

Utilization of Waste Products as Alternative Fuels for Cement Industry

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Abstract

Cement production is an energy intensive industry and is mostly dependent on fossil fuels like coal and natural gas to fulfil the energy demand. Excessive usage of fossil fuels leads to higher CO₂ emissions. About 5%–6% of anthropogenic CO₂ is released from the cement industry which is a significant concern for the environment. Besides CO₂, other greenhouse gases like NO_x and SO₂ and some heavy metal discharges from cement industry place it under continuous scrutiny of local government and environmental protection agencies. In contrast to fossil fuel, waste derived alternative fuels offer cheaper energy sources which are capable of reducing the pollutant emissions and are environmentally sustainable. Still there are concerns on using alternative fuel regarding the quality of the cement and some emission issues as not all waste derived fuel reduces the greenhouse gas emissions. Previous studies show that no single alternative fuel could replace the entire energy requirement for cement manufacturing. In this context there is a need to identify a perfect blend of alternative fuels which could replace the fossil fuel for cement production.

The main aim of this study is to investigate the utilisation of waste products as alternative fuels in cement manufacturing and maximise their usage. This study explored the impact of using waste-derived alternative fuels on pollutant emissions and on the quality of clinker. This thesis determined the maximum substitution rate of major alternative fuels in the cement industry. The study was divided into four major sections with specific research goals. Firstly, a feasibility study was undertaken to identify the potentialities of alternative fuel sources in Australia, in particular solid alternative fuels. The second part of the study was to develop a novel computational process model capable of predicting the outcomes of using different solid alternative fuels in terms of emissions and clinker quality. The process model was developed in three stages: the preheater tower model, the kiln model and the integrated model. The third part of the study consisted of using the computational model to optimise the usage of solid alternative fuels in cement production. This part also determined a perfect blend of alternative fuels which could replace all or a major portion of the fossil fuel that was being used for energy supply. Finally, the simulation model predicted the potential opportunity of energy saving by

reducing the energy requirement for clinker production without altering the process parameters and clinker quality.

Alternative fuel substitution rates in Australia are way below best practice all over the world. This study is the first of its kind in the Australian context to investigate and determine the maximum substitution rates of potential alternative fuels for cement manufacturing. Many alternative fuels were considered throughout the study, but only five were examined using the integrated model, namely waste tyres, MSW, MBM, plastic waste and bagasse.

Based on the simulation results of the investigated model, it was found that the maximum substitution rates of selected alternative fuels for the operating conditions of local plants are: waste tyres 18%, MSW 15%, MBM 20%, plastic waste 12% and bagasse 5%. Emission results indicate that, in optimised operating conditions, each alternative fuel can reduce CO₂ emissions and about a 5% reduction in CO₂ was achieved for MSW and MBM. It is to be noted that the selected alternative fuels have very minimal influences on clinker quality. In the process of determining maximum substitution rates, a baseline emission standard was set as no such standard is available at the Australian national level. The baseline standard outlined in this study could be the starting point for policy makers to develop a national emissions standard for Australia. The integrated model identified the potential energy saving opportunity through employing alternative fuels and a maximum of 6.4% energy saving can be achieved by using MBM in optimised conditions.

This study provided a clear understanding and guidelines to Australian cement manufacturers and stakeholders on using different alternative fuels in optimal proportion. The computational model presented in this thesis could be one of the important tools for the cement industry to identify new alternative fuels before being tested and implemented. This study also promoted alternative fuels as a climate friendly sustainable energy source for the cement industry which may help the community to develop a green future.

Declaration

I, Azad Rahman, hereby declare that this thesis is entirely my own original work and has not been presented elsewhere for any other degree or diploma. All the work presented in this thesis is original, except where otherwise indicated. To the best of my knowledge and belief, any material presented by any person or institute is duly referenced and a complete list of all references is presented in the bibliography.

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April 2016

Table of Contents

i. Abstract	ii
ii. Declaration	iv
iii. Copyright Statement	v
iv. Table of Contents.....	vi
v. List of Tables.....	xii
vi. List of Figures	xiv
vii. List of Symbols.....	xviii
viii. Acronyms.....	xx
ix. Acknowledgements	xxii
x. List of Publications	xxiii
1 Chapter One: Introduction.....	1
1.1 Background and Significance.....	1
1.2 Scope of the Study	3
1.3 Aim and Objectives of the Study	5
1.4 Major Contributions	6
1.4.1 Contribution 1: Feasibility study of alternative fuel.....	6
1.4.2 Contribution 2: development of process model.....	7
1.4.3 Contribution 3: Optimal usage of alternative fuel	7
1.4.4 Contribution 4: Potential impact on emission and clinker quality.....	7
1.4.5 Contribution 5: Reduction of energy requirement for the process	7
1.5 Limitations of the study.....	8
1.6 Thesis framework.....	8

2	Chapter Two: Literature Review.....	10
2.1	Ancient History of Cement and Current Usage	10
2.2	Cement Manufacturing Process	12
2.2.1	Raw Materials	14
2.2.2	Preparation of Raw Materials	14
2.2.3	Preheater and Precalciner.....	15
2.2.4	Kiln	16
2.2.5	Clinker Cooling and Grinding	16
2.2.6	Storage and Transportation	16
2.3	Chemistry of Cement	17
2.4	Fuels in Cement Manufacturing.....	20
2.5	Thermal and Environmental Performance of Cement Plant	21
2.6	Emission	24
2.6.1	Global emission standard.....	27
2.7	Process Modelling and Simulation.....	30
2.7.1	Aspen plus.....	33
2.7.2	Aspen HYSYS	33
2.7.3	ANSYS Fluent	34
2.7.4	CHEMCAD	34
2.7.5	Selection of Software.....	35
2.8	Concluding Remarks.....	35
3	Chapter Three: Alternative Fuels.....	37
3.1	Introduction	37
3.2	Kiln as the destination of waste.....	37
3.3	Usage of Alternative Fuels.....	38

3.4	Advantages of Using Alternative Fuels	40
3.5	Disadvantages of Using Alternative Fuels	41
3.6	Criteria of Alternative Fuels.....	41
3.7	Classification of Alternative Fuel	44
3.8	Alternative Fuel Options	45
3.8.1	Used Tyre.....	46
3.8.2	Spent pot liner	50
3.8.3	Spent Solvent and Used Oil	52
3.8.4	Municipal Solid Waste (MSW)	55
3.8.5	Plastic Waste	59
3.8.6	Meat and Bone Meal	60
3.8.7	Sewage Sludge	61
3.8.8	Agricultural Biomass	64
3.8.8.1	Agricultural biomasses in Australia	66
3.8.9	Others	67
3.9	Discussion and recommendation.....	68
3.9.1	Availability	68
3.9.2	Substitution rate	70
3.9.3	Emission factor	70
3.9.4	Storage handling and installation.....	71
3.9.5	Comparison	71
3.9.6	Recommendation	73
3.10	Conclusion.....	74
4	Chapter Four: Research Methodology	75
4.1	Introduction	75

4.2	Synergy opportunities among the industries	77
4.3	Data Collection.....	80
4.4	Modelling and Simulation approach	82
4.4.1	Sub stage of the simulation process	83
4.4.2	Selection of operation block	85
4.4.3	Selection of stream class.....	87
4.4.4	Component specification	88
4.4.5	Selection of property method.....	89
4.4.6	Energy and Mass Balance	91
4.5	Report option.....	92
4.5.1	Setup for emission results	92
4.5.2	Quality control of clinker.....	93
4.5.2.1	Lime saturation factor (LSF).....	93
4.5.2.2	Silica ratio (SR).....	93
4.5.2.3	Alumina ratio.....	94
4.6	Analysis for Coal.....	94
4.6.1	Scenario analysis of coal.....	95
4.6.2	Coal combustion model	97
4.7	Sensitivity analysis of coal combustion	101
4.8	Conclusion.....	106
5	Chapter Five: Preheater Tower Modelling.....	108
5.1	Introduction	108
5.2	Calciner	109
5.2.1	Classification of calciner.....	109
5.2.2	Alternative fuel for calciner model	110

5.2.3	Calciner model development	111
5.2.4	Calciner Model Validation.....	113
5.2.5	Modified Calciner Model for Alternative Fuel Burning.....	115
5.2.6	Simulation results and discussion for calciner.....	116
5.2.7	Concluding remark on calciner model.....	120
5.3	Preheater tower.....	121
5.3.1	Preheater tower model	122
5.3.2	Results and discussion for preheater tower model.....	124
5.3.3	Improvement on energy demand	128
5.3.4	Concluding remark on preheater tower model.....	130
5.4	Conclusion.....	130
6	Chapter Six: Development of Process Model for Kiln	132
6.1	Introduction	132
6.2	Pyroprocessing reactions in kiln	133
6.3	Alternative fuels for kiln	135
6.4	Agricultural biomass as alternative fuel in cement kiln.....	136
6.4.1	Chemical composition of alternative fuels	137
6.5	Kiln process model.....	138
6.5.1	Model Principle.....	138
6.5.2	Model Assumption.....	140
6.5.3	Model Validation	142
6.6	Simulation results and discussion	143
6.7	Concluding remark on kiln model.....	149
6.8	Modified Kiln Model	150
6.8.1	Alternative fuels for modified kiln model	152

6.8.2	Results and discussion for modified kiln model	154
6.8.3	Concluding comments on modified kiln model	159
6.9	Conclusion	159
7	Chapter Seven: Integrated Model for Cement Manufacturing	162
7.1	Introduction	162
7.2	Alternative fuels for process model	163
7.3	Development of Integrated Model	165
7.4	Simulation results and discussion	168
7.5	Blended alternative fuels for integrated model	175
7.6	Analysis for blended alternative fuels	176
7.7	Conclusion	182
8	Chapter Eight: Conclusions and Recommendations	185
8.1	Introduction	185
8.2	Outcomes of the Thesis	185
8.2.1	Feasibility study	186
8.2.2	Computational model development	187
8.2.3	Maximum substitution rate of alternative fuel	188
8.2.4	Impact analysis	190
8.2.5	Energy savings opportunity	191
8.3	Contributions	192
8.4	Recommendation for future research	192
	References	194
	Appendix	214

List of Tables

Table 1.1: Usage of alternative fuels in different countries.....	4
Table 2.1: Cement production in the world.....	11
Table 2.2: Typical composition of Portland cement.....	17
Table 2.3: Reactions and reaction enthalpies.....	19
Table 2.4: Reactions occurring stage.....	19
Table 2.5: Specific thermal energy consumption in different kiln process	20
Table 2.6: Fuel mix for burning clinker (% of total fuels only based on thermal energy)	21
Table 2.7: Baseline Performance of the Cement Industry	22
Table 2.8: Thermal efficiency of cement manufacturing group	23
Table 2.9: Environmental performance of five cement manufacturing group	24
Table 2.10: Air Emissions Limits for cement co-processing plants from EU Waste Incineration Directive.....	28
Table 2.11: Average Emissions from cement plant Gladstone, Queensland	29
Table 2.12: Emissions standard for different country for SO ₂ and NO _x	29
Table 3.1: Percentage of different type of waste used as alternative fuels	39
Table 3.2: Typical quality parameters for co-firing in cement manufacturing process.....	43
Table 3.3: Category of solid alternative fuel	44
Table 3.4: Advantages and disadvantages of different forms of tyre derived fuels	47
Table 3.5: Ultimate analysis of tires and coal by percentage of weight	49
Table 3.6: Typical SPL composition	52
Table 3.7: Elementary composition of waste solvent & heavy fuel oil.....	54
Table 3.8: Waste generation in selected countries in 2005	55
Table 3.9: Typical composition of MSW by material	57
Table 3.10: Chemical composition of MSW and RDF.....	58
Table 3.11: Proximate and ultimate analysis of fuels	63
Table 3.12: Typical heating values for several types of sewage sludge	63
Table 3.13: Proximate analyses of selected biomass fuels (wt%).	65
Table 3.14: Ultimate analyses of selected biomass fuels (wt% fuel with ash)	66

Table 3.15: Crop production of Australia	67
Table 3.16: Proximate, Ultimate and Ash analysis of different alternative fuels	69
Table 3.17: Comparison of different Alternative fuels	72
Table 4.1: Synergy opportunities for cement industry in Gladstone	79
Table 4.2: Preliminary process breakdown.....	84
Table 4.3: Aspen plus operation blocks.....	86
Table 4.4: Material stream class	88
Table 4.5: List of component used in the model.....	88
Table 4.6: property method for coal processing	89
Table 4.7: Property model for nonconventional component	90
Table 4.8: elemental analysis of coal from different source.....	96
Table 5.1: Elemental analysis of fuel.....	111
Table 5.2: Comparison of simulation results and literature values.....	114
Table 5.3: Elemental analysis of waste tyre, MBM and RDF	125
Table 5.4: Simulation results for energy efficiency.....	129
Table 6.1: Elemental analysis of fuel.....	138
Table 6.2: Validation of simulation results against plant data.....	143
Table 6.3: Simulation results for energy saving	148
Table 6.4: Modified model validation	152
Table 6.5: Chemical composition and elemental analyses of fuels	153
Table 7.1: Analysis of alternative fuels	164
Table 7.2: Integrated model validation	167
Table 7.3: Analysis of potential improvement in emission and energy savings.....	174
Table 7.4: Thermal energy substitution by alternative fuels in different fuel blend.....	176

List of Figures

Figure 1.1 Percentage of ingredients in concrete.....	1
Figure 1.2: Usage of alternative fuel by Australian cement industry	4
Figure 2.1: Cement & Clinker production in Australia	12
Figure 2.2: Schematic presentation of the cement manufacturing process from quarry to dispatch	13
Figure 2.3: Clinker production in Australia by kiln type.....	14
Figure 2.4: Preheater Tower and Precalciner.....	15
Figure 2.5: Cement manufacturing process: Release of pollutants into atmosphere.....	27
Figure 3.1: Waste recovery by cement industry reduces emission.....	40
Figure 3.2: Tonnes of alternative fuel required to replace 1 tonne of coal.....	43
Figure 3.3: List of fuels (conventional & alternatives) in cement industry	45
Figure 3.4: Tyre as alternative fuel in cement manufacturing	46
Figure 3.5: a) Landfill of tyre, b) Scrape tyre, c) Used tires being fed to a cement kilns....	48
Figure 3.6: Air emission data for burning tyre	49
Figure 3.7: a) Aluminium smelting cells, b) Hall-Heroult Aluminium reduction cell,.....	51
Figure 3.8: a) Spent Solvent, b) Waste oil, c) Paint residue, d) Paint sludge	53
Figure 3.9: a) Municipal solid waste, b) Municipal solid waste is shredded and ground into a uniform particle size, c) Refuse-derived fuels	56
Figure 3.10: a) Mixed plastic waste, b) Bundled plastic waste,.....	59
Figure 3.11: a) Waste from slaughter house, b) Meat and Bone Meal (MBM).....	61
Figure 3.12: a) Waste water disposal, b) Wastewater treatment plant, c) Sewage Sludge after treatment	62
Figure 4.1: Flowchart of the research activities.....	76
Figure 4.2: Existing and possible synergies with industries in Gladstone region	78
Figure 4.3: Australian black coal resources.....	95
Figure 4.4: Coal combustion model.....	97
Figure 4.5: CO ₂ emission from coal combustion.....	98
Figure 4.6: NO _x emission from 4000 kg/hr coal combustion	99

Figure 4.7: Heating value and outlet temperature from combustion of coal from different source.....	99
Figure 4.8: a) Correlation between heating value and outlet temperature, b) correlation between moisture content and outlet temperature.....	100
Figure 4.9: Variation of temperature with air flow in the burning zone.....	102
Figure 4.10: Changes in CO ₂ and CO emission with air flow.....	102
Figure 4.11: Variation in NO _x emission with air flow rate.....	103
Figure 4.12: Effect of moisture content on outlet temperature.....	104
Figure 4.13: Effect of moisture content on CO ₂ and CO emission.....	104
Figure 4.14: Sensitivity curve of temperature against the heating value of coal.....	105
Figure 4.15: Variation in NO _x emission against the heating value of coal.....	106
Figure 5.1: Schematic diagram of ILC with single string pre-heatre tower.....	110
Figure 5.2: Calciner model for coal firing.....	112
Figure 5.3: Modified Calciner model for alternative fuel burning.....	115
Figure 5.4: CO ₂ emission from calciner (kg/tonne clinker).....	117
Figure 5.5: CO emission from calciner (kg/tonne clinker).....	118
Figure 5.6: NO _x emission from calciner (mg/Nm ³).....	118
Figure 5.7: SO ₂ emission from calciner (kg/tonne clinker).....	119
Figure 5.8: Outlet gas Temperature (°K).....	120
Figure 5.9: flow sheet of preheater tower model with calciner.....	123
Figure 5.10: CO ₂ emission from preheater tower (kg/tonne clinker).....	126
Figure 5.11: NO _x emission from preheater tower (mg/Nm ³).....	126
Figure 5.12: SO ₂ emission from preheater tower (mg/Nm ³).....	127
Figure 5.13: Calciner Outlet Temperature (K).....	127
Figure 6.1: Temperature profile and the qualitative profile of the heat of reaction.....	134
Figure 6.2: Multi-channel burner nozzle.....	135
Figure 6.3: a) Almond shell, b) Coffee husks used as alternative fuel.....	137
Figure 6.4: Typical mass balance of the kiln system.....	139
Figure 6.5: Kiln proces model for agricultural biomass as alternative fuel.....	142
Figure 6.6: CO ₂ emission from kiln (kg/tonne clinker).....	144
Figure 6.7: CO emission from kiln (kg/tonne clinker).....	145

Figure 6.8: NO _x concentration in the kiln gas (mg/Nm ³).....	145
Figure 6.9: SO ₂ emission from calciner (kg/tonne clinker)	146
Figure 6.10: Daily clinker production from simulation results (tonne/day)	146
Figure 6.11: Outlet gas temperature (°C).....	147
Figure 6.12: Percentage of free lime present in the clinker	148
Figure 6.13: Modified kiln proces model	151
Figure 6.14: CO ₂ emission from kiln (kg/tonne clinker)	154
Figure 6.15: Concentration of NO _x and SO ₂ in kiln gas (mg/Nm ³)	155
Figure 6.16: composition analysis of clinker	156
Figure 6.17: LSF and percentage of free lime in clinker	157
Figure 6.18: kiln outlet temperature.....	158
Figure 6.19: Daily production rate of clinker	158
Figure 7.1: Integrated process model for cement manufacturing	166
Figure 7.2: Net CO ₂ emission (kg/tonne clinker)	169
Figure 7.3: NO _x concentration in stack gas (mg/Nm ³)	170
Figure 7.4: SO ₂ concentration in stack gas (mg/Nm ³).....	170
Figure 7.5: Excess amount of oxygen in calciner	171
Figure 7.6: Impact on clinker quality a) LSF b) AR and c) SR.....	172
Figure 7.7: a) Kiln outlet temperature (°C), b) clinker production (tonne/day).....	173
Figure 7.8: Net CO ₂ emission (kg/tonne clinker) for different blend of alternative fuels	177
Figure 7.9: NO _x concentration in stack gas	178
Figure 7.10: Excess amount of O ₂ in calciner	179
Figure 7.11: SO ₂ concentration in stack gas (mg/Nm ³).....	179
Figure 7.12: Clinker composition for different blend of alternative fuels.....	180
Figure 7.13: Changes in a) LSF and b) SR & AR for different blend of alternative fuels ...	181
Figure 7.14: daily production of clinker (tonne/day).....	182
Figure A.1: Global specification sheet in Aspen Plus simulation	214
Figure A.2: Component specification sheet.....	215
Figure A.3: Global property specification information in Aspen plus	216
Figure A.4: User defined property parameter sheet for heating values of fuels.	216
Figure A.5: Assigning Enthalpy and Density model nonconventional component.....	217

Figure A.6: Coal input stream specification	217
Figure A.7: Specify the elemental analysis of coal.....	218
Figure A.8: Specification sheet for alternative fuel input.....	218
Figure A.9: Operating conditions for RGibs reactor	219
Figure A.10: Entering reaction stoichiometry for RStoic reactor.....	220
Figure A.11: Specification sheet for Cyclone block.....	220
Figure A.12: CO ₂ emission summary from simulation results.....	221
Figure A.13: Custom stream summary containing input and output results for all stream and block.....	222
Figure A.14: Material stream summary results for clinker stream	222

List of Symbols

$w_{i,j}$	Mass fraction of the j th constituent in component i
$\rho_{i,j}^s$	Density of the j th constituent in component i
C_p	Heat capacity (J/kgK)
h	Specific enthalpy (J/kg)
$\Delta_c h$	Specific heat of combustion
$\Delta_f h$	Specific heat of formation
T	Temperature (K)
t	Temperature (°C)
w	Weight fraction
ρ	Specific density (kg/m ³)
Subscripts	
A	Ash
C	Carbon
Cl	Chlorine
FC	Fixed carbon
H	Hydrogen
H_2O	Moisture
MM	Mineral matter
N	Nitrogen
O	Oxygen
So	Organic sulphur
Sp	Pyritic sulphur
St	Total sulphur

<i>S</i>	Other sulphur
<i>VM</i>	Volatile matter
Superscripts:	
<i>d</i>	Dry basis
<i>m</i>	Mineral-matter-free basis
<i>s</i>	Solid Property

Acronyms

ABARES	Australian Bureau of Agricultural and Resource
AF	Alternative Fuels
AR	Alumina Ratio
ASPEN	Advanced System for Process Engineering
ASR	Automobile Shredder Residue
BAT	Best Available Technique
BSE	Bovine Spongiform Encephalopathy
CFD	Computational Fluid Dynamics
CIF	Cement Industry Federation
CKD	Cement Kiln Dust
CV	Calorific Value
DDC	Dual Combustion and Denitration Calciner
EC	European Commission
ESP	Electrostatic Precipitators
EU	European Union
GCV	Gross Calorific Value
GERIAP	Greenhouse Gas Emission Reduction from Industry in Asia and the Pacific
GHG	Green House Gas
GUI	Graphical User Interface
HAL	Horticulture Australia Limited
HHV	Higher Heating Value
HM	Hydraulic Modulus
IEA	International Energy Agency

ILC	In Line Calciner
KPI	Key Performance Indicator
LHV	Lower Heating Value
LSF	Lime Saturation Factor
MBM	Meat & Bone Meal
MSW	Municipal Solid Waste
OECD	Organisation for Economic Cooperation and Development
OPC	Ordinary Portland Cement
PCA	Portland Cement Association
PCDD	Polychlorinated Dibenzodioxins
PCDF	Polychlorinated Dibenzofurans
PM	Particulate Matter
RDF	Refuse Derived Fuel
SETIS	Strategic Energy Technologies Information System
SLC	Separate Line Calciner
SPL	Spent Pot Liner
SR	Silica Ratio
SR	Shredder Residue
SRF	Solid Recovered Fuel
SS	Sewage Sludge
TDF	Tyre Derived Fuel
TOC	Total Organic Compounds
USGS	U.S. Geological Survey
VOC	Volatile Organic Compound
WBCSD	World Business Council For Sustainable Development

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List of Publications

The following articles were produced for publication during the course of my candidature:

Refereed Book Chapter

1. Azad Rahman, M.G. Rasul, M.M.K. Khan, S. Sharma 2015, Cement Kiln Process Modelling to Achieve Energy Efficiency by Utilizing Agricultural Biomass as Alternative Fuels in *Thermofluids Modeling For Energy Efficiency Applications* edited by M. Masud K. Khan and Nur Md. Sayeed Hassan, Elsevier 2015 (in press).

Referred Journal Papers

1. Azad Rahman, M.G. Rasul, M.M.K. Khan, S. Sharma, Recent development on the uses of alternative fuels in cement manufacturing process. *Fuel*, vol. 145, 2015, pp. 84-99.
2. Azad Rahman, M.G. Rasul, M.M.K. Khan, S. Sharma, Aspen Plus based simulation for energy recovery from waste to utilize in cement plant preheater tower. *Energy Procedia*, vol. 61, 2014, pp. 922 – 927.
3. Azad Rahman, M.G. Rasul, M.M.K. Khan, S. Sharma, Impact of alternative fuels on the cement manufacturing plant performance: an overview. *Procedia Engineering*, vol. 56, 2013, pp. 393 – 400.
4. K.T. Kaddatz, M.G. Rasul, Azad Rahman, Alternative fuels for use in cement kilns: process impact modelling. *Procedia Engineering*, vol. 56, 2013, pp. 413 – 420.

Referred Conference Papers

1. Rahman, A., Rasul, M.G., Khan, M.M.K, Sharma, S., Industrial waste as alternative fuels in cement industry: its impact on environment. *Proceedings of the 7th WSEAS International Conference on Energy & Environment (EE'12)*, pp. 108-114; 14-17 July, 2012, Kos Island, Greece.
2. Azad Rahman, M.G. Rasul, M.M.K. Khan, S. Sharma, Cement calciner model development for optimizing the usage of alternative fuels. *Proceeding of 12th International Conference on Sustainable Energy Technologies (SET-2013)*, pp. 1784-1794; 26-29th August, 2013, Hong Kong, Paper ID: SET2013-307.

Chapter One

Introduction

1.1 Background and Significance

Given the facts of a high energy demand for the modern world and the limited amount of non-renewable fossil fuel, there is a need to identify potential alternative energy sources which are sustainable and environment friendly. Cement as an energy intensive industry and heavily dependent on fossil fuel; the urge is even higher along with a requirement to mitigate pollutant emission. Alternative fuel and raw material provide a realistic solution of the problem up to some extent. Acceptance of varieties of waste as an alternative fuel in the cement industry opens up the field of research to identify and optimise the usage of alternative fuel in the manufacturing process.

Cement is a fine grained powder made of limestone and clay minerals and acts as a binding agent of concrete. Second only to water, concrete is the most consumed material on earth. Almost three tonnes of concrete are produced in the world per person, twice as much as the rest of materials together, including wood, steel, plastics and aluminium (Strategic Energy Technologies Information System [SETIS], 2001). Concrete is formed by mixing water, sand, gravel and other material with cement in a certain proportion. Figure 1.1 shows the typical ratio of concrete ingredients by volume where cement constitutes 11% (Portland Cement Association [PCA], 2011). Though cement comprises only 10–15% of the mass of concrete, it plays a significant role in determining the cost of concrete, its environmental impact, and the properties of concrete.



Figure 1.1 Percentage of ingredients in concrete

To meet the requirements of the modern world, about 4 billion metric tonnes of cement was produced across the world in 2014 (U.S. Geological Survey [USGS], 2014). The cement manufacturing process requires approximately 3.2 to 6.3 GJ of energy and 1.7 tonnes of raw materials (mainly limestone) per tonne of clinker produced (van Oss & Padovani, 2002, 2003), which makes it one of the energy intensive industries. A major share of thermal energy is required for calcination and pyro-processing of clinker in the burning zone. Typical electrical energy consumption of a modern cement plant is about 110–120kWh per tonne of cement which is mainly used during cement grinding (Madloul et al. 2011). In general, the energy cost in a cement plant is around 30%–40% of the total production costs (Rasul et al. 2005).

Generally fossil fuels such as coal, petroleum coke (petcoke) and natural gas accomplish the thermal energy requirement of the cement industry. Usage of alternative fuel (AF) becomes more warranted to the cement manufacturer due to increasing fossil fuel prices, limited fossil fuel resources and environmental concerns (Rahman et al. 2013). Alternative fuel includes all non-fossil fuels and waste from other industries including tyre-derived fuels, biomass residues, sewage sludge and other household wastes (Nielsen et al., 2011).

The rotary kiln used in cement manufacturing is favourable to burn a wide range of waste due to the long exposure time at high temperatures, intrinsic ability for clinker to absorb and lock contaminants into the clinker and the alkalinity of the kiln environment (Rahman et al. 2013). Materials like waste oils, plastics, waste tyres, municipal solid waste and sewage sludge are often proposed as alternative fuels for the cement industry. Meat and bone meal and several agricultural biomasses are also considered now as effective alternative fuel (Kaantee et al., 2004). Spent pot linings, an industrial waste of aluminium smelters, are recently identified as a potential alternative fuel for the cement industry (Lechtenberg, 2009). In order to utilise certain waste as alternative fuel in a cement kiln, it is necessary to analyse the physical, chemical and thermal characteristics of each waste and its compatibility to the clinkering process.

Beside the conservation of non-renewable energy sources, environmental advantage can be achieved by using alternative fuels in the cement industry through the reduction of waste disposal sites and reduction of emission. The cement industry is one of the heavy pollutant industries and accountable for the 5%–6% releases of all carbon dioxide generated by

human activities, which causes about 4% of global warming (Rodrigues & Joeke, 2011). Along with carbon dioxide other greenhouse gases (GHG) like NO_x and SO₂ discharge from the cement manufacturing system which has a severe impact on the environment. Heavy metal emission from the cement industry is another concern and needs to be suitably controlled. The environmental impact of alternative fuels needs to be assessed before implementing them in the manufacturing process.

The quality of the clinker is strictly controlled in the process and any alteration of the process, by introducing new alternative fuel, could change it drastically which may affect the performance of the concrete. Alternative fuels could possibly change the kiln environment (temperature, pressure) which may lead to an improper chemical combination for clinker as a certain temperature is required for the chemical reactions of clinkerization. Beside this, due to the nature of the manufacturing process, all combustion residue remains inside the kiln and take part in the clinker formation reaction. It suggests that the ash quality of any fuel used in cement manufacturing needs to be taken into account to identify potential change in the clinker quality. Any adverse effect on the clinker quality may obliterate the potential benefits that may be derived by using alternative fuel.

Maximum benefit can be achieved by increasing the substitution rate of alternative fuels or by a blend of alternative fuels depending on the process, adaptability of the process, emission and the clinker quality. During the last two decades several researches were carried out regarding the usage of alternative fuel in cement kilns but scant literature is found in the direction of optimal proportion of different alternative fuel which can possibly replace the part or entire fossil fuels requirement. The aim of this study is to investigate the feasibility of different alternative fuels that can be used in cement manufacturing at maximum proportion and examine the impact of different blends of alternative fuels.

1.2 Scope of the Study

Under increasing pressure from the environmental protection agencies, cement manufacturers lean towards the alternative fuels to reduce pollutant emission and to attain other ecological benefits like conserving non-renewable resources (Trezza & Scian, 2000). The substitution rate of alternative fuels varies from country to country and most of the European countries are way ahead in the usage percentage of alternative fuels than the rest of the world. The substitution rate of different countries is shown in Table 1.1 (Rahman et

al., 2015) which indicate that Australia only achieved 7.8% substitution rate in contrast to 85% substitution rate in the Netherlands.

Table 1.1: Usage of alternative fuels in different countries

Country or Region	% Substitution	Country or Region	% Substitution
Australia (2013)	7.8	Germany (2010)	53.6
Japan (2012)	15.5	EU (2012)	18
Sweden (2011)	45	Poland (2010)	45
Switzerland (2012)	41	Spain (2011)	22.4
(Only Holcim)			
Netherlands (2011)	85	Belgium (2011)	60
Canada (2008)	11.3	USA (2004)	8

Source: Rahman et al., 2015

Australia's abundance of coal has helped to keep energy prices low but makes it one of the world's highest per-capita GHG emission producing countries (Organisation for Economic Cooperation and Development [OECD], 2013) because of its reliance on coal-fired power. The cement industry is also heavily dependent on coal and natural gas and its usage of alternative fuels is way below to the best practice in the world. Along with the fuel generated CO₂, the cement industry releases process CO₂ through calcination which cannot be reduced immensely without lowering the production. CO₂ generated from fuel combustion from the cement industry can be reduced and alternative fuels become the redeemer in this case. The progress on usage of alternative fuel in Australia since 1991 is illustrated in Figure 1.2 which indicates inconsistent and slow growth over the last two decades.

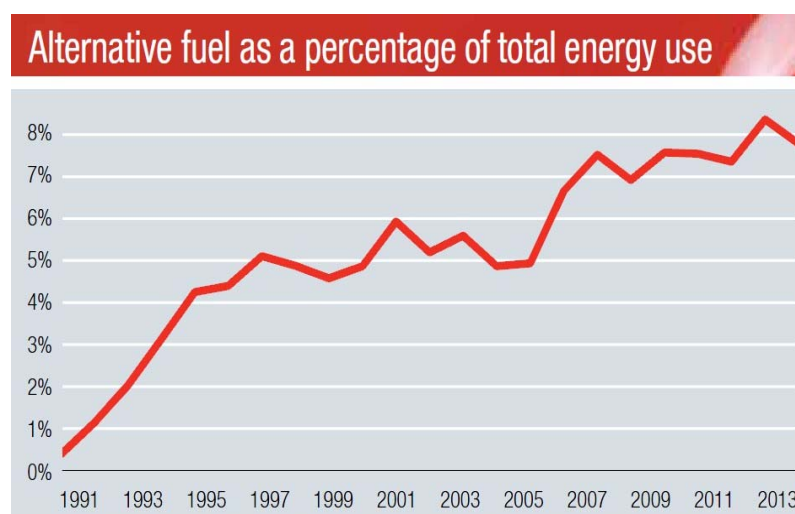


Figure 1.2: Usage of alternative fuel by Australian cement industry

Source: Cement Industry Federation (CIF), 2013

Waste tyres, used oil, demolition timber and solvent based fuel are a few alternative fuels which are currently being used by the Australian cement industry (CIF, 2013). There is a significant scope to increase the safe use of alternative fuel in the Australian cement industry and this study aims to identify a few alternative fuels to be used in optimum proportion.

This study explores most of the feasible alternative fuels that can be utilised in Australia and focuses on the potential environmental impact and variation in clinker quality. To fulfil the requirement of this study, a process model is developed to carry out simulation results. Computational process models are frequently used in industries like cement to reduce the financial risk of experimental study. The scope of this study is not limited to identify the alternative fuels but to maximise their usage and to find out a perfect blend of alternative fuels to substitute the major portion of coal requirement. Based on the available information for the selection of the tools for this study, Advanced System for Process Engineering (Aspen plus) was found to be suitable and relevant. The simulation model was validated against the real life data from a local cement plant. In simulation only solid alternative fuels were considered due to their availability and similar feeding technique like coal.

1.3 Aim and Objectives of the Study

The main aim of this study is to *investigate how the maximum quantity of selected alternative fuels can be efficiently utilised in cement manufacturing without negative impact on the environment and process performance.*

Due to increasing pressures to implement sustainable and environmentally friendly manufacturing techniques, there has been an increased exploration of alternative fuels to power the cement kiln. Testing of possible alternative fuels has been limited by the economic risks associated with real world experimentation with alternative fuels. The focus of this research is to develop a valid computational model of cement manufacturing process to investigate the feasibility of using numerous alternative fuels. The key research questions which have been addressed in this study are:

Question 1: Which are the potential alternative fuels in the Australian context?

Question 2: What are the optimum substitution rates of fossil fuels by these alternative fuels?

Question 3: What are the impacts on air emission and on the clinker quality due to the optimal use of selected alternative fuels?

Question 4: Is there any opportunity to reduce the energy demand for the cement industry by introducing alternative fuels or a blend of alternative fuels?

With a view of getting the answers to these questions, the specific objectives that were achieved are to:

- Identify the best practice of using alternative fuels in the cement industry around the world.
- Identify the potential alternative fuels in the Australian perspective.
- Develop a valid computational model of the cement manufacturing process for thermal and environmental performance by using process engineering software Aspen plus.
- Explore the optimised combustion process for different alternative fuels.
- Analyse the environmental impact in terms of air emission results from a computational model.
- Analyse the chemical composition of clinker to determine the effect of using alternative fuels.
- Identify a possible energy improvement scenario.
- Make a recommendation on the optimal usage of selected alternative fuels and identify an optimum blend of alternative fuels.

1.4 Major Contributions

This study contributed into five major areas. These are: feasibility of usage of solid alternative fuels in the Australian cement industry; development of a valid process model for cement manufacturing; determination of maximum usage percentage of selected alternative fuels; assessment of environmental impact and clinker quality; clinker quality; and investigation of energy saving opportunity in cement kiln.

1.4.1 Contribution 1: Feasibility study of alternative fuel

Recent statistics show that only about 7.8% substitution rate for alternative fuel is achieved by the Australian cement industry which is way lower than most of the European countries. Some legislative regulation and definitional barriers restrict the usage of alternative fuels in maximum proportion. Identifying potential alternative fuels with their positive impact on the environment could assist policymakers to change the law regarding the usage of

waste derived fuels. This study explores most of the feasible alternative fuels in the Australian context through extensive literature review. Potential substitution rates for different alternative fuels were also revealed from literature.

1.4.2 Contribution 2: development of process model

A novel computational process model was developed by using Aspen plus software to assess the impact of alternative fuels on emission and clinker quality. Initially a different section of the manufacturing process was modelled and finally an integrated model for the entire process was developed. The model was validated with data obtained from local cement plant. The integrated model was used to analyse different blends of alternative fuels.

1.4.3 Contribution 3: Optimal usage of alternative fuel

The substitution rate used for different alternative fuels is available in literature but with variations due to the fact that they depend on the operating conditions of an individual plant. On the basis of available data from a local cement plant, a maximum substitution rate of selected alternative fuels was proposed from the simulation results. The maximum substitution rate was also used in search of a perfect blend of alternative fuel.

1.4.4 Contribution 4: Potential impact on emission and clinker quality

The impact of using alternative fuels in different operating conditions was revealed in this study. Greenhouse gas emission was extensively studied to identify any reduction below the existing Australian standard. As the binding agent of concrete, cement quality needs to be up to the standard and any fluctuation may lead to devastating destruction. The quality of clinker in terms of composition ratio was also studied in this section. Variation on the kiln environment in terms of temperature was included in this section to justify the changes in clinker quality.

1.4.5 Contribution 5: Reduction of energy requirement for the process

The energy saving aspects of using alternative fuels was studied, which is another contribution of this thesis. As an energy intensive industry, cement is always aiming to reduce its thermal energy requirement by introducing modern technologies. The reduction of fuel to produce clinker with desired quality implies the reduction of thermal energy requirements. A small improvement in energy demand was observed in the simulation

results. This improvement comes at the expense of daily production; additional raw meal is required to maintain a consistent production rate.

1.5 Limitations of the study

The main objective of this study was to investigate the usage of alternative fuels in cement production. Scope of this research is only in the cement burning process and in evaluating the feasibility of alternative fuels. A computational model has been used to assess the optimal usage proportion of different alternative fuels and to analyse the process performance and environmental impact. This study deals with simulation based results obtained from a computational model and no experimental investigation was carried out due to the extreme process conditions of cement manufacturing and the financial risk involved. To obtain valid results, actual plant data from a local industry was used for model validation which implies that presented results may not be applicable to every cement plant as it is dependent on the process route and operating conditions. Consideration in terms of the effect of alternative fuels on the hydration of cement was beyond the scope of this thesis. Transport, storage, handling and delivery of alternative fuels were also not included in this research work.

1.6 Thesis framework

A computational process model was presented in this study to assess the impact of alternative fuels in the cement industry. A comprehensive literature review followed by the feasibility study of alternative fuels in the Australian context were done to identify potential alternative fuels for the cement industry. The Aspen plus based process model was developed using available data from a local cement plant along with the available information from literature. A process model was used to identify the pros and cons of selected alternative fuels and to maximise their usage in the manufacturing process. Performance of the alternative fuels in terms of emission and clinker quality was explored from the simulation results. Finally, a potential energy efficiency improvement opportunity was identified from simulation results. The outline of this thesis is given below to provide a glance of the chapter content.

Chapter 1 summarises the general background and significance of the study. The objective of the study along with the research questions are identified as a consequence. Research contributions are also described in this chapter.

Chapter 2 reviews the relevant literature regarding the cement manufacturing process and the cement chemistry. Energy sources for the cement industry and pollutant emissions from the same are also discussed in this chapter. Information regarding current practices of fuel mix and emission standard are included to identify the improvement opportunity for different sectors. Research efforts to develop process models are appraised to facilitate the selection of tools for this study.

Chapter 3 presents a detailed review of alternative fuels in the cement industry with their advantages, disadvantages, substitution rate and environmental impact. Through the review, research gaps are identified and the objective of this study is outlined.

Chapter 4 explains detailed methodology of current research work along with the selection of process simulation software. Collection of cement plant data and their nature are also discussed in this chapter.

Chapter 5 offers the development of a process model for the preheater tower section of a cement plant and runs the model with a set of solid alternative fuels. On the course of model construction an in-line calciner (ILC) model has been developed as an important section of the preheater tower.

Chapter 6 describes the structure of a kiln model based on mass and energy balance. A selection of agricultural biomass from the Australian context is studied in this chapter. Furthermore, a set of alternative fuels which is considered to form a perfect blend is finalised in this chapter.

Chapter 7 presents an integrated model of the entire manufacturing process and five selected alternative fuels from different categories are considered for a simulation run. This chapter also investigates a number of blends of the given five alternative fuels in search for a perfect blend. A potential improvement on energy demand is determined in this chapter.

Chapter 8 summarises the findings of the study and describes achievements made. This chapter also proposes future research directions related to this study.

Chapter Two

Literature Review

2.1 Ancient History of Cement and Current Usage

From the very beginning of structural construction, human being were looking for a material that would bind stones into a solid mass. The Assyrians and Babylonians used clay for this purpose and the Egyptians used lime and gypsum cement (Bellis, 1997). Ancient Egyptians mixed lime, clay and water to make concrete and mortar which they used to build the Great Pyramid some 4500 years ago (Cement Australia, 2011). The Greeks and Romans made further improvements to develop cement that produced structures of remarkable durability (Buckley Rumford Fireplaces, 2001). The Romans mixed lime with the volcanic sand of Mount Vesuvius and with water to form a strong cement. This was combined with aggregates to produce the concrete for aquaducts, harbours and buildings including the Colosseum in Rome (80AD) (Cement Australia, 2011).

The discovery of Portland cement is attributed to Joseph Aspdin in 1823 (James & Chanson, 2000). Aspdin took a patent on his invented cement in 1824, which was lightly calcined lime with limited lime-silica reaction. His son, William Aspdin, made the first in-depth CaO-SiO_2 reaction by accident when he used a rejected sample of over-burnt clinker (Akkapeddi, 2008). By the end of the nineteenth century, Portland cement became a highly appreciated construction material throughout the world. Since the invention of Portland cement the basic principles of the process have not changed much. The most remarkable additions were the invention of rotary kilns, ball mills to grind the clinker and the addition of gypsum to control the setting speeds (WHD Microanalysis Consultants, 2011).

Joseph Aspdin established a plant in Wakefield to manufacture Portland cement which was used in the construction of the Thames River Tunnel in 1828 (Buckley, 2001). Twenty years later J. D. White and Sons set up a factory in Kent for Portland cement production, which led the early expansion of the Portland cement industry in Europe (Buckley, 2001). In Australia, Portland cement was first produced in 1882 at Brighton, in South Australia (Cement Australia, 2011). The rotary kiln was an important milestone in the cement

industry. Frederick Ransome is credited with the first successful rotary kiln, which he patented in England in 1885. The first economical rotary kiln was developed by Hurry and Seaman of the Atlas Cement Company, America and went into production in 1895 (Peray, 1986).

In 2014, around 4.18 billion metric tonnes of Portland cement was produced globally making it the most widely used and manufactured material in the world (USGS, 2015). Various countries' production of cement from 2001 to 2014 are shown in Table 2.1. China is the largest cement producer of the world with 2.44 billion metric tonnes of annual production, while India is the second largest cement manufacturing country. In 2014 Australia produced about 9 million metric tonnes of cement (CIF, 2013). Figure 2.1 represents the growth of the Australian cement industry over the year in production of cement and clinker.

Table 2.1: Cement production in the world

Country	Year	Cement production (Million metric tonnes)			
		2001	2008	2012	2014
China		661	1,388.40	2,137.00	2,438.00
India		102.9	185	239	300
European Union		225.6	250.8	170.5	159.4
USA		88.9	86.3	74	81
Brazil		39.4	51.6	68	72
Turkey		30	51.4	63.9	71.2
Russian Federation		28.7	53.5	53	68.4
Japan		79.5	67.6	59.3	62
Korea, Rep. of		52	51.7	46.9	47.1
Saudi Arabia		20	37.4	43	51.8
Indonesia		31.1	38.5	53.5	54.2
Mexico		33.2	37.1	36.8	39.4
Germany		32.1	33.6	32.4	32
Italy		39.8	43	26.2	21.4
France		19.1	21.2	18	16.4
Canada		12.1	13.7	12.5	12.8
Argentina		5.5	9.7	10.7	11.4
South Africa		8.4	13.4	13.8	13.8
Australia		6.8	9.4	8.8	9
United Kingdom		11.9	10.5	7.9	9

Source: (USGS, 2015)

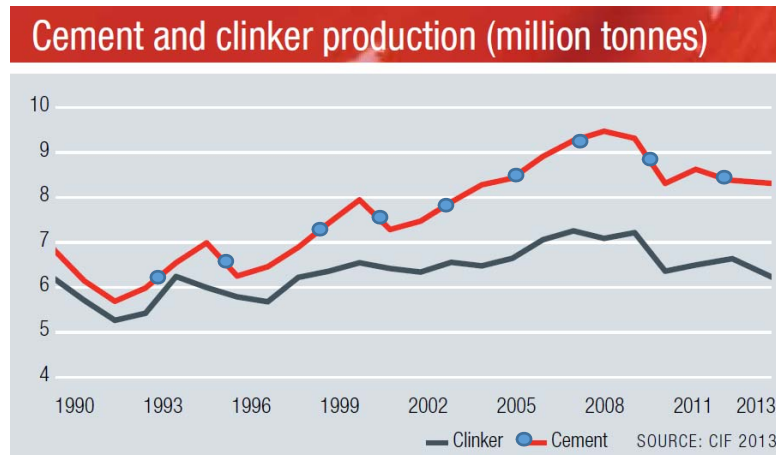


Figure 2.1: Cement & Clinker production in Australia

Source: (CIF, 2013)

2.2 Cement Manufacturing Process

The technology of cement production has developed significantly from the days of its innovation. One of the most noteworthy advances was the addition of extremely high temperatures, which causes the raw materials to chemically alter and hence to form clinker. Clinker is ground with a small quantity of gypsum and other additive to become Portland cement, which is the most commonly used type of cement. The main process routes for the manufacture of cement vary with respect to equipment design, method of operation and fuel consumption (European Commission, 2001). The cement manufacture process can be split into three main stages: raw material preparation, Pyroprocessing (clinker generation) and cement milling. Figure 2.2 shows a basic process flow from initial quarrying through to shipment of the final product.

The process of cement manufacturing can be classified into four categories namely dry, semi-dry, semi-wet and wet. All these processes use the same basic equipment setup as shown in Figure 2.2. These processes can be shortly characterised as follows (Cembureau, 1999):

- **Dry process:** Dry raw meal is fed to a cyclone preheater or precalciner kiln
- **Semi-dry process:** Dry raw meal is pelletised with water and fed to a travelling grate preheater prior to the rotary kiln.
- **Semi-wet process:** Raw slurry is first dewatered in filter presses. The resulting filter cake is either extruded into pellets and fed to a travelling grate preheater or

fed directly to a filter cake drier for (dry) raw meal production prior to a preheater/precalciner kiln.

- **Wet process:** The raw slurry is fed directly to a long rotary kiln equipped with an internal drying/pre-heating system.

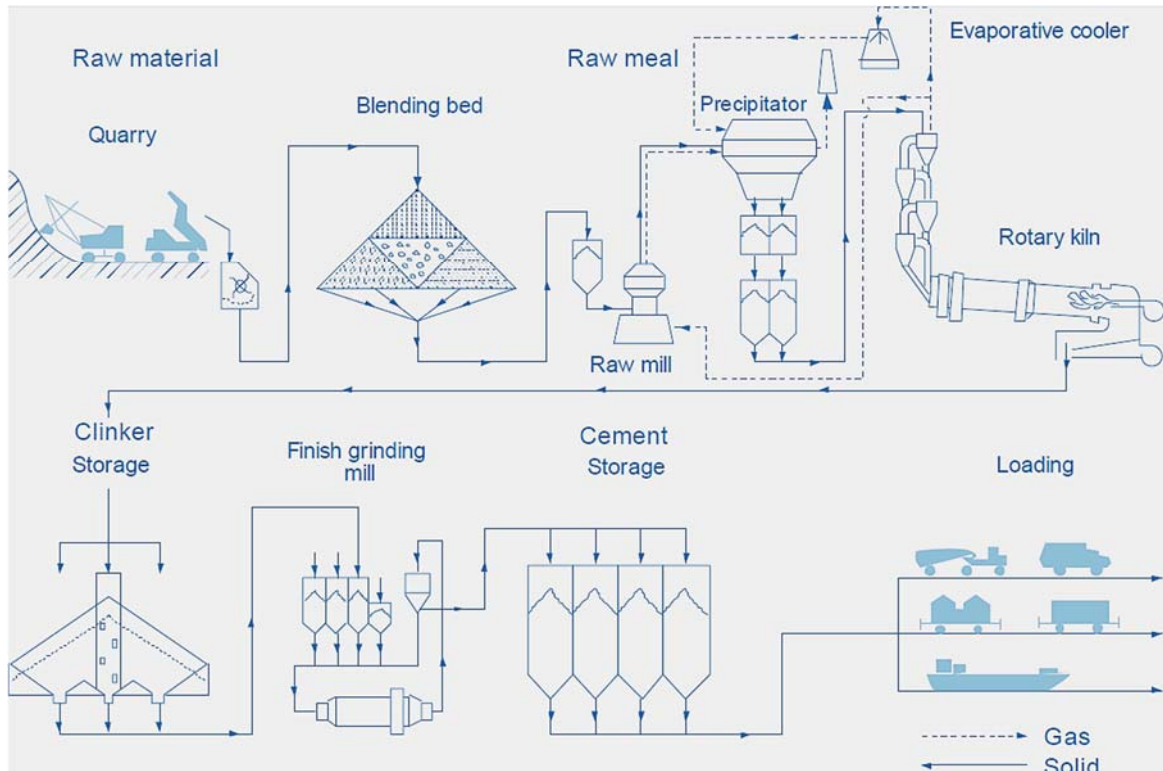


Figure 2.2: Schematic presentation of the cement manufacturing process from quarry to dispatch

Source: vdz, 2009

Cement companies have tended to phase out older, less efficient wet and long dry kilns and replace them with new kilns that use more efficient processes and technologies such as pre-heating, pre-calcination. New installations have come on stream in emerging markets, with high efficiency and high clinker-blending factors (Klee et al., 2011). Vertical shaft kilns are still used in some parts of the world, predominately in China, to produce cement. A shaft kiln essentially consists of a large drum set vertically with a packed mixture of raw material and fuel travelling down through it under gravity (Murray and Price, 2008). In 2012-13 over 90% of clinker was produced using precalciner kilns in the Australian cement industry. Figure 2.3 illustrates the current trend of the cement manufacturing process in Australia. This research focused only on the precalciner type of kiln considering its dominance over the other processes.

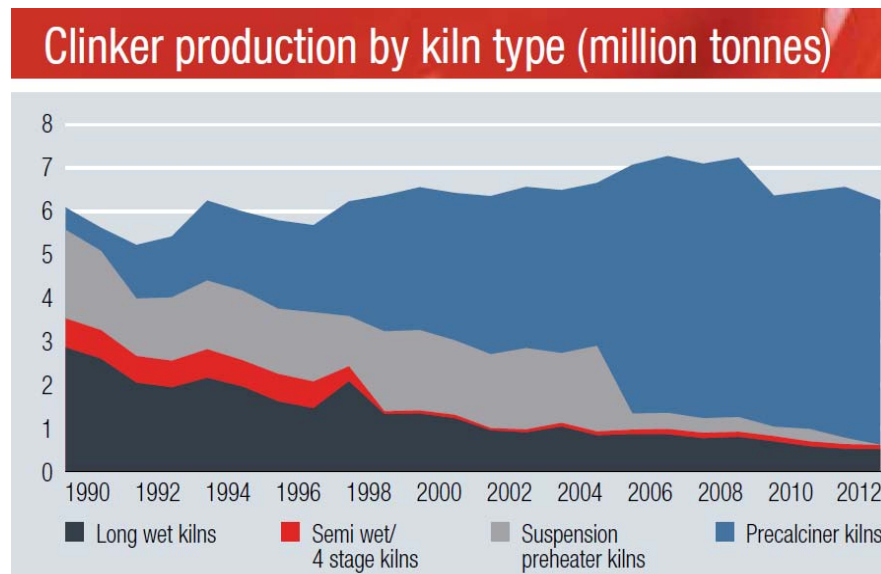


Figure 2.3: Clinker production in Australia by kiln type

Source: CIF, 2013

Cement manufacturing basically includes the following steps:

2.2.1 Raw Materials

The main raw materials used for Portland cement manufacturing are combinations of limestone, shells or chalk, clay and sand. Limestone and chalk are the source of calcium while clay and sand provide silicon, aluminium and iron (Hewlett, 1998). About 1.7 tonnes of raw materials are needed to produce 1 tonne of cement (van Oss & Padovani, 2002, 2003). These natural raw materials are extracted from quarries which, in most cases, are located close to the cement plant. After extraction, these raw materials are crushed at the quarry site and transported to the cement plant for intermediate storage, homogenization and further preparation (Cembureau, 1999). In recent years, different types of alternative raw materials have been used to reduce the amount of raw material and to reduce the clinker cement ratio which helps to reduce energy consumption. Coal fly ash from power plants, water treatment sludge or slag from alumina, phosphorus and steel production are some examples of alternative raw materials for the cement industry (Bhatty et al., 2004).

2.2.2 Preparation of Raw Materials

After intermediate storage and pre-homogenisation, the raw materials are dried and ground together in the raw mill with defined proportions to produce a raw meal for the dry process. The proportions are typically 75%-80% limestone, 20%-25% clay on weight basis and small amounts of iron ore and sand to meet the requirements for Portland cement (Nielsen

et al., 2011). Raw meal is stored and further homogenised in raw meal silos to achieve and maintain the required uniform chemical composition before entering the kiln system (Cembureau, 1999).

2.2.3 Preheater and Precalciner

In this stage the raw meal is passed through the preheater tower which consists of a series of vertical counter-current flow cyclones, through which a raw material is passed from the top (Madloul et al., 2011). The cyclones remove finer particles from the gas stream while mixing the feed material with the gas to recycle the maximum amount of energy.

The latest preheater towers contain a combustion chamber, known as the precalciner. Currently different types of precalciner are used in the cement industry which are constructed to speed up the calcination process. Hot kiln gas, often combining some additional fuel with air from the clinker cooling stage, is generally taken to the precalciner to facilitate the calcination process more rapidly (Lakshmikanth, 2011). Calcination is the decomposition process of calcium carbonate (CaCO_3); it occurs at about 900°C to leave calcium oxide (CaO , lime) and liberate gaseous carbon dioxide (CO_2). A schematic diagram of a Preheater tower along with precalciner and kiln is given in Figure 2.4.

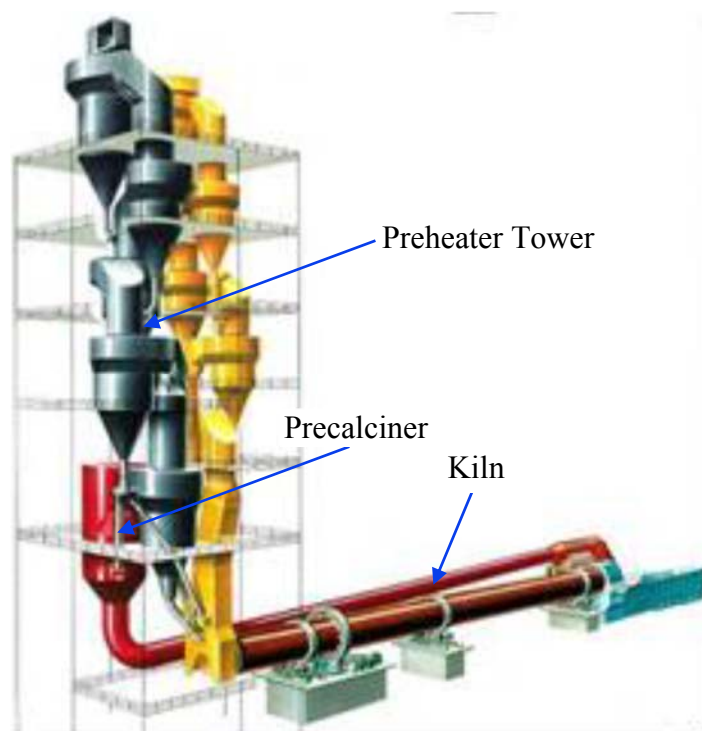


Figure 2.4: Preheater Tower and Precalciner

Source: Caruso, 2006

2.2.4 Kiln

The kiln is the most important component of a cement manufacturing plant as most of the chemical reactions take place in it with high temperature. Rotary kiln is a huge rotating steel furnace with a length and diameter ratio between 10 and 40 metres (Cembureau, 1999). The range of its length varies from 60-200 metres with the diameter ranging from 3 to 9 metres (Madloul, 2011). The slight inclination (2.5% to 4.5%) together with the slow counter-current rotation (0.5 – 4.5 revolutions per minute) allow for a material transport sufficiently long to achieve the thermal conversion processes required (Cembureau, 1999). Gases and solids flow in opposite directions through the kiln, providing for more efficient heat transfer. The raw meal is fed at the upper end of the rotary kiln, and the slope and rotation cause the meal to move toward the lower and hot end. The kiln is fired at the lower end, usually with coal or petroleum coke as the primary fuel. As the meal moves through the kiln and is heated, it undergoes drying and pyroprocessing reactions which cause chemical and physical changes to form the clinker. The red-hot clinker is discharged from the end of the kiln and passed through coolers to cool down.

2.2.5 Clinker Cooling and Grinding

The clinker leaves the hot end of the kiln at a temperature of about 1,500° C. It falls into a cooler, typically a moving grate through which cooling air is blown. Cooling air assists the clinker to reduce its temperature to approximately 170° C (Madloul, 2011). The heated air is used for combustion in the rotary kiln and in the precalciner. The clinker has a variable particle size, typically of diameter 3-25mm. It is generally stored in a silo for a short period of time and then it is ground to achieve a more uniform particle size. The clinker is ground with gypsum and other additives, usually in a ball mill, to produce the final product – cement. The different cement types are stored separately in cement silos prior to bagging and dispatch. Other additives such as coal fly ash, sand or alternative materials are also added to increase the strength-giving properties of the cement (Hewlett, 1998).

2.2.6 Storage and Transportation

The cement is conveyed from the finish cement mill to large, vertical storage silos in the pack house or shipping department. Usually processed cement is transported in bulk via heavy trucks, rails and barge. Only a small amount of cement is bagged and sent for retail sale; transportation of bagged cement is the same as bulk transport (Lakshmikanth, 2011).

2.3 Chemistry of Cement

Understanding the fundamental chemistry of the cement manufacturing process is one of the essential parts of this research work. The chemical changes in clinker production occur almost exclusively through the pyroprocessing stage and are the same regardless of the process. Pyroprocessing is the process in which materials are changed chemically or/and physically subject to high temperature. Four primary materials, namely Alite, Belite, Calcium Aluminate and Ferrite are formed during the production of clinker. Each of these constituents has a specific effect on the properties of the final material. A large amount of chemical reactions take place in order to form the clinker and these reactions begin as soon as the raw feed enters the pre-heating tower and continue until the clinker is cooled. The chemical process during the pyroprocessing can be divided in the following three stages (WHD Microanalysis Consultants, 2011).

- 1. Decomposition:** This stage mainly occurs in the preheater tower and the precalciner stage. All water from the feed materials is evaporated and CO₂ liberated from limestone. Decomposition of the siliceous and aluminosilicate portion of the feed and the formation of the sulphate melt also take place in this stage.
- 2. Burning in kiln:** Alite and Belite formation is the key feature of this stage. Nodule form of clinker and evaporation of some volatile phases also come up.
- 3. Cooling and stabilisation:** Hydraulically-reactive silicates are formed through faster cooling and they settle the setting speeds and strengths of clinker. Waste heat is recovered from the cooling stage to improve plant efficiency.

The typical mineral composition of Portland cement is given in Table 2.2 along with their weight percentage.

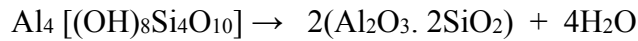
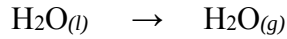
Table 2.2: Typical composition of Portland cement

<i>Chemical formula</i>	<i>Abbreviated notation</i>	<i>Description</i>	<i>Amount %</i>
3CaO.SiO ₂	C ₃ S	Tricalcium silicate (“Alite”)	50-55
2CaO.SiO ₂	C ₂ S	Dicalcium silicate (“Belite”)	19-24
3CaO.Al ₂ O ₃	C ₃ A	Tricalcium aluminate	6-10
2CaO.(Al ₂ O ₃ , Fe ₂ O ₃)	C ₄ AF	Tetracalcium aluminoferrite	7-11
CaSO ₄ •2H ₂ O	CSH ₂	Calcium sulfate dihydrate (gypsum)	3-7

Source: Van Oss and Padovani 2002

In detail chemical reactions of the manufacturing process are available in literature (Tokheim, 1999) and included here for better understanding of the process.

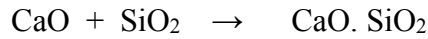
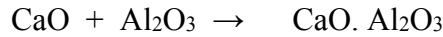
The first stage in the process is the drying of feed meal. Free water is driven off from the raw meal at temperatures ranging up to 200°C, and the absorbed water escapes at the temperature range of 100°-400°C. Chemically bonded water is dehydrated at 400-750°C temperature.



The decomposition of calcium carbonate (CaCO_3) takes place around 900°C. The MgCO_3 is dissociated in the temperatures between 600°C to 900°C. $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ also decomposed within this range. The oxidization of organic carbon takes place in this stage.



In the same time the rapid neutralization of free lime occurs.



When the temperature rises above 800°C CaO reacts with the formed oxides to form clinker.



A liquid phase appears in temperature 1250°C and above. Alite is formed through a very slow reaction between Belite and free lime.



At approximately 1450°C the mixture fuses into balls of 0.3 to 2.5 cm diameter clinker. The final stage in pyroprocessing is the cooling of the clinker. A rapid cooling system needs to be incorporated to maintain the desired mineralogical composition of clinker. Slow cooling allows the Alite to decompose to Belite and free lime effectively spoils the cement. The standard reaction enthalpies for the most important reactions occurring are given in Table 2.3. The occurrence stages of different reactions are stated in Table 2.4.

Table 2.3: Reactions and reaction enthalpies

Reaction	Reaction equation	Standard reaction enthalpy [kJ/kg]
I. Formation of oxides and decomposing reactions		
Evaporation of water	$\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)}$	2453
Decomposition of kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O}$	780
Oxidation of carbon	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	-33913
Dissociation of MgCO_3	$\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$	1395
Dissociation of CaCO_3	$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	1780
II. Formation of intermediates		
Formation of CA	$\text{CaO} + \text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3$	-100
Formation of C_2F	$2\text{CaO} + \text{Fe}_2\text{O}_3 \rightarrow 2\text{CaO} \cdot \text{Fe}_2\text{O}_3$	-114
Formation of $\beta\text{-C}_2\text{S}$	$2\text{CaO} + \text{SiO}_2 \rightarrow 2\text{CaO} \cdot \text{SiO}_2$	-732
III. Sintering reactions		
Formation of C_4AF	$\text{CA} + \text{C}_2\text{F} + \text{CaO} \rightarrow \text{C}_4\text{AF}$	25
Formation of C_3A	$\text{CA} + 2\text{CaO} \rightarrow \text{C}_3\text{A}$	25
Formation of C_3S	$\beta\text{-C}_2\text{S} + \text{CaO} \rightarrow \text{C}_3\text{S}$	59

Source: Tokheim, 1999

Table 2.4: Reactions occurring stage

Temperature	Reaction	Stage of process
100°C	Evaporation of free water	Preheater
500°C and above	Evolution of combined water from clay	Preheater
900°C and above	Crystallisation of amorphous dehydration products of clay	Preheater, Early kiln
900°C and above	Evolution of calcium carbonate to form carbon dioxide	Preheater, Early kiln
900°C -1200°C	Reaction between lime and clay	Early to mid kiln
1250°C -1280°C	Commencement of liquid formation	Mid to late Kiln
Above 1280°C	Further formation of liquid and completion of formation of cement compounds	Mid to late kiln

Source: Hewlett, 2003

2.4 Fuels in Cement Manufacturing

The main energy intensive phases of the cement production process take place inside the precalciner and kiln during the formation of clinker. A large amount of thermal energy is required to create enough heat for the cement kiln and precalciner. Typical thermal energy consumption of clinker manufacturing with different kiln processes is illustrated in Table 2.5 (Greenhouse Gas emission Reduction from Industry in Asia and the Pacific [GERIAP], 2005).

Table 2.5: Specific thermal energy consumption in different kiln process

Kiln process	Thermal energy consumption (GJ/tonne clinker)
Wet process with internals	5.86–6.28
Long dry process with internals	4.60
1-stage cyclone preheater	4.18
2-stage cyclone preheater	3.77
4-stage cyclone preheater	3.55
4-stage cyclone preheater plus calciner	3.14
5-stage preheater plus calciner plus high efficiency cooler	3.01
6-stage preheater plus calciner plus high efficiency cooler	<2.93

Source: GERIAP, 2005

Fossil fuels such as coal, petroleum coke and natural gas are the main sources to provide the thermal energy requirement in clinker production. Due to limited resources and the high price of fossil fuel, waste-derived fuels have been used in the cement industry for the last three decades. Used tyres, spent solvents, waste oils, plastics and biomass are few to name among the established alternative fuels in the cement industry. The proportion of different fuels currently being used by cement manufacturers is available on their annual sustainable reports. Table 2.6 summarises these data from five selected leading cement producer groups (Heidelberg, 2014; Holcim, 2014; Lafarge, 2014; Cemex, 2014; Italcementi, 2014). This table shows that coal and petcoke are mainly burnt as fuel in the cement industry. An extensive literature review on the usage of alternative fuels in cement manufacturing is included in the next chapter.

Table 2.6: Fuel mix for burning clinker (% of total fuels only based on thermal energy)

Fuel (%) In 2014	Holcim Group	Cemex Group	Heidelberg Group	Lafarge Group	Italcementi Group
Coal	52	22.5	58.1	37.1	36.8
Petcoke	25	38.2	10.6	22.9	31.9
Heavy fuel Oil	0	8.5	0.4	-	0
Light fuel oil	-	-	0.3	7.7	6.6
Natural gas	7	3.0	6.2	14.8	13.9
Shale and lignite	2	-	3.1	-	-
Other fossil fuel	-	-	0.5	-	-
Alternative fossil fuels	10	16.3	13.0	10.6	5.4
Alternative biomass fuels	4	11.4	7.6	6.8	5.4

2.5 Thermal and Environmental Performance of Cement Plant

The cement industry needs to ensure sustainable and environmentally friendly use of natural resources while increasing profit margins. This is the responsibility of the cement producers to develop new strategies that will optimise the performance of the manufacturing process in response to changing conditions. To measure the performance of the manufacturing process a number of companies utilise some Key Performance Indicators (KPI). Selecting appropriate KPIs at the company level and implementing them in the operational level is also a new challenge faced by the cement industry (Rahman et al., 2013).

To move towards sustainable development, an important requirement for the cement companies is performance measurement. Investigation of a cement plant's performance requires data from different sources, which need to be collected and evaluated properly (Rahman et al., 2013). The raw data from the sources are often unavailable due to their confidential nature. Inconsistency of data because of the limited accuracy of the instruments is also another problem (Gallestey et al., 2005). Within the cement industry, many companies are operating environmental indicators as facility level KPIs and some companies have introduced indicators based on energy efficiency and use of alternative fuels and raw materials (Fiksel, 2002). Base lining and benchmarking are two related approaches for performance measurement. Base lining involves comparing plant

performance over time, while benchmarking involves comparing performance relative to an established best practice level of performance (Boyd and Zhang, 2012).

The potential KPIs for cement plant performance can be categorized by energy efficiency, environmental performance, economic benefits, social performance etcetera. According to the World Business Council for Sustainable Development (WBCSD) report on sustainable cement industry (Fiksel, 2002), the most important KPIs are:

- Tonnes of cement per mega joule of energy
- Fuel and raw material substitution rates (%)
- Non-product output (kg of waste) per tonne of cement
- Net CO₂ (kg) per tonne of cement
- Incident rate (injury, illness) per 200,000 hours/

The first two of these indicators are related to thermal performance of the plant while the third and fourth are environmental performance indicators. There are several ways to measure these performance indicators, amongst them exergy analysis is the best option as it can be used to determine the thermal and environmental performance of the plant. Base lines of the KPI are summarised in Table 2.7.

Table 2.7: Baseline Performance of the Cement Industry

Indicator	Approximate Value
Tonnes of cement per MJ	Each tonne of cement consumes roughly 3000 MJ of total thermal energy
Fuel & raw material substitution rates (%)	Fuel ranges from 0 to 25% Raw material from 0 to 10%
Non-product output (waste per tonne of cement)	Airborne and waterborne releases are generally known, but definitions of solid waste vary
Net CO ₂ (kg) per tonne of cement	Each tonne of Cement generates approximately 900 kg of net CO ₂ emissions
Incident rate (injury, illness) per 200,000 hours	Ranges from 1 to 5 incidents per 200,000 hours

Source: Fiksel, 2002

To understand the current trend of the performance indicators five selected cement manufacturing groups' data has been presented. Excluding China, three out of the five

world's largest cement producers are located in the EU-27: Lafarge (France), Heidelberg Cement (Germany) and Italcementi (Italy), with the other two being Holcim (Switzerland) and Cemex, Mexico (European Commission, 2010). As the plant level data are not available in literature, the group level data (Heidelberg, 2014; Holcim, 2014; Lafarge, 2014; Cemex, 2014; Italcementi, 2014) have been presented in this section. All those data have been collected from the sustainability reports of the manufacturing groups which are published biannually. Table 2.8 summarises the percentage of alternative fuel in fuel mix and the average thermal energy efficiency of the manufacturing group. The annual sale of cement is also included to indicate the annual production of the groups. From Table 2.8 it is found that except Heidelberg group all have increased the percentage of alternative fuels in their fuel mix. Thermal energy efficiency was achieved with the increment of alternative fuel usage with an exception of Cemex group.

Table 2.8: Thermal efficiency of cement manufacturing group

Company	Sales of cement (million tonnes)		% of thermal energy from alternative fuel		Thermal energy efficiency (MJ/tonne clinker)	
	2012	2014	2012	2014	2012	2014
Holcim Group	142.3	140.3	12.9	14	3499	3469
Cemex Group	-	-	27.1	27.7	3876	3854
Heidelberg Group	89	81.8	20.1	20.6	3724	3704
Italcementi Group	45.9	43.4	6.5	10.8	3820	3806
Lafarge Group	141	116.4	13	17.4	3633	3613

The most important KPI for cement manufacturing plants from the environmental point of view is the gross and net CO₂ emission. This and other KPIs for the cement manufacturing group are assembled in Table 2.9. In the table air emission data includes the amount of NO_x, SO₂, dust and other heavy metal and organic compounds. Clinker cement ratio is also included in the table as it is also considered as an important KPI (Fiksel, 2002) and directly involved with thermal energy consumption and CO₂ emission. Lafarge group managed to improve their clinker cement ratio and in the course they managed to reduce net CO₂ emission which occurs during the calcination process of clinker production.

Table 2.9: Environmental performance of five cement manufacturing group

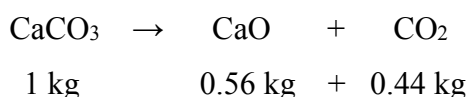
Company	Gross CO ₂ emission (Million tonnes)		Net CO ₂ emission (kg per ton of cement)		Air emission (kg of waste) per ton of cement		Clinker cement ratio	
	2012	2014	2012	2014	2012	2014	2012	2014
Holcim Group	95.9	98.7	595	594	1.36	1.4	70.1	69.8
Cemex Group	42.6	42.8	770	769	1.54	1.6	76.5	76.5
Heidelberg Group	49.9	51.5	615.2	609.1	2.2	1.8	75.8	75.3
Italcementi Group	31.7	29.0	712	692	2.09	1.9	81.8	81.1
Lafarge Group	94	93	600	594	2.09	1.75	71.9	72

It is found from Table 2.8 that the thermal substitution rate was highest for Cemex Group in 2014, while Holcim was the most energy efficient manufacturing group among the selected manufacturers. On the basis of environmental performance, Holcim group is found to be the best among the other manufacturing groups (Table 2.9).

2.6 Emission

Cement manufacturing is a highly pollutant process which is accountable for releasing greenhouse gases and some heavy metal in the environment. Among the gaseous pollutant carbon dioxide (CO₂), nitrogen and sulphur oxides (NO_x and SO_x) are the major concern for the environment along with minor discharge of carbon monoxide (CO), dioxins and furans (D/F), metals, particulate matter (PM), and volatile organic compounds (VOCs). The emission factor of the process depends on three fundamental aspects which are chemical composition of the raw materials, the chemical and physical properties of the fuel and the kiln conditions (Marengo et al., 2006).

The main source of CO₂ emissions from cement manufacturing are through calcination and fuel combustion. Calcination is the thermal decomposition process of CaCO₃ to liberate CO₂ and leave CaO. The typical mass balance of calcination reaction is.



Portland cement contains about 63.5%CaO, consequently, about 1.135 units of CaCO₃ are required to produce 1 unit of cement, and the amount of CO₂ released in the calcining

process is about 500 kg per tonne of cement produced. The net process CO₂ emission also depends on the clinker/cement ratio, which varies normally from 0.5 to 0.95 (Hendriks et al., 2003). Gross CO₂ emissions depend on the fuel used and energy consumption rate which is about 0.977 tonnes of CO₂ per tonne of cement production. Collectively the process and combustion are accountable for 5%–6% of anthropogenic CO₂ emission (Rodrigues & Joeke, 2011).

Oxides of nitrogen are formed during the oxidation of chemically-bound nitrogen in the fuel and by thermal fixation of nitrogen in the combustion air. The amount of thermally generated NO_x increases with higher flame temperature. The nature of the fuels, combustion air flow and the temperature of the burning zone are the key parameters which control the NO_x emission (Walters et al., 1999). About 1.5 to 10 kg of NO_x is emitted into the atmosphere for every tonne of cement produced (Naik 2005). Larsen (2007) reviewed the effect of co-firing alternative fuels on NO_x-emissions and reported that NO_x emissions generally decrease when alternative fuels are used.

Sulphur dioxide may be generated in the manufacturing process both from the sulphur compounds in the raw materials and from sulphur content in the fuel (Van Oss and Padovani 2003). The sulphur content of both raw materials and fuels varies from plant to plant and with geographic location. However, the alkaline nature of the cement provides the advantage for direct absorption of SO₂ into the clinker. More than 50% to 90% SO₂ is absorbed by the kiln feed, clinker, cement kiln dust, or left in the kiln as a coating that helps preserve the brick lining (Van Oss and Padovani 2003).

In the presence of chlorine, two aromatic hydrocarbons, polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF), occur as by-products of combustion below 400°C in a cement kiln (Kirk, 2000). Improper mixing of fuel and combustion air in the calciner are the main reason for formation of dioxins and furans as residence time and temperature of the precalciner are lower than the rotary kiln (Karstensen, 2008). Dioxin and furan emissions from cement kilns are generally very low because of oxygen concentrations and high temperatures (Nielsen, 2012).

Heavy metals like lead and mercury are present in the fuels and raw materials and they have a potential chance of exposure to the environment during the cement production

(Schuhmacher et al., 2004). Thankfully the kiln system has the ability to incorporate many metals into the clinker and those metals are normally not emitted in measurable quantities. However, some metals, such as mercury and thallium, are extremely volatile in the kiln, and could be found in the stack gases. Mercury, lead, cadmium, and chromium emission from the cement manufacturing process are generally monitored as they are a potential threat to the environment.

Carbon monoxide (CO) is a product of incomplete combustion of carbon molecules and it can be produced in the precalciner or kiln. If the combustion reactions do not reach completion, volatile organic pollutants, typically measured as total organic compounds (TOC), volatile organic compounds (VOC) or organic condensable particulate, can also be emitted. Small quantities of ammonia (NH₃), chlorine, and hydrogen chloride (HCl), also may be emitted from the cement manufacturing process.

The emission of dust has been one of the main environmental concerns in cement manufacture. Dust and particulate matter emissions originate mainly from the raw mills, kiln system (CKD), clinker cooler, and the cement mills. This includes coarse and fine particulates, with 10 µm serving as the isolating line between these two (Van Oss and Padovani 2003). Often, dust from the kiln is collected and recycled into the kiln, thereby producing clinker from the dust. However, if the alkali content of the raw materials is too high, some or all of the dust is discarded or leached before being returned to the kiln. A Particulate matter control devices such as a fabric filter or electrostatic precipitators (ESP) are used to collect cement kiln dust (CKD). Additional sources of PM are raw material storage piles, conveyors, storage silos, and unloading facilities.

Fly ash, which is a biggest concerns for the coal fired power plant is actually added some extra value for the cement plant as fly ash is considered as supplementary cementitious material now a day. Fly ash is actually generated from the combustion of fuel and release in the air with stack gas. In modern cement plant fly ash is captured from stack gas by using bag house filter or electrostatic precipitator (ESP). Australian standard AS3582.1 state the criteria for the fly ash to be considered as a cementitious material in concrete and mortar. It can be used in Portland cement and blended cement up to 5% according to the Australian standard (ADDA, 2009). The local cement plant, from where data has been collected, sales fly ash as one of their product beside cement and lime.

According to temperature and released substances, three major sections of cement manufacturing are (i) dehydration, (ii) calcination and (iii) clinkering zones (Rodrigues & Joekes, 2011). Figure 2.5 shows a schematic diagram of the generation of particles, generation of organic pollutants and the release of carbon dioxide from different sections of cement manufacturing.

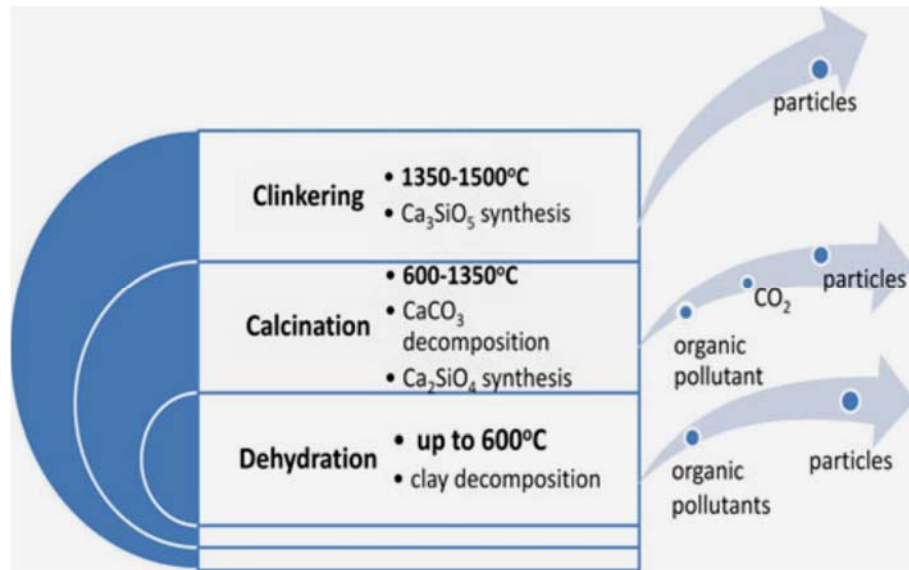


Figure 2.5: Cement manufacturing process: Release of pollutants into atmosphere
Source: Rodrigues and Joekes, 2011

Measuring total emission from a cement plant can also be done through a life cycle assessment (LCS) where the emission due to the transportation and other reason is considered along with the process emission. This thesis only considering the emission regarding the combustion and calcination. This study is not an LCA study and hence the emission regarding the transportation of fuel and clinker is beyond the scope of this thesis.

2.6.1 Global emission standard

Cement plants are known as one of the sources of today's environmental pollutions and local, regional and national governments provide the guidelines for maximum tolerable limits for different types of emissions. In different parts of the world, local environmental protection agencies also play a vital role to set emission standards. Cement kilns are also used for waste incineration in the form of alternative fuels which is the reason to monitor and control any possible pollutant discharge besides process emission to the environment.

Table 2.10 shows the European Union (EU) emissions limits (daily average values for continuous measurements) for cement co-processing plants that treat nonhazardous wastes or less than 40% hazardous wastes. Dust from de-dusting equipment can be partially or totally recycled into cement manufacturing processes (Hasanbeigi et al., 2012).

In Australia pollutant emission limits and environmental impact assessment for process industries are monitored by state governments. Unfortunately in Australia no specific emission standard is set to be practiced nationwide. A detailed report on the emission from Cement Australia in Gladstone, Queensland is presented by Campin (2008) which is only a local based data and not representing the state standard. Table 2.11 summarises average emission from Gladstone cement plant as reported by Campin (2008). In the table the mean specific emission for each contaminant (grams per tonne of clinker product) has been calculated based on the average emission divided by the average plant capacity.

Table 2.10: Air Emissions Limits for cement co-processing plants from EU
Waste Incineration Directive

Pollutant	Limit for cement co-processing plants (average value) [mg/m³]
Total Dust	30
HCl	10
HF	1
NO _x for existing plants	800
NO _x for new plants	500
Cd + Tl	0.05
Hg	0.05
Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V	0.5
Dioxins and furans	0.1
SO ₂	50
TOC	10
CO	Set by competent authority

HCl: hydrogen chloride; HF: Hydrogen Fluoride; NO_x: nitrogen oxides; Cd: cadmium; Tl: Thallium; Hg: mercury; Sb: Antimony; As: Arsenic; Pb: lead; Cr: Chromium; Co: Cobalt; Cu: Copper; Mn: Manganese; Ni: Nickel; V: Vanadium; SO₂: sulphur dioxide; TOC: total organic compounds; CO: carbon monoxide;

Source: European Commission (EC) 2012

Table 2.11: Average Emissions from cement plant Gladstone, Queensland

Pollutant	Mean specific emission (g/tonne)
HCl	23
SO ₂	170
NO _x	2200
Cd + Tl	0.0053
Hg	0.039
Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V	1.772
Dioxins and furans	0.00000120
Particulate matter	140
CO	1000

HCl: hydrogen chloride;; NO_x: nitrogen oxides; Cd: cadmium; Tl: Thallium; Hg: mercury; Sb: Antimony; As: Arsenic; Pb: lead; Cr: Chromium; Co: Cobalt; Cu: Copper; Mn: Manganese; Ni: Nickel; V: Vanadium; SO₂: sulphur dioxide; CO: carbon monoxide;

Source: Campin, 2008

As it was mentioned earlier that the emission standards are different in countries, regions, manufacturing groups and even in individual plants, it is really difficult to set a worldwide standard. To identify the versatility of data among the countries, Edwards (2014) presented the emissions regulations for four key pollutants: sulphur dioxide (SO₂), nitrogen oxides (NO_x), mercury (Hg) and dust / particulate matter (PM). For the purpose of this study only the sulphur dioxide (SO₂) and nitrogen oxides (NO_x) data is presented in table 2.12 in concise form. It is observed from table 2.12 that for most of the nations the limits for SO₂ and NO_x varied between 200 – 500 mg/Nm³ and 500 – 1000 mg/Nm³ respectively.

Table 2.12: Emissions standard for different country for SO₂ and NO_x

Country / Region	SO ₂ (mg/Nm ³)	NO _x (mg/Nm ³)
Australia (New South Wales)	50	800
Australia (Victoria)	250g/min	3600g/min
Austria	350	500
Bolivia	600	1800
China	200	400-800
Colombia	200-550	200-800
Egypt	400	600
European Union (EU)	<50-400	200-450
Germany	50	500
Indonesia (Proposed)	800(400)	800

Lebanon (as SOx)	850 (old) / 800 (new)	2500 (old), 1500 (new)
Nigeria	2000	600-800
Norway	400-500	800
Pakistan	1700	400-1200
Saudi Arabia	365	600
South Africa	50-250	1200-2000
Switzerland	500	800
Trinidad & Tobago (Proposed)	1000	500
Turkey (Conventional fuel)	300	400
UAE	125 μ g/Nm ³	400
UK	200	900
USA (From 9 September 2015)	0.4 lb/ton (clinker)	1.5 lb/ton clinker

Source: (Adapted from Edwards, 2014)

2.7 Process Modelling and Simulation

The environmental impact of alternative fuels needs to be assessed before employing them in the manufacturing process. Economic risks associated with the experimentation of alternative fuels restrict the researchers conducting tests in the cement plant. Besides this it is really difficult to mimic the similar environment of a cement kiln in an experimental set up. Modern computers enable the usage of process modelling for the physical and chemical changes in industrial production. Computer process models are important tools to predict the effects of alternative fuels on plant performance and emissions. Process simulation models allow testing a wide range of alternative fuels with minimal cost, time and risk.

Tscheng and Watkinson (1979) published a research article which described a method to calculate the convective heat transfer between the walls of a rotary kiln and the clinker. Jenkins and Moles (1981) have developed a mathematical model to predict the temperature profiles of the gas and refractory in a kiln. Gorog et al. (1983) developed a heat transfer model in the burning zone, and validated it partially with some laboratory experiments. A complex heat transfer model for a rotary kiln was developed by Silcox and Pershing (1990) including all three types of heat transfer. A steady-state heat transfer model for the pre-heating zone of a wet rotary kiln in cement manufacturing was presented by Ghoshdastidar and Aanandanunni (1996).

As the most vital part of the process cement kiln was modelled by researchers in different aspects which mainly includes (Saidur et al. 2011)

- Structural modelling by the finite element methods
- Static nonlinear analysis of the model
- Dynamic linear analysis of model and
- Structural verification including fatigue and ovalization of the kiln body

To identify the possible emission from the cement process that may cause potential environmental threat, static nonlinear analysis could be the most useful method among the aforementioned methods. This analysis consider the input flow rate and calculate the output irrespective to time. Energy efficiency improvement can also be calculated by using such model. Scheuer and Sprung (1990) investigated energy consumption and prospective energy savings method for German cement industry. For the period between 1970 and 1997 a detailed investigation was performed by Worrell (2000) for US cement industry which includes CO₂ reduction and energy efficiency improvement. In this thesis, a computational model was developed on the basis of static nonlinear analysis to predict emission due to the introduction of alternative fuels. Basically a steady state model determine the differences between two different scenario in terms of change in the raw material compositions, change of fuels or change in operating conditions.

Computational fluid dynamics (CFD) based software is dominantly used to model the kiln section of the process (Mastorakos et al., 1999; Mujumdar & Ranade, 2006; Mujumdar et al., 2007; Mujumdar & Ranade, 2008, Spang, 1972; Boateng & Barr, 1996; Martins et al., 2002; Paul et al., 2002; Giddings et al., 2002; Marin et al., 2001). Due to the complexity of modelling the behaviour of solid particles in conventional CFD framework, researchers used one-dimensional models with material and energy balance equations. Numerical techniques associated with solving boundary value problems were incorporated to achieve accurate temperature profiles and specific mass fractions (Spang, 1972; Boateng & Barr, 1996; Martins et al., 2002; Paul et al., 2002; Giddings et al., 2002; Marin et al., 2001). These models were used to study flame shape, temperature of the kiln, velocity profile of particles in the kiln system and oxygen enrichment in the burning zone. Mikulcic et al., (2012) presented a CFD model of calciner to use in reduction of CO₂ emission during cement production. Numerical simulation was also used to obtain gas velocity, gas

temperature, and gas components in a cement rotary kiln (Wang et al., 2006). A different approach of modelling the cement manufacturing process can be found in literature by using Aspen Plus software which focuses on the clinker chemistry, reaction stoichiometric and thermodynamic property of the material in the process (Kaantee et al., 2004; Zhang et al., 2011; Rahman et al. 2013a; Rahman et al., 2014).

Aspen Plus is a powerful process engineering software with a rich databank of pure components, reaction constant and a vast number of thermodynamic models. Kaantee et al. (2004) used Aspen plus to model the entire process of a four-stage preheater kiln system. Two types of alternative fuels were used to identify the relationship between the amount of combustion air and process performance. Zhang et al. (2011) proposed an Aspen plus model for the Dual Combustion and Denitration calciner to study the pollutant emission.

Another approach of integrated modelling of preheater, calciner, kiln and clinker cooler was reported by Mujumdar et al. (2007). In this effort, individual models for preheater, calciner, kiln and cooler were coupled with each other to develop a simulator for the entire system. This simulator known as ‘Rotary cement kiln simulator’ (RoCKS) requires the physical dimension of every processing unit as well as the physical properties, particle size and composition of fuel and raw meal. The model and the RoCKS software are very convenient to determine the optimum percentage calcinations desired for minimizing net energy consumption.

Recently Vatopoulos and Tzimas (2012) used commercial software ChemCAD to make assessment on different CO₂ capture technologies for the cement industry. Mass and energy balances have been calculated by using ChemCAD, according to the process configurations. The thermodynamic models used in this simulation were chosen based on the chemical composition, process operating conditions and the thermodynamic equilibrium. Previously Weil et al. (2006) used ChemCAD Software to study a thermo-chemical concept hydrogen energy from coupled waste gasification and cement production. The software was used to minimise Gibbs free energy for the calculation of product gas composition, assuming a constant temperature. Recently CFD modelling of cement process were used to assess the impact of alternative fuels in the cement kiln, for example uses of shredded tyre and pine wood (Mtui, 2013) and meat and bone meal (Ariyaratne et al. 2015).

The manufacturing of cement is a very complex process which includes several endothermic and exothermic reactions along with heat transfer in solid liquid and vapour phases of different materials. To predict the performance of a cement plant, researchers use numerous computational and process simulation software among which Aspen Plus, Aspen HYSYS, Ansys Fluent and ChemCAD are widely known. Some features of these software packages are listed below

2.7.1 Aspen plus

Aspen Plus is a chemical process simulation package commonly used to design and optimise a chemical process. Currently, Aspen Plus has been widely used in the simulation of iron manufacture, metallurgical process, coal and biomass gasification and combustion, solid waste combustion, and gas pollutants capturing processes, etcetera (Zhang et al., 2011). It can be utilised in the conceptual design phase to predict the plant performance. Aspen Plus uses a flow sheet simulator to graphically represent each stage of the process. The flow sheet system allows the user to build a model small or large as necessary by adding each stage as a single or group of blocks. It contains a large number of predefined operation blocks which are helpful to create and understand the flow diagram easily. A rich database of over 30,000 physical and chemical properties for chemicals, solids and polymers are available in Aspen plus. It also allows to create user defined compounds and reactions. It enables quick and easy alterations to a process, and allows the users to trial a number of different system configurations without requiring a new model for each change. Aspen Plus consists of a predefined library of heat exchanger processes which can be altered by the user to imitate real world situations. It is designed to allow calculation of solid based reactions and heat transfer cases. The built-in plot wizard of Aspen plus allows generating plots of results of a simulation. It is also able to provide results in a number of exportable formats to allow further manipulation of the results and improve readability.

2.7.2 Aspen HYSYS

Aspen HYSYS is also a product of AspenTec company, provider of Aspen plus. It contains almost every feature of Aspen Plus. This process modelling software is specially designed for modelling of oil and gas production processes, petroleum refining and air separation applications. Aspen HYSYS is able to predict the performance of yet to be built installations along with forecasting changes to process performance due to process alterations. It is specifically designed for new users with a larger focus on interaction with

the process flow diagram than data tables. Predefined blocks and a rich databank of the chemical property of different components are key features of Aspen HYSYS. It also includes a predefined library of distillation column. Aspen HYSYS automatically generates a greenhouse emission report containing a breakdown for all stages of the process.

2.7.3 ANSYS Fluent

ANSYS Fluent software contains the broad physical modelling capabilities needed to model flow, turbulence, heat transfer, and reactions for industrial applications. Air flow over an aircraft wing, blood flow in the human body, combustion in a furnace and design for wastewater treatment plants are some examples of the application of ANSYS Fluent. Thousands of companies around the world are benefited by using ANSYS Fluent software as an integral part of the design and optimization phases of their product development. Advanced solver technology of ANSYS Fluent provides fast, accurate CFD results. Fluent is capable to work with any geometry through mesh grid generation. User-defined functions allow the implementation of new user models and the extensive customization of existing ones. The interactive solver setup, solution and post-processing capabilities of ANSYS Fluent allow it to pause a calculation, examine results with integrated post-processing, change any setting, and then continue the calculation within a single application.

2.7.4 CHEMCAD

CHEMCAD is a powerful and flexible chemical process simulation software. CHEMCAD combines a graphical user interface (GUI), an extensive chemical component database, a large library of thermodynamic data, and a library of the most common unit operations. In addition, the software is capable to deal with user defined thermodynamics, unit operations, calculations, and reporting. This program is used extensively around the world for the design, operation, and maintenance of chemical processes in a wide variety of industries, including oil and gas exploration, production, and refining; gas processing; pharmaceuticals; bio-fuels; and process equipment manufacturing. The challenges regarding design and rating of process equipment such as vessels, columns, heat exchangers, piping, valves, and instrumentation can be met by this software. Economic comparisons of process alternatives are another advantage of using CHEMCAD.

2.7.5 Selection of Software

Modelling of cement manufacturing became a recent trend to minimise the experimental cost as well as to get most reliable results while trialling new alternative fuel. In cement manufacturing a large amount of chemical reactions take place both in the course of clinker formation and fuel combustion. The chemical reactions as well as the reaction kinetics are reported in different literatures. Considering the availability of these data, commercial software Aspen Plus is selected to simulate the manufacturing process and to carry out this research work. Aspen Plus has the unique capability of modelling the cement manufacturing process with a strong focus on clinker chemistry and thermodynamics in the entire process. It can easily identify the effect of alternative fuels on material flows, thermal performance, emissions and product quality. Beside this, the rich data bank of pure and compound components allows to replicate almost every single chemical reaction that occurs during the manufacturing process. The sensitivity analyser and optimization subroutine in Aspen Plus are suitable for simulating cement plant operation in different conditions. The built-in sensitive analysis and optimization subroutine option of Aspen Plus offers additional advantage to users to simulate cement plant operation in different conditions. A large model library of block and stream of Aspen Plus is very helpful to construct a process flow diagram.

2.8 Concluding Remarks

Cement has been being produced in commercial level for about 200 years and numbers of modifications were incorporated meanwhile to obtain an energy efficient process and improve the clinker quality. The general chemistry of cement manufacturing is studied extensively and recorded through different literature. Initially only coal and natural gases were used as energy sources for the cement industry but for the last three decades different types of alternative fuels were introduced in the production line to minimise the cost and pollutant emission. To assess the plant performance, different key performance indicators (KPIs) along with the base line value were set by the manufacturers.

Pollutant emission from cement plants has been discussed in this chapter to get an indication of the potential threat to the environment by the cement industry. Local and national governments and environmental protection agencies legislated maximum tolerable emission limits for different types of pollutant. A brief description on the variation of the

emission standard in different countries was included in this chapter for better understanding of common practice. In Australia emission standards are available only at state level and national air emission standards are not available yet (International Energy Agency [IEA], 2010). No data was found regarding the emission standard in Queensland State where this research is carried out. An average value of pollutant emission from the cement plant in Queensland was found in literature (Campin, 2008) and included in this chapter. Recent data apart from the air emission from the same plant was collected to validate the simulation work in this study. Unfortunately the air emission data was not disclosed by the authority due to its sensitivity and current study hinges on the previously published data.

CFD based simulation for cement manufacturing are available in the literatures and most of them are related with the structural modelling. A few researchers used a Static nonlinear model to predict the chemical behaviours and changes inside the kiln. Some of them used some well-known alternative fuels like waste tyre and municipal solid waste in their model to enhance energy efficiency and mitigate emissions. There are plenty of alternative fuels available now a days which can be used in the cement kiln effectively. There is a research gap on using versatile alternative fuels in a cement manufacturing process model. Beside this, a wide spread area of research on dealing with a blend of alternative fuels has been untouched, while using blend of alternative fuels is a common practice in the cement industry. In this thesis a set of major alternative fuels of the cement industry in Australian prospect were focused by using a static process model and tried to find their optimum usage percentage in cement industry. This thesis also investigated the impact of the blends of alternative fuels and attempted to replace major portion of coal by a suitable blend of alternative fuels. In my knowledge this is the first attempt to study the alternative fuels for Australian cement industry and assessing the feasibility of different blend of alternative fuels is also a new approach in the world context. In the next chapter, a set of alternative fuels have been discussed along with the ongoing research on them in different operating conditions. Detailed literature review of these alternative fuels also revealed the research gaps in this area.

Chapter Three

Alternative Fuels

3.1 Introduction

Cement manufacturing is an energy intensive process and a huge amount of thermal energy is required to complete the pyroprocessing reaction of clinker formation. Fossil fuels such as coal, petroleum coke and natural gases are the primary candidates to provide the thermal energy required for the cement industry. In recent years, due to increasing prices of fossil fuel and concerns over climate change, industry has been looking for alternative fuel sources which could possibly replace fossil fuels partially or completely. In the past couple of decades a large amount of research on alternative fuels and their impact on plant performance have been carried out to identify the feasibility of different alternative fuel. The cement kiln is capable to serve as a waste incinerator due to its characteristics such as high temperatures, alkaline environment and long residence times for complete combustion. Cement kilns can combust hazardous waste as alternative fuels which are normally considered dangerous to burn in a low temperature waste processing furnace. While burning the wastes cement kilns can utilise the energy content to fulfil the energy requirement of the manufacturing process. This chapter reviews most common alternative fuels used in the cement industry with emphasis on the impacts and challenges faced due to switching from conventional to alternative fuel. The content of this chapter has been published in Elsevier journal *Fuel* 2015 (vol. 145).

3.2 Kiln as the destination of waste

Germany used waste tyres as alternative fuel in cement manufacturing at the beginning of the 1950s (Lechtenberg, 2008). The two worldwide economic recessions during 1980-1982 and 1990-1991, directed many cement manufacturers to reduce their operational cost and alternative fuels helped to cut the fuel cost. In the late 1980s and early 1990s, a number of hazardous waste fuels were burnt in cement plants at US and Europe. Over the years, the burning of non-hazardous waste fuels such as tyres also became well established and accepted in the cement industry (Gossman, 2009).

Alternative fuel utilization at a commercial level in the cement industry is as old as about 30 years; still the manufacturers face some barriers in regards to environmental, social and product quality issues. In calciner lines, almost 100% alternative fuel firing at the precalciner was achieved at a very early stage (Schneider et al., 2011) but the usage of alternative fuel in the rotary kiln is still in progress. Reports show that some kilns reached 100% substitution rates for a shorter period (Cemex, 2011) and researches are being continued to reveal new alternative fuels. In any case, alternative fuel utilization requires adaptation by the cement industry. Modern multi-channel burners and thermograph systems help in controlling the alternative fuel feed rate and the flame shape to optimise the burning behaviour of the fuels (Schneider et al., 2011).

The manufacturing process of cement is perfect for incinerating waste-derived alternative fuel due to the intrinsic ability for clinker to absorb and lock contaminants such as heavy metals into the cement. Other key factors of burning waste in cement kilns are:

- High temperature in the burning zone of cement kiln, which is about 1500°C, is capable of incinerating high molecular hydrocarbons, as well as the de-chlorination of dioxins and furans (Mokrzycki et al., 2003).
- Long residence time at high temperature due to the length and slow rotation speed of the kiln.
- Large inner surface area of the kiln and continuous fuel supply.
- Additional supply of O₂ which ensures the complete combustion of the alternative fuel.
- Alkaline environment of the kiln, which leads to sulphur and chlorine neutralisation (Giannopoulos et al., 2007).
- Highly turbulent gas flow velocities in the high temperature zones fall within the range of 12.1–13.5 m/s (Mokrzycki et al., 2003).
- The usage of electrostatic precipitators (ESP) in a modern cement plant allows to control cement kiln dust (CKD) and particulates contained in the exhaust and hence reduce emission (Giannopoulos et al., 2007).

3.3 Usage of Alternative Fuels

Implementation of alternative fuel in cement manufacturing has several environmental benefits including reduction of pollutant emission and conservation of non-renewable

energy resources (Trezza & Scian, 2000). The substitution rate of fossil fuel by alternative fuels varies from country to country and most of the European countries are way ahead in the usage percentage of alternative fuels than the rest of the world (World Business Council for Sustainable Development [WBCSD], 2005). The world's leading cement producers are currently using alternative fuels in a large extent and pursuing to increase it even more by 2020. Conventional fossil fuel substitution rate and the percentage of different alternative fuel usage by different cement production groups are available in their sustainable development reports. Table 3.1 summarises the percentage of different wastes which are currently being used as alternative fuels in five selected leading cement producer groups (Heidelberg, 2014; Holcim, 2014; Lafarge, 2014; Cemex, 2014; Italcementi, 2014). Cemex group are currently using industrial and household waste as a major portion of their alternative fuel. Heidelberg, Holcim and Italcementi groups are using a range of alternative fuels but Lafarge group is stuck with only four types of alternative fuels. It is also found from Table 3.1 that the most common alternative fuel is waste tyres which are being utilised by all the selected manufacturing groups up to some extent.

Table 3.1: Percentage of different type of waste used as alternative fuels

Waste type used as Alternative fuel (%)	Holcim Group (2014)	Cemex Group (2014)	Heidelberg Group (2014)	Italcementi Group (2014)	Lafarge Group (2014)
Waste oil	3	—	1.7	5.8	15.5
Solvent & liquid waste	9	—	4.0	12.1	—
Tires	9	9.0	9.3	20.5	13.2
Impregnated sawdust	3	—	—	—	—
Plastic	13	—	28.9	2.6	32.2
Industrial & household waste (solid)	—	49.7	—	16.1	—
Industrial waste & other fossil based fuel	31	—	—	—	—
MBM	1	2.5	5.0	9.4	—
Agricultural Waste	13	7.2	4.3	24.3	—
Wood chip & Other Biomass	17	31.6	23.5	—	39.1
Sewage sludge	1	—	3.9	2.1	—
RDF	—	—	—	7.3	—
Other alternative fuel	—	—	19.2	—	—

Generally the cement producers choose the alternative fuels on the basis of price and their availability but lots of other criteria need to be taken into consideration before introducing

them in the production line. Availability of a certain alternative fuel varies with the location and hence different cement plants are hinged with different locally available alternative fuels. In some countries usage of alternative fuel is restricted by some regulations set by local government. For instance, in Spain, Meat and Bone Meal (MBM) can be used up to 15% of total energy demand while there is no limit in Switzerland on using MBM (Conesa et al., 2005).

3.4 Advantages of Using Alternative Fuels

Initially alternative fuels are opted to be used in the cement industry due to their low price and they can be even more cost effective if they are used in the kiln with minimal preparation (Wellington & Dhanjal 2008). Apart from reducing the cost there are other significant advantages of using alternative fuels and among them the preservation of non-renewable energy sources ensure the storage of coal and natural gas for future generations (Trezza & Scian 2000). Co-combustion of waste in cement plants as alternative fuels reduces the emissions; otherwise that waste has to be incinerated separately with corresponding emissions and final residues (Figure 3.1).

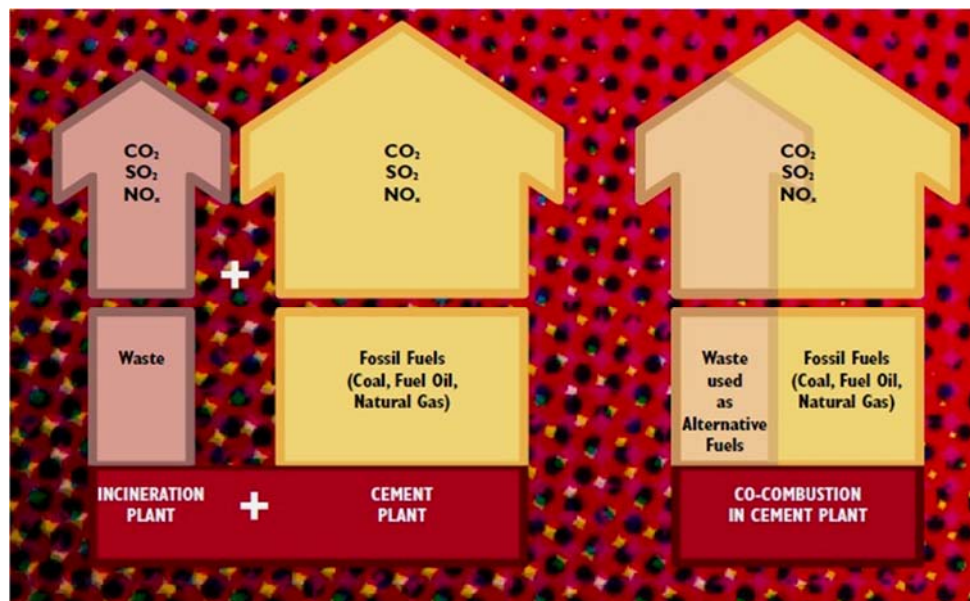


Figure 3.1: Waste recovery by cement industry reduces emission

Source: Cembureau, 1997

Among the multitude of energy recovery options from waste, cement kilns offer one of the best options as additional disposal sites for ash and slag are not required since both are locked in the clinker (Cembureau, 1997). Waste product from other industry or agricultural

processes are generally landfilled or combusted in dedicated incinerators which is total wastage of energy value of those waste products. Cement kilns offer an environmentally safe and secure alternative for conventional waste disposal which reduces the number of waste disposal sites and incineration facilities which may have detrimental impacts on the environment (Murray & Price, 2008).

In cement production, ash produced from fuel combustion generally is retained by the clinker and acts as alternative raw material, which means less raw meal requirement. For example, the steel belts in tyres may be used to replace a portion of the iron required in the raw materials (Kaantee et al., 2004). Another example is agricultural biomass which contains a high silica, an essential component of raw feed meal.

3.5 Disadvantages of Using Alternative Fuels

Switching from conventional fuels to alternative ones presents several challenges as they have different characteristics compared to conventional fuels. Poor heat distribution, unstable precalciner operation, blockages in the preheater cyclones, build-ups in the kiln riser ducts, higher SO₂, NO_x, and CO emissions, and dusty kilns are some of the major challenges which need to be addressed (Chinyama, 2011). Additional logistical supports are needed for using alternative fuel in the manufacturing process, such as fuel preparation and conditioning, storing, dosing and feeding of alternative fuels (Wurst & Prey 2002).

Chemical composition of clinker is one of the concerns in implementation of alternative fuels since the combustion by-products are incorporated into clinker. Usage of alternative fuel should be restricted if it affects the quality of the cement (Akkapeddi, 2008). Replacement of traditional fossil fuels by alternative fuels essentially requires investment costs associated with adjustment or replacement of a burner, alternative fuel delivery systems, new fuel storage facilities, and fuel distribution systems (Greco et al., 2004).

3.6 Criteria of Alternative Fuels

Most waste materials contain some heating value and thus can be considered as an alternative fuel in the cement industry for heat generation. To be considered as alternative fuel for cement industry a particular waste needs to meet certain criteria which are generally set by individual plant. Composition of the fuel including the energy content, moisture and volatile contents, size and shape of waste, and physical state of waste are some of the

criteria which need to be taken into consideration. Alternative fuel could be in different forms including liquid, solid, semi-solid, powdered or in the form of big lumps. Depending on the form of alternative fuel a flexible fuel feeding system might be required, through which alternative fuel could be fed either directly into the burning zone at the kiln or in the pre-heating system (Kaantee et al., 2004).

There are no set criteria for selecting alternative fuels today for the cement industry. The specific criteria that a material must meet in order to be considered as a fuel is typically set by the individual cement producer according to their own needs. Alternative fuels are generally derived from wastes and therefore consistency in their composition cannot be guaranteed. There is a need for ensuring the chemical contents of the alternative fuel that meets regulatory requirements for environmental protection. The following properties are expected to be considered for any potential candidate of alternative fuels (Madloul et al., 2011; Mokrzycki & Uliasz-Bochenczyk, 2003):

- Availability,
- Physical state (solid, liquid, gaseous) and physical properties (scrap size, density, homogeneity) of the fuel,
- Content of circulating elements (Na, K, Cl, S),
- Toxicity (organic compounds, heavy metals),
- Composition and content of ash and content of volatiles,
- Calorific value — over 14.0 MJ/kg,
- Chlorine content — less than 0.2% and Sulphur content — less than 2.5%,
- Polychlorinated biphenyl (PCB) content—less than 50 ppm, heavy-metals content — less than 2500ppm [out of which: mercury (Hg) less than 10 ppm, and total cadmium (Cd), thallium (Tl) and mercury (Hg) less than 100 ppm],
- Grinding properties,
- Moisture content,
- Proportioning technology,
- The emissions released,
- The cement quality and its compatibility with the environment must not decrease,
- Alternative fuels must be economically viable.

The production of clinker requires an even combustion of fuels in order to heat the raw materials consistently. Energy content or calorific values of the alternative fuels are the

measure of thermal energy that can be produced by a specific alternative fuel. According to Ibbetson and Wengenroth (2007) the limit of energy content may vary depending on the process where alternative fuels is employed. Table 3.2 shows a range of different quality parameters of alternative fuel in the burning process.

Table 3.2: Typical quality parameters for co-firing in cement manufacturing process

Quality parameter	Kiln feeding	Calcliner feeding
Calorific value (MJ/kg)	Min. 20	Min. 15
Particle size (mm)	< 20	< 25 as soft pellet
Ash content (%)	low	Can be higher up to 20%
Chlorine (%)	In general < 1%	In general < 1%

Source: Ibbetson and Wengenroth (2007)

Generally the substitution rates of fossil fuels by alternative fuels depend on the calorific value and moisture content. A general illustration of the requirement of alternative fuels to replace one tonne of coal is shown in Figure 3.2 (Murray & Price, 2008), where the calorific value of coal is assumed to be 26.3 MJ/kg. Less requirement of replacement fuel is found in the case of petroleum based fuels to replace coal due to their high calorific value. On the other hand, sludge requires a higher amount of fuel due to high moisture content.

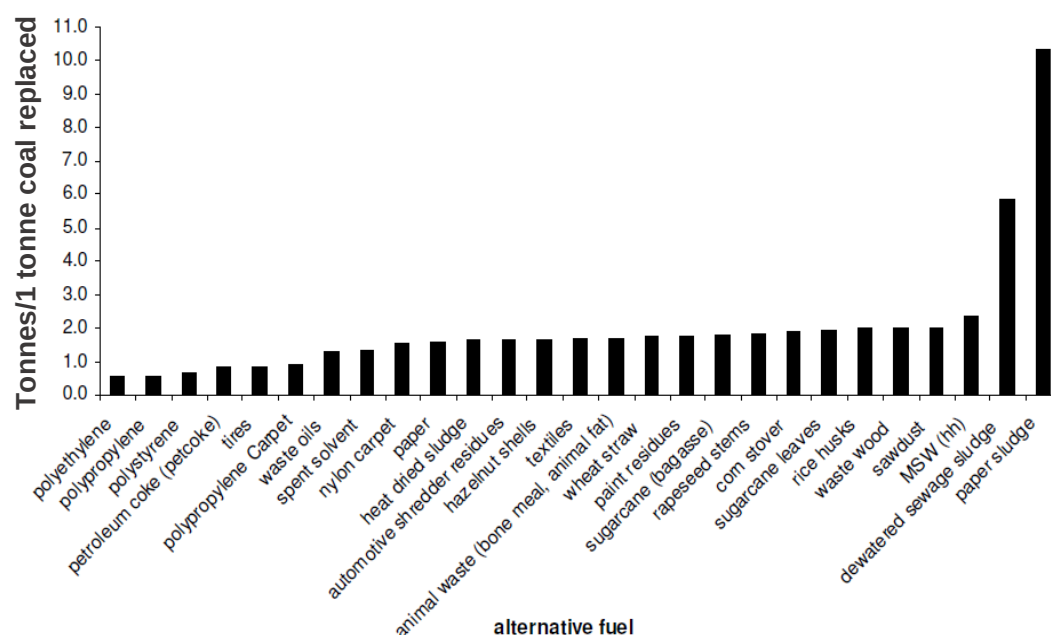


Figure 3.2: Tonnes of alternative fuel required to replace 1 tonne of coal

Source: (Murray & Price, 2008)

3.7 Classification of Alternative Fuel

The range of alternative fuels is extremely wide and they can be divided into three distinct categories: solid, liquid, and gaseous fuels (Greco et al., 2004; Chinyama, 2011). Ranges of alternative fuels are listed in Figure 3.3 based on their physical state. Mokrzycki and Uliasz-Bochenczyk (2003) also categorised solid alternative fuel in four groups according to their size which are stated in Table 3.3.

Table 3.3: Category of solid alternative fuel

Description	Dimension mm	Moisture content	Examples
solid, dry fuels of relative fine size, which do not adhere	< 2	<10–15%	wood dust, bark powder, rice husk,
solid, dry fuels of coarse size, which do not adhere	< 20	<10–15%	plastic waste, wood chips, waste wood
solid, dry fuels which tend to stick	< 20	<10–15%	Meat and bone meal, impregnated wood dust,
mixtures of different lumpy fuels	<200	<20%	fluff, paper, cardboard

Source: Mokrzycki and Uliasz-Bochenczyk, 2003

Cement manufacturers also use a blend of different alternative fuels to achieve maximum benefit. In such case the mixture should be produced considering certain issues (Lemarchand, 2000):

- The quality of the fuel must meet regulatory standards assuring environmental protection,
- The calorific value must be stable enough to allow the control of the energy supply to the kiln; the objective being to arrive at a fairly homogeneous composition, and
- The physical form must allow easy handling of the material for transportation and a stable, adjustable flow of material in the cement plant.

The Cement industry can acquire alternative fuels from a wide variety of sources. The diversity of sources and inconsistent nature of these waste materials pose a difficult challenge to the cement producers regarding the storage, handling and feeding of alternative fuels into the system. Utilization of a modern dryer and shredder, conveyer belt

and multi-channel burner facilitates the maximum usage of alternative fuel in the cement industry currently.

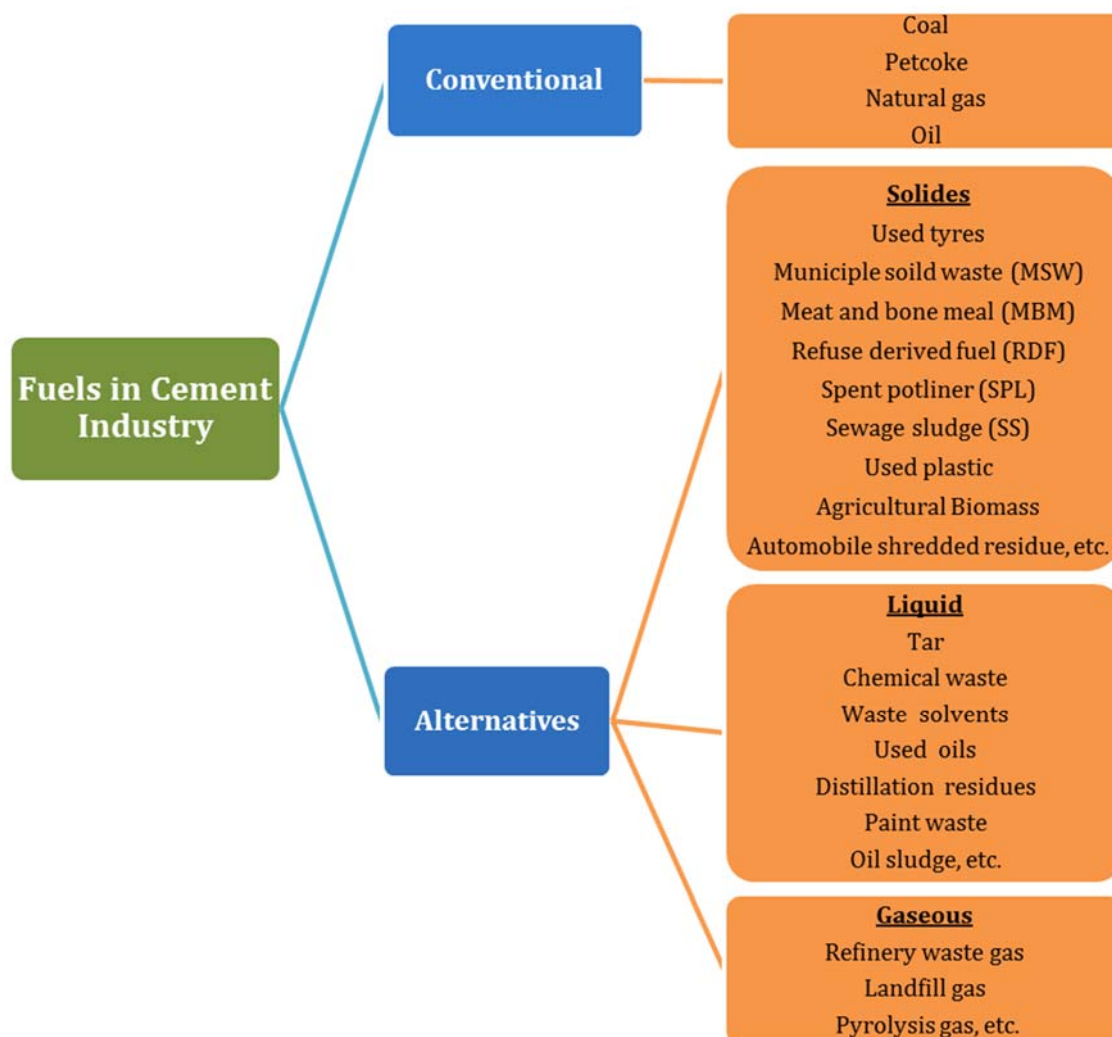


Figure 3.3: List of fuels (conventional & alternatives) in cement industry

3.8 Alternative Fuel Options

A wide range of materials can be considered as viable alternative fuels. In this section most of the common alternative fuels are discussed along with their composition, usage and environmental impact. Elemental analyses of different alternative fuels are collected from literature and appended herewith to facilitate comparison. Apart from the moisture content, the volatile content of alternative fuels is closely monitored as it is related with the amount of combustion residue which remains with the clinker. Generally the volatile content of the alternative fuels ranges from 54-100 wt. %, which is higher than coal and petcoke (Nielsen, 2012) and leads to significant low char content.

3.8.1 Used Tyre

End life tyre is a waste from the automobile industry and generally disposed of in landfills or stockpiles. Landfilling or stockpiling tyres has potential environmental, safety and health hazards. Amongst them rodent and insect infestation are well known. In the mid 1980's tyre became very popular to the cement manufacturer as alternative fuel to cope with the increasing fossil fuel costs. High carbon content, high heating value of 35.6 MJ/kg (Kaantee et al., 2002) and low moisture content make tyre derived fuel (TDF) one of the most used alternative fuels in the cement industry all over the world. Tyre derived fuel (TDF) costs are significantly lower than natural gas costs and the overall unit costs of tyre derived fuel are even less expensive than coal. Using whole tyres as fuel one will receive a tipping fee for collecting the whole scrap tyres which will help offset the transportation costs (Smith & Martin 2008). Reinforcing wires of tyres can be consumed as a replacement of raw material containing iron (Kaantee et al., 2002) when the whole tyre is used as alternative fuel. Figure 3.4 represents a schematic diagram of the process involved in the cement industry while using tyres as alternative fuel (Corti & Lombardi, 2004). The diagram indicates the saving of coal and iron minerals as input materials.

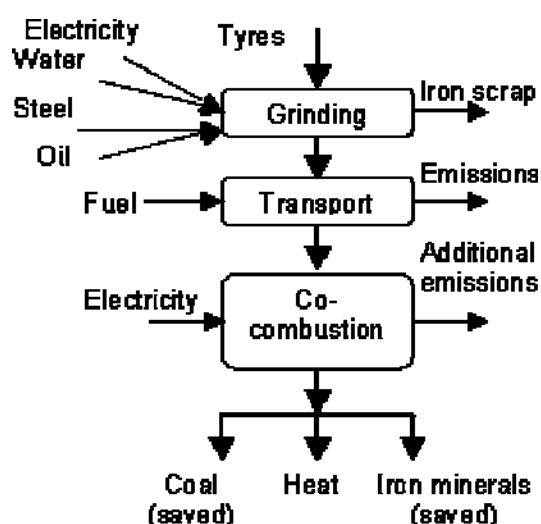


Figure 3.4: Tyre as alternative fuel in cement manufacturing

Source : Corti and Lombardi, 2004

In terms of the clinker quality, researchers found no significant differences in the chemical composition of the clinker manufactured by using TDF as opposed to fossil fuel (Puertas & Blanco-Varela, 2004). Different forms of tyre, from whole to fine grained, can be used in cement kilns as alternative fuel. The advantage and disadvantage of using different forms

of tyre are listed in Table 3.4 while Figure 3.5 illustrates the tyre dumping facility, size of tyre chip and feeding tyres into the kiln with a conveyer belt facility.

Table 3.4: Advantages and disadvantages of different forms of tyre derived fuels
(Adapted from Ariyaratne 2009)

Form	Advantages	Disadvantages
Ground tyres (crumb)	▪ The crumb can be blown in with powdered coal fuel directly. ▪ The transportation storage and management of the crumb is very similar to managing coal fines.	▪ The removal of the steel is unnecessary since cement kilns have a need for iron in its process. ▪ Producing the crumb is quite expensive. ▪ Dust and fire suppression on storage may be required due to high bulk density.
Tyre chips (from 2x2 cm ² to 15x15 cm ²)	▪ Feed rate can be continuous and carefully regulated. ▪ There is very little manual labour involved in handling chips versus whole tires.	▪ Expensive. ▪ The wires in radial belts do not shear smoothly when the tires are chipped. Consequently, the chips are ragged with these wires hooking onto everything they come in contact with. ▪ Dust suppression and fire suppression on storage is required.
Whole tyres	▪ No processing costs in addition to the acquisition costs. ▪ Do not migrate throughout the facility. ▪ Dust and fire suppression on storage are not required.	▪ Transportation, storage and management of whole tires require more logistical care and more manual labour and difficult to automate.

The composition of tyres is variable with respect to the source and levels of bracing material within the tyre or tyre chips. Ultimate analysis on weight percentage of passenger car tyre and truck tyres in comparison with bituminous coal are given in Table 3.5 (Karell and Blumenthal, 2000). It is found that heating values of tyre are higher than bituminous coal.

Waste tyre as an alternative fuel was intensively studied to identify possible environmental impact as it is the most common alternative fuel in the cement industry. Contradictory results are available in literature regarding SO₂ and NO_x emissions while using TDF as

alternative fuel. Prisciandaro et al. (2003) reported that SO_2 and NO_x emissions increase in an Italian cement plant with TDF replacing up to 20% of fossil fuel. In contrast Carrasco et al. (2002) found a decrease in NO_x emissions but an increase in SO_2 while studying a Canadian cement plant that used a combination of coal and scrap tyres as fuel. Schrama et al. (1995) and Lemarchand (2000) reported that the emission of NO_x decreased when whole tyres are used as alternative fuel. Schematic data of air emission while burning 1 tonne of scrap tyre are shown in Figure 3.6.



Figure 3.5: a) Landfill of tyre, b) Scrape tyre, c) Used tires being fed to a cement kilns

Source: a) Oracle Think Quest Education Foundation, Recycling, <http://library.thinkquest.org/07aug/02051/Tires.htm> b) Tire-Derived Fuels, Scrap Tires, Beta Analytic Inc. <http://www.betalabservices.com/renewable-carbon/tire-derived-fuels.html>, c) Wikipedia, the free encyclopedia, http://en.wikipedia.org/wiki/Cement_kiln

Table 3.5: Ultimate analysis of tires and coal by percentage of weight

Fuel Type	Passenger Tires	Truck Tires	TDF	Bituminous Coal
Weight percentage (wt%)				
Carbon	89.48	89.65	89.51	75.8
Hydrogen	7.61	7.50	7.59	5.1
Oxygen	<0.01	<0.01	<0.01	8.2
Nitrogen	0.27	0.25	0.27	1.5
Sulphur	1.88	2.09	1.92	1.6
Chlorine	0.07	0.06	0.07	Not listed
Ash	3.9	5.5	4.2	7.8
Lower Heating value (MJ/kg)	36.7	34.7	36.1	31.4

Source: Karell and Blumenthal, 2000

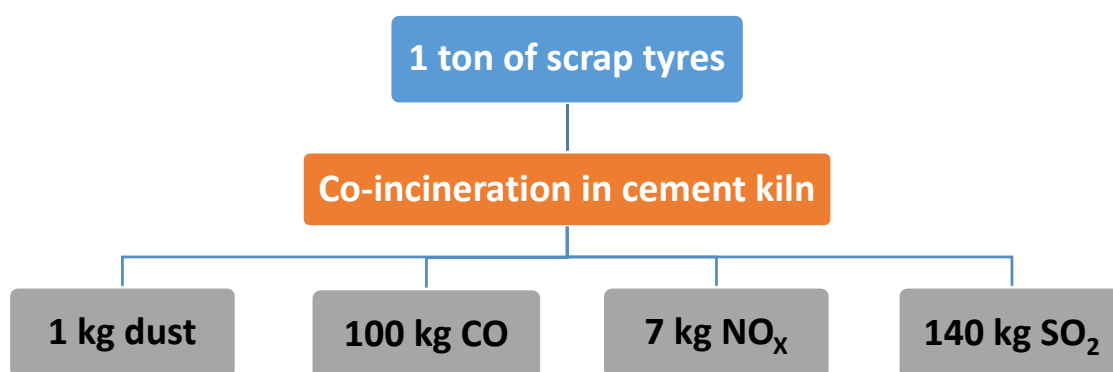


Figure 3.6: Air emission data for burning tyre

Source: Silvestraviciute and Karaliunaite, 2006

Contrary results are also available in terms of metal, dioxin and furan emissions. In a real plant scenario, Conesa et al. (2008) showed that dioxin and furan emissions increased while using scrap tyre as alternative fuel. By contrast, Carrasco et al. (2002) found that using scrap tyres in cement kilns reduced the amount of dioxins and furans emitted. However, Prisciandaro et al. (2003) reported that the emissions of dioxins and furans remained unchanged (and well below the limit).

CO emissions in most cases are found higher (average 35% higher) (Pegg et al., 2007) when TDF is used. HCL emission was found to be higher than normal (Carrasco et al.,

2002). During rubber compounding to control the rate of vulcanization, zinc is added to tyre. This zinc has the potential to release on environment (Clark et al., 1991).

3.8.2 Spent pot liner

Spent pot liner (SPL) is a solid waste produced from aluminium industry during the manufacture of aluminium metal in electrolytic cells. In the process of aluminium production, alumina is dissolved in Cryolite in electrolytic cells which consist of steel shells lined with carbon. A number of pots, usually more than 100, are arranged in series to form a potline. The lining of the cell is composed of carbon, which is backed by insulation and contained within a steel container called a potshell. The carbon portion of the lining serves as the cathode for the electrolysis process. After a certain period the cell lining become impregnated with fluoride-containing salts and then the cell is taken off-line and the cathode lining material is removed from the potshell by mechanised digging equipment. This spent cathodic material is referred to as spent pot liner (SPL). The life cycle of a cathode typically varies from about 3 to 10 years (Silveira et al., 2002). A potline with a series of pot shell in an aluminium smelter, impregnated pot shell and raw spent pot liner are given in Figure 3.7.

In 2010, U.S.-generated SPL was recycled up to 79% in cement kilns in 2010 (Alcoa, 2012). In 2009, 7449 tonnes of spent pot lining (SPL) were recycled in Australia. Most of them are used in cement manufacturing as alternative fuel (Alcoa in Australia, 2012). Three smelters in Canada generated a combined 17,400 metric tonnes of SPL in 2010, of which 90% was recycled mainly as valuable raw material and alternative fuel source for use in the manufacture of cement, steel, and other products (Alcoa, 2011).

The heating value of SPL is 25.2 MJ/kg (Mikša et al., 2003) which is almost equal to bituminous coal. The total SPL generation in the world was about 800,000 tonnes in the year 2003 which implies the abundance of SPL to be used as alternative fuel (Mikša et al., 2003). SPL can be fed in to the kiln as fine grounded powder along with powdered coal and hence some processing is required. SPL contains a small amount of cyanide and a few heavy metals, primarily lead and chromium. Sodium and fluoride are also found in the composition of SPL in small amounts. Table 3.6 summarises chemical compositions of SPL from literature and variation was found in terms of composition and heating value based on the location of collection point.

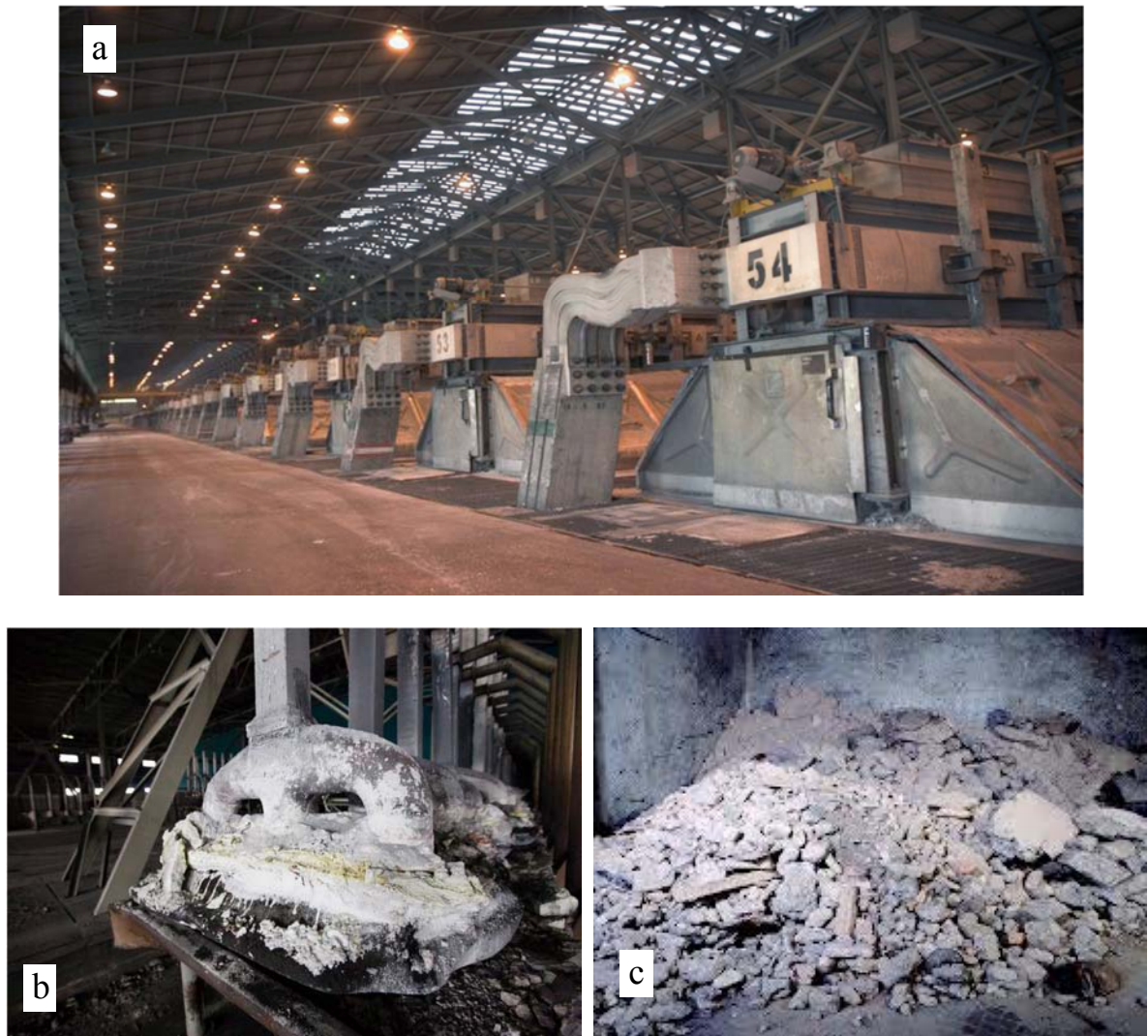


Figure 3.7: **a)** Aluminium smelting cells, **b)** Hall-Heroult Aluminium reduction cell, **c)** Raw spent potliner

Source: **a)** Lechtenberg, D 2009, *Global Cement Magazine*, January, pp. 36-37. **b)** Angelova. K 2012, <http://www.businessinsider.com/rusal-aluminum-factory-oleg-deripaska-2011-12?op=1>, **c)** Regain Services Pty Ltd., regain.com.au

Scant literatures were found regarding the environmental impact of SPL while using it as fuel in cement kilns. A test study showed that almost 99.9% of the cyanide contained in the SPL is destroyed when it is used as a supplemental fuel in a cement kiln (Kohnen, n.d.). Lechtenberg (2009) reported the reduction of NO_x and CO₂ emission while using SPL. Lechtenberg (2009) also indicated that use of SPL would supply raw materials such as silica, alumina and ferrous components. Due to high fluorine content, handling and transportation could be an issue. Another problem of SPL is the high pH level, which is 11.18 on average (Silveira, 2002). SPL is highly water reactive and it can generate

ammonia, methane, hydrogen and heat on contact with humid air (Gossman, 2006). The finer the material is ground, for injecting it into a cement kiln, the greater the potential for hazardous gas release; extra precautions is required when handling SPL.

Table 3.6: Typical SPL composition

Material	Composition (wt%)		
	Lechtenberg 2009	Pong et al. 2000	Mikša et al, 2003
Moisture	0.5–2%	—	0.72
Carbon	15–30%	13-69	56.13
Na ₂ O	14–20%	8.6-22	9.42
K ₂ O	0.4–0.8%	—	—
Fluorine	9–15%	7.5-22	7.16
Al ₂ O ₃	25–35%	7-22	5.23
SiO ₂	14–20%	0.7-10.9	0.61
Fe ₂ O ₃	1–3%	0.3-2.8	—
CaO	1–3%	0.5-6.4	0.86
Sulphur	0.05–2%	0.1-0.6	0.17
Chlorine	0.01–0.04%	—	—
Total cyanides	0.01–0.1%	0.04-0.6	3.3
Magnesium	—	0.1-0.17	—
Ash	—	—	42.9
Net heating value	5–18 MJ/kg	—	25.2 MJ/kg

3.8.3 Spent Solvent and Used Oil

Waste oils are a hazardous waste; they originate from automotive, railway, marine, farm and industrial sources. In European Union countries approximately 1.07 million tonnes of waste oil is used by cement kilns as alternative fuel (Murray & Price, 2008). Solvent and spent oil from different industries generally have high calorific value and those can be used in cement kilns as alternative fuel with minimal processing cost (De Vos et al., 2007). De Vos et al. (2007) reported that the maximum and minimum calorific values of solvent and spent oil were 29 MJ/Kg and 36 MJ/Kg respectively and the variation occurred due to the ratio of different chemical in it. Cement plants established in the vicinity of industrial areas can makes the solvent and spent oil a highly acquirable fuel with minimum transportation cost. In Figure 3.8 some samples of spent solvent and used oil are given to illustrate the physical state of these alternative fuels.



Figure 3.8: a) Spent Solvent, b) Waste oil, c) Paint residue, d) Paint sludge

Source: a) *The concept of Generator's Knowledge*, <http://normanswei.wordpress.com/2011/11/08/the-concept-of-generators-knowledge/>, b) Gupta, R, *Waste Oil: Burners, Heaters and Boilers*, <http://www.buzzle.com/articles/waste-oil-burners-heaters-and-boilers.html>, c) Anonymous, d) *Burning alternative fuels at cement plants*, www.pmsolid.com/psp/data/IP_3776_2_GB_Cement.pdf

Australian industries purchase in excess of 500 million litres of oil annually (Australian Government report, 2011). Some of this oil can be recycled into new products through filtration and treatment; still there is a portion which cannot be reused. Used oil becomes unusable if it is exposed to other substances such as water, dirt or chemicals used in conjunction with the oil to improve performance. The unusable portion often contains trace amounts of lead, cadmium, arsenic, dioxins, benzenes and polycyclic aromatics (Australian Government report, 2011) all of which are highly toxic materials to humans, animals and plants. Burning of the non-recyclable used oil is an effective means of disposal as the temperatures of the kiln is high enough to burn all organic materials and any remaining non organic compounds are chemically trapped in the clinker (Bhatty, 2006). Compositions of waste solvent and used oil are available in literature and a typical composition is shown

in Table 3.7. Heavy fuel oils are more contaminated with heavy metals, sulphur, phosphorus and total halogens depending on the source of origin.

Table 3.7: Elementary composition of waste solvent & heavy fuel oil

Composition	Waste solvent	Heavy fuel oil
H ₂ O	16.5 (wt%)	--
C	47.7 (wt%)	84 (wt%)
H	8.2 (wt%)	--
O and rest	23.1 (wt%)	14.73 (wt%)
N	1.0 (wt%)	0.44 (wt%)
S	0.7 (wt%)	0.83 (wt%)
P	0.06 (wt%)	traces
Cl	2.4 (wt%)	20 (g/t)
Br	2500 (ppm)	--
I	130 (ppm)	--
Fe	85 (ppm)	--
Ni	4.6 (ppm)	15 (g/t)
Cu	6.2 (ppm)	3(g/t)
Zn	57 (ppm)	0.9(g/t)
As	--	0.8(g/t)
Cd	--	2(g/t)
Cr	--	1(g/t)
Hg	--	0.006(g/t)
Pb	--	3.5(g/t)
Net heating value [MJ/kg]	21.7	40.4

Source: Seyler et al., 2005, Seyler et al., 2005a

Solvent and waste oil contain less minerals compared to petcoke and coal hence an additional amount of raw meal may be needed to ensure the quality of the cement (De Vos et al., 2007). One study shows a reduction of nitrogen oxides while using spent solvents compared to fossil fuels (Seyler et al., 2005a). De Vos et al. (2007) reported that CO₂ emission was reduced while solvents and paint sludge were used as alternative fuel. The literature is inconclusive with respect to the changes in SO₂ emission. Mlakar et al. (2010) showed a reduction in mercury emissions while Seyler et al. (2005a) showed a reduction in heavy metal emissions when waste solvents were mixed with fossil fuel.

3.8.4 Municipal Solid Waste (MSW)

Municipal solid waste (MSW) is an intricate waste due to their heterogeneous composition (Kara et al., 2010) and the physical or chemical properties are inconsistent compared with other alternative fuels (Carrasco et al., 2006). Still the availability of the MSW makes it one of the most desirable alternative fuels in cement manufacturing. Table 3.8 summarised the MSW generation rate of different countries which is a clear indication of the availability of this waste.

Refuse derived fuel (RDF) is the homogenous portion of MSW and preferred as alternative fuel due to their high calorific value and low moisture content. In the late 1980's Dorn (1977) presented a research work indicating the pros and cons of using municipal waste as alternative fuel in the cement industry. At that point it was really difficult to predict the future trend of energy utilization in the cement industry and it was predicted that RDF may not be a feasible option as an alternative fuel due to uncertain supply of waste. Over the time as the world population grows the excess amount of MSW has become an environmental concern and the cement industry has grabbed that opportunity to replace coal by the alternative fuel MSW. In 1990 Haley presented a cost benefit analysis of burning RDF in a cement kiln which encouraged the cement producer even more to choose RDF as alternative fuel. Figure 3.9 presents the landfill site of MSW, processing of MSW and RDF.

Table 3.8: Waste generation in selected countries in 2005

Countries	Total amount of MSW generation (1000 tonnes)	MSW generation rate (kg/capita/day)
USA	222,863	2.05
France	33,963	1.48
Germany	49,563	1.64
Denmark	3,900	2.03
Switzerland	4,855	1.78
Poland	9,354	0.68
Portugal	5,009	1.29
Hungary	4,632	1.26
Mexico	36,088	0.93
Japan	51,607	1.10
Korea	18,252	1.04
China	212,100	0.98

Source: Zhang et al., 2010



Figure 3.9: **a)** Municipal solid waste, **b)** Municipal solid waste is shredded and ground into a uniform particle size, **c)** Refuse-derived fuels

Source: **a)** http://www.environment.tn.nic.in/SoE/waste_pho.htm,
b) <http://www.percwte.com/index.php?id=14>
c) <http://www.betalabservices.com/renewable-carbon/refuse-derived-fuels.html>

Garg et al. (2009) reported that cement kilns are potentially the best option over incineration of MSW in a thermal power plant and co-combustion in a biomass combustor. During incineration of MSW, toxins and heavy metals are produced which can leach into the water supply and soil. With energy recovery in cement manufacturing, these substances

are partially transferred to the clinker (Genon & Brizio, 2007). A major concern of using MSW in cement kilns is the variable heating value and moisture content due to the heterogeneous composition of MSW. Depending on these, MSW can be substituted up to 30% of the fuel mix in cement manufacturing (Kara et al., 2010; Lockwood & Ou, 1993). Generally MSW contains various components including plastic, paper, rubber, wood and textile. Table 3.9 shows a typical composition of MSW regarding different material by weight percentage and volume percentage.

Table 3.9: Typical composition of MSW by material

Material	Percentage by weight	Percentage by volume
Pulp and paperboard	37.5	37.0
Glass	6.7	2.3
Ferrous metals	6.3	8.8
Aluminium	1.4	3.1
Plastics	8.3	18.3
Rubber and leather	2.4	5.8
Textiles	2.8	5.4
Wood	6.3	5.9
Food wastes	6.7	2.7
Yard wastes	17.9	9.2
Other	3.7	1.5

Source: Ruth, 1998

Refuse derived fuel (RDF) can be produced from MSW through a number of different processes consisting in general of:

- Separation at source;
- Sorting or mechanical separation;
- Size reduction (shredding, chipping and milling);
- Separation and screening;
- Blending;
- Drying and pelletising;
- Packaging; and
- Storage (EC, 2003).

MSW typically has a calorific value of 8-11 MJ/kg, while the calorific value of RDF ranges from 15–20 MJ/kg (Ariyaratne, 2009). Typical chemical composition of MSW and RDF is

presented in Table 3.10 (Garg et al., 2009). Generally a belt conveyor and pneumatic channel are used to feed MSW or RDF directly to the burning zone.

Table 3.10: Chemical composition of MSW and RDF

Component	MSW	RDF
	Dry solids%	Dry solids%
Carbon	34.88	47.1
Hydrogen	4.65	7.1
Nitrogen	1.02	0.7
Sulphur	0.15	0.24
Chlorine	1.02	0.6
Oxygen	23.11	29.4
Moisture	31.2	15
VM	64.83	82.06
Ash	35.17	10.9
Lower heating value	15.4 MJ/kg	21.2 MJ/kg

Garg et al. (2009) reported that SO_x emissions increase for MSW while using it in cement kilns compared to the other disposal option of MSW. Still the emission of SO_x is way below the environmental regulation limit. On the contrary, Genon and Brizio (2008) reported that the nitrogen and sulphur content are lower in MSW than fossil fuel, meaning less emission of NO_x and SO_2 . The use of MSW implies a reduction of the use of fossil fuels which leads to a net reduction in CO_2 and CO emissions in comparison to fossil fuel combustion (Hashimoto et al., 2010; Genon & Brizio, 2008, Mokrzycki et al., 2003; Cheung et al., 2006). Incomplete combustion of MSW and a high level of chlorine content may lead to highly toxic dioxin and furan emissions (Choy et al., 2004; Genon & Brizio, 2008). In a study Mokrzycki et al. (2003) showed that the quality of the MSW can affect the HCL emission. Among the heavy metal, an increase in mercury emissions has been reported (Genon & Brizio, 2008).

Overall the substitution of MSW as alternative fuel has a positive effect on greenhouse gas formation over traditional schemes. The formation of conventional gaseous pollutants, such as sulphur and chlorine are well retained by the alkaline environment of a cement kiln (Genon & Brizio, 2008). The generation of nitrogen oxides can be reduced by lowering flame temperatures and decreasing excess air.

3.8.5 Plastic Waste

Plastic waste is one of the most readily available alternative fuels in the cement industry due to its worldwide production. Plastic wastes are also present in municipal waste and industrial waste as a fraction but individually plastic waste has higher calorific value which ranges from 29-40 MJ/kg (European Commission, 2003).

The major concern of using plastic waste is the Chlorine content which is mainly found in PVC. According to Al-Salem et al. (2009) the accepted particle size for the incineration process is $10 \times 10 \times 10$ cm and a shredder is needed when larger parts are offered in the kiln. Isolation of materials from plastic waste and retrofitting requires additional capital and labour costs. The material preparation can be done on-site or off-site and can be conveyed either to the kiln or to the precalciner through a belt-conveyer. Figure 3.10 shows the plastic waste at collection point and shredded plastic waste which is ready to be fired in the burning zone.



Figure 3.10: **a)** Mixed plastic waste, **b)** Bundled plastic waste, **c)** Shredded plastic waste

NO_x emission, while burning plastic waste, might depend on the nitrogen content of the plastic and some other parameters such as the flame temperature and amount of excess air (Al-Salem et al., 2010). Emission of volatile metals like mercury and thallium have the potential to increase, however by using ESPs in the dust stream this could be removed (Ariyaratne, 2009). Strazza et al. (2011) investigated the co-incineration of plastic waste in an Italian cement plant by using a life cycle assessment tool. They have considered five parameters to assess environmental impact which are global warming potential (GWP) in 100 years (for CO₂), ozone-depleting potential (ODP) in 20 years (for CFC), acidifying potential (for SO₂), ozone-creating potential (POCP) and oxygen consumption potential (EP). Strazza et al. (2011) affirmed the positive effect of using plastic waste by reporting relative reductions in every impact category. Shortage of research articles on the complete environmental impact assessment of using plastic waste as alternative fuel indicates that this field has not been well studied.

3.8.6 Meat and Bone Meal

In 1994 European Union banned the uses of meat and bone meal (MBM) as cattle feed and land filling due to the BSE pathogens (publicly known as mad cow disease). This change increased the interest in using MBM as fuel in the cement industry to ensure that any living organism is thermally destroyed totally and its energy potential is utilised (Chinyama, 2011). In recent days most of the cement producers are using MBM as alternative fuel (Table 3.1). In France about 45% of the annual production of MBM were burnt in cement plants (Deydier et al., 2005). The availability of MBM is higher than most of the other alternative fuel commonly used in cement kilns (Kowalski & Krupa-Żuczek, 2007). The substitution rates of MBM in cement kilns vary from country to country. For example, in Spain the limit is 15% of the energy needed in the kilns, but there is no limit in Switzerland (Conesa et al., 2005). Images of slaughterhouse residue and processed MBM are given in Figure 3.11.

MBM have calorific value (LHV) 14.47 MJ/kg (Senneca, 2008) which is almost half that of coal. The high content of calcium in MBM offers the advantage of reducing SO₂ emission as it could act to retain most of SO₂ formed during MBM combustion (Chinyama, 2011). Presence of an excess amount of calcium can produce free lime while burning in cement kilns, which may affect the clinker quality (Ariyaratne et al., 2010). Another

potential barrier of using MBM in the cement industry as fuel is the moisture content which is about 70%. Pre-treatment is required to reduce that, hence increasing the processing cost.

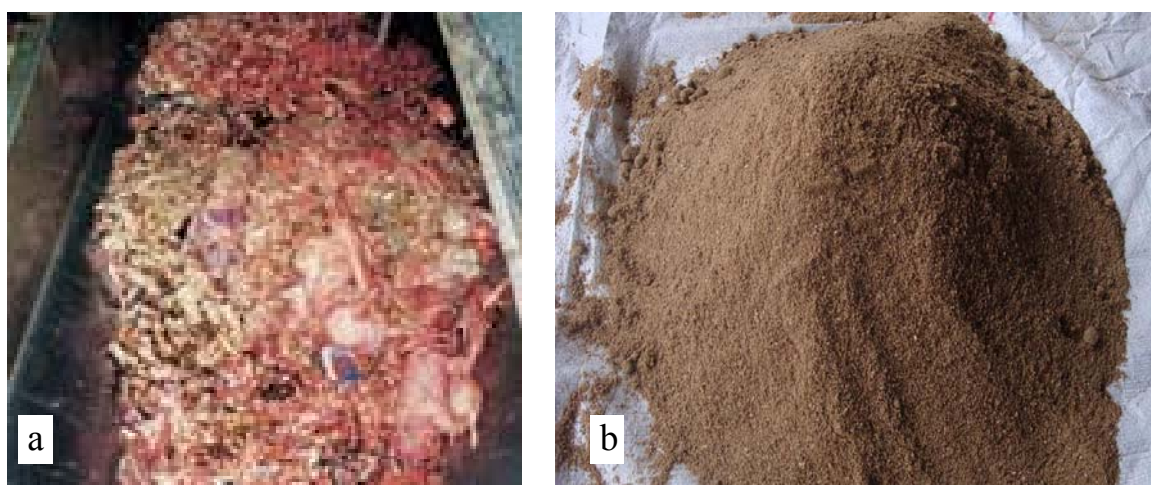


Figure 3.11: **a)** Waste from slaughter house, **b)** Meat and Bone Meal (MBM)

Source: **a)** *Burning alternative fuels at cement plants,*

www.pmsolid.com/psp/data/IP_3776_2_GB_Cement.pdf

b) http://www.aboissa.com.br/produtos/view/643/meat_and_bone_meal?language=en

MBM are generally fed in the kiln burner and an additional amount of air may be required if it is used in precalciner riser (Ariyaratne, 2009). Kaantee et al. (2002) reported that approximately 5% to 10% more air is needed for combustion if MBM meal is fed to the burning zone. Compared with coal, MBM has less fixed carbon and high chlorine. Due to higher chlorine content there is a potential chance of build-up and blockages occur in preheater units resulting in the reduction of the efficiency of the plant (Chinyama, 2011). Abad et al. (2004) found that animal and bone meal combustion has no impact on dioxin and furan emissions. Nitrogen content in the MBM is about 7-8 times higher than that in coal; hence one would expect that NO_x emissions would increase. But it was observed that NO_x decrease with increasing MBM content in coal-MBM fuel blend (Gulyurtlu et al., 2005). In contrast Denafas et al. (2004) mentioned that the emission of nitrogen oxides might increase during incineration of MBM with heavy fuel oil.

3.8.7 Sewage Sludge

A large amount of sewage sludge is produced worldwide during wastewater treatment. Landfill, agricultural use as organic fertiliser and soil conditioner are the main conventional methods of disposal; most of which are not environmentally friendly (Chinyama, 2011).

The most common sewage sludge disposal alternative is to incinerate it in a cement kiln and to confine the ash in the clinker. In 2006 the Swiss cement industry used 54,964 tonnes of dried sewage sludge, 22% of the total used tonnage of alternative fuels. In Germany around 200,000 tonnes of dewatered municipal sewage sludge and around 40,000 tonnes of dried municipal sewage were used in 2006 (Lechtenberg 2011). Werthera and Ogadab (1999) suggested that the maximal sewage sludge feed rate should not be more than 5% of the clinker production capacity of the cement plant. The wet sewage sludge is better for blending into wet process slurries and use in wet process kilns. In the dry cement process the sludge must be dried to 1% moisture before firing. Figure 3.12 illustrates the source, treatment plant and final product dried sewage sludge.



Figure 3.12: **a)** Waste water disposal, **b)** Wastewater treatment plant, **c)** Sewage Sludge after treatment

Table 3.11: Proximate and ultimate analysis of fuels

	Sludge A	Sludge B
<i>Proximate analysis (dry, wt%)</i>		
Moisture	0.2	0.6
VM	47.3	70.8
Ash	20.2	23.0
FC	32.3	5.6
<i>Ultimate analysis (wt%)</i>		
C	52.5	54.8
H	6.4	7.8
N	9.2	8.7
S	0.8	0.1
O ^a	31.1	28.6

^a By difference.

Source: Ninomiya et al., 2004

The range of different elements on the sewage sludge and its calorific value depend on the characteristics of the source and the treatment process of the sludge. Proximate and ultimate analyses of two different types of sewage sludge are listed in Table 3.11. While the heating value of different types of dried sludge are given in Table 3.12.

Table 3.12: Typical heating values for several types of sewage sludge

Source: Fytili and Zabaniotou, 2008

Type of sludge	Lower heating value of dried sludge (MJ/kg)	
	Range	Typical
Raw sludge	23–29	25.5
Activated sludge	16–23	21
Anaerobically digested primary sludge	9–13	11
Raw chemically precipitated primary sludge	14–18	16
Biological filter sludge	16–23	19.5

One study (U.S. Environmental Protection Agency, 2008) showed that NO_x emissions are reduced while using sewage sludge compared to fossil fuels. Cartmell et al. (2006) reported an increment of SO₂ emissions. The level of mercury (Hg) is high in sewage sludge which comes from the cleaning process at the sewage plant and from the source (Ariyaratne, 2009). To use sewage sludge in the cement industry, the suggested maximum mercury content is 0.5 mg/kg (Zabaniotou & Theofilou, 2008). Conesa et al. (2008) stated that there

was no correlation between sewage sludge usage rate and heavy metal emissions. But Cartmell et al. (2006) reported earlier that sewage sludge causes an increase in heavy metal emissions compared to fossil fuels. More intensive studies are needed to increase the reliability of these findings.

3.8.8 Agricultural Biomass

The usage of agricultural biomass in power generation is a recent trend, mostly in rural developing countries like India, Thailand and Malaysia (Chinyama, 2011). In 2001, agricultural biomass accounted for 0.25% of thermal energy substitution in the cement industry around the world (Murray & Price, 2008). The share of kiln fuel replaced by agricultural biomass is about 5% (Müller & Harnisch, 2009) and it is increasing slowly. Rice husk, corn stover, hazelnut shells, coconut husks, coffee pods, palm nut shells and bagasse are the most common varieties of biomass currently being used in the cement industry (Murray and Price, 2008). Most of the agricultural biomasses have moderate heating value ranges from 14 to 21 MJ/kg (Chuah et al., 2006), which is suitable to burn in cement kilns as well as in calciners. Research showed that 20% substitution of the thermal energy in cement by agricultural biomass can be achieved without a major capital investment (Demirbas, 2003).

Numerous studies on the impact of alternative fuel on cement manufacturing were carried out over the last two decades. Unfortunately not many studies are found in the literature regarding the usage of agricultural biomass as alternative fuels in the cement industry. Researchers have done experimental and numerical studies to determine the heating value and combustion characteristics of different agricultural biomass (Demirbas, 1997, 2003; Jenkins et al., 1998; Raveendran and Ganesh, 1996; Friedl et al., 2005; Skodras 2006). During the last decade researchers concentrated on the impact of co-firing biomass and coal on emissions (Demirbas. 2003; Sami et al., 2008), flame characteristic (Lu et al., 2008) and cost effectiveness (Tillman, 2000). Specific agricultural biomass for example bagasse (Ramakrishna and Babu, 2001), coffee husk (Suarez & Luengo, 2003), rice husk (Afzal et al., 2011) and saw dust (Sharma et al., 2013), were studied to justify their performance in power generation. In spite of worldwide usage of agricultural biomass as alternative fuel in the cement industry, scant literature was found regarding the effect on clinker quality and emission from cement plants. Sharma et al. (2013) studied the usage of saw dust in cement manufacturing along with the effect on clinker quality. Warnken and Giurco (2003)

identified the benefits and barrier of using various biomass fuels including wood, wheat residues and rice husks in the cement industry. Table 3.13 and 3.14 respectively represent the proximate analysis and ultimate analysis of different agricultural biomasses which are currently used in the cement industry as alternative fuel.

Agricultural biomass is considered as a CO₂ neutral fuel since CO₂ consumed by them during their life is almost the same amount of CO₂ that releases during combustion (Sami et al., 2008). Different studies showed that co-firing of agricultural biomass results in the reduction of NO_x, SO_x and some heavy metal emissions (Murray & Price, 2008; Sami et al., 2008; Royo et al., 2007). Inconsistent supply of biomass and fluctuation of the heating value of some biomasses may restrict their usage as alternative fuels (Chinyama, 2011).

Table 3.13: Proximate analyses of selected biomass fuels (wt%).

Agricultural biomass	Moisture	Ash	Volatile Matter	Fixed carbon	References
Rice husk	9.96	20.61	54.68	15.02	Demirbas, 2003
Switch grass	15.00	7.63	65.19	12.19	Tillman, 2000
Coffee husk	10	2.4	78.5	19.1	Suarez and Luengo, 2003
Corn Stover	35.0	3.25	54.6	7.15	Demirbas, 2003
Coconut shell	4.4	3.1	70.5	22.0	Werther and Saenger, 2000
Wheat straw	8.5	13.5	63.0	23.5	Demirbas, 1997
Olive husk	9.2	3.6	70.3	26.1	Demirbas, 1997
Soya husk	6.3	5.1	69.6	19.0	Werther and Saenger, 2000
Sugarcane bagasse	—	11.27	—	14.95	Sami et al. 2001
Almond shell	9.7	3.36	66.9	20	Skodras et al., 2006

Table 3.14: Ultimate analyses of selected biomass fuels (wt% fuel with ash)

Fuel sample	C	H	N	S	O	Calorific	References
						value MJ/kg	
Rice husk	34.94	5.46	0.11	–	38.86	13.5	Demirbas, 2003
Switch grass	39.68	4.95	0.65	0.16	31.77	10.39	Tillman, 2000
Coffee husk	47.5	6.4	–	–	43.7	18.39	Suarez and Luengo, 2003
Corn Stover	42.5	5.04	0.75	0.18	42.6	10.7	Demirbas, 2003
Coconut shell	51.2	5.6	0.0	0.1	43.1	14.0	Werther and Saenger, 2000
Wheat straw	45.5	5.1	1.8	–	34.1	17.0	Demirbas, 1997
Olive husk	50.0	6.2	1.6	–	42.2	19.0	Demirbas, 1997
Soya husk	45.4	6.7	0.9	0.1	46.9	–	Werther and Saenger, 2000
Sugarcane bagasse	44.8	5.35	0.38	0.01	39.55	17.3	Sami et al. 2001
Almond shell	51.6	8.5	1.08	–	38.82	29.86	Skodras et al., 2006

3.8.8.1 Agricultural biomasses in Australia

In the world scale, Australia is a relatively small producer of agricultural crops. In spite of that, every year Australia exports a large amount of crops after fulfilling the demand of the local population. Australian crops production can be divided into two parts based on the period of production, namely winter crops and summer crops. Winter crops include barley, canola, chickpeas, field peas, lentils, linseed, lupins, oats, safflower, triticale and wheat, while summer crops include cottonseed, grain sorghum, corn (maize), mung beans, rice, peanuts, soybeans and sunflower (Australian Bureau of Agricultural and Resource Economics and Sciences [ABARES], 2014). Most regions in Australia are only able to produce one crop per year; however, a few areas are capable of producing two crops in the same year due to favourable soil and climate conditions (PricewaterhouseCoopers [PwC], 2012). In year 2013-14 the area and production of the winter crop in Australia was 2,245,900 ha and 44,101 kt respectively while the same for the summer crop were 113,000 ha and 3705 kt respectively (ABARES, 2014). Table 3.15 summarises the production of different crops in Australia in the years 2012-13 and 2013-14 (ABARES, 2014).

Table 3.15: Crop production of Australia

Winter Crop	2012–13 kt	2013–14 estimated kt	Summer Crop	2012–13 kt	2013–14 estimated kt
Wheat	22 856	27 013	Grain sorghum	2 230	1 107
Barley	7 472	9 545	Cottonseed	1 439	1 287
Canola	4 142	3 760	Cotton lint	1 018	910
Chickpeas	813	629	Rice (paddy)	1 161	825
Faba beans	377	328	Corn (maize)	507	335
Field peas	320	342	Soybeans	92	63
Lentils	185	254	Sunflower	44	32
Lupins	459	625			
Oats	1 121	1 326			
Triticale	171	263			

Source: ABARES, 2014

The amount of production of different crops indicates that there is plenty of agricultural waste that needs to be treated in an economic and environmentally friendly way. The major portion of agricultural waste is utilised as cattle feed and the rest is burnt and their ash used as soil fertilizer. The second option causes serious environmental damage in terms of air pollution and leaching of heavy metal into the soil. This study recommends a sustainable way to incinerate agricultural waste inside cement kilns to reduce air pollution and heavy metal emission.

3.8.9 Others

Apart from the above-mentioned wastes there are varieties of other alternative fuels which can be found in the literature. Amongst them, carpet waste (Realff, 2007; Konopa et al., 2008), automobile shredder residue (Cossua et al., 2012; Boughton, 2006), waste wood (Mackes & Lightburn, 2003), poultry litter (Hains, 2011), liquefied natural gas (Bernatik et al., 2011), fluff, textile waste, paper residue, packing boxes, livestock manure, oil soaked rags, are few to name. Unfortunately not much information regarding their usages and impacts are available and there is a need for more research to justify their candidature.

3.9 Discussion and recommendation

The usage of wastes in cement kilns is a useful alternative to landfill. However only for few wastes, like waste oil and plastic, recycling or reusing are preferred over burning in kilns. Throughout the years researchers have studied the impact of using alternative fuels on the cement quality as well as on the environment emission. This chapter summarised most of the research efforts made towards the uses of alternative fuels in recent years. Chemical composition of the alternative fuel is one of the factors which influence the cement manufacturer to choose a particular alternative fuel for their plant. Table 3.16 summarises the information regarding the proximate, ultimate and ash analysis of different alternative fuels along with the reference case coal. Those analyses are an early indicator for the performance of the alternative fuels regarding emission. For instance an alternative fuel containing more sulphur is likely to emit more SO_x during combustion. As the combustion residue of alternative fuels stays with the clinker, ash analyses of alternative fuels are important to identify any adverse effect on the clinker. Table 3.16 also summarises the energy content of different alternative fuel which will be helpful to calculate the replacement ratio over coal in terms of heating value.

3.9.1 Availability

Generally the availability of the alternative fuels is high and cement manufacturers prefer locally available alternative fuel to reduce the cost of accruing. The availability of some alternative fuels is low not because of their low production but due to the availability of other suitable disposal options for them such as recycle and reuse. In terms of availability used tyre and MSW are the best options for the cement industry as their number of production increases day by day. SPL and plastic waste also have very high production rates but not that much utilised in the cement industry as alternative fuel. Among the studied alternative fuels only the agricultural biomasses do not have a continuous supply due to the fact that a particular crop is not cultivated all year round. MBM is one of the emerging alternative fuels in the cement industry and their availability increases due to the restriction of their usage in other sectors such as cattle feed.

Table 3.16: Proximate, Ultimate and Ash analysis of different alternative fuels

Description	Coal (Kaantee et al. 2004)	Used tyre (Karell and Blumenthal, 2001)	MBM (Gulyurtlu et al. 2005)	Sewage Sludge (Ninomiya et al. 2004, Fytli and Zabaniotou, 2008)	SPL (Vick, and von Steiger 2001)	MSW Garg et al. 2009, Kikuchi 2001)	Plastic waste (Feng et al. 1996)	Waste oil (ECOFLUID*) (Prisciandaro et al. 2003)	Biomass (Rice Husk) (Demirbas ,2006, Zhang et al 1996)
Proximate Analysis									
Moisture (ar)	3.0	0.62	6.8	0.2	0.6	31.2	0.01	9.1	9.96
Ash	11.1	4.78	34.4	20.2	71.0	35.17	0.45	2.37	20.61
Volatile Matter	35.9	66.64	32.7	47.3	4.1	64.83	98.80		54.68
Fixed Carbon	53.0	27.96	26.1	32.3	24.3	--	0.74		15.02
Ultimate Analysis									
Moisture	3.0	0.62	6.8	0.2	0.6	31.2	0.01	9.1	9.96
Ash	11.1	4.78	34.4	20.2	71.0	35.17	0.45	2.37	20.61
Carbon	70.6	83.87	35.3	52.5	26.2	34.88	84.65	68.3	34.94
Hydrogen	4.3	7.09	4.9	6.4	0.3	4.65	13.71	10.5	5.46
Nitrogen	1.2	0.24	8.4	9.2	0.6	1.02	0.65	4.4	0.11
Sulfur	1.3	1.23	0.5	0.8	0.3	0.15	0.01	0.04	--
Oxygen (by difference)	11.8	2.17		31.1	1.2	23.11	0.95	4.69	38.86
Chlorine	0.07	0.149	0.26			1.02	0.03	0.6	--
Elemental Mineral Analysis (Oxide form)									
Calcium (CaO in ash)	0.18	0.378	10.6	15.5	2.6	36.6			0.55
Iron(Fe ₂ O ₃ in ash)	0.31	0.321	0.03	8.7	2.8	4.7			0.16
P (P ₂ O ₅ in ash)	0.016		6.4	24.3	<0.1	1.5			0.50
Na (Na ₂ O in ash)	0.05		0.55	0.4	26.6	1.8			1.12
Al (Al ₂ O ₃ in ash)	1.07		0.02	12.7	39.9	15.6			0.15
K (K ₂ O in ash)	0.12		0.26	9.7	0.8	1.3			3.68
Si (SiO ₂ in ash)	2.0		0.15	26.3	13.6	15.1			87.2
Mg (MgO in ash)	0.08		0.25	1.9	0.4	2.0			0.35
Lead (PbO in ash)		0.0065							
Zinc (ZnO in Ash)		1.52							
Mn (MnO)					<0.1				
V (V ₂ O ₅)					<0.1				
As (mg/kg)					8.0				
Chromium (Cr ₂ O ₃)		0.0097			<0.1				
Fluorine		0.0010							
Cadmium (mg/kg)		0.0006							
Heating value									
LHV (MJ/kg)	27.4		13.06		9.29	15.4	29-40	25.9	13.5
HHV (MJ/kg)	28.4	37.8	14.19	25.5	9.36				

*ECOFLUID: mixture of different organic waste oils

3.9.2 Substitution rate

Previous studies suggest that none of the alternative fuels solely could fulfil the entire thermal requirement of cement manufacturing, but a blend of different alternative fuels can achieve the goal. In fact most of the cement manufacturers are using varieties of alternative fuels to minimise their production costs. Cemex, UK's South Ferriby cement plant in Lincolnshire, has replaced 100% of the fuel by alternative fuel which is a blend of industrial liquid waste (paint, solvent etcetera) and Climafuel, which is made from household residue and commercial waste (Cemex, 2011). There are different opinions regarding the maximum substitution rate of different alternative fuels and they might be different from plant to plant based on the operating conditions. Literature suggests that MBM can replace 40% of fossil fuel in the kiln (Ariyaratne et al., 2010) while waste tyre and MSW can do the same up to 30% (Pipilikaki, et al., 2005; Kara, et al., 2010). By the rule of thumb, researchers suggest for a 20% substitution by any alternative fuel. In real scenario the substitution rates are even lower than that depending on the quality of the alternative fuel and operating condition of the kiln. For example due to high chlorine content, usage of SPL and sewage are restricted up to 8% and 5% respectively. Scant literatures are available to study a blend of different alternative fuel in the kiln system and none identify the optimal blending ratio. It is difficult to determine a correct proportion due to variable composition of alternative fuels which depends on the source. Extensive research is needed to draw conclusions about the perfect blend of alternative fuels.

3.9.3 Emission factor

The great concern of using alternative fuel is the environmental impact and a large amount of research works are directed toward this. It is found that four major categories of emission were targeted by the researchers which are NO_x, CO₂, SO₂ and heavy metal emission. The information regarding emission collected in this review has been summarised in Table 3.17 with some other selection criteria of alternative fuels. The emission data presented in Table 3.17 are with respect to the reference case of an only coal burning facility. It is found from the review that with very few exceptions all alternative fuels are capable to reduce the emission compared to coal. CO₂ emission from the cement industry is one of the major environmental concerns and Table 3.17 indicates that all prime alternative fuels can reduce it up to some extent. It is found from literature that used oil and spent solvent could reduce 2.02 tonne of CO₂ by replacing 1 tonne of coal in the burning zone (de Vos et al., 2007). Literature suggested that CO₂ release may decrease about 1.16kg per kg of RDF used

(Genon & Brizio, 2008). A decrease of 15%, 12% and 10% of CO₂ are also reported in the literature for plastic waste, MBM and used tyre respectively (Hashimoto et al., 2010; Gulyurtlu et al., 2005; Courtemanche and Levendis, 1998). NO_x emission is found to have similar results like CO₂ for all alternative fuel. There is a potential chance of increasing SO₂ emission for the case of used tyre, MSW and sewage sludge. There are some research gaps regarding the pollutant emission from a cement manufacturing system while using a blend of alternative fuels and further research needs to be done to maximise the usage of alternative fuel simultaneously.

3.9.4 Storage handling and installation

Form review it is found that apart from MSW and sewage sludge the installation and operating cost of alternative fuels are relatively low. The heterogeneous nature of MSW and high moisture content of sewage sludge incur more cost for sorting and drying respectively. Storage requirements are high for SPL, MSW and sewage sludge compared to the other alternative fuels. Extra caution needs to be taken for those as they might have explosion hazard (SPL) and odour problems. Used oil and spent solvent also have the potential of fire and explosion, hence additional measures need to be taken for safe storage.

3.9.5 Comparison

Used tyre and biomass could be the most attractive alternative fuels to the cement producer due to their low operational cost and high substitution rate. Solvent and used oil have the highest calorific value among the alternative fuels and they can be introduced in the burning zone without processing. On the other hand MSW, MBM and sewage sludge need to be processed to meet the requirements of the cement kiln. TDF has been widely used in the cement industry for a long period of time. Literature reports TDF usage of more than 30% of the kiln fuel may alter the chemistry of the cements and affect the hardening process adversely. From the emission standpoint, agricultural biomass could be the best option but the unavailability of a particular agricultural biomass all year round restricts their usage. The usage of SPL is restricted due to high florin content. SPL is relatively new in the cement industry as alternative fuel and its impact on the environment has not been studied comprehensively yet.

Table 3.17: Comparison of different Alternative fuels

Alternative Fuels Criteria	Used tyre	Spent linear pot	MSW	MBM	Dried Sewage Sludge	Biomass (Rice husk, wheat residue)	Plastic Waste	Used and Oils Spent Solvent
Heating value (MJ/kg)	35.6	9.29	15.4	14.47	15.28	14-21	29-40	43-45
Moisture content %	0.62	0.6	31.2	6	variable	6-12	variable	<3
Availability	High	High	High	Moderate	High	Moderate	High	Moderate
NO _x emission	Unchanged	Reduced	Reduced	Reduced	Reduced	Reduced	Unchanged	Reduced
CO ₂ emission	Reduced 10%	Reduced	Reduced -1.61kg/kg RDF	Reduced 12%	Reduced -0.88 ton/ ton coal replaced	Reduced	Reduced 15%	Reduced -2.02 ton/ton coal replaced
SO ₂ emission	Increase	ND	Increased	Reduced	Increased	Reduced	Reduced	ND
Heavy metal emission	Reduced	ND	increased	ND	Unchanged	Reduced	increased	Reduced
Maximum substitution rate (of total fuel)	30%	8%	30%	40%	5%	20%	ND	ND
Storage requirement	Moderate	High	Moderate	Moderate	High	Low	Moderate	Moderate
Effects on clinker quality	Unchanged	Unchanged	Low	Low	Low	ND	Moderate	Low
Installation cost	Low	Low	High	Moderate	High	Low	Moderate	Low

*ND: not detected

Source: Rahman et al., 2015

Availability of MSW and MBM are high and their environmental impacts are comparatively low but in contrast the processing costs are very high in the case of MBM and MSW. High moisture content is also an issue for using MBM and MSW in a large scale. Among the discussed alternative fuels, sewage sludge has the lowest calorific value but the ash derived from the sludge substitutes raw material, which is an additional advantage.

In spite of numerous researches to identify the potential benefits and barriers of using different alternative fuel, none of those studies indicate which fuel is better than the others. This is only because there are lots of criteria which need to be considered from different perspectives. Table 3.17 shows different criteria of the alternative fuels that have been discussed in this review. On the grounds of environmental, economic and social impact many other criteria can be added to this table. Table 3.17 indicates there are a few regions which are not yet revealed by the researchers.

3.9.6 Recommendation

It is really difficult to claim a particular alternative fuel to be the best amongst the discussed candidates. The reason being these are neither tailor made nor factory produced where constituent types and their quantities could be controlled. In regards to calorific values plastic waste is the best option but presence of dioxins and furans emissions pose some restrictions on their usage. Solvent and spent oil also has high calorific value and it reduces greenhouse gas emission. Still recycling and reusing of solvent and spent oil is preferred over the incineration in cement kilns. Multi-criteria analysis for decision making using AHP Fuzzy logic can be applied in accordance with the criteria given in Table 3.17 in order to identify the best alternative fuel.

The guide line to give preference to a particular alternative fuel over the others may vary depending on the region, time frame and local environmental regulations. In Australia the selection of alternative fuels may vary from state to state due to the versatility of nature and local government rules. Unfortunately Australia does not have national air emission standards. Environment protection authorities in different states set such standards. From the emission point of view, most of the alternative fuels discussed in this chapter are suitable to use in Australia. Currently the share of alternative fuel for energy production in the Australian cement industry is only 7.8%. Used tyre is dominantly used in Australia as

alternative fuel along with SPL, used oils, dewatered sludge, solvent based fuel, and some other agricultural biomass like wood chip and rice hull. From literature review it is found that MBM could be a potential candidate of alternative fuel in Australia. The Australian meat industry is well established and the slaughterhouse residue is converted to MBM and currently is being used as cattle and poultry feed. MBM could replace 40% of fossil fuel and the calcium content of MBM may also reduce the amount of raw feed. Along with that the emission factors associated with MBM combustion are comparatively low. MBM can be fed in the kiln with the existing alternative fuel insertion facility which implies low installation cost. Apart from MBM, municipal solid waste could be another potential alternative fuel in Australia as they are currently used as landfill. But the processing cost for MSW could be marginally higher than MBM.

3.10 Conclusion

In this chapter several alternative fuels have been critically reviewed and analysed on the grounds of their calorific values, advantages, disadvantages, greenhouse gas emissions and environmental impact. Among the alternative fuels, waste tyre has been studied extensively as it is used by most of the cement producers while scant literature is found regarding the usage and impact of SPL as alternative fuel. Solvent based fuel and plastic waste have higher energy content than classical fossil fuel but research on maximum substitution rates by these alternative fuels are not adequate. *Though a large amount of research works have been carried out, still there is an urge to identify the maximum usage percentage of different feasible alternative fuels.* MBM is suggested as the most suitable alternative fuel option for Australia beside the current practice. Municipal solid waste (MSW) was also found as the most easily achievable alternative fuel option in Australia. Further analyses are recommended using a multi-criteria decision making approach.

The current solid alternative fuels have been selected on the basis of their availability in the local region to ensure the regional industrial synergies. This study aims to maximise the usage of these alternative fuels in cement manufacturing without any degradation on the thermal and environmental performance of the plant. A complete methodology of research is presented in the following chapter (chapter 4).

Chapter Four

Research Methodology

4.1 Introduction

This thesis focuses on the usage of alternative fuels in the cement industry and identifies their impact on emission and clinker quality. Major objectives of this thesis have been described in section 1.3 and to fulfil those objectives the following tasks have been undertaken.

- Extensive literature review on the usage of alternative fuels in the cement plant to identify the research gaps and to set the purpose of this research based on these findings. The literature review also aids to recognise potential alternative fuel for the local region as well as for Australia.
- Identify a suitable software to accomplish the numerical work relevant to this study.
- Collect data from the regional cement plant as well as from literature to develop and validate the computational model.
- Develop a cement manufacturing process model to assess the impact of alternative fuels on the environment and clinker quality. Model development has been done in three stages namely preheater tower model, kiln model and integrated model.
- Selection of a range of alternative fuels from different categories.
- Determine the maximum substitution of alternative fuels without any adverse effect on the emission and clinker quality.
- Run the process model with a set of parameters to identify the energy performance improvement.
- Select a blend of alternative fuels which could replace entire or major portion of fossil fuel in clinker production.
- Analyse the results and make recommendations on the maximum substitution rate and mixing ratio for the blend of alternative fuels.

A flowchart of research activity is given in Figure 4.1 which clearly demonstrates the research strategy and the order of specific tasks.

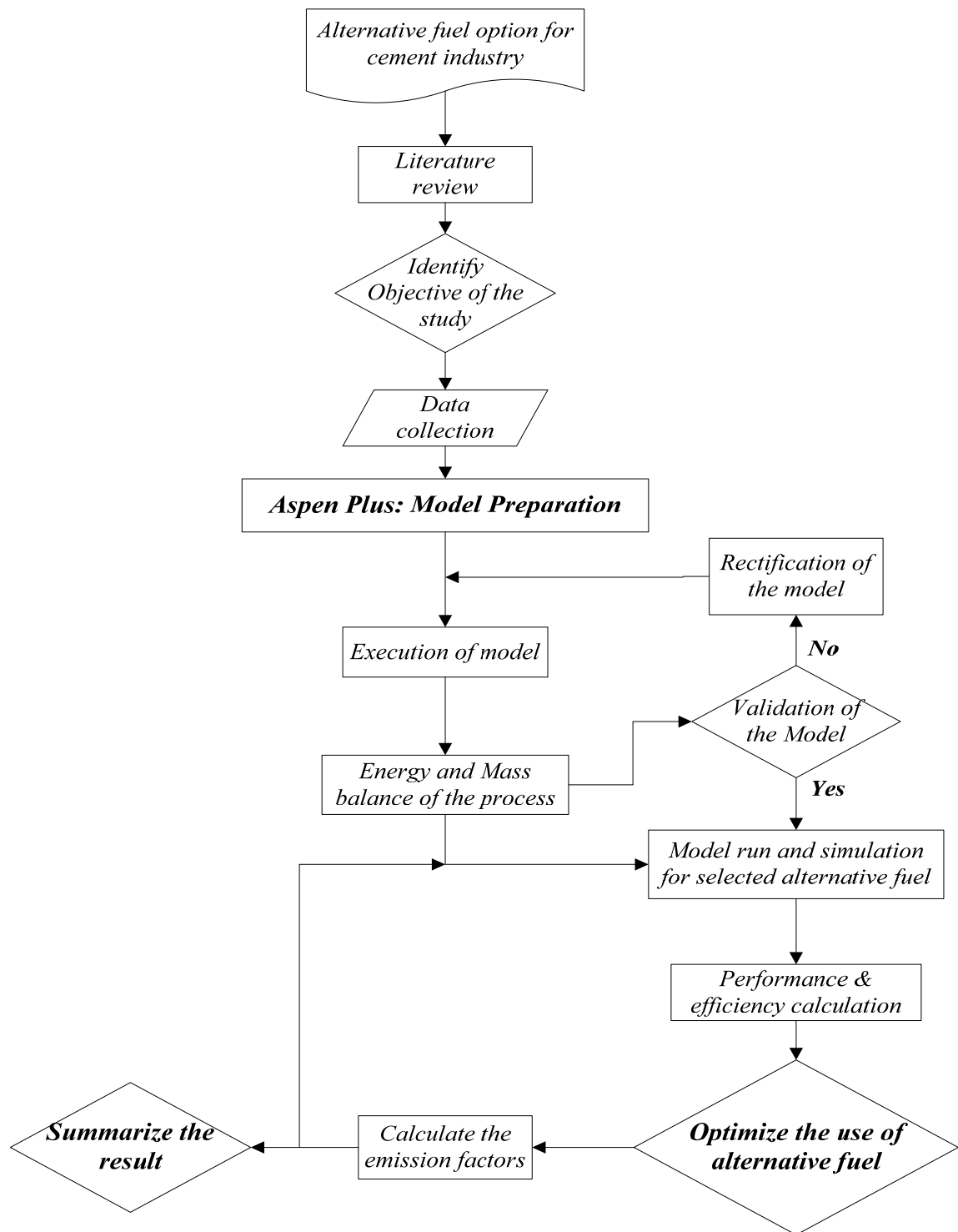


Figure 4.1: Flowchart of the research activities

In the course of selecting alternative fuel for this study, importance has been given on the local regionally based alternative fuels to facilitate availability and to minimise the transportation cost. This research focuses on solid alternative fuels and Gladstone industrial area in Queensland is taken as the region of consideration.

The outcomes of this research will be useful for the local cement plant as well as other stakeholders nationally and internationally in terms of thermal energy substitution through alternative fuels. In addition, the study helps to understand the impact of using particular alternative fuel in cement kilns. Local government will benefit from this study by legislating the usage of waste-derived alternative fuels which currently does not exist in their policy.

4.2 Synergy opportunities among the industries

A wide range of waste materials can be used as alternative fuel in a cement kiln due to the alkaline environment, long residence times at high temperatures and the intrinsic ability for clinker to absorb and lock contaminants into it. Generally waste materials with high calorific values are most suitable as alternative fuels in the cement industry but waste with low energy content and high availability can also be the same. If the wastes are available in the vicinity of the plant and can be used as alternative fuel without any processing, it implies the energy cost will be minimal. Waste from other industry can be such candidates if they are located in the same industrial region where the reference cement plant is situated. In the Gladstone region there is a unique opportunity to create a number of synergies between local industry and the regional cement plants. Corder (2008) has studied on developing local synergies in the Gladstone industrial area and suggested different alternative fuel options for the local cement industry.

Regional synergies, or waste and by-product exchanges among the industries, can make a significant contribution to sustainable development. An extensive study on the Gladstone Regional Synergies Project was carried out by Corder (2008) and an alternative fuels scheme for Cement Australia has been proposed in the report. Figure 4.2 illustrates potential and existing synergies among the industries located in Gladstone region.

Annual production of different wastes, which can be utilised as alternative fuel in the cement industry, are summarised in Table 4.1 along with the source of those wastes. Corder (2008) found that the spent cell lining (also known as spent pot lining) is the most promising waste which can be used as alternative fuel or alternative raw material. From 2004 Cement Australia started using SPL as alternative raw material on a trial basis. Currently they are using solvent based fuel as an alternative to fossil fuels. Used tyres were also employed as an alternative fuel in Cement Australia's Gladstone plant but needed to stop a few years ago due to some clinker quality concern. This research targeted some solid alternative fuels along with used tyres and SPL. This study will examine the justification of using those alternative fuels and try to maximise their usage.

Table 4.1: Synergy opportunities for cement industry in Gladstone

Synergy	Sources	By-products	Annual Amount	Receiver
Alternative fuel	Orica	Decontaminated boxes	300 tonnes	Cement Australia
	Orica	Contaminated oil and grease	0.2 tonne	
	Orica	Bags and containers	50 - 100 tonne	
	BSL	Met coke fines and dust	1381 tonnes	
	BSL	Waste tar	61 tonnes	
	BSL	Spent cell linings	13,290 tonnes	
	CAR	Oily waste	910 tonnes	
	NRG/CAR	Fabric Filters	~70 tonnes	

Source: Corder, 2005

From table 4.1 it is found that SPL has the highest annual production and the other waste productions are not adequate enough to be considered as an alternative fuel option for the cement industry. Figure 4.2 represents existing and potential synergies options in Gladstone industrial region. In Figure 4.2 a stream of calcined ash is connected from Boyne smelters to Cement Australia which is one form of SPL and used as alternative raw material. Figure 4.2 showed that tyres were used as alternative fuels, however currently they are not being used to avoid some quality issues.

Synergy opportunities in an industrial area near a cement plant is always helpful to detect the potential alternative fuels though this synergy may change over time and alternative

fuel option may alter. In the current study all the major alternative fuels in cement industry has been considered and emphasis was given on the findings of the synergy study that was conducted by Corder (2008). The simulation model presented in this study has the flexibility to incorporate any kind of solid alternative fuels and hence any change in the local synergy can be dealt with the modification of input stream. It is worth mentioning that a wide range of data regarding the composition and physical properties of the alternative fuels are required to run the model properly.

4.3 Data Collection

To carry out this research work successfully, the objective of this study needs to be addressed with a clearly defined process. This process can be split into two discrete steps: finding the required information and implementing the information in the model. The first part of this research deals with understanding that the cement manufacturing process and collection of adequate data to run a process model. An extensive literature review leads to the proper understanding of the manufacturing process along with the chemical reactions associated with the process. From the recent research work on the regional synergies, potential alternative fuels have been selected for this study. Chemical breakdowns of these alternative fuels are revealed from numerous literatures and stored for the model development.

Proximate analysis of different types of fuel is one of the most important parts to build the model correctly. These data can be found in literature and may vary on the basis of the origin of the alternative fuels. Proximate analysis consists of four constituents: fixed carbon, moisture content, volatile matter (gases emitted during the thermal decomposition of coal in an inert atmosphere) and ash (inorganic matter left after combustion). As the ash content of the alternative fuel plays an important role on the clinker quality and emission, exact measure is essential to ensure the effectiveness of the model.

In order to develop a realistic model, actual plant data is specially required. Real plant data from the regional cement industry was collected through institutional and personal communication. The model required a large range of data to be entered ranging from the composition of the fuels, the feed materials, reactions and reaction rates through to the dimension of the cyclones and kiln. As it was mentioned earlier the properties of each of

the fuels are a critical component of the model and this information should be very accurate. The majority of this information has been obtained primarily from journal articles. A baseline feed requirement along with weight percentage of different constituents must be known to model the process accurately. This feed requirement needs to be related to the output of the plant in order to allow the calculation of the effect of the different alternative fuels. Ideally this information would come from an active cement plant and will be collected from the regional cement plant.

The physical layout of the plant is required to create a model as it varies from plant to plant. As most of the plant based data was collected from the local cement plant hence the layout of the same plant is more appropriate to model. The local cement plant currently consists of a five stage double string preheater tower with an in-line calciner and two rotary kilns for cement and lime production. In addition to the physical layout of the plant, Aspen Plus required the physical dimensions of different operating blocks and those were collected from the regional cement plant. The range of collected data is very wide and consists of the following

- Chemical composition of primary fuel coal and raw meal
- Chemical composition of kiln feed which enter to the kiln from the last stage of cyclone.
- Clinker composition both in compound and ratio form and daily production rate.
- Feed rate of coal, raw meal primary and secondary air.
- Temperature and pressure at reference points
- Dimensions of the kiln and the cyclones with separation efficiency of the cyclones.
- Constituent of kiln gas and tertiary air.

Simulation results were verified against the measured data which were collected from the local cement plant. The data consisted of the constituents of raw feed, clinker and fuel (coal), temperature and pressure at reference points, mass flow rate, thermal energy requirements and other operating parameters.

To validate model air emission data was required but unfortunately due to its sensitive nature, recent air emission data was not provided by the regional plant authority. Instead they provided average air emission data from the plant which was previously published in

literature (Table 2.11). This average air emission data along with the available national air emission standard provides sufficient information to validate the process model.

The reactions which take place during cement manufacturing are critical to the success of the model. These reactions are readily available but complex in nature as the clinker is composed of different non-conventional components. The reaction kinetic and stoichiometric data is also needed to model a real world situation and those are collected from literature and included in chapter 2. The data collected from local cement plant from both the preheater tower and the kiln section along with ultimate and proximate analysis of coal are provided in the respective chapters (Chapter 5 & 6) in model validation section.

4.4 Modelling and Simulation approach

The most important part of this research work is to develop an Aspen Plus model for the cement manufacturing process according to the real plant specifications. It is required to utilise complex models for the physical–chemical property calculation of stream components and for the process unit operation design during the process design. The model is built by using software – Aspen plus V7.3 (Advanced System for Process Engineering) which includes: construction of a process flowsheet, specify the stream classes and property method, enter all required information for model run and development of Aspen FORTRAN-code sub-models for simulating the processes if required. Initially the model was run by using the primary fuel option, which is coal in this case, to validate results with collected plant data. In the later part of this study, after validation, the model was executed by using selected solid alternative fuels. Simulation results were presented graphically with analysis regarding emission and impact on the final product of the process.

Aspen Plus is powerful process engineering software. It is capable of modelling a cement plant and simulating the effects of alternative fuels. Modelling parameters, such as the choice of blocks to imitate the process stage, need to be selected carefully. It is important to note that a single operation block in real life may or may not be modelled by a single model block and in a later case a series must be used. In order to create the model correctly the process must first be thoroughly understood and broken down into its most basic components. Once the process has been understood and all stages, chemicals and reactions

have been identified the model can be created. Creating the model can be broken down to the following stages.

- Identify the major process stages
- Select model blocks to represent each stage
- Create a flow diagram for the process identifying all linking streams
- Place the required model blocks
- Make stream linkages between each block
- Set the thermodynamic and chemical properties and feed rates of each stream
- Set the properties of each block
- Define sensitivity calculations
- Run simulation, verify the results

Before construction of the model, a few basic assumptions need to be made to reduce the complexity of the model without affecting the simulation results. Throughout the thesis different segments of the process were modelled separately and finally an integrated model was presented. Hence the assumption related to the different stage modelling is described in the later part of this thesis. Still some basic assumptions which are considered for all stages of modelling are given below.

- ✓ Combustion units of the calciner and kiln are modelled by using two reactor blocks. The combustion process consists of a fuel decomposition section and a decomposed products combustion section, which are simulated respectively using reactor modules namely RYield and RGibbs.
- ✓ In preheater section, the cyclones act as separators in which also the calcination reaction takes place. This will be modelled with a series of reactors and cyclone separators (Kaantee, 2002).
- ✓ All feed materials were considered to take part in the chemical reaction.
- ✓ Only CaCO_3 and MgCO_3 of raw feed were decomposed within the calciner.
- ✓ Any pressure losses, turbulent motions, and air leakages in the system were not considered throughout the model.
- ✓ All the reactions in each section will take place with chemical equilibrium.

4.4.1 Sub stage of the simulation process

For modelling purposes the cement manufacture process was broken down into its basic stages. It is necessary to understand the operation of different stages in order to select the

correct modelling block. The major stages of this process are shown in Table 4.2. This broad overview of the process facilitates the system to split into a number of manageable subsystems. In terms of modelling, the entire process was considered in two split systems: preheater tower with calciner and kiln with cooler section. These two models were combined together to construct the integrated model which covered the entire process. To simplify the model at every stage, different sets of assumptions have been made before unit operation blocks were chosen.

Table 4.2: Preliminary process breakdown

Process	Description	Primary Function
Preheat tower	A combination of the preheater burner and the dust separation cyclones	Preheat the incoming feed material
Calciner	A combustion chamber which uses additional fuel and preheated combustion air from cooler and/or kiln exit.	Use fuel combustion heat to complete almost 95% of calcination before the raw material enters in to the kiln
Kiln	Feed material is heated and mixed in order to create the clinker	- Heat feed material to approx. 1400°C - Formation of Belite and Alite. - Large number of complex chemical reactions occurs.
Fuel burning	The burning of the coal and alternative fuels takes place in two stages of the process the kiln and the preheater raiser.	- Combustion of the fuels. - Mixing of the alternative fuels
Cooler	Quickly cools the clinker to produce the required chemical composition. Heated air then passed into the burners	- Use air to cool the clinker - Heated air is bypassed to the preheater tower

To complete the flow diagram of the entire process, predefined blocks of Aspen Plus are chosen in such a way that the chemistry in the different parts of the process can be specified as realistically as possible (for example, equilibrium or non-equilibrium reactors).

In the manufacturing process, both primary and alternative fuels are fed at two different points, at the back end of the kiln and raiser section of the calciner, at a split of 40% and

60% respectively of the entire requirement. Raw meal for cement production is fed at the top end of the preheater tower. Apart from the fuel and raw feed only the combustion air is taken to the combustion zone through an air duct and by means of an electric fan. In the cooler section ambient air is blown in the same manner to cool red hot clinker. Hot exhaust air from the cooler section is taken to the calciner and/or preheater tower to heat the raw meal and to burn fuel in the raiser of the preheater tower. Additional air may be required in the raiser to complete the fuel combustion properly. The output stream of the system is clinker from the cooler section and exhaust gas from preheater tower. Every other stream is confined and circulating within the system.

4.4.2 Selection of operation block

A number of unit operation blocks are available in Aspen plus with distinct capacity to model specific parts of the process. Choosing the correct unit operation block is the key to develop a model successfully. There are three types of reactor block in Aspen plus which are classified as their job description and they are:

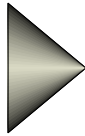
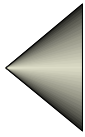
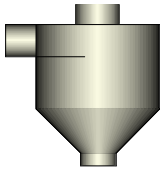
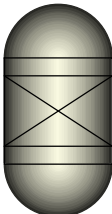
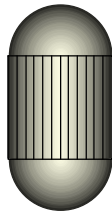
- Balance based: RYield, RStoic
- Equilibrium based: REquil, RGibbs
- Kinetics based: RCSTR, RPlug, RBatch

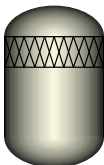
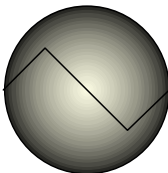
To facilitate the fuel combustion in model two of the reactor was used namely RYield and RGibbs. Fuel is decomposed by the RYield reactor based on their elemental analysis and combustion reaction is carried out by the RGibbs reactor with minimum Gibbs free energy. A real plant preheater tower, which consists of a string of cyclone, simultaneously plays two roles: separation of dust from raw meal and decomposition of carbonate of raw meal. In Aspen plus software there is a unit operation block called Cyclone, which is only suitable for dust separation and no chemical reaction occurs within the block. Hence to imitate the real life cyclone an additional reactor block is considered for modelling purposes.

Crafting a kiln model with Aspen plus was most challenging as complex reactions occur in this stage for clinker formation. To facilitate a clear understanding of the model, an entire kiln was modelled by using a series of RStoic reactors since the reaction stoichiometric is well known. This series of reactors also assists to divide clinkerization reactions based on the temperature range. For the cooler section, MHeatX block was used as it allows the heat transfer between hot and cold streams which are clinker and air at ambient temperature respectively for the current case. Apart from the aforementioned blocks, a few others were

used to mix different, separate streams. Table 4.3 summarises all unit operation blocks which were used to model the different stages of the process.

Table 4.3: Aspen plus operation blocks

Aspen operation blocks	Description	Used in model
 Mixer	✓ Mixes the incoming streams into a single stream. ✓ No reactions take place	✓ Used to mix all the outgoing gaseous stream.
 FSplit	✓ Splits the incoming stream by sub stream, percentage of total flow or both. ✓ Reactions do not take place	✓ Used where flows need to be split. ✓ Separate ash from decomposed fuel
 Cyclone	✓ Able to calculate the separation of particles from a gas stream ✓ Requires the dimensions of the cyclone ✓ Works on the particle size distribution of the incoming stream	• Used to Model the cyclones in preheater tower. • The particle size distributions of the outlet solids streams can be determined.
 RYield	✓ Requires mass balance only. Reaction stoichiometry is unknown or unimportant. ✓ Yield distribution needs to be known. Hence only need to know outlet products and the total mass of the input ✓ Phase is not considered	✓ Simulating decomposition of fuels into components for reaction (components and energy output). ✓ Used in fuel burning stage along with RGibbs reactor.
 RGibbs	✓ Reaction stoichiometry is not required. ✓ Uses Gibbs free energy used to determine lowest energy products. ✓ Only block capable of dealing with three phases of equilibrium	✓ Used to calculate the chemical equilibrium between any number of conventional solid components and the fluid phases. ✓ Used for combustion of fuel and thermal energy generation.

 RStoic	✓ RStoic can model reactions occurring simultaneously or sequentially. ✓ Reaction kinetics is not required. ✓ Stoichiometry and the molar extent or conversion need to be known for each reaction	✓ Used to model the kiln where several chemical reactions occur. ✓ It can also be used to calculate the heat of reaction.
 Separator	✓ Performs vapour-liquid or vapour-liquid-liquid equilibrium calculations. ✓ It can determine the thermal and phase conditions of a mixture of one or more inlet streams.	✓ Used to separate clinker and kiln gas from the outlet stream of kiln section. ✓ Also used to separate clinker after the cooling stage.
 MHeatX	✓ Can be used to represent heat transfer between multiple hot and cold streams. ✓ MHeatX ensures an overall energy balance but does not account for the exchanger geometry. ✓ Thermodynamic condition of a stream can be set.	✓ Used in clinker cooling stage by using cool ambient air.

4.4.3 Selection of stream class

Different stream classes are available in Aspen plus to enable different types of components to be transferred from one unit operation block to another. There are three stream classes available in Aspen Plus, namely, material, heat and work streams. Material streams are used to define chemical composition, thermodynamic condition and flow rates of each feed stream. The heat streams are used to transfer heat from one process unit to another and work streams exchange power between two blocks. Three basic substream classes exist in Aspen plus and a new stream class can be defined with their combination with an optional particle size distribution (PSD) specification. Basic stream classes are described in Table 4.4.

For current study a combination of these three streams is considered and the stream class is called MCINCPD which includes MIXED, CISOLID and NC streams with PSD option. All fuels are considered as nonconventional and raw meal are composed of conventional component.

Table 4.4: Material stream class

▪ Mixed	Used to handle conventional components that reach vapor-liquid-solid phase equilibrium
▪ CISOLID (Conventional Inert Solid)	Used to handle conventional components that appear in the solid phase but do not participate in phase equilibrium
▪ NC (Nonconventional)	Used to handle nonconventional components

4.4.4 Component specification

In the actual cement manufacturing process, several chemical components take part in the reactions and considering all the components is beyond the scope of this study. Only the major chemical compounds and reactions are considered for this study. All the components considered for the model need to be specified before construction of the process model. A list of components and their types considered in this study are given in Table 4.5. Along with coal and ash all the alternative fuels are considered non-conventional (NC).

Table 4.5: List of component used in the model

Component ID	Type	Component ID	Type	Component ID	Type
H ₂ O	CONV	CaO*Fe ₂ O ₃	SOLID	Mg	SOLID
NO ₂	CONV	C ₃ S	SOLID	K	SOLID
NO	CONV	C ₃ A	SOLID	Na	SOLID
S	CONV	C ₂ S	SOLID	F	SOLID
SO ₂	CONV	C ₄ AF	SOLID	SiO ₂	SOLID
SO ₃	CONV	Al ₂ Si ₂ O ₇ *2H ₂ O	SOLID	Al ₂ O ₃	SOLID
H ₂	CONV	MgCO ₃ *3H ₂ O	SOLID	CaO	SOLID
Cl ₂	CONV	CaO*Al ₂ O ₃	SOLID	MgO	SOLID
HCl	CONV	C	SOLID	K ₂ O	SOLID
CO ₂	CONV	COAL	NC	Na ₂ O	SOLID
O ₂	CONV	ASH	NC	Fe ₂ O ₃	SOLID
N ₂	CONV	Si	SOLID	TiO ₂	SOLID
CO	CONV	Al	SOLID	P ₂ O ₅	SOLID
(CaO) ₃ *Al ₂ O ₃	CONV	Fe	SOLID	CaCO ₃	SOLID
(CaO) ₃ *Al ₂ O ₃ *6H ₂ O	SOLID	Ca	SOLID	ZnO	SOLID

4.4.5 Selection of property method

In Aspen plus a property method is a collection of property calculation routes which are needed by unit operation models to execute their operation properly. Property method is used to calculate thermodynamic properties and relevant thermodynamic properties are:

- Fugacity coefficient (or equivalent: chemical potential, K-value)
- Enthalpy
- Entropy
- Gibbs energy
- Volume

It is important to choose the right property method for an application to ensure the accurate property calculation. There are ten different classes of property methods available in Aspen plus and each class contains a set of specific property methods for different processes. A list of recommended property methods can be found in Aspen user guide (Aspen, 2000). Table 4.6 presents the recommended property method for coal processing.

Table 4.6: property method for coal processing

Coal Processing	
Application	Recommended Property Methods
Size reduction crushing, grinding	SOLIDS
Separation and cleaning sieving, cyclones, precipitation, washing	SOLIDS
Combustion	PR-BM, RKS-BM (combustion databank)

As all the fuels for cement manufacturing are considered to be nonconventional, property methods for nonconventional components need to be specified. The properties calculated for nonconventional components are enthalpy and density. Table 4.7 lists the available model in Aspen plus. Detailed descriptions are available in Aspen physical property system guide (Aspen, 2001).

Table 4.7: Property model for nonconventional component

Property Model	Attribute	Requirements
<i>General Model</i>		
ENTHALPY	ENTHGEN	GENANAL
DENSITY	DNSTYGEN	GENANAL
<i>Coal and coal derive material</i>		
ENTHALPY	HCOALGEN HCJ1BOIE HCOAL-R8 HBOIE-R8	ULTANAL, PROXANAL, SULFANAL
DENSITY	DCOALIGT DCHARIGT	ULTANAL, SULFANAL

For the current study, a property method has been chosen according to the guideline provided in Aspen plus user manual. IDEAL, SOLIDS and RKS-BM are three property methods which were used in this study to model different segments of the cement manufacturing process. For nonconventional elements, which include coal and alternative fuel, HCOALGEN and DCOALIGT attribute are selected for enthalpy and density calculation.

HCOALGEN model includes a number of different correlations for the following:

- Heat of combustion
- Heat of formation
- Heat capacity

Any one of these three correlation can be used in the model depending on the condition and available data. Heat of combustion calculate the gross and net calorific value, which is already available in collected plant data. Heat of formation correlation is based on the assumption that combustion results in complete oxidation of all elements except sulphatic sulphur and ash, which are considered inert. The numerical coefficients are combinations of stoichiometric coefficients and heat of formation for CO₂, HO₂, HCl and NO₂ at 298.15°K and given by

$$\Delta_f h_i^d = \Delta_c h_i^d - [1.418 \times 10^6 w_{H,i}^d + 3.278 \times 10^5 w_{C,i}^d + 9.264 \times 10^4 w_{S,i}^d - 2.418 \times 10^6 w_{N,i}^d - 1.426 \times 10^4 w_{Cl,i}^d] 10^2 \dots\dots\dots(4.1)$$

where $\Delta_c h$ is the specific heat of combustion and $\Delta_f h$ stands for specific heat of formation.

In heat capacity correlation nonconventional component are considered to be a mixture of moisture, ash, fixed carbon, and primary and secondary volatile matter. Primary volatile

matter is any volatile matter equal to the total volatile matter content, up to 10%. The correlation developed by Kirov treats the heat capacity as a weighted sum of the heat capacities of the constituents:

$$C_{p,i}^d = \sum_{j=1}^{ncn} w_j C_{p,ij} \dots \dots \dots (4.2)$$

$$C_{p,ij} = a_{i,j1} + a_{i,j2}T + a_{i,j3}T^2 + a_{i,j4}T^3 \dots \dots \dots (4.3)$$

Where i = component index, j =constituent index, 1= moisture, 2=fixed carbon, 3= primary volatile matter, 4= secondary volatile matter, 5=ash and w_j =mass fraction of j th constituent on dry basis.

The DCOALIGT model gives the true density of nonconventional component on a dry basis by using ultimate and sulphur analyses. Formulations are given by

$$\rho_i = \frac{\rho_i^{dm}}{\left[\rho_i^{dm} (0.42 w_{A,i}^d - 0.15 w_{Sp,i}^d) + 1 - 1.13 w_{A,i}^d - 0.5475 w_{Sp,i}^d \right]} \dots \dots \dots (4.4)$$

$$\text{where } \rho_i^{dm} = \frac{1}{a_{1i} + a_{2i} w_{H,i}^{dm} + a_{3i} (w_{H,i}^{dm})^2 + a_{4i} (w_{H,i}^{dm})^3} \dots \dots \dots (4.5)$$

$$\text{and } w_{H,i}^{dm} = \frac{10^2 (w_{H,i}^d - 0.013 w_{A,i}^d + 0.02 w_{Sp,i}^d)}{(1 - 1.13 w_{A,i}^d + 0.02 w_{Sp,i}^d)} \dots \dots \dots (4.6)$$

It was required to specify all the options discussed in this section to construct a model successfully. Detail description of the model for preheater tower and kiln section are given in following chapters, i.e. Chapter 5 and 6 respectively.

4.4.6 Energy and Mass Balance

Process simulation with Aspen plus allows to predict the behaviour of a process using basic engineering relationships such as mass and energy balances. Aspen plus performs a mass balance check around each block as it is executed at the end of the simulation. A default relative tolerance of 0.0001 was set for mass balance checking. Imbalances can occur for numerous reasons such as improper stoichiometry or yield fraction specifications, inconsistent user kinetic rates, etcetera. Mass balance checking will point out these imbalances and in many cases provide the reason for the imbalance. If reaction stoichiometry is known, Aspen plus checks the mass-balance of stoichiometry based on the stoichiometric coefficient and molecular weight of the components. The mass balance can be specified for blocks or for streams. The mass balance equations can be any one of these:

- Overall mass balance, for which components, component groups, or sub-streams need not to be specified.
- Mass balance for sub-streams.
- Component balances.

Aspen Plus provides energy balances and convergence calculations by default. The only available option for energy balance in Aspen Plus is the overall energy balance. As the current model involves lots of chemical reactions of solids, enthalpy data is required for energy balance calculation. Ultimate and Proximate analyses of all types of nonconventional solids are also required to ensure an unaffected energy balance calculation.

In this study both mass and energy balance was considered after setting all essential parameters to simulate the result. Mass and energy balance is a good indicator of the accuracy of the model, hence calculating this is one of the major parts of this study.

4.5 Report option

This thesis presents a computational model for the cement manufacturing process which is capable of predicting pollutant emission and possible changes in clinker quality due to the introduction of solid alternative fuel in the system. Results obtained from simulation are available in a report file and can be exported directly to an Excel worksheet. Report options are available for flowsheet, block and for the stream. The sensitivity analysis option of Aspen Plus allows to plot the variation in any output parameter due to the changes in input parameter for a selected range. Alternatively results can be exported to Excel file to plot them to visualise the outcomes. For the current study, the second option is preferred as it allows to combine data for a set of alternative fuel. Results obtained from this study were presented graphically to identify and compare potential changes in emission and clinker quality.

4.5.1 Setup for emission results

Pollutant emission from the cement process is widespread and reporting all possible emissions is way beyond the scope of this study. Only four types of air emission is considered for this study which are CO₂, NO_x, SO₂ and CO. Emission standards for these pollutants are set according to the available local standard and baseline practice by the

regional cement plant. The thermal substitution rate by any alternative fuels is controlled by the emission standard. The maximum substitution rate of a single alternative fuel is also determined by measuring pollutant emission. Based on the emission results alternative fuels are suggested or rejected for the regional cement plant.

4.5.2 Quality control of clinker

An important part of the current study is to ensure the quality of the clinker while alternative fuel is burnt to generate the energy for the process. Cement manufacturing is a closed type process and all combustion residue is confined within the kiln and mixed with the clinker. Hence there is a possibility that alternative fuel may change the clinker composition and that might affect the binding quality of clinker.

In the cement industry three basic ratios are used to identify the quality of the clinker and these are lime saturation factor (LSF), silica ratio (SR) and alumina ratio (AR).

4.5.2.1 Lime saturation factor (LSF)

Lime Saturation factor is a ratio of CaO to the other three main oxides and the formula for the case of MgO<2% is given by (Aldieb & Ibrahim, 2010, Taylor 2004),

$$LSF = \frac{100(CaO + 0.7MgO)}{2.8SiO_2 + 1.2Al_2O_3 + 6.5Fe_2O_3} \quad (4.7)$$

where CaO, MgO, SiO₂, Al₂O₃ and Fe₂O₃ are all expressed in weight percentage.

The LSF is proportional to the ratio of Alite to Belite in the clinker and indicates the amount of unacceptable free lime present in the clinker. The typical values of LSF for modern clinkers are 92%-98% (Taylor, 2004). Theoretically free lime will exist in the clinker if LSF is more than 100% but practically mixing of raw materials is never perfect and residual free lime exists in clinker even when the LSF is considerably below 100%.

4.5.2.2 Silica ratio (SR)

Silica ratio (also known as the Silica Modulus) governs the proportion of silicate phase in the clinker and is defined by,

$$SR = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \quad (4.8)$$

Silica ratio (SR) is related with the liquid phase of the clinker at high temperature and controls the burnability of the clinker. For Portland cement SR ranges from 2.0 to 3.0 (Taylor, 2004).

4.5.2.3 Alumina ratio

Alumina ratio (AR) is defined as the ratio of aluminate to ferrite phase and determines the quantity of liquid formed at low temperature. The formula for AR is given by:

$$AR = \frac{Al_2O_3}{Fe_2O_3} \quad (4.9)$$

A high alumina ratio together with a low silica ratio could result in a fast setting property of the cement which needs to be controlled by adding higher amounts of gypsum. The value of AR between 1.0 and 4.0 is suitable for Portland cement.

Apart from these three ratios another one known as Hydraulic modulus (HM) is often used for chemical analysis of clinker which is defined by,

$$HM = \frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3} \quad (4.10)$$

If the value of HM is too high, additional heat will be required to burn clinker. Consequently, the initial strength and heat of hydration increases and the resistance to chemical attack decreases. HM value of less than 1.7 implies insufficient strength and over 2.3 results poor stability of volume. To assess the clinker quality while alternative fuels are in operation, the aforementioned ratio was calculated and any scenario where these ratios fail to lie within the accepted range was rejected.

4.6 Analysis for Coal

It was mentioned in section 4.3 that chemical analysis of primary fuel, coal was collected from local cement plant. There is a possibility that the coal quality of the plant may not be same as the other cement plants and coal quarry. In this section a simple coal combustion model was developed by Aspen plus to identify the impacts on the output due to the change of coal quality. Apart from that a sensitivity analysis is executed to visualise the effect of some input parameter like moisture content and heating value.

4.6.1 Scenario analysis of coal

Australia has a range of energy sources and among them coal is the largest. The largest share of recoverable black coal are contained in Queensland (56 per cent) and New South Wales (40 per cent). About 70 per cent of Australia's black coal are located in the Sydney and Bowen basins (ABARE 2010). Apart from those two basins, major coal basins for black coal are Gunnedah, Tarong, Clarence Moreton, Surat and Galilee which are situated in Queensland, and New South Wales. Figure 4.3 indicates the black coal resources in Australia and the location of different basin.

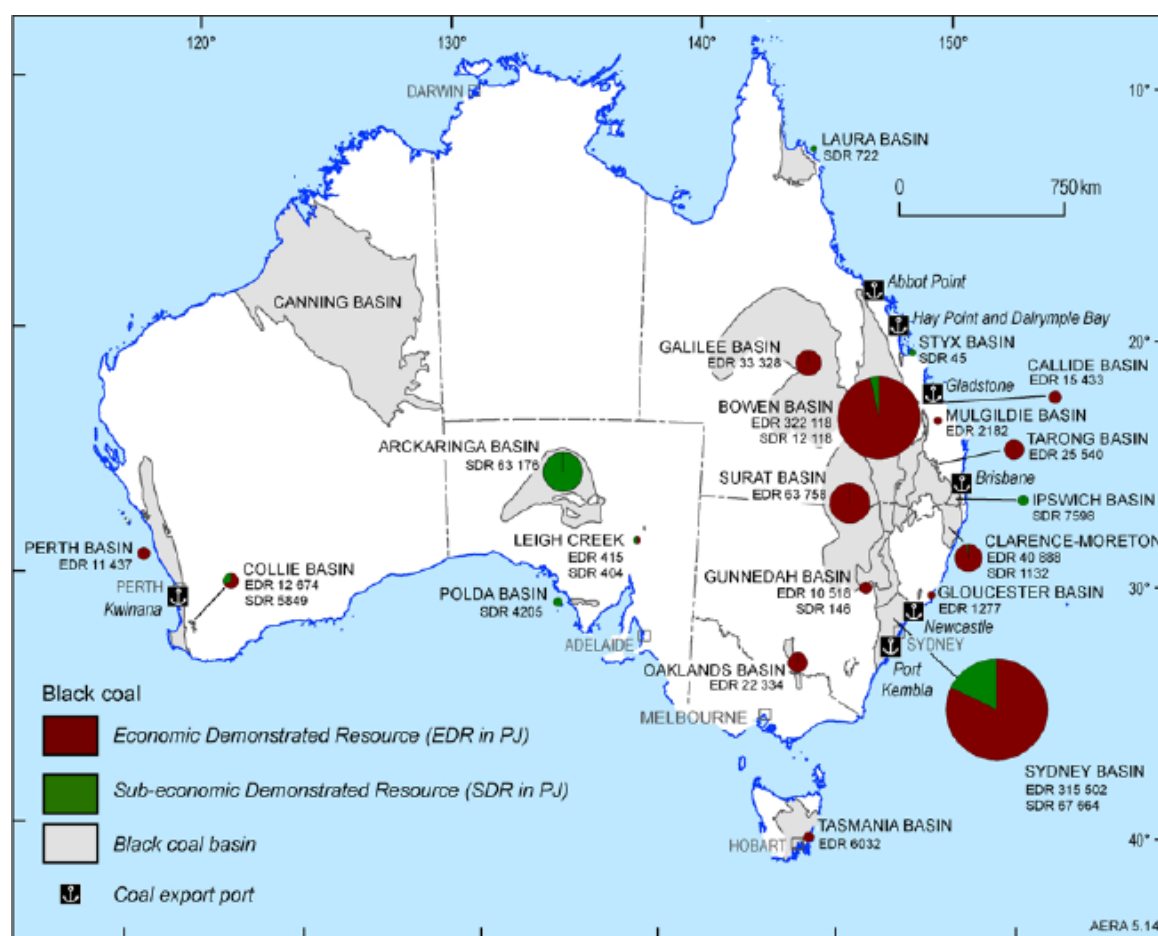


Figure 4.3: Australian black coal resources (ABARE 2010)

As coal is the primary fuel for cement industry and responsible for pollutant emission, the source point of the coal need to be taken into consideration for any environmental impact assessment. The composition and heating value of coal varies from basin to basin and hence the coal requirement and amount of pollutant emission may not be same for coal acquired from different sources. In the current study local plant data including the composition of

coal were considered to develop a process model for cement manufacturing. In this section a scenario analysis was carried out for coal from different basins and compared with the results obtained from plant data. A simple coal combustion model was developed to identify the variation that may occur due to the different sources of coal. For this section, coal from eight different basins of QLD and NSW were considered along with the reference plant data to measure the difference that may occur in output results. Selected basins are Bowen Basin (BB), Callide district Basin (CB), Tarong Basin (TB), Clarence-Moreton Basin (CMB), Surat Basin (SB), Gunnedah Basin (GB), Sydney Basin Hunter coalfield (SBH) and Sydney Basin Newcastle coalfield (SBNC) and all data is collected from renowned book ‘Handbook of Australian Black Coal’ by M.B. Huleatt (Australian Government Publishing service, 1991). Selected basins produce almost 90% of black coal from Queensland and New South Wales region. Table 4.8 shows the elemental analysis of the coal from selected basins.

Table 4.8: elemental analysis of coal from different source

	Plant Data	BB	CB	TB	CMB	SB	GB	SBH	SBNC
Proximate analysis									
Ash	18.55	14.69	18.41	29.57	16.41	18.03	12.52	8.76	15.38
Fixed Carbon (FC)	57.3	64.84	53.98	41.39	52.82	41.04	54.35	55.67	50.77
Volatile Matter (VM)	24.15	20.47	27.61	29.04	30.77	40.93	33.13	35.57	33.85
Moisture	1.35	1.3	10.9	5.3	2.2	5.7	3.4	3	2.5
Ultimate analysis									
Ash	18.55	14.69	18.41	29.57	16.41	18.03	12.52	8.76	15.38
C	69.13	74.73	63.69	56.696	70.29	64.346	72.87	75.73	70.403
H	3.79	4.18	3.19	3.732	4.597	5.246	4.46	5.119	4.662
N	1.51	1.53	0.94	1.056	1.27	1.393	1.575	1.596	1.793
Cl	0	0.03	0.02	0.002	0.002	0.001	0.001	0.003	0.003
S	0.36	1.19	0.18	0.282	0.267	0.656	0.525	0.92	1.286
O	6.66	3.65	13.57	8.662	7.164	10.328	8.049	7.872	6.473
Heating value MJ/kg	27.4	30.57	21.74	22.95	28.05	26.28	28.72	30.56	28.05

It can be observed from the table that the composition of coal can be drastically changed based on its source. Throughout the thesis only the data from local cement plant was considered, hence this section highlighted the capability of Aspen plus to handle any changes in coal composition and demonstrate the expected changes in the outcomes.

4.6.2 Coal combustion model

To study the scenario analysis for coal from different sources a coal combustion model was developed in this section. The model basically consisted of two reactor namely DECOMP (Ryield) and BRNKiLN (RGibbs) along with a separator to separate solid and gaseous output. Dry coal directly carried to the Ryield reactor where the coal was decomposed in accordance to its elemental analysis. A huge amount of heat was generated in this decomposition process which was carried in to the combustion reactor RGibbs with the decomposed coal. Combustion air was supplied in the burning zone with a separate stream and combustion occurred in the RGibbs reactor to produce the ash and gaseous product. To ensure the complete combustion was occurred, stoichiometric air is supplied in the system for every scenario. Separator block was used to separate gas stream and solid stream which was only ash for the present case. For the model run different operating parameters were specified in the input stream including flow rate, pressure and temperature. The output results consisted of the gaseous emission, ash generation, temperature and pressure. This was a sample model from Aspen Plus user manual ‘Getting Started Modeling Processes with Solids’ (2010).

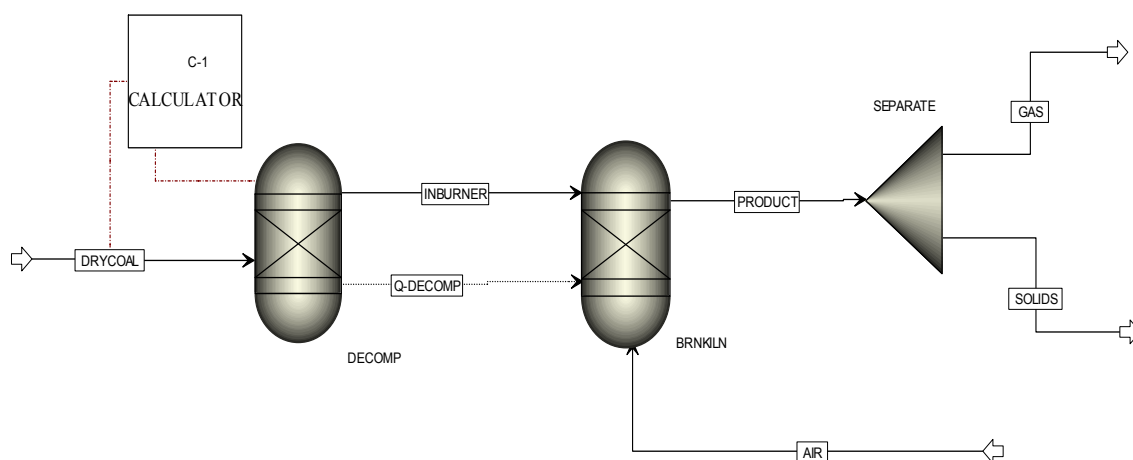


Figure 4.4: Coal combustion model

For the current section a constant flow rate of 4000 kg/hr of coal was used for different scenario. Flow rate of air was varied with the stoichiometric air needed which was calculated based on the elemental analysis. Air emission results and the outlet temperature of output stream were presented in graphical form for analysis.

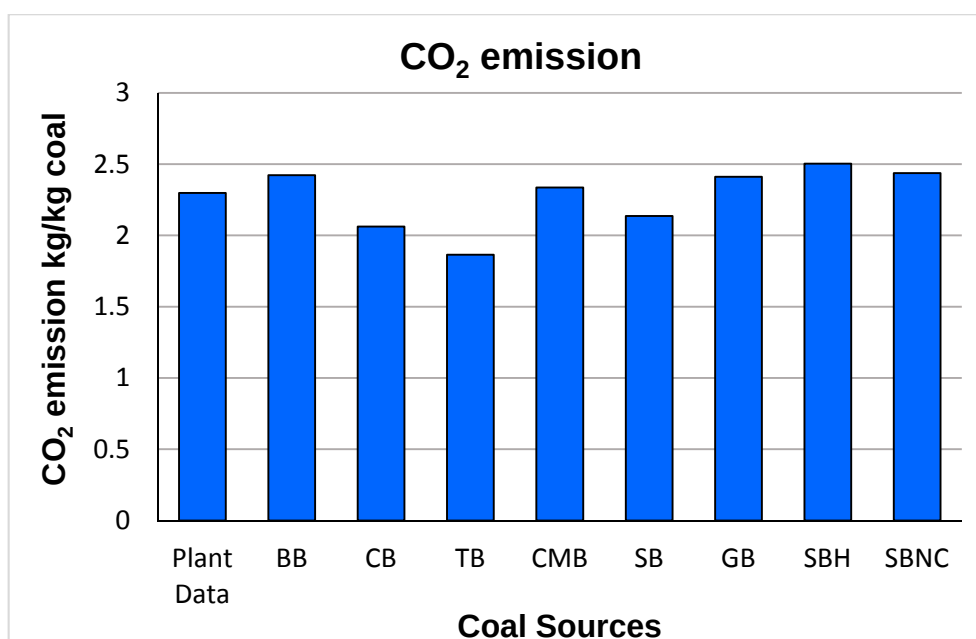


Figure 4.5: CO₂ emission from coal combustion

CO₂ emission from coal combustion depends on the amount of carbon in the coal and the degree of combustion. As the model was prepared to allow stoichiometric air in the system it should ascertain the maximum CO₂ production. Figure 4.5 indicated the amount of CO₂ produced by burning 1kg of coal from different sources. The figure indicated that the coal from Tarong basin (TB) generates lowest amount of CO₂ which was expected as the carbon content was only 56.696 (Table 4.8). All the other coals from different sources generated about 2 kg to 2.5 kg of CO₂. While the coal from the plant was expected to produce about 2.3 kg of CO₂ per kg of coal which was very much representative to the coal of Australia irrespective to its source.

Several variables are involved regarding the NO_x emission from coal combustion including the quality of coal, feed rate, combustion air and the temperature in the burning zone (Walters et al., 1999). NO_x emission is comparatively lower than CO₂ emission and figure 4.6 indicated the amount of NO_x emission during the model run, which was burning 4000 kg of coal per hour. Interestingly the coal from the Bowen basin generated more NO_x than others though the amount of Nitrogen in the coal analysis was not the highest. The other factors such as temperature and excess air in the burning zone played decisive role in NO_x emission. The coal from cement plant generated about 120 kg of NO_x per hour where the average emission from the samples used in the model was 130 kg per hour.

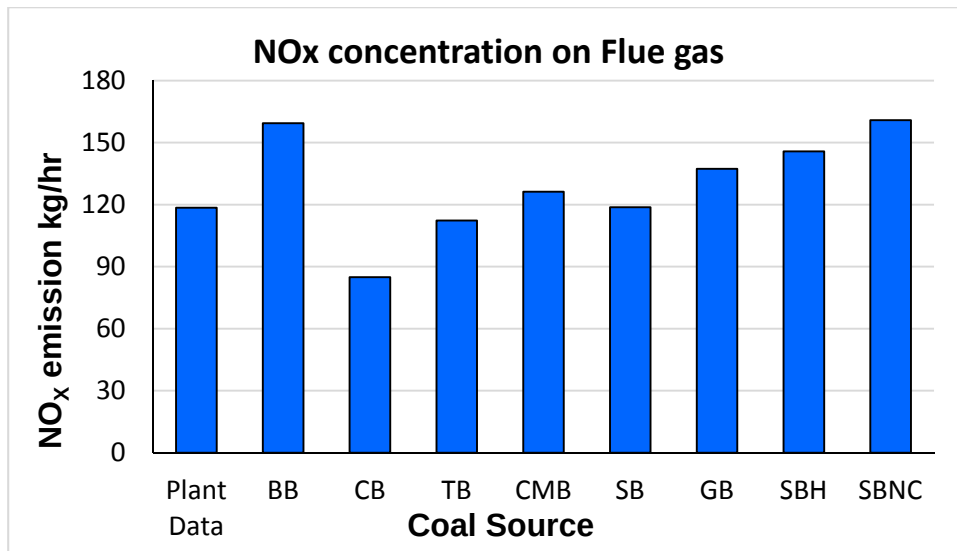


Figure 4.6: NO_x emission from 4000 kg/hr coal combustion

It is always difficult to measure the exact temperature in the burning zone due to the intense condition. However, the outlet temperature provides a good indication of the condition of the burning zone. The heating value of the fuels are the main decisive factor for heat generation and raise of temperature. Figure 4.7 indicated the outlet temperatures during burning coal from different sources. The measure of heating value of coals were also included in the figure as secondary vertical axis to point out the correlations between heating value and outlet temperature.

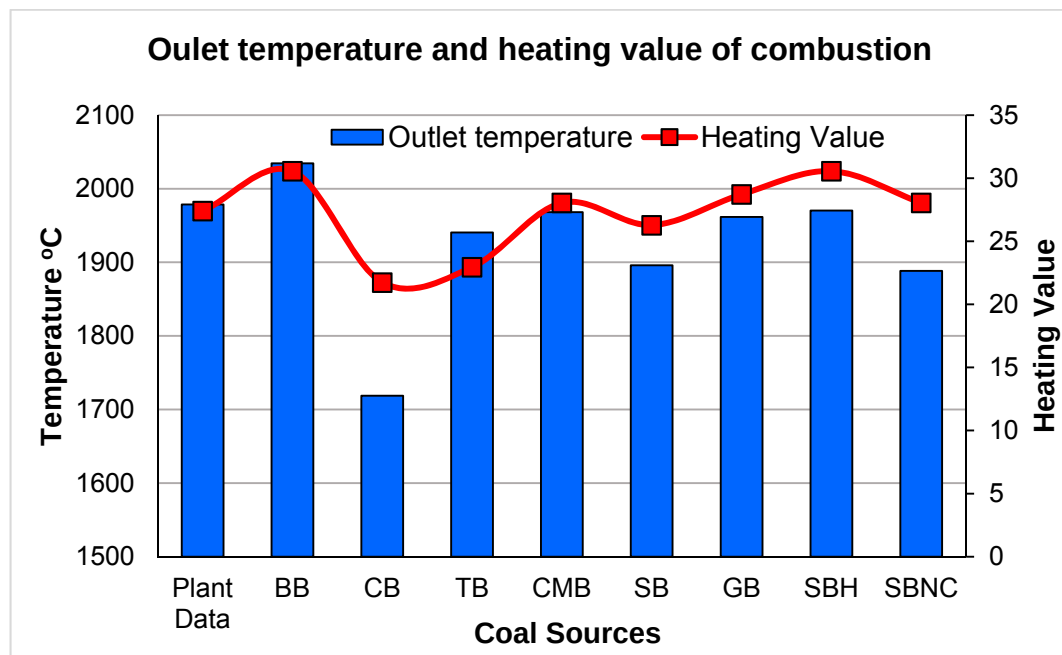


Figure 4.7: Heating value and outlet temperature from combustion of coal from different source.

It was found the coal from the Bowen basin possess highest heating value and consequently the outlet temperature was maximum among the samples. This high temperature for the case of Bowen basin coal also justified the higher NO_x emission that was reported in Figure 4.6. One interesting observation was that the coal from Callide district Basin (CB) generated less temperature though its heating value was not that low. This implied that there was other parameter which affect the outlet temperature and in this case it was the moisture content which was 10.9 wt% for Callide district basin coal.

To get a better picture of the influence of heating value and moisture content on the outlet temperature two scatter plots were presented in Figure 4.8 (a) and (b) to illustrate the correlation. Also the standard correlation coefficient was calculated and which were +0.761 for heating value & temperature and -0.906 for moisture content & temperature.

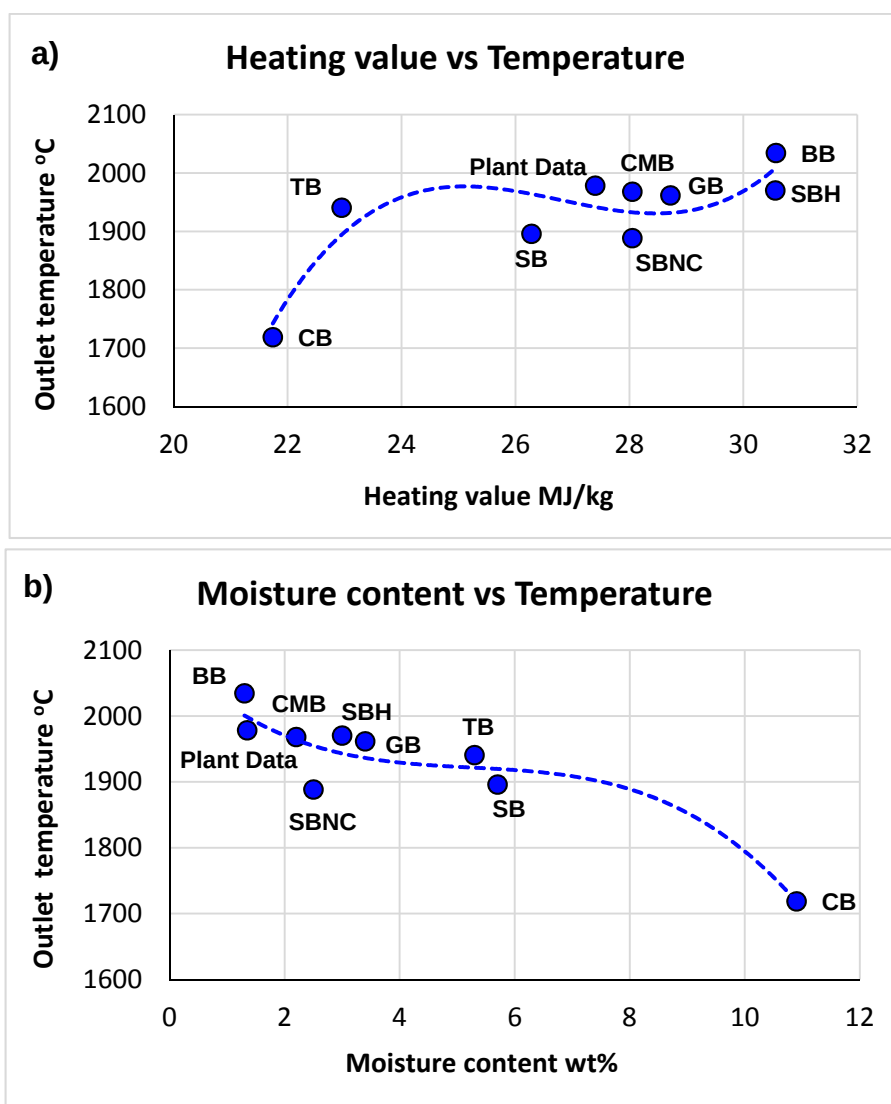


Figure 4.8: a) Correlation between heating value and outlet temperature, b) correlation between moisture content and outlet temperature

Figure 4.8(a) showed that outlet temperature was strongly correlated with the heating value and to get a steady temperature the heating value needed to be in between 26 to 29 MJ/kg. The coal specimen from plant had the heating value 27.4 MJ/kg which was perfect for this study. On the other hand Figure 4.8 (b) indicated that moisture content of the coal affect the temperature hugely as heat was needed to convert those moisture into steam. This was to be mentioned that all the moisture content considered here is after air drying the coal sample. To analyse the effect of moisture content and heating value a detailed sensitivity analysis was presented in next section.

The results presented in this section by using a simple coal combustion model shows that the selected software Aspen Plus is capable to handle the variation of the coal analysis and any sample of coal can be used in the model irrespective to its source provided the elemental analysis is known. This analysis also reveals that the coal data collected from the plant are very much representative to the black coal of Australia.

4.7 Sensitivity analysis of coal combustion

In section 4.6 a details scenario analysis was done with sample of coal from different sources where it was revealed that some parameters involve in coal analysis and combustion environment can affect the combustion outcome. In this section a sensitivity analysis is carried out with the coal sample collected from local plant to identify the effect of some decisive parameter such as amount of air in the combustion zone, moisture content and heating value of coal. The coal combustion model describe in the section 4.6 is used for sensitivity analysis and Aspen built-in sensitivity analysis tools are used to visualize the outcomes. For the sensitivity analysis a mass flow of 4000 kg/hr of coal is considered and stoichiometric air needed for combustion is calculated by using the ultimate analysis.

Air in the combustion zone is the most important factor as it contain the oxygen which is essential for burning and it is always suggested that a little excess air than the theoretical air required ensure the complete combustion. The stoichiometric air fuel ratio for the sample coal of cement plat is approximately 9.037 and hence about 36000 kg of air per hour is theoretically required for the current model. By using the sensitivity analysis tool in the Aspen plus model variable amount of air is feed in the burning zone with in the range

5000 kg to 5500 kg. The variation of outlet stream in terms of temperature, CO₂, CO and NO_x emission are plotted in figures 4.9-4.11. Figure 4.9 indicate that the maximum temperature of outlet attain when about 36000 kg of air is feed. The temperature drops down on the both side of that point which is expected.

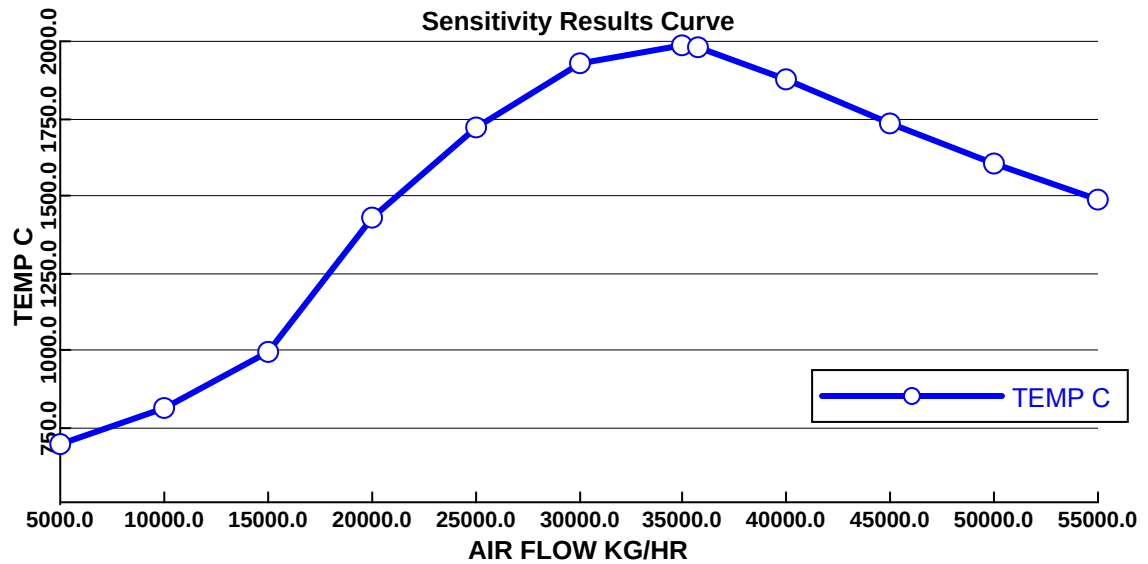


Figure 4.9: Variation of temperature with air flow in the burning zone

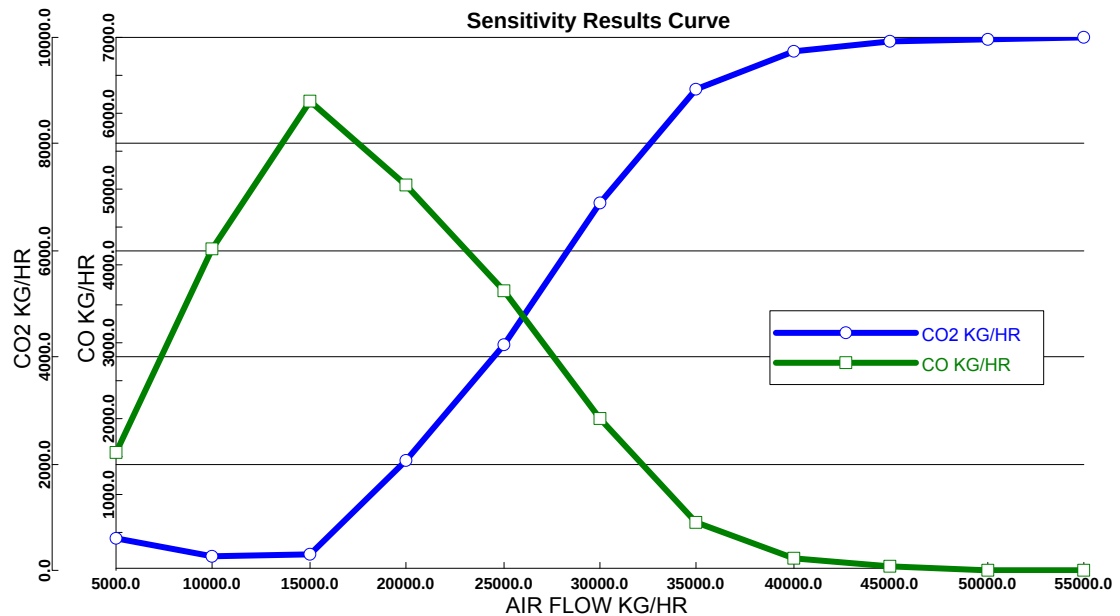


Figure 4.10: Changes in CO₂ and CO emission with air flow

Insufficient air may leads to more CO emission than CO₂ as not much O₂ are available for the conversion of CO₂ from CO. This trend is visible in figure 4.10 and it is found that the emission of CO₂ and CO become stable when the air flow is about 40000 kg per hour which is little bit higher than the stoichiometric air. This results point out that about 10% of excess air in the burning zone will ensure the complete conversion of CO into CO₂.

NO_x emission from coal combustion is more dependent with the temperature rather than the amount of N₂ in the combustion zone. However, the temperature is dependent with the air flow as it is illustrated in figure 4.9. Figure 4.11 shows that the NO_x emission reaches to its maximum when air flow is between 40000 kg/hr and 45000 kg/hr where temperature is very high (figure 4.9). This figure also justify the choice of 10% excess air in the combustion zone for our rest of the study which will eventually allow to examine the worst case scenario.

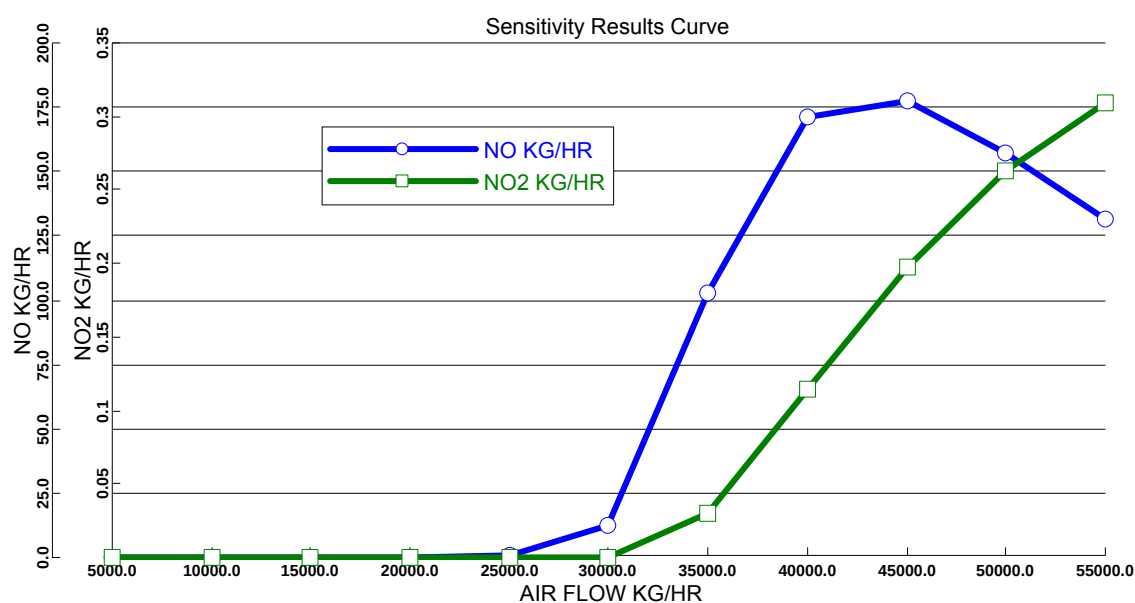


Figure 4.11: Variation in NO_x emission with air flow rate

Moisture content of the coal is another influential parameter in the case of coal combustion. Generally the coal is air dried before it is taken to the burning zone. In spite of air dried process there is some moisture remain in the coal which can reduce the temperature in the burning zone. For this sensitivity analysis a range of 0% -15% of moisture content is considered and the figure 4.12 shows that the outlet temperature can be dropped about 11% due to the presence of 15% moisture. This is because of the heat loss during the vaporization of moisture content.

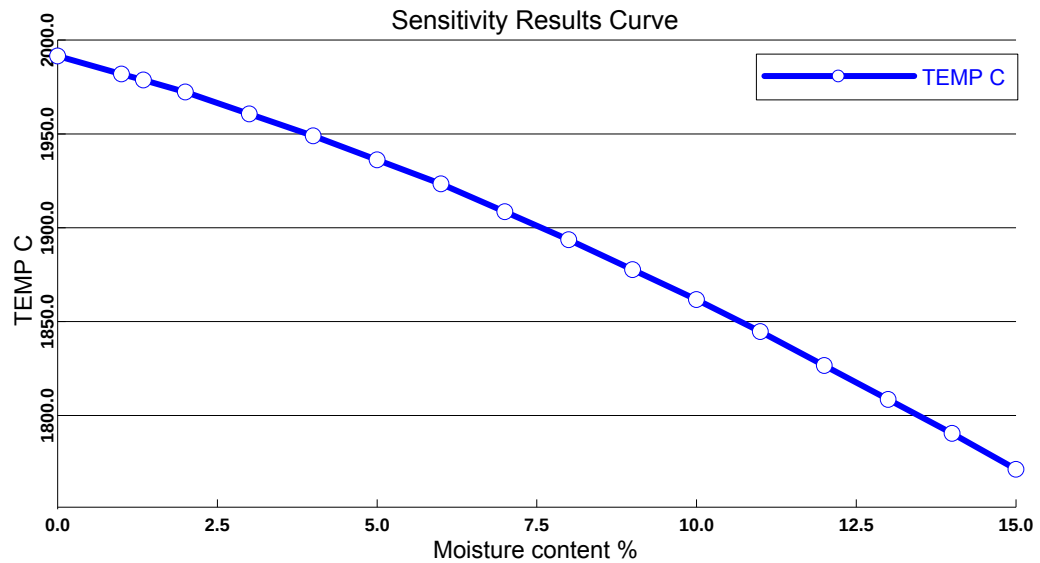


Figure 4.12: Effect of moisture content on outlet temperature

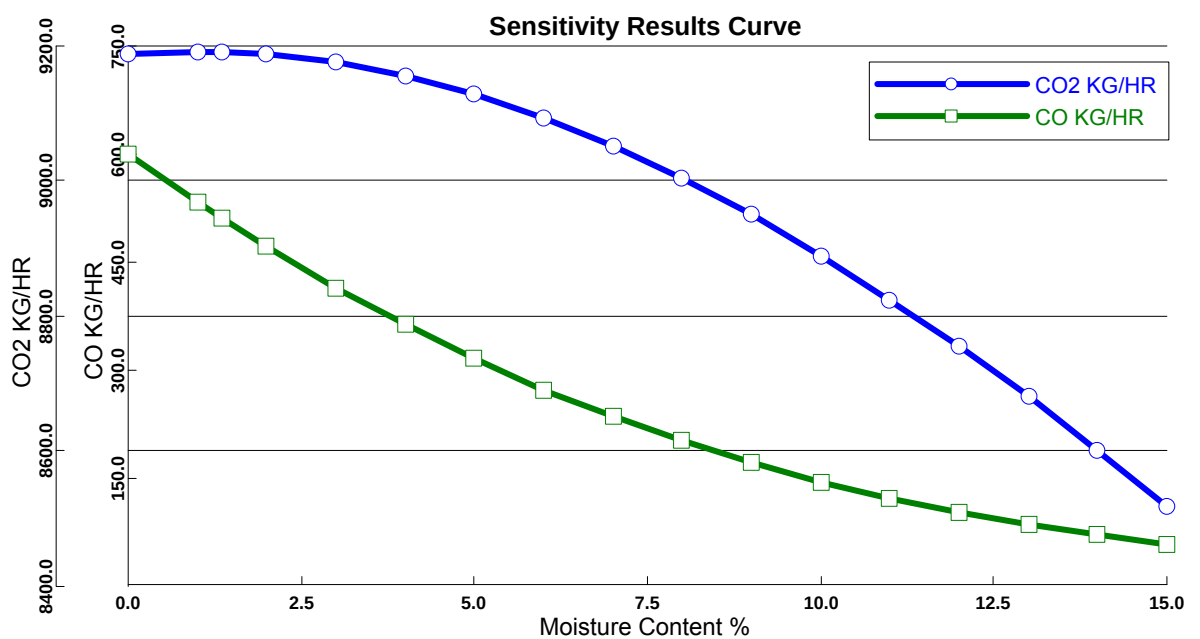


Figure 4.13: Effect of moisture content on CO₂ and CO emission

Figure 4.13 indicate that additional moisture content can possibly reduce the CO₂ and CO emission because extra amount of water in the coal implies the less amount of C in the coal since the mass flow rate of the coal is kept constant. It will be an ideal situation if the coal used for combustion are moisture free, but additional energy is required to do so and hence not an energy efficient procedure. Based on the results shown in figure 4.12 and 4.13 it can be concluded that moisture content need to be kept below 5% to ensure the ideal

temperature in the outlet stream. This range will also allow this study to deal with the highest possible CO₂ emission.

Heating value of coal also play a vital role in the outlet temperature and the amount of NO_x emission. Figure 4.14 shows the effect of heating value on the outlet temperature when coal mass flow rate and the air flow rate in the burning zone are kept constant. As expected it is found that the higher heating value increase the outlet temperature. Excessive temperature in the outlet stream may pose detrimental impact on cement manufacturing and hence ideal heating value should be in between 26 MJ/kg to 28 MJ/kg when the outlet temperature remains about 2000°C. It was mentioned earlier that the generation of NO_x is temperature dependent and the figure 4.15 also support that statement where the NO_x emission is plotted against the variable heating value. The figure indicate that the coal with higher heating value could produce more NO_x in results of high temperature in the combustion zone.

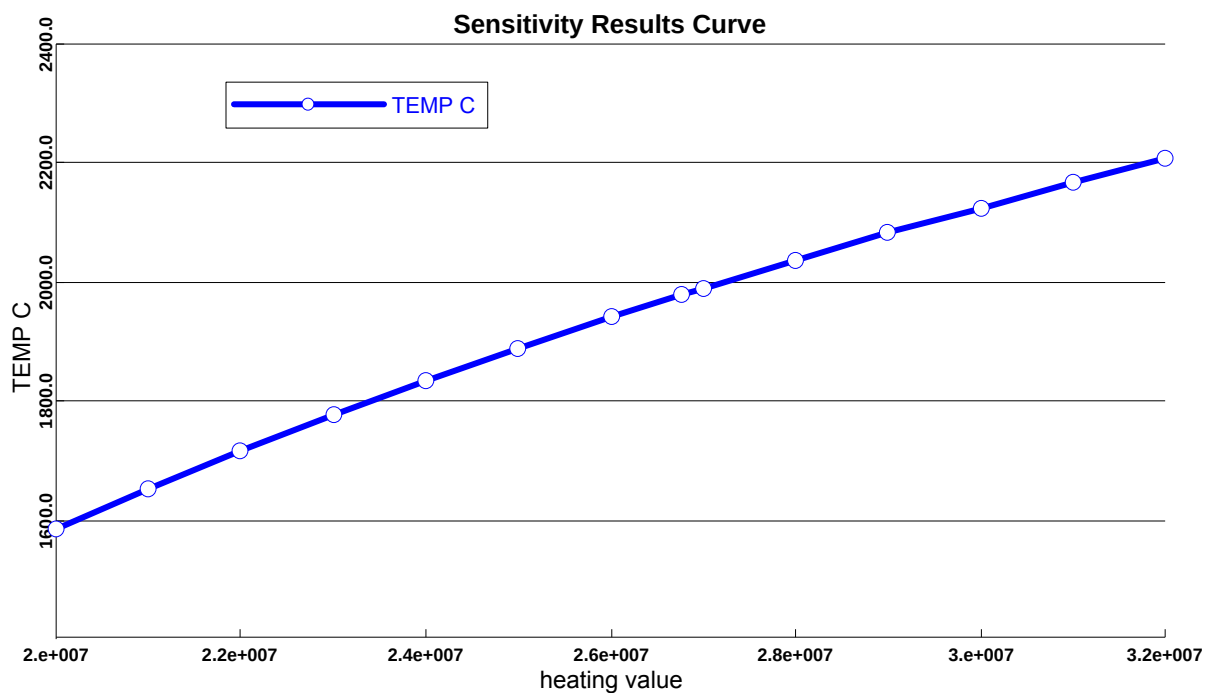


Figure 4.14: Sensitivity curve of temperature against the heating value of coal

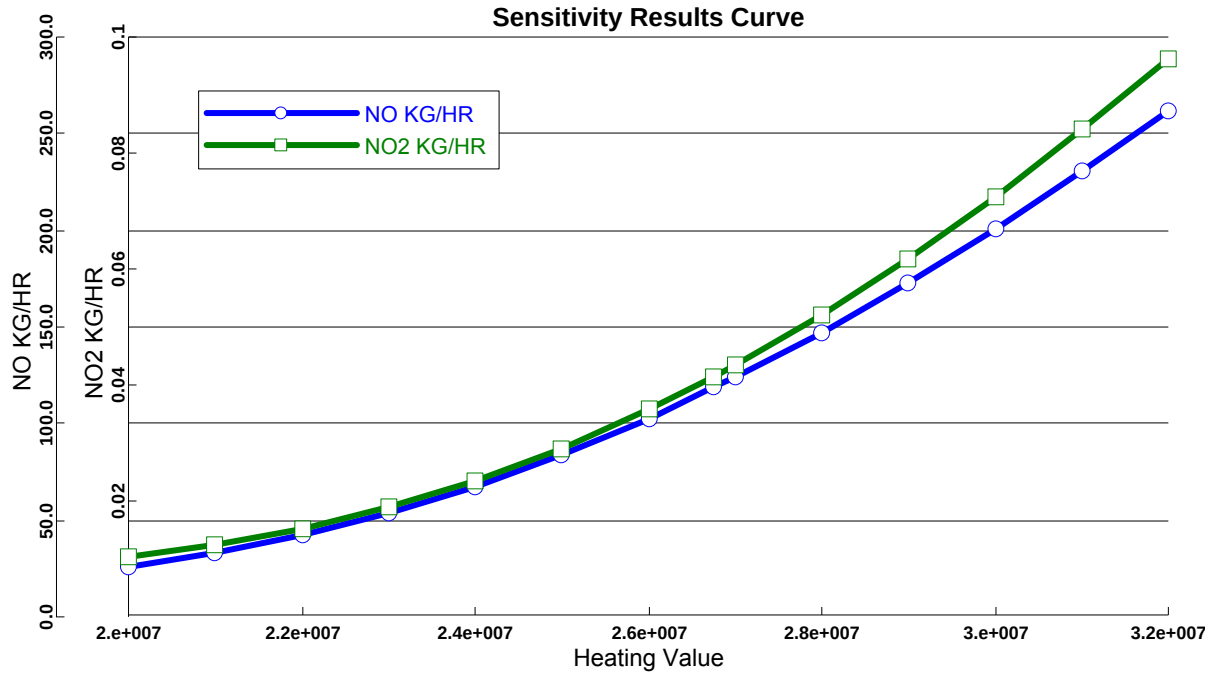


Figure 4.15: Variation in NO_x emission against the heating value of coal

The above sensitivity analysis reveals that the selected parameters are very influential on the output results of the simulation model. In the later part of this thesis, these three parameters will be closely observed to discuss the outcomes for different alternative fuels.

4.8 Conclusion

This chapter summarised the research plan and methodology which is essential for success of any research project. Aspen plus was chosen to carry out the simulation work due to its unique ability to handle component chemistry, reaction stoichiometric and thermodynamic property of the material in the process. From the local synergy report, SPL was identified as one prospective alternative fuel according to its production. Along with SPL, different types of solid alternative fuel were also considered for this study. For modelling purposes the entire process was broken down into sub stages and all sub stages were merged to form the integrated model. Specification of stream blocks and components were clarified in this section to make the modelling easier in the proceeding chapter. The presentation approach of results in the form of emission and clinker quality has also been discussed in this chapter. A detail scenario analysis for coal from different sources has been discussed in this chapter to indicate that the coal from the sample plant is very much representative to the coal of Australia. The scenario analysis also reveals the strength of Aspen plus software in case of

manipulation of data regarding the elemental properties of coal. To identify the decisive parameter a sensitivity analysis is presented in this chapter by using a coal combustion model and the sample of coal from the local plant. Moisture content, amount of air in the combustion zone and heating value are recognized to have impact on the simulation results. Based on the strategy presented in this chapter, simulation models for the preheater tower and kiln are presented in the next two chapters respectively.

Chapter Five

Preheater Tower Modelling

5.1 Introduction

The Suspension preheater is the basis of all modern cement manufacturing systems. Raw meal of cement, in powder form, is injected into the vertical tower which consists of a series of cyclones and raiser ducts. Hot air from the kiln exhaust and/or tertiary air from the cooler section is taken to the string of cyclones to preheat the raw meal. The upward gas velocity is strong enough to lift up the powdered raw meal in the duct ‘in suspension’ to the gas. The cyclones then separate the gases and solids and within the string of cyclones the same things happen four to six times. Heat exchange occurs repeatedly within the large surface area of duct and cyclone, which allows the raw meal to capture most of the heat from kiln gas and tertiary air. Hot raw meal exits from the bottom of the last cyclone of the string and is then ready for calcination and pyroprocessing. The preheater tower enables energy recovery from the kiln gas and makes the process more energy efficient.

In addition to the string of cyclones and raiser ducts, a combustion chamber is offered to the preheater tower which is known as the calciner/precalciner. In the calciner, most of the decomposition of raw meal occurs in the presence of hot air and with additional fuel burning. The calciner reduces the amount of heat load for the kiln and gas pollutant formation in the kiln. The calciner vessel even reduces the heat waste from the system as most of the heat is used for calcination. Almost 60% of total fuel is needed in the calciner to maximise the calcination process. This chapter describes model development of the calciner and preheater tower in two segments by using Aspen plus software and process data collected from the regional cement plant. A set of alternative fuels was used in the model to predict their impact on pollutant emission. The model was validated against the available data from literature for the case of only coal burning. The results were presented in graphical form for better understanding. The results presented in this chapter were also presented in Sustainable Energy and Technology Conference (SET 2013) and International Conference on Applied Energy (ICAE 2014).

5.2 Calciner

In a modern dry process cement manufacturing system, a suspension preheater and precalciner is used to reduce the chance of fuel and heat wastage. The main component of a preheater is a cyclone and the number of cyclones used in preheater towers varies from 1 to 6. According to the principle of the cyclone for heat exchange, the greater number of cyclones should create a more efficient preheater. But in the real picture, adding an extra stage in the preheater increases the pressure drop and more than six stages are prohibited as additional energy, in the form of kiln fan-power, is required to draw the gases through the string of cyclones. Hot air from the clinker cooling stage is generally by-passed through the preheater tower to dry and preheat the raw feed.

Using a precalciner in the preheater tower is a great milestone achieved by the cement manufacturer. Hot raw feed enters the calciner from the cyclone string of the preheater tower. Combustion air from the lower end of the kiln through the cooler is carried to the calciner, which is known as tertiary air. Also the kiln exhaust-gas with high temperature and rich NO_x is taken to the calciner to increase the efficiency of the calciner. Around 90% of calcination of raw feed occurs in the calciner and to make that happen 60% of the total fuel used is burnt in the calciner (GERIAP, 2005). After calcination, the process materials enter the kiln at around 750°-900°C. As the calciner is operated in a lower temperature compared to the kiln, fuel need not be of as high quality as fuel burnt in the kiln.

5.2.1 Classification of calciner

There are two main types of calciners, which are in-line calciners (ILCs) and separate-line calciners (SLCs). In an ILC the tertiary air and kiln exhaust gas passes through the burning zone of the calciner. This type of calciner is useful to burn waste-derived alternative fuel as well as coal and natural gas. The low-oxygen content of tertiary air makes the ILC more compatible with fuels that have relatively high volatile content. On the other hand the SLC only uses the tertiary air and the kiln gas bypasses the combustion area of calciner. Oxygen-rich air from the cooler section is used in SLCs for fuel combustion. In the current study, an in-line calciner prototype with a capacity of 2200t/d is considered. Figure 5.1 shows the schematic diagram of an ILC unit with single-string cyclone preheater kiln (Neuffer & Laney, 2007).

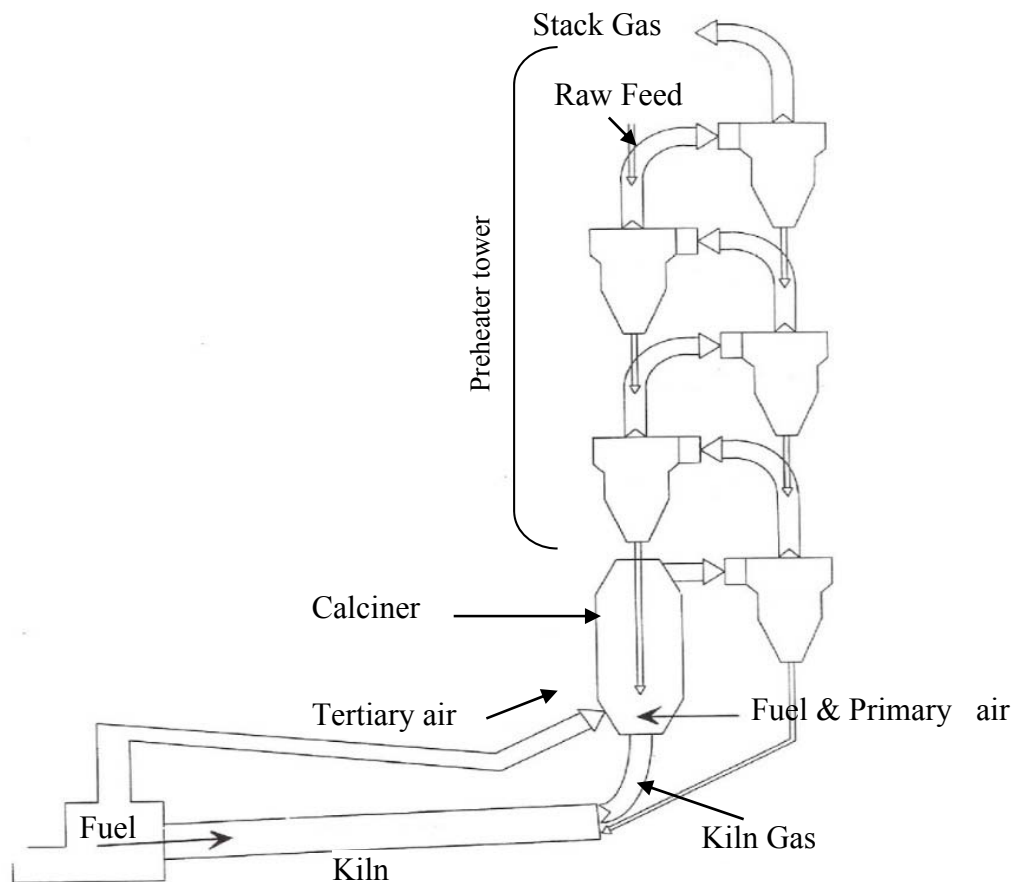


Figure 5.1: Schemetic diagram of ILC with single string pre-heatre tower

5.2.2 Alternative fuel for calciner model

Several alternative fuel options are available for cement calciners and most of them were discussed in chapter 3. According to the local industrial synergy SPL could be one of the attractive options for the local cement plant. From the discussion provided in chapter 3 MSW is another option which can be chosen due to availability and low price. Used tyre as an alternative fuel was used for over 30 years and the local cement plant also used them a few years back. Unfortunately the local cement plant discontinued their usage of waste tyre as a problem was identified on clinker quality. Along with these three alternative fuels, sewage sludge is also considered for this section. Detailed description of these alternative fuels can be found in chapter 3.

In order to create a proper model, the full chemical breakdowns of each of the fuels are required; this information was gathered from the literature (Karell & Blumenthal 2001, Vick & von Steiger, 2001, Garg et al. 2009 Ninomiya et al. 2004) as well as from the local cement plant. Table 5.1 summarises an elemental analysis of selected alternative fuels

which is essential to construct the model. To obtain the most realistic result, actual plant data regarding the chemical breakdown of coal, feed material and constituents of tertiary air and kiln gas along with temperature and pressure, were collected from the local cement plant. Also the mass flow rates of different input items have been collected from the same plant. Table 5.1 indicates that waste tyre had the highest energy content but a higher fraction of carbon content may also increase CO₂ emission.

Table 5.1: Elemental analysis of fuel

	Coal (Plant data)	Waste tyre (Karell & Blumenthal 2001)	SPL (Vick & von Steiger, 2001)	MSW (Garg et al., 2009)	SS (Ninomiya et al., 2004)
Proximate					
analysis (wt%)					
Moisture	1.35	0.62	0.6	31.2	0.2
Ash	18.55	4.81	71.43	35.17	20.25
Volatile matter	24.15	67.06	4.1	64.83	47.4
Fixed carbon	57.3	28.13	24.3	-	32.35
Elemental analysis					
on dry basis (wt%)					
C	69.13	84.39	26.2	34.88	52.5
H	3.79	7.13	0.3	4.65	6.4
N	1.51	0.24	0.6	1.02	9.2
S	0.36	1.24	0.3	0.15	0.8
Cl	0	-	-	1.02	-
O	6.66	2.19	1.2	23.11	31.1
HHV (MJ/kg)	-	37.72	9.36	-	-
LHV (MJ/kg)	27.4	35.97	9.29	15.4	25.5

5.2.3 Calciner model development

For the current study an Aspen Plus model for the ILC has been developed, based on the model proposed by Zhang et al. (2011). Zhang et al. (2011) proposed a single air staging model of a Dual Combustion and Denitration calciner (DD-calciner) with a production rate of 2500 tonne/day. In this section the simplified model of Zhang et al. (2011) has been reproduced and modified for alternative fuel firing. Before constructing the model, a few

basic assumptions were made to reduce the complexity of the model without affecting the simulation results. These are:

- In the calciner, the coal and other fuel combustion has taken place in two different reactors. The combustion process consists of the fuel decomposition section and decomposed products combustion section. These have been simulated by using two reactor modules of Aspen Plus namely RYield and RGibbs.
- Throughout the model, N_2 of air has been considered inert and NO_x generation from the processes due to the combustion of the fuel and concentration in the kiln gas.
- CO_2 has been produced through the calcination process and combustion of fuels.
- Only $CaCO_3$ and $MgCO_3$ of raw feed are decomposed within the calciner. For convenience it is assumed that only 90% of $CaCO_3$ will decompose in the calciner and liberate CO_2 .
- Ash has been considered to be nonreactive in the combustion process.
- Any air leakages in the calciner system have not been considered.

Figure 5.2 shows the calciner process model flow sheet in Aspen Plus. Raw feed has been inserted in the model through a separate reactor block, RStoic. Calcination of the raw feed up to 90% (as per assumption) has occurred in this reactor in the presence of heat carried out from the fuel combustion reactor block.

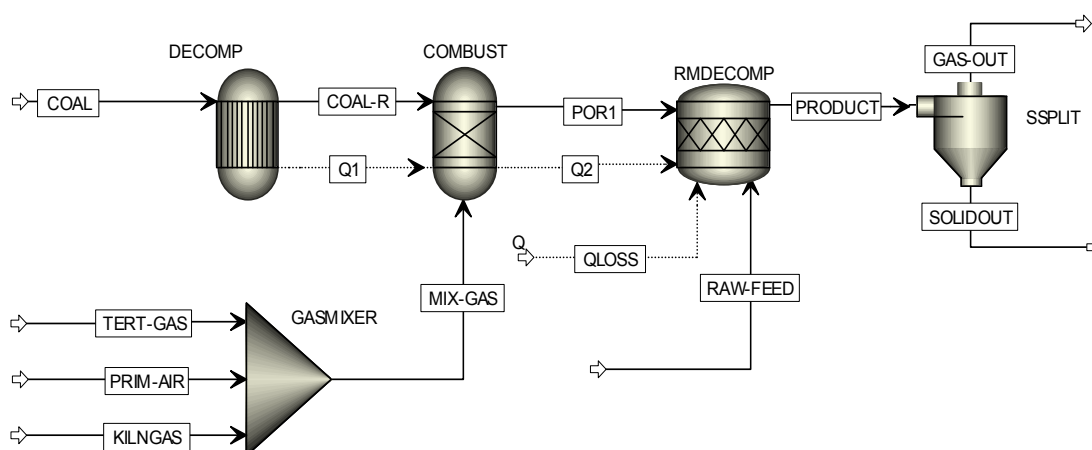


Figure 5.2: Calciner model for coal firing

In an Aspen Plus simulation model, user can specify the name of the unit operation block as well. In the current model the name of the unit operation blocks are specified based on their function to make the model more accessible to the readers. For instance, DECOMP

reactor will decompose the coal, COMBUST reactor will perform the combustion process and RMDECOMP reactor will perform the decomposition of raw materials.

The global property method for this model was selected on the basis of thermodynamic properties computation criteria and the selected property method is PENG-ROB method, a built in method in Aspen plus software. HCOALGEN and DCOALIGT models was used for enthalpy and density calculation for both fuels and ash. The operation conditions, temperature and pressure of combustion were determined by the supplied data from the local cement plant.

To run the model properly, operating parameters for each block and streams need to be specified. Then input parameters for material and heat streams have to be installed in the model. A wide range of data was required for the model run which includes:

- Mass flow rates of all incoming streams including fuel, raw feed, tertiary air, primary air, and kiln.
- Temperature and pressure of material streams.
- Heating values and chemical composition in the form of Proximate and Ultimate analysis of the fuels with particle size distributions.
- Chemical constituent of incoming gas streams.
- Composition of raw feed with particle size distribution.

After all the input parameters were introduced in to the model, the model was ready to run. The simulation produced output results in the form of:

- Mass and mole flow rate of all products component.
- Temperature, enthalpy, entropy, density, and average molecular weight of each output stream.
- Material and energy balance data from each reactor block along with temperature and pressure.
- Results from user defined calculator block compiled by FORTRAN.

5.2.4 Calciner Model Validation

The developed model was verified using available data from literature and data collected from the local cement plant. As the chemical constituent of different input stream was not available in the literature, this study relies upon the data provided by the local cement plant.

The mass flow rate of input stream and the percentage of different components in exhaust flue gas were available in literature. Based on those two sets of data, the calciner process model was run for three different scenarios given in Table 5.2. Comparisons between the published results and simulated results are summarised in Table 5.2.

Table 5.2: Comparison of simulation results and literature values

Input		Literature data (Huang,2006, Zhang et al. 2011)		
Material streams (kg/s)		Ex 1	Ex 2	Ex 3
Raw material		44.69	48.84	56.24
Coal		2.1	2.12	3.13
Tertiary air		21.94	23.87	24.38
Kiln gas		15.34	14.84	19.56

Output	Ex. 1			Ex. 2			Ex. 3		
Parameter	Huang (2006)	Zhang (2011)	Simulation results	Huang (2006)	Zhang (2011)	Simulation results	Huang (2006)	Zhang (2011)	Simulation results
Outlet Temperature (K)	1176	1175	1195	1163	1193	1166.6	1154	1194	1261.8
NO _x (mg/Nm ³)	776	774.7	772.1	-	765.3	656.6	-	498	554.8
O ₂ (%)	2.282	2.47	2.39	1.35	1.14	1.97	1.46	1.65	1.58
CO (%)	0	1.54E-08	2.99E-05	-	2.43E-08	3.23E-05	-	1.63E-08	4.00E-05
CO ₂ (%)	-	39	40.44	36	40.3	42.83	40.12	38.9	41.28

Comparison of results in Table 5.2 indicates that the simulation results are in very good agreement with published values. The variation in the Outlet temperature ranges from 0.3% to 9%. CO₂ concentration in the flue gas are strongly dependent on the degree of calcination that occurred in the calciner. Results of the percentage of CO₂ in outlet gas between literature values and simulation values differ only 3.7% for example 1 (Table 5.2). For example 2, simulation results of CO₂ concentration are about 21% outlying the results of Huang (2006) but only 6.3% higher than Zhang et al. (2011) results. Excess O₂ in outlet streams are found higher in the case of example 2 but for example 1 and 3, the model generated similar results as published in the literature. The O₂ level in the exhaust gas varies due to the percentage of flow rate of tertiary air and primary air.

Weight percentages of CO in stack gas were found higher in simulation results but the total amount was very negligible and not mention-worthy. Variation has occurred in the concentration of NO in the flue gas, only for the case of examples 2 and 3. This was due

to the different constituent data for the kiln gas and tertiary air. Generally kiln gas carries a rich amount of NO but the actual amount may vary from plant to plant due to the process type and different compositions of raw material and fuels (US Environmental Protection Agency, 1994) The comparison results indicated that the model can be used to predict the behaviour of different alternative fuels on the pollutant emission

5.2.5 Modified Calclner Model for Alternative Fuel Burning

Alternative fuel substitution in the calciner needs to be done with utmost care so that any pollutant emission or the quality of the clinker is not compromised. According to the rule of thumb most of the alternative fuels can substitute 20% of the total thermal energy required in clinker production (Prisciandaro et al., 2003, Chinyama, 2011). The actual scenario is not as simple as that, since there are lots of constraints which need to be minimised. The validated model was modified in this section to enable alternative fuel burning. An additional reactor block for alternative fuel decomposition is required to update the exiting model. A modified model is presented in Figure 5.3 and an additional reactor ‘AFUELDCO’ can be seen at the combustion section of the model.

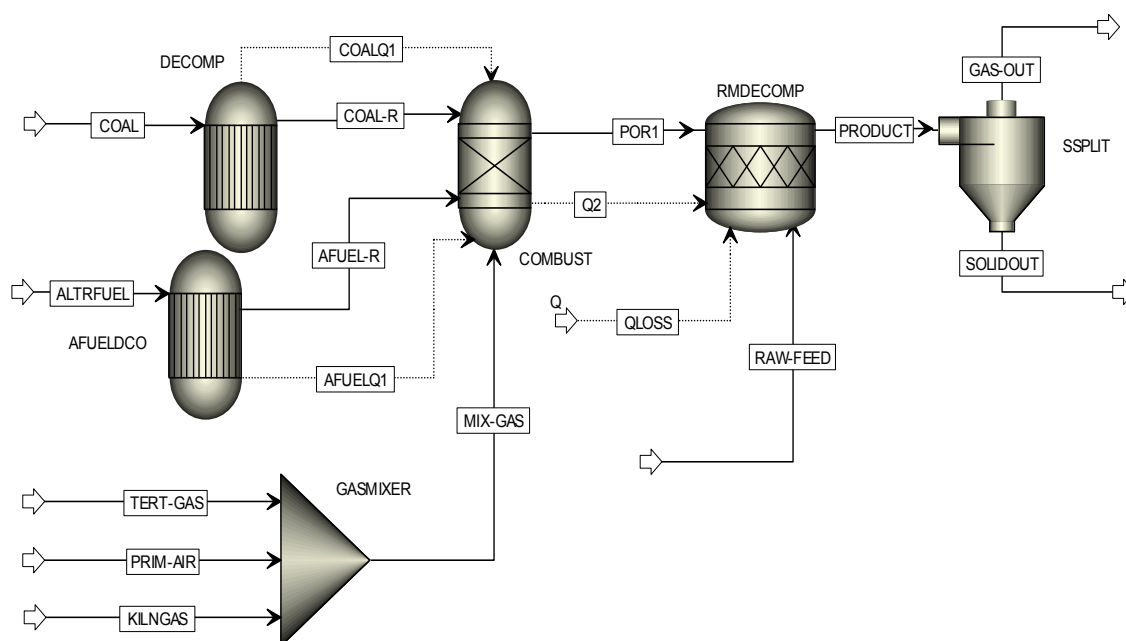


Figure 5.3: Modified Calclner model for alternative fuel burning

The proposed model was prepared to simulate a 2250t/d calciner double fuel injection system which means only two different types of fuel can be introduced at a time in the burning zone of the calciner. For the current section four solid alternative fuels were

selected and examined on the ground of pollutant emission. A few additional assumptions were made to reduce the complexity of alternative fuel burning system. The energy requirement in the calciner was determined using the data of energy consumption collected from the local plant assuming that only 60% of the total thermal energy is required in the calciner. Required thermal energy for the process was generated by primary fuel coal and a single alternative fuel. It was discussed in the sensitivity analysis in chapter 4 the air flow has a decisive effect on the emission and according to that discussion the amount of excess air in the burning zone is assumed to be 10% for the rest of the study. The thermal substitution rates by alternative fuels were kept variable and these varied from 5% to 25%. The range of the substitution rates is considered based on the available information in the literature which is presented in the Table 3.17 and the fact that theoretically 20% substitution rate is feasible for most of the alternative fuels (Prisciandaro et al., 2003). According to Van Oss & Padovani (2003) single waste fuel component should not exceed 30%. In some other cases like sewage sludge and SPL the substitution rate need to be kept below 10%. Considering all these fact the substitution rates ranges from 5% to 25% is chosen for this thesis which is reasonable for all sorts of alternative fuels. Throughout the simulation, the mass flow of kiln gas, tertiary air and raw feed were kept constant to identify the sole impact of alternative fuel on the pollutant emission. Primary air was controlled in accordance to the assumption of 10% excess air in the combustion zone. Stoichiometric air fuel ratio for each alternative fuel has also been determined to ensure an oxygen-rich combustion environment.

5.2.6 Simulation results and discussion for calciner

Impact of four solid alternative fuels on the pollutant emission was investigated for an in-line calciner by using an Aspen plus process model. Concentration of CO₂, CO, NO_x and SO₂ in the flue gas was examined along with the outlet temperature while the substitution rate varied from 5% to 25%. Throughout the simulation the mass flow rate of raw feed, tertiary gas and kiln gas were kept constant, while the amount of primary air was modified with the proportion of fuel mix to meet the assumption of 10% excess air. In the simulation model the energy requirement for the process was set by the specification of local plant and the mass flow rate of fuels was determined accordingly.

Total CO₂ emissions from the pyroprocess depend on energy consumption and nearly 977 kg of CO₂ was produced for each tonne of clinker (Choate, 2003) while the calciner is

responsible for about 70% of this CO₂ emission. CO₂ and CO emission from the modelled calciner are presented in Figures 5.4 and 5.5 respectively. It was found from both cases that using MSW as a substitution of coal reduces CO₂ and CO emission in large scale. CO₂ emission reduced about 6% when 25% of thermal energy is substituted by MSW. As it is seen from Table 5.1 that the percentage of carbon is way lower in MSW compared to coal and waste tyre, the reduction of CO₂ emission is much anticipated. It is also found from Figure 5.4 and 5.5 that net CO₂ and gross CO emission increases when SPL is used as substitute fuel while a slight decrease for the same case is observed for waste tyre. Though the carbon percentage is very low in SPL, it requires about 2.42 times of coal to replace the required thermal energy (Kaddatz et al., 2013). This leads to higher CO₂ emission for the case of SPL. Sewage sludge (SS) was found to perform better than waste tyre in terms of reduction of CO₂ and CO emission. About 2% reduction of CO₂ was observed while SS substitute was 25% of coal.

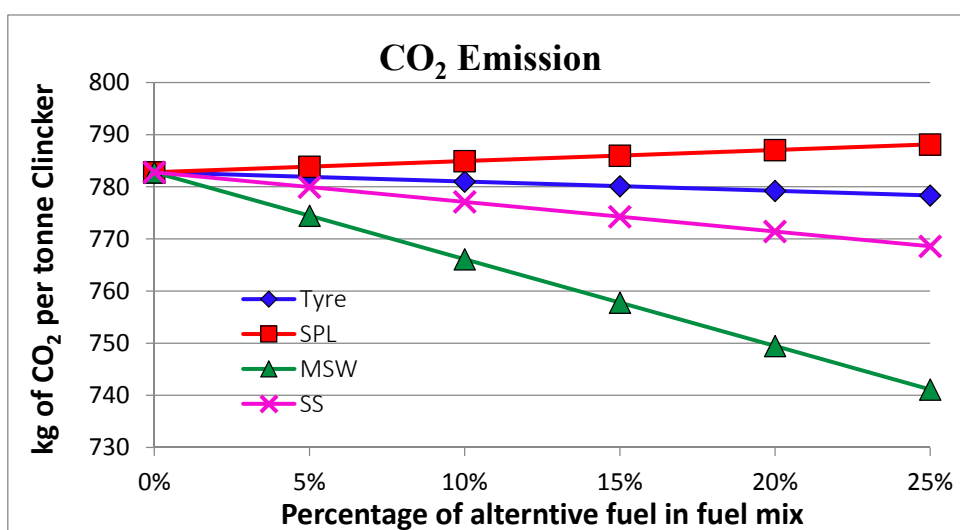


Figure 5.4: CO₂ emission from calciner (kg/tonne clinker)

Variables which have influence on NO_x emission in cement manufacturing are fuel type, feed rate, amount of air flow and the temperatures in the burning zone of the kiln (Walters et al., 1999). About 1.5 to 10 kg of NO_x is emitted into the atmosphere per tonne of cement produced (Naik, 2005). Figure 5.6 illustrates NO_x emission from the system for alternative fuel options. NO_x emission was found markedly increased when MSW is used as alternative fuel. The nitrogen content of coal and MSW were similar but the heating value of MSW was almost half of coal and hence extra amount of MSW was needed to meet the energy requirement of clinker productions. This extra amount of fuel lead to a higher NO_x emission. Using waste tyre and SPL did not affect the NO_x emission while 1% increase of

NO_x was detected in simulation results for SS. According to global emission standard NO_x should lie between 500-1000 mg/Nm³ (Edwards, 2014). Simulation results indicated that up to 25% substitution of selected alternative fuels did not result an emission beyond that range.

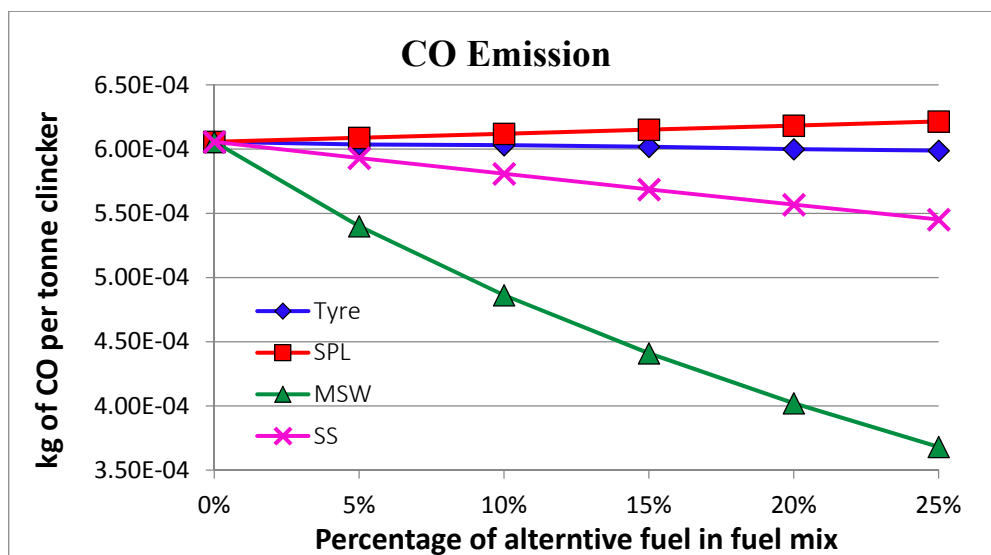


Figure 5.5: CO emission from calciner (kg/tonne clinker)

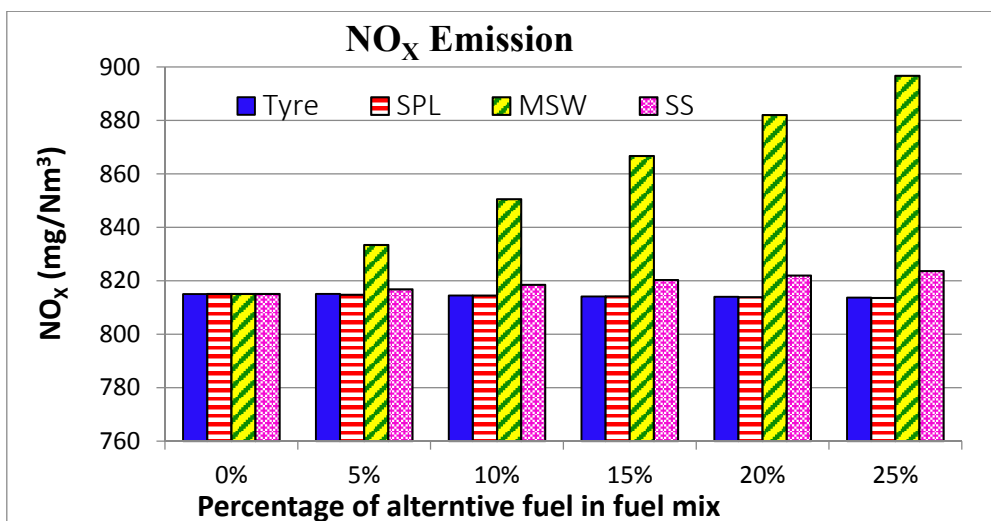


Figure 5.6: NO_x emission from calciner (mg/Nm³)

Sulphur dioxide may be generated both from the Sulphur compounds in the raw materials and from Sulphur in the fuel (Van Oss & Padovani, 2003). SO₂ emission per tonne of clinker production is illustrated in Figure 5.7. Waste tyre, SPL and SS are found to produce more SO₂ when mix with coal compared to the case of only coal burning. While MSW and

coal mix leads to lower SO₂ emission which is predictable as Table 5.1 shows that MSW has the lowest amount of sulphur. Unexpectedly, SPL showed about 35% increase of SO₂ in the stack gas when it was used at 25% substitution rate, though it had almost similar sulphur content like coal. Since SPL had very low heating value hence additional amount of fuel, which was about 2.42 times of coal (Kaddatz et al., 2013), was required to meet the energy demand. This extra amount of SPL released the additional amount of SO_x.

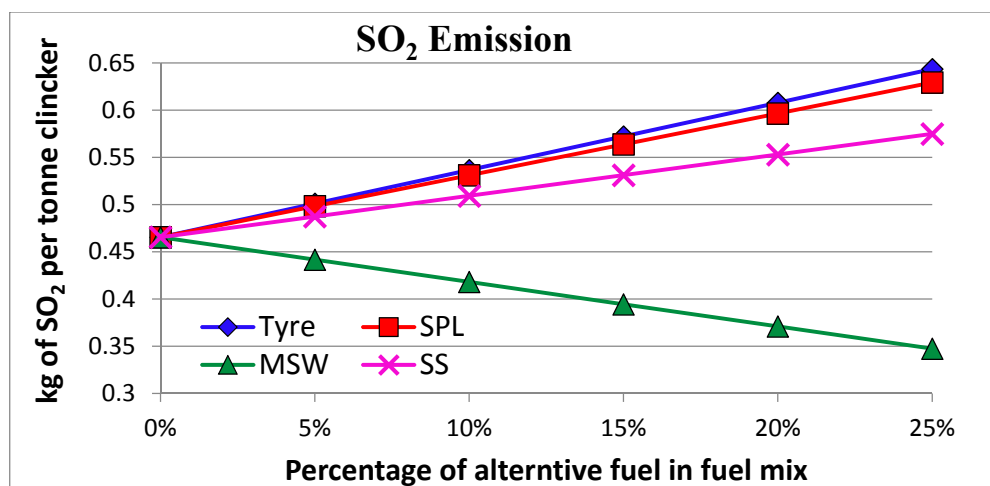


Figure 5.7: SO₂ emission from calciner (kg/tonne clinker)

Outlet temperature is a good indication of at what temperature raw feed is decomposed and liberates CO₂. To complete the calcination up to a desired degree, temperature of the calciner needs to be kept as high as 800°C (1075°K). Figure 5.8 shows the outlet temperature of the modelled calciner for alternative fuel options. A rapid drop in the outlet temperature is observed when usages of MSW is increases. This was only because of high moisture content of MSW and the results suggest that MSW needs to be air dried to keep the performance of the calciner up to the mark. Temperatures in the case of waste tyre and SPL were slightly higher than only coal burning while SS increased the temperature of 1%, consequently more heat was supplied in the calciner.

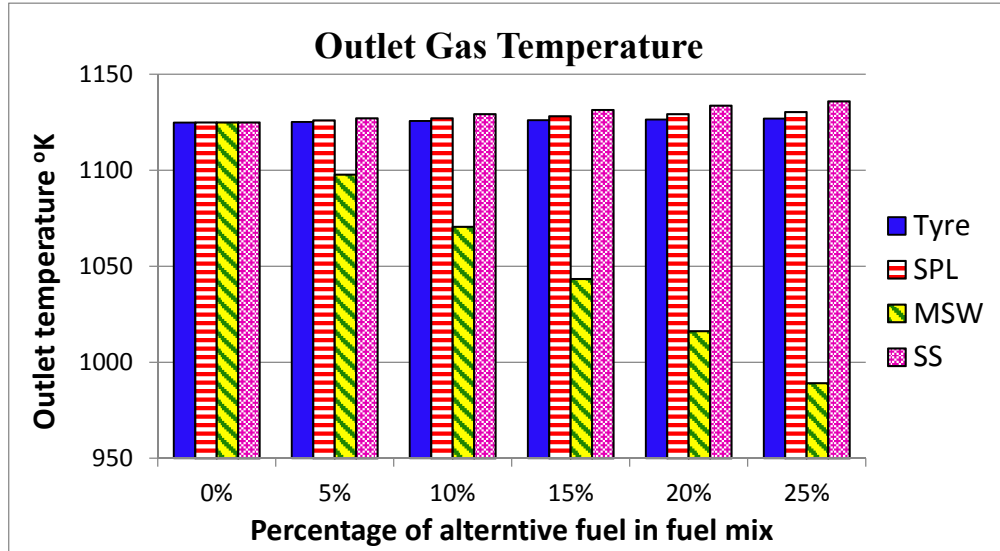


Figure 5.8: Outlet gas Temperature (°K)

Based on the result it was evident that MSW could be the best option as alternative fuel from an emission standpoint. Unfortunately, MSW cannot replace more than 10% of thermal energy due to its high moisture content which leads to less heat generation in the calciner. This phenomena was discussed in the sensitivity analysis of coal in section 4.7. Using SPL as alternative fuel could increase CO₂ and CO emission which is undesirable. Also SO₂ release from burning SPL restricted its use up to as much as 5% of total thermal energy. Waste tyre could be a better option as it reduces several pollutant emissions including CO₂, CO and NO_x without lowering the temperature of the calciner. The only downside of using waste tyre is SO₂ emission. However, considering the decrease of CO₂, this study suggested that a maximum 12% of thermal energy can be substituted by waste tyre. This substitution rate will keep the SO₂ emission below 0.55kg per tonne of clinker production. Based on the results presented above, SS was a more compatible alternative fuel than MSW, waste tyre and SPL. Apart from SO₂, SS was capable of reducing all other pollutant emission without reducing the amount of heat in the calciner. To keep the SO₂ below the same level that was set for tyre, the maximum suggested substitution rate for SS was 19%.

5.2.7 Concluding remark on calciner model

This section concentrated on four solid fuels to maximise their usage in a cement calciner by using a process model of a calciner. From the outcomes of an Aspen plus model for a calciner, the suggested substitution rate for waste tyre, MSW, SPL and SS were, 12%, 10%,

5% and 19% respectively. The substitution rate of MSW could be increased if it was fed in the burning zone after reducing the moisture content, by drying, in to a desirable level. Though SPL was found to be a potential alternative fuel from literature review, this study did not show promising results for SPL in terms of pollutant emission.

Three alternative fuels were examined with calciner model in terms of potential emission. Available literature on the environmental impact of using different alternative fuels were summarized in the chapter 3 of this thesis. Most of the previously published results were region or specific plant based and hence there were differences among the process of the plants, operating conditions, quality of the fuel and raw materials. The previously published results was not considered in this thesis for comparison with the current simulation results due to the incomparable nature of the data because of all those differences. To get a better idea on the similarity and difference of the current simulation results and previously published results, readers are advised to see table 3.17 where a comparisons of all different alternative fuel have been summarized based on the literature review. In terms of ranking, it is always difficult to rank the alternative fuels as different parameters need to be taken into consideration and all those parameter are not compatible. Even ranking those on basis of single criteria, for example CO₂ emission, may not be possible as contradictory results are available in the literature.

5.3 Preheater tower

Preheater tower is the stage where raw meal is inserted to the closed process system after homogenisation. The main function of the preheater tower is to evaporate moisture and elevate the temperature of the precalciner feed. All surface and inherent moisture are removed from the feed in the preheater tower. The feed is partially calcined at the last cyclone of the string.

The preheater/precalciner system uses an induced draft fan, which draws hot kiln gas through the kiln. Raw meal is injected into the gas flow of the preheater which are suspended in the hot gas stream. Raw meal is then pulled by the fan to the first stage of cyclone where the materials are separated from gas centrifugally. Within the preheater tower quick heat transfer occurs between the material and gas flow. Throughout the process the material travels by gravity to the next stage of cyclone and the gas phase containing

remaining solids flows to the cyclone stage above. At the exit of the preheater tower raw meal becomes dried and the clay minerals dehydrated and decomposed. The temperature of the meal has increased to about 700°C and the temperature of gas flow towards the opposite direction has reduced to about 350°C. Preheated raw meal then enters in the calciner where fuel is burnt to produce enough thermal energy to complete the calcination process.

5.3.1 Preheater tower model

The preheater tower model was an extension of the calciner model that was described in the previous section (section 5.2). In addition to the existing model a series of cyclones was added to imitate the preheater tower. Usually two smaller cyclones with separation efficiency of about 95% are used in the top most stage of a cyclone string. The efficiency of the lower stage cyclone is typically 75% to 80%. In the cyclone string, heat transfers and calcination occur simultaneously beside the dust separation from raw meal. In the Aspen plus model there was no specific unit operation block which could perform both dust separation and calcination reactions, hence two blocks, namely cyclone and RStoic reactor, were used in series to carry out these task. The number of cyclones in the string normally vary between 2 to 6 and the local cement plant, from where plant data was collected, had a 5 stage preheater tower. In the model it was not necessary to put the same numbers of cyclones in the flow sheet as it was in the real plant. The reason behind this is all the cyclones had the same function but in variable temperature. It was found that only three stages of cyclones in the model were sufficient to replicate the preheater tower with any number of cyclones. These three cyclones and reactors need to operate in separate temperature range. As it was mentioned in section 2.3 that raw feed enter into the cyclone string at room temperature and after completion of major calcination feed enters to the kiln at an approximate temperature. Detailed description of reactions in different temperature range are given in section 2.3. In the preheater tower model temperature will rise up to 200 °C in the first stage of cyclone and in the second stage it will go as high as 600 °C. In the third stage of cyclone the heat stream from the calciner chamber is carried through and eventually the temperature of this stage will rise above 900 °C (in simulation results it is about 940 °C) to ensure maximum amount of calcination. In the real plant the preheater tower contains only cyclone where all the reactions occur and has variable temperature range. In the process model, additional reactors for the chemical reaction were included as Aspen plus unit operation block CYCLONE cannot perform any chemical reactions. To

For the preheater tower model three alternative fuels were selected, namely waste tyre, refuse derived fuels (RDF) and meat and bone meal (MBM). In this thesis, different alternative fuels in different section were considered to cover all the major alternative fuels in cement industry. Throughout the analysis best possible options of alternatives are selected for the integrated model. In this process MBM is introduced in this section and the other alternative fuel RDF is actually a fraction of MSW with less moisture content. To compare any potential changes in emission with the case of the calciner model, waste tyre was included to be studied in the preheater tower model. Detailed description of all three alternative fuels can be found in chapter 3. As all the elemental analysis of fuels were collected from published literature and since there are variation of data, in this thesis the worst case data is considered to identify maximum impact on the environment. Refuse derived fuels cover a wide range of waste materials which includes residues from MSW recycling, industrial/trade waste, industrial hazardous waste, biomass waste, etcetera (EC, 2013). MBM is used as fuel in the cement industry to ensure that any living organism is thermally destroyed and its energy potential is utilised (Chinyama, 2011). Chemical breakdown of the selected alternative fuel is presented in Table 5.3. It is found from Table 5.3 that RDF had a higher heating value and lower moisture content in contrast to MSW. It was expected that RDF perform better than MSW as alternative fuel. Though the calorific value of MBM is low, it was chosen with expectation that it will reduce CO₂ emission as the carbon content is way lower than coal. Simulation results for the preheater tower model are presented in the next section with discussion and recommendation.

5.3.2 Results and discussion for preheater tower model

A preheater tower for cement manufacturing was modelled by using Aspen plus to investigate the impact of using selected alternative fuels on pollutant emission. The cyclones in the tower enable the pollutant to circulate within the process and use the waste heat from the kiln exhaust to achieve energy efficiency. Emission results are presented in the form of CO₂, NO_x and SO₂ and the results are used to determine the maximum substitution rate of alternative fuels. Like the calciner model, alternative fuels were set to substitute up to 25% of the energy requirement for modelling purposes.

Table 5.3: Elemental analysis of waste tyre, MBM and RDF

	Coal (Plant data)	Waste tyre (Karell & Blumenthal, 2001)	MBM (Gulyurtlu et al. 2005)	RDF (Garg et al. 2009)
Proximate analysis (wt%)				
Moisture	1.35	0.62	6.8	15
Ash	18.55	4.81	36.91	10.9
Volatile matter	24.15	67.06	35.09	82.06
Fixed carbon	57.3	28.13	28	7.04
Elemental analysis on dry basis (wt%)				
C	69.13	84.39	35.3	47.1
H	3.79	7.13	4.9	7.1
N	1.51	0.24	8.4	0.7
S	0.36	1.24	0.5	0.24
Cl	0	-	0.26	0.6
O	6.66	2.19	13.73	33.36
HHV (MJ/kg)	-	37.72	14.19	-
LHV (MJ/kg)	27.4	35.97	13.06	21.2

According to model assumption, about 95% of raw meal should be calcined within the preheater tower and hence there was a chance of increase in CO₂ release compared to the calciner model. CO₂ emission results are presented in Figure 5.10 which indicate a similar kind of results as presented in the calciner model. It was found that, in spite of higher degree of calcination CO₂ emission per tonne of clinker production is marginally lower for the reference case where only coal is used as fuel. This might be because of the cyclone string which confined and circulated CO₂ in the process. Maximum reduction of CO₂ was observed for the case of RDF (about 1.28%). Waste tyre also reduced CO₂ emission to a certain level and these results agreed with the calciner model results. MBM was found to emit slightly more CO₂ than the reference case (only coal) though it had lower carbon content than coal. Since the heating value of MBM is almost half of the coal it implies that almost twice as much MBM will be required to replace coal to meet the energy requirement. This additional amount of fuel in the fuel mix leads to a higher CO₂ emission. It is worthy to mention that there are huge variation of MBM elemental analysis in literature. A better quality MBM might be helpful to reduce CO₂ emission.

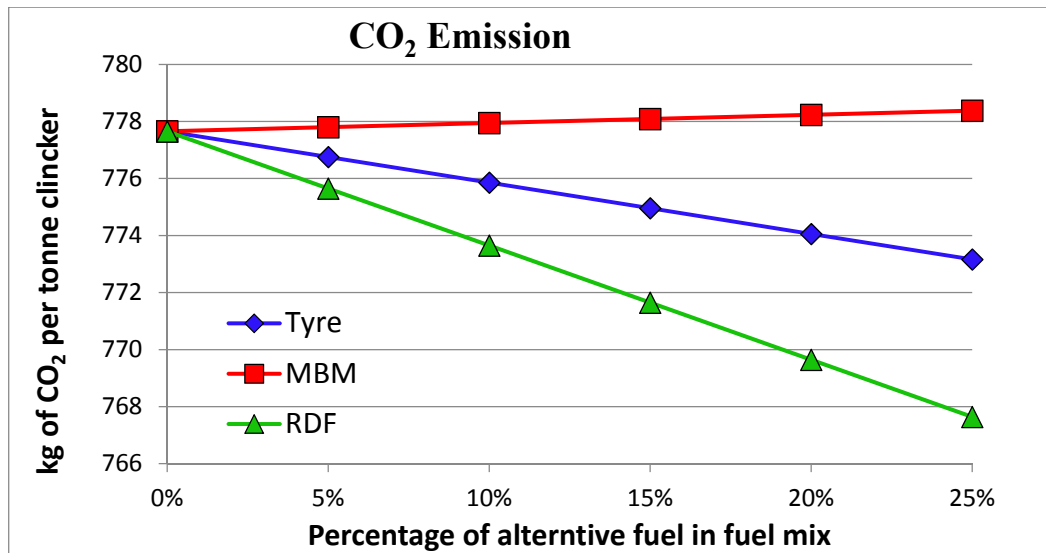


Figure 5.10: CO₂ emission from preheater tower (kg/tonne clinker)

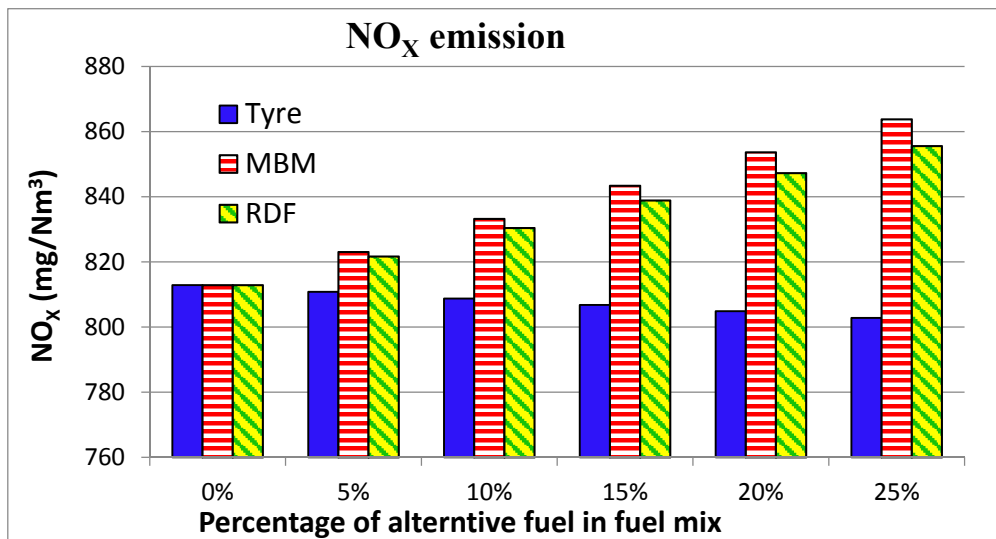


Figure 5.11: NO_x emission from preheater tower (mg/Nm³)

NO_x and SO₂ emission results are presented in Figures 5.11 and 5.12 respectively. The results indicate that using RDF and MBM might raise the concentration of NO_x in the stack gas while waste tyre managed to lessen NO_x concentration slightly. The increment of NO_x for MBM and RDF were about 6% and 5% respectively. If the tolerable limit for NO_x was set to 850mg/Nm³ then the results suggest that MBM and RDF can be used up to 15% and 20% of the thermal energy requirement respectively. In terms of SO₂ emission a marked intensification was noticed for the case of waste tyre and MBM which was predictable due to higher sulphur content compared to coal. The amount of SO₂ concentration in stack gas increased about 39% and 44% when MBM and waste tyre were used to substitute 25% of

energy demand. In contrast RDF was able to reduce the SO₂ emission to 12.5%. Setting 350mg/Nm³ as the upper limit of SO₂ emission (which is average of the range of global emission standard), the simulation results measuring safe substitution rates for MBM and waste tyre, which are about 13.5 and 14.5%

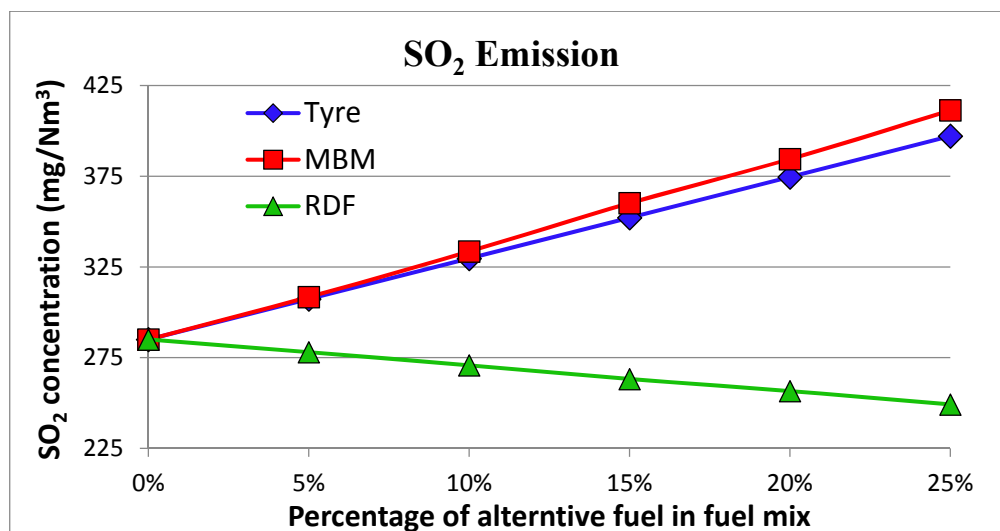


Figure 5.12: SO₂ emission from preheater tower (mg/Nm³)

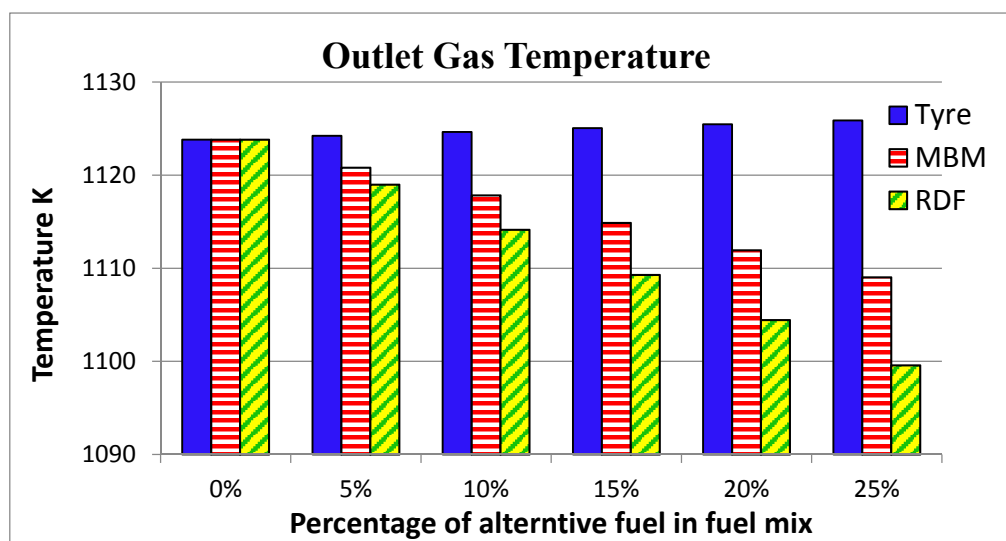


Figure 5.13: Calciner Outlet Temperature (K)

As mentioned in the calciner model, outlet temperature could be a useful parameter to justify the performance of the alternative fuel. Outlet gas temperature from the calciner is plotted in Figure 5.13 which indicates the vulnerability of RDF as an alternative fuel. For the case of RDF, outlet temperature dropped about 2.2% while MBM also showed the same

phenomena with approximately 1.3% drop, while both the alternative fuels were used with 25% substitution rate. Lower temperature was an indication that the combustion was not complete and as a result the calcination was not reached up to desired degree. A possible reason for the lower temperature was high moisture content for RDF and low heating value for MBM. Suggested substitution rates for RDF and MBM were 8.5% and 14% respectively to maintain the outlet temperature above 1115K.

Based on the simulation results in this section it can be concluded that none of the selected alternative fuels were capable of substituting the energy demand more than 20%. Combining all the outcomes it was revealed that maximum substitution rates for waste tyre, RDF and MBM are given as 14.5%, 8.5% and 13.5% respectively without affecting the process adversely.

5.3.3 Improvement on energy demand

Cement manufacturing is an energy intensive process and any opportunity to reduce the energy requirement are welcomed to curb the energy cost. This study was designed to analyses the impact of alternative fuels and the only possible ways of achieving improvements on energy demand was to reduce the amount of fuel used as no retrofitting was considered in this study. Reducing the amount of fuel was a challenging thing to do as it might affect the process and lead to an unstable product. The parameters that needed to be monitored in this process were the temperature, degree of calcination and the amount of pollutant emission. Lowering the amount of fuels also implies the reduction of emissions.

To investigate potential improvement in energy demand, the preheater tower model was run with a set of fixed parameters and with a variable fuel feed rate. Outlet temperature of the calciner was set to 1113.15K (840°C) and the desired degree of calcination was set to 94%. Energy requirement was calculated from the simulation results in terms of MJ/kg clinker. It was worthy to mention that according to the model's assumption, only 60% of total energy was required in the preheater tower and presented results were calculated accordingly for the entire manufacturing process. Along with the energy requirement, CO₂ emission rate was also considered and a reduction was expected because of the reduced amount of fuel used. Substitution rates for the alternative fuels were fixed according to the finding of this

section. Simulation results are summarised in Table 5.4 where the case of only coal was calculated based on the set of parameters predefined in this section.

Table 5.4: Simulation results for energy efficiency

Fuels (% of thermal energy)	Simulation results			
	Degree of calcination	Outlet temperature °C	Energy requirement MJ/kg clinker	CO ₂ emission kg/ton clinker
Only Coal	94.13%	840.6	3.18	768.9
Tyre 14.5%+Coal 85.5%	94.13%	839.9	3.07	746.1
RDF 8.5%+Coal 91.5%	94.12%	840.3	3.17	752.5
MBM 13.5%+Coal 86.5%	94.12%	840.2	3.13	755.6

The results presented in Table 5.4 show that all three alternative fuels are capable of reducing the energy requirement as well as the CO₂ emission. Data from the local plant were collected for modelling purposes, and with the amount of coal used in the process, it was calculated that the energy requirement was 3.236 MJ/kg clinker for the cement plant. Simulation results presented in Table 5.4 reveal that energy requirements can be reduced to 3.178 MJ/kg clinker without affecting the process when only coal was burnt in the calciner. Even more improvement can be achieved by using alternative fuels with a prescribed substitution rate. Use of waste tyre with a substitution rate of 14.5% could reduce the energy demand of about 3.3% along with a 3% reduction of CO₂. RDF could only replace 8.5% of primary fuel coal and very small improvement could be achieved in terms of energy demand. Nevertheless, RDF reduced CO₂ from stack gas by up to 2% as the simulation results suggested.

As per simulation results, the substitution rate of MBM is 13.5% and at that rate about 1.7% of reduction in CO₂ emission and 1.7% reduction in energy requirement is observed in Table 5.4. In terms of energy saving, MBM was found to be a better option than RDF. The substitution rate of RDF can be increased by drying and reducing the moisture content. Waste tyre was identified as the best option among the three selected alternative fuels.

5.3.4 Concluding remark on preheater tower model

A process model for the cement preheater tower with calciner has been presented in this section and run with three selected alternative fuels. Simulation results discovered that maximum substitution percentage rates are 14.5, 8.5 and 13.5 for waste tyre, RDF and MBM. Maximum 3% reduction of CO₂ was reported when waste tyre was used at suggested substitution rate. Energy saving was also observed for the same case and the percentage of energy saving was 3.3. RDF and MBM also alleviated CO₂ emission from the process with a slight improvement in energy savings. There was an indication that using RDF and MBM might drop the temperature inside the calciner, hence the calcination process might not reach to the desired degree. Drying RDF to reduce moisture and using better quality MBM (with higher heating value) could remove this barrier on using RDF and MBM with a higher substitution rate.

5.4 Conclusion

A preheater tower model has been presented in this section which was developed using Aspen plus software. The preheater tower was considered to have a calciner, a separate combustion chamber to enable most of the calcination, according to the local plant specifications. A few assumptions were made prior to develop the model to make it simple yet effective for serving the purpose of this study. A set of alternative fuels was studied in this chapter to investigate potential improvement on pollutant emission and energy saving. Results presented in this chapter have some encouraging prospects regarding pollutant emission as well as energy savings.

Almost every single alternative fuel studied in this chapter showed their capability to reduce CO₂ concentration on stack gas. MSW was found to reduce CO₂ most compared to the other selected alternative fuel and its magnitude was 6% when MSW was used to substitute 25% of thermal energy. Similar results were observed for RDF which was actually the homogenous portion of MSW. Waste tyre and SS also reduced CO₂ emission up to some extent.

NO_x emission was found to increase for MSW, RDF and MBM which were contradictory to previously published results (Genon & Brizio, 2008; Gulyurtlu et al., 2005). NO_x emission was controlled by a lots of parameters including excess air, flame temperature,

quality of fuel and these parameters vary from plant to plant. Other alternative fuel of this section managed to reduce or keep the NO_x level the same as for the case of coal. In contrast to the NO_x results it was found that only MSW and RDF reduced SO₂ emission compared to the reference case of coal. Apart from MSW and RDF all other alternative fuels released high amounts of SO₂ in the environment. Simulation results of the preheater tower showed that the amount of SO₂ emission could be elevated up to 44% by using waste tyre as alternative fuel at a substitution rate of 25%.

As an indicative parameter, outlet temperature of the calciner is studied in this chapter, knowing that low temperatures might occur for incomplete combustion and affect the degree of calcination. High moisture content of MSW and RDF reduced the temperature in the calciner, as it was suggested by simulation results. It was recommended that MSW and RDF should dry with hot air to reduce moisture before introduction to the calciner. A possible energy saving scenario was investigated by lowering the amount of fuel feed and it was found that about 3.3% of energy saving can be achieved by using waste tyre with 14.5% substitution rate.

Results presented in this chapter reveal several facts, a few of which agreed with previously published literature and a few did not. It needs to be mentioned that emission data from a real plant might vary due to the quality of the alternative fuels and their collection source and with the type of process setup. For simulation results the deciding factors were the elemental analysis of alternative fuel and excess air in the combustion zone. In literature a different set of elemental analysis can be found for a single alternative fuel. Hence if possible, data needs to be collected from the vicinity of the plant or the next best option should be chosen according to the literature. In this chapter it is recommended that MBM with higher calorific value should be used for simulation to increase the substitution rate.

As clinker is not formed at the end of preheater tower, a kiln model is required to study the quality of clinker. The kiln is the next section of the process, whereby hot kiln feed enters the kiln at the end stage of the preheater tower. In next chapter a kiln model is presented with simulation results for different alternative fuels. In the kiln model quality of clinker on the basis of the basic ratios of the oxides is studied.

Chapter Six

Development of Process Model for Kiln

6.1 Introduction

Cement kiln is the most important part of the manufacturing process as most of the complex clinker formation reactions occurs in this stage. The rotary kiln was introduced in the cement manufacturing in the later part of nineteenth century. Rotary kiln consist of a huge rotating steel furnace which is placed at a slope and turns slowly to transport material from the high end to the lower one. The inside of the kiln is lined with refractory brick to protect the metal from extreme heat. The lower end of the kiln contains the burner where fuel is ignited to produce a high temperature flame. The other end of the kiln is referred to as the feed end where preheated raw meal from the preheater tower enters the kiln for pyroprocessing.

At the feed end of the kiln, the temperature of pre-calcined material is about 900°C and gas temperature is about 1100°C. Small inclination and slow revolution of the kiln allows the material to progress slowly toward the hot end of the kiln. Within the extreme condition of the kiln, several reactions occur. Among the most important reactions are the remaining calcination and the reactions between the oxides of calcium, silicon, aluminium and iron to produce the final product clinker. The red-hot clinker is discharged from the end of the kiln and passed through coolers to cool down. Depending on the manufacturing process, rotary kilns can be classified into the following types (Cembureau, 1999):

- Wet process kilns.
- Semi-dry process kilns.
- Dry process kilns.
- Preheater kilns.
- Precalciner kilns.

For the current study only a precalciner kiln is considered and the description of the precalciner system can be found in chapter 5.

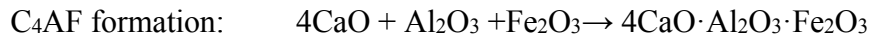
Considering the importance of the kiln, numerous attempts were taken to model the kiln. Procedures involved for kiln model analysis include structural modelling, static nonlinear analysis, dynamic linear analysis and structural verification. Most of the researches concentrated on structural modelling by using CFD software and finite element method (Mastorakos et al., 1999; Mujumdar & Ranade, 2006; Mujumdar et al., 2007; Spang, 1972; Boateng & Barr, 1996; Martins et al., 2002; Paul et al., 2002; Giddings et al., 2002; Marin et al., 2001). Numerical technique for solving the boundary value problem was incorporated to study flame shape, temperature of the kiln, velocity profile of particles in the kiln system (Giddings et al., 2002) and oxygen enrichment in the burning zone (Marin et al. 2001). Unlike CFD based modelling, Kaantee et al. (2004), Zhang et al. (2011) and Rahman et al. (2013, 2014) used Aspen Plus software to simulate the cement clinker production focusing on clinker chemistry and thermodynamics in the rotary kiln and in the calciner.

In this chapter an Aspen plus based model is presented for the kiln which is validated by the results available from the local cement plant and from literature. To facilitate alternative fuel firing in the kiln, the model was modified accordingly. Different types of solid alternative fuels are examined in this chapter to predict the emission factor and clinker quality. Among the alternative fuels emphasis was given to a set of agricultural biomass which has a great potential in the context of the local region.

6.2 Pyroprocessing reactions in kiln

The main energy intensive phases of the cement production process take place inside the calciner and kiln during the production of clinker. A large amount of thermal energy is required to create enough heat for calcination in the calciner and pyroprocess in the cement kiln. The split of energy requirements for calciner and kiln are 60% and 40% respectively. At the calciner, raw meal is preheated and almost 90% of calcination takes place in the calciner to release CO₂ by decomposing CaCO₃ and MgCO₃. The rest of the calcination occurs in the kiln to enable all CaO for pyroprocessing reactions. The main constituent of clinkers is formed by the reaction of CaO with other oxides which are the key of kiln pyroprocessing. Apart from the calcination reaction at the opening end of the kiln the major reactions in the kiln are:





The formation of these four constituents in the kiln is not straight forward and detailed breakdowns of reactions with reaction enthalpy were given in Chapter 2.

A schematic diagram of the temperature profile along with the qualitative phase of the main reaction in the kiln is given in Figure 6.1 (Stadler et al., 2011). Exact temperature of the kiln flame is not typically measured, as adequate temperature sensors are not generally incorporated with the kiln. However, a predicted temperature profile can be constructed based on the temperature of the kiln gas and the state of the solid inside the kiln (Stadler et al., 2011). About 40% of total thermal energy is required in the kiln to complete the clinkerization process. Depending on the process type, one or more alternative fuels can be utilised in the kiln along with the primary fuel, coal. Typically, alternative fuels are injected with the primary fuel by using a multi-channel burner, which is capable of introducing solid and liquid fuel at the same time in the burning zone. A usual arrangement of multi-channel burner is given in Figure 6.2 (Wellington & Dhanjal, 2008).

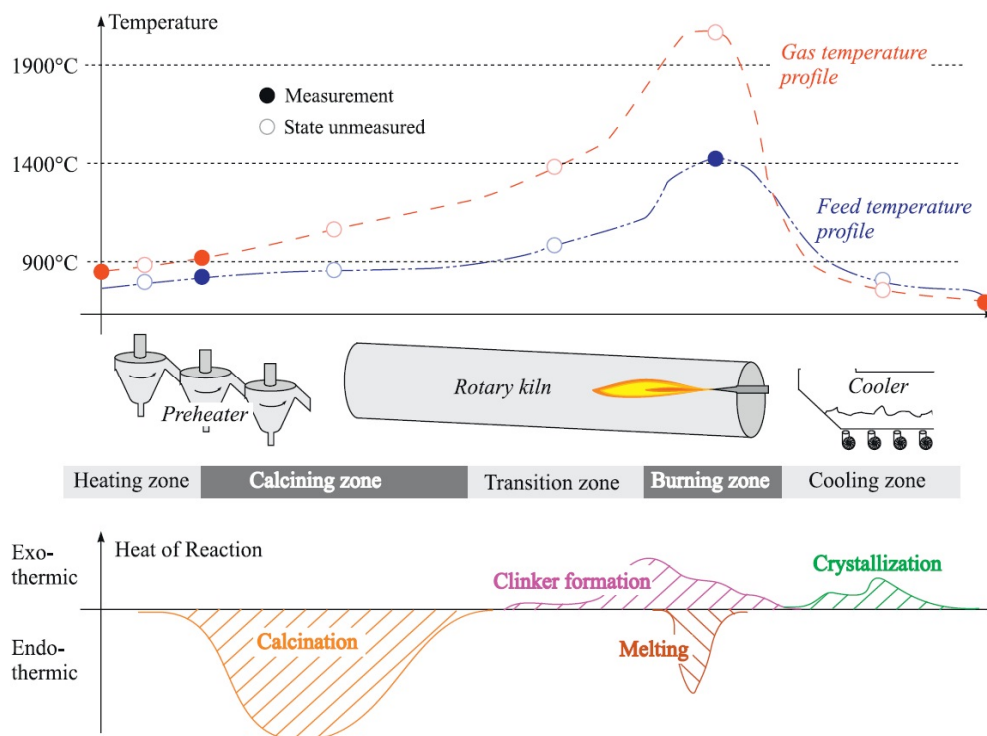


Figure 6.1: Temperature profile and the qualitative profile of the heat of reaction

Source: Stadler et al., 2011

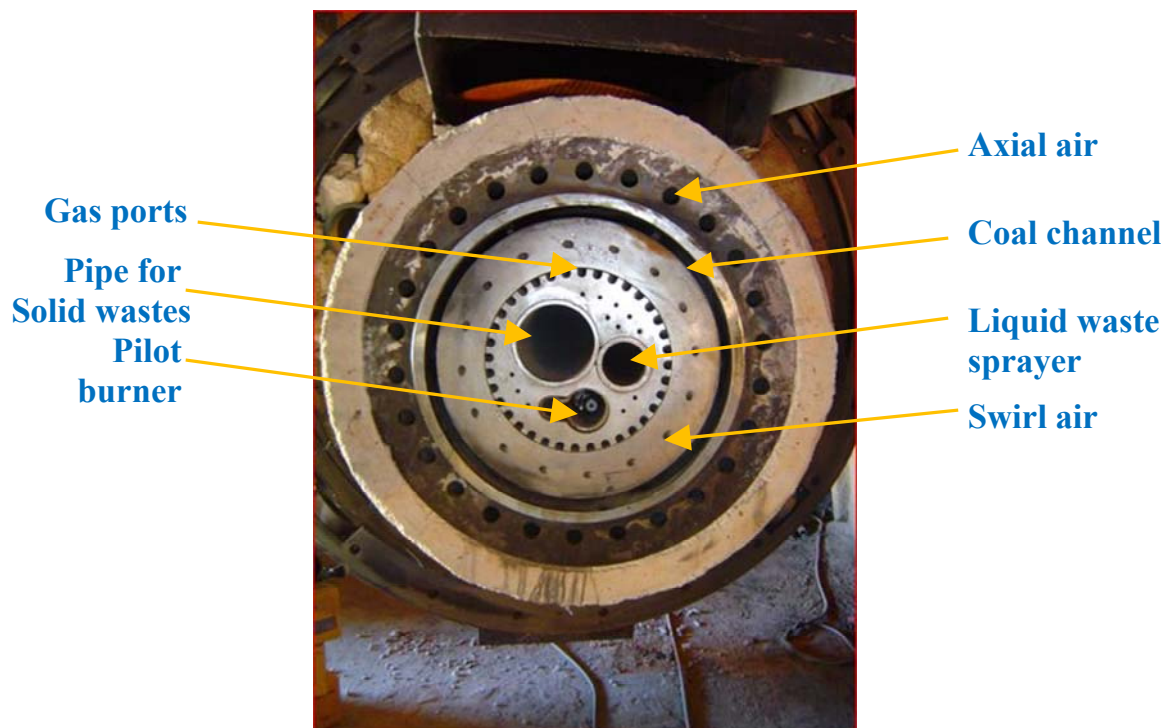


Figure 6.2: Multi-channel burner nozzle
Source: Wellington and Dhanjal, 2008

6.3 Alternative fuels for kiln

Introduction of new technology to cement manufacturing make the process much easier to deal with alternative fuels. Utilization of a modern dryer and shredder, conveyer belt and multi-channel burner facilitates the maximum usage of alternative fuel in the cement industry. Almost all types of alternative fuel can be fed in the rotary kiln. Detailed description of different types of alternative fuels were given in chapter 3. As the clinker formation occurs in the kiln and a very high temperature flame is required for that, it is recommended to use alternative fuels with high heating value and low moisture content. The cement industry can acquire alternative fuels from a wide variety of sources. The diversity of sources and inconsistent nature of these waste materials pose a difficult challenge to the cement producers regarding the storage, handling and feeding of alternative fuels into the system.

In this chapter, two different types of alternative fuels are considered to study with a process model. These are agricultural biomass and industrial wastes with MSW. The major challenges of implementing alternative fuels are to ensure that pollutant emission and the

quality of the clinker are within acceptable levels. Using alternative fuels in the kiln system may lower the flame temperature which will affect the clinker quality. Also introducing alternative fuel should not reduce the daily production of clinker which may offset the advantage achieved by energy saving. Alternative fuel can substitute 20% of the total thermal energy requirement according to the rule of thumb (Prisciandaro et al., 2003, Chinyama, 2011). In real plant instance, this may not be true due to lots of constraints.

6.4 Agricultural biomass as alternative fuel in cement kiln

Numerous studies are available in literature regarding co-firing of agricultural biomass with coal but only a few identifies the impact of burning them in cement kilns. This section examines the feasibility of five agricultural biomasses, namely bagasse, almond shell, rice husk, coffee husk and olive husk, as alternative fuels in cement kilns. The biomasses were selected on the basis of their availability, world wide application and inadequate disposal option.

The sugar cane industry waste bagasse is generally consumed by the same industrial plant for heat and electricity generation. Incinerating bagasse in a cement kiln ensures that all the combustion residue is confined within the clinker and enhances the quality of cement. In Australia the total annual sugar cane crop is about 35.5 million tonnes (Mt), of which 14% is cane fibre, resulting in a total available energy of above 90 PJ (Clean Energy Council, 2008).

The rice husk (or hull) is the outermost layer of the paddy could be one alternative fuel option for Australian cement industry (Santiago, 2013). In 2013-14 Australia produced about 852 kt of rice which implies over 170 kt of rice husk production (ABARES, 2014). Another potential source of alternative fuels is waste from almond industry as Australia is the second highest almond producer of the world (7%) and the total production in 2013 is about 73,361 tonnes (Almond Board of Australia, 2013, 2012). The major wastes from the almond industry are the husk and the shell (Figure 6.3a.).

During the last decade Australian olive oil production has increased significantly and it is expected that the production will reach 90,000 tonnes or 15M litres of olive oil for 2014-15 (Horticulture Australia Limited [HAL], 2012). This expansion in the Australian olive

industry can be expected to result in the production of over 62,500 tonnes of solid waste and over 350×10^6 litres of liquid waste per annum (Nair and Markham, 2008). The cement industry can be the destination of the solid waste from the olive industry to achieve sustainable production under a clean environment. Coffee husk is being used as alternative fuel in the cement industry in major coffee producing countries like Brazil (Lafarge, 2008). In this study we include coffee husk to promote local coffee production by improving the cost competitiveness of the local coffee industry and produce an environmental friendly fuel for the cement industry at the same time (Figure 6.3b).



Figure 6.3: a) Almond shell, b) Coffee husks used as alternative fuel

Source: Lafarge, 2008

6.4.1 Chemical composition of alternative fuels

Before the implementation of any alternative fuel in the cement industry the manufacturer needs to examine the impact of the alternative fuel on emission and quality of the clinker. The chemical composition of the chosen alternative fuels could provide an initial insight into the potential emission from combustion. For instance an alternative fuel containing more fixed carbon is expected to produce higher CO_2 , and higher sulphur content may cause higher SO_x emission. Still proper modelling and simulation is required to estimate the amount of pollutant emission since many chemical reactions occur in the kiln. Researchers have studied comprehensively the chemical composition of different agricultural biomass along with the combustion characteristics. Table 6.1 presents the proximate and ultimate analysis of the selected five alternative fuels (Demirbas, 1997, 2003; Skodras et al., 2006; Sami et al., 2001; Suarez & Luengo, 2003).

Table 6.1: Elemental analysis of fuel

	Coal (Plant data)	Baggasse (Sami et al. 2001)	Almond shell (Skodras et al. 2006)	Rice Husk (Demirbas 2003)	Coffee Husk (Suarez and Luengo, 2003)	Olive Husk (Demirbas 1997)
Proximate analysis (wt%)						
Moisture	1.35	10	9.7	9.96	10	9.2
Ash	18.55	11.27	3.72	22.88	2.4	3.6
Volatile matter	24.15	73.78	74.12	60.55	78.5	70.3
Fixed carbon	57.3	14.95	22.16	16.63	19.1	26.1
Elemental analysis on dry basis (wt%)						
C	69.43	44.8	49.68	33.96	47.5	48.2
H	3.83	5.35	8.18	5.31	6.4	5.98
N	1.5	0.38	1.04	0.11	-	1.54
S	0.36	0.01	-	-	-	-
Cl	0.2	0.01	-	-	-	-
O	5.58	38.13	37.38	37.8	43.7	40.68
LHV (MJ/kg)	27.4	17.3	29.86	13.5	18.39	19.0

6.5 Kiln process model

Kiln is the key equipment for the cement manufacturing process as several complex chemical reactions along with heat transfer in solid liquid and vapour phases of different materials occur in this stage. In this section an Aspen Plus model was developed to identify the impact of alternative fuels on process and product quality. Aspen plus has the unique capability to simulate chemical reactions within solid, liquid and vapour phases and has a database comprising a wide range of physical and chemical properties for chemicals, solids and polymers. Unit operation blocks from Aspen database was used to construct the model and the operation blocks were connected with material stream and/or heat stream. Descriptions of a set of operation blocks were presented in chapter 4 along with their specific function in the model. The kiln model was developed with mass and energy balance principle and with some basic assumptions.

6.5.1 Model Principle

In this study Aspen Plus software is used to model a cement kiln on the basis of energy and mass balance principle with known stoichiometry of the chemical reactions. Different unit operation blocks were used to carry out specific tasks of the process such as fuel

decomposition, combustion, chemical reactions, cooling and separation. In the current model all combustion was carried out on an energy balance basis. Combustion of the conventional fuel as well as the alternative ones took place in two Aspen Plus operation blocks. These blocks were RYield and RGibbs where decomposition and the combustion occur respectively. Stoichiometric air was fed directly in the RGibbs reactor block. Decomposition heat from RYield reactor was transferred directly to the RGibbs reactor block. The combustion residue and generated heat were then carried to the next series of operating blocks where clinkerization reactions occur in the presence of heat.

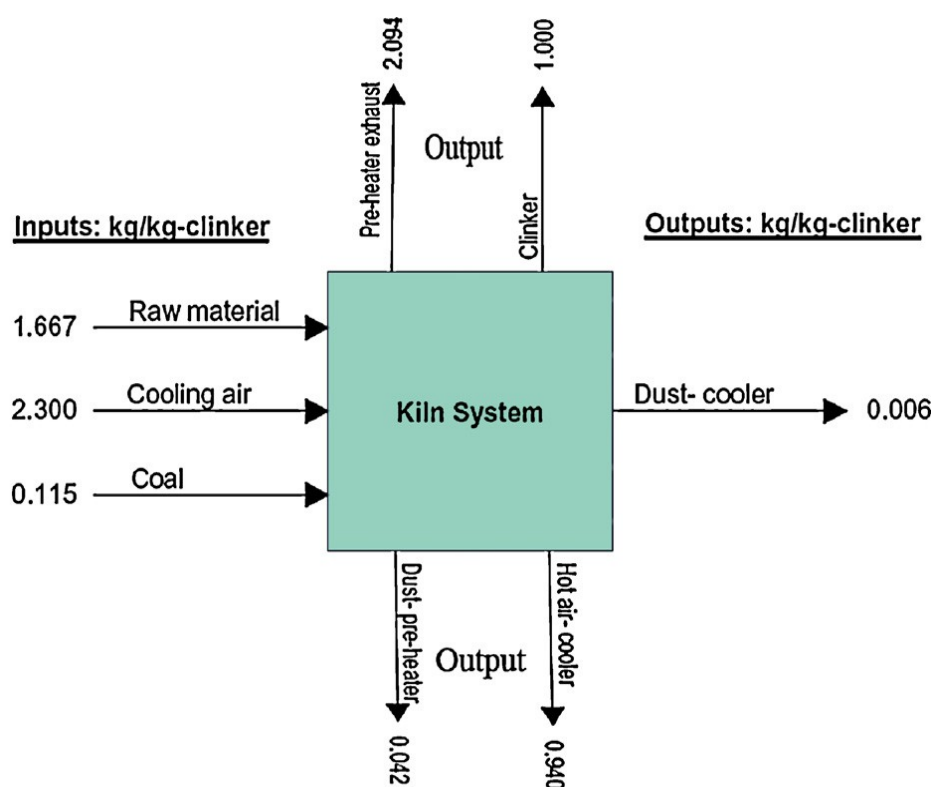


Figure 6.4: Typical mass balance of the kiln system

Source: Engin and Ari, 2005; Saidur et al., 2011

The clinkerization process of the kiln was carried out by using three reactor blocks with the mass balance principle. A typical mass balance system of the kiln is given in Figure 6.4 which shows the required input and predicted output from the kiln to produce 1kg of clinker. The reaction stoichiometry of the clinkerization process are well established to maintain the quality of the clinker. The mass balance principle along with the reaction stoichiometry allows the usage of the Aspen plus RStoic reactor block to model the kiln. A series of reactor blocks were used for the different phases of clinkerization that occur at

increasing temperatures inside the kiln. Kiln gas is separated from the product flow and hot product is cooled down by using a heat exchanger operation block. Air with ambient temperature is used to cool the hot clinker and finally the stack gas and clinker is separated by a separator block.

Large number of methods are available in the Aspen Physical Property System and three property methods namely IDEAL, SOLIDS and RKS-BM have been used for the kiln model. IDEAL property method enables the model to deal with gaseous and liquid material inside the kiln which accommodates Raoult's law and Henry's law. Permanent gases may be dissolved in the liquid and can be modelled by using Henry's law. The properties of solids and fluid phases cannot be calculated with the same type of models. Therefore the components are distributed over the sub streams of types MIXED, CISOLID and NC and their properties are calculated with appropriate models. During the mechanical processing of raw materials and fuel, physical properties can often be handled as nonconventional components with an overall density and an overall heat capacity. Beside this when the solids are decomposed into individual components (coal and alternative fuels decomposition) they normally occur in the CISOLID sub stream. To handle the nonconventional (NC) component and CISOLID sub stream and to facilitate solid material processing inside the kiln, 'SOLIDS' was the appropriate property method available in Aspen plus property method database. For coal and solid fuel combustion, the property method RKS-BM was used in the model. The RKS-BM property method uses the Redlich-Kwong-Soave (RKS) cubic equation of state with Boston-Mathias alpha function for all thermodynamic properties. As mentioned earlier the coal and alternative fuels were categorised as a nonconventional component, therefore a set of models needs to be incorporated to the stream. HCOALGEN and DCOALIGT models were used for enthalpy and density calculation which is suitable for coal and other solid alternative fuels.

6.5.2 Model Assumption

For the current study an Aspen Plus model was developed for a proposed alternative fuel kiln. The production capacity of the kiln was assumed to be 2200t/day with an option of burning alternative fuel along with the primary one, coal. To reduce the complexity of the model a few basic assumptions were made without any loss of generality. Assumptions for the current study were:

- ✓ Unlike the real process, fuel combustion took place in two different reactors: fuel decomposition unit and combustion unit namely RYield and RGibbs respectively.
- ✓ Throughout the model, N_2 of air was considered inert and NO_x generation from the processes was due to the combustion of the fuel in the kiln.
- ✓ CO_2 was produced through calcination of kiln feed and the combustion of fuels.
- ✓ For simplicity the entire kiln was modelled by using three unit operation blocks which distribute all the chemical reactions in a continuous manner.
- ✓ Ash was considered to be nonreactive in the combustion process.
- ✓ Any air leakage in the calciner system was not considered throughout the model.
- ✓ The thermal energy requirement in the kiln was assumed to be 40% of the total energy requirement which is the specification provided by the local cement plant.
- ✓ The energy requirement for the process was set according to the reference plant specification.
- ✓ 10% of excess air was considered in the burning zone of the kiln as it was discussed in section 4.7.

The process model of the kiln in Aspen Plus flow sheet is given in Figure 6.5 which consists of reactors, separator and cooler unit operation block. All the blocks were connected with material and heat streams. The operating conditions of the kiln in terms of mass flow, temperature and pressure were set according to the collected data from the reference plant. The kiln feed data were also collected from the local cement plant.

A wide range of operating parameters was required for the successful construction of the model which includes:

- ✓ Mass flow rates of all incoming streams.
- ✓ Temperature and pressure of all incoming material streams.
- ✓ Heating values and chemical composition of the fuels.
- ✓ Composition of kiln feed in terms of mass or mole fraction.
- ✓ Percentage of excess air in the kiln and mass flow rate of primary air.
- ✓ Particle size distribution of solid fuel and kiln feed.

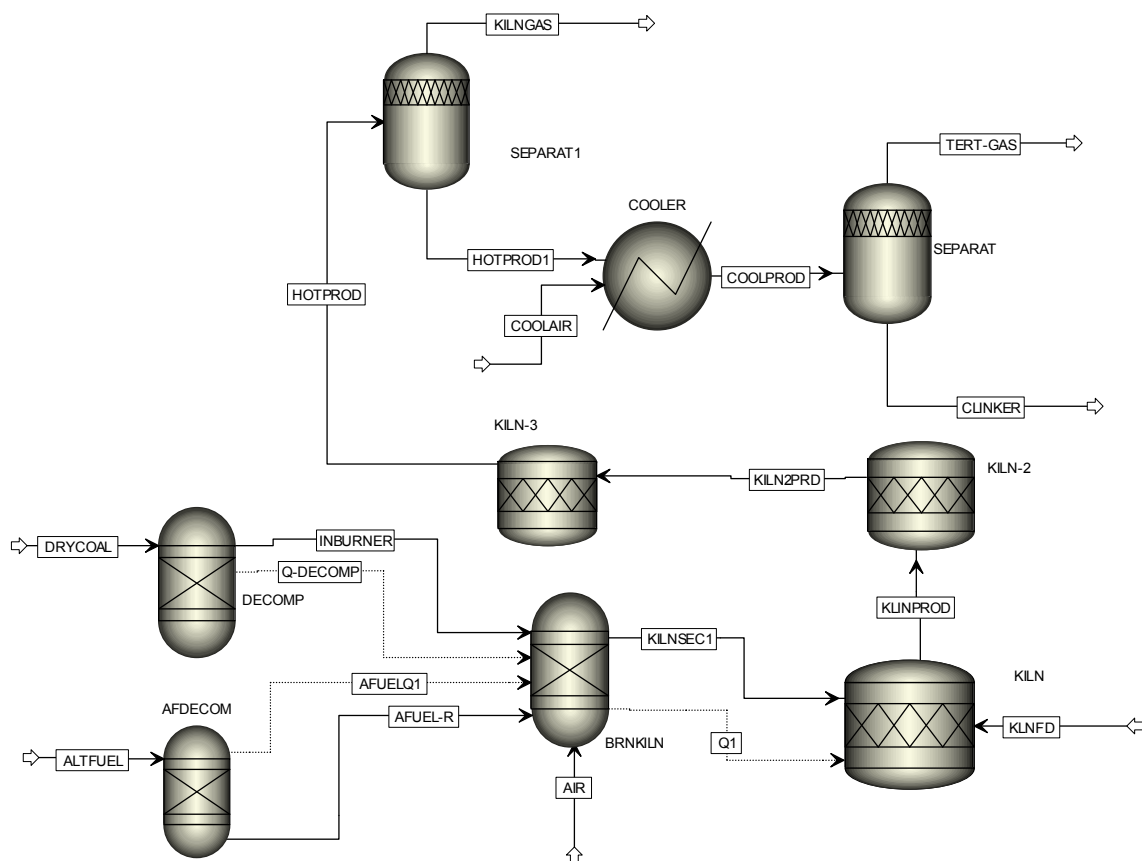


Figure 6.5: Kiln proces model for agricultural biomass as alternative fuel

6.5.3 Model Validation

Simulation results were verified against the measured data which were collected from the local cement plant. The data consisted of the constituents of raw feed, clinker and fuel (coal), temperature and pressure at reference points, mass flow rate, thermal energy requirements and other operating parameters. Data related to the clinker in terms of component as well as chemical breakdown were also available in literature. For validation only coal was considered as fuel in the process, hence no mass flow was considered for the stream ALTFUEL.

The simulation results in terms of clinker composition were in very good agreement with the plant data and the data available in literature. Simulation results are presented along with the plant data in Table 6.2 which indicate that the proposed model has the capability to predict the outcomes of the cement manufacturing process. Small variations were found in the chemical component of some minor constituents such as MgO , Na_2O , K_2O and SO_3 which may be due to the assumptions used when constructing the model. Ash content was

assumed to be inert in the system while actually ash can be highly reactive in the high temperatures inside the kiln and may increase those aforementioned minor constituents.

Table 6.2: Validation of simulation results against plant data

Input						
Material streams			Plant Data			
Kiln feed (kg/s)			27.902			
Coal (kg/s)			1.181			
Excess air in the system			10%			
Output						
Component of Clinker	Plant Data	Simulation results	Chemical breakdown of clinker	Reference data (Hewlett, 2003)	Plant Data	Simulation results
C ₄ AF	11.84	11.7	CaO	60-67	66.79	66.72
C ₃ A	8.58	8.93	SiO ₂	17-25	21.84	21.68
C ₂ S	15.95	15.99	Al ₂ O ₃	3-8	5.72	5.81
C ₃ S	61.26	60.92	Fe ₂ O ₃	0.5-6.0	3.89	3.84
LSF	96.0	93.93	MgO	0.1-5.5	1.1	0.14
AR	1.47	1.51	Na ₂ O+ K ₂ O	0.5-1.3	0.68	0.19
SR	2.273	2.25	SO ₃	1-3	0.22	0.02
HM	2.124	2.13				
Free lime	1.1	1.19				

* LSF=Lime Saturation Factor, AR= Alumina Ratio, SR= Silica Ratio, HM=Hydraulic Modulus

6.6 Simulation results and discussion

A processes model for cement kilns was constructed with the option of alternative fuel firing. Five agricultural biomasses were selected to be used in the kiln model to assess their performance. The model was run with different substitution rates of alternative fuels. The concentrations of pollutants in the flue gas were examined along with amounts of free lime present in the clinker.

Total CO₂ emissions from the clinker production process depend on the fuel and quality of raw feed. Approximately 977 kg of CO₂ is produced for each tonne of clinker (Choate,

2003). In a preheater and calciner kiln system about 75% of the CO₂ emitted from the preheater tower. This indicates that the kiln itself is accountable for about 200 kg CO₂ generation per tonne of clinker. Figures 6.6 and 6.7 represent the simulation results in terms of CO₂ and CO emission from the kiln system while burning alternative fuels in a fixed ratio.

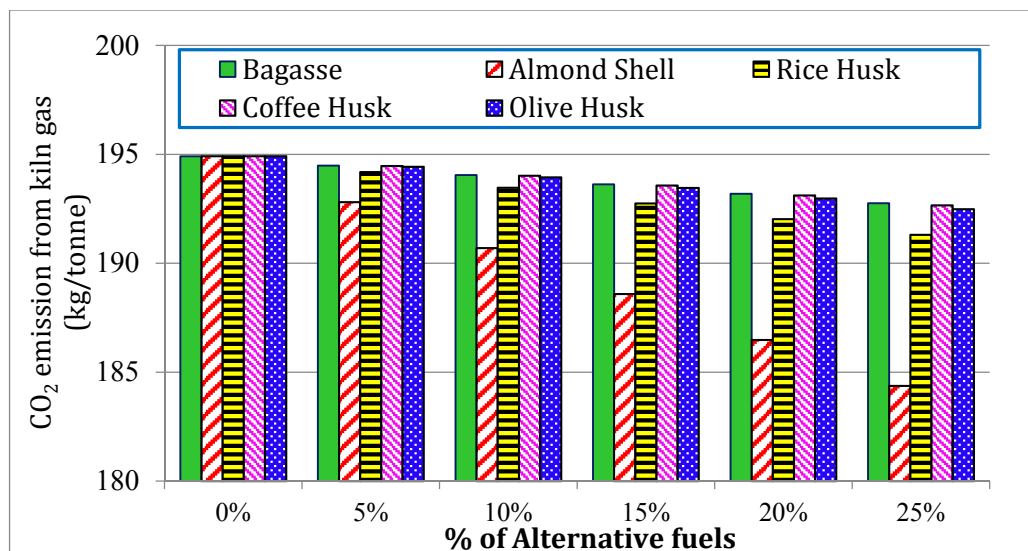


Figure 6.6: CO₂ emission from kiln (kg/tonne clinker)

It is found that all selected alternative fuels are competent to reduce the CO₂ emission from the kiln to some extent. Among the selected alternative fuels almond shell is found to reduce the CO₂ about 5.4% while for others the reduction was between 1 to 2%. Almond shell has higher heating value than coal and all other selected agricultural biomass, which implies that less amount of fuel is required to meet energy requirement for clinker production as per local plant specification. Less amount of fuel mix in the kiln leads to a reduced CO₂ emission in spite of the higher carbon content in the almond shell. The same phenomena can be seen in CO emission from the kiln, where again almond shell is found to be the best option among the selected agricultural biomasses. On contrary, rice husk has very low carbon content but its low heating value did not allow to reduce CO₂ emission as much as almond shell. Thermal energy substitution of 25% by almond shell leads to a 3.6% reduction of CO. In the European standard CO emission from cement plants is allowed to be as high as 2000 mg/Nm³ (WBCSD, 2012) whereas in the present study it was found to be within 1050 mg/Nm³. Unfortunately in Australia, a national emission standard is not available for a cement plant. Available data for emission varies from state to state (Edwards, 2014) and in Victoria the emission limit of CO is 2500mg/Nm³. In order to keep CO concentration on the kiln gas below 3.1 kg/tonne clinker, which is equivalent to 1000mg/Nm³, alternative fuel substitution was allowed up to 20%, 15%, 12% and 13.5% for bagasse, rice husk, coffee husk and olive

husk respectively. In the case of almond shell, it can fulfil at least 25% of the thermal energy requirement without any increase in CO emission.

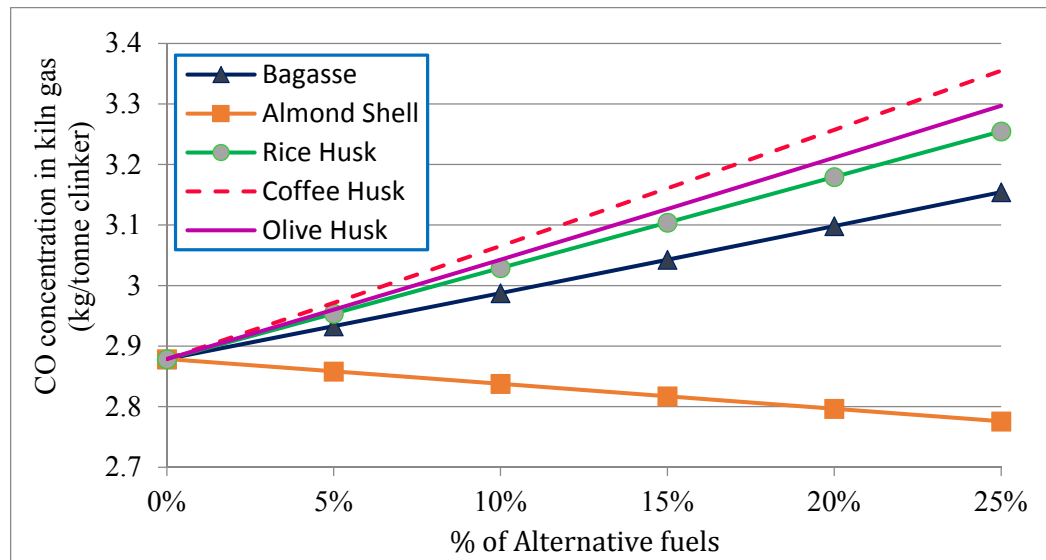


Figure 6.7: CO emission from kiln (kg/tonne clinker)

Percentages of NO_x and SO₂ in the kiln gas are dependent on the fuel type, feed rate, excess air in the burning zone and flame temperature (Walters et al., 1999). One tonne of cement production is accountable for 1.5 to 10 kg of NO_x emission (Naik, 2005). Figure 6.8 illustrates NO_x concentration in the kiln gas. In Australia (New South Wales) the maximum limit of NO_x emission from a cement kiln is 800 mg/Nm³ (Edwards, 2014). The results show that thermal substitution up to 15% for each selected alternative fuel is permissible regarding NO_x emission. In fact the substitution of almond shell up to 25% will keep the NO_x concentration in the kiln gas below the limit.

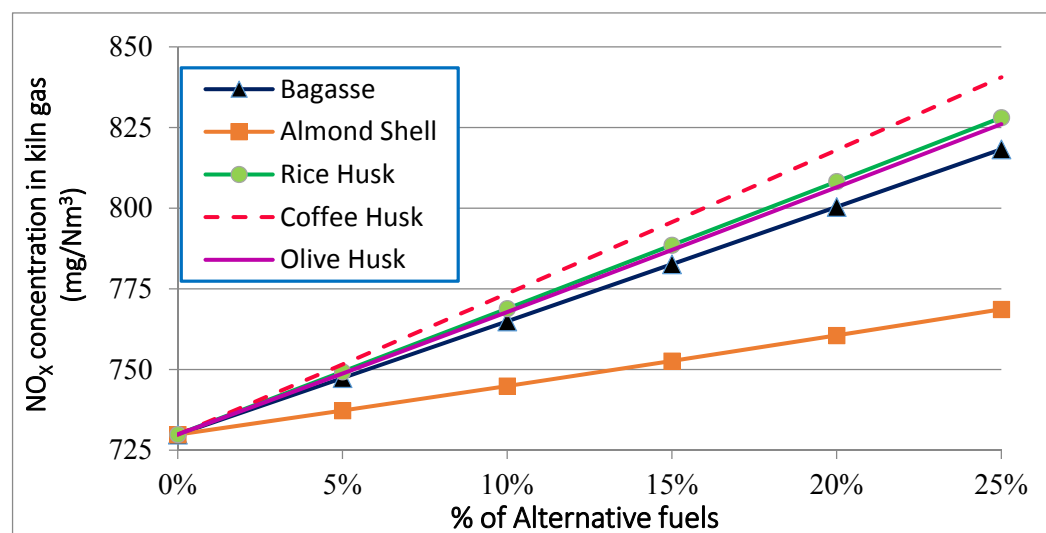


Figure 6.8: NO_x concentration in the kiln gas (mg/Nm³)

Figure 6.9 indicates that using any of the selected agricultural biomass leads to a consistent reduction of SO_x in the kiln gas, which agrees with the earlier published results (Sami et al., 2001). It is worthy to mention that the tolerable limit of SO_x emission around the world is 200 to 500 mg/Nm³ (Edwards, 2014) and in the model results it is below 100 mg/Nm³. This rate of emission is acceptable though it is higher than the limit of New South Wales (Australia) which is 50 mg/Nm³.

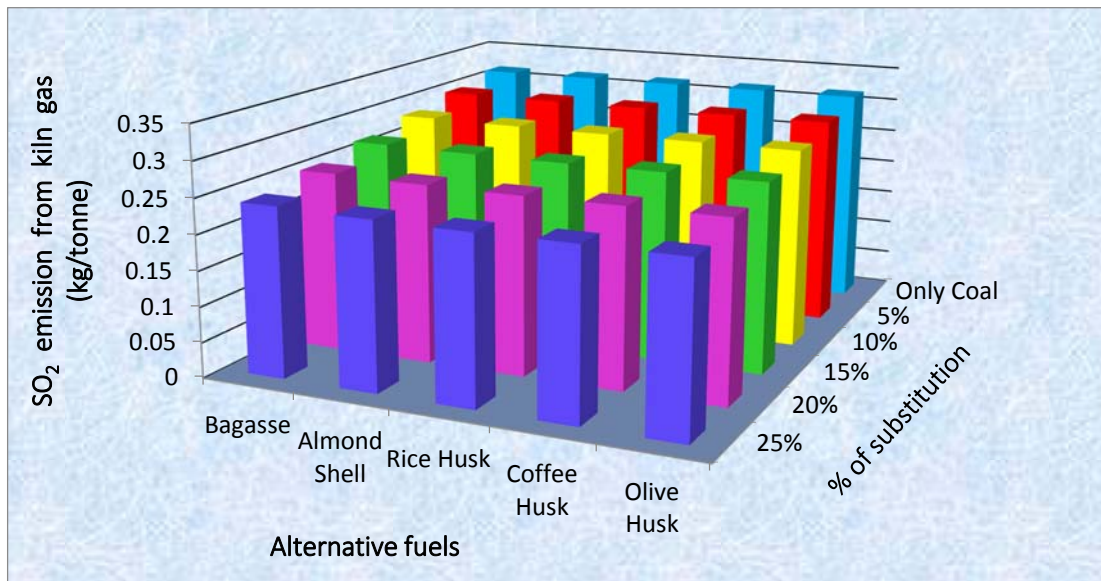


Figure 6.9: SO₂ emission from calciner (kg/tonne clinker)

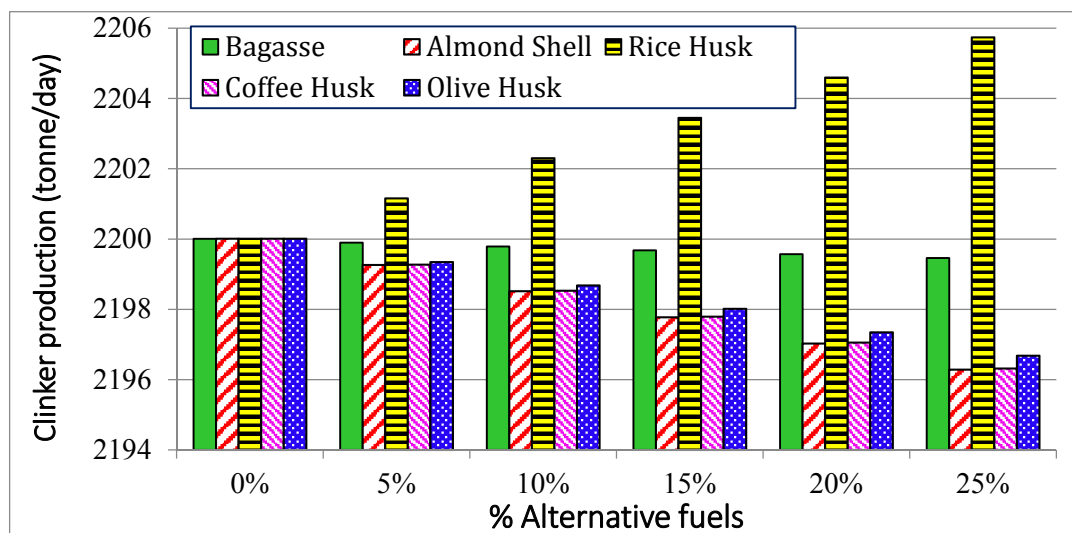


Figure 6.10: Daily clinker production from simulation results (tonne/day)

Clinker production may be affected due to introducing alternative fuels to the kiln system and the economic benefits gained by using alternative fuel can be eliminated with the

reduced production. Results illustrated in Figure 6.10 indicate that apart from rice husk all the other alternative fuels of this study may cause a reduction of clinker production. The modelled kiln capacity was 2200 tonne/day and if allowed up to 2198 tonne per/day all the alternative fuels can be used to substitute 15% of thermal energy.

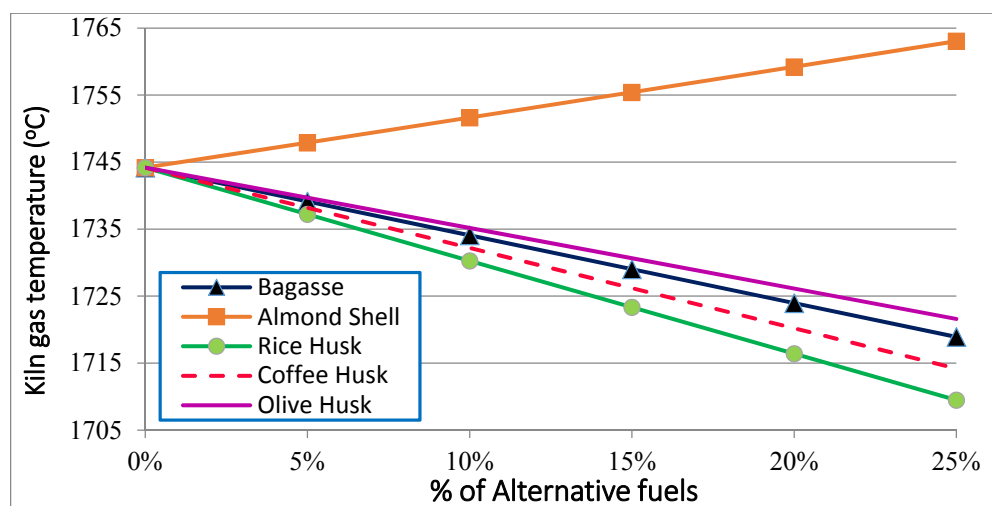


Figure 6.11: Outlet gas temperature (°C)

Temperature of the flame in the kiln is another property of kilns which controls the quality of the clinker. Low flame temperature may result in rapid crystallisation of clinker which change the constituent percentage in the clinker. Since there is no suitable sensor to measure the flame temperature, kiln gas temperatures are often used to estimate the environment inside the kiln. Standard kiln gas temperature varies from 1700°C to 2100°C. Figure 6.11 shows the simulated kiln gas temperature while using different alternative fuels. All the alternative fuels except almond shell were found to reduce the kiln gas temperature within the allowable limit.

An important parameter in clinker production is free lime which is usually used to identify how the clinker is burnt (Aldieb and Ibrahim, 2010). The appropriate free lime level is useful to monitor the kiln process and to achieve considerable thermal energy savings (Buman et al., 2009). Figure 6.12 shows the free lime data generated from the simulation. The result shows that only the usage of rice husk reduces the free lime content in the clinker. The increases of free lime due to the usage of other agricultural biomasses are not substantial and may not affect the clinker quality.

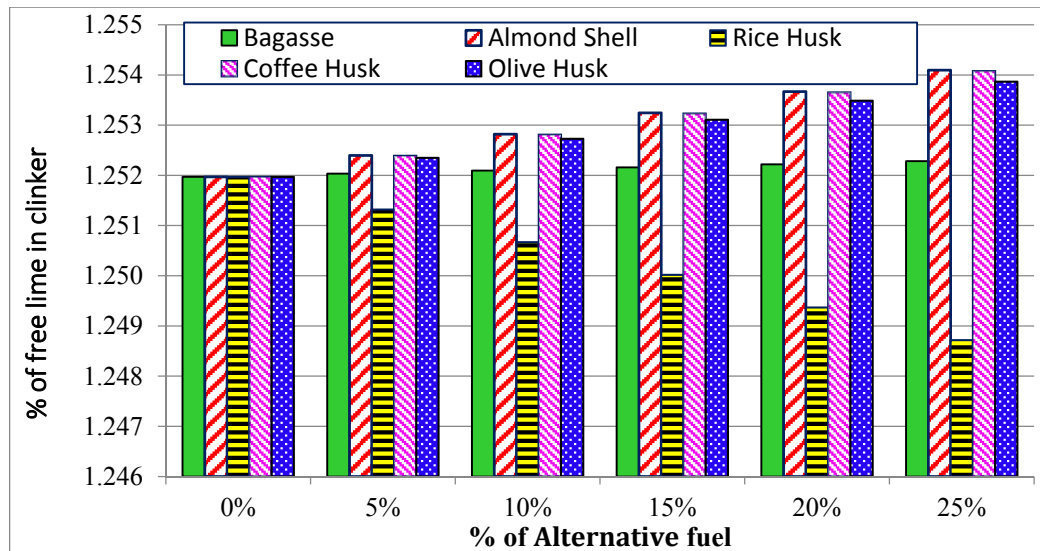


Figure 6.12: Percentage of free lime present in the clinker

To examine the energy saving, the kiln model was used with the substitution rates for the alternative fuels of 20%, 15%, 15%, 12% and 13.5% for bagasse, almond shell, rice husk, coffee husk and olive husk respectively. Those percentage values were determined by the pollutant emission restrictions and daily production of clinker required. After fixing the substitution rate the amount of total fuel feed in the system was reduced until the model generates the results which agree with all the cut-off points. The substitution of any alternative fuel leads to an improvement in terms of energy savings. The results obtained from the simulation are summarised in Table 6.3.

Table 6.3: Simulation results for energy saving

Fuels (% of thermal energy)	Simulation results		
	Kiln Gas temperature °C	Energy requirement MJ/kg clinker	CO ₂ Emission kg/tonne clinker
Only Coal	1744	3.18	194.91
Bagasse 20%+Coal 80%	1724	3.13	192.67
Almond shell 15%+Coal 85%	1756	3.13	188.17
Rice husk 15%+ Coal 85%	1723	3.09	191.63
Coffee Husk 12% + Coal 88%	1729	3.08	192.33
Olive husk 13.5% +Coal 86.5%	1731	3.11	192.79

The results presented in Table 6.3 show that the selected biomasses are capable of reducing the energy requirement as well as the CO₂ emission. A potential 3% energy savings along with a 1.3% decrease in CO₂ emission is observed when substitution rates of coffee husk is 12%. Almond shell is capable of reducing the CO₂ by 3.5% but that comes at the price of reduction in total clinker production and a lower flame temperature. From the simulation results it was found that using rice husk for 15% of thermal energy substitution may increase the total clinker production around 3 tonne per day. Along with that it reduces the energy requirement and CO₂ emission about 2.6% and 1.7% respectively. Kiln gas temperature was found to be low while using rice husk as alternative fuel and that may be a concern for the clinker quality issue. Bagasse can be used up to 20% of total thermal energy which will lower the CO₂ emission by 1.2% and improve the energy savings about 2%. Olive husk has the potential to achieve 2.3% energy improvement with a 1.1% reduction in emitted CO₂.

6.7 Concluding remark on kiln model

The cement industry is considered a major emission source of greenhouse gas (mainly CO₂) and acidic gases (mainly NO_x and SO₂) in the industry sector. Reducing pollutant emissions along with the energy savings becomes a challenge for cement manufacturers due to the recent environmental regulations. Alternative fuels offer a feasible option to the manufacturer to mitigate the emission. Based on the available data from plant and literature, this section presented an Aspen plus based cement kiln process model to examine the impact of five agricultural biomasses as alternative fuel. Aspen Plus was used to study the operation parameters which influence the constituent of clinker and kiln gas composition.

Simulation results presented in this section showed that thermal energy substitution of 20%, 15%, 15%, 12% and 13.5% can be done by bagasse, almond shell, rice husk, coffee husk and olive husk respectively. Coffee husk was found to gain about 3% of energy efficiency over the reference case of 100% coal burning in spite of a small reduction in the total production of clinker. On contrary rice husk could increase the daily production with a 2.6% reduction in the CO₂ emission. NO_x emission was found to be higher than the reference case for all selected alternative fuels; this can be kept below the regulation limit by lowering the substitution rate. SO₂ emission was found to be reduced for all five agricultural biomasses, while except almond shell the other alternative fuels are

accountable for a higher discharge of CO. Simulation results show that the temperature inside the kiln becomes lower while using the agricultural biomasses with an exception for almond shell. Kiln temperature is one of the key factors which control the quality of the clinker and needs to be monitored closely. Results for the amount of free lime present in the clinker show that only rice husk has the ability to reduce it and for the other alternative fuels it might increase by a small amount which may not affect the clinker quality.

6.8 Modified Kiln Model

The kiln model presented in the previous section was validated by local plant data and was found effective to predict emission factor due to introduction of alternative fuel in the process. One of the biggest drawbacks of the model was its incapability to identify the true amount of constituent present in the clinker as it was assumed that the combustion ash did not take part in the clinker formation reaction and stayed as it was in the clinker. To overcome this problem a modified kiln model was developed in this section. An additional reactor block and calculator block were placed in the model to decompose the ash into its elemental composition. The decomposed component was then carried to the kiln reactor block to take part in the clinker formation reactions. It is worthy to mention that in the model, ash was considered as a nonconventional component while the decomposed components are in conventional form and hence can take part in the chemical reaction. Another modification was done in the cooler section by using a MHeatX operation block which enables a much matured approach for heat exchange between two different streams, red hot clinker and cool air. A process flow sheet of the modified kiln model is given in Figure 6.13. Apart from the assumption regarding the reactivity of ash, all basic assumptions remain the same.

The model was constructed on the basis of mass and energy balance principle. Like the previous version of the kiln model, three property methods were considered to handle all sorts of chemical components effectively. Selected property methods are IDEAL, SOLIDS and RKS-BM. Along with the previously mentioned operating parameter, ash analysis of coal and all other alternative fuels were required to run the model successfully. To validate the model, plant data were used and only coal was considered as the fuel. Ash analysis of coal was also collected for the same cement plant. Validation results are presented in Table 6.4.

Table 6.4: Modified model validation

Input						
Material streams			Plant Data			
Kiln feed (kg/s)			26.77			
Coal (kg/s)			1.18			
Excess air in the system			10%			
Output						
Component of Clinker	Plant Data	Simulation results	Chemical breakdown of clinker	Reference data (Hewlett, 2003)	Plant Data	Simulation results
C ₄ AF	11.84	11.77	CaO	60-67	66.79	67.04
C ₃ A	8.58	8.43	SiO ₂	17-25	21.84	21.63
C ₂ S	15.95	15.82	Al ₂ O ₃	3-8	5.72	5.66
C ₃ S	61.26	61.25	Fe ₂ O ₃	0.5-6.0	3.89	3.87
LSF	96.003	95.79	MgO	0.1-5.5	1.1	1.09
AR	1.47	1.46	Na ₂ O+ K ₂ O	0.5-1.3	0.68	0.65
SR	2.273	2.27	SO ₃	1-3	0.22	0.21
HM	2.124	2.15				
Free lime	1.1	0.94				

Simulation results presented in Table 6.4 agree with the local plant data and the results are even better than previous validation. It was mentioned in section 6.5.3 that considering ash to take part in the kiln reaction would correct the amount of minor constituents in simulation results. It was found that for the current validation, simulation results of all major and minor constituents vary with plant data only by a maximum of 3%. In validation results free lime data were found to be marginally lower than the plant data. The amount of free lime depends on the Alite and Belite formation reaction and is somewhat unpredictable. It was found from the results that less amounts of kiln feed were required to keep the clinker production at the rate same.

6.8.1 Alternative fuels for modified kiln model

In the previous section a kiln process model was developed by using the unit operation block available in Aspen Plus. The alternative fuel firing option of the model allows to test any solid alternative fuel to evaluate their impact. The combustion residue ash of the solid waste

can be supplements to the clinker which leads to less raw material required and less production cost. The current kiln model is capable of calculating the amount of ash produced along with chemical constituents of ash in weight percentage. This allows the model to consider ash in the clinker formation process. Four alternative fuels were considered for the modified kiln model, which are municipal solid waste (MSW), spent pot liner (SPL) sewage sludge (SS) and plastic waste. Apart from the plastic waste the other three solid wastes are known from the literature, to reduce the raw meal requirement in cement production as their ash acts as alternative raw material for clinker production. Literature review on the usage of the selected alternative fuels are given in chapter 3. Elemental analyses of the alternative fuels along with their ash analysis are given in Table 6.5.

Table 6.5: Chemical composition and elemental analyses of fuels

	Coal (Plant data)	SPL (Vick & von Steiger, 2001)	MSW (Garg et al., 2009; Kikuchi.2001)	SS (Ninomiya et al., 2004; Fytili & Zabaniotou, 2008)	Plastic waste (Kim et al., 2011; Xiao et al., 2007)
Proximate analysis (wt%)					
Moisture	1.35	0.6	31.2	0.2	0.6
Ash	18.55	71.43	35.17	20.25	0.4
Volatile matter	24.15	4.1	64.83	47.4	94.77
Fixed carbon	57.3	24.3	-	32.35	4.83
Elemental analysis on dry basis (wt%)					
C	69.43	26.2	34.88	52.5	77.02
H	3.83	0.3	4.65	6.4	12.14
N	1.5	0.6	1.02	9.2	0
S	0.36	0.3	0.15	0.8	0
Cl	0.2	-	1.02	-	1.09
O	5.58	1.2	23.11	31.1	4.92
HHV (MJ/kg)	-	9.36	-	-	-
LHV (MJ/kg)	27.4	9.29	15.4	25.5	41.5
Ash analysis (wt%)					
SiO ₂	46.09	13.6	15.1	26.3	46.61
Al ₂ O ₃	20.64	39.9	15.6	12.7	17.69
Fe ₂ O ₃	7.84	2.8	4.7	8.7	14.14
CaO	16.19	2.6	36.6	15.5	4.47
MgO	1.16	0.4	2	1.9	3.33
SO ₃	2.45	0.5	1.7	9.7	2.08
TiO ₂	1.3	0.4	-	-	2.63
P ₂ O ₅	2.45	0.1	1.5	24.3	2.72
Na ₂ O	0.31	26.6	1.8	0.4	0.79
K ₂ O	1.57	0.8	1.3	0.5	0.15
Cl ₂	-	-	9.7	-	-

6.8.2 Results and discussion for modified kiln model

According to the process configuration almost 200 kg of CO₂ is produced only from the kiln which includes the process CO₂ and combustion CO₂. It was predicted that CO₂ emission will reduce with the reduction of the amount of fuel. For the current model combustion ash takes part in the clinker formation, resulting in less raw material and less fuel. CO₂ emission results are presented in Figure 6.14 which indicate that MSW, SS and plastic waste reduce the CO₂ emission significantly (about 5%) while SPL increases the amount of CO₂ about 2%. This phenomena for SPL was also observed in calciner model results and it was identified that due to lower heating value extra amounts of SPL need to be burnt which cause the raise of CO₂.

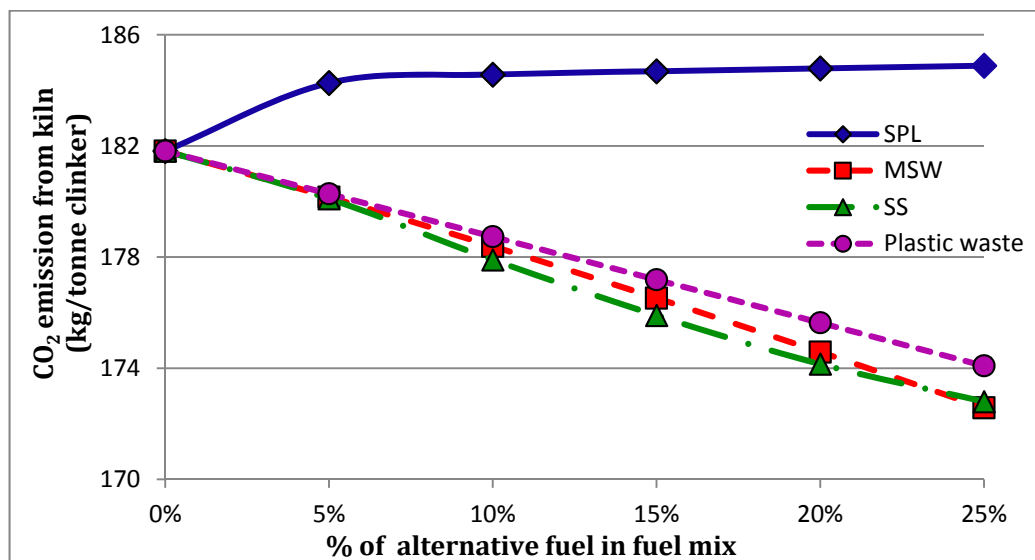


Figure 6.14: CO₂ emission from kiln (kg/tonne clinker)

Simulation results for NO_x and SO₂ are illustrated in Figure 6.15 in concentration unit mg/Nm³. Interestingly, it was found that SPL reduces the NO_x emission about 95% when its share in the fuel mix was 25%. This result is unusual and that may be because of other parameters involved in the process. About 19% reduction of NO_x is observed in the simulation results when MSW is used at 25% substitution rate. The concentration of NO_x raise slightly when sewage sludge or plastic waste was used as alternative fuel. Apart from the plastic waste similar results are found for SO₂ emission from the kiln. SPL and MSW reduce SO₂ in kiln gas about 15% and 6% respectively. SS increases about 22% SO₂ in the kiln gas which is much anticipated as the sulphur content of SS is almost double than coal.

For the plastic waste the amount of SO_x dropped about 33% when plastic waste cover 25% share of the fuel. Since there is no sulphur content in the elemental analysis of plastic waste, hence the huge drop of SO_x is observed in the outlet stream.

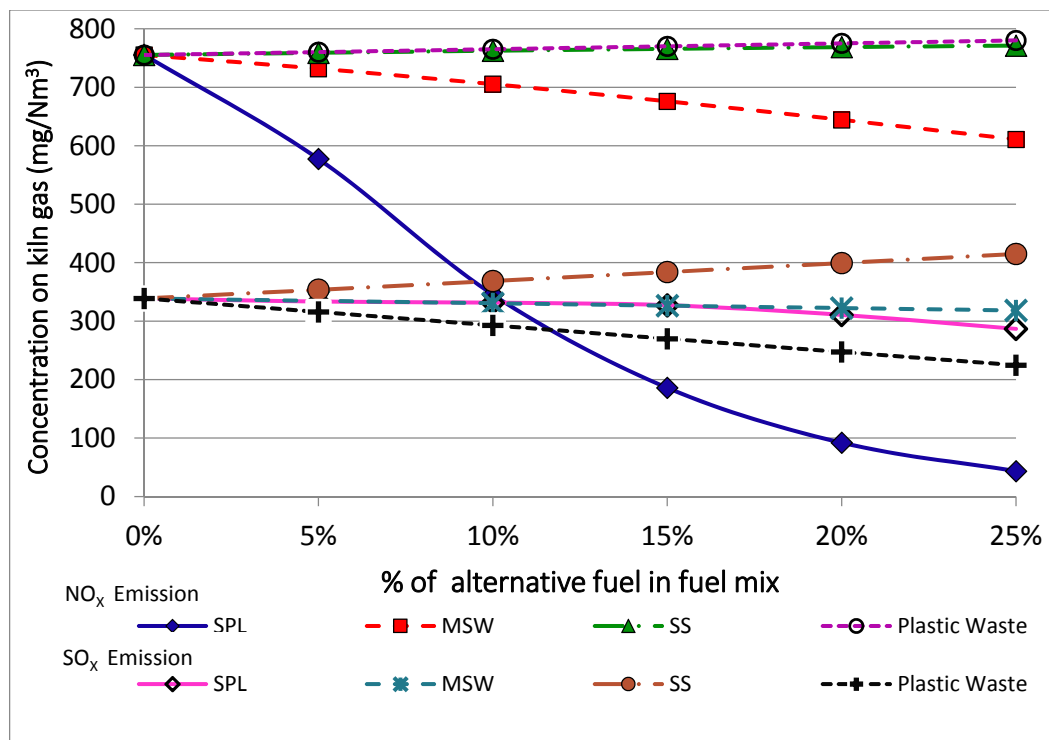
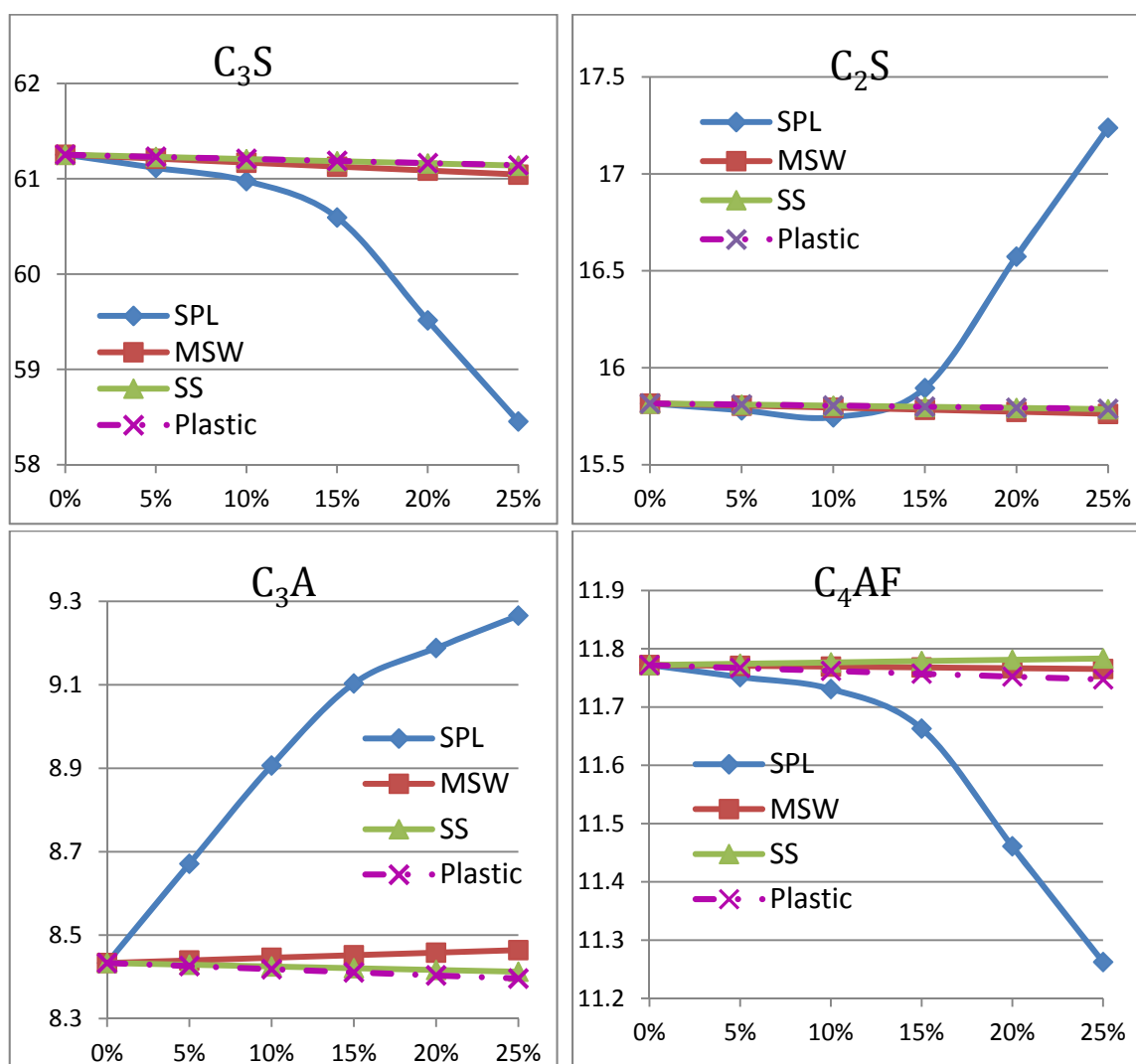


Figure 6.15: Concentration of NO_x and SO₂ in kiln gas (mg/Nm³)

The main constituents of clinkers are Alite (C₃S), Belite (C₂S), Tricalcium aluminate (C₃A) and Tetracalcium aluminoferrite (C₄AF). Weight percentage of these elements is controlled by the manufacturer to ensure the quality of the clinker. The modified kiln model presented in this section is capable to predict the weight percentage of these four components while alternative fuel is introduced to the process. Simulation results regarding the weight percentage of these components are given in Figure 6.16.

Figure 6.16 suggests that using alternative fuel can change the clinker composition and for the case of SPL it is drastic. It was found that when the substitution rate of SPL exceeds 10%, rapid change occurs for all four components. C₃S reduces about 4.5% and C₂S and C₃A increases around 9% and 10%. The ash analysis of the alternative fuel given in Table 6.5 shows that ash of SPL contains high Al₂O₃ and low CaO. Excess amounts of Al₂O₃ lead to the increase of C₃A as it was assumed that all components will take part in the clinker formation reactions. C₃S formed by the chemical reactions of C₂S and CaO, and any

reduction in the amount of total CaO will affect C_2S and C_3S formation. According to the sequence of clinker formation reactions C_2S formed before C_3S and in a lower temperature. Increasing amounts of C_2S in Figure 6.16 suggest that most of the CaO react with the SiO_2 to form C_2S but it left less CaO to form the C_3S in a higher temperature. In the model, rotary kiln was modelled with three reactors in series to separate the temperature range in the kiln and to simulate the reaction sequentially. That means when the components enter the high temperature zone, already there are some shortages of CaO. Consequently less amounts of C_3S is produced. Ash analysis also indicates that SPL has less Fe_2O_3 content, which explains the reduction (about 4%) of C_4AF in the simulation results. Clinker composition is found not to be affected much by using MSW, SS and plastic waste as alternative fuel.



- Variable along X axis: % of alternative fuels
- Variable along Y axis: weight % in clinker

Figure 6.16: composition analysis of clinker

To endorse the explanation for C_3S reduction, simulation results for free lime and lime saturation factor are presented in Figure 6.17. Results indicate that free lime in the clinker drops to 0% when SPL is fed to cover 15% of thermal energy. Lack of presence of CaO in the kiln restricts the C_3S formation and left extra amounts of C_2S in the composition. Lime saturation factor also dropped 2% while SPL is used 25%. In case of other three alternative fuels a similarity is found in terms of the presence of free lime in the clinker. For MSW, SS and plastic waste, the amount of free lime increases steadily with the increase of the percentage of alternative fuel in the fuel mix. The level of free lime is higher in the case of plastic waste comparing to the other two and the same phenomenon is observed for LSF.

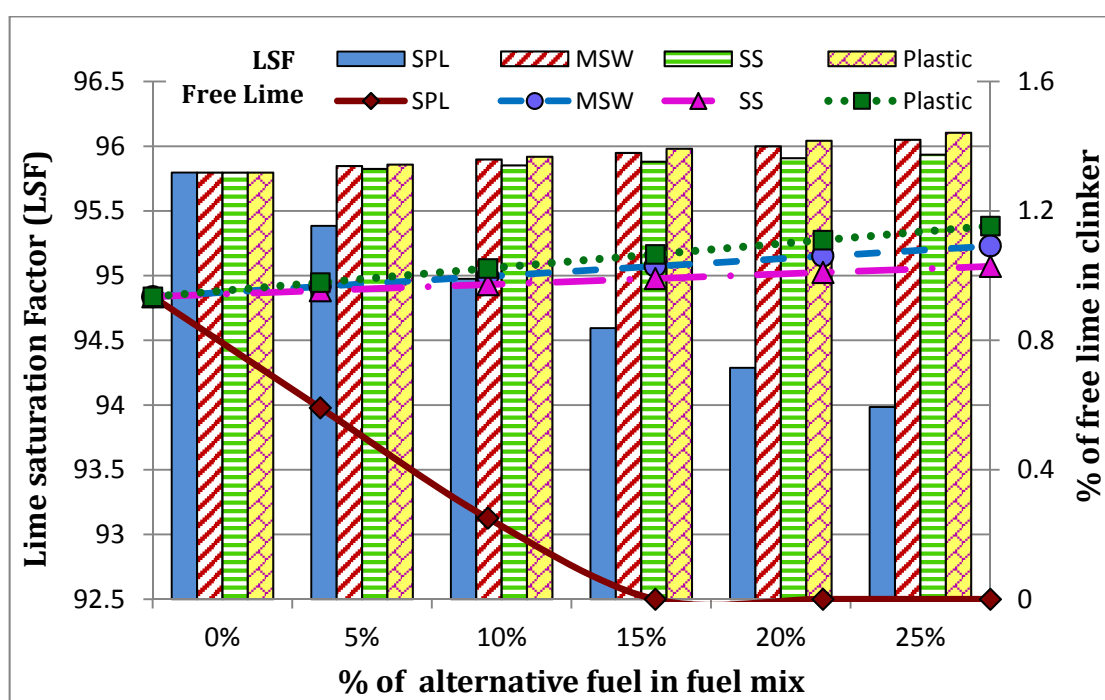


Figure 6.17: LSF and percentage of free lime in clinker

Kiln outlet temperature is generally measured to identify the kiln environment and to identify the state of material at the hot end of the kiln. Simulation results regarding the outlet temperature (Figure 6.18) show a rapid drop for the case of SPL and for the case of 25% substitution the outlet temperature is 1583.99°C in contrast to the reference case (only coal) outlet temperature is 1746.39°C. That huge difference of temperature affects the clinker composition as well as the NO_x formation as it was mentioned in Figure 6.15. It is found from Figure 6.18 that the outlet temperature increases slightly for the case of SS, while MSW and plastic waste manages to keep the outlet temperature almost the same as the reference case.

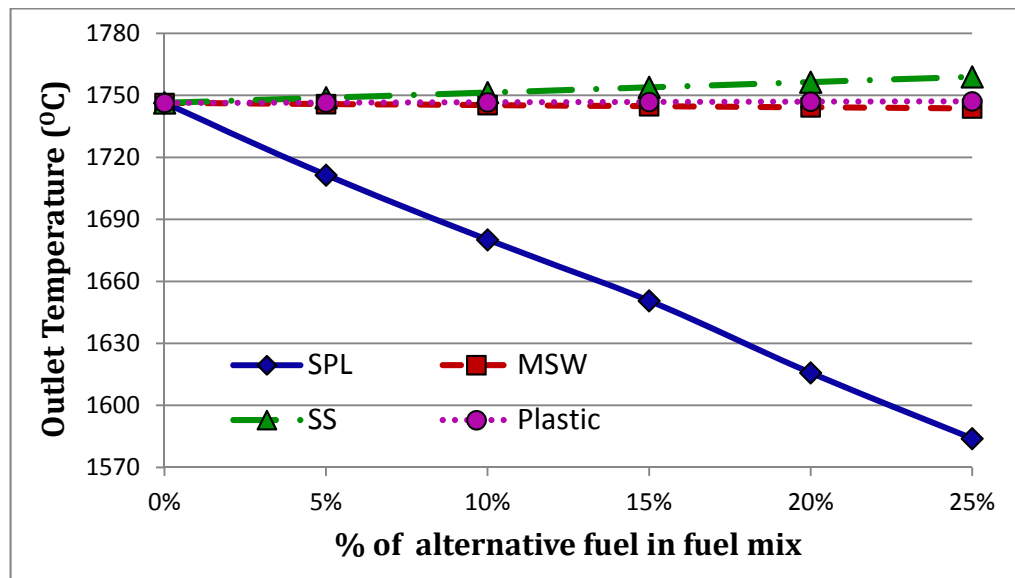


Figure 6.18: kiln outlet temperature

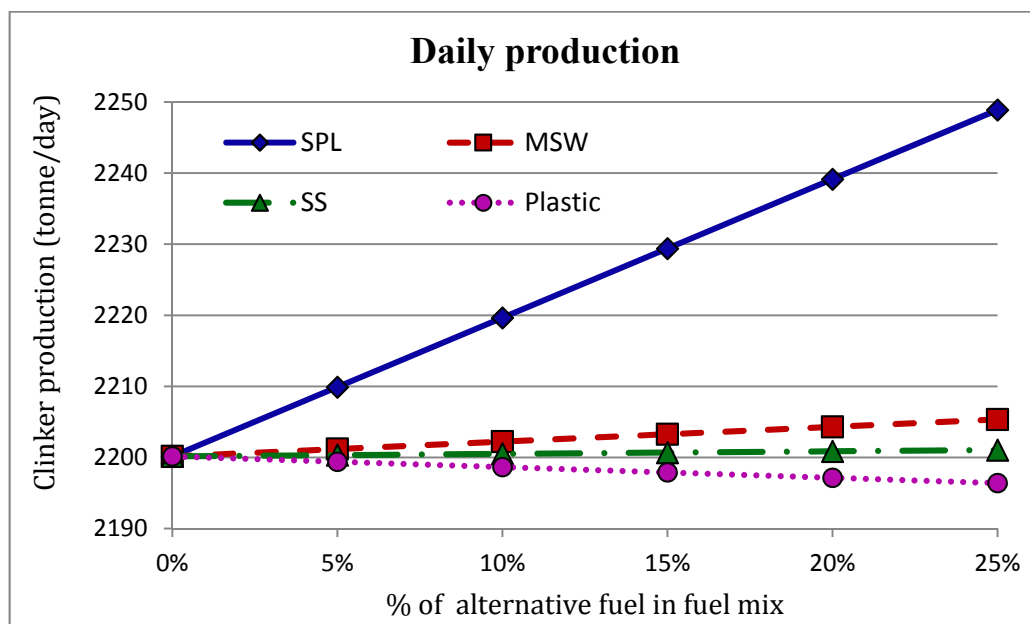


Figure 6.19: Daily production rate of clinker

The current kiln model is designed for a 2200 tonne per day production and all the data associated with that was collected from the local cement plant. In the kiln, combustion residue remains inside and reacts with other components to form clinker. Hence with better quality ash, the production of clinker might increase a bit. Daily production of the kiln while using alternative fuels is plotted in Figure 6.19, which indicates that using SPL will improve

the production rate immensely. But this result is not commendable as it was identified that the composition of clinker may be altered by utilising SPL in the kiln. From the results it is revealed that using MSW up to 25% could add an extra 5 tonne in daily production. On the other hand, using SS could produce an extra tonne of clinker daily. Since the amount is not too large, using these two alternative fuels could not add much value to the clinker production. In contrast to the other three alternative fuels, plastic waste could potentially reduce the daily production about 4 tonne per day. This is only because the amount of ash produce from plastic combustion is very small and not rich enough to be treated as alternative raw materials

6.8.3 Concluding comments on modified kiln model

A modified kiln model is presented in this section which is capable of dealing with the ash constituent of fuels. According to the model setup the ash decomposed in a separate reactor block to enable the constituent to take part in the clinker formation reaction. Three alternative fuels were studied with this model in terms of pollutant emission and clinker quality. Simulation results presented in this section revealed that using SPL as alternative fuel may change the composition of clinker which is not desired. Though SPL was suggested by the local synergy report as a potential alternative fuel for the cement industry, the current study rejected the effectiveness of using SPL as alternative fuel. Only a small amount of SPL, less than 5% substitution rate, is recommended to grab the advantage of NO_x reduction. MSW, SS and plastic waste are found to keep the integrity of the clinker intact while using them as alternative fuels. Based on the NO_x emission data MSW is preferred over SS and plastic waste to burn in the kiln. Using plastic waste as alternative fuel can reduce the SO_x emission, however, one downside of using plastic waste is that the reduction of clinker production as the ash of plastic is not rich enough. Plastic waste can be considered as a viable alternative fuel option due to its availability and high heating value.

6.9 Conclusion

Cement kilns are complex process equipment due to their extreme heat, pyroprocessing reactions and unpredictable environment inside. Due to its importance for cement manufacturing, numerous approaches were carried out to model a kiln from a different perspective. This chapter presents an Aspen plus process model of a cement kiln based on its thermodynamic principle and reaction stoichiometry. The process model was verified

against the plant data as well as data from literature. Five agricultural biomasses were studied by using the kiln model. Results in terms of the pollutant emission were presented and maximum substitution rate of the selected alternative fuels were determined based on the results. The potential energy saving aspect of using selected alternative fuels was also determined by using the kiln process model. Some modification for the kiln model was also recommended to identify the impact of using alternative fuel on the clinker quality.

A modified version of the kiln model was presented in the second part of this chapter which considered the combustion ash to take part in clinker formation reactions. A modified kiln model was used to examine four solid alternative fuels, namely, SPL, MSW, SS and plastic waste. Effects on the clinker quality while using alternative fuels in the system were thoroughly discussed and pros and cons of the selected alternative fuels were identified.

Among the agricultural biomasses 20%, 15%, 15%, 12% and 13.5% substitution rate was suggested for bagasse, almond shell, rice husk, coffee husk and olive husk respectively. Simulation results revealed that the cement industry could save a maximum of 3% of energy by using coffee husk at 12% substitution rate without exceeding the pollutant emission standard. It was found that agricultural biomasses were a good option to mitigate SO_2 emission. The simulation results suggested that the kiln outlet temperature could be on the lower side while using agricultural biomasses with an exception for almond shell.

A modified kiln model was presented in later part of this chapter and the validation results suggested that it could effectively predict the quality of clinker in terms of chemical compositions. Simulation results presented in this section pointed out the drawback of using SPL as alternative fuel and suggested not to use it over 5% substitution rate. Richness of SiO_2 and Al_2O_3 in SPL ash posed some problem regarding the formation of C_3A which is one of the major constituents of clinker. Beside this the fraction of C_4AF in clinker was found to drop due to the inadequacy of Fe_2O_3 in SPL ash. To overcome these problems additional amounts of raw material will be required which will attract higher production cost and hence is not recommended. The other three alternative fuels examined in this section are found to be competent to reduce the emission without affecting the clinker quality.

In the next chapter an integrated model is presented which is a combination of preheater tower and kiln model. A set of alternative fuels, selected according to the outcomes of the kiln and preheater model, is studied with the integrated model to identify their individual impact on the process. In addition to that, an integrated model is used to study blends of alternative fuels in search of an optimal blend.

Chapter Seven

Integrated Model for Cement Manufacturing

7.1 Introduction

Manufacturing cement is one of the most complex processes due to its high energy requirement and pyroprocessing reaction for clinker formation. Computational models are widely used to study extreme processes like cement to predict the outcomes due to any changes in the process setup. CFD based models are dominantly used to imitate different sections of the process by using the heat and mass transfer principle. These models were used to study different operating parameters and conditions including flame shape, temperature and velocity profile of particles in the kiln system and oxygen enrichment in the burning zone. Scant literature is found to deal with the entire process as lots of parameters involved with the extreme conditions of a kiln are not known. Beside this all chemical reactions that occur in different physical phases of material inside a kiln can only be predicted not measured.

Developing a model for the entire process can still be done in a simple form where only main pyroprocessing and clinkerization reactions are taken into consideration in their equilibrium form. A four-stage preheater kiln system was modelled by Kaantee et al. (2004) using Aspen plus software to identify the relationship between the amount of combustion air and process performance. Mujumdar et al. (2007) modelled preheater, calciner, kiln and cooler separately and combined them to develop a simulator for the entire system. The model was identified as very convenient to determine the optimum percentage calcinations desired for minimizing net energy consumption. Both the models were constructed on a set of assumptions which made the model simple yet still effective.

An integrated model for cement manufacturing is presented in this chapter which is developed by Aspen plus software. The model simulates results on the basis of mass and energy balance principle of the process. An alternative fuel firing facility in the model generates results for varieties of alternative fuel. Reduction of emission and potential

energy savings are the main two targets of this study. It needs to be remembered that the quality of the clinker should not be compromised. Based on the emission results, a maximum substitution rate of the selected alternative fuel is determined. Finally the process model was modified to enable alternative fuel blends that can be introduced to the system. Simulation results are used to suggest an optimum blending ratio.

7.2 Alternative fuels for process model

Alternative fuels are mostly waste-derived and hence economically cheaper than fossil fuels. Alternative fuel has been used for over 30 years on a commercial basis. Still the manufacturers are facing some challenges regarding environmental, social and product quality issues. In this chapter, five alternative fuels are considered to study with a valid process model. Alternative fuel selection is done on the basis of the results presented in the previous two chapters. Waste tyre, MSW, MBM, bagasse and plastic waste are the alternative fuels used in this section.

In the preheater tower model it was identified that waste tyre can be substituted up to 15% of the total fuel requirement. With that substitution rate potential energy savings and reduction of emission was reported in chapter 5. MBM was also recognised to be a better alternative fuel option for the cement industry. In chapter 6, simulation results for five agricultural biomasses in a kiln model were presented and bagasse was identified as the best option among them. A modified version of the kiln was also presented in chapter 6 and three alternative fuels namely SPL, MSW and SS were studied by the kiln model. Simulation results rejected SPL as alternative fuel due to its adverse impact on clinker quality. It was also discovered that MSW can reduce emission without affecting the constituent of clinker. Plastic waste has the highest calorific value among all solid alternative fuels that have been discussed in this thesis. Generally recycling or reusing of plastic waste is preferred over incineration. Apart from chlorine build up in the preheater tower, plastic waste was reported to be a favourable option for the cement process as alternative fuel. Plastic waste was examined in chapter six by using the modified kiln model to identify its impacts and it was found to be effective to reduce SO_x. It was also revealed the plastic waste can be used as alternative fuel without any negative impact on the clinker quality. Beside this, plastic waste is one of the most available waste in our modern society and hence need to be treated in an environment friendly process.

To develop the process model, elemental analyses of all alternative fuels are required along with the ash analysis. The chemical composition of the alternative fuels in terms of elemental analysis and ash analysis data was collected from literatures (Karell & Blumenthal, 2001; Trezza & Scian, 2009; Garg et al., 2009; Kikuchi, 2001; Fryda et al., 2007; Kim et al., 2011; Xiao et al., 2007; Jenkins et al., 1998) and has been summarized in Table 6.1. It is to be mentioned that as per the recommendation from chapter 5 a better quality of MBM in terms of heating value is chosen for the current study. Ash analysis is used in the model to identify changes in clinker composition as the ash remains in the kiln and takes part in the clinker formation reactions.

Table 7.1: Analysis of alternative fuels

	Coal (Plant data)	Tyre	MSW	MBM	Plastic waste	Bagasse
Proximate analysis on dry basis (wt%)						
Moisture	1.35	0.62	31.2	1.35	0.6	0
Ash	18.55	4.81	35.17	10.54	0.4	11.95
Volatile matter	24.15	67.06	64.83	80.74	94.77	85.61
Fixed carbon	57.3	28.13	0	8.72	4.83	2.44
Elemental analysis on dry basis (wt%)						
C	69.43	84.39	34.88	55.7	77.02	48.64
H	3.83	7.13	4.65	8.03	12.14	5.87
N	1.5	0.24	1.02	7.15	0	0.16
S	0.36	0.01	0.15	0	0	0.03
Cl	0.2	1.24	1.02	0.05	1.09	0.04
O	5.58	2.18	23.11	18.53	4.92	42.82
LHV (MJ/kg)	27.4	37.8	15.4	30.705	41.5	18.99
Ash analysis (wt%)						
SiO ₂	46.09	14.1	15.1	5.97	61.35	46.61
Al ₂ O ₃	20.64	2.7	15.6	1.81	25.13	17.69
Fe ₂ O ₃	7.84	1.1	4.7	0.59	5.44	14.14
CaO	16.19	47.0	36.6	45.6	4.72	4.47
MgO	1.16	0.7	2	1.43	0.94	3.33
SO ₃	2.45	1.2	1.7	-	0.03	2.08
TiO ₂	1.3	<0.01	-	1.1	-	2.63
P ₂ O ₅	2.45	<0.01	1.5	37.3	-	2.72
Na ₂ O	0.31	<0.01	1.8	2.07	0.42	0.79
K ₂ O	1.57	<0.01	1.3	1.86	1.52	0.15
Cl ₂	-	-	9.7	0.11	-	-
ZnO	-	33.1	-	-	-	-

7.3 Development of Integrated Model

The integrated process model for cement manufacturing was constructed by combining the preheater tower model and modified kiln model which have been presented in chapter 5 and chapter 6 respectively. The process model was built according to the reference plant specification with 2200 tonne/day clinker production capacity with an ILC preheater tower. Energy split between precalciner and kiln section was assumed to be 60% and 40% respectively. The basic assumptions for an integrated model are same as for modified kiln model. Aspen plus process flow sheet for the integrated model is illustrated in Figure 6.1 which clearly indicates the input and output stream of the system.

Combining two process models to develop a new one apparently seems easy but in the real world it is not. In a separate model, some parameters need to be installed in the model as input form but in the integrated model sometimes the same parameters need not to be specified. For instance the output stream KILNFEED of the preheater model is an input stream for the kiln model. Hence in a separate kiln model one has to specify the temperature, pressure and mass flow of the stream along with the chemical breakdown of the material of the stream. In an integrated model the same stream directly enters in the kiln reactor hence any of the above mentioned parameters need not to be specified. In the kiln model those parameters stay constant but in contrast in the integrated model they are variable depending on the operating condition. Similar aspects can be found for KILNGAS stream which is an output stream of the kiln model and an input stream of the preheater tower model.

RKS-BM property method along with SOLID and IDEAL was considered for an integrated model like the kiln model. Enthalpy and density calculations for coal and alternative fuels, were carried out by nonconventional property methods. Ten percent of excess air in the kiln section was maintained while the amount of excess oxygen in the calciner was calculated by using a calculator block. Required data to run the model were collected from the local plant and also from literature which includes:

- Mass flow rates of all incoming streams.
- Temperature and pressure of all incoming material streams.
- Heating values and chemical composition of all fuels and raw meal.

- Particle size distribution of all fuel and raw feed.
- Dimension and efficiency of cyclone string

As the conditions are different from the separate models, the integrated model itself needed to be verified. The same set of plant data was used to validate the model as for the kiln model. Though air emission data is not available for a particular instance, average air emission data were used to check the effectiveness of the model. Table 7.2 summarises the validation results which contain the input and output data collected from the local cement plant and simulation results.

Table 7.2: Integrated model validation

Input data (From plant)											
Coal analysis	Proximate analysis	Moisture		Fixed carbon		Volatile matter		Ash		Calorific Value	
		1.35		57.3		24.15		18.55		27.4 MJ/kg	
	Ultimate analysis	C		H		N		Cl		S	
		69.13		3.79		1.51		0		0.36	
	Ash analysis	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	TiO ₂	P ₂ O ₅	Na ₂ O	K ₂ O
		0.4609	0.2064	0.0784	0.1619	0.0116	0.0245	0.013	0.0245	0.0031	0.0157
Raw meal (wt%)	SiO ₂	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Fe ₂ O ₃	TiO ₂	SO ₃	L.O.I.	CaCO ₃
	13.68	3.54	43.49	0.66	0.23	0.15	2.49	-	0.16	35.39	78.13
Output data											
Clinker composition (oxide form)											
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	P ₂ O ₅	TiO ₂	Na ₂ O	K ₂ O	SO ₃	Free CaO
Range (wt%)	60.2–66.3	18.6–23.4	2.4–6.3	1.3–6.1	0.6–4.8	--	--	0.05–1.20	1.7–4.6	--	--
Plant data	66.79	21.84	5.72	3.89	1.1	--	--	0.31	0.37	0.22	1.1
Simulation results	66.7793	21.6564	5.7106	3.8798	1.0089	0.052	0.028	0.245	0.362	0.2227	0.5369
Clinker composition (Compound form) and ratios											
	C ₄ AF	C ₃ A		C ₂ S		C ₃ S		LSF		AR	
Plant data	11.84	8.58		15.95		61.26		96.003		1.47	
Simulation results	11.80692	8.55310		15.90564		61.23595		95.14625		1.47190	
Air emission data											
Pollutant	Unit			Source			Available data			Simulation results	
CO ₂	kg/tonne clinker			Standard limit			977			803.6919	
NO _x	gm/tonne clinker			Average plant data			2200			1776.50498	
SO ₂	gm/tonne clinker			Average plant data			170			175.893923	

Model validation results indicate that the process model agrees well with the plant data and could be useful to predict the changing conditions with different sets of operating parameters. Some variation is observed in air emission data which is obvious since

available data of CO₂ emission was not the actual plant data but rather a standard limit. According to the model assumption NO_x is formed only from N content of fuel and air N₂ is considered non-reactant. Hence there is some variation in the NO_x emission data. In spite of those variations the model can predict the pollutant emission

After validation, the model is executed with selected alternative fuels replacing fossil fuel coal up to 30% of total thermal energy requirement. Simulation results in terms of pollutant emission and kiln outlet temperature were presented to identify the possible impact of using alternative fuel. To quantify potential improvement in energy demand, the process model was run with less fuel feed while maintaining the kiln temperature at a fixed point and with a fixed production rate.

7.4 Simulation results and discussion

An integrated process model for cement manufacturing with a daily production of 2200 tonne of clinker is presented in this section to study five selected alternative fuels. According to the model set up, fuel requirement for the process is calculated on the basis of energy requirement data from the reference plant. Selected alternative fuels were set to substitute up to 30% of total thermal energy and each alternative fuel was used separately to identify their impact. Throughout the simulation the mass flow rate of raw feed is kept constant, while the amount of primary air is modified with the proportion of fuel mix to meet the assumption of 10% excess air. In the simulation model the energy requirement for the process is set by the specification of local plant and the mass flow rate of fuels is determined accordingly. The amount of air in the cooler was kept constant and the temperature and pressure at different point are inserted in the model on the basis of plant specifications.

Total CO₂ emissions from the pyroprocess depend on energy consumption and nearly 977 kg of CO₂ were produced for each tonne of clinker. Simulation results for CO₂ are presented in Figure 7.2 which indicates that apart from bagasse all other selected alternative fuels potentially reduce CO₂ emission up to some extent. MSW was found as the best option to reduce CO₂ emission up to 4.7% while substituting 30% of thermal energy requirement. As the raw meal flow rate remains the same throughout the simulation, the reduction of CO₂ occurs from the fuel combustion stage. Carbon percentage in the elemental analysis of

the alternative fuels plays a vital role in CO₂ emission. The heating value of MSW is very low compared to coal and hence amount of fuel is higher than only coal burning. One might assume that additional amount of fuel could release more CO₂ but due to low carbon content MSW produce less CO₂ than the other selected alternative fuels.

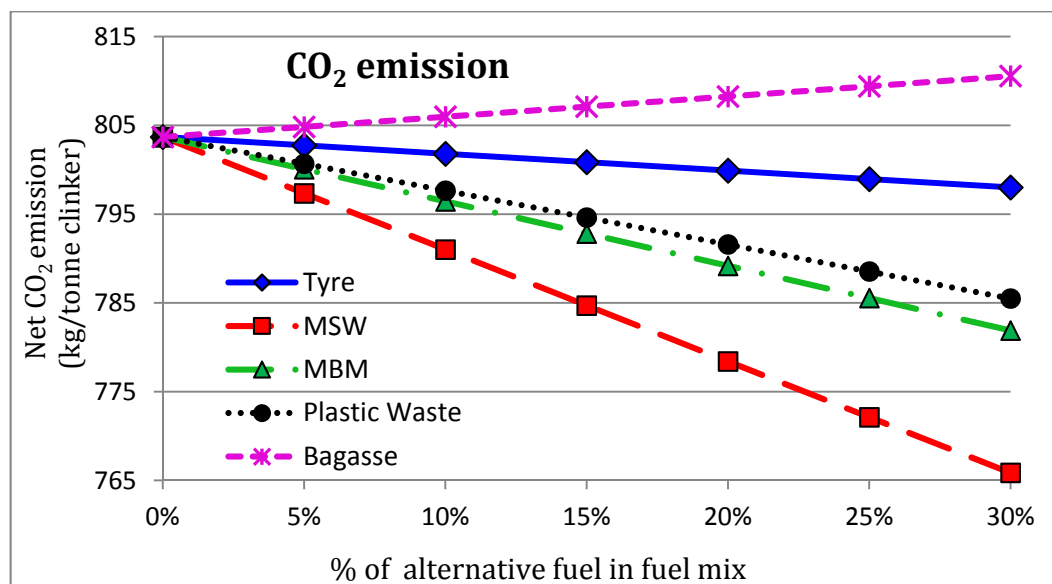


Figure 7.2: Net CO₂ emission (kg/tonne clinker)

NO_x and SO₂ emission results are presented in Figures 7.3 and 7.4 respectively. For the reference case the NO_x and SO₂ emissions are found to be a little higher from the standard baseline which is due to the excess air in the burning zone. As per plant specification, the kiln model was operated with 10% excess air. A constant flow of tertiary air in the calciner increases the oxygen level of the calciner up to 20%. Though MSW potentially reduces the CO₂ emission, a completely opposite scenario was observed in the case of NO_x emission with 29.5% increase in the stack gas. It was mentioned earlier that the amount of MSW required in the fuel mix is higher than other alternative fuels due to its low heating value and the additional amount of MSW leads to high NO_x emission since the Nitrogen contents are almost similar to coal. All the other selected alternative fuels were found to increase the NO_x emission at a certain level. The nitrogen content of MBM is way higher than all other alternative fuel options and expected to release more NO_x. However, NO_x emission for the case of MBM was not as high as expected. This outcome can be explained by the fact that less fuel is required due to the high heating value of MBM. SO₂ emission remained almost constant for the case of MSW while tyre produced about 11% more SO₂ than the reference

case which was actually expected. All the other alternative fuels had the potential to reduce the SO₂ emission significantly.

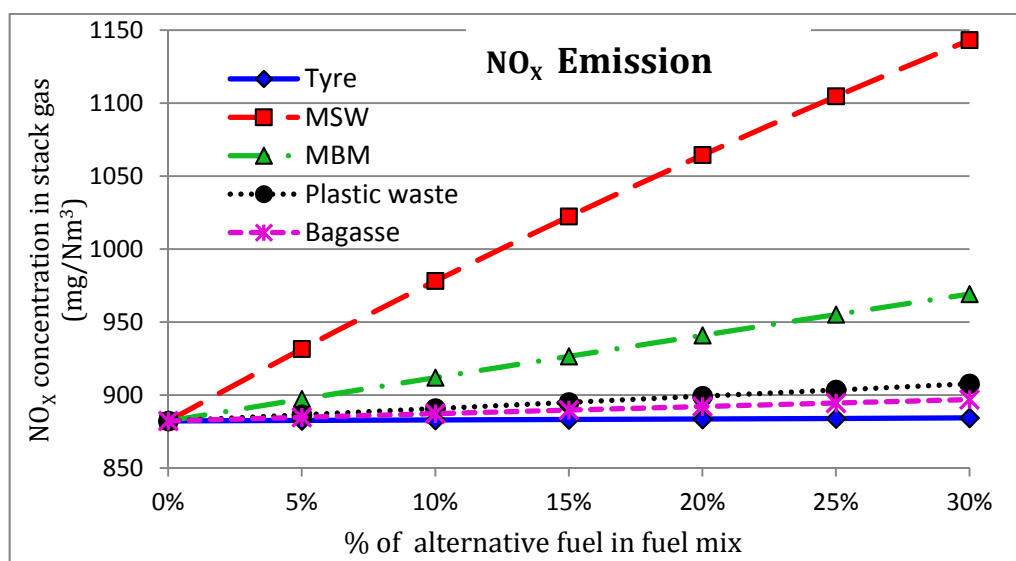


Figure 7.3: NO_x concentration in stack gas (mg/Nm³)

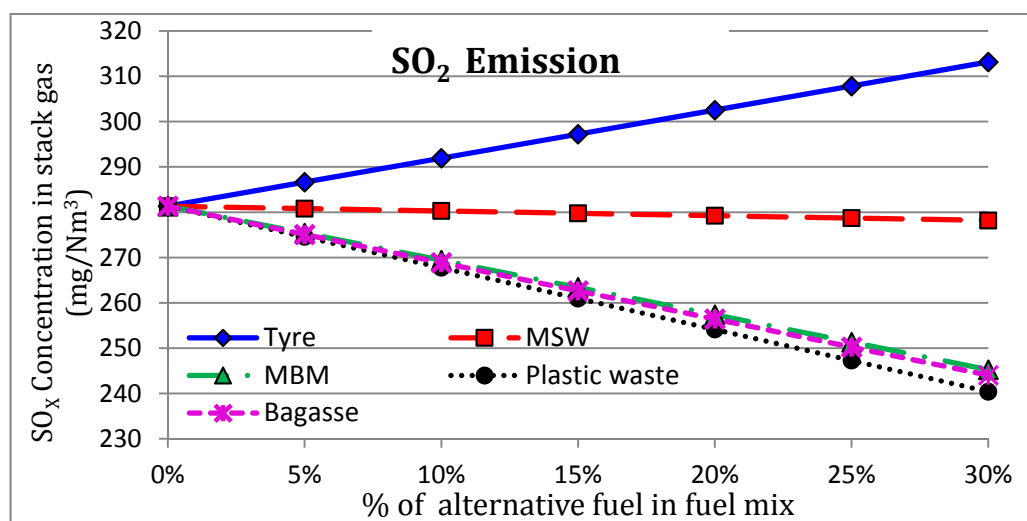


Figure 7.4: SO₂ concentration in stack gas (mg/Nm³)

The excess amount of NO_x also depends on the amount of excess air in the burning zone. Since the excess air in the kiln was kept at a constant 10% limit, the amount of oxygen in the calciner had an impact on the NO_x emission. Figure 7.5 represents the amount of excess oxygen in the calciner with different alternative fuel feed. Figure 7.5 indicates that there is a positive correlation between the amount of excess oxygen in the calciner and the NO_x concentration in the stack gas.

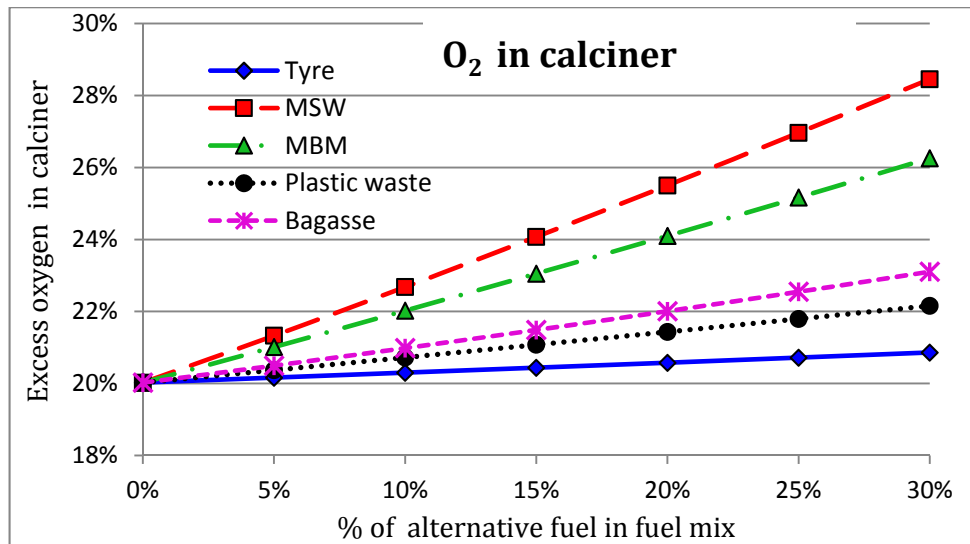


Figure 7.5: Excess amount of oxygen in calciner

Impact on the clinker quality in terms of basic ratios is presented in Figure 7.6. Results suggested that for all five alternative fuels LSF has a common trend of increasing. For MBM a maximum 1.5% increase is observed. Using MSW as alternative fuel affects the silica and alumina ratio in a small amount and the rest of the alternative fuels seem to have no impact on AR and SR. Based on the analysis it is evident that selected alternative fuels have minimum influence on the clinker quality.

Outlet temperature of the kiln outlet is a good indication of the kiln environment to understand the clinkerization phase inside the kiln. A reduction of temperature inside the kiln could possibly cause an incomplete pyroprocessing which may lead to a downgraded clinker quality. The outlet temperature of a kiln is illustrated in Figure 7.7a for different feed rates of alternative fuel where 0% alternative fuel indicates the reference case of only coal as fuel. The simulation results showed that kiln temperature was remarkably low for the case of MSW which could really change the clinker chemistry. Meanwhile apart from bagasse all other three alternative fuels are capable to maintain the kiln temperature up to the reference case.

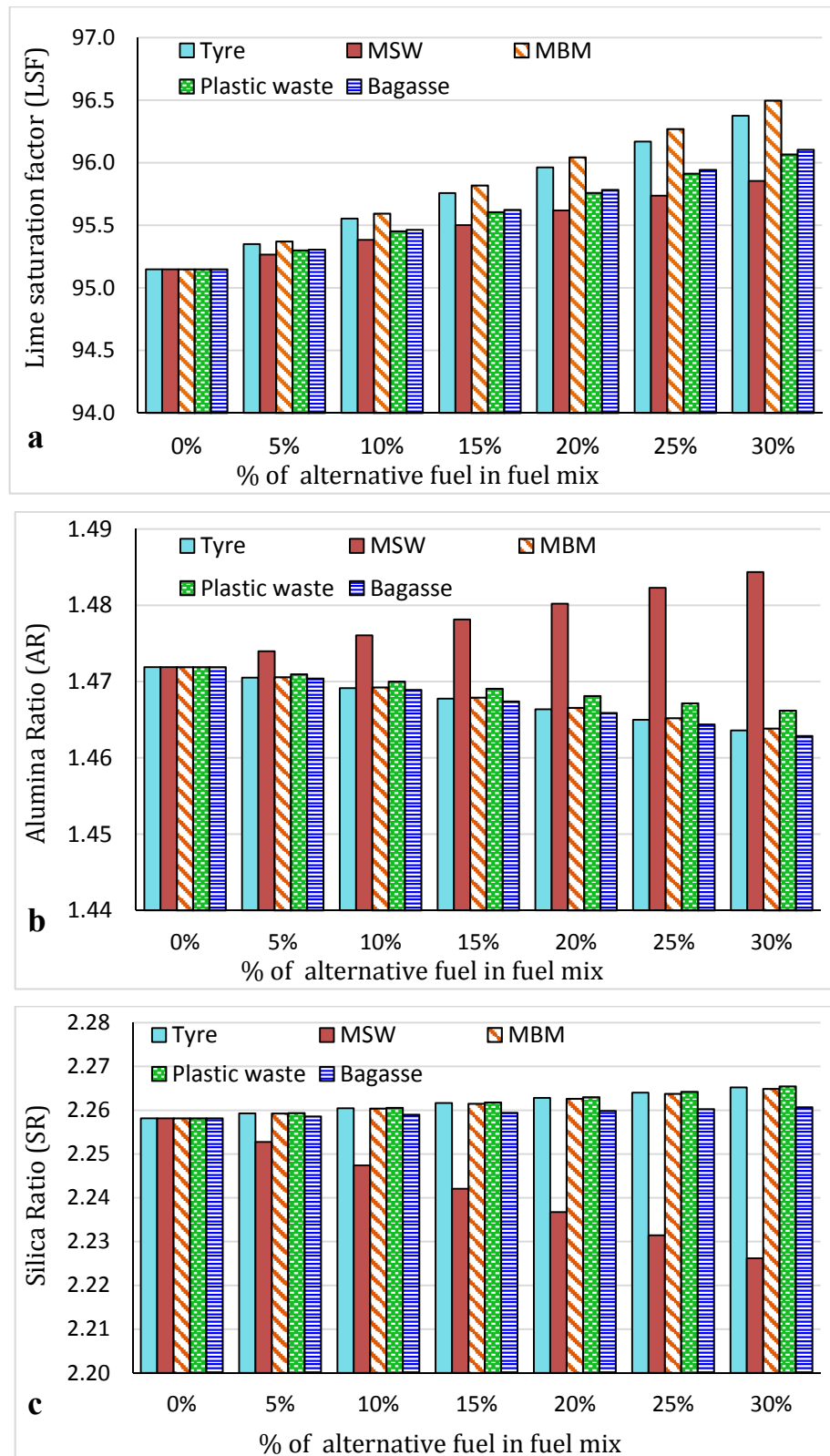


Figure 7.6: Impact on clinker quality a) LSF b) AR and c) SR

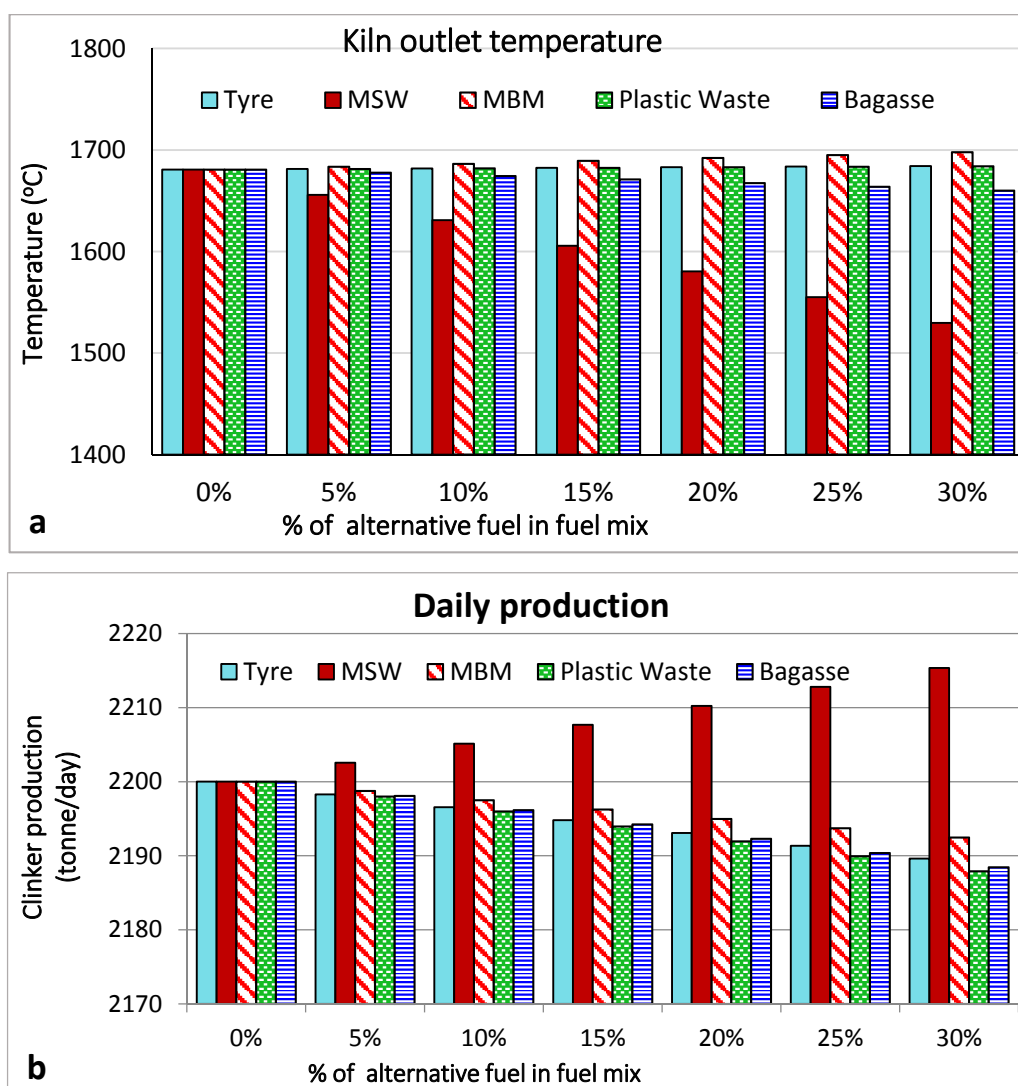


Figure 7.7: a) Kiln outlet temperature (°C), b) clinker production (tonne/day)

Clinker production is another key feature to measure the efficiency of the plant. Drop in production will diminish all the economic benefit that could possibly be gained by introducing alternative fuel in the system. Simulation results regarding the clinker production with a fixed raw meal feed are presented in Figure 7.7b. Simulation results showed that usage of plastic waste and bagasse could reduce the production of up to 0.4% while MSW could possibly increase the production rate about 0.6%. Since the amounts are negligibly small, all the alternative fuel could be used up to 30% based on these criteria.

To examine the potential reduction of energy requirements of the system, a maximum percentage of alternative fuel in the fuel mix was determined from the emission analysis. Waste tyre could be used up to 18% to keep the SO₂ emission below 300 mg/Nm³ while

bagasse could be used up to 5% to keep the CO₂ emission below the baseline limit set by the reference plant. Based on the kiln outlet temperature, the usage percentage of MSW was set at 15% and NO_x level needs to be controlled by reducing excess air in the calciner for this case. Usage of 20% MBM will keep the NO_x emission below 950mg/Nm³ which could even be lowered by controlling the air in the calciner. Plastic waste could be used up to 12% to avoid the clinker production dropping below 2195 tonne/day. The model was run with the prescribed substitution rate and by lowering the total feed rate as well as adjusting the air flow in the calciner to investigate potential improvement in energy demand. Throughout this simulation the kiln outlet temperature and daily production were kept the same as the reference case. Lowering the fuel feed could reduce clinker production as the combustion ash stays with the clinker to increase the volume. Additional raw meal was required for a consistent production rate.

Table 7.3: Analysis of potential improvement in emission and energy savings

Fuel mix Properties	Only coal	Coal 82% & tyre 18%	Coal 85% & MSW 15%	Coal 80% & MBM 20%	Coal 88% & Plastic waste 12%	Coal 95% & Bagasse 5%
Excess air in the kiln	10%	5%	2%	5%	5%	5%
Excess air in the calciner	20.025%	13.58%	6.866%	15.277%	10.7879%	8.64%
Kiln outlet temperature (°C)	1680.665	1680.708	1680.441	1679.998	1680.722	1680.205
Raw feed (kg/hr)	137856	138365	137510	138530	138475	138320
[change %]		[+0.369%]	[-0.25%]	[+0.489%]	[+0.449%]	[+0.337%]
Energy requirement (MJ/kg clinker)	3.178	3.059	3.185	2.975	2.983	2.982
[change%]		[-3.72%]	[+0.22%]	[-6.39%]	[-5.15%]	[-5.18%]
CO ₂ emission (kg/tonne clinker)	803.692	781.275	780.585	768.543	778.564	786.632
[change %]		[-2.79%]	[-2.88%]	[-4.37%]	[-3.13%]	[-2.12%]
NO _x emission (mg/Nm ³) [change%]	882.28	598.048	762.317	740.352	647.238	589.91
		[-32.22%]	[-13.6%]	[-16.09%]	[-26.64%]	[-33.14%]
SO ₂ emission (mg/Nm ³) [change%]	281.36	315.37	301.66	271.082	279.386	291.36
		[+12.09%]	[+7.21%]	[-3.65%]	[-0.70%]	[+3.55%]

Simulation results presented in Table 7.3 indicate that a reduction of pollutant emission and energy demand in the cement industry can be achieved by using alternative fuel in suitable proportion. Thermal energy requirement in the manufacturing process could be reduced a maximum of 6.39% by using 20% MBM in the fuel mix. As MBM was used with maximum substitution rate among the selected alternative value and the heating value of MBM is higher than coal potential energy savings was expected. Tyre is the most widely used alternative fuel in the cement industry but it always returns some risk of extra SO₂ emission. The current simulation results for tyre, agrees with previously published results about SO₂ emission and indicate an increase 12%. In contrast to other alternative fuel MSW showed prospect to reduce the raw meal; still it was a less favourable option to reduce pollutant emission. Like MSW, Bagasse also generate more pollutant compared to the other three and release to the environment. A close look the elemental analyses revealed that the O₂ content in the ultimate analysis of MSW and Bagasse are higher than the other, which implies extra amount of O₂ in the burning zone cause more CO₂ and SO₂ release. MBM was found to be the best option among the selected alternative fuels though an additional 0.49% of raw meal is required to secure the benefits. With a similar amount of additional feed meal, plastic waste was found to reduce the energy demand and NO_x emission. Plastic waste has the highest heating value which helps it save some energy from the process. Bagasse could be used in a small amount in the fuel mix as the amount of CO₂ in stack gas is likely to increase.

7.5 Blended alternative fuels for integrated model

To maximise the usage percentage of alternative fuels, a blend is preferred and practiced worldwide. The advantage of using a blend of alternative fuels is that the user can adjust the fraction of a single alternative fuel in the blend or can omit that from the blend if it is unavailable. The omission of an alternative fuel can be adjusted by increasing the weight fraction of other alternative fuels in the blend. Literatures regarding the impact of the blend of alternative fuels are very limited as most of the research work is focused on a single alternative fuel at a time. Kookos, et al. (2011) considered four alternative fuels (residue derived fuel, tyre derived fuel, meat and bone meal and sewage sludge) and used mathematical programming to optimize fuels mix in cement production. Organic and inorganic pollutant emission from a real plant kiln was studied by Conesa et al. (2008) while using a mixture of two alternative fuels on an experimental basis. Gabel and Tillman

(2005) used different sets of data for alternative raw material and alternative fuel mix to identify the consequence in clinker production from the life cycle perspective. Tsiliyannis (2012) presented a mass and energy balance model and used the model to study seven different scenarios of fuel mix to quantify the effect of operational parameters. The integrated model presented in this chapter could be a useful tool to cement manufacturers as it can assess the impact of blends of alternative fuels which can be modified based on the availability of individual alternative fuels. In the current section five different alternative fuels were considered namely waste tyre, municipal solid waste (MSW), meat and bone meal (MBM), waste plastic and sugarcane bagasse. Six different blends of these alternative fuels were chosen to run in a valid process model. Randomly selected blending ratio of the five s alternative fuels for the current study is given in Table 7.4. Among the cases that were studied in this paper, blend 5 was composed according to the optimum usage percentage of the selected alternative fuels suggested in the previous section. Blend 6 was chosen in a way that the entire thermal energy requirement was covered by the selected alternative fuels.

Table 7.4: Thermal energy substitution by alternative fuels in different fuel blend

Option Fuel	Only coal	Blend 1	Blend 2	Blend 3	Blend 4	Blend 5	Blend 6
Coal	100%	50%	50%	40%	40%	30%	—
Tire	—	10%	15%	20%	15%	18%	30%
MSW	—	10%	10%	15%	10%	15%	20%
MBM	—	10%	15%	15%	20%	20%	25%
Plastic waste	—	10%	5%	5%	10%	12%	15%
Bagasse	—	10%	5%	5%	5%	5%	10%

7.6 Analysis for blended alternative fuels

Alternative fuels are generally utilized in the cement manufacturing process to reduce the pollutant emission and production costs. Any alteration in the clinker composition may neutralise the potential benefit of using alternative fuel. The integrated model presented in this chapter is capable of identifying the impact of using a blend of alternative fuels. Alternative fuels used in this section for the model run are waste tyre, municipal solid waste (MSW), meat and bone meal (MBM), waste plastic and sugarcane bagasse. The choice of alternative fuels was based on the analysis that was carried out in the preceding chapters.

Alternative fuel selection for a cement plant depends on their availability locally and they could be different for the other plants due to location equipment design and local waste generation trends.

Excess air in the burning zone is one important parameter which can affect the emission factor as well as the quality of clinker. In the current section the excess air in the kiln section is considered to be variable. On the other hand, tertiary air flow rate in the calciner is kept constant. Tertiary air is the main source of O₂ in the calciner to enable the combustion of fuel. In addition to the tertiary air, kiln exhaust gas and some cool air is fed in the calciner to ensure complete combustion of fuel. The model was also run with a fixed amount of raw meal which was used for the reference case to produce 2200 tonne of clinker per day. Excess air in the kiln was set to be increased from 0% to 15% throughout the model run where 0% indicates that only stoichiometric air was supplied in the burning zone. Stoichiometric air for coal and alternative fuel is calculated from the ultimate analysis data and the amount of excess air was determined from the ratio of actual air and stoichiometric air.

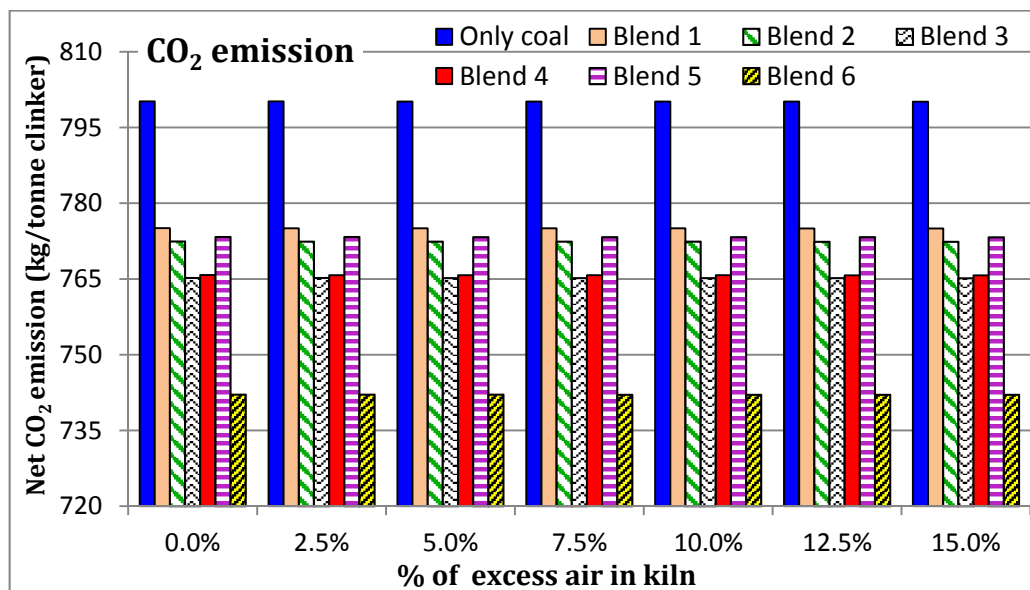


Figure 7.8: Net CO₂ emission (kg/tonne clinker) for different blend of alternative fuels

CO₂ emissions from the cement plant are the biggest concern for the manufacturer due to the high carbon tax. Simulation results for CO₂ are presented in Figure 7.8 which indicate that each blend (Table 7.4) can reduce the CO₂ emission regardless of the amount of excess air in the kiln. Simulation results show that CO₂ emission can be reduced about 7.25% by

replacing total fossil fuel with the selected blend of alternative fuels (blend 6). Blend 5, which was supposed to be the best option, was found less efficient than blends 3 and 4 and almost equal to blend 1.

NO_x emission results are presented in Figure 7.9 which indicates that there is a strong correlation between the excess air and the concentration of NO_x in the stack gas. The amount of excess oxygen in the calciner, which was plotted in Figure 7.10, also affects the NO_x concentration. Zhang et al. (2011) reported that excess oxygen could reach up to 40% when 100% tertiary air was carried to the calciner because of its high concentration of O₂. Results presented in this section agree with Zhang et al. (2011) observation. It shows that excess oxygen in the calciner reaches about 21% and 36% when only coal and blend 6 are used respectively. It can be concluded that the introduction of a blend of alternative fuels could shoot the NO_x level sky high hence choosing a perfect blend is crucial. NO_x emission can be reduced by bypassing some kiln gas from the kiln exit which might reduce the temperature in the calciner. Oxy-fuel combustion could be another valid option to reduce the NO_x emission from cement manufacturing. Figures 7.9 and 7.10 reveal that in spite of high excess air in the calciner blend 5 produced comparatively less NO_x. One could conclude from that, blend 5 is capable of producing less NO_x without lowering the amount of excess air in the calciner too much. Blend 1 was found to produce almost the same amount of NO_x as blend 5.

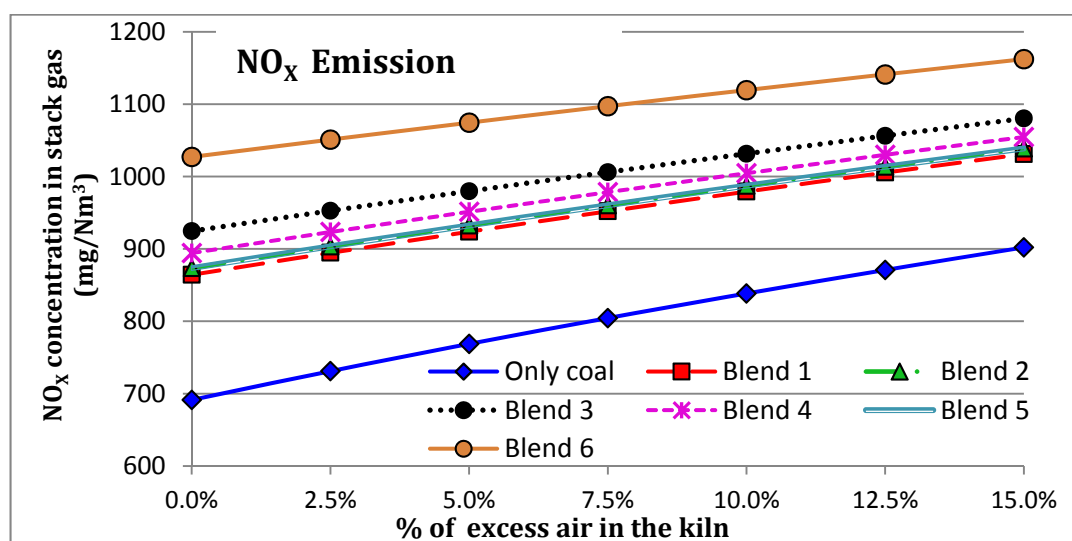


Figure 7.9: NO_x concentration in stack gas

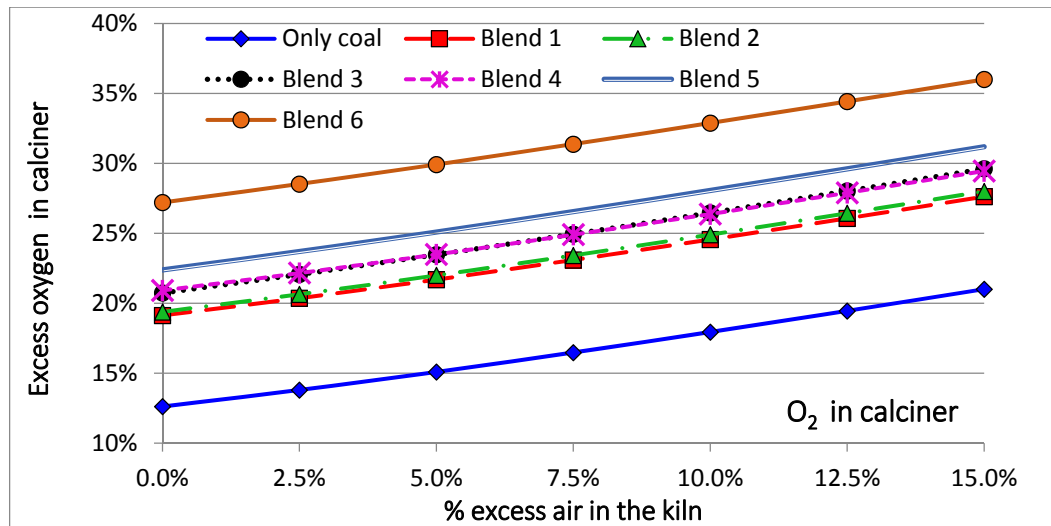


Figure 7.10: Excess amount of O₂ in calciner

SO₂ emission results presented in Figure 7.11 suggest that every single blend is proficient to reduce SO₂ emission up to some extent. One interesting outcome observed that blend 1, where only 50% coal is replaced by alternative fuel, is as good as any other blend with an exception for blend 6 to reduce SO₂ emission. It was also evident that an excess amount of air in the kiln section results in a reduction of SO₂ emission.

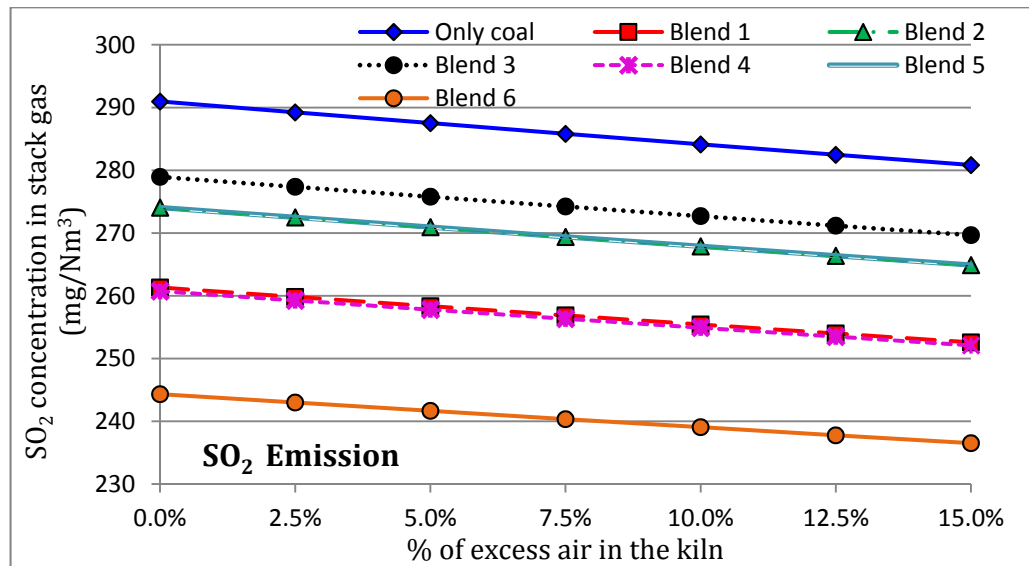


Figure 7.11: SO₂ concentration in stack gas (mg/Nm³)

Clinker composition can be presented in oxide form or in compound form and both are related by the Bogue's Correlation. From the simulation results it was found that the amount of excess air in the kiln did not alter the composition of clinker but a variation was found for different blends of alternative fuels. Figure 7.12 clarifies the impact of different blends

(Table 7.4) of alternative fuels on the clinker composition while the excess air is 10% in the kiln. The amounts of reduction are 2.5%, 2.9%, 3.5% and 2.1% for four major compounds of clinker C_3S , C_2S , C_3A and C_4AF respectively when fuel mix was changed from only coal to blend 6 option. The changes in the composition occur due to the presence of the four major components (Ca, Si, Al, Fe) in the fuel mix. The introduction of the alternative fuels in the fuel mix certainly changes the ratio of these four components as every singel alternative fuel has different elemental composition. Beside this the ash generated from the alternative fuels may not be as rich as the coal ash. This will affect the daily production of clinker as well and this variations are discussed later in this section.

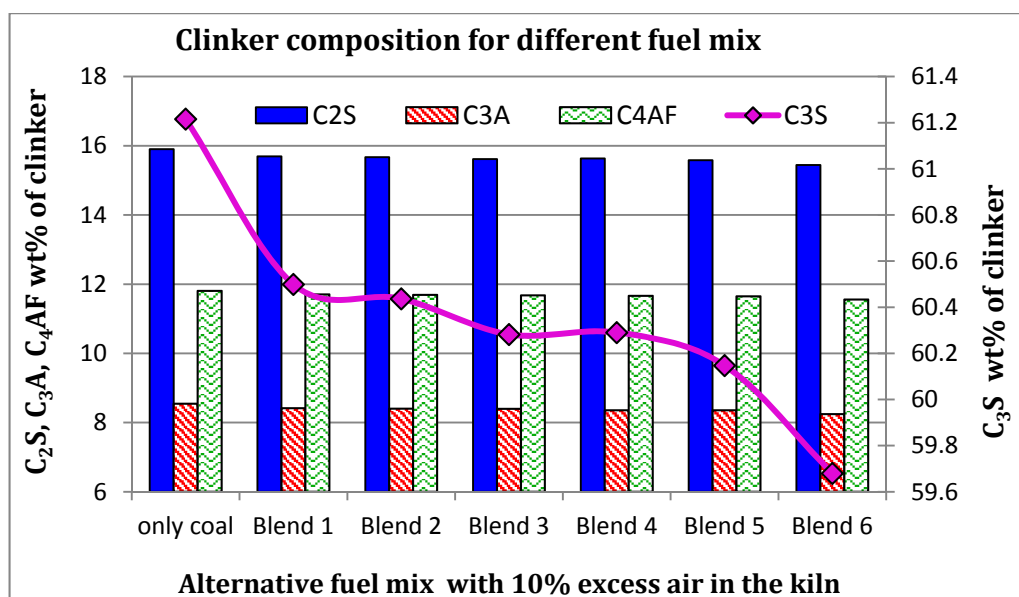


Figure 7.12: Clinker composition for different blend of alternative fuels

The quality of the clinker produced is often determined by three ratios, namely LSF, SR and AR. Any fluctuation from the reference data indicates a downgraded clinker which may lead to an unwanted change in setting time for cement. Simulation results are summarised in Figures 7.13a and 7.13b to observe potential changes in LSF, SR and AR. Excess air in the kiln is considered constant for this case as no substantial variation was observed with the changing amount of excess air. LSF is found to be on the higher side while an alternative fuel blend is used in the model. LSF reaches about 99% for blend 6 compared to the reference case (only coal) of 95.2% because of the additional amount of free lime in the clinker. An excess amount of free lime occurs due to the reduced amount of SiO_2 in the composition to be reacted with CaO to produce C_2S . Simulation results also point out a reduction of alumina ratio with the usage of alternative fuel. Silica ratio also had the same

tendency with an interesting exception for blend 4 and blend 6 where SR was almost the same as the reference case.

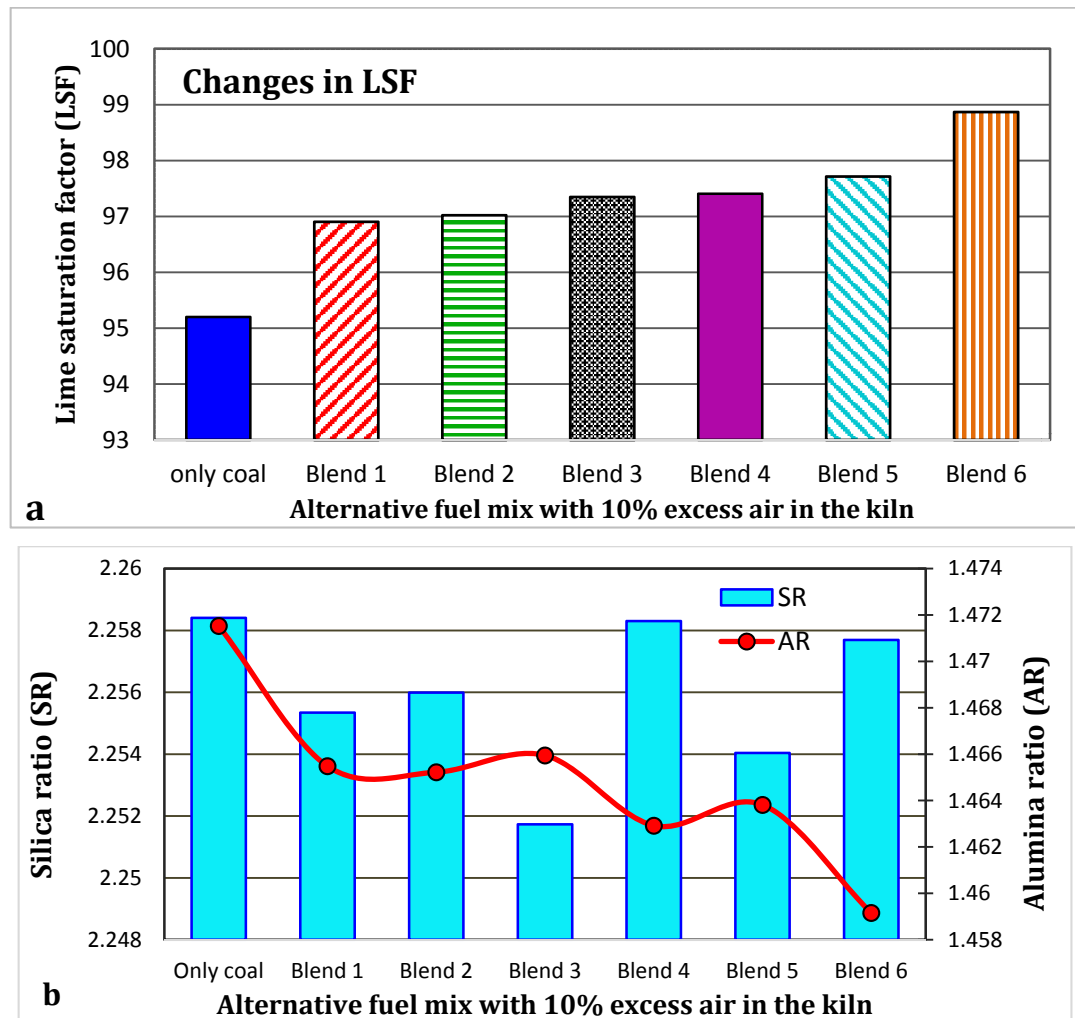


Figure 7.13: Changes in a) LSF and b) SR & AR for different blend of alternative fuels

As clinker is comprised of combustion ash some alternative fuels ash substitutes the raw material for clinker which may lead to an increased clinker production. Unfortunately that is not the case for the current study. For each blend of alternative fuel, a reduction in the clinker production was observed in the simulation results, which is presented in Figure 7.14. Hence additional amounts of raw meal will be required to maintain a consistent amount of clinker production.

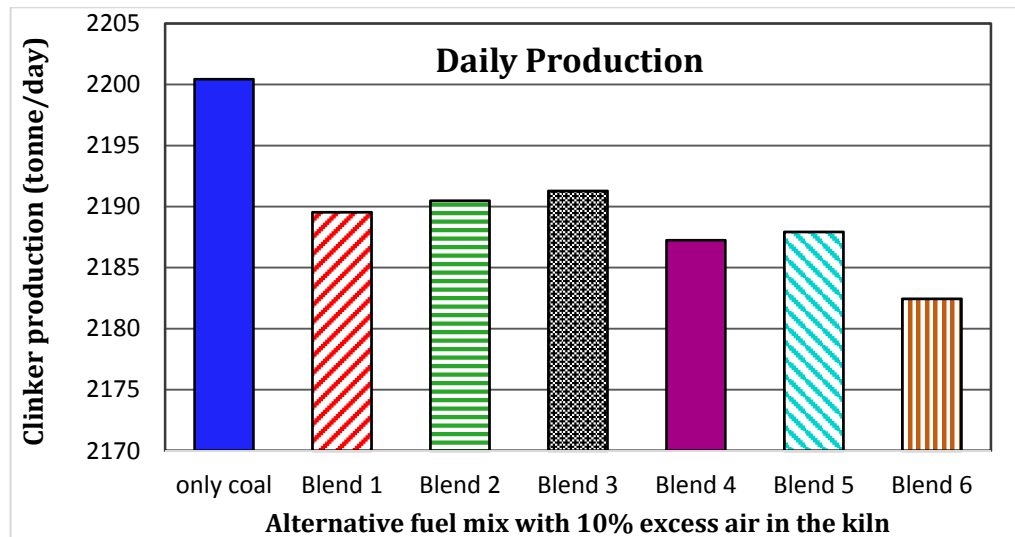


Figure 7.14: daily production of clinker (tonne/day)

7.7 Conclusion

This chapter presents an integrated model for cement manufacturing to identify the maximum usage percentage of selected alternative fuels on the basis of pollutant emission and clinker quality. Alternative fuels were selected by their performance in the preheater tower model and kiln model described in previous chapters. Selected alternative fuels are waste tyre, MSW, MBM, bagasse and plastic waste. A baseline emission standard was set to detect the maximum usage percentage of the selected alternative fuels. Based on the emission results from the simulation the maximum usage percentage is determined as 18%, 15%, 20%, 12% and 5% for waste tyre, MSW, MBM, plastic waste and bagasse respectively. It is to be noted that the have been found based on the data of local cement plant, hence the recommended usage percentages are applicable to that plant at least. Usage percentage may vary for other plants depending on the process setup of the plant, operating conditions and quality of alternative fuels.

In reference to condition, selected alternative fuels are capable of reducing CO₂ emission with an exception for bagasse, which is an encouraging sign as CO₂ is one of the main concerns for the manufacturer due to costs associated with carbon tax. About 4.7% of CO₂ reduction could be achieved by using MSW but that reduces the kiln temperature and affects the clinker composition. In simulation results, it is found that using MSW increases the LSF and decreases SR in clinker composition which may affect the cement setting time.

In a modified operating condition MBM is found to reduce the CO₂ emission about 4.37% without changing the integrity of the clinker.

NO_x emission is found to be on the higher side for each alternative fuel. Using MSW at a substitution rate of 30% increases the NO_x emission almost 29.5% of the reference case (only coal). One interesting feature of NO_x emission is that it is strongly correlated with the amount of O₂ in the calciner. It is suggested that the amount of O₂ in the calciner should be reduced by controlling the tertiary air in the burning zone of the calciner. It is revealed from the simulation results that NO_x emission can be reduced over 30% (for the case of waste tyre and bagasse) by controlling the excess air. Promising results are obtained for SO₂ emission, as all selected alternative fuel except waste tyre reduce SO₂ emission significantly.

A potential energy saving opportunity is identified in this chapter by lowering the fuel feed rate and by keeping the output parameter fixed. About 6.39% of energy saving can be achieved by using MBM, which was also identified as the best option among the alternative fuels. Nowadays most cement plants use energy efficient equipment and further efficiency gained through retrofitting seems unrealistic. In this scenario, even the smallest amount of energy saving through the usage of alternative fuels is appreciable. Plastic waste and bagasse also show great prospect in energy savings though plastic waste is not commonly used in the cement industry and bagasse releases more CO₂ than the reference case.

In the second part of this chapter a set of alternative fuel blends is studied in search for an optimal blend. Six different blends of alternative fuels are considered for study and their impacts on emission and clinker quality are observed. Alternative fuels blend 5 (coal 30%, waste tyre 18%, Msw 15%, MBM20%, plastic waste 12%ans bagasse 5%) is composed with the suggested maximum percentage of alternative fuels and was expected to be the best option. Unfortunately simulation results did not support that expectation. Blend 5 is found to produce better results for NO_x emission compared to the other blends but the emission rate is higher than the reference case. On every other prospect a better blend than blend 5 can be found from simulation results.

In terms of CO₂ emission Blend 1, 2 and 5 produced similar types of results (about 2% reduction). Blend 6, which entirely substitutes coal with alternative fuels, can reduce CO₂ emission up to 7%. But for blend 6, the release of NO_x is way higher than the reference case. Considering these two main pollutant emissions, blend 1 is found to be the best option among the selected blends. In terms of clinker composition, blend 1 generates more acceptable results than the other blends as the reduction of the major four constituents (C₃S, C₂S, C₃A, C₄AF) of clinker are in the tolerable range. Even the changes in the basic ratios (LSF, SR, AR) while using blend 1 are endurable. This analysis shows the importance of the process model as the case of an individual alternative fuel may not agree with the case of a blend of alternative fuels. As per the above discussion this study suggests blend 1 as the best alternative fuel blend for the local cement plant which is composed of coal 50% and five selected alternative fuels with 10% each.

The process model presented in this study could be a useful tool for researchers and stakeholders to determine the impact of a wide range of alternative fuels in cement production. The process model can also be used to study different blends of alternative fuels to optimise energy savings and minimise pollutant emission.

Chapter Eight

Conclusions and Recommendations

8.1 Introduction

The energy intensive nature of the cement industry makes it vulnerable to increasing fossil fuel prices as energy costs are about 30-40% of the total production costs. Besides, recent legislation on pollutant emission and the imposed high carbon tax forces the manufacturer to search for alternative energy sources which are cheaper and environment friendly. Waste derived alternative fuels provide the solution and currently utilise worldwide to meet the energy requirement of the cement industry. Due to the extreme environment inside a cement kiln, almost every type of waste is offered as alternative fuel for the manufacturing process. Unfortunately, not all wastes are found to be environment friendly or can keep the clinker quality up to its basic standard. Though the trend of using alternative fuels in the cement industry is as old as 30 years, research is still ongoing to identify the impact of using waste as alternative fuel.

From this perspective, this study has been undertaken to assess the prospects of alternative fuels in the context of the Australian cement industry and investigated the maximum substitution rate and potential impacts both on emission and clinker quality. Most of the common solid alternative fuels are considered for this study in a process set up of a local cement plant. The local cement plant provided the required data to develop a process model to carry out this study numerically. Findings from this study are expected to be used as a guideline by the policy makers, manufacturer and stakeholders for employing maximum usage of alternative fuels in the cement sector of Australia. The community will also be benefited by this study with an environment friendly and sustainable process option for cement manufacturing.

8.2 Outcomes of the Thesis

This study investigated and examined the impacts of selected solid alternative fuels on the manufacturing process, pollutant emission and clinker quality. The objective and key

research questions were set at the beginning of this study. The current section of the thesis summarises the outcomes of the study and emphasises how the research objectives of the study were met.

Comprehensive literature reviews on manufacturing process and usage of alternative fuels were documented in Chapters 2 and 3. In the review, the detailed process of cement production was described which lead to the development of the framework necessary for setting research methodology. The literature indicated the energy intensity and the complexity of the process in terms of endothermic and exothermic chemical reactions. The literature review also showed the effectiveness of a computational model to study such extreme processes. Among a range of simulation software, a suitable one to study the cement process was identified through the literature review and the selected one is Aspen plus. Literature review revealed that in Australia, national regulation for air emission does not exist and for the purpose of current research a base line standard was considered in conjunction with the local plant specification and worldwide practice.

Literature review on alternative fuels shows a wide range of waste that can be used as fuel in the cement process. In terms of substitution rates of alternative fuels in the cement sector, Australia was found way below the world's best practice. In the Australian cement industry only few alternative fuel options are currently being used, as literature suggested. This study discussed & identified a need to identify potential alternative fuels for the Australian cement industry and their maximum substitution rates. This thesis offers a first-time study on a set of alternative fuels with maximum substitution rates in Australian cement industry

Outcomes of this study into five major areas outlined in chapter1, are summarised below.

8.2.1 Feasibility study

The thesis presented a feasibility study to identify the potential alternative fuels from an Australian perspective with support from a local synergy report, waste generation trends and common practice in the world. The feasibility study of alternative fuels has been discussed in chapter 3. The synergy report of Gladstone industrial area suggested that SPL, a waste from an aluminium smelter, could be one of the potential alternative fuels for the local cement plant. In terms of worldwide waste production, waste tyre and municipal solid

waste (MSW) are considered most readily available alternative fuel options for the cement industry. These two alternative fuels are also suggested for the Australian cement industry as they are currently being used in current practice. Central Queensland has a well-developed beef industry. Meat and bone meal (MBM), a processed waste from the beef industry, can be an attractive option for the cement industry. Agricultural biomasses are considered as a carbon neutral fuel option as the amount of CO₂ they consumed from the atmosphere during their growth is almost the same as the amount of CO₂ released during their combustion. Australia is a relatively small producer of agricultural crops in the world scale. However, to grasp the advantages offered by agricultural biomass, a small amount is recommended as alternative fuel in the cement industry. Plastic waste has the highest calorific value among the solid alternative fuels, so it is recognised as a potential alternative fuel. However its recycling is preferred over its combustion option due to toxic emission while burning.

The substitution rate of the aforementioned alternative fuels are available in literature except plastic waste. Literature suggests MBM could replace up to 40% of thermal energy requirement of the cement process. The proposed substitution rate for waste tyre and MSW in literature is up to 30%. Throughout the review it was revealed that the substitution rate depends on the location of plant, process mechanism of the plant and the collection source of alternative fuel. Hence it was essential to identify the substitution rate for local interest.

8.2.2 Computational model development

Literature review suggests that computational models for the process are an effective tool to predict the behaviour of alternative fuels in a risk free, cost effective and timely manner. In this thesis Aspen plus was identified as the appropriate software to model the entire manufacturing process. A process model was developed in the course of this study and utilized to predict the outcomes of using suggested alternative fuels. The process model was developed in three stages: the preheater tower model, the kiln model and the integrated model. Each stage of the model was verified against the published data and the data collected from the local cement plant. The novelty of the integrated process model is its ability to consider combustion ash as a reactant to the clinker formation equation and to handle multiple alternative fuels simultaneously. These two unique features of the process model allow to predict the clinker composition accurately for quality control and to recognise an optimal blend of alternative fuels. A detailed description of the novel

integrated process model has been presented in Chapter 7 while the construction of the preheater tower model and the kiln model have been attached in Chapter 5 and 6 respectively.

Cement manufacturing process is as old as about 200 years. During those years the process has been change drastically and a modern cement plat contain all the component that ensure the maximum amount of energy is saved and the environmental impact is minimum. In spite of all the technological changes occurred in cement industry the basic process and chemical reactions involved in the process remains same. The model presented in this thesis contain all the basic information of the process and deals with major chemical reactions for clinker productions. On that note it can be said that the model presented in this thesis should be valid unless some drastic change take places in the manufacturing process. Technology is ever changing so as the research approach to the problems. New technology may be introduced in the manufacturing process in near future and that can also be modelled with appropriate unit operation block. Aspen plus has the flexibility to include additional block in an existing model.

8.2.3 Maximum substitution rate of alternative fuel

A wide range of waste materials can be used as alternative fuels in the cement industry due to the extreme nature of the cement manufacturing process. Examination of every single alternative fuel was beyond this study, hence a set of alternative fuels were selected for the feasibility study in Australian context. The substitution rate of most of the selected alternative fuels are available in literature but not in precise form. This is in consideration of the fact that the substitution rate might change on the basis of process setup, operating conditions of the plant and with the quality of alternative fuels.

To identify the maximum substitution rate of selected alternative fuels a base line performance for air emission was set in this thesis as there is no national air emission standard. The proposed tolerable emission limit of CO₂, NO_x and SO₂ according to world emission standard are;

CO₂ emission limit: 805 kg/tonne clinker

NO_x emission limit: 950mg/Nm³

SO_x emission limit: 300mg/Nm³

It is worthy to mention that most of the cement producing countries follow the standard emission limits for SO₂ and NO_x which are 200 – 500 mg/Nm³ and 500 – 1000 mg/Nm³ respectively. The average NO_x emission data was found slightly higher than the global emission standard but for analysis purposes the base line emission is considered to be within the limit. Along with these emission baselines, a few other parameters were considered to identify the maximum substitution rates of selected alternative fuel. Among them kiln outlet temperature (>1600°C), clinker composition (with a maximum 5% variation with reference case), daily production (2200±5 tonne/day) are noteworthy. The substitution rate of alternative fuels was increased until any of the base line standard limit is crossed. Based on the simulation results of the integrated model, the maximum substitution rates of selected alternative fuels for the local plant's operating condition are;

Waste tyre:	18%
MSW:	15%
MBM:	20%
Plastic waste:	12%
and Bagasse:	5%

A few more alternative fuels were also studied separately in the kiln model and the preheater tower model. According to the simulation results from those two models, the maximum substitution rates for the alternative fuels were suggested. They are: SPL(<5%), RDF (8.5%), SS (8%) almond shell (15%), Rice Husk (15%), Coffee Husk (12%), Olive husk (13.5%).

One important finding from this analysis is the rejection of SPL as a potential alternative fuel for the local cement plant. Some adverse effects on clinker quality was observed when SPL was offered as alternative fuel in the cement kiln. Hence over 5% substitution rate was not encouraged for the local plant. A substitution rate for the plastic waste and its impact on the clinker quality was not found in the literature. Both of these information are considered important outcome of this thesis.

In addition to identify the maximum substitution rates, a selection of alternative fuel blends was examined to identify an optimal blend. It was expected that a blend of five alternative fuels which were blended with their maximum substitution rates would produce the best results. Interestingly, simulation results did not support that assumption and a blend

composed with 50% coal and 10% of each alternative fuel produced the best results in terms of pollutant emission and minimal effect on the clinker quality. Outcomes summarised in this section can be found in Chapter 5, 6 and 7.

8.2.4 Impact analysis

Impact assessment of alternative fuels are essential prior to commercial implementation. This thesis presented a detailed impact analysis on the emission and on the clinker quality. Five alternative fuels were studied by the integrated model with variable feed rates and variable amounts of excess air in the burning zone. Results are presented in the reference condition and in the optimized condition to identify potential improvement in air emission results. In the optimized condition, the minimum amount of fuel was fed in the system without altering the kiln environment and the integrity of the clinker. In the reference condition, operating parameters and energy demands of the system were set in agreement with the collected data from the local cement plant.

In the reference condition about 5% reduction of CO₂ was observed in the case of 30% thermal substitution of MSW. Unfortunately for this case NO_x concentration increased by about 30%. On the other hand, in optimized condition, a maximum of 4.37% reduction of CO₂ was reported in this thesis. This scenario was observed for the case of 20% MBM firing with 80% coal. In addition to CO₂ reduction, a 16% decrease of NO_x emission and 3.65% decrease of SO₂ were also detected. In optimized condition a high percentage (about 33%) reduction of NO_x was spotted for the case of waste tyre and bagasse. But that reduction came at the price of increasing SO₂ in the stack gas. In optimized condition, waste tyre was found to raise SO₂ emission of about 12%.

The clinker quality in terms of basic ratios of oxides were also studied in this thesis. Apart from the case of SPL it was found that the impact of using alternative fuel on clinker quality is minimum. In the numerical study of the kiln model it was found that, using SPL as alternative fuel reduces the amount of CaO in the composition which leads to a lower percentage of C₃S and an excess amount of C₂S. Due to this erroneous outcome, SPL is only recommended for use with a substitution rate below 5%. In the analysis of the integrated model, it was found that LSF increases in a tiny proportion (around 1.5%) for all the selected alternative fuels. In terms of SR and AR selected alternative fuels showed almost no variation except MSW. For MSW a small rise (<1%) was observed for AR while

SR suffered a reduction of about 1.8%. The variation in the clinker composition was minimal, hence it was concluded that *selected alternative fuels have minimum influence on the clinker quality*.

In the analysis of the integrated model, simulation results for a selection of alternative fuel blend were included to provide extra dimension to this thesis. Simulation results indicate that any composition of alternative fuel blend was capable of reducing CO₂ and SO₂ emission from the cement plant. On the contrary, NO_x emission was found to be on the higher side for each alternative fuel blend. It was revealed through the analysis that NO_x concentration in stack gas is positively correlated with an excess amount of oxygen in the kiln and the calciner. Excess air is required in the burning zone to ensure the complete combustion of fuels. Controlling the air in the burning zone with a cautious manner could possibly reduce the NO_x concentration in the stack gas.

The clinker quality was found to be affected when the blends of alternative fuels were used in the process. A maximum of 2.5%, 2.9%, 3.5% and 2.1% reduction of C₃S, C₂S, C₃A and C₄AF respectively was found when the total thermal energy requirement was fulfilled by an alternative fuel blend (blend 6). Changes in the basic ratios (LSF, AR, SR) were also observed for different blends of alternative fuels. Variations of LSF, AR and SR for different blends were found to be similar to the results of individual alternative fuel firing. The maximum difference observed in the simulation results is less than 4% and hence may not be significant enough to alter the basic property of the clinker.

8.2.5 Energy savings opportunity

Energy savings is one of the desired outcomes that the cement manufacturers are always looking for. Modern technology like the calciner, waste heat capture, energy efficient cooler allows the cement industry to produce cement using minimum energy. Most cement manufacturers in Australia are currently using energy efficient equipment to grab every single opportunity of energy saving. Literature suggests that achieving further energy efficiency through retrofitting is unlikely. The only option of energy saving through the usage of alternative fuel is to reduce the amount of fuel required without affecting the process. Energy saving opportunities were studied for the preheater tower, the kiln and the integrated model. Encouraging results were observed for the integrated model as a maximum of 6.39% of energy savings was reported for the case of MBM combustion with

coal. Plastic waste and bagasse also showed some energy savings opportunity with about 5% reduction in energy requirement. Details of these outcomes were presented in Chapter 7.

8.3 Contributions

On reflection, the contributions of this study are:

- Feasibility study and clear understanding of identifying the potential alternative fuels for the Australian cement industry.
- Novel computational model development which can be utilised for predicting the outcomes on implementing alternative fuels in the cement industry.
- Detailed environmental impact analysis through simulation results to identify potential changes in emission and clinker quality while using different alternative fuels.
- Comprehensive analysis that identifies the maximum substitution rates of selected alternative fuels for a reference operating condition.
- Numerical analysis on the selection of alternative fuel blends to discover the optimal fuel blend.
- Analysis to identify potential energy saving opportunities by introducing alternative fuels in the manufacturing process.
- Information on guideline development for cement manufacturers, local government, policy makers, researchers and the entire community to update the definition of wastes in the Australian context so that they can be utilised in maximum proportion in the cement industry.
- Information for a baseline emission standard development for the local government to be considered as none currently existing.
- Environment friendly and sustainable cement manufacturing process that might help ensure a green future for the community.

8.4 Recommendation for future research

In the current study a simulation based investigation was carried out to investigate and identify the impact of alternative fuels in the cement manufacturing. Maximum usage of alternative fuels and potential energy saving opportunities were also pointed out in the thesis. Before implementing any alternative fuel or any blend of alternative fuels in the

process, simulation results need to be supported with experimental results. As per the scope of research a few areas were not considered in this study and recommended for future work.

- This study recommends the experimental investigation in real plant scenario to justify the outcomes and to establish the simulation results even stronger.
- A comprehensive literature review on alternative fuels is provided in this thesis, however multi criteria analysis is recommended to identify the best option of selection of alternative fuels. .
- In this study only solid alternative fuels were considered and a similar study is recommended for liquid alternative fuels like waste oil, solvent and paint residue.
- Some minor pollutant like heavy metal and Dioxin and furans were not considered in this thesis. A modified model of the presented version can be used to examine the impacts of alternative fuels on the emission of those pollutants.
- Life cycle assessment of the alternative fuels can be done as an extension of the current study.
- Recently oxy-fuel combustion was suggested in the cement industry to reduce the NO_x emission. The model presented in this thesis can also be used to simulate oxy-fuel combustion process.
- In this thesis blends of five selected alternative fuels were studied. Different blends with different set of fuels can be studied to use the locally available alternative fuels for different region.

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Appendix

In this section a brief description of how the Aspen plus software works is given to help the reader to understand the simulation process. To simulate the model properly all the required information need to be specify in five categories

- Global data specifications
- Components specifications
- Properties
- Streams
- Blocks

Figure A.1 shows a typical Global specification sheet where measurement units, stream class and flow basis need to be specified. In the stream class MCINCPD was chosen which represents mixed, conventional inert and non-conventional components with particle size distribution.

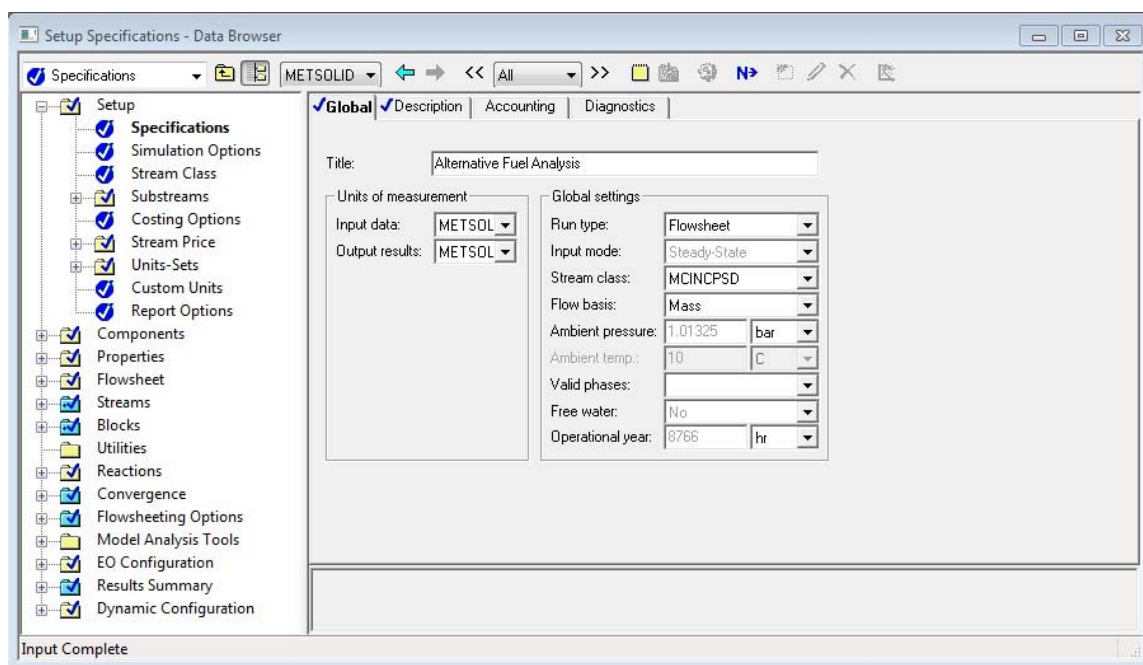


Figure A.1: Global specification sheet in Aspen Plus simulation

All the chemical component that is used in the model are entered in the component specification sheet. Pure component databanks contain parameters such as molecular

weight and critical properties. The component ID is used to identify the component in the simulation inputs and results. Each component ID can be associated with a databank component represented by either a formula or the component's full name. All nonconventional component also need to be entered in this section. If the conventional component is not available in the Aspen data bank it can be inserted by using user defined button and basic property of the component such as molecular weight, boiling point, enthalpy of formation also need to be specified in order to add the component to the user defined data bank. Figure A.2 shows a component specification sheet in Aspen plus.

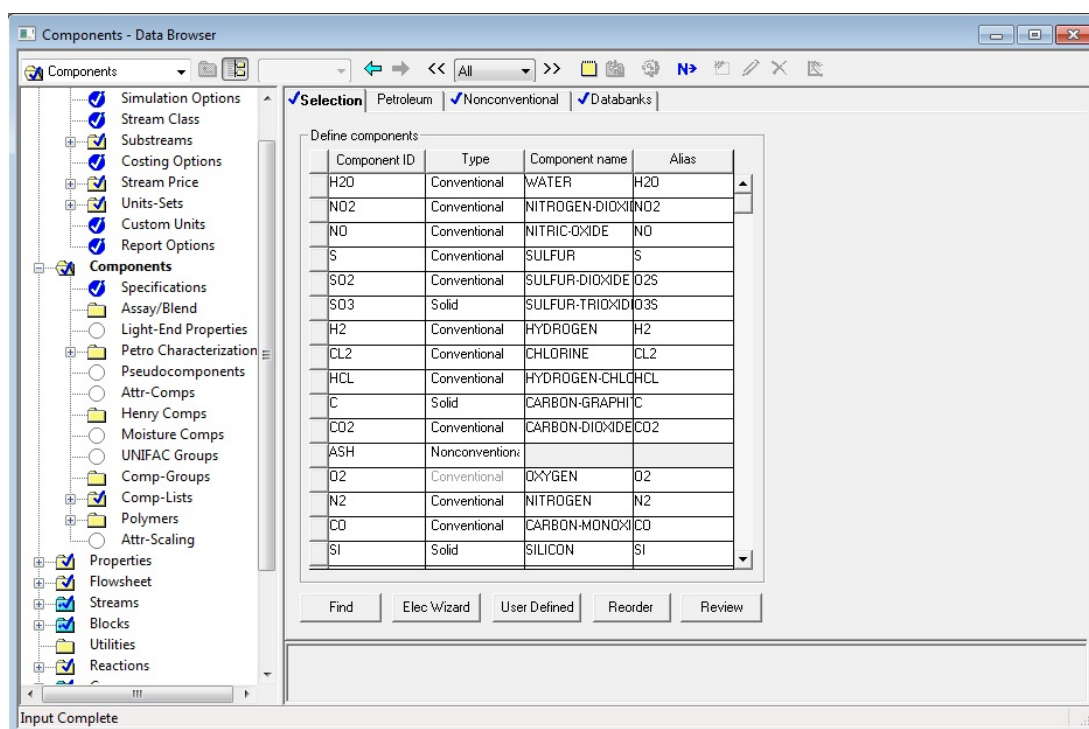


Figure A.2: Component specification sheet

In the properties specification sheet the property method need to be specified for the simulation (Figure A.3). A wide range of property method are available in Aspen plus and can be viewed by using the drop down list. Choosing the right physical properties is critical for obtaining reliable simulation results. Heating value of coal and alternative fuels also need to be specified in this section (Figure A.4).

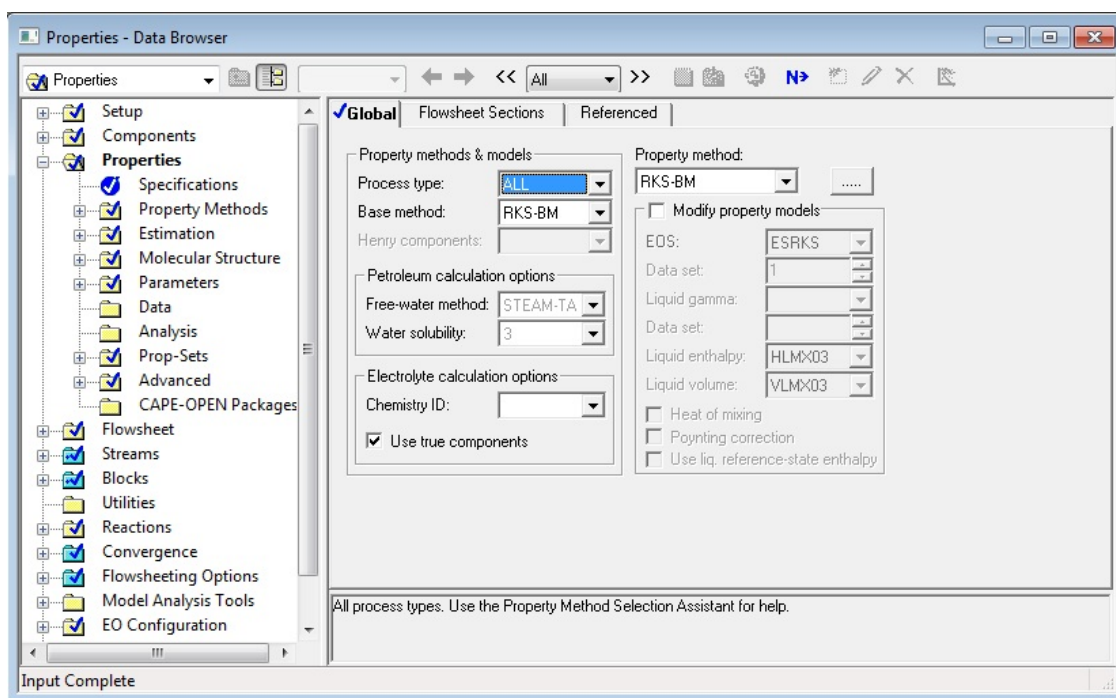


Figure A.3: Global property specification information in Aspen plus

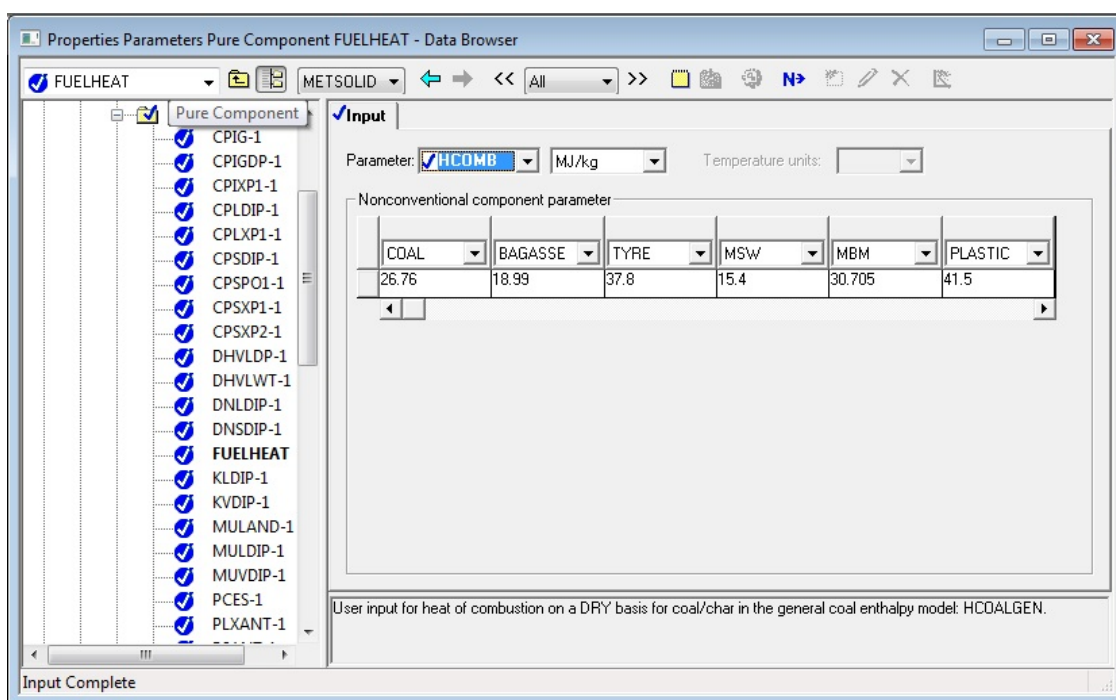


Figure A.4: User defined property parameter sheet for heating values of fuels.

Enthalpy and density model for all the nonconventional component listed in the component specification sheet, need to be entered as a part of property specification (Figure A.5).

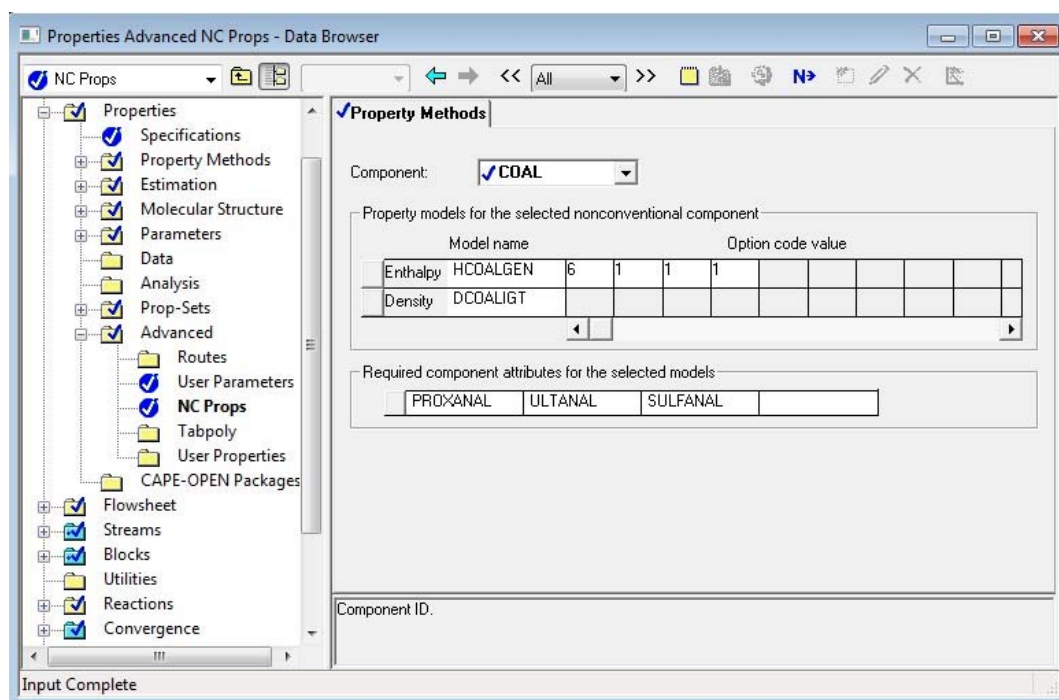


Figure A.5: Assigning Enthalpy and Density model nonconventional component

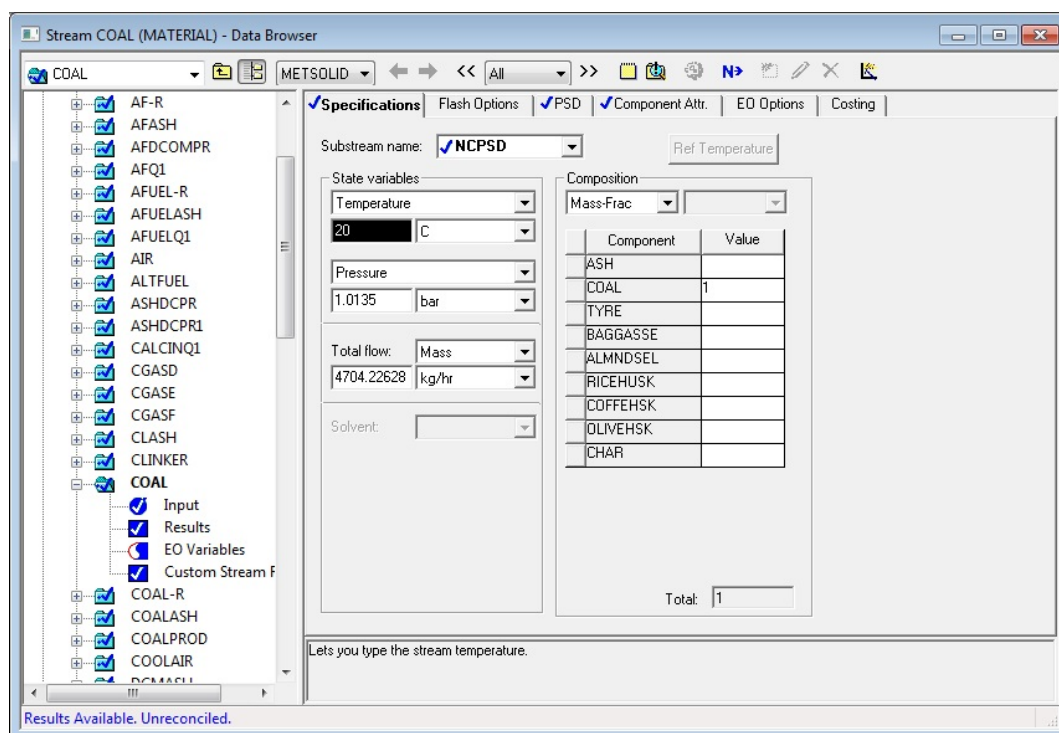


Figure A.6: Coal input stream specification

Property setting for each stream and block are decisive for the modelling. In the input stream composition specification, physical properties (temperature, pressure), particle size distribution and total flow rate need to be quantified. Figure A.6 and A.7 represents the coal

stream specification and component attribute specifications respectively while Figure A.8 shows the alternative fuel stream specifications.

Stream COAL (MATERIAL) - Data Browser

COAL

METSOLID

Specifications | Flash Options | PSD | **Component Attr.** | EO Options | Costing

Substream name: **NCPSPD**

Component ID: **COAL**

Attribute ID: **PROXANAL**

Element	Value
MOISTURE	1.35
FC	57.3
VM	24.15
ASH	18.55

Total: 100

Lets you select the substream name.

Results Available. Unreconciled.

Figure A.7: Specify the elemental analysis of coal.

Stream ALTFUEL (MATERIAL) - Data Browser

ALTFUEL

METSOLID

Specifications | Flash Options | PSD | **Component Attr.** | EO Options | Costing

Substream name: **NCPSPD**

State variables

Temperature: 20 C

Pressure: 1.035 bar

Total flow: 499.015873 kg/hr

Solvent:

Composition

Mass-Frac

Component	Value
ASH	
COAL	
TYRE	1
BAGGASSE	
ALMNDSEL	
RICEHUSK	
COFFEHSK	
OLIVEHSK	
CHAR	

Total: 1

Lets you select the substream name.

Results Available. Unreconciled.

Figure A.8: Specification sheet for alternative fuel input

The reactor blocks performs the chemical reactions on the basis of minimum Gibbs free energy (RGibbs reactor) and reaction stoichiometry (RStoic reactor). Figure A.9 and A.10 display the specification sheet for RGibbs and RStoic reactors respectively.

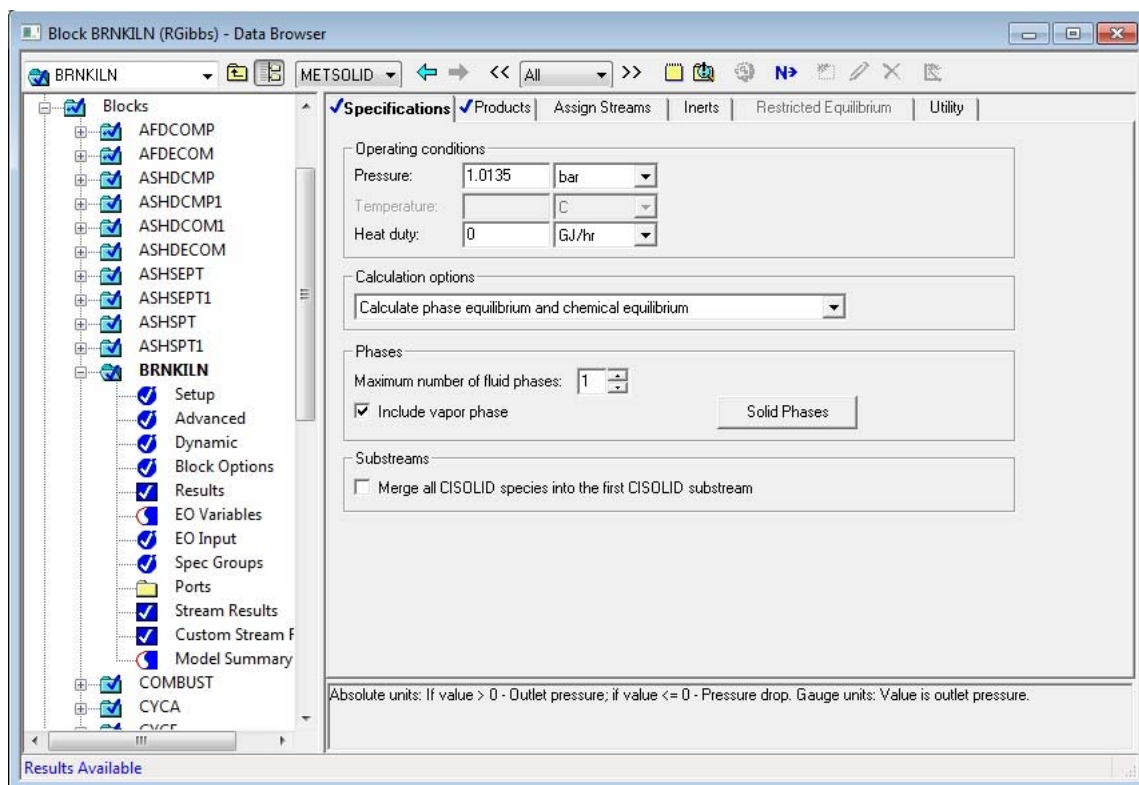


Figure A.9: Operating conditions for RGibbs reactor

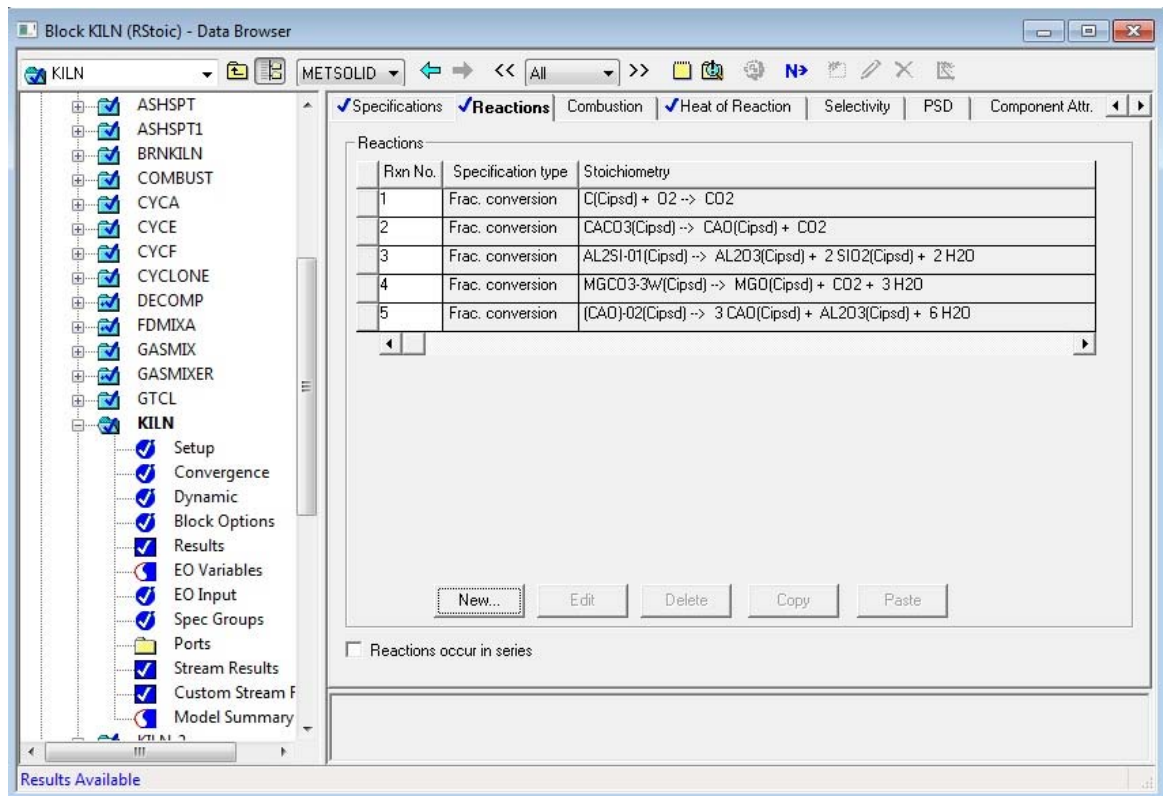


Figure A.10: Entering reaction stoichiometry for RStoic reactor

For the cyclone block, the dimension and the efficiency of the cyclone need to be entered in the specification sheet (Figure A.11)

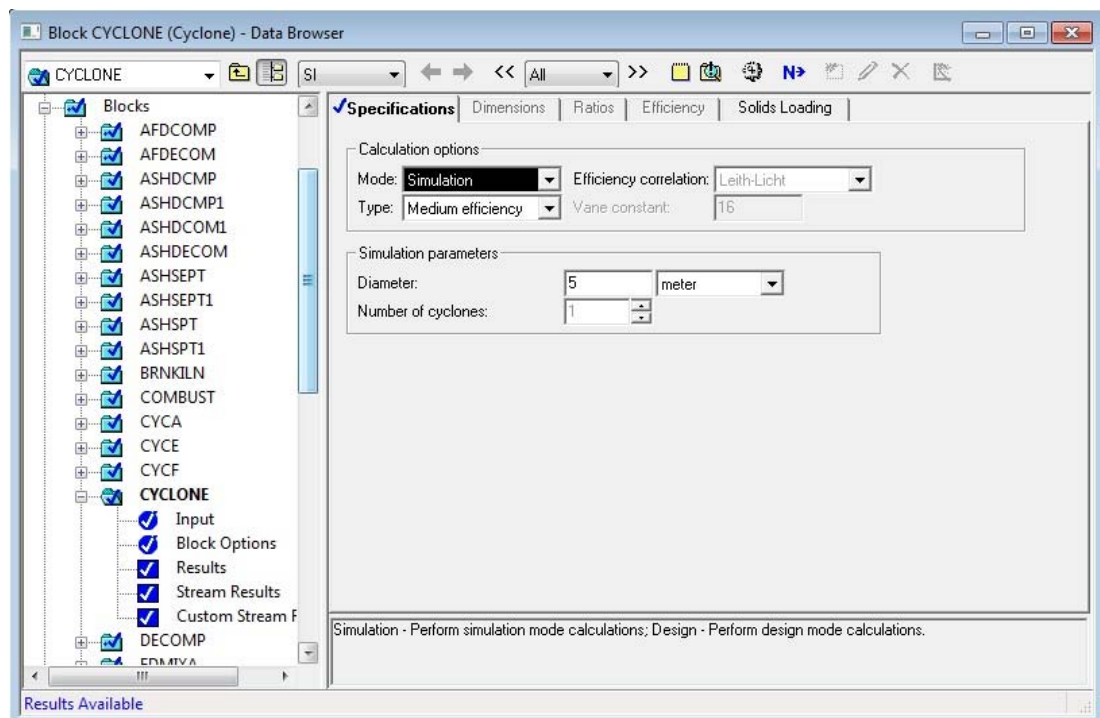


Figure A.11: Specification sheet for Cyclone block

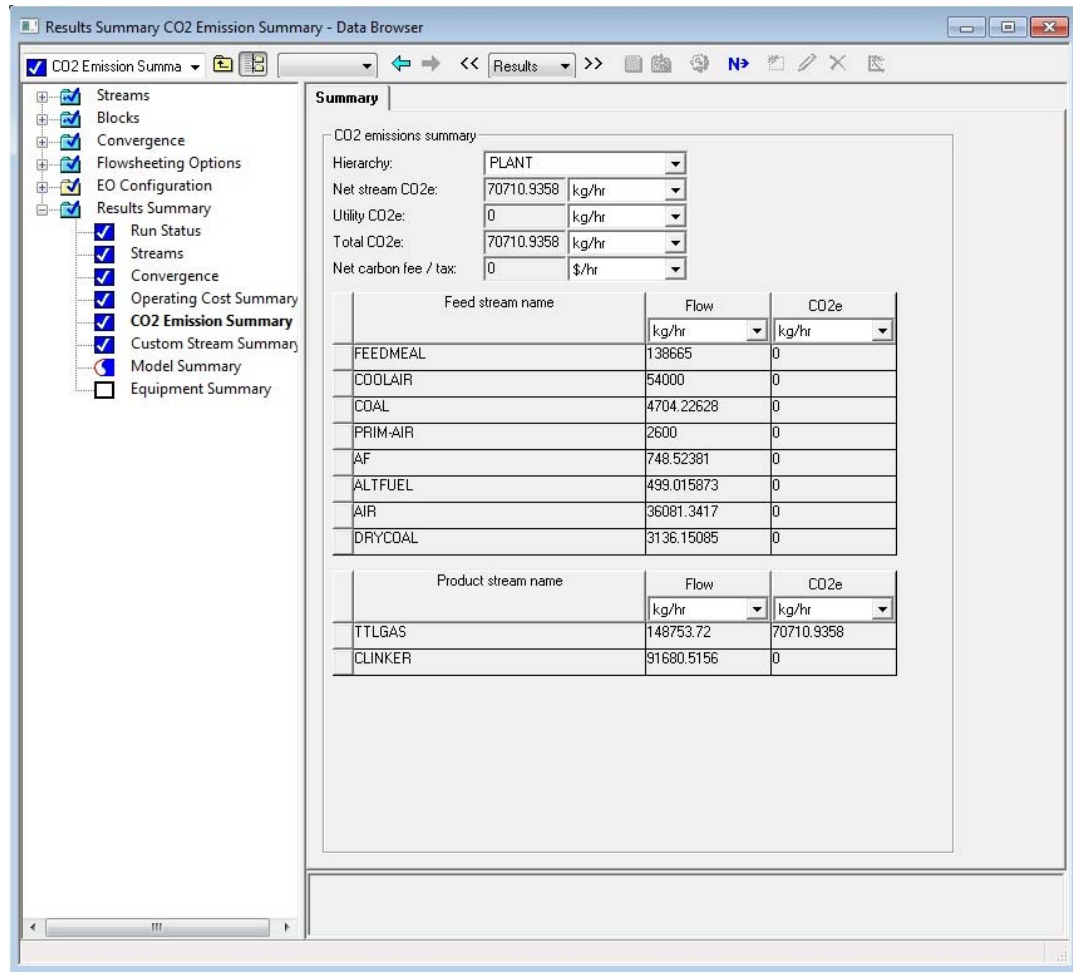


Figure A.12: CO₂ emission summary from simulation results

After running the model without error and warning the simulation results are stored and can be seen under results summary heading. Aspen plus generate CO₂ emission summery as a part of the simulation (Figure A.12). Results can be viewed in combine form in the custom stream summary format (Figure A.13) or by opening individual stream (Figure A.14) or block results.

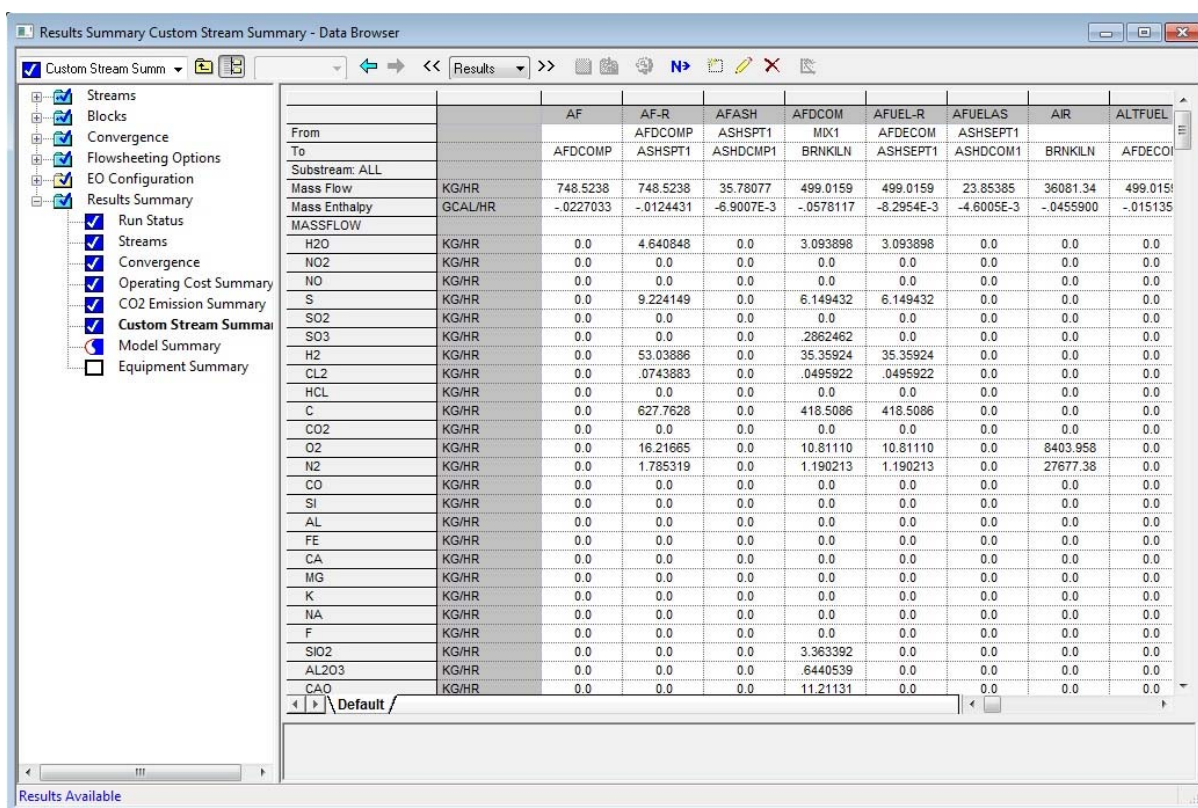


Figure A.13: Custom stream summary containing input and output results for all stream and block

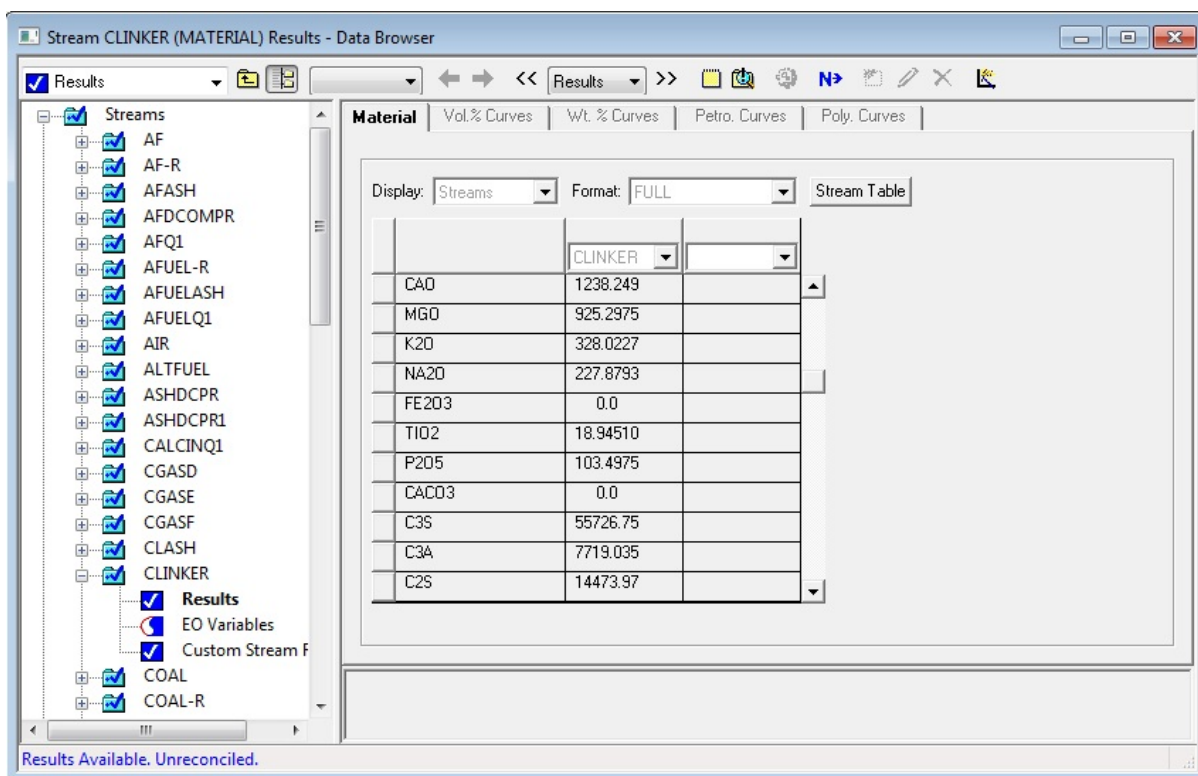


Figure A.14: Material stream summary results for clinker stream