kept below 900°C.

- The measured NO_X and SO_X concentration levels in the flue gas were within the permissible limit in coal-fired power plants in Victoria. Therefore, additional NO_X removal system (such as selective catalytic reduction or low- NO_X burner) and SO_X removal system (such as flue gas desulphurization unit or scrubber) may not be required during oxy-fuel fluidized bed combustion using Loy Yang coal.
- The emission of gaseous mercury, especially the harmful elemental mercury, was considerably higher under oxy-fuel combustion compared to air combustion. Therefore, mercury removal system may be required to avoid corrosion in the CO₂ separation units if CO₂ capture and transportation is intended.
- These conventional pollutants and trace elements emission characteristics are of great importance for the design of the gas cleaning systems for CO₂ capture and storage (CCS) purposes.
- By performing experiments using 8% limestone mixed with Morwell ash over 6 hours isothermal period at different carbonation temperatures (300 800°C), highest (up to 70%) carbonation conversion was observed at 700°C. These results have practical implications for the extent of carbonation as a function of time at different downstream locations where the temperature drops below 800°C.

All these findings have important implication for the selection of optimum operating parameters during scale-up using Victorian brown coal. Overall, the information generated will be useful for a wide range of stakeholders including research organizations, technology developers, environmental agencies and policyholders for the development of brown coal utilization.

9.3. RECOMMENDATIONS FOR FUTURE RESEARCH AND DEVELOPMENT

Being the first-ever study on Oxy-FB combustion of Victorian brown coal, this research has identified the need for follow up work:

- To perform long term (greater than 8 h) experiments in the bench scale Oxy-CFB rig to investigate the agglomeration characteristics, and characterize the generated fly and bed ashes in different size bins.
- To study the carbonation kinetics by performing a series of experiments in TGA to establish the associated reaction mechanisms.
- To expand the process simulation model coupled with full power generation cycle for concentrated CO₂ production.
- To carry out longer-term tests in a large pilot plant, such as the one in CIUDEN, Spain.

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APPENDICES

APPENDIX A: CALCULATIONS FOR THE FLUIDIZED BED RIG DESIGN

Detailed calculations for the design of oxy-fuel fluidized bed (Oxy-FB) rig are given in the following tables (Table A.1 to Table A.6).

Inner diameter of the	Gas composition		
combustor : 0.1 m		O ₂	N ₂
Excess oxygen: 6% Gas velocity at 900°C: 2 m/s Coal feed rate: 2.055 kg/h	Volumetric percentage (v/v) Mass flow rate (kg/h)	21% 3.95	79% 12.51

Table A.1: Design calculation for air combustion

Table A.2: Design calculation for Oxy-FB combustion with different gas composition

Inner diameter of the combustor : 0.1 m	Gas composition	Case 1	Case 2	Case 3	Case 4	Case 5
Excess oxygen: 2%	O ₂ Volumetric percentage	10.23%	10.23%	10.23%	10.23%	10.23%
Gas velocity at 900°C: 2 m/s	(v/v)	1.00	1.02	1.02	1.02	1.02
Coal feed rate: 1 kg/h	Mass flow rate (kg/h)	1.92	1.92	1.92	1.92	1.92
Total flow rate : 0.00365 m ³ /s	CO ₂ Volumetric percentage (v/v)	64.6%	78.28%	72.81%	75.55%	75.23%
	Mass flow rate (kg/h)	16.91	20.45	19.03	19.74	19.18
	N ₂ Volumetric percentage (v/v)	0.54%	0.54%	0.54%	0.54%	0.54%
	Mass flow rate (kg/h)	0.09	0.09	0.09	0.09	0.09
	Steam Volumetric percentage (v/v)	24.63%	10.95%	16.42%	13.68%	15.00%
	Mass flow rate (kg/h)	2.6	1.16	1.74	1.45	1.59

Inner diameter of the	Coal feed rate (kg/hr)	1	2	1.5
combustor : 0.15 m	Gas Velocity at 900°C (m/s)	0.824	1.19	0.79
Excess oxygen: 2%	Gas composition O ₂			
	Volumetric percentage (v/v)	9.3%	12.9%	14.52%
	Mass flow rate (kg/h)	1.77	3.54	2.66
	CO ₂			
	Volumetric percentage (v/v)	39.47%	27.35%	9.74%
	Mass flow rate (kg/h)	10.33	10.33	2.45
	N_2			
	Volumetric percentage (v/v)	35%	48.5%	54.64%
	Mass flow rate (kg/h)	5.83	11.65	8.74
	Steam			
	Volumetric percentage (v/v)	16.22%	11.24%	21.1%
	Mass flow rate (kg/h)	1.74	1.74	2.17

Table A.3: Design calculation for Oxy-FB combustion with different coal feed rates with 0.15 m inner diameter of the combustion

Table A.4: Design calculation for Oxy-FB combustion with different coal feed rates with 0.1

m inner diameter of the combustion

Inner diameter of the combustor : 0.1 m	Coal feed rate (kg/hr)	1	2	1.5
	Gas Velocity at 900°C (m/s)	0.0037	0.0042	0.00355
Excess oxygen: 2%	Gas composition O ₂			
	Volumetric percentage (v/v) Mass flow rate (kg/h)	9.3% 1.77	16.48% 3.54	14.52% 2.66
	CO_2			
	Volumetric percentage (v/v)	39.47%	0%	9.74%
	Mass flow rate (kg/h)	10.33	0	2.45
	N_2			
	Volumetric percentage (v/v)	35%	61.98%	54.64%
	Mass flow rate (kg/h)	5.83	11.65	8.74
	Steam			
	Volumetric percentage (v/v)	16.22%	21.54%	21.1%
	Mass flow rate (kg/h)	1.74	2.6	2.17

Inner diameter of the combustor : 0.1 m		Without steam	With Steam
Excess oxygen: 2%	Gas composition O ₂		
Coal feed rate: 1 kg/h	Volumetric percentage (v/v) Mass flow rate (kg/h)	9.3% 1.77	9.3% 1.77
Gas velocity at 900°C: 1.855 m/s	CO₂ Volumetric percentage (v/v) Mass flow rate (kg/h)	55.69% 14.57	39.47% 10.33
	N ₂ Volumetric percentage (v/v) Mass flow rate (kg/h)	35% 5.83	35% 5.83
	Steam Volumetric percentage (v/v) Mass flow rate (kg/h)	0% 0	16.22% 1.74

Table A.5: Design calculation for Oxy-FB combustion with or without steam

Table A.6: Design calculation for Oxy-FB combustion with different excess oxygen at 900°C

Inner diameter of the	Excess oxygen	0%	1%	2%
combustor : 0.1 m	Gas Velocity at 900°C (m/s)	2	1.93	1.855
Coal feed rate: 1 kg/h	Gas composition O ₂			
	Volumetric percentage (v/v)	8.46%	8.87%	9.3%
	Mass flow rate (kg/h)	1.74	1.75	1.77
	CO ₂			
	Volumetric percentage (v/v)	59.71%	57.78%	55.69%
	Mass flow rate (kg/h)	16.84	15.71	14.57
	N_2			
	Volumetric percentage (v/v)	31.83%	33.36%	35%
	Mass flow rate (kg/h)	5.71	5.77	5.83