Experimental and mathematical modelling of biowaste gasification in a bubbling fluidised bed reactor

Thesis presented for the award of Doctor of Philosophy


Department of Chemical Sciences
Faculty of Science and Engineering
University of Limerick, Ireland

Supervisors:
Dr. Witold Kwapisz
Prof. James J. Leahy

Submitted to the University of Limerick
November 2016
DECLARATION

The work presented in this thesis is the original work of the author, under the supervision of Dr. Witold Kwapinski and Prof. James J. Leahy. Other sources of information, when used, have been acknowledged. No part of this thesis has been previously submitted to this or any other university.

Daya Shankar Pandey

Date
ACKNOWLEDGEMENT

During my PhD, I treasured moments filled with delight, frustration, apathy, confidence and success. It was a great learning experience indeed. This is the time to express my gratitude to thank many people who provided various help during my stay and work at the University of Limerick, Ireland.

I would initially like to thank my supervisors Dr. Witold Kwapinski and Prof. J. J. Leahy for accepting me to do a PhD in the Carbolea Research Group and for giving unwavering support and providing a trustful environment with opportunities, challenges and also enough freedom to develop as a researcher. I am very grateful for their suggestions and motivation to take part in various workshops and conferences. I thankfully acknowledge their efforts and advice to improve the structure of manuscripts and thesis. To the great extent a special thanks goes to Dr. Marzena Kwapinska for her continuous support, suggestions and discussions throughout the course of my work. Thank you Dr. Michael P. Ryan for proof reading the thesis.

I would like to thank the principle coordinator of the ReUseWaste project, Prof. Lars Stoumann Jensen, Dr. Myles Oelofse, all the ReUseWaste fellows and partners. The project meetings, scientific and generic training activities, workshops, site visits were truly inspiring, motivating and fun. Being part of ReUseWaste was a life changing experience that opened doors for my future scientific career.

During the course of this research, I gained an opportunity to undertake a Marie-Curie secondment at the Grupo de Bioenergia, Universidade de Sevilla, Spain under the guidance of Prof. Alberto Gómez-Barea. A very special thanks goes to him for his concrete inputs in the work related to pseudo-equilibrium modelling and the entire group for making my research stay in Sevilla so enjoyable. I am indebted for his sound and friendly advices, fruitful comments, scientific feedback and discussions.

During this research, I was also awarded a BRISK research grant and went to ECN (the Netherlands) for conducting the experiments under the guidance of Dr. L.P.L.M. Rabou and Dr. Lydia E. Fryda. The research trip has provided valuable data for my
thesis, for model development and I learned a great deal of knowledge. I would like to thank them and all the staff involved for making the visit valuable and enjoyable.

I am also thankful to Dr. Indranil Pan and Dr. Saptarshi Das for their concrete inputs in the work related to data-driven modelling approaches. Their valuable discussions and recommendations always inspired me to bring the best out of this work. They critically read and improved the manuscripts.

A big thanks to all the members of Carbolea Research Group and friends in UL for their consistent support, advices and friendship. I specially thank my project colleague as well as friend Dr. Natalie Taupe for her helpful advice and cheerful company during work and trips.

This work would have not been possible without financial support from the People Programme (Marie Curie Actions) of the European Union’s Seventh Framework Programme FP7/2007-2013/under REA grant agreement n° [289887], research grant from EU’s BRISK project, Postgraduate Research scholarship and Plassey Campus Centre scholarship received from the University of Limerick, Ireland.

Above all, I am grateful to the almighty god for giving me such wonderful parents. I owe everything to them. I will always be indebted to my sisters Asha and Luxmi, my brother Shiv Shankar Pandey and my brothers in-law who always stood by me and became my strength. I am also grateful to my in-laws for their unequivocal support in all possible ways. This would have been impossible without their support.

Before I finish, a very special thanks to you my beloved wife Dr. Pooja, for being with me even from miles apart. Thank you for your love and patience, without your support I would never have been able to come to this point.

Thank you all for your unending support, I could have not done this without you!
DEDICATION

This thesis is dedicated to my mother and
in memory of my father.
Abstract

The production of clean, economically affordable energy with minimum impact on the environment is posing the most significant challenge of the 21st century. According to World Bank data, about 4 billion tonnes of waste is generated per year, out of which cities’ alone contribute 1.3 billion tonnes of solid waste. This volume is forecast to increase to 2.2 billion tonnes by 2025. Three-quarters of this waste is disposed of in landfills while only one-quarter is recycled. In addition to this, livestock production is among the most rapidly growing sectors of the agricultural economy, driven primarily by the growing demand for animal protein. Waste from this sector presents a massive disposal problem throughout the world while also offering the potential of being a source of energy and nutrients. In this context, biowaste, originating from households and animal production, could contribute significantly to achieving the ambitious goal set by EU’s Renewable Energy Directive, which commits the EU to produce 20% of its total primary energy demand from the renewables by 2020.

This thesis is focused on optimising the bioenergy production from biowaste by employing a thermochemical conversion technology (gasification). To date gasification of municipal solid waste (MSW) and poultry litter has not been explored. In this work, experiments and process simulations are performed which demonstrates the feasibility of biowaste gasification. An additive (limestone) is blended with poultry litter during its gasification in a bubbling fluidised bed to prevent bed agglomeration. Furthermore, a pseudo equilibrium based model (PEM) complemented with experimental data is developed to predict the product gas composition, lower heating value (LHV) and optimised process parameters using Aspen Plus. The carbon conversion, \( \text{CH}_4 \) formation and the equilibrium factor for the water-gas shift reaction were corrected based on experimental data from the gasifier. Data-driven modelling approaches are also developed for simulating the fluidised bed gasification of MSW. Genetic programming (GP) and an artificial neural network (ANN) model using Monte Carlo simulation are exploited. Published experimental datasets are used for model training and validation purposes. A genetic programming based modelling strategy provides analytical expressions which can deliver an insight into determining if the selected feedstock would be an appropriate fuel for gasification or not. A simple and rigorous ANN approach is also developed for deciding hidden layers, number of neurons in the hidden layer and activation function in a network using multiple Monte Carlo simulations. These data-driven models have shown better predictive accuracy over the previously developed PEM. Another advantage of these models is their flexibility to be easily extended for other types of feedstocks/process.
List of papers included in this thesis

The thesis is based on a number of peer-reviewed articles already published and presented in international conferences. They are the following:


**Conferences**


Pandey, D.S., Leahy, J.J., Kwapinski, W. **Oral:** Simulation of synthesis gas production from gasification process of poultry litter, 10th RRB Conference, Valladolid, Spain, 4–6 June, 2014.
List of papers not included in this thesis


Conference

# Table of Contents

1  Introduction.................................................................................................................. 1

  1.1  Background .............................................................................................................. 1

  1.2  Waste generation – An Irish perspective............................................................... 6

  1.3  Energy recovery from waste....................................................................................... 7

        1.3.1  Anaerobic digestion .................................................................................. 10

        1.3.2  Electrochemical method............................................................................ 11

        1.3.3  Combustion................................................................................................. 11

        1.3.4  Pyrolysis....................................................................................................... 12

  1.4  Gasification ......................................................................................................... 12

        1.4.1  Introduction................................................................................................. 12

        1.4.2  Types of gasifier......................................................................................... 19

        1.4.3  Moving/fixed bed gasifiers....................................................................... 20

        1.4.4  Fluidised bed gasifier............................................................................... 22

        1.4.5  Entrained flow gasifier.............................................................................. 24

  1.5  Mathematical modelling of gasification................................................................... 25

  1.6  The ReUseWaste project ......................................................................................... 28

        1.6.1  An Overview................................................................................................ 28

  1.7  Overall scientific objectives and approach............................................................. 29

  1.8  Scope of the proposed work...................................................................................... 32

  1.9  Thesis structure....................................................................................................... 32

  1.10 References................................................................................................................ 35

2  Materials and methods .................................................................................................. 47

  2.1  Fuel characterisation............................................................................................... 47

        2.1.1  Feedstock sampling methods.......................................................................... 47
2.1.2 Moisture content ................................................................. 47
2.1.3 Volatile matter content ...................................................... 48
2.1.4 Ash content .......................................................................... 49
2.1.5 Fixed carbon content ............................................................. 50
2.1.6 Determination of carbon, hydrogen, nitrogen and sulphur in the feedstock ................................................................................................. 51
2.1.7 Determination of higher heating value, lower heating value and chlorine content ................................................................. 52
2.1.8 Cellulose, hemicellulose and lignin analysis ......................... 54
2.1.9 Thermogravimetric analysis .................................................. 54
2.1.10 Bed material characterisation .............................................. 55
2.2 Fluidised bed gasification test rig ............................................ 56
2.2.1 Fluidisation regime ................................................................. 57
2.3 Gasification process parameters ............................................. 59
2.3.1 Equivalence ratio .................................................................... 59
2.3.2 Calculation of LHV of the product gas ................................. 59
2.3.3 Gasification efficiencies ......................................................... 60
2.3.4 Mass balance analysis ......................................................... 61
2.4 Product gas measurement ...................................................... 62
2.4.1 Micro-gas chromatography .................................................... 62
2.4.2 Moisture analysis in product gas ......................................... 64
2.4.3 Gas yield calculation ............................................................. 65
2.5 Modelling of fluidised bed gasifier ......................................... 65
2.5.1 Aspen Plus simulation software ......................................... 65
2.5.2 Structure ............................................................................... 65
2.5.3 Stream classes ...................................................................... 66
2.5.4 Solver method ................................................................. 66
2.5.5 Result output ................................................................. 66
2.6 Genetic programming approach ...................................... 67
2.6.1 Methodology: ............................................................... 68
2.7 References ................................................................. 71

3 Poultry litter gasification in a fluidised bed reactor: Effects of gasifying agent and limestone addition ............................................................... 75
3.1 Introduction ................................................................. 77
3.2 Experimental details .................................................. 81
3.2.1 Materials ................................................................. 81
3.2.2 Experimental facility and test procedure ................ 82
3.2.3 Ash Chemistry ......................................................... 85
3.2.4 Measurement methods ........................................... 86
3.2.5 Performance analysis ............................................. 88
3.3 Results and discussion ................................................ 91
3.3.1 Thermogravimetric analysis (TGA) of poultry ash .... 92
3.3.2 Effect of limestone addition ..................................... 95
3.3.3 Effect of temperature on gasification performance .... 97
3.3.4 Effect of ER on poultry litter gasification ............. 100
3.3.5 Effect of steam injection ........................................ 103
3.3.6 Mass balance analysis and fate of N, S and Cl of the feed (poultry litter) .... 105
3.4 Conclusion .................................................................... 108
3.5 References ................................................................. 110

4 Model development and application to the poultry litter gasification .......... 117
4.1 Introduction ................................................................. 118
4.2 Experimental facility and procedure .............................................. 120
  4.2.1 Test facility .................................................................................. 120
  4.2.2 Materials .................................................................................... 121
  4.2.3 Test procedure ............................................................................ 122
  4.2.4 Data Analysis ............................................................................. 122

4.3 Experimental results in supports of PEM ....................................... 123
  4.3.1 Hydrocarbon yields ...................................................................... 123
  4.3.2 Char conversion .......................................................................... 125

4.4 Pseudo-equilibrium model and performance evaluation ............... 126
  4.4.1 Methodology of the pseudo-equilibrium gasification model ....... 127
  4.4.2 Model validation .......................................................................... 130

4.5 Results and discussion .................................................................... 130
  4.5.1 Effect of gasifier pressure ............................................................. 130
  4.5.2 Effect of gasifier temperature ....................................................... 131
  4.5.3 Effect of ER ................................................................................ 133
  4.5.4 Effect of steam injection ............................................................... 134
  4.5.5 Equilibrium prediction for WGSR ............................................... 135

4.6 Conclusion ....................................................................................... 136

4.7 References ...................................................................................... 137

5 Artificial neural network based modelling approach for municipal solid waste gasification in a fluidised bed reactor ............................................... 143
  5.1 Introduction ..................................................................................... 145
  5.2 Material and methods ...................................................................... 149
    5.2.1 Theory of artificial neural network based modelling ................. 149
    5.2.2 Proposed approach of ANN based learning methodology and optimisation of the model parameters ........................................ 154
5.3 Results ........................................................................................................... 158

5.3.1 Single layer MISO and MIMO models ...................................................... 158

5.3.2 Double layer MISO and MIMO model ...................................................... 160

5.4 Discussion .................................................................................................... 163

5.4.1 Predictive performance of the single layer MISO ANN model ............ 164

5.4.2 Predictive performance of the single layer MIMO ANN model .......... 165

5.4.3 Predictive performance of the double layer MISO ANN model ........... 166

5.4.4 Predictive performance of the double layer MIMO ANN model ........... 167

5.4.5 Comparison of MISO and MIMO ANN models ..................................... 168

5.5 Conclusion .................................................................................................. 169

5.6 References .................................................................................................. 171

6 Multi-gene genetic programming based predictive models for municipal solid waste gasification in a fluidised bed gasifier ........................................................... 177

6.1 Introduction ............................................................................................... 178

6.2 Method of GP modelling .......................................................................... 181

6.2.1 Parameter setting of GP algorithm ...................................................... 186

6.3 Results and Discussion ........................................................................... 187

6.3.1 Multi-gene GP based model for LHV calculation ............................. 187

6.3.2 Multi-gene GP based model for syngas yield production ................. 191

6.3.3 Multi-gene GP algorithm and comparison with single-gene GP model 193

6.4 Conclusion ............................................................................................... 197

6.5 References .................................................................................................. 198

7 Conclusions and future recommendations ................................................... 203

7.1 Conclusions ............................................................................................. 203

7.2 Future recommendations ........................................................................... 205
Appendix 1. Fundamental data used for the calculations ......................................... 207
Appendix 2. Computational time ............................................................................. 208
List of tables

Table 1.1: Typical gasification reactions at 25 °C (Basu 2010) ........................................ 18

Table 1.2: Selection of gasifier design (Basu 2010) ...................................................... 19

Table 1.3: Overview of each study and their objectives .............................................. 31

Table 2.1: Classification of bed material ................................................................. 55

Table 3.1: Chemical characteristics of poultry litter .......................................... 81

Table 3.2: Chemical composition of the poultry litter ash on an as received basis (ash at 550 °C) ............................................................... 82

Table 3.3: Summary of experimental tests ........................................................... 90

Table 3.4: Experimental test results ........................................................................ 94

Table 3.5: Mass balance of gasification tests ....................................................... 106

Table 3.6: Fate of nitrogen, sulphur and chlorine from the feedstock ................. 108

Table 4.1: Description of Aspen Plus unit operation .......................................... 129

Table 4.2: Simulation vs. experimental results .................................................. 130

Table 5.1: Pros and cons of different gasification modelling approach (Gómez-Barea and Leckner 2010; Mikulandric’ et al. 2014) ................................................. 148

Table 5.2: Training performance of the best ANN configuration ....................... 162

Table 5.3: Statistics of the best solutions of single and double layer model variants ................................................................. 169

Table 6.1: Parameter settings for the multi-gene GP and single-gene GP variants 186

Table 6.2: Statistics of the best solutions of two GP variants for LHV prediction and syngas yield production .......................................................... 195

Table 6.3: Statistics of the best solution for 30 independent runs of two GP variants for LHV prediction and syngas yield production ......................................... 195
List of figures

Figure 1.1: Compound and sector-specific emissions of greenhouse gases, associated radiative forcing and global ruminant numbers over the past 50 years (a) Estimates of direct radiative forcing in 2008 for CO$_2$ and non-CO$_2$ greenhouse gases from anthropogenic sources. (b) Projections of radiative forcing in four different scenarios: constant future emissions at 2008 levels (red); 80% reduction in only non-CO$_2$ emissions (orange), 80% reduction in only CO$_2$ emissions (blue), and 80% reductions in both non-CO$_2$ and CO$_2$ emissions (green). (c) Estimated annual anthropogenic emissions from major sources of methane in recent years. Error bars represent 1 standard deviation. (d) Global ruminant numbers from 1961 to 2011 (Ripple et al. 2014). Data for a–c (Montzka et al. 2011), data for d (FAOSTAT 2013) ................. 2

Figure 1.2: Development of municipal waste management in 32 European countries, EU-27, Croatia, Iceland, Norway, Switzerland and Turkey, between 2001–2010 (Fischer et al. 2013) ..................................................................................................... 5

Figure 1.3: Biomass sources and categories (Xue 2014) .................................................. 10

Figure 1.4: Worldwide gasification capacity and growth, input from Gasification Technology Centre (GTC) database, 2014 (Higman 2014) ................................................. 14

Figure 1.5: Schematic presentation of gasification process, adapted from (Gómez-Barea and Leckner 2010) ............................................................................................................. 17

Figure 1.6: Schematic of fixed bed gasifiers (a) updraft, (b) downdraft and (c) crossdraft, source (Knoef and Ahrenfeldt 2005) ................................................................. 22

Figure 1.7: The two type of fluidised bed gasifier (a) bubbling fluidised bed (b) circulating fluidised bed, adapted from (Gómez-Barea and Leckner 2010) .............. 24

Figure 1.8: Schematic of entrained flow gasifier, Source: GE ChevronTexaco entrained flow gasifier (NETL 2013) .................................................................................... 25

Figure 1.9: ReUseWaste project overview and objectives of each work package (WP) (ReUseWaste 2016) ................................................................................................. 29

Figure 1.10: Flowchart of work presented in this thesis .................................................. 30

Figure 2.1: Schematic diagram of the Vario EL Cube Elemental analyser ........ 51
Figure 2.2: A schematic diagram of the bomb calorimeter (Averill and Eldredge 2007) .......................................................................................................................... 53

Figure 2.3: The change of fluidisation regimes with the increase of air velocity (Yang 2003) ................................................................................................................. 57

Figure 2.4: Variation of differential pressure across the bed with gas velocity (Wang et al. 2007) ............................................................................................................. 58

Figure 2.5: Schematic diagram of the TCD (Toonen and van Loon 2013) .............. 64

Figure 2.6: A typical representation of an evolved GP algorithm ......................... 68

Figure 2.7: Flowchart of the GP-based problem solving process (Affenzeller et al. 2009) ............................................................................................................................................. 69

Figure 3.1: Schematic diagram of WOB gasifier (1) biomass hopper; (2) feeding screws; (3) air preheater; (4) gasifier reactor; (5) cyclone; (6) valve; (7) hot filter; (8) cold filter; (9) flare .................................................................................................................................................. 84

Figure 3.2: Bed and freeboard temperature and gas composition evolution in a poultry litter test at 700 °C and ER= 0.18: (a) temperature profile (b) product gas composition ............................................................................................................................................. 91

Figure 3.3: Weight loss and heat flow curve of poultry litter ash using TGA at constant heating rate (10 °C/min) in nitrogen atmosphere (100 ml/min) ............... 92

Figure 3.4: Effect of limestone on the composition of the product gas and gasifier performance (gas yields are on a N₂ free basis) ................................................................. 95

Figure 3.5: Effect of temperature on the composition of the product gas at ER ≈ 0.30 (a) yield of major gas species (b) yield of light hydrocarbon gas species in the product gas .......................................................................................................................... 98

Figure 3.6: Effect of temperature on (a) LHV, product gas (N₂ free) and total tar yields (b) the performance of gasification at ER≈0.30 (experiments number 5, 10 and 14) ............................................................................................................................................. 99

Figure 3.7: Effects of ER on the composition of product gas and gasifier performance (gas yields are on an N₂ free basis) ................................................................. 101
Figure 3.8: Effects of SBR on the composition of product gas and gasifier performance

Figure 4.1: Experimental setup

Figure 4.2: Gas and char yields during devolatilisation of poultry litter, \( u = 0.35 \text{ m/s} \)

Figure 4.3: Experimental gas yield of the main components (mass fraction) \( u = 0.35 \text{ m/s} \)

Figure 4.4: Gas yield during (a) gasification process (under steam 20\% flow rate) and (b) combustion (under air), \( u= 0.35 \text{ m/s} \)

Figure 4.5: Aspen Plus flowsheet model of poultry litter gasifier

Figure 4.6: Effect of pressure on product gas composition

Figure 4.7: Effect of gasifier temperature on product gas composition, \( \text{ER} = 0.25 \)

Figure 4.8: Effect of ER on the product gas composition, \( T = 800 \text{ °C} \)

Figure 4.9: Effect of SBR on product gas composition, \( \text{SBR} = 0.20 \)

Figure 4.10: Temperature dependency of experimental \( (K_{\text{exp}}) \), thermodynamic equilibrium \( (K_{\text{eq}}) \) and equilibrium factor \( (f) \)

Figure 5.1: Schematic diagram of the MIMO ANN model (a) single hidden layer (b) double hidden layer

Figure 5.2: Flowchart of the proposed methodology

Figure 5.3: Box plot of single layer MISO model. Each box plot shows variation across multiple optimisation runs

Figure 5.4: Box plot of single layer MIMO model. Each box plot shows variation across multiple optimisation runs

Figure 5.5: Surface plot of MSE for double layer MISO models (a) LHV (b) LHV\(_p\) and (c) Gas yield

Figure 5.6: Surface plot of MSE for double layer MIMO models (LHV-LHV\(_p\)-Gas yield)
Figure 5.7: Convergence characteristics of the optimum double layer MISO model for the LHVp (4/13, logsig/logsig and LM algorithm) .................................................. 163

Figure 5.8: Prediction of single layer MISO ANN model with R² and MSE on the training, validation and the testing datasets (a) LHV (b) LHVp and (c) Gas yield . 165

Figure 5.9: Prediction of single layer MIMO ANN model with R² and MSE on the training, validation and the testing datasets ............................................................. 166

Figure 5.10: Prediction of double layer MISO based ANN model with R² and MSE on the training, validation and the testing datasets (a) LHV (b) LHVp and (c) Gas yield .......................................................................................................................... 167

Figure 5.11: Prediction of double layer MIMO based ANN model with R² and MSE on the training, validation and the testing datasets ............................................ 168

Figure 6.1: Schematic diagram of the tree structure of a multi-gene GP model..... 184

Figure 6.2: The Pareto front and convergence of the multi-gene GP solutions for LHV calculation (top row) and syngas yield production (bottom row) .............. 187

Figure 6.3: Prediction results of the multi-gene GP solutions with R² and RMSE on the training and the testing datasets: LHV prediction Solution A (a1), Solution B (b1), Solution C (c1) and syngas yield production Solution A (a2), Solution B (b2), Solution C (c2) .................................................................................................................................. 189

Figure 6.4: Prediction results of the multi-gene GP solutions with R² on the training and the testing datasets: LHV prediction Solution A (a1), Solution B (b1), Solution C (c1) and syngas yield production Solution A (a2), Solution B (b2), Solution C (c2) .................................................................................................................................. 190

Figure 6.5: The Pareto front and convergence of the best single-gene GP solution for LHV calculation (top row) and syngas yield production (bottom row) .......... 194

Figure 6.6: Prediction results of the best single-gene GP solution with R² and RMSE on the training and the testing datasets: for the LHV (top) and syngas yield production (bottom) ........................................................................................................... 194
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{bed}$</td>
<td>Cross section area of the bed</td>
<td>m²</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Neon flow rate</td>
<td>ml/min</td>
</tr>
<tr>
<td>$\gamma_i$</td>
<td>Flow rate of dry product gas</td>
<td>m³/min</td>
</tr>
<tr>
<td>Ne</td>
<td>Concentration of Neon</td>
<td>ppm</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>Absolute particle density</td>
<td>kg/m³</td>
</tr>
<tr>
<td>$\eta_{cc}$</td>
<td>Carbon conversion efficiency</td>
<td>%</td>
</tr>
<tr>
<td>$\eta_{eg}$</td>
<td>Cold gas efficiency</td>
<td>%</td>
</tr>
<tr>
<td>$\eta_{hc}$</td>
<td>Hydrogen conversion efficiency</td>
<td>%</td>
</tr>
<tr>
<td>A</td>
<td>Ash content dry basis</td>
<td>wt.%</td>
</tr>
<tr>
<td>ER</td>
<td>Equivalence ratio</td>
<td>-</td>
</tr>
<tr>
<td>FC</td>
<td>Fixed carbon</td>
<td>wt.%</td>
</tr>
<tr>
<td>MC</td>
<td>Moisture content</td>
<td>wt.%</td>
</tr>
<tr>
<td>m</td>
<td>Mass of</td>
<td>g</td>
</tr>
<tr>
<td>$\dot{m}_f$</td>
<td>Feed rate of solid fuel</td>
<td>kg/h</td>
</tr>
<tr>
<td>$\dot{m}_g$</td>
<td>Product gas flow rate</td>
<td>kg/h</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
<td>atm</td>
</tr>
<tr>
<td>SBR</td>
<td>Steam to biomass ratio</td>
<td>-</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>ºC</td>
</tr>
<tr>
<td>$\dot{Q}_g$</td>
<td>Gas flow rate</td>
<td>Nm³/s</td>
</tr>
<tr>
<td>$U_{fl}$</td>
<td>Superficial fluidisation velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$U_{mf}$</td>
<td>Minimum fluidisation velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
<td>ml</td>
</tr>
<tr>
<td>VM</td>
<td>Volatile matter</td>
<td>wt.%</td>
</tr>
</tbody>
</table>
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ash content</td>
</tr>
<tr>
<td>AD</td>
<td>Anaerobic digestion</td>
</tr>
<tr>
<td>ar</td>
<td>As received (weight of fresh sample)</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>ANN</td>
<td>Artificial neural network</td>
</tr>
<tr>
<td>BFGS</td>
<td>Broyden-Fletcher-Goldfarb-Shanno quasi-Newton</td>
</tr>
<tr>
<td>CaO</td>
<td>Limestone</td>
</tr>
<tr>
<td>CCE</td>
<td>Carbon conversion efficiency</td>
</tr>
<tr>
<td>CGE</td>
<td>Cold gas efficiency</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>Acetylene</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>Ethylene</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>Ethane</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>Propane</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>Benzene</td>
</tr>
<tr>
<td>C₆H₇</td>
<td>Toluene</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>COS</td>
<td>Carbonyl sulphide</td>
</tr>
<tr>
<td>daf</td>
<td>Dry ash free basis (weight after ashing at 550 °C)</td>
</tr>
<tr>
<td>DCENR</td>
<td>Department of Communications, Energy and Natural Resources</td>
</tr>
<tr>
<td>db</td>
<td>Dry basis (weight after drying at 105 °C)</td>
</tr>
<tr>
<td>ECN</td>
<td>Energy Research Centre of the Netherlands</td>
</tr>
<tr>
<td>EEA</td>
<td>European Environmental Agency</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>EM</td>
<td>Equilibrium model</td>
</tr>
<tr>
<td>ER</td>
<td>Equivalence ratio</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>FAO</td>
<td>Food and Agriculture Organisation</td>
</tr>
<tr>
<td>FC</td>
<td>Fixed carbon</td>
</tr>
<tr>
<td>FFNN</td>
<td>Feed forward neural network</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>GDX</td>
<td>Gradient descent with momentum and adaptive learning rate</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gas(es)</td>
</tr>
<tr>
<td>GP</td>
<td>Genetic programming</td>
</tr>
<tr>
<td>GTC</td>
<td>Gasification Technology Centre</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HCN</td>
<td>Hydrogen cyanide</td>
</tr>
<tr>
<td>HCE</td>
<td>Hydrogen conversion efficiency</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>H₂S</td>
<td>Hydrogen sulphide</td>
</tr>
<tr>
<td>HHV</td>
<td>Higher heating value</td>
</tr>
<tr>
<td>IEO</td>
<td>International Energy Outlook</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>IQR</td>
<td>Interquartile range</td>
</tr>
<tr>
<td>LHV</td>
<td>Lower heating value</td>
</tr>
<tr>
<td>LHVₚ</td>
<td>Lower heating value of product gas including tars and entrained char</td>
</tr>
<tr>
<td>Symbol</td>
<td>Term</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>logsig</td>
<td>Logarithmic sigmoid function</td>
</tr>
<tr>
<td>LM</td>
<td>Levenberg–Marquardt</td>
</tr>
<tr>
<td>MC</td>
<td>Moisture content</td>
</tr>
<tr>
<td>MAE</td>
<td>Mean absolute error</td>
</tr>
<tr>
<td>MIMO</td>
<td>Multiple input and multiple output</td>
</tr>
<tr>
<td>MISO</td>
<td>Multiple input and single output</td>
</tr>
<tr>
<td>MSD</td>
<td>Mass selective detector</td>
</tr>
<tr>
<td>MSE</td>
<td>Mean squared error</td>
</tr>
<tr>
<td>MSW</td>
<td>Municipal solid waste</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Ne</td>
<td>Neon</td>
</tr>
<tr>
<td>NH₃</td>
<td>Ammonia</td>
</tr>
<tr>
<td>NETL</td>
<td>National Energy Technology Laboratory</td>
</tr>
<tr>
<td>NM</td>
<td>Not measured</td>
</tr>
<tr>
<td>NMSE</td>
<td>Normalised mean squared error</td>
</tr>
<tr>
<td>NREL</td>
<td>National Renewable Energy Laboratory</td>
</tr>
<tr>
<td>OCED</td>
<td>Organisation for Economic Co-operation and Development</td>
</tr>
<tr>
<td>RMSE</td>
<td>Root means squared error</td>
</tr>
<tr>
<td>SBR</td>
<td>Steam to biomass ratio</td>
</tr>
<tr>
<td>SCG</td>
<td>Scaled conjugate gradient</td>
</tr>
<tr>
<td>SD</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>SEAI</td>
<td>Sustainable Energy Authority of Ireland</td>
</tr>
<tr>
<td>SPA</td>
<td>Solid phase adsorption</td>
</tr>
<tr>
<td>tansig</td>
<td>Hyperbolic tangent sigmoid function</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>PEM</td>
<td>Pseudo equilibrium model</td>
</tr>
<tr>
<td>purelin</td>
<td>Pure linear function</td>
</tr>
<tr>
<td>QET</td>
<td>Quasi-equilibrium model</td>
</tr>
<tr>
<td>UN</td>
<td>United Nations</td>
</tr>
<tr>
<td>UL</td>
<td>University of Limerick</td>
</tr>
<tr>
<td>VM</td>
<td>Volatile matter</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compound</td>
</tr>
<tr>
<td>WtE</td>
<td>Waste to energy</td>
</tr>
<tr>
<td>WP</td>
<td>Work Package</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Background

A rapidly growing world population has triggered a substantial rise in food consumption and energy demand. Global population rose from 2.5 billion in 1950 to 7.3 billion in 2015 (Population Reference Bureau 2015) and the United Nations (UN) has estimated that it will further increase to 11.2 billion by 2100 (UN 2015). The key drivers for population growth are the industrial revolution, industrialisation of agriculture sector/practices including the use of inorganic fertiliser, pesticides etc. (Tilman et al. 2002) and better medical services. Increasing wealth has led to the increasing demand for animal protein. The global meat consumption/capita in 2014 was 34 kg which is expected to increase to 35.5 kg by 2024 (OECD 2015). According to the Organisation for Economic Co-operation and Development (OECD) report, poultry meat is expected to account for half of the increase in global meat production as it surges past pork as the most consumed meat by 2020. Livestock production now uses 30% of the earth’s entire land surface and 33% of the global arable land area used for producing feed for livestock (Steinfeld et al. 2006). In addition, maximising clean water and energy production with minimum impact to the environment is posing the significant challenges in the 21st century (Omenn 2006).

The feeding crop is in direct competition with land for producing crops for humans and climate mitigation (bioenergy crop and carbon sequestration) (Smith et al. 2013). Approximately one-third of all greenhouse gas (GHG) emissions come from the agricultural sector. The whole food sector contributed 9,800–16,900 megatonnes of carbon dioxide (CO2) equivalent into the atmosphere in 2008, including indirect emissions from deforestation and land-use changes (Gilbert 2012). In addition, GHG emissions from ruminant meat production are significant, with ruminant and cattle contributing 11.6 and 9.4% respectively to GHG emissions globally from anthropogenic sources. It was suggested that reductions in ruminant numbers would substantially reduce the burden in achieving climate change mitigation goals while having social and environmental co-benefits (Ripple et al. 2014).
Figure 1.1: Compound and sector-specific emissions of greenhouse gases, associated radiative forcing and global ruminant numbers over the past 50 years (a) Estimates of direct radiative forcing in 2008 for CO\textsubscript{2} and non-CO\textsubscript{2} greenhouse gases from anthropogenic sources. (b) Projections of radiative forcing in four different scenarios: constant future emissions at 2008 levels (red); 80% reduction in only non-CO\textsubscript{2} emissions (orange), 80% reduction in only CO\textsubscript{2} emissions (blue), and 80% reductions in both non-CO\textsubscript{2} and CO\textsubscript{2} emissions (green). (c) Estimated annual anthropogenic emissions from major sources of methane in recent years. Error bars represent 1 standard deviation. (d) Global ruminant numbers from 1961 to 2011 (Ripple et al. 2014). Data for a–c (Montzka et al. 2011), data for d (FAOSTAT 2013).
Figure 1.1a shows the compound and sector specific GHG emission over the past 50 years. It is evident that non-CO₂ contributes about a third of total anthropogenic CO₂ equivalent and among them methane (CH₄) is the most abundant from the different sectors (Figure 1.1c). The Food and Agriculture Organisation (FAO) figures estimate that an average, 25 million domestic ruminants have been added every year over the past 50 years as depicted in Figure 1.1d (FAOSTAT 2013). The share of poultry meat in world meat production increased from 15 percent three decades ago to 30% (FAO 2006) and is expected to grow by an additional 60% by 2030 (MacLeod et al. 2013).

According to the European Environmental Agency (EEA) data in June 2016, GHG emissions in the EU-28 in 2014 amounted to 4,286 million tonnes CO₂-equivalent. The share of GHG emissions from the agriculture sector was 11.3% (EEA 2016). The IPCC suggests that the uncertainty in total GHG emissions trends is ~ 4 % - 5%. Whereas, for the EU, the trend uncertainty estimated is close to 1 % since total GHG emissions estimates are quite reliable and the limited number of interpolations used. Enteric fermentation and manure together account for approximately 80% of agricultural CH₄ emissions and about 35% to 40% of the total anthropogenic CH₄ emissions (Steinfeld et al. 2006). The formation of CH₄ is dependent on the surrounding environment, such as temperature, and the physical and chemical properties of the manure. Also microorganisms can be a significant factor effecting GHG emissions depending on the source of nutrients available to them. CH₄ production in the slurry most likely depends on the activity of slow-growing acetotrophic methanogens (Sommer et al. 2013a). Considerable amounts of methane (CH₄) emissions may be emitted from manure or slurry storage. CH₄ belongs to the GHG emitted from livestock along with carbon dioxide (CO₂) and N₂O. The global warming potential of CH₄ and N₂O are around 25 and 298 times higher than CO₂ over a 100-year time period respectively (IPCC, 2014).

Animal waste includes manure, faeces, urine, compost, litter and lagoon effluents. Primarily, animal waste has been used a source of nutrient for agriculture crop land since it is high in nutrients such as nitrogen, phosphorous and potassium (N-P-K). However, the amount of manure based nutrients (preliminary N and P) generated is
much more than that actually can be taken up by crops on nearby farm land (Ribaudo et al. 2003). Over application of animal manure on agricultural land would result in environmental issues such as surface water contamination, odour problem, heavy metal contamination, pathogens and air pollution (Burton and Turner 2003). However, animal manure not only has negative environmental issues but is also identified as a potential source of energy and nutrients (Lynch et al. 2013).

Municipal solid waste (MSW) includes commercial (construction and demolition debris) or residential wastes (household waste, waste from hotel or restaurant, sanitation waste etc.) generated in municipal areas either in the form of solid or semi-solid excluding industrial hazardous waste. The improvement in economic activity and changing lifestyles has led to the situation of a rapid increase in MSW generation. The generation rate of MSW is growing even faster than the rate of urbanisation (Hoornweg and Bhada-Tata 2012). According to World Bank data, about 4 billion tonnes of waste is generated per year and about 30% of solid waste comes from urban areas. As of now, three quarters of this waste is disposed of in landfills, with only one quarter being recycled. It is expected that in lower income countries waste generation will double in the next 25 years due to rapid industrial growth. It is also anticipated that the per capita MSW generation rate will increase from 1.2 kg to 1.42 kg per day in next fifteen years. The traditional method of MSW disposal is landfill. Moreover, landfilling could lead to serious environmental problem such as air and water pollution and only less than 0.02% heavy metal leached from the landfill after 30 years (Belevi and Baccini 1989). Therefore, landfilling of MSW is not an environmentally friendly disposal method. The problem caused by landfilling can be mitigated by adopting waste-to-energy (WtE) technologies which would process the waste and produce bioenergy.

The share of MSW generation from OECD countries is almost half of the world’s waste with an average 2.2 kg/capita/day (Hoornweg and Bhada-Tata 2012). The European Union recognised that improved waste management is a key element to make Europe more resource efficient. To achieve sustainable waste management, a waste hierarchy system must be adopted — reducing waste disposal (landfill) instead focusing on waste prevention, reuse, recycle and recovery. The development in
municipal waste management in Europe reflects a collective initiative taken by both the EU and individual countries. These pillars have been integrated into the EU’s roadmap of a resource efficient Europe (EU, 2011) and the Waste Framework Directive (EU 2008).

Figure 1.2: Development of municipal waste management in 32 European countries, EU-27, Croatia, Iceland, Norway, Switzerland and Turkey, between 2001–2010 (Fischer et al. 2013)

Figure 1.2 shows that landfilling of MSW decreased by 40 million tonnes whereas incineration and recycling grew by 15 and 29 million tonnes respectively from 2001. It is also evident that amount of MSW recycled has declined slightly since 2008. It
should be noted that total recycling includes material recycling as well as composting and digestion of biowaste (Fischer et al. 2013).

In conclusion, landfilling wastes from concentrated animal farms and municipalities is not a sustainable disposal method. In this regard, alternative disposal strategies have been proposed (anaerobic digestion, thermochemical conversion, mechanical separation and recycling), addressing environmental problem while recovering energy and nutrients from the waste.

1.2 Waste generation – An Irish perspective

The potential sources of possible feedstock categories in Ireland include agricultural and forestry residues, digestate from anaerobic digestion (AD) plants, MSW and energy crop (Miscanthus x giganteus) grown on posture land. While AD facilities are suitable for wet waste such as cow and pig manure, thermal treatment such as combustion, pyrolysis and gasification are widely recognised for energy recovery from dry lignocellulosic material including dehydrated MSW and digestate while addressing both waste management and energy challenges (Murphy and McKeogh 2004).

Agriculture is the single largest source of waste producer in Ireland. Straw, a by-product of cereal crops has been pointed out as the most abundant agricultural residue in Ireland at 1.1 million tonnes (Caslin and Finnan 2016). However, only 5% of the total straw generated is used for energy production as 95% is being recycled for animal bedding, animal feed and mushroom composting (Clancy et al. 2012). The livestock density in the republic of Ireland is 1.16 per hectare which is higher than the EU member states of 0.77 (Eurostat 2012). According to the Environmental Protection Agency (EPA) of Ireland’s National Waste Database, of a total of 85 million tonnes of waste generated in 2004, 60 million tonnes (70.6%) were generated in a managed environment from agriculture. Approximately 42 million tonnes out of total agricultural waste comes from animal manure of which the contribution of poultry litter was about 172 kilo tonnes (Forfás 2007).
MSW generation in Ireland in 2006 was 794 kg/capita/year and by 2010 it had reduced by 20% to 636 kg/capita/year, which could be due to economic recession following the financial problems beginning in 2007 (Watson 2013). In Ireland, MSW is predominantly landfilled. Moreover, Ireland has recently achieved the target set by Waste Framework Directive i.e. 50% recycling of waste by 2020 from MSW (Watson 2013). The recycled and the organic fraction from MSW is digested or composted and the remaining dry residues are mostly landfilled with a portion being incinerated as refuse derived fuel. The landfilled MSW contains plastic, rubber, cloth, wood, organic matter, paper, metal and glass. Nevertheless, advanced thermal treatment processes (pyrolysis and/or gasification) can be employed to recover energy from the pre-processed MSW (free from metal and glass) (Defra 2013).

1.3 Energy recovery from waste

International Energy Outlook (IEO 2016) has projected that worldwide energy consumption of marketable energy will increase by 48% between 2012 and 2040. As an alternative to depleting fossil fuel reserves researchers have been attracted to explore clean and renewable energy alternatives. In this regard, recovering energy from biomass and waste is important for countries like Ireland. The energy demand in Ireland is met by natural gas, oil, coal, peat, wind & hydro and in 2014 Ireland imported 96.5% of natural gas (Howley et al. 2015). The target for Ireland under the EU Renewable Energy Directive (2009/28/EC) is to achieve 16% renewable energy in overall energy consumption by 2020. As per Energy in Ireland Statistics – 2015 Report, the total primary energy demand was 13.3 Mtoe. The end use of thermal and electrical energy accounted for 32% and 33% of total primary energy supply respectively. However, the consumption of electricity by the end user accounted for only 19% and transformation & transmission losses represented 51% of the total energy input (Howley et al. 2015). In 2014, the share of energy production from the renewable resources was 7.7% of the total Irish primary energy demand of which 4.5% was bioenergy. Energy from biomass and waste grew by 13.9% and is regarded as the second largest renewable energy resource after wind energy in Ireland with a potential for 12.73 PJ or 29.8% of the total renewable energy share (Howley et al. 2015). The Sustainable Energy Authority of Ireland (SEAI) forecasts wide
availability and variety of biomass resources in Ireland, from waste products to energy crops, suitable for thermochemical conversion (Clancy et al. 2012). The National Bioenergy Plan for Ireland focused on harnessing more energy from Ireland’s bioenergy resources such as forests, energy crops, animal by-products and waste (DCENR 2015).

Regulations on air pollutions and GHG emissions make biomass an attractive source of energy as the use of biomass has the potential for significant carbon emission reduction over traditional fossil fuel resources (Tester et al. 2005). Biomass has been used for the energy production but the state of commercialisation is limited mainly due to the high prices of clean biomass. These reasons explain the renewed interest in dirty residues such as refused derived fuel (RDF), MSW, agricultural waste (harvested crops), animal waste etc., which has opened great perspectives during the last few years. Biowaste (poultry litter and MSW) is an ideal source of energy because of its geographical diversification. Using biowaste as a fuel reduces disposal issues and provides a fuel which will contribute to meet the challenges of climate change. There are several ways to utilise biowaste as a feedstock for bioenergy production including thermochemical (pyrolysis, gasification, and combustion), chemical (hydrolysis) and microbiological (anaerobic digestion and fermentation technologies) conversion. It has been demonstrated that low moisture waste such as poultry litter can be subject to thermal treatment, such as combustion, pyrolysis and gasification (McKendry 2002a). In a quest for a sustainable waste treatment technology, WtE technology (bioenergy production) has recently been reviewed by Brunner and Rechberger (2015). WtE can reduce the original volume of wastes disposed by 80-95% along with energy recovery depending on the waste composition (Rand et al. 1999). Additionally, processing biowaste via thermochemical processes has several advantages over chemical or biological conversion routes such as shorter conversion time, pathogens elimination and is quite adaptable to different kinds of waste.

Processing biowaste via thermochemical processes has several advantages over chemical or biological conversion routes such as shorter conversion time, pathogens elimination and is quite adaptable to different kinds of waste. Biochemical
conversion processes are suggested to be relatively inherently inflexible in terms of processing feedstocks, two phase process, fall in pH leading to inhibition of bacterial activity, high retention time, and requires a large collection area to provide the necessary biomass supply for a large scale facility (Bouallagui et al. 2005; Huang et al. 2009; Balan et al. 2012). In addition, biofuels produced using thermochemical conversion processes resulted in lower GHG emission per MJ of fuel than that of using biochemical conversion pathways (Daystar et al. 2015).

Even though all nutrients are equally important for plant growth, usually nitrogen (N), phosphorous (P) and potassium (K) are the most limiting. Bottom ash can be used as a soil amender provided silica sand was used as a bed material, otherwise the separation of bed material and char/ash is required. The by-product from poultry litter gasification (a mixture of char and ash) contains considerable amounts of nutrients, which can have potential application on agricultural lands. This is permitted in the UK under the Poultry Litter Ash Protocol. Due to the porous structure of the biochar, it can be helpful in improving soil permeability, reducing nutrient run-off and biochar in soil acts as a carbon sequester. Thermal treatment of animal manures, such as poultry litter (Kelleher et al. 2002; Abelha et al. 2003; Font-Palma 2012), swine manure (Ro et al. 2009; Tsai et al. 2012) and cattle manure (Cantrell et al. 2012) have increasingly been subjected to nutrient recovery investigation. Valuable macro- and micronutrients can be recovered in the obtained ash and biochar fractions, especially non-volatile minerals like P (Thygesen and Johnsen 2012; Wang et al. 2012). However, most of the N forms NH₃ during thermochemical conversion (Pandey et al. 2016). Nevertheless, the main aim of the research conducted is to assess thermochemical conversion technologies to recover energy from poultry litter and MSW.
1.3.1 Anaerobic digestion

Anaerobic digestion (AD) involves the breakdown of organic matter through microbial fermentation in an oxygen-free environment. The end product is biogas which primarily consists of CH₄, CO₂, small amount of water and trace gases such as hydrogen sulphide, oxygen, nitrogen, ammonia and hydrogen. The produced gas can be used directly for energy or can be upgraded to transportation fuels and chemicals. The remaining residue (digestate) is sterile, rich in nutrients and emits less odour compounds compared to the original waste. There are four steps involved during anaerobic digestion, namely hydrolysis, acidogenesis, acetogenesis, and methanogenesis. AD takes place in the mesophilic (30 °C to 35 °C) or thermophilic (50 °C to 55 °C) temperature range. The rate of decomposition depends on several factors, such as temperature, retention time and abundance of microorganisms (Li et
al. 2011; Sommer et al. 2013b). The pH of the AD process can affect the digestion process significantly. The optimum range of pH in an AD process is 6.8-7.2 (Wu et al. 2009; Kumar et al. 2010; Romano and Zhang 2011).

1.3.2 Electrochemical method

The electrochemical conversion method refers to microbial fuel cells. These fuel cells convert chemical energy of carbon based fuel directly into electricity or hydrogen without a reforming process (Dudek and Socha 2014). Although the technology offers many advantages for an extensive range of applications (energy conversion, storage, and hydrogen production) further improvements to their low energy conversion efficiencies, lifetime, reliability and low power density are required. Furthermore, the technology has not been commercialised yet (Badwal et al. 2014; Im et al. 2016).

1.3.3 Combustion

Combustion is the oldest, the most developed and therefore most frequently used thermochemical conversion technology. It is an exothermic phenomenon that occurred between a fuel and oxidant and gives off heat. The heat released from this exothermic reaction currently represents the largest source of energy for human consumption. Combustion units exist at a small scale for cooking and heating or at district or industrial scale using steam generated in biomass-fired boilers. The ash residue can be used in the fertilising industry and as a component in building materials (Pels et al. 2005). Biomass combustion takes place in three steps (1) heating and drying of feedstock, (2) devolatilisation and combustion of volatiles and (3) combustion of char (Basu 2010). Incomplete combustion may lead to the formation of gaseous pollutants such as SOx, NOx, carbon monoxide, volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAHs) and chlorinated hydrocarbons such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) dioxin. Deposit formation and corrosion are particularly a concern with fuels containing high chlorine and potassium, such as biomass (Yin et al. 2008).
1.3.4 Pyrolysis

Pyrolysis or devolatilisation is a thermochemical method involving heating a carbonaceous feedstock material at a moderate temperature (typically higher than 300 °C) in an oxygen free atmosphere during which the unstable carbonaceous species will decompose giving permanent gases (mainly CO, CO$_2$, CH$_4$, H$_2$ and other light hydrocarbons) and condensable liquid bio-oil (mainly oxygenates, aromatics, water, products of low degree of polymerisation, etc.) and solids (a carbon residue called biochar). The operating parameters for pyrolysis, such as temperature and residence time, depend on which streams of products is desired. For instance, low temperature and long residence time (slow pyrolysis) give higher char yield (Williams and Besler 1996) while gas production is favoured with high temperatures and short residence time (fast pyrolysis) (Bridgwater 2012).

1.4 Gasification

1.4.1 Introduction

One thermochemical technology is gasification, which converts solid fuels into clean combustible gas called product gas (synthesis gas) by partial combustion. Gasification is an “old” technology dating back some 180 years (Higman and Van der Burgt 2011) but regained attention recently for solid fuel conversion due to the perceived depletion of fossil fuels and environmental concerns. The application of gasification technology in the field of WtE process has been recognised as a promising method to provide an alternative approach for disposing wastes such as agricultural waste, sewage sludge, poultry litter and other biomass. Gasification processes provides flexibility for the production of fuels, heat and power based on a clean biomass/waste derived product gas while complying with emission standards (Arena 2012; Pandey et al. 2016b).

Gasification is considered a process between pyrolysis and combustion that converts the solid fuel into a gaseous energy carrier called “product gas” or “producer gas/synthesis gas” via partial oxidation of a substance (Arena 2012). The amount of oxygen supplied into the gasifier is not sufficient (below the stoichiometric) to allow the fuel to be completely oxidised (combusted). The essential difference between
combustion and gasification is that the former releases the heat by breaking chemical bonds while the latter relocates/repacks the energy into chemical bonds in gaseous products. The product gas consists of gases which are not completely oxidised and vary in composition depending on the feedstock, process type and process parameters. Typically the temperature employed is higher than 650 °C. The product gas quality and yield largely rely on the gasifying medium (oxidation agent), feedstock properties, gasifier reactor type and operating conditions. Air, steam and/or oxygen are mainly used as the gasifying media. Air is commonly used as a gasifying medium since it is inexpensive however, the calorific value of the gas is lower compared to gas produced from oxygen or steam gasification due to dilution with N₂ and subsequently increases the burden of downstream gas cleaning equipment. Additionally, feedstock properties such as shape, size, moisture content and chemical composition, significantly affect the composition of product gas and impurities. The LHV can range from 4-7 MJ/m³ when oxidised with air to 10-15 MJ/m³ when oxidised with pure oxygen. Oxidation with steam produces a better LHV in the range of 15-20 MJ/m³ (McKendry 2002b; Lombardi et al. 2015).

In the past, gasification processes have been extensively used for converting low quality coal into gaseous carrier gas but recently it has been employed to process biomass/waste for bioenergy production. The US Department of Energy report prepared by the National Renewable Energy Laboratory (NREL) indicated biomass and waste gasification processes represents only 0.33% of the total worldwide gasification capacity compared to other feedstocks (approximately 99.67%) such as peat and coke (NREL 2010). Figure 1.4 shows the worldwide gasification capacity and expected growth. Generally, gasification produces a mixture of CO, H₂, CH₄, CO₂, H₂O, N₂ and contaminants, such as particulates, tar, alkali metals, hydrochloric acid (HCl), sulphide (H₂S, COS) and NH₃, HCN. The low to medium calorific value gas (4 and 6 MJ/m³) can either be burned directly or used as a fuel for gas engines and turbines after the necessary gas cleaning steps. The main components CO and H₂ are also called “syngas”. Syngas is considered as a building block for further processing and production of chemicals (e.g. methanol, ethanol) and Fisher Tropsch synthesised gasoline (McKendry 2002b; Spath and Dayton 2003). A techno-economic analysis of ammonia production (Huber-Bosch process) via an integrated
biomass gasification process in an existing pulp and paper mill was performed and compared with a standalone plant. It was concluded that the integrated plant has better process economics and energy performance over the standalone production unit. However, the study also recommended that a high NH$_3$ selling price is required to make this process economically feasible (Andersson and Lundgren 2014). By-products of the gasification process are unconverted carbon (char) and ash. These by-products can be used for improving soil productivity, carbon storage mitigation of climate change and nutrient recycling (Lehmann and Joseph 2009).

**Figure 1.4:** Worldwide gasification capacity and growth, input from Gasification Technology Centre (GTC) database, 2014 (Higman 2014)

Gasification includes a sequence of endothermic and exothermic reactions. There are different kinds of technologies for gasification. The gasification process can for example be either direct (autothermal) or indirect (allothermal). In autothermal gasifiers, part of fuel is combusted to provide the necessary heat for gasification whereas heat is supplied from an external heat source in allothermal gasification (Gómez-Barea and Leckner 2010; Arena 2012). The amount of heat required for converting a unit mass of solid fuel into gaseous products at standard temperature and pressure is called the heat of gasification. The heat of gasification is the sum of
the heat required to raise the temperature of the solid fuel and gasification medium to
the gasification temperature, and the energy needed for the endothermic gasification
reactions (Zhang 2011).

\[
\Delta H_{\text{gasif}} = \int_{T_0}^{T_{\text{fuel}}} \left( m_{\text{fuel}} C_{p,\text{fuel}} T + m_{\text{agent}} C_{p,\text{agent}} T \right) dT + \Delta H_r \quad (1.1)
\]

The gasification process involves drying, devolatilisation, partial oxidation and
reduction (gasification). These processes occur simultaneously in a real gasifier. A
brief description of these processes is provided here:

- **Heating and drying of the biomass:** this phenomenon takes place when fuel
  is fed into the gasifier, it uses heat transferred from the heating zone to
  remove the free and the chemically bound water. Typically, the moisture
  content of biomass ranges from 5% to 35% but freshly harvested biomass can
  have a moisture content as high as 60% (Cummer and Brown 2002). Therefore,
  drying of the feedstock is usually desirable and sometimes
  essential before gasification in order to ensure satisfactory gasifier operation
  and improve product gas quality (Brammer and Bridgwater 1999).

\[
\left(C_{n}H_{m}O_{p}\right)_{\text{fuel,ar}} + \text{Heat} \rightarrow \left(C_{x}H_{y}O_{z}\right)_{\text{fuel,dry}} + \sum \text{moisture} \quad (1.2)
\]

- **Pyrolysis (devolatilisation):** after the drying process the biomass is heated in
  an oxygen free environment and the biomass releases light permanent gases
  (non-condensable gases), primary tar (condensable gases) and char arising
  from thermal decomposition. Tar is a black and sticky material formed during
  the pyrolysis process that potentially gives rise to system malfunction if
  condensation occurs (Horvat et al. 2016). In other words, tar is a mixture of
  organic molecules including acids, aldehydes, ketones, alcohols, phenols,
  larger polycyclic aromatic hydrocarbons, and particulate matter whose
  amount in the product gas depends on the operating conditions (González et
  al. 2012). The composition of the volatiles depends on the original feedstock,
temperature, pressure, atmosphere and heating rate (Arena 2012). Char may also contain ash from the biomass which generally contains inorganic mineral and alkali metals. Light permanent gases are mixture of H₂, CO, CO₂ and CH₄ but it also contains a small amount of C₂H₆, C₂H₄, C₃H₈ and C₃H₆. The condensed primary tar is also called bio-oil and is composed of oxygenated hydrocarbons (levoglucosan, acetic acid and alcohols). At elevated temperature (>800 °C), primary tar is further cracked to permanent gases (CO, CO₂, H₂, CH₄, steam) and secondary tar. The secondary tars are comprised of a mixture of phenols, cresol, benzene and methyl- and hydroxyl-derivates. Cracking of secondary to ternary tars produces methyl-derivate of aromatic components (toluene and xylene) and polycyclic components like naphthalene (Buah et al. 2007).

\[
C_xH_yO_z + \text{Heat} \rightarrow \sum_{\text{liquid}} C_aH_bO_c + \sum_{\text{gas}} C_jH_kO_l + \sum_{\text{solid}} C
\]  

(1.3)

- **Partial combustion**: it is the only exothermic process in gasification. The heat that drives the gasification process comes from combusting the products of pyrolysis process, either tar and gases or char. Partial combustion of tar or char provides heat for drying, devolatilisation, endothermic gasification reactions and maintaining the temperature in the gasifier.

- **Gasification (reduction)**: during gasification endothermic reactions between gas-gas and solid-gas phases take place in a reducing environment. Instead of burning the char and the other volatiles produced in the pyrolysis process, they react with oxygen, steam and CO₂ to produce partially oxidised compounds called product gas or synthesis gas. The final product gas predominantly contains H₂, CO, CO₂, CH₄ and water. The gasification reactions generally occur in excess of 750 °C. Steam reforming reaction produces carbon monoxide and hydrogen whereas carbon monoxide is consumed in water-gas shift reaction.

Table 1.1 lists the most important gas forming reactions. The endothermic gasification reactions are all equilibrium reactions. The water gas and Boudouard
reactions are the most important reactions which increase the concentration of CO and H₂ in the product gas at higher temperature. The final gas composition is determined by the reaction rates and catalytic effects. For example, the pyrolysis process is several orders of magnitude faster than char gasification with CO₂ and H₂O. This is relevant for biomasses with high moisture and volatile matter (VM) content, as oxygen fed into the gasifier first reacts with the volatile gases then the char with CO₂ and H₂O. Since the char gasification reaction is slow and the time available for char conversion is limited due to attrition and elutriation of chars. The reactivity of the char particles is kinetically limited and depends on the composition of the original feedstock. For example, elements in the biomass ash, such as alkaline (K, Na), alkaline earth (Ca, Mg) and transition (Fe) metals, can act as catalysts to promote the carbon reaction (Dupont et al. 2011). The condensable produced during the pyrolysis process are thermally cracked at higher temperature. A schematic of these processes is presented in Figure 1.5.

Figure 1.5: Schematic presentation of gasification process, adapted from (Gómez-Barea and Leckner 2010)
### Table 1.1: Typical gasification reactions at 25 °C (Basu 2010)

**Carbon reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 (Boudouard)</td>
<td>C + CO&lt;sub&gt;2&lt;/sub&gt; ↔ 2 CO</td>
<td>+172</td>
</tr>
<tr>
<td>R2 (Water-gas or steam)</td>
<td>C + H&lt;sub&gt;2&lt;/sub&gt;O ↔ CO + H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>+131</td>
</tr>
<tr>
<td>R3 (Hydrogasification)</td>
<td>C + 2 H&lt;sub&gt;2&lt;/sub&gt; ↔ CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>−74.8</td>
</tr>
<tr>
<td>R4 (Partial oxidation)</td>
<td>C + 0.5 O&lt;sub&gt;2&lt;/sub&gt; → CO</td>
<td>−111</td>
</tr>
</tbody>
</table>

**Oxidation reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R5</td>
<td>C + O&lt;sub&gt;2&lt;/sub&gt; → CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>−394</td>
</tr>
<tr>
<td>R6</td>
<td>CO + 0.5 O&lt;sub&gt;2&lt;/sub&gt; → CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>−284</td>
</tr>
<tr>
<td>R7</td>
<td>CH&lt;sub&gt;4&lt;/sub&gt; + 2 O&lt;sub&gt;2&lt;/sub&gt; ↔ CO&lt;sub&gt;2&lt;/sub&gt; + 2 H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>−803</td>
</tr>
<tr>
<td>R8</td>
<td>H&lt;sub&gt;2&lt;/sub&gt; + 0.5 O&lt;sub&gt;2&lt;/sub&gt; → H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>−242</td>
</tr>
</tbody>
</table>

**Water-gas shift reaction**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R9</td>
<td>CO + H&lt;sub&gt;2&lt;/sub&gt;O ↔ CO&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>−41.2</td>
</tr>
</tbody>
</table>

**Methanation reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R10</td>
<td>2 CO + 2 H&lt;sub&gt;2&lt;/sub&gt; → CH&lt;sub&gt;4&lt;/sub&gt; + CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>−247</td>
</tr>
<tr>
<td>R11</td>
<td>CO + 3 H&lt;sub&gt;2&lt;/sub&gt; ↔ CH&lt;sub&gt;4&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>−206</td>
</tr>
<tr>
<td>R12</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt; + 4 H&lt;sub&gt;2&lt;/sub&gt; → CH&lt;sub&gt;4&lt;/sub&gt; + 2 H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>−165</td>
</tr>
</tbody>
</table>

**Steam-Reforming Reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R13</td>
<td>CH&lt;sub&gt;4&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O ↔ CO + 3 H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>+206</td>
</tr>
<tr>
<td>R14</td>
<td>CH&lt;sub&gt;4&lt;/sub&gt; + 0.5 O&lt;sub&gt;2&lt;/sub&gt; → CO + 2 H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>−36</td>
</tr>
</tbody>
</table>

**Pyrolysis**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>R15</td>
<td>Biomass → permanent gases + tar + char + steam</td>
</tr>
</tbody>
</table>

**Tar reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>R16 (Partial oxidation)</td>
<td>C&lt;sub&gt;n&lt;/sub&gt;H&lt;sub&gt;m&lt;/sub&gt; + (n/2) O&lt;sub&gt;2&lt;/sub&gt; → n CO + (m/2) H&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>R17 (Dry reforming)</td>
<td>C&lt;sub&gt;n&lt;/sub&gt;H&lt;sub&gt;m&lt;/sub&gt; + n CO&lt;sub&gt;2&lt;/sub&gt; → 2n CO + (m/2) H&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>R18 (Steam reforming)</td>
<td>C&lt;sub&gt;n&lt;/sub&gt;H&lt;sub&gt;m&lt;/sub&gt; + n H&lt;sub&gt;2&lt;/sub&gt;O → n CO + (m/2+n) H&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>R19 (Hydrogenation)</td>
<td>C&lt;sub&gt;n&lt;/sub&gt;H&lt;sub&gt;m&lt;/sub&gt; + (2n-m/2) H&lt;sub&gt;2&lt;/sub&gt; → n CH&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>R20 (Thermal cracking)</td>
<td>C&lt;sub&gt;n&lt;/sub&gt;H&lt;sub&gt;m&lt;/sub&gt; → (n-m/4) C + (m/4) CH&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
</tbody>
</table>
1.4.2 Types of gasifier

The type of gasification system can be defined in different ways (McKendry 2002b; Gómez-Barea and Leckner 2010; Arena 2012).

- According to the gasifying agents used: air, oxygen or steam blown gasifier.
- According to the heat of gasification: autothermal (direct) or allothermal (indirect).
- According to the pressure inside the reactor: atmospheric or pressurised.
- According to the design of the reactor: fixed/moving bed, fluidised bed, entrained bed or twin-bed.
- According to the bottom ash status: dry ash or vitrified (slagging) ash.
- According to the application of the gasifier: heat or power generation.

The main difference between different types of gasifier is how feedstock and oxidising agents move inside the reactor. The selection of gasifier type is dependent on feedstock’s characteristics. In general, all types of feedstock require pre-treatment/preparation due to their heterogeneous nature. A biomass gasification plant consists of consecutive parts, including biomass handling and feeding system, gasifier reactor, gas clean-up system and ash or solid residue removal system. Fuel requirement and an appropriate design of the gasifier for different capacities are presented in Table 1.2.

**Table 1.2: Selection of gasifier design (Basu 2010)**

<table>
<thead>
<tr>
<th>Gasifier type</th>
<th>Fixed bed</th>
<th>Fluidised bed</th>
<th>Entrained flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (mm)</td>
<td>20-100</td>
<td>&lt; 10</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Moisture content (ar)</td>
<td>&lt; 50</td>
<td>&lt; 40</td>
<td>&lt; 15</td>
</tr>
<tr>
<td>Ash content (db)</td>
<td>&lt; 5</td>
<td>&lt; 20</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>Ash melting point (°C)</td>
<td>&gt; 1250</td>
<td>&gt; 1000</td>
<td>&gt; 1250</td>
</tr>
<tr>
<td>Bulk density (kg/m³)</td>
<td>&gt; 500</td>
<td>&gt; 100</td>
<td>&gt; 400</td>
</tr>
<tr>
<td>Application area</td>
<td>10 kW_{th} - 10 MW_{th}</td>
<td>&gt; 5-100 MW_{th}</td>
<td>&gt; 50 MW_{th}</td>
</tr>
<tr>
<td>Nature of ash produced</td>
<td>Dry</td>
<td>Dry</td>
<td>Slagging</td>
</tr>
<tr>
<td>Problem areas</td>
<td>Tar Production</td>
<td>C conversion</td>
<td>Raw-gas cooling</td>
</tr>
</tbody>
</table>
For waste biomasses the feedstock costs are often negligible; however, additional operational costs might be involved. Waste treatment plants at large scale are very often not accepted by local communities. Small scale plants are more compatible, since the perception is that small scale plants encourage waste recycling. Small scale gasifiers can be implemented in developing countries supplying communities with heat and electricity and encouraging rural development. In western society the incentive for producing renewable energy derived from a sense of responsibility to mitigate environmental problems and climate change, especially due to increasing consumerism and waste production (McKendry 2002b).

1.4.3 Moving/fixed bed gasifiers

This type of gasification has been used for a long time and the technology is quite simple and robust. A cyclone is not needed for char and ash separation due to the ash and char removal in the bottom of the gasifier. The bed is fixed in a compartment where fuel needs to be feed and the ash/char retrieved at the bottom of the reactor. This type of reactor is also known as a moving bed gasifier as fuel fed into the gasifier moves down in the reactor. The size of the gasifier is limited in terms of thermal energy capacity (10 kW_{th}-10 MW_{th}) due to problems with achieving a homogenous bed. Another big challenge involved in this reactor is that the quality of product gas and the amount of tar in the product gas will vary due to large variations in temperature along the bed. The disadvantages are the upscale limit, no real process control and varying gas quality (Higman and Van der Burgt 2011). Fixed bed gasifiers are mainly categorised into updraft, downdraft and crossdraft gasifiers according to where gasifying medium is introduced.

Updraft gasifier

The updraft gasifier is the oldest and simplest design. In an updraft gasifier (counter-current gasifier), the feedstock is fed into the gasifier from the top and moves down in a counter-current fashion to the product gas flow (Figure 1.6a). The feedstock passes through drying, devolatilisation, reduction and oxidation zones. Warmed air enters from the bottom of the reactor and meets the hot ashes and any unconverted carbon (char) descending from the top. The temperature in the bed is higher than the
ignition temperature of carbon initiating exothermic reactions (R4 and R5). The hot gases (mixture of CO and CO$_2$) move up in the reduction zone where char from pyrolysis zone is gasified (R1 and R2). High char combustion, internal heat exchange and low exit temperature of the product gas results in relatively high gasification efficiency. Due to the upward movement of hot gases, the feedstock is dried in the upper section allows fuel with higher moisture, up to 60% to be used. The CH$_4$ content in the product gas is relatively high indicating that the temperature in the devolatilisation zone is not high enough to reform the CH$_4$ (Arena 2012). However, the presence of high amounts of tar in the product gas is a major drawback because the temperature in the devolatilisation zone is not high enough to crack the tar which is ultimately carried away by the upward moving product gas. Therefore, the product gas from such a type of gasifier is only suitable for direct combustion in Kiln/furnace otherwise extensive cleaning is required. Downstream gas cleaning equipment is necessary for the use of the product gas in gas turbines and engines, which includes the removal of particulates, tar, and trace impurities associated with fuel bound nitrogen sulphur and chlorine (Basu 2010).

**Downdraft gasifier**

Downdraft (co-current) reactors are designed in a way that the gasifying agent is injected at a certain height below the top (Figure 1.6b). Both the product gas and solid (char and ash) move down along with the gasifying medium. Therefore, a part of volatile gases and char get partially combusted before the gasification zone. The hot gases flow downwards through the remaining hot char bed where gasification takes place. Since the product gas passes through hot bed, tars are easily cracked and their production rate is kept very low but the product gas contains more entrained particles. Furthermore, the tar content in the product gas is dependent on load. Since producer gas from downdraft gasifiers is tar free (low tar), it can be used in an internal combustion engine/gas turbines (Arena 2012). Nevertheless, it requires that the feedstock should have a relatively low moisture content (< 25%) and uniform particle size to avoid blockages in the throated section. The temperature of the exit gas is high which lowers the cold gas efficiency and it has high ash content and fines in the gas (Basu 2010).
Crossdraft gasifier

The design of the crossdraft (con-current) gasifier is similar to the updraft gasifier. The fuel fed from the top of the reactor and gasification reaction occurs as fuel descends into the reactor (Figure 1.6c). The only difference between the crossdraft and updraft gasifier is that the air is fed from the side of the reactor rather than from the bottom. The product gas is released opposite to the entry point of the air. The start-up time is relatively short and very high temperature can be attained (≈ 1500 °C) in the hearth zone therefore this type of gasifier is not suitable for a fuel with high ash content. Tar production is low (0.01-0.1 g/Nm$^3$) hence a relatively simple gas cleaning system required. The biomass units are usually very small (< 10 kW$_e$). The particle size of the biomass is also an important consideration (Basu 2010).

![Figure 1.6: Schematic of fixed bed gasifiers (a) updraft, (b) downdraft and (c) crossdraft, source (Knoef and Ahrenfeldt 2005)](image)

1.4.4 Fluidised bed gasifier

Fluidised bed gasifiers have several advantages over fixed bed gasifiers, especially excellent solid-gas mixing, reaction rates, the possibility of scale-up and temperature uniformity in the bed. A fluidised bed is made of granular solids (inert material) called the bed material that is kept in a semi-suspended condition throughout the experiments by the fluidising medium. The most normal bed material is quartz sand with a size distribution around 250 μm. Other active materials may be used such as...
dolomite or blast furnace slag if they can be supplied in large enough amounts. The sand/bed-material enhances the heat transfer to the fuel particles and increases the mixing and kinetics, this will give an upswing in the gasification efficiency and fuel throughput. The production of tars lies between that for updraft and downdraft gasification. Compared to fixed bed, fluidised bed gasifiers are complex in design and operation and require additional particle size reduction to about < 10 mm (McKendry 2002b).

Fluidised bed gasifiers can be further categorised into bubbling fluidised beds and circulating fluidised beds. Bubbling fluidised bed gasifiers (Figure 1.7a) are the most popular for biomass and are designed in medium size units (< 25 MWth). The bed temperature is usually kept below 900 °C for biomass to avoid ash fusion and agglomeration. Bubbling fluidised bed gasifiers can be operated at low or high temperature as well as under an atmospheric or pressurised system.

The circulating fluidised bed gasifier (Figure 1.7b) is built with the provision of recirculation of fine particles which leads to greater carbon conversion efficiency due to longer residence time (Gómez-Barea and Leckner 2010). It is especially suitable for fuels with high volatiles. This type of gasifier is comprised of a riser, which acts as the reactor, a cyclone and a solid recycle device. The hot gas passes through the cyclone, which collects the solid particles, and these are then returned to the bottom gasifier by a loop seal. In Finland, a circulating fluidised bed gasifier of 60 MWth is built to provide a cheap supplementary fuel by gasifying waste wood and refuse-derived fuels. (Basu 2010).
Figure 1.7: The two type of fluidised bed gasifier (a) bubbling fluidised bed (b) circulating fluidised bed, adapted from (Gómez-Barea and Leckner 2010)

1.4.5 Entrained flow gasifier

Entrained flow (Figure 1.8) is the most effective and widely used gasifier for large/industrial scale application. This type of gasifier is suitable for high ranked coal and coke. High ash content coal is not suitable because the cold gas efficiency decreases with an increase in ash content. For the economic operation the limit of ash in the slurry fed coal and dry feed is 20 and 40% respectively (Higman and Van der Burgt 2011). The feedstock is fed co-currently with gasifying medium and the working temperature is in the range of 1200-1500 °C. Entrained flow gasification has several advantages over other types of gasifier such as high carbon conversion, almost tar free product gas, low CH₄ in the product gas and slagging ash conversion. Moreover, because it has shorter residence time therefore the fuel needs to be pulverised before gasification. Secondly oxygen is used as a gasifying medium which substantially increases the operational and capital cost. It should be noted that ash from biomass has a high amount of alkali metal which can be converted into
corrosive species at high temperature and could shorten the life of the gasifier’s refractory linings. Considering the above mentioned points, entrained flow gasifier is not a preferred choice for biomass/waste gasification (Basu 2010).

![Figure 1.8](image)

**Figure 1.8:** Schematic of entrained flow gasifier, Source: GE ChevronTexaco entrained flow gasifier (NETL 2013)

### 1.5 Mathematical modelling of gasification

In order to achieve high gasifier performance, process parameters such as temperature, pressure, flow inside the gasifier need to be optimised. In this regard, experiments have been frequently performed but are quite time consuming and costly. One possible solution to this problem is mathematical modelling where the model can be exploited to optimise process conditions quickly and cheaply (Sikarwar et al. 2016). The gasification model can be divided into time dependence gasification models such as kinetic models and kinetic free models or the type of gasification can be divided into zero-dimensional models, one-dimensional models, two-dimensional models and three dimensional models as well as non-mechanistic, non-equilibrium based models. These models can be categorised as follows:
1. Thermodynamic Equilibrium Model
2. Kinetic Model
3. Computational Fluid Dynamics (CFD) Model
4. Artificial Neural Network (ANN) Model

The earliest and simplest gasification models are thermodynamic equilibrium models. The equilibrium models are independent of the gasifier design and zero-dimensional kinetic free models, where the reaction system archives the equilibrium condition by minimising its Gibbs free energy (Barman et al. 2012). The equilibrium based model can be further divided into: stoichiometric or non-stoichiometric model. The input data needed in the equilibrium based model is the elemental composition of the fuel (Li et al. 2004). The drawback of the equilibrium models is that it overestimates CO and H₂, underestimates CO₂ and the product gas is almost free from methane and tar. A novel approach called “Multi-box” based on the thermodynamic model has been developed where authors have divided the gasification stage into multiple boxes (Vakalis et al. 2016). Researcher have also employed thermodynamic models to study the influence of process parameters on product gas composition (Kaushal et al. 2011; Loha et al. 2011; Hannula and Kurkela 2012; Sandeep and Dasappa 2014) and unique gasifiers (Deydier et al. 2011; Nilsson et al. 2012). An equilibrium model for MSW gasification coupled with a solid oxide fuel cell was developed (Rokni 2015).

Kinetic modelling considers essential information of the kinetic mechanism of biomass conversion and hydrodynamics of the reactor. The working principle of this model is based on the first principle of law of conservation (mass, momentum and energy). Kinetic models are more precise and accurate in predicting the overall performance of the gasifier, but are computationally more expansive (Sharma 2008).

The model uses the Arrhenius equation \( k = A \exp\left(\frac{-E_a}{RT}\right) \) to reflect the kinetic parameters, where, \( k \) is the reaction rate constant; \( A \) the pre-exponential factor; \( E_a \) the activation energy; \( R \) is the universal gas constant; and \( T \) the absolute reaction temperature.
Lately, several contemporary researchers have focused on kinetic based modelling (Wang and Kinoshita 1993; Di Blasi 2000; Fiaschi and Michelini 2001; Yang et al. 2003; Radmanesh et al. 2006; Nikoo and Mahinpey 2008; Zhong et al. 2009; Gordillo and Belghit 2011; Saucedo et al. 2014; Sreejith et al. 2015). There are multiple mathematical software packages available such as Mathematica, MATLAB and Aspen Plus which can be extremely useful. However, kinetic rate models are dependent on feedstock and gasifier type, which limit their applicability to different plants and become cumbersome (Baruah and Baruah 2014). To facilitate the modelling of gasification processes, lumped model supported with chemical kinetics of tar were developed and validated with experimental data. Tar species are modelled as classified and/or single compounds.

CFD based models emerged as a powerful tool in modelling thermochemical conversion processes due to advancements in computing power. However, CFD models are dependent on the hydrodynamics of reactors, dense particle flow and chemistry as well as information of different stages of the gasification process i.e. drying, devolatilisation, char combustion and reduction which makes it more complicated (Di Blasi 2008). A detailed CFD model of a cyclone gasifier was developed on a Fluent software package to study the temperature inside the gasifier and composition of the product gas (Gao et al. 2012). A 2D CFD model based on the Eulerian–Eulerian approach has been proposed to study the influence of O2 rich air on biomass gasification employing coffee husks as a feedstock (Couto et al. 2015). Recently, an attempt has been made using a CFD code to evaluate the behaviour of catalytic filters situated inside the freeboard of the reactor and to analyse their performance in steam reforming of CH4 and tar species (Savuto et al. 2015).

Recently, artificial intelligence techniques (ANNs and GP) have been exploited. The major advantage of these techniques is that they do not require detailed information. These are data driven modelling approaches, which try to mimic the behaviour of a human brain and leaning processes to solve complex mathematical (non-linear) equations (Xiao et al. 2009; Puig-Arnavat et al. 2013; Pandey et al. 2015; Pandey et al. 2016). Even though ANN modelling has shown an encouraging approach, it requires large amount of data. Furthermore, the models might not work well for a
drastically new configuration of a gasifier which is not similar to the training dataset. Nevertheless, this is a limitation of the dataset and not of the ANN based modelling methodology. The readers can follow this general design philosophy for ANNs and build models which would work in a wider variety of situations if they had large enough and more representative datasets.

1.6 The ReUseWaste project
1.6.1 An Overview

The ReUseWaste Initial Training Network project (under the Marie Curie action of the EU-FP7-PEOPLE-2011 program) was initiated to bring together research groups from universities and other institutes, agri-environmental technology companies and public regulatory authorities, located in the countries and regions of most intensive livestock production in Europe. The overall objective of ReUseWaste was to rethink the currently established manure management systems and develop and apply new technologies to improve the utilisation of manure organic matter and nutrients in a sustainable manner. The knowledge should provide companies with improved and new technologies to produce both bioenergy and bio-fertilisers, leading to improved soil, water and air quality (ReUseWaste 2016).

Figure 1.9 presents an overview of the ReUseWaste network and the objectives of the different work packages (WP), which include developing new characterisation tools for manure components (WP3), finding new technologies for treatment and separation of manure organic matter and nutrients (WP4), developing new technologies for bioenergy and nutrient recovery (WP5), assessment of the performances of the manure treatment products through land recycling (WP6) and finally implementation of integrated assessments and stakeholder dialogues to integrate the gained knowledge into new manure management systems (WP7).
The energy crisis and the processing of biowaste generated are both emerging issues. A potential solution that is capable of solving these issues is to further develop gasification of biowaste. The key scientific aim of this thesis was to investigate the gasification process of two different types of feedstock (poultry litter and MSW) using experimental and mathematical approaches. This thesis focuses on investigating gasification technology as an alternative for waste management and to determine the potential of poultry litter and MSW for bioenergy production. Two projects are referred to in this thesis towards the development of traditional and data driven modelling approaches and experimental work was carried out on a bench and lab-scale fluidised bed gasifier.

The specific aims of the project were:

1. To investigate the process parameters on the product gas composition and gasifier performance.
3. Artificial neural network modelling of the fluidised bed gasifier.
4. Optimising the prediction capability of the multi-gene genetic programming approach.

The supplements presented in Figure 1.10 are presented in Table 1.3.
Figure 1.10: Flowchart of work presented in this thesis
<table>
<thead>
<tr>
<th>Supplement</th>
<th>Event</th>
<th>Objectives</th>
</tr>
</thead>
</table>
| I          | Experimental test of poultry litter gasification | • Product gas composition with temperature, ER and SBR  
• Product gas composition with and without limestone addition  
• Gasifier performance and mass balance analysis  
• Development of zero-dimensional fluidised bed gasifier using Aspen Plus  
• Pseudo equilibrium model complemented with experimental data  
• Sensitivity analysis of process parameters  
• Developing a data-driven modelling of fluidized bed gasifiers for MSW gasification  
• Demonstrated a methodology how to decide hidden layers, number of neurons in the hidden layer and activation function using Monte Carlo runs  
• Exploited developed model to predict lower heating value and product gas yield  
• GP is used to predict the performance of the fluidised bed gasifier  
• The performance of the multi-gene GP models is compared with the single-gene GP model  
• GP modelling is useful for prediction with analytical expressions |
| II         | Zero-dimensional simulation of fluidised bed gasifier | |
| III        | Artificial Neural Network model | |
| IV         | Genetic Programming (GP) modelling approach | |
1.8 Scope of the proposed work

Considering the energy potential of poultry litter and MSW, there seems to be an opportunity for bioenergy production at farm (to give farmers energy independence) or municipality level as animal manure/solid waste can be used as renewable and carbon neutral feedstock in energy production unit which will eventually off-set fossil fuel consumption.

In order to determine the optimum use of poultry litter and MSW in gasification systems, the present study investigated fluidised bed gasification process for poultry litter and MSW both experimentally and numerically. Poultry litter gasification experiments were performed on a lab-scale bubbling fluidised bed gasifier at the Energy Research Centre of the Netherlands (ECN). Gasification experiments were performed using different combinations of air and air-steam mixture as the gasifying medium under steady state conditions. The experimental data obtained from the bubbling fluidised bed gasifier are analysed. In fluidised bed gasification, agglomeration and defluidisation are known problem, so a novel approach is proposed to prevent such problem while gasifying feedstock with high ash content.

The results from the ECN gasifier and dedicated devolatilisation experimental data are used to develop a zero-dimensional model to simulate the fluidised bed gasifier so as to study the influence of different process parameters. In addition, in this thesis simplified but rigorous mathematical models are developed for simulating the fluidised bed gasifier performance and optimisation.

1.9 Thesis structure

Chapter 1: Introduction – Introduces the topic of animal feedlot and solid waste management. The focus lies on thermal treatment of poultry litter and MSW feedstocks to produce bioenergy through gasification processes. The by-product of gasification i.e. ash and char can be used to improve soil quality, enhance plant growth and mitigate environmental pollution in the manure management chain.


**Chapter 2: Materials and methods** – This chapter provides the reader with a detailed description of the methods including the mathematical approach and operational details of the equipment used throughout the course of this research project.

**Chapter 3: Poultry litter gasification in a fluidised bed reactor: Effects of gasifying agents and limestone addition** – The gasification of poultry litter is experimentally investigated in a bubbling fluidised bed gasifier at lab-scale. A novel technique is proposed to gasify animal manure (poultry litter) in a bubbling fluidised bed gasifier to avoid agglomeration problems. This chapter was published in the American Chemical Society’s (ACS) journal ‘Energy & Fuels’.


**Chapter 4: Model development and application to the poultry litter gasification**– This chapter presents a pseudo equilibrium based model (PEM) complemented with experimental data to predict the product gas composition, gasifier performance and optimised process parameters using ASPEN PLUS. Results discussed in this chapter were presented in an international ‘WasteEng 2016’ conference in Albi, France. This research chapter will be submitted for publication.


**Chapter 5: Artificial neural network modelling approach for municipal solid waste in a fluidised bed reactor** – This chapter gives insight into the developed artificial neural network (ANN) model’s definition, architecture, working principle and its application to a fluidised bed gasifier. The ANN model using Monte Carlo simulation is exploited and validated with the published experimental datasets. This chapter is accepted for publication in the Elsevier’s journal ‘Waste Management’.

Chapter 6: Multi-gene genetic programming based predictive models for municipal solid waste gasification in a fluidised bed gasifier – This chapter presents the development of a data-driven modelling approach for simulating fluidised bed gasification of MSW. A genetic programming based modelling strategy provides analytical expressions which can provide an insight if the selected feedstock would be appropriate fuel for gasification or not. This chapter was published in the Elsevier’s journal ‘Bioresource Technology’.


Chapter 7: Conclusions and recommendations for future work – Summarises the key findings of the investigations and gives suggestions for future research work in the area.
1.10 References


2 Materials and methods

2.1 Fuel characterisation

2.1.1 Feedstock sampling methods

The feedstock used in the fluidised bed gasifier was poultry litter, which was collected from a farm in the Netherlands according to BS EN 14778 (2011a). Considering the heterogeneity, the samples collected were carefully prepared (collected, partially dried, sieved etc.) to make it representative before being used in the gasifier.

2.1.2 Moisture content

The moisture content in the feedstock was measured according to BS EN 14774-3 (2009a). Due to the hygroscopic nature of feedstock, ultimate, proximate analyses and heating value of the poultry litter was carried out on the same day to avoid any discrepancies in the measurements.

Method:

A crucible along with lid was dried in an oven at 105 ± 2 °C until the mass of the crucible had become constant. Once the mass was constant, it was taken out from the oven and cooled to room temperature in a desiccator. It was then weighed on a mass balance with a precision of 0.1 mg. Thereafter, the crucible was loaded and weighed along with the lid and sample of 1 g to the nearest accuracy of 0.1 mg. The crucible was transferred to the oven and the uncovered crucible was heated to 105 ± 2 °C leftover night. The covered crucible with the lid was transferred to a desiccator to cool it to room temperature before weighing. To reduce the uncertainties involved in measurements, each sample was analysed in duplicate. The standard deviation associated between the duplicates result was calculated and reported.
**Calculation:**

The moisture content in the feedstock was calculated according to equation (2.1)

\[
MC = \left( \frac{m_1 - m_i}{m_2 - m_i} \right) \times 100
\]  

(2.1)

where,

- MC is the moisture content in the feedstock (% basis).
- \(m_1\) is the weight of dry empty crucible and lid (in grams).
- \(m_2\) is the weight of wet sample along with crucible and lid before drying (in grams).
- \(m_3\) is the weight of dry sample along with crucible and lid after drying (in grams).

### 2.1.3 Volatile matter content

Volatile matter content was determined in accordance with BS EN 15148 (2009b). The volatile matter is defined as a mass loss of dried sample when it is heated at 900 ± 10°C for the period of 7 minutes in the absence of ambient air.

**Method:**

A specially designed crucible along with lid for measuring volatile matter was placed in a furnace and heated to 900 ± 10°C for 7 minutes. The heated crucible was taken out of the furnace and allowed to cool on a heat resistant plate before transferring it into the desiccator. The weight of crucible was noted down, it was loaded with 1 g of sample, covered with the lid and returned to the furnace at 900 ± 10°C for 7 minutes. A similar cooling protocol was adopted as the one applied for an empty crucible. The crucible was weighed and recorded for calculation.

**Calculation:**

The volatile matter content was calculated according to equation (2.2)

\[
VM = \left( \frac{m_1 - m_i}{(m_2 - m_1) \times \left(1 - \frac{MC}{100} \right)} \right) \times 100
\]  

(2.2)

where,
VM is the volatile matter content in the feedstock (% basis).
MC is the moisture content in the feedstock (% basis).

$m_1$ is the weight of an empty crucible and lid (in grams).

$m_2$ is the weight of sample along with crucible and lid before volatilisation (in grams).

$m_3$ is the weight of sample along with crucible and lid after volatilisation (in grams).

### 2.1.4 Ash content

Ash in the feedstock represents inorganic compounds that remain after the complete combustion of the feedstock (biomass). Ash content and its composition can have a significant influence on the smooth operation of a fluidised bed gasifier therefore, it is important to have ash analysis beforehand. The ash content presented in this study is reported as a percentage mass of dried feedstock. The ash content measurement was done according to the BS EN 14775 (2009c).

**Method:**

An empty crucible was placed in a furnace and heated to 550 ± 10 °C for an hour. The crucible was taken out and placed on a heat resistant plate for cooling for about 10 minutes followed by continued cooling to ambient temperature in a desiccator without desiccant. The weight of the empty crucible was noted and thereafter the crucible was loaded with 1 g of dry sample (evenly spread) and put in the cold furnace. The furnace was programmed to reach 250 °C from ambient temperature with a heating rate of 5 °C/min and was maintained for another two hours to drive off the volatile matter. After that, the temperature of the furnace was set to 550 °C and heating rate increased to 10 °C/min and it was held at that temperature for another two hours until the mass change was less than 200 mg. The sample was taken out and the same cooling and weighing procedure was followed as the one used for an empty crucible. Again, duplicate samples were analysed to provide better accuracy in results. It is likely that some carbon may be present indicating that combustion was not complete, if that occurs, the sample has to be returned to the furnace for another
30 minutes at 550 °C and this process has to be repeated until the mass change is less than 200 mg.

**Calculation:**

The ash content was calculated by equation (2.3)

\[
A = \left( \frac{m_3 - m_1}{(m_2 - m_1) \times \left(1 - \frac{MC}{100}\right)} \right) \times 100
\]

(2.3)

where,

A is the ash content in the feedstock (% dry basis).
MC is the moisture content in the feedstock (% basis).
\(m_1\) is the weight of an empty crucible and lid (in grams).
\(m_2\) is the weight of sample along with crucible and lid before ash generation (in grams).
\(m_3\) is the weight of sample along with crucible and lid after ash generation (in grams).

The elemental analysis of ashes (major and minor) were analysed by inductively coupled plasma (ICP) according to BS EN 15290 (2011b) and BS EN 15297 (2011c) respectively

**2.1.5 Fixed carbon content**

The fixed carbon content represents the solid carbon in the feedstock that remains after the volatilisation process. The fixed carbon was calculated by difference according to equation(2.4)

\[
FC = 100 - (MC + VM + A)
\]

(2.4)

where,

FC is the fixed carbon (%).
MC is the moisture content in the feedstock (%).
VM is the volatile matter content of the feedstock (%, dry basis).
A is the ash content in the feedstock (%, dry basis).

2.1.6 Determination of carbon, hydrogen, nitrogen and sulphur in the feedstock

The ultimate analyses of feedstock (C, H, N and S) were determined using a Vario EL cube Elemental Analyser. A schematic diagram of elemental analyser is shown in Figure 2.1. The analyser was calibrated using sulphalnic acid before it was used for determining the elemental composition. The measurements were undertaken in triplicate and the elemental composition was reported on a dry and dry ash free basis.

![Schematic diagram of the Vario EL Cube Elemental analyser](image)

**Figure 2.1:** Schematic diagram of the Vario EL Cube Elemental analyser

For the elemental analysis, room dried sample (about 10 mg) were weighed in alumina boats and placed in the automatic cartridges of the device. The samples were sequentially flushed by a helium carrier gas into the combustion zone (1150 °C) and samples were combusted in the presence of oxygen and tungsten trioxide (WO₃). Tungsten trioxide acts as an oxidation catalyst to make sure that sample has been
completely combusted as well as to prevent the formation of non-volatile sulphates and binds with heavy alkali metals which might cause the disruption of the analysis. After combusting the sample the evolved gases (CO$_2$, SO$_x$, NO$_x$ and H$_2$O) pass through a reduction tube at 850 °C, containing copper which acts as a catalyst to convert NO$_x$ and SO$_x$ to N$_2$ and SO$_2$ respectively. The top of the reduction tube was filled with silver wool to trap volatile halogen compounds. The remaining CO$_2$, H$_2$O and SO$_2$ were retained in three different thermal adsorption columns. Moisture content present in the mixture of the gases was removed with Sicapent (Phosphorous Pentaoxide, P$_2$O$_5$).

A thermal conductivity detector (TCD) is used to measure the composition of the different components in the gases. Once the analysis was finished, the analyser computed the elemental composition of the sample which was further corrected for moisture and ash contents. The analyses were carried out in triplicate and reported as the mean and standard deviation. The elemental oxygen content in the sample was calculated by difference.

2.1.7 Determination of higher heating value, lower heating value and chlorine content

The higher heating value (HHV) of the sample was determined using an adiabatic oxygen Bomb Calorimeter (Isoperibol Calorimeter 6200 Parr Instrument Company) as per the British Standard BS EN 14918 (2009d). The bomb calorimeter was calibrated with a standard sample (Benzoic acid), prior to analysing the samples. The bomb was loaded with 1 g (approximately) of sample, the bomb was sealed and pressurised with oxygen (25 bar). The bomb was submerged in a known volume of water (200 ml) before the charge was electrically ignited to combust the sample (closed system – no escape of combustible gases). The temperature of the surrounding water was increased due to the combustion process and the change in water temperature was recorded. The temperature difference along with a bomb factor (heat capacity of the bomb, depends on metal parts of the bomb) was used to calculate the HHV of the sample. A correction was made to take into account the electrical energy supply and burning of the fuse. The excess pressure of the bomb
was released after measuring the rise of temperature. To ensure the precision of the measurement, at least two duplicates were analysed and an average value was reported. A schematic of the device is shown in Figure 2.2. The lower heating value (LHV also referred to as the net calorific value) is calculated by equation (2.5)

\[
LHV_{dry} = HHV_{dry} - 2.442 \times 8.936 \times \left( \frac{H}{100} \right)
\]

(2.5)

where, \(HHV_{dry}\) is the HHV of the sample on a dry basis (MJ/m\(^3\)) and \(H\) is the percentage of hydrogen content in the biomass (dry).

Figure 2.2: A schematic diagram of the bomb calorimeter (Averill and Eldredge 2007)

The liquid samples generated during the measurement of HHV were used to determine the chlorine content using a chlorine ion selective electrode according to CEN/TS 15408 (2006).
2.1.8 Cellulose, hemicellulose and lignin analysis

Lignocellulosic samples were analysed using a standard developed by the National Renewable Energy Laboratory (Sluiter et al. 2008). Samples were carefully prepared (grind, sieved) with a particle size in the range of 180-850 µm (FOSS Cyclotec 1093 Mill, Retsch AS200 sieve shaker). An ethanol extraction was carried out by means of a Dionex Accelerated Solvent Extractor 200 according to a modified NREL method (Ruiz et al. 2005) before analysing the carbohydrate and lignin content in the samples. The purpose of solvent extraction is to remove non-structural material from the sample to avoid any interference with later analytical steps.

Following solvent extraction, the samples were hydrolysed with sulphuric acid in two stages. The hydrolysed mixture was filtered and the solid residues were collected. The solid was dried at 105 °C for 24 h and then it was heated at 550 °C for 24 h in a muffle furnace and weighed and the acid insoluble lignin and ash content were calculated. The Klason lignin content was determined gravimetrically as an ash-free acid insoluble residue fraction. The filtered hydrolysate was analysed using an Agilent HP 8452A Diode Array Spectrophotometer (set to 205 nm) to estimate the acid soluble lignin fraction (TAPPI 1991). The structural carbohydrates, cellulose and hemicellulose, were determined by high performance liquid chromatograph (HPLC).

2.1.9 Thermogravimetric analysis

Prior to the gasification experiment, thermogravimetric analysis (TGA) was performed to study the weight loss of the sample as a function of temperature using a SDT Q600 (TA Instruments) analyser. A crucible loaded with 10 mg of sample was analysed where the dynamics of weight loss of the sample was measured as a function of increasing temperature/time. The heating rate was programmed in such a way that the sample was in a drying stage (105 °C) for 10 minutes followed by temperature ramping to a final temperature of 900 °C at a heating rate of 10 °C/min. All the experiments were performed in a nitrogen environment. A purge flow of nitrogen (100 ml/min) was used to prevent oxidation and to remove gaseous products formed during the pyrolysis process.
2.1.10 Bed material characterisation

Bed material (an inert material) was used in a bubbling fluidised bed gasifier as a heat and mass transfer medium to ensure uniform temperature within the bed. Normally, silica sand is used as a bed material whereas other bed materials with catalytic activity such as olivine, magnesite or dolomite can also be used. The fluidisation regime depends on the bed material used in the gasifier (Yang 2003). The bed material was sieved using a Retsch AS 200 sieve shaker. The sieves (Endecotts Ltd.) were 200 mm in diameter and 25 mm in height. The three sizes used were 0.50, 0.40, 0.30, 0.25 and 0.20 mm. A known weight of solid samples was placed into the shaker and shaken for 45 min at amplitude of 60 to determine the mean particle size of the bed material. It should be noted the properties of the bed material (silica sand) has a significant influence on the hydrodynamics of the fluidisation. A method was established by Geldart (2007) to classify the bed material according to the behaviour of solids when they were fluidised by gases. As can be seen in Table 2.1, different powders show their inherent dynamic patterns. Only group B is suitable for the bubbling fluidised bed gasification according to this classification.

**Table 2.1: Classification of bed material**

<table>
<thead>
<tr>
<th>Group A</th>
<th>The bed particles exhibit dense phase expansion after minimum fluidisation and before the beginning of bubbling. Gas bubbles appear at the minimum bubbling velocity.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group B</td>
<td>Gas bubbles appear at the minimum fluidisation velocity.</td>
</tr>
<tr>
<td>Group C</td>
<td>The bed particles are cohesive and difficult to fluidise.</td>
</tr>
<tr>
<td>Group D</td>
<td>Stable spouted beds can be easily formed in this group of powders.</td>
</tr>
</tbody>
</table>

The bulk density (ratio of mass of a batch of particles and volume occupied by particle including voids) was calculated according to the ASTM D6683-14 (ASTM 2014). Measuring the bulk density is highly dependent how samples were handled. A fixed amount (500 g) of bed material (as received) was thoroughly mixed before pouring it into a 100 ml cylindrical tube (empty weight $m_1$, g). Once the material was
poured into the cylindrical flask, it was gently tapped on the bench to avoid any
unnecessary voids then weighed again ($m_2$, g). The reported result was an averaged
value of the triplicate samples.

The absolute density of the bed material was also calculated considering the void
volume is negligible. The measuring procedure involved weighing of 10 ml
cylindrical tube (empty weight $m_1$, g) followed by pouring a small amount of bed
material particles and weighing ($m_2$, g); 5 ml of water was added into the cylinder
and then it was placed in an ultrasonic bath for 20 minutes to remove any bubbles,
after which the volume was recorded ($V$, ml). The absolute density of the particles
was calculated according to equation (2.6) given as follows:

$$
\rho_p = \left( \frac{m_{2,q} - m_{1,q}}{10\text{ ml} - (10\text{ ml} - V'_{ml})} \right) \times 1000
$$

(2.6)

where, $\rho_p$ is the absolute density of the particle (kg/m$^3$). Calculations were performed
three times and the final result was reported on an average basis.

### 2.2 Fluidised bed gasification test rig

The gasification reactor consisted of a bed section (500 mm high and 74 mm internal
diameter (i.d.)) and a freeboard section (600 mm high and an i.d. of 108 mm). Both
sections were externally heated. The throughput was in the range of 113-155 kg/h-
m$^2$. The temperature of the gasifier was controlled by an external heating source and
the gasifier was operated at 1 atmospheric pressure. The average residence time was
about 5 seconds. A detailed description of the fluidised bed gasifier used for the
purpose of this thesis can be found in the Chapter 3. However, in the section below
the theory of the fluidisation process is explained.
2.2.1 Fluidisation regime

The fluidisation regime in a gas-solid system is determined by several factors, including the mean particle size and particle size distribution of the bed material, temperature and pressure of the reactor and the flow rate of the fluidising medium. The fluidisation regime not only describes the hydrodynamic nature of the bed, but also fundamentally defines the operating characteristics and the possible applications of a reactor. There are at least five distinguishable regimes for gas-solid mixing systems: For example fixed bed, particulate fluidisation, bubbling fluidisation, slugging fluidisation and turbulent fluidisation (Figure 2.3) (Yang 2003). With regards to the gasification process in air-blown bubbling fluidised bed gasifiers, a term known as the minimum fluidisation velocity \( U_{mf} \) is of substantial significance. The minimum fluidisation velocity (at specific temperature) is defined as the superficial velocity \( U, \text{ m/s} \) of the air when the drag force of the gasifying air equals to the gravitational force on the bed material at which point the bed transforms into a incipiently fluidised bed and behaves as a pseudoliquid (Basu 2010).

![Diagram showing fluidisation regimes](image)

**Figure 2.3:** The change of fluidisation regimes with the increase of air velocity (Yang 2003)
From the perspective of practical operation, the detection of the minimum fluidisation is very important because it represents the onset of fluidisation (Caicedo et al. 2002). There are basically two ways to determine the $U_{mf}$, specifically numerical calculation and pressure drop analysis. Empirical mathematical relations have been developed to calculate the $U_{mf}$ according to the geometric and physical parameters of the gasifier and bed material. Lin et al. (2002) reported a comprehensive list in their paper. But it should be noted that the equations and models were developed based on individual reactors with their own geometry characteristics especially the design of their air distributors at different conditions e.g. temperature and pressure. That means they are not universally applicable but they can still be used to provide approximate values. Another way is through pressure drop analysis which is based on the fact that the pressure drop across the bed increases proportionally with the air flow when the $U$ is lower than the $U_{mf}$ (Lin et al. 2002).

\[ \text{Figure 2.4: Variation of differential pressure across the bed with gas velocity (Wang et al. 2007)} \]

When the $U$ is increased to a critical point equal to the $U_{mf}$, the value of the pressure drop reaches its peak. After that, the pressure drop will decrease slightly (Figure 2.4)
and remain relatively constant with any further increase of U because the gas-solid bed is well aerated and can deform easily without appreciable resistance (Kunii and Levenspiel 1991). This method was used in this study because it can avoid the errors from the physical parameters and geometry structures and give more accurate results.

2.3 Gasification process parameters

2.3.1 Equivalence ratio

The equivalence ratio (ER) is defined as the ratio of the actual amount of air fed into the reactor per unit mass of biomass (dry and ash free basis) to the stoichiometric amount of air required for the complete combustion per unit biomass. The ER is defined as follows (2.7)

$$ER = \left(\frac{\text{Air flowrate}}{\text{Biomass flowrate}}_{\text{actual}}\right) / \left(\frac{\text{Air flowrate}}{\text{Biomass flowrate}}_{\text{stoichiometric}}\right)$$ (2.7)

where, the stoichiometric amount of air required ($M_{\text{air}}$) for complete combustion of per unit mass of biomass can be calculated by equation (2.8) (Basu 2010) using the ultimate and proximate analysis of the biomass. Since the temperature inside the gasifier is not high enough for the conversion of nitrogen in the biomass to NO$_x$, therefore, the N is not considered in the combustion reaction.

$$M_{\text{air}} = \left[11.53C + 34.34\left(H - \frac{O}{8}\right) + 4.34S + A\times S\right] \text{kg} / \text{kg biomass}$$ (2.8)

2.3.2 Calculation of LHV of the product gas

The LHV and HHV of the product gas (MJ/Nm$^3$) were determined according to equations (2.9) and (2.10) respectively.
\[
LHV_p = \frac{\sum C_i H_j \times LHV_{C,H_j} + H_2 \times LHV_{H_2} + CO \times LHV_{CO} + H_2 S \times LHV_{H_2 S} + COS \times LHV_{COS}}{100}
\]

(2.9)

\[
HHV_p = \frac{\sum C_i H_j \times HHV_{C,H_j} + H_2 \times HHV_{H_2} + CO \times HHV_{CO} + H_2 S \times HHV_{H_2 S} + COS \times HHV_{COS}}{100}
\]

(2.10)

where, \(LHV_p\) and \(HHV_p\) are net and gross calorific value of the product gas, \(C_i H_j\) is the concentration of the specific gas within the product gas and \(LHV_{C,H_j}\) and \(HHV_{C,H_j}\) is their corresponding net and gross calorific value respectively. The net and gross calorific values of the specific gases present in the product gas are tabulated in Appendix 1.

### 2.3.3 Gasification efficiencies

The efficiency of a gasifier is normally expressed in terms of the cold gas efficiency (CGE). CGE is defined as the ratio of the chemical energy of the produced gas to the chemical energy of the feedstock. It is imperative to mention that while calculating the CGE, both the heating value of the gas produced and feedstock have to be in the same units i.e. either LHV or higher heating value (HHV). In this study the LHV of the biomass and product gas is used in calculating CGE. Carbon conversion efficiency (CCE) and hydrogen conversion efficiency (HCE) were calculated by dividing the carbon and hydrogen in the dry product gas by the amount of carbon and hydrogen fed into the gasifier. To assess the gasification process performance CGE, CCE and HCE are determined according to following equations (Basu 2010).

\[
CGE(\eta_g) = \frac{LHV_g(ER,T) \times \dot{m}_g}{LHV_f(ER,T) \times \dot{m}_f} \times 100
\]

(2.11)
\[
CCE(\eta_{ce}) = \left( \frac{C_{o,dry\text{gas}}}{C_{i,daf}} \right) \times 100
\] (2.12)

\[
HCE(\eta_{hc}) = \left( \frac{H_{o,dry\text{gas}}}{H_{i,daf}} \right) \times 100
\] (2.13)

Where, \( m_g \) is the product gas flow rate in kg/hr, \( m_f \) is the feed rate of solid fuel, \( LHV_g(ER,T) \) and \( LHV_f(ER,T) \) are the calorific values of the product gas and solid fuel at a particular temperature and ER respectively. \( C, C_O, H \) and \( H \), where the subscript \( i \) represents the feeding rate of carbon and hydrogen on a dry and ash free (daf) basis and \( o \) the flow rate of carbon and hydrogen in the product gas.

### 2.3.4 Mass balance analysis

A mass (material) balance accounts for material entering and leaving from the enclosed system which is used to identify the measurement errors. The elemental compositions of input and output streams are taken into account for calculating the mass flow rate (kg/hr) while applying the law of conservation of mass. Dry air fed to the gasifier consists of oxygen and nitrogen only with a mass ratio of 23.2 - 76.8. The flow rate of different gas species was calculated as the concentration (% vol), their corresponding densities at room temperature (kg/m\(^3\)) and yield of product gas (m\(^3\)/hr). The following assumptions were made for calculating the mass balance (i) elutriation of bed material is negligible (ii) \( \sum_{i=1}^{n} M_i = \sum_{j=1}^{n} M_o \) where, \( i \) and \( j \) represent the input and output constituents of each element (iii) added limestone is bound with bottom ash (iv) accumulation rate of ash and char in the bed is averaged over the day. All possible measurements like elemental composition in the gas phase, cyclone fines (elutriated char) and bed material were taken into account while calculating the mass balance. The ultimate and proximate analyses were performed for cyclone fines and bed material. Char elutriation (collected from the cyclone) was estimated as the average value over the entire period of gasification. Char samples collected after
gasification were analysed for moisture, ash and elemental composition. Each stream was included in the CHNO output. The sum of CHNO from all the streams was the overall mass output. Moisture content in the product gas was measured during the gasification process. It is necessary to point out that tar composition was not taken into account in this calculation. In addition, fines that escaped from the cyclone and end up in the filters was not collected and measured in this study that could be another source of error since the exact cut point of the cyclone was not known. The mass input from the biomass was converted to the input of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) (kg/h) on a moisture and ash free basis (corresponding to the elemental analysis). The moisture from the biomass was divided into H and O input. The mass flow of air was calculated from its volumetric flow rate (dm$^3$/min) and density (at room temperature and 1 atm). The mass flow of the gas species in the air ($N_2$, $O_2$ and $CO_2$) was calculated according to their mole fractions and converted to CHNO flow (kg/h). The sum of all elements represented the overall mass input. The mass flow rate of each gas species (kg/h) in the product gas was calculated as the product of its density (kg/m$^3$) (at room temperature and 1 atm), concentration (vol.%) and yield of the product gas (m$^3$/h).

2.4 Product gas measurement

2.4.1 Micro-gas chromatography

The measurement of permanent gases (CO, CO$_2$, C$_2$H$_2$, CH$_4$, C$_2$H$_4$, C$_2$H$_6$, C$_6$H$_6$, C$_3$H$_8$, N$_2$, COS, H$_2$S and Ne) were analysed online using a Varian, CP4900 micro-gas chromatography ($\mu$-GC). The micro gas chromatograph was calibrated with a known gas mixture containing a specified concentration of measured gases. Precautions were taken into account to make sure the H$_2$ and Ne peaks were well separated. Ne concentration (in ppm) in the outlet stream of the reactor was measured by micro GC using a Molsieve 5A (10m) column. It is imperative to stress that the product gas that analysed by $\mu$-GC passed was free from particulates and other impurities. The $\mu$-GC was equipped with 4 channels, each with a thermal conductivity detector for the determination of permanent gases and light hydrocarbons. Helium was used as the carrier gas. Channel 1 was fitted with a CP-4900 Backflash Column Module 10 MSS to analyse Ar/O$_2$, N$_2$, CH$_4$ and CO.
Channel 2 was fitted with a CP-4900 Backflash Column Module 10 PPU to analyse CH₄, CO₂, C₂H₄, C₂H₆, C₂H₂, H₂S and COS (carbonyl sulphide). Channel 4 was equipped with a CP-4900 Column Module to analyse benzene and toluene. Channel 3 was not used in this study. An ABB gas analyser was used to determine the H₂ and O₂ content in the product gas. It was fitted with three modules: an Uras26 (infrared photometer) for CO, CO₂ and CH₄ concentration, a Magnos27 module (thermo-magnetic) for O₂ content and a Caldos27 (thermal conductivity silicon sensor) for H₂ content. The gas analysis was carried out according to the method described by van Paasen et al. (2006). The interval time for the μ-GC was 4 minutes and for the ABB analyser was 1 second.

Gas chromatograph is used in analytical chemistry to analyse the different gas components in a sample by vaporising it. Gas chromatograph consists of sample injector, separator column (capillary tube) and detectors. In gas chromatography, the mobile phase is a carrier gas (inert gas He, Ne or sometimes N₂), a microscopic layer of solid adsorbent or non-volatile liquid acts as a stationary phase. The gas sample is carried through the column by the carrier gas where gaseous molecules are adsorbed by the stationary phase and desorbed by the mobile phase (He). The gaseous compounds elute at different times according to their own adsorbing and desorbing capacity (partial pressure of sample components). The separated gaseous species exit the separator column at different times (retention time) and reach the detectors. The detector signals were integrated over time to determine the quantity of specific component present in the product gas. The peak area of the signal represents the quantity of each material. Peak shapes depend on isotherms that establish a relationship between concentrations of solute in the stationary phase to the solute concentration in carrier gas. If the isotherms are linear, the peaks are Gaussian in shape indicating that separation proceeds with little or no problem, where as if the isotherms are non-linear, the peaks become asymmetric (Grob and Barry 2004). Gas samples were analysed by thermal conductivity detectors (TCD) due to their simplicity, large linear dynamic range and non-destructive nature.

The working principle of TCD is based on thermal conductivity which depends on the gas type. A typical TCD detector is heated with an electric heater (constant
electrical power) where its temperature depends on thermal conductivity of the surrounding gas. In general, twin detector are used, one is located before the sample injector port and other one immediately after the stationary phase column. A Wheatstone bridge circuit (Figure 2.5) is arranged to nullify the effect of thermal conductivity of the carrier gas. A detailed description of the working principle of TCD detectors can be found elsewhere (Toonen and van Loon 2013).

![Wheatstone bridge circuit](image)

**Figure 2.5:** Schematic diagram of the TCD (Toonen and van Loon 2013)

### 2.4.2 Moisture analysis in product gas

The moisture content in the product gas was measured once a day. Although, moisture present in the feedstock will be vaporised or consumed in the gasification reaction (water gas or water gas shift reaction) however, at the same time moisture vapour will be generated by the oxidation reactions. Therefore, moisture content in the product gas will inevitably be higher than in the tar. A syringe packed with 10 g of P₂O₅ with a strong desiccant was weighed. Once gasifier achieved steady state conditions, 100 ml of hot product gas was drawn through the desiccant (50 ml/min) to adsorb all the moisture (including tar compounds) and it was weighed again immediately. The moisture content was determined by the mass difference of the before and after the sampling.
2.4.3 Gas yield calculation

To calculate the product gas flow rate, a known amount of neon gas (10 ml/min) was continuously fed into the gasifier and was detected by µ-GC in the outlet stream (in ppm) along with the product gas. The flow rate of the product gas (m$^3$/min) was calculated as follows (2.14):

$$\gamma_i = \left( \frac{\beta}{Ne} \right)$$  \hspace{1cm} (2.14)

where, $\gamma_i$ represent the flow rate of dry product gas (m$^3$/min), $\beta$ the Ne flow rate (ml/min) and $Ne$ the concentration of Ne (ppm) in the product gas.

2.5 Modelling of fluidised bed gasifier

2.5.1 Aspen Plus simulation software

The poultry litter gasification process was simulated on Aspen Plus software (AspenTech 2010). Aspen Plus is a powerful process simulation tool which allows simulating a wide range of industrial application. It works on the principle of mass and energy balance. Calculations in Aspen Plus are performed in unit operational blocks. Aspen Plus has several unit operation blocks consisting of heat exchangers, mixers, reactors, separators, pumps, compressors etc. In addition to these blocks, Aspen Plus allows one to build user defined models using Microsoft Excel spreadsheets or by writing a FORTRAN code. Unit blocks are connected by material, heat or work streams.

2.5.2 Structure

An Aspen Plus model consists of different stages. The first step is the layout of a flowsheet (a graphical representation of the process) where unit blocks are connected with the desired streams. Secondly, the user has to define chemical components, temperature, pressure and flow of the stream. Finally, the operating conditions of the unit blocks are defined. Aspen Plus has an extensive library of chemical and
thermodynamic databases which provide an advantage over other process simulation software. The user can also add additional components by supplying the necessary dataset. In addition, Aspen Plus also provides the flexibility to incorporate other numerical methods and optimisation convergence options which can be implemented based on the need and requirement for more rigorous calculations.

2.5.3 Stream classes

Streams represent mass or energy flow. An energy stream can be defined as a heat or work flow. Moreover, the heat stream contains the temperature information. A mass stream is classified into three categories: mixed, solid and non-conventional. A mixed stream can be a mixture of gases, liquids or solids. A solid stream can only have solid components. Mixed and solid streams are classified as conventional components which mean their chemical and thermodynamic properties are already in the Aspen library. Components which are not included in the Aspen Plus library can be defined as a non-conventional stream. Non-conventional components do not have a defined phase and are thermodynamically partially defined. These components are defined by their proximate, ultimate and sulphate analysis. They can also be defined by standard enthalpy of formation, coefficient of heat capacity and density vs. temperature polynomials.

2.5.4 Solver method

Aspen Plus solves the equations given in the unit blocks and streams using calculator or design specification blocks sequentially or spontaneously. It also allows using iterative processes and iteration methods. Aspen Plus software can be exploited to perform the sensitivity analysis of the process parameters and for the optimisation.

2.5.5 Result output

After the simulation is finished, the results properties of the stream, process unit block along with calculator or design specification block (if any) are available in Aspen Plus results section which can also be exported to other programs for processing. Based on requirement, user defined result properties can be obtained.
Moreover, gasification performance parameters are not defined in the Aspen Plus software therefore the user has to use the calculator block or export the gas composition data for calculating the performance parameters.

2.6 Genetic programming approach

Genetic programming (GP) is a domain dependent evolutionary algorithm inspired by a high-level biological computer program that performs user defined computational tasks (Koza and Poli 2005). GP works on the Darwinian principal of survival of the fittest (selection), recombination (crossover) and mutation. It is a machine learning technique which is used to optimise a computer program based on the mathematical operators to solve the given task while minimising the prediction error in the objective function. The solution variables are encoded in what is known as the genes or trees. Unlike other evolutionary algorithms, GP is represented in the form of syntax trees. It is directly manipulating a coded chromosome of the problem. Therefore, GP based programs are articulated as a fixed-length character string called a syntax tree rather than as lines of code. Variables and constants used in the program represent leaves of the tree (Poli et al. 2008). In GP, variables and constants are leaves of the tree called terminals and arithmetic operations are internal nodes called functions. It is a systematic, domain- independent method to solve problems automatically. The programs evolved by GP consist of a set of instructions or functions used for symbolic regression (athematic operator) and terminals (constants, variables and logical expressions). A simple tree representation of GP algorithm is shown in Figure 2.6. The detailed description of the GP based algorithm can be found elsewhere (Koza 1992).
2.6.1 Methodology:

GP is an extension of the genetic algorithm which also uses crossover and mutation operators to find a solution. At the start of the algorithm, the genes or expression trees are randomly initialised within the feasible space. Then they undergo reproduction, crossover and mutation to evolve fitter individuals in the succeeding generations. Crossover is an important generic operator; it takes two individuals called parents and produces a new offspring called a child by swapping generic material between before and after a randomly chosen crossover point. The second generic stage called mutation is an arbitrary modification to prevent premature convergence by random changes within the gene. Mutation is applied by simply flipping one element by another randomly in a string with a certain probability called the mutation rate.
The crossover and mutation operations are stochastic and their probability of occurrence is pre-specified by the user. It is an optimisation process which tries to find the optimum solution $s^*$ such that

$$s^* = \arg \min_{s \in S} f(s)$$  \hspace{1cm} (2.15)

where $S$ is the search space of the probable solutions and $f$ is a suitably defined fitness function. The optimal solution $s^* \in S$ minimises $f$. In GP the candidate solutions $s \in S$ are functions of the form $s: \Gamma \rightarrow \Psi$ where $\Gamma$ and $\Psi$ are the spaces of the input and the output data of the programs from $S$. The strength of these evolutionary algorithms is that they do not try a brute force method for all the solutions in the input space $\Gamma$. The fitness function can be expressed as (2.16)

$$f(s) = \sum_i y_i - s(x_i)$$

(2.16)
where, $s(x_i)$ is the output of evolved program, for the input set $x_i$. $\cdot$ represents a metric like the Euclidean norm or 2-norm or the root mean square error on the output space $\psi$ and $i$ is an iterator for all the given fitness cases. The output of the GP regression model can be represented as (2.17)

$$\hat{y} = w_0 + \sum_{i=1}^{T} w_i \Phi_i$$

(2.17)

where, $w_0$ is bias term, $T$ is number of tree, $w_i \forall i \in [1,T]$ are the gene or tree weights and $\Phi_i \forall i \in [1,T]$ represents the individual trees (Pan et al. 2013).
2.7 References


BS EN/CEN/TS 15408: *Solid recovered fuels. Methods for the determination of sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content* (2006) London: British Standards Institute.


3 Poultry litter gasification in a fluidised bed reactor: Effects of gasifying agent and limestone addition

Abstract

Air and air-steam gasification of poultry litter was experimentally studied in a laboratory scale bubbling fluidised bed gasifier at atmospheric pressure using silica sand as the bed material. The effects of equivalence ratio (ER), gasifier temperature, steam-to-biomass ratio (SBR) and addition of limestone blended with the poultry litter, on product gas species yields and process efficiency, are discussed. The optimum conditions (maximum carbon conversion, gas yield, heating value and cold gas efficiency) was achieved at an ER 0.25 and 800 °C, using air (SBR = 0) and poultry litter blended with 8% w/w limestone, yielding a product gas with a lower heating value (LHV) of 4.52 MJ/Nm³ and an average product gas composition (dry basis) of H₂: 10.78%, CO: 9.38%, CH₄: 2.61 and CO₂: 13.13. Under this optimum processing conditions, the cold gas efficiency (CGE), carbon conversion efficiency (CCE) and hydrogen conversion efficiency (HCE) were 89, 73 and 43% respectively. The reported NH₃ measurement at an ER of 0.28 and 750 °C is 2.7% (equivalent to 19,300 mg/Nm³) with 14.7 mg/Nm³ of HCl observed the dry product gas. High temperature and steam injection favour production of CO and H₂ while their effect on CH₄ was almost negligible. It is demonstrated that poultry litter can be gasified by blending with limestone, making it possible to overcome the fluidisation problems caused by the mineral composition of poultry litter ash (high K and P content), yielding a gas with a similar heating value compared to gasifying without limestone addition, but with a significantly lower tar content.
Published as


D.S. Pandey defined the goal and scope of poultry litter gasification experiments in consultation with Luc Rabou, J.J. Leahy and W. Kwapinski. Experiments were performed on the ECN’s WOB gasifier by D.S. Pandey together with A. Horvat and a technician at the ECN. The calculations were all performed by D.S. Pandey. The draft of the manuscript was critically reviewed by M. Kwapinska, A. Gómez-Barea, L.E. Fryda, Luc Rabou, J.J. Leahy and W. Kwapinski, who also acted as discussion partners throughout the research leading to this paper. Chapter 3 of this thesis corresponds to the paper published in ACS journal Energy & Fuels.
3.1 Introduction

Livestock production is among the most rapidly growing sectors of the agricultural economy driven primarily by growing demand for animal protein. New livestock production has shifted progressively from ruminants such as cattle to pigs and poultry which is forecast to grow by more than 60% between by 2030, the vast majority of which will occur in intensive farming units (MacLeod et al. 2013). Intensive livestock production, while more efficient than traditional farming practice poses significant challenges in terms of its effects on the natural environment due to the accumulation of large quantities of waste with estimates of 1.4 billion tonnes (Foged et al. 2011) of manure in EU states. This accumulation of manure often results in its over application as a nutrient source for crops giving rise to social and environmental problems, such as odours, pathogens and eutrophication of surface waters. Within the EU the livestock industry has to adapt to an EU regulatory framework including the Nitrates (91/676/EEC) and Water (2000/60/EC) Directives which demand improved environmental performance (Gerber et al. 2007).

Waste management of organic streams can effectively be achieved with thermal recycling (combustion, pyrolysis, gasification, liquefaction) and bio-chemical conversion (digestion, fermentation), with the choice of conversion process dependent on the feedstock properties and availability, the desired end products, the economic value and relevant environmental standards. The main advantages of thermal processes are their ability to convert the waste to a sterile material with a significant reduction in volume by 80-95% (depending on feedstock composition and treatment technologies)(Rand et al. 1999; Hoornweg and Bhada-Tata 2012) and to recover energy either directly as heat or as energy carriers (Bujak 2015).

Poultry litter is a heterogeneous fuel, composed of bedding material, excreta, waste feed and feathers (Lynch et al. 2013). In the past, several reviews (Kelleher et al. 2002; Cantrell et al. 2007) explored the advances in disposal technology for poultry litter and for producing bioenergy from livestock waste. These studies clearly indicated that thermochemical conversion processes have capabilities to convert animal by-products into combustible gases, bio-oils and biochar (soil
amender/fertiliser). Most of the published research studies on poultry litter have focused on combustion, co-combustion with coal and fixed bed (updraft and downdraft) gasification. Poultry litter combustors (incinerators) are currently used for electricity production and ash recycling in the UK, the USA and the Netherlands (Billen et al. 2015). Thermal gasification provides some advantages and greater flexibility over direct combustion as it produces a product syngas that can either be used in gas engines or boilers for heat and electricity production. Additionally the gas can be cleaned before burning, opening the potential processing of wastes and dirty biomass feedstocks. For small and medium scale systems, gasification has emerged as an alternative viable technology with higher energy conversion efficiency to electricity than traditional combustion processes, while complying with present EU’s emission standards (Arena 2012). Solid by-products from the gasifier can be used on agricultural lands to improve the soil permeability and reduce nutrient run-off. However, leachate tests have yet to be performed to understand the fate of residues and their effect on contaminating surface and ground water. The European parliament has adopted the animal by-product Regulation (1069/2009/EU) supplemented with Regulation (142/2011/EU), to pave the way for processing animal by-products locally for nutrient recycling while producing bioenergy.

Gasification is a thermochemical conversion process which converts carbonaceous material into a useful gaseous product at elevated temperature in the presence of a limited amount of air. Thermal gasification can be used for the conversion of a wide range of fuels (wood, coal, etc.) as well as low calorific value feedstocks such as animal by-products and organic wastes. Gasification is a complex thermochemical process involving drying, devolatilisation, partial oxidation and reforming of both gaseous and solid carbon species. Gasification can be undertaken either in fixed/moving bed (updraft and downdraft configurations or some variation of these), fluidised bed or entrained flow reactors (Basu 2010).

Several fixed bed gasification studies on feedlot manure and poultry litter have been performed over the past decade. Poultry litter gasification has been carried out in small-scale fixed bed gasifiers in order to recover energy (Priyadarsan et al. 2004; Joseph et al. 2012; Thanapal et al. 2012; Hamilton et al. 2014; Taupe et al. 2016) to
reduce odour emission and nutrient run-off as well curtailing land spreading. In contrast, relatively few attempts have been made to gasify animal manure in a fluidised bed gasifier, mainly due to the higher ash content compared to other biomass. Raman et al. (1980) gasified dried swine manure in a fluidised bed gasifier using air as a fluidising medium and silica sand as the bed material. This study concluded that both the product gas yield and energy recovery increased with temperature. Recently, poultry waste was gasified in a pre-pilot scale atmospheric air-blown fluidised bed gasifier to investigate the behaviour of ash composition (Di Gregorio et al. 2014), and the authors concluded that while it is a feasible process, proper fuel characterisation is essential due to the feedstock heterogeneity and the risk of sintering and agglomeration arising from some ash constituents.

The presence of a higher fraction of low melting compounds (K, Na) and a smaller amount of higher melting species (Ca, Mg) in the feedstock ash can give rise to ash melting and agglomeration in the bed (Zevenhoven-Onderwater et al. 2001; Scala and Chirone 2008). In particular, low CaO content in the fuel ash is found to increase the likelihood of ash melting (Scala and Chirone 2008). Billen et al. (2014) concluded that the higher amount of phosphorous (P) present in poultry litter can lead to problems with bed defluidisation, and they suggested that calcite addition might lower the risk of bed agglomeration during fluidised bed combustion of poultry litter. Prevention or mitigation of defluidisation may be achieved by mixing limestone with poultry litter in the fuel intake. This provides calcium for the reaction with phosphorus, forming a high melting temperature calcium phosphate which coats onto the silica particles preventing reaction between potassium phosphate and silica (Barišić et al. 2008). Fryda et al. (2008) tested the agglomeration tendency of olive bagasse in an atmospheric fluidised bed gasifier with quartz sand (SiO$_2$ with a mean particle size 0.27 mm) and olivine. They concluded that tests with olivine resisted defluidisation at higher temperature because MgO interacts with the fuel ash and elevates the melting temperature. Walawender et al. (1981) gasified feedlot manure with steam in a bench scale fluidised bed reactor using a mixture of 25 wt% limestone and 75 wt% silica sand as the bed material. These authors reported that limestone addition in the silica bed could prevent agglomeration.
Bed agglomeration and fuel ash cause problems during fluidised bed gasification processes leading to unwanted defluidisation and shutdown of the installation. Inorganic alkali components of the fuel ash such as K, P and Na can be a source of agglomeration problems due to the formation of low-melting phosphates (sodium phosphate, potassium phosphate) and silicates with the silica present in the bed (Bartels et al. 2008). Various additives (Al, Ca, Mg) or alternative bed materials (olivine, bauxite or Ilmenite) have been used to prevent agglomeration problems. The beneficial effect of calcium oxide (CaO) addition in suppressing agglomeration has been presented by (Öhman et al. 2000) because a small addition of calcium can shift the melting temperature to 1080 °C but the melting behaviour is also dependent on the relative amounts of potassium and calcium. The authors concluded that a major fraction (>90%) of the coating is limited to the ternary system K$_2$O–CaO–SiO$_2$. The behaviour of calcium and magnesium during fluidised-bed combustion of South Australian lignite was investigated. The experimental results indicated that both Ca/Mg-bearing minerals and Ca-treated coal were effective to a certain extents in reducing bed defluidisation (Vuthaluru and Zhang 2001b). Calcite (limestone) has previously been used as bed material in a lab-scale fluidised bed combustor (Vuthaluru and Zhang 2001a), 1 MW$_{th}$ cylindrical bubbling fluidised bed combustor (Llorente et al. 2006) and was compared with silica sand. The authors concluded that calcium was diluting the low-melting silicates and did not yield any agglomerates. Silica sand was selected as a bed material because it is readily available and cheap compared to other bed materials like olivine or bauxite.

This study present the results obtained from experiments of poultry litter gasification using a bubbling fluidised bed gasifier. The main objectives of this study are (a) to investigate the influence of equivalence ratio (ER, i.e. fed to stoichiometric air ratio) (b) steam to biomass ratio (SBR, i.e. steam to poultry litter mass ratio), (c) reactor temperature ($T_g$) and (d) the effect of limestone (blended with the poultry litter), on the performance of the gasification process.
3.2 Experimental details

3.2.1 Materials

Poultry litter was collected from a local poultry farm in the Netherlands. Since, poultry litter is a heterogeneous fuel with a bulk density of 360 kg/m$^3$, it was carefully prepared (collected, partially dried, sieved etc.) with particle size in the range of 0.7-2.8 mm before gasifying. The moisture and ash content in the feedstock were 22.1 as received and 17.6% dry basis, respectively. Ultimate and proximate analyses as well as heating value of the poultry litter are reported in Table 3.1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Poultry litter (%w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (a.r.)</td>
<td>22.10</td>
</tr>
<tr>
<td>Ash content (d.b.)</td>
<td>17.55 ± 0.06</td>
</tr>
<tr>
<td>Volatile Matter (d.b.)</td>
<td>73.65 ± 0.02</td>
</tr>
<tr>
<td>Fixed carbon* (d.b.)</td>
<td>8.81 ± 0.02</td>
</tr>
<tr>
<td>C (d.a.f.)</td>
<td>54.70 ± 0.37</td>
</tr>
<tr>
<td>H (d.a.f.)</td>
<td>6.43 ± 0.07</td>
</tr>
<tr>
<td>N (d.a.f.)</td>
<td>6.48 ± 0.01</td>
</tr>
<tr>
<td>Cl (d.a.f.)</td>
<td>0.70 ± 0.02</td>
</tr>
<tr>
<td>S (d.a.f.)</td>
<td>0.90 ± 0.03</td>
</tr>
<tr>
<td>O* (d.a.f.)</td>
<td>30.79 ± 0.25</td>
</tr>
<tr>
<td>LHV (MJ/kg) (a.r.)</td>
<td>13.53 ± 0.41</td>
</tr>
<tr>
<td>Cellulose (d.b.)</td>
<td>12.88</td>
</tr>
<tr>
<td>Hemicellulose (d.b.)</td>
<td>11.72</td>
</tr>
<tr>
<td>Lignin (d.b.)</td>
<td>14.16</td>
</tr>
<tr>
<td>Extractives* (d.b.)</td>
<td>39.21</td>
</tr>
</tbody>
</table>

*calculated by difference, a.r. – as received, d.b. – dry basis, d.a.f – dry and ash free basis, *containing water and ethanol extractives.

The composition of poultry litter can be represented by the empirical formula CH$_{1.40}$O$_{0.42}$N$_{0.10}$ (dry and ash free basis). Fixed carbon content was calculated by subtracting the moisture, ash and volatile matter content from 100%. The elemental composition (C, H, N and S) was determined by a Vario EL cube elemental analyser. Oxygen content in the poultry litter was calculated by the difference, whereas higher heating value was measured using an Isoperibol Calorimeter 6200 (Parr Instruments). Chlorine content in the poultry litter, cyclone fines and bottom ash was determined.
according to CEN/TS 15408:2006. Poultry litter ash (generated at 550 °C according to BS EN 14775:2009 standard) was digested and analysed by inductively coupled plasma (ICP) and the results for the individual metals are reported as their corresponding oxides in Table 3.2. The elemental analysis of poultry litter ash shows that it has high amounts of silica, sodium, potassium, phosphorous and aluminium oxides.

Table 3.2: Chemical composition of the poultry litter ash on an as received basis (ash at 550 °C)

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Concentration (wt. %)</th>
<th>Oxides</th>
<th>Concentration (10^{-3} wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>35.67</td>
<td>TiO₂</td>
<td>32</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>17.51</td>
<td>BaO</td>
<td>17</td>
</tr>
<tr>
<td>CaO</td>
<td>12.29</td>
<td>NiO</td>
<td>12</td>
</tr>
<tr>
<td>SO₃</td>
<td>11.90</td>
<td>Cr₂O₃</td>
<td>3.7</td>
</tr>
<tr>
<td>MgO</td>
<td>9.23</td>
<td>MoO₃</td>
<td>2.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>5.27</td>
<td>V₂O₅</td>
<td>2.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.32</td>
<td>SeO₃</td>
<td>1.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.40</td>
<td>HgO</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.51</td>
<td>PbO</td>
<td>0.57</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.37</td>
<td>As₂O₃</td>
<td>0.50</td>
</tr>
<tr>
<td>MnO</td>
<td>0.34</td>
<td>CoO</td>
<td>0.29</td>
</tr>
<tr>
<td>CuO</td>
<td>0.10</td>
<td>CdO</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BeO</td>
<td>0.11</td>
</tr>
</tbody>
</table>

3.2.2 Experimental facility and test procedure

The experiments were carried out within the BRISK EU FP7 framework project using an air-blown bubbling fluidised bed gasifier at the Energy Research Centre of the Netherlands (ECN). The experimental set-up consists of: biomass hopper with two feeding screws, air preheater, bubbling fluidised bed gasification reactor, cyclone, hot and cold particulate filters and afterburner/flame for combustion of the product gas, as shown in Figure 3.1. The biomass hopper was equipped with a stirrer.
which was used to prevent settling and bridging of the feedstock and to ensure the fuel supply was consistent. The gasification reactor consists of a bed section (500 mm high and 74 mm internal diameter (ID) and a freeboard section (600 mm high and an ID of 108 mm). External heat was supplied to maintain the temperature within the reactor. Poultry litter was fed through a mechanical screw feeder under N₂ (1 dm³/min) to prevent backflow of the product gases. The feeding point was 50 mm above the bottom plate. The fluidising media were heated to 160 ºC before being introduced from the bottom of the reactor Table 3.3. The experiments were carried out at various air, N₂ and steam mixtures at different temperatures. The cyclone at the outlet stream was used to separate the solid particles (elutriated char and ashes) from the product gas. After each experiment, cyclone fines were collected and weighed and the char elutriation rate was calculated over the period of gasification test. The amount of downstream dust that escaped from the cyclone was not collected and measured in this study. The downstream sections of the gasifier up to cold filter were well insulated, heated and maintained at 400 ºC to avoid tar condensation. Tar and moisture samples were taken through a sampling port located after the cyclone and hot filtration unit in the downstream section. The product gases were combusted in a flare.
Figure 3.1: Schematic diagram of WOB gasifier (1) biomass hopper; (2) feeding screws; (3) air preheater; (4) gasifier reactor; (5) cyclone; (6) valve; (7) hot filter; (8) cold filter; (9) flare

Silica sand with a particle size in the range 0.25-0.50 mm (mean particle size of 0.31 mm) and bulk and absolute densities of 1422 and 2620 kg/m$^3$ respectively was used as the bed material. To avoid any influence of accumulated ash from previous experiments, 1.2 kg of fresh silica sand was used for each test. The minimum theoretical fluidising velocity was around 0.097 m/s at 20 ºC, calculated using Wen and Yu’s correlation (Wen and Yu 1966).

Gasification tests were conducted in such a way that the gas velocity (based on total flowrate fed and the average temperature of the gasifier) of the fluidising medium (air and N$_2$) was constant throughout the tests. The feed rate of poultry litter was varied to achieve the required ER in the tests (Table 3.3). Air, N$_2$ and steam were injected from the bottom of the gasifier. The ER was varied from 0.18-
0.41 by adjusting the air and N\textsubscript{2} flow rate. The experimental campaigns were performed using either a mixture of poultry litter (92\%) and limestone (8\%) or solely poultry litter. The limestone was supplied by Rheinkalk GmbH (Brilon, Germany) with particle size in the range 0.9 to 1.2 mm. The feed rate of the fuel was between 0.49 to 0.66 kg/hr. Four experiments were performed each working day and the feeding rate was reported on an averaged basis over the period of gasification time. The bed temperature of the reactor remained constant during each test. The flow rate of air, N\textsubscript{2} and steam was adjusted to ensure that the bed was properly fluidised. At higher ER, N\textsubscript{2} flow rate was decreased while increasing the air flow rate to keep constant the fluidisation velocity. Therefore, decrease in N\textsubscript{2} concentration was evident in product gas with an increase in ER. Three gasification tests were carried out to investigate the effect of steam injection on the product gas composition and its heating value. Experiments were performed at different temperatures (700 ≤ T\textsubscript{g} ≤ 800 °C), equivalence ratios (0.18 ≤ ER ≤ 0.41) and steam to biomass mass ratios (0.26 ≤ SBR≤ 0.33).

### 3.2.3 Ash Chemistry

Ash from the fuels with a high content of alkali metals (K, P and Na) has a lower melting point. The chemical reaction between bed material and alkali compounds (gaseous or liquid form) are described as follows (Öhman \textit{et al.} 2005; Hupa 2011)

\[ \text{SiO}_2(s) + 2\text{KCl}_g + \text{H}_2\text{O}_g \leftrightarrow \text{K}_2\text{SiO}_3(l) + 2\text{HCl}_g \]  \hspace{1cm} (3.1)

\[ \text{SiO}_2(s) + 2\text{KOH}_g \leftrightarrow \text{K}_2\text{SiO}_3(l) + \text{H}_2\text{O}_g \]  \hspace{1cm} (3.2)

Since poultry litter has a high S and Cl content, CaO in the bed might act as a desulphuriser during combustion/gasification (Zevenhoven \textit{et al.} 2010)

\[ \text{CaO}_s + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CaSO}_4(g) \]  \hspace{1cm} (3.3)

In fact, phosphorus has a higher affinity for calcium compared to potassium that produces stable solid products in the residual ash (Bostr.m \textit{et al.} 2011)

\[ \text{P}_2\text{O}_5(g) + 3\text{CaO}_s \leftrightarrow \text{Ca}_3\text{P}_2\text{O}_8(s) \]  \hspace{1cm} (3.4)
The influence of limestone addition on the retention of chlorine under bubbling fluidised bed combustion conditions has been experimentally investigated. The authors proposed to remove gaseous Cl according to the following path (Coda et al. 2001)

\[
CaO(s) + 2HCl(g) \rightarrow CaCl_2(s) + H_2O(g)
\]  

(3.5)

Below mentioned reactions summarise the sulfation of the alkali chlorides, where A is Na or K (Boonsongsup et al. 1997; Iisa et al. 1999).

\[
SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)
\]  

(3.6)

\[
2ACl(g) + SO_3(g) + H_2O(g) \leftrightarrow A_2SO_4(s,j) + 2HCl(g)
\]  

(3.7)

### 3.2.4 Measurement methods

The composition (CO, CO₂, C₂H₂, CH₄, C₂H₄, C₆H₆, C₇H₈, N₂, COS, H₂S and Ne) of the filtered dry product gases were analysed an online micro gas chromatograph (GC) (Varian, CP-4900). The micro GC was calibrated with a gas mixture containing a specified neon concentration. Precautions were taken to make sure the H₂ and Ne peaks were well separated. An ABB gas analyser was used to determine the H₂ and O₂ content in the product gas. The online gas analyser measures permanent gases as well as sulphur containing compounds (H₂S and COS). Ne gas (10 ml/min) was introduced into the gasifier continuously to measure the product gas flow rate, which was calculated according to equation (3.8) using the concentration of Ne in the product gas.

\[
\gamma_i = \left( \frac{\beta}{Ne} \right)
\]  

(3.8)

where, \( \gamma_i \) represent the flow rate of dry product gas (m³/min), \( \beta \) the Ne flow rate (ml/min) and \( Ne \) the concentration of Ne (ppm) in the product gas. Char elutriation rate was calculated by dividing the mass of char collected in the cyclone by the time of the experiment. Permanent gas measurements were carried out as per the method described by van Paasen et al. (2006). The N₂ fed into the gasifier was corrected for
the gas yields and gas compositions. Gas composition measurements were performed continuously at 4 minutes intervals for around 30 minutes and 4 samples of tar were taken at the same instants.

A short description of solid-phase adsorption (SPA) cartridge preparation, extraction, tar sampling methodology and chromatographic analysis is provided here. SPA cartridges were assembled by packing 500 mg of aminopropyl silica sorbent. A stainless steel needle with the plastic cap was attached to one side and a conical rubber stopper closed the other side of the SPA cartridge. The extraction procedure and chromatographic analysis described by Osipovs (2009) has been modified for the purpose of this work. Tar compounds were extracted from the sorbent by addition of $3 \times 600 \mu l$ of dichloromethane. Tert-butylcyclohexane and 4-ethoxy phenol were added as internal standards to the tar solutions. Calibration curves using naphtalene /tert-butylcyclohexane and phenol/4-ethoxy phenol were applied to integrate the aromatic and phenolic tars respectively.

A Thermo Scientific Trace 1310 GC with flame ionisation detector (GC-FID) was used to analyse the tars. Helium flow, column, injection volume, injection port and oven settings were kept the same as for GC mass selective detector (GC-MSD) analysis. The FID temperature was maintained at 240 °C. Air, hydrogen and carrier gas (N$_2$) flow were adjusted to 350, 35, and 40 ml/min respectively.

Tar yields are expressed on a mass basis as $g_{\text{tar}}/kg_{\text{daf-poultry litter}}$ in order to eliminate any dilution effect of the product gas when the biomass feed rate is reduced (Padban et al. 2000) or when the oxygen to nitrogen ratio is reduced to adjust for lower ER (Kinoshita et al. 1994). Tar in this paper refers to GC detectable tar including those tar compounds eluted from phenol ($M \approx 94$ g/mol) to benz[a]anthracene ($M \approx 228$ g/mol). Due to the poor measurement reliability of the lighter tars (e.g. benzene, toluene), the SPA results are not included in the present work, but instead the micro-GC results are used for the discussion.

Moisture, ammonia (NH$_3$) and hydrochloric acid (HCl) content was measured once a day at each temperature. An impinger bottle containing 100 ml of 0.1 M HNO$_3$ was
placed in bath at 4°C after the hot filter for the sampling of moisture, NH₃ and HCl. The moisture content was determined by the mass difference of the impinger bottle before and after the sampling. The principle of NH₃ measurement was based on membrane diffusion and its content was measured using an electro-conductivity detector. HCl content was determined by the means of ion chromatography (conductivity detection) using a Dionex IonPac AS18 analytical column.

Table 3.3 presents a summary of the experiments. The experimental tasks focused on the analysis of the product gas composition, ammonia emissions and tar concentration at different temperatures, ER and SBR to identify the optimum operating conditions for feedstock’s which have high ash content.

### 3.2.5 Performance analysis

The efficiency of a gasifier is normally expressed in terms of the cold gas efficiency (CGE). CGE is defined as the ratio of the chemical energy of the produced gas to the chemical energy of the feedstock. It is imperative to mention that while calculating the CGE, both the heating value of the gas produced and feedstock have to be in the same units i.e. either LHV or higher heating value (HHV). In this study the LHV of the biomass and product gas is used in calculating CGE. Carbon conversion efficiency (CCE) and hydrogen conversion efficiency (HCE) were calculated by dividing the carbon and hydrogen in the dry product gas by the amount of carbon and hydrogen fed into the gasifier. To assess the gasification process performance CGE, CCE and HCE are determined according to following equations (Basu 2010).

\[
CGE(\eta_{CG}) = \left( \frac{LHV_g \times m_g}{LHV_f \times m_f} \right) \times 100
\]  
(3.9)

\[
CCE(\eta_{CC}) = \left( \frac{C_{o,dry \text{gas}}}{C_{i,def}} \right) \times 100
\]  
(3.10)
\[ HCE(\eta_{hc}) = \left( \frac{H_{o,dry,gas}}{H_{i,daf}} \right) \times 100 \] (3.11)

Where, \( \dot{m}_s \) is the feed rate of solid fuel, \( \dot{m}_g \) is product gas flow rate in kg/hr, \( LHV_g \) and \( LHV_j \) are calorific values of produced gas and solid fuel respectively. \( C_i, C_o, H_i \) and \( H_o \), where the subscript \( i \) represents the feeding rate of carbon and hydrogen on a daf basis and \( o \) the flow rate of carbon and hydrogen in the product gas. The superficial fluidisation velocity of the product gas (at the reactor temperature) presented in Table 3.3 is calculated according to the formula given by Siedlecki et al. (2011).

\[
U_{fl} = \left( \frac{\text{actual volumetric feed gas flow rate}}{\text{cross-sectional area of the bed}} \right) = \left( \frac{\dot{Q}_{gas} \times T_{process} \times P_{atm}}{A_{bed} \times 273.15 \times P_{process,abs}} \right) \] (3.12)

where, \( U_{fl} \) is superficial fluidisation velocity in m/s, \( \dot{Q}_{gas} \) is product gas flow rate in Nm\(^3\)/s, \( T_{process} \) is the gasifier temperature in the bed in Kelvin, \( P_{atm} \) is atmospheric pressure in bar, \( A_{bed} \) is cross section area of the bed m\(^2\), \( P_{process,abs} \) is an absolute pressure in the bed in bar.
### Table 3.3: Summary of experimental tests

<table>
<thead>
<tr>
<th>Test number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock type</td>
<td>Poultry litter</td>
<td>PL with limestone</td>
<td>PL with lime</td>
<td>PL with lime</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poultry litter feed rate, kg/hr (a.r.)</td>
<td>0.66</td>
<td>0.49</td>
<td>0.61</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limestone (kg/hr)</td>
<td>0.0</td>
<td>0.04</td>
<td>0.05</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Throughput (kg/hr-m²)</td>
<td>155</td>
<td>113</td>
<td>141</td>
<td>132</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature of gasifier, ºC</td>
<td>700</td>
<td>700</td>
<td>750</td>
<td>800</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature of gasifying medium, ºC</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam to biomass ratio, SBR (-)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equivalence ratio, ER (-)</td>
<td>0.18</td>
<td>0.22</td>
<td>0.30</td>
<td>0.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air flow rate, (dm³/min)</td>
<td>6</td>
<td>7.2</td>
<td>10</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen flow rate, (dm³/min)</td>
<td>6</td>
<td>4.8</td>
<td>2</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam flow rate, kg/hr</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.125</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluidising medium flow rate, dm³/min</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>13.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluidisation velocity, m/s (20 ºC)</td>
<td>0.098</td>
<td>0.097</td>
<td>0.094</td>
<td>0.095</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Superficial gas velocity based on the total product gas yield, m/s (Tg)</td>
<td>0.21</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3 Results and discussion

Figure 3.2 shows the concentration of the major gas components and temperature profiles in the bed and freeboard over the run time of a typical experiment. The temperature and gas composition profiles had effectively stabilised after 10 min. However, to ensure steady state had been reached, an additional 40 minutes were allowed before sampling the product gas for tars and other gas measurement.

![Figure 3.2: Bed and freeboard temperature and gas composition evolution in a poultry litter test at 700 °C and ER= 0.18: (a) temperature profile (b) product gas composition](image)

Table 3.4 presents the main results of the experimental campaign. It should be noted that the gas compositions presented in Table 3.4 are on an as measured basis whereas gas compositions and yields reported in figures are presented on a N$_2$ free basis. At higher ER, N$_2$ flow rate was reduced while increasing the air flow rate to keep initial
fluidisation velocity of the bed the same. Consequently, a decrease in $N_2$ concentration was evident in the product gas with an increase in ER. The mean value of the concentration of individual product gas compounds and the total tar measured were reported. The corresponding standard deviations (SD) were calculated to be less than 3%, therefore other calculations such as LHV, CGE, CCE, HCE and gas yield were performed on an averaged basis of product gas compositions. SD of the gas yields are reported in figures.

3.3.1 Thermogravimetric analysis (TGA) of poultry ash

The ash content in poultry litter is higher than the proposed limit of ashes for feedstock considered suitable to be used in fluidised bed gasifier (Arena 2012). To understand the effect of ash softening temperature in this study, TGA analysis was performed. The result of TGA analysis of a poultry litter ash sample is shown in Figure 3.3.

Figure 3.3: Weight loss and heat flow curve of poultry litter ash using TGA at constant heating rate (10 °C/min) in nitrogen atmosphere (100 ml/min)
The reported result is mean of three TGA runs which present the percentage weight loss with respect to temperature. It can be seen from Figure 3.3 that the total weight loss is about 8%. It is evident that the weight loss occurs at around 650 ºC which might be due to calcination of CaCO$_3$ as farmers use this supplement as a food additive to improve the egg shell quality (Giuntoli et al. 2009). Blamey et al. (2010) have proposed that under atmospheric conditions degradation of CaCO$_3$ is possible in this temperature range provided the concentration of CO$_2$ in gas phase is low (e.g. 3.5% at 700 ºC). The TGA analysis was performed under a nitrogen atmosphere which could provide a compatible condition for CaCO$_3$ degradation. TGA analysis was performed to check the softening temperature of the poultry litter ash. It indicates that the chances of ash sintering are highly likely at higher temperature. To avoid ash sintering/defluidisation problems, limestone was added to the poultry litter.
<table>
<thead>
<tr>
<th>Test number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>7.34</td>
<td>11.60</td>
<td>12.04</td>
<td>17.58</td>
<td>5.78</td>
<td>5.16</td>
<td>2.44</td>
<td>6.62</td>
<td>10.29</td>
<td>9.48</td>
<td>9.00</td>
<td>14.98</td>
<td>10.49</td>
<td>8.95</td>
</tr>
<tr>
<td>Ar</td>
<td>0.41</td>
<td>0.42</td>
<td>0.55</td>
<td>0.53</td>
<td>0.47</td>
<td>0.57</td>
<td>0.79</td>
<td>0.78</td>
<td>0.42</td>
<td>0.53</td>
<td>0.61</td>
<td>0.53</td>
<td>0.40</td>
<td>0.51</td>
</tr>
<tr>
<td>N₂</td>
<td>69.00</td>
<td>58.53</td>
<td>53.88</td>
<td>46.50</td>
<td>69.39</td>
<td>68.13</td>
<td>69.87</td>
<td>64.22</td>
<td>60.66</td>
<td>60.36</td>
<td>58.83</td>
<td>52.10</td>
<td>60.27</td>
<td>62.35</td>
</tr>
<tr>
<td>CO₂</td>
<td>5.41</td>
<td>8.52</td>
<td>9.69</td>
<td>9.35</td>
<td>5.06</td>
<td>5.01</td>
<td>4.23</td>
<td>4.38</td>
<td>8.40</td>
<td>8.32</td>
<td>8.08</td>
<td>7.57</td>
<td>9.14</td>
<td>7.50</td>
</tr>
<tr>
<td>CO</td>
<td>11.36</td>
<td>13.22</td>
<td>15.60</td>
<td>17.74</td>
<td>12.29</td>
<td>13.74</td>
<td>15.03</td>
<td>16.08</td>
<td>12.69</td>
<td>13.68</td>
<td>15.25</td>
<td>16.92</td>
<td>12.78</td>
<td>14.15</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.89</td>
<td>1.14</td>
<td>1.11</td>
<td>1.10</td>
<td>0.91</td>
<td>0.82</td>
<td>0.81</td>
<td>0.86</td>
<td>1.42</td>
<td>1.30</td>
<td>1.26</td>
<td>1.26</td>
<td>1.40</td>
<td>1.27</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.19</td>
<td>0.29</td>
<td>0.29</td>
<td>0.32</td>
<td>0.18</td>
<td>0.17</td>
<td>0.14</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td>0.18</td>
<td>0.19</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>0.017</td>
<td>0.019</td>
<td>0.016</td>
<td>0.013</td>
<td>0.018</td>
<td>0.017</td>
<td>0.019</td>
<td>0.017</td>
<td>0.025</td>
<td>0.028</td>
<td>0.020</td>
<td>0.017</td>
<td>0.023</td>
<td>0.015</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.046</td>
<td>0.062</td>
<td>0.057</td>
<td>0.091</td>
<td>0.042</td>
<td>0.051</td>
<td>0.026</td>
<td>0.070</td>
<td>0.023</td>
<td>0.030</td>
<td>0.028</td>
<td>0.042</td>
<td>0.019</td>
<td>0.023</td>
</tr>
<tr>
<td>COS</td>
<td>0.003</td>
<td>0.004</td>
<td>0.003</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>C₅H₈</td>
<td>0.092</td>
<td>0.115</td>
<td>0.112</td>
<td>0.112</td>
<td>0.097</td>
<td>0.083</td>
<td>0.078</td>
<td>0.086</td>
<td>0.155</td>
<td>0.133</td>
<td>0.13</td>
<td>0.121</td>
<td>0.166</td>
<td>0.156</td>
</tr>
<tr>
<td>C₇H₈</td>
<td>0.041</td>
<td>0.054</td>
<td>0.055</td>
<td>0.055</td>
<td>0.040</td>
<td>0.038</td>
<td>0.034</td>
<td>0.038</td>
<td>0.048</td>
<td>0.046</td>
<td>0.050</td>
<td>0.047</td>
<td>0.033</td>
<td>0.037</td>
</tr>
<tr>
<td>NH₃ (ppmv in dry gas)</td>
<td>-</td>
<td>-</td>
<td>39552</td>
<td>-</td>
<td>-</td>
<td>29540</td>
<td>-</td>
<td>-</td>
<td>-27031</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Moisture in the product gas (%vol)</td>
<td>-</td>
<td>-</td>
<td>19.6</td>
<td>-</td>
<td>-</td>
<td>19.5</td>
<td>-</td>
<td>-</td>
<td>-16.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HCl (mg/m³, dry gas)</td>
<td>-</td>
<td>-</td>
<td>20.9</td>
<td>-</td>
<td>-</td>
<td>88.5</td>
<td>-</td>
<td>-</td>
<td>-14.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total GC detectable tar (g/kgₐdaf poultry litter)</td>
<td>4.40</td>
<td>6.25</td>
<td>7.22</td>
<td>8.59</td>
<td>6.36</td>
<td>5.85</td>
<td>3.72</td>
<td>3.97</td>
<td>6.42</td>
<td>5.19</td>
<td>3.89</td>
<td>2.89</td>
<td>5.66</td>
<td>3.25</td>
</tr>
<tr>
<td>Gas yield (m³/kgₐdaf poultry litter N₂ free)</td>
<td>0.75</td>
<td>1.09</td>
<td>1.15</td>
<td>1.36</td>
<td>1.12</td>
<td>1.14</td>
<td>1.03</td>
<td>1.13</td>
<td>1.15</td>
<td>1.10</td>
<td>1.12</td>
<td>1.25</td>
<td>1.39</td>
<td>1.24</td>
</tr>
<tr>
<td>LHV (MJ/Nm³, dry gas)</td>
<td>3.11</td>
<td>4.53</td>
<td>4.72</td>
<td>5.36</td>
<td>2.91</td>
<td>2.69</td>
<td>2.17</td>
<td>2.87</td>
<td>4.55</td>
<td>4.24</td>
<td>4.12</td>
<td>4.74</td>
<td>4.52</td>
<td>3.95</td>
</tr>
<tr>
<td>C entrainment in the cyclone (g/kgₐdaf poultry litter)</td>
<td>53.17</td>
<td>78.51</td>
<td>98.27</td>
<td>104.22</td>
<td>58.51</td>
<td>77.25</td>
<td>47.28</td>
<td>63.26</td>
<td>72.11</td>
<td>76.47</td>
<td>70.51</td>
<td>70.51</td>
<td>33.43</td>
<td>33.43</td>
</tr>
<tr>
<td>Carbon conversion efficiency (%)</td>
<td>49.1</td>
<td>72.5</td>
<td>81.8</td>
<td>88.0</td>
<td>70.8</td>
<td>73.1</td>
<td>70.0</td>
<td>71.8</td>
<td>78.2</td>
<td>76.4</td>
<td>79.0</td>
<td>80.2</td>
<td>89.2</td>
<td>81.0</td>
</tr>
<tr>
<td>Cold gas efficiency (%)</td>
<td>42.3</td>
<td>69.7</td>
<td>72.5</td>
<td>83.6</td>
<td>55.2</td>
<td>43.0</td>
<td>33.0</td>
<td>48.4</td>
<td>75.6</td>
<td>68.0</td>
<td>65.2</td>
<td>73.5</td>
<td>84.6</td>
<td>69.3</td>
</tr>
<tr>
<td>Hydrogen conversion efficiency (%)</td>
<td>27.3</td>
<td>40.2</td>
<td>41.0</td>
<td>39.8</td>
<td>32.3</td>
<td>29.2</td>
<td>20.7</td>
<td>24.1</td>
<td>41.1</td>
<td>37.6</td>
<td>36.3</td>
<td>36.7</td>
<td>42.9</td>
<td>37.8</td>
</tr>
</tbody>
</table>
3.3.2 Effect of limestone addition

This section describes the product gas composition and performance of the poultry litter gasification process without and with limestone addition at 700 °C and an ER 0.30 (experiments numbers 3 and 5). Limestone was one of the first additives used in gasifiers to improve the gasification in terms of tar reduction (Devi et al. 2003). However, since the effect of limestone addition on biomass gasification with air at atmospheric pressure is not well documented, an attempt was made to understand how limestone might affect the gasification performance for the poultry litter used in this study. The total tar content decreased by 12% without having much influence on product gas yield (Table 3.4). A similar conclusion has been drawn by Gómez-Barea et al. (2006) while gasifying orujillo and meat and bone meal waste in an air-blown bubbling fluidised bed at atmospheric pressure using lime as a bed material (or blend with ofite).

![Figure 3.4: Effect of limestone on the composition of the product gas and gasifier performance (gas yields are on a N₂ free basis)](image_url)
Limestone addition proportionally reduced the poultry litter feed rate (8% by weight) and also changed gas composition significantly with a consequent effect on its heating value (calculated on the basis of gas composition without the contribution of tar content) and CGE. From Figure 3.4, it can be seen that limestone addition has a significant influence on product gas composition. The concentration of the major product gas components fell except for C2H2 and C6H6 when poultry litter was blended with limestone. Moreover, reported errors are well within the acceptable range (∼3%). The total gas yield remained stable (between 1.15 and 1.12 Nm³/kg_daf) while the LHV dropped from 4.72 to 2.91 MJ/Nm³. As a consequence, a significant decrease in CGE is observed from 72.5% to 55.2%. Limestone addition does not have as significant an effect on CCE as it does on the CGE and LHV, which indicates that its addition might have reduced the char elutriation rate in the cyclone. The measurements presented in Table 3.4 confirmed this by inspection of the calculated elutriation rate of carbon/char. About 10.69% (58.51 g/kg_daf) of total carbon fed into the gasifier was collected from the cyclone fines in the case of blended poultry litter and limestone whereas without limestone blending the percentage of carbon recovered in cyclone fines is 17.96% (98.27 g/kg_daf).

In general, the bed material acts as a reservoir of generated ash and its elements (especially the less volatile elements such as Si, Al, Ca, Mg and P). The collected elutriated char and ash fines form the cyclones were analysed and the results revealed that, without limestone about 58% of total Cl and 44% of total S end up in the cyclone fines whereas the corresponding values when limestone was added to the feed were 3 and 53% respectively at a temperature of 700 ºC and an ER ≈0.30 (experiment numbers 3 and 5). As shown in Table 3.4, the concentration of H2S and COS in the product gas decreases with limestone addition suggesting that it might have favoured the S and Cl recoveries in the bed and/or cyclone fines, similar results have been reported elsewhere (Llorente et al. 2006; Piotrowska et al. 2010). However, in contrast to the findings of other researcher, HCl content in the gas phase increases with limestone addition at 700 ºC and an ER of 0.35. Nevertheless, at elevated temperature (750 ºC and an ER of 0.28) the results are in line with findings reported (Llorente et al. 2006; Piotrowska et al. 2010). The fate of N, S and Cl bound with the feedstock is presented in the Section 3.3.6 (Table 3.6).
While gasifying poultry litter without any limestone addition, the bed agglomeration could be seen at a gasifier temperature of 750 °C. Therefore, as a counter measure to avoid defluidisation and agglomeration issues at higher temperature in a fluidised bed gasifier with feedstock’s of higher ash content, limestone addition has become a necessity. Further, discussion will focus on comparing the influence of different process parameters on poultry litter gasification blended with limestone.

### 3.3.3 Effect of temperature on gasification performance

The effect of reactor temperature on the gasification performance of poultry litter blended with limestone was investigated over different temperature (700 ≤Tg≤ 800 °C) and an ER of ≈ 0.30 (experiments number 5, 10 and 14). The variables analysed include gas composition, product gas yield (N₂ free basis), heating value, tar yield, CCE, CGE and HCE and the results are shown in Figure 3.5 & Figure 3.6. It is evident from Figure 3.5 that the gasifier temperature has a significant influence on the product gas composition since, higher temperature favours endothermic reactions i.e. char gasification, water gas shift reaction, cracking of higher hydrocarbons and tars (Kumar et al. 2009). The increase in CO and H₂ production is due to the improved Boudouard reaction and water gas reactions, as well as tar cracking and reforming reactions. The concentrations of CH₄, C₂H₄ and benzene shows similar trend and increases with temperature. On the other hand, gasification temperature has almost no effect on the yields of C₂H₂, C₇H₈ over the tested range of temperature while, the production of C₂H₆ and H₂S decreased with temperature. The elevated temperature favours thermal cracking and steam reforming reactions, explaining the observed decreased in C₂H₆ concentration in this study. A similar conclusion was drawn by Turn et al. (1998) in the temperature range 750 to 800 °C.

Sulphur concentration in the product gas depends on sulphur content in the fuel and the gasifier temperature. Mass balance analysis in Section 3.3.6 shows that approximately 45-70% of the sulphur is bound to the cyclone fines. The sulphur in the gas phase is present in the form of H₂S and COS which accounts for about 8% of total sulphur fed into the gasifier at 800 °C and an ER of 0.25. The concentration of H₂S decreases with an increase in the gasification temperature whereas the
concentration of COS remains fairly constant throughout the temperatures studied (Figure 3.5). It is considered that the balancer of the sulphur remains in the bed.

**Figure 3.5:** Effect of temperature on the composition of the product gas at ER ≈ 0.30 (a) yield of major gas species (b) yield of light hydrocarbon gas species in the product gas

Normally, the HCl concentration in the gas phase increases with temperature due to chlorinated tar cracking at higher temperature (van Paasen *et al.* 2006). However, it is observed from Table 3.4 that the concentration of HCl in the gas phase decreased with increasing gasifier temperature from 700 to 750 °C. Since poultry litter ash has higher concentration of K, P and Ca (due to the addition of limestone), the probability of forming potassium chloride (KCl), phosphorous chloride (PCl₃) and calcium chloride (CaCl₂) compounds are highly likely and consequently most of the Cl is bounded in the bottom ash and/or cyclone fines. Normally, KCl condenses on cold surfaces whereas fines are collected from the hot cyclones therefore part of the Cl cannot be measured. The amount of Cl recovered from the cyclone fines increases
from 2.94 to 25% with increase in temperature from 700 to 750 °C. Detailed analysis of mass closure is presented in Section 3.3.6 (Table 3.5) which will provide a better insight into the fate of the S, Cl and N bound to the feedstock’s for experiments number 3, 6 and 10.

The high concentration of NH$_3$ in the product gas indicates that NH$_3$ is the main nitrogenous compound formed during the gasification of poultry litter (Table 3.4). NH$_3$ concentration further correlated to the nitrogen content in the feedstock. The measured NH$_3$ decreased with an increase in the temperature of gasification which is in-line with investigations performed on a lab-scale bubbling fluidised bed gasifier by Zhou et al. (2000). Furthermore, it confirms the theory proposed by Zhou et al. (2000) that at higher temperature the conversion of NH$_3$ to N$_2$ ($3H_2 + N_2 \leftrightarrow 2NH_3$) is the dominant thermochemical process which consequently decides the fate of fuel bound nitrogen in a fluidised bed gasifier. It is worth mentioning that the amount of chlorine and sulphur in the product gas are well below the required maximum allowable concentration limit of the fuel to be used in a boiler or gas engine (van Paasen et al. 2006).

![Figure 3.6](image)

**Figure 3.6:** Effect of temperature on (a) LHV, product gas (N$_2$ free) and total tar yields (b) the performance of gasification at ER≈0.30 (experiments number 5, 10 and 14)

Figure 3.6 clearly shows that a higher temperature increases the product gas yield (from 1.12 to 1.24 Nm$^3$/kgdaf) and LHV (from 2.91 to 4.24 MJ/Nm$^3$) while decreasing total tar content (from 7.22 to 6.26 g/kgdaf). This is attributed to the fact
that increasing the temperature improves char and tar cracking (into light hydrocarbon gases and secondary tar species). However, at higher temperature in the gasifier, CO oxidation and the water gas shift reaction are dominating which increases the yield of CO2 and consequently lowered the LHV of the product gas. The influence of temperature on the gasifier’s performance is reported in Figure 3.6b. It is apparent that an increase in temperature improved the CCE over the range of temperatures investigated. Similarly, an increase in temperature has a significant effect on CGE which increased from 55.2% at 700 0C to more than 69.3% at 800 0C under the same operating conditions (ER =0.30). The main reason for a carbon conversion in the range of 80% could be due to unconverted carbon from cyclone, which accounted for 6-14% of the total carbon fed into the gasifier. The hydrogen conversion into the dry product gas is relatively low compared to the carbon conversion; the reason could be due to loss of hydrogen in moisture and tar compounds. In the temperature range from 700-750 ºC, HCE was observed to increase by 5%. However, higher gasification temperature does not show any significant effect on hydrogen conversion. The moisture content in the product gas was measured on a daily basis, which decreased with gasification temperature (Table 3.4).

### 3.3.4 Effect of ER on poultry litter gasification

The profiles of the product gas composition, gas yield, LHV, CGE, CCE, HCE and tar yield from poultry litter gasification under different combination of ER and temperature are presented in Figure 3.7. An increase in ER results in a reduction of H2 and CO contents in the product gas due to increased amount of O2 available in the reactor for reaction with the volatiles and char combustion which results in increase of CO2 production and degrades the quality of product gas.

It is important to note that the ER does not have much influence on CH4. Regarding light hydrocarbons, Figure 3.7b shows that the concentration of ethane, benzene and toluene fell slightly with ER. At the same time, acetylene and H2S do not show any consistent trend over the range of temperatures and ER studied. At lower
temperatures, acetylene concentration was fairly constant but showed declining behaviour with ER at elevated temperatures.

**Figure 3.7**: Effects of ER on the composition of product gas and gasifier performance (gas yields are on an N₂ free basis)

Since, the product gas yield is reported on an N₂ and dry and ash free basis, the ER does not have a noticeable effect on product gas yields as evident from the Figure 3.7c. Moreover, LHV decreases slightly due to dilution of the product gas with nitrogen and diminishing combustible gas contents (calculation of LHV was done on an as measured basis). In contrast to the product gas yield, the ER does impact total tar yield and a significant drop from 6.36 to 2.93 g/kg_{daf} is observed at 750 °C due to the oxidation reaction of aromatics (Hanping et al. 2008). Moreover, an increase in ER does not benefit in terms of the chemical energy of the product gas except for the tar reduction during the gasification process.
The maximum product gas yield, LHV, CCE and CGE is achieved at an ER of 0.25 when the gasifier was operating at 800 °C. This process condition (refer to Figure 3.7) yielded a product gas with a chemical composition (on dry basis) of H₂: 10.78%, CO: 9.38%, CH₄: 2.61 and CO₂: 13.13 and LHV of 4.52 MJ/Nm³. The carbon entrainment at this operating condition was the lowest (5.2% of the total carbon fed into the gasifier) amongst all other conditions and resulted in the highest CGE of 89.2%.

In line with the findings of several other reports in the scientific literature, it is found that increasing the ER above 0.25 produces a low quality product gas due to dilution with N₂ and other non-combustible gas components. CGE decreased with ER due to the lower chemical energy of the product gas. The reason is that at higher ERs, more air is fed to the gasifier promoting the char/carbon combustion reactions (producing more CO₂ and H₂O, lowering the heating value of the product gas) but resulting in higher carbon conversion efficiency. HCE on the other hand decreased with ER, this could be due to the dominant combustion reactions (char combustion and oxidation of H₂) promoting the moisture yield in the product gas. As outlined in Gómez-Barea et al. (2013) selection of the optimum condition of ER and tar evolution can be achieved once the product gas application is defined. For example, the gasifier has to be operated below an ER of 0.25 when the aim is having higher heating value of the product gas. On the other hand, if product gas is to be used in combustion engines where low tar content is mandatory, the gasifier has to be operated at high ER, which will reduce the tar content.

In conclusion, it is not recommended to have too low or too high ER in biomass/waste gasification processes. However, the optimum operating condition of ER totally depends on other process conditions and potential application of the product gas. Narvaez et al. (1996) proposed an optimum operating range of ER of 0.18<ER<0.45 in the gasifier. The research findings of this study proposed a narrow and more accurate condition of the ER of 0.25 to optimise the performance of poultry litter gasification.
3.3.5 Effect of steam injection

The influence of steam to biomass ratio (SBR) on the product gas yield is investigated at 700 and 750 °C. Steam gasification experiments are performed to optimise the hydrogen production while increasing the CCE. It can be seen that steam injection improves the gas yield and LHV of dry gas while it decreases the tar yield. The steam injection increases the product gas yield because steam injection favours tar steam reforming and the water gas shift reaction. Figure 3.8 shows that steam injection has a significant influence on hydrogen production. The addition of steam resulted in an increase of 53% in hydrogen production (0.26 Nm³/kg daf vs 0.41 Nm³/kg daf) when compared with no steam injection at ER of 0.28 and temperature of 750 °C. It is found that H₂ and CO₂ concentration increases with steam injection while CH₄ and CO decreased. Similar conclusions have been drawn by varying the SBR (Wang and Kinoshita 1992). It confirms that the water gas shift reaction plays a dominant role to improve the hydrogen production. In contrast, it does not have much influence on the other hydrocarbon concentrations. At 700 °C with SBR of 0.33 and 750 °C with SBR of 0.26, the total tar content decreased during the process, from 5.85 to 3.97 and 5.19 to 2.89 g/kg daf poultry litter respectively. A significant drop in total tar concentration is observed in Figure 3.8c which confirms that steam tar reforming reactions are enhanced with the steam injection in the gasifier even at so relatively low temperature level, most probably due to the catalysed action of lime in the bed.
Figure 3.8: Effects of SBR on the composition of product gas and gasifier performance

Figure 3.8 shows that, in spite rising the H\textsubscript{2} yield in the gas, SBR does not have influence much the LHV as compared to other parameters analysed, probably because the increase in H\textsubscript{2} is outweighed by the decrease in CO and CH\textsubscript{4}. However, steam injection improves the chemical energy content of the product gas, resulting in an increase in CGE and CCE of around 5%. It can be seen in Figure 3.8d that HCE is significantly lower at 700 °C when steam is added (as compared to the case without steam), indicating that the use of steam at low temperature is not consumed and so it leads to a decrease in HCE. Although it is evident that steam injection improves the hydrogen production, it decreases the yield of higher hydrocarbons such as C\textsubscript{2}H\textsubscript{6}, C\textsubscript{6}H\textsubscript{6} and C\textsubscript{7}H\textsubscript{8}. Considering the energy required to product steam, it might not be economically feasible to operate at high SBR. Most importantly, if the gasification process is conducted in autothermal mode, as it will most probably be in small to medium plants, steam injection at constant ER reduced the temperature and therefore, it could lead to a reduction of gas quality and higher tar yield, lowering the
process efficiency. It may be concluded that SBR has significant effects on hydrogen production, reforming the tars, CCE and CGE. It can be recommended that steam injection is desirable for the production of hydrogen rich product gas.

### 3.3.6 Mass balance analysis and fate of N, S and Cl of the feed (poultry litter)

The mass balance calculations for the main elemental species are presented in Table 3.5. The input stream comprises of feed, air, steam and moisture content in the feed whereas the outlet stream consists of dry gas, unconverted char collected from the bed and cyclone fines, NH₃, HCl and moisture present in the gas. The elemental compositions of input and output streams are taken into account for calculating the mass closure while applying the law of conservation of mass. Dry air fed to the gasifier consists of oxygen and nitrogen only, with a mass ratio of 23.2-76.8. The following assumptions are made for calculating the mass balance (i) elutriation of bed material is negligible (ii) \[ \sum_{j=1}^{n} M_i = \sum_{j=1}^{n} M_o \] where, \( i \) and \( j \) represent the input and output constituents of each elemental (iii) added limestone is bound with the bottom ash (iv) accumulation rate of ash and char in the bed is averaged over the day.
Table 3.5: Mass balance of gasification tests

<table>
<thead>
<tr>
<th>Elements</th>
<th>Poultry litter without limestone at 700 °C and ER= 0.30</th>
<th>Poultry litter with limestone at 700 °C and ER= 0.35</th>
<th>Poultry litter with limestone at 750 °C and ER= 0.28</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Input (kg/hr)</td>
<td>Output (kg/hr)</td>
<td>Rel. Error (%)</td>
</tr>
<tr>
<td>C</td>
<td>0.234</td>
<td>0.224</td>
<td>-4.16</td>
</tr>
<tr>
<td>H</td>
<td>0.044</td>
<td>0.043</td>
<td>-3.04</td>
</tr>
<tr>
<td>O</td>
<td>0.433</td>
<td>0.436</td>
<td>0.81</td>
</tr>
<tr>
<td>N</td>
<td>0.734</td>
<td>0.680</td>
<td>-7.34</td>
</tr>
<tr>
<td>S</td>
<td>0.004</td>
<td>0.003</td>
<td>-15.30</td>
</tr>
<tr>
<td>Cl</td>
<td>0.002</td>
<td>0.001</td>
<td>-37.03</td>
</tr>
<tr>
<td>Ash</td>
<td>0.091</td>
<td>0.089</td>
<td>-2.76</td>
</tr>
</tbody>
</table>

where,

$$ relative\ error = \left( \frac{input - output}{input} \right) \times 100\% $$  \hspace{1cm} (3.5)$$

Table 3.5 shows that the relative errors are in the range of ±15% (except for Cl), which are within an acceptable limit. The amount of Cl present in the bottom ash was not measured, explaining the poor mass balance closure obtained for Cl. Table 3.5 indicates that Cl mass closure without limestone has a lower relative error compared to when limestone is added. The presence of high amounts of mineral elements such as K, P, Na in poultry litter and Ca from the limestone might have led to a high retention of S and Cl in the ash in the bed and elutriated cyclone fines which is in agreement with previous finding (Meng et al. 2009). The possible reasons for the observed discrepancies in relative errors might be (1) measurement errors (2) the error associated with measurement might have accumulated and exaggerated after several calculations made. Despite the fact that the uncertainties involved with fluidised bed gasifier processes, in this study efforts are made to close the mass
balance to maximise the accuracy of the results. Lately, an attempt has been made for addressing uncertainties in the gasification process. It was concluded that by incorporation of the uncertainties involved with the process can be helpful in the study of different alternative energy pathways (Pan and Pandey 2016).

An attempt was made to explain the fate of N, S and Cl from the poultry litter based on measurements. Table 3.6 illustrates the detailed analysis of the measurements. It can be seen from Table 3.6 that without limestone, major fraction of Cl is measured in cyclone fines (57.6%) whereas 4.5 and 0.57% are in the bed ash and gas phase respectively. Moreover, about 37% is still missing; the reason could be that Cl was also present in the form of KCl which condenses on the cold surfaces. The percentage Cl increased from 0.87 to 5.05% in the vapour phase with limestone addition but a significant change in Cl percentage is observed in the cyclone fines at ER=0.35 and 700 °C. A similar trend is observed in case of S content in the gas phase at lower temperature. It is interesting to see that most of the nitrogen associated with feedstock is converted into ammonia (NH₃). Furthermore, the research findings revealed that NH₃ formation decreased with an increase in gasifier temperature in agreement with literature (Zhou et al. 2000). In conclusion, limestone addition has shown a positive influence on reduction of S and Cl content in the gas phase when the gasifier was running at relatively high temperature (>750 °C). Table 3.6 indicates that Cl is mostly bound to bottom ash whereas a large portion of S is collected from the cyclone fines when poultry litter was blended with limestone.
### Table 3.6: Fate of nitrogen, sulphur and chlorine from the feedstock

<table>
<thead>
<tr>
<th>Elements</th>
<th>Gas</th>
<th>Cyclone</th>
<th>Bed</th>
<th>Gas</th>
<th>Cyclone</th>
<th>Bed</th>
<th>Gas</th>
<th>Cyclone</th>
<th>Bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>100</td>
<td>0.87</td>
<td>57.66</td>
<td>4.44</td>
<td>5.05</td>
<td>4.71</td>
<td>*</td>
<td>0.67</td>
<td>25.10</td>
</tr>
<tr>
<td>S</td>
<td>100</td>
<td>21.56</td>
<td>44.42</td>
<td>18.71</td>
<td>26.55</td>
<td>77.84</td>
<td>10.01</td>
<td>12.22</td>
<td>71.26</td>
</tr>
<tr>
<td>N^^</td>
<td>100</td>
<td>101.12</td>
<td>0.34</td>
<td>0.10</td>
<td>94.94</td>
<td>7.45</td>
<td>0.05</td>
<td>75.70</td>
<td>7.50</td>
</tr>
</tbody>
</table>

\^\^Nitrogen associated with poultry litter, *not measured

### 3.4 Conclusion

Despite having high ash content, poultry litter blended with limestone was successfully gasified in a bubbling fluidised bed without agglomeration problems. Therefore, limestone addition (0.08 kg limestone/kg poultry litter in the present work) is recommended for the smooth running of a gasifier with reasonable efficiency when poultry litter is gasified. Total tar and Cl content in the gas phase were relatively low compared to other biomass and wastes. In contrast, higher N\(\text{2}\) content in the feed resulted in high concentration of NH\(\text{3}\) in the gas. The effects of several process parameters on product gas production were experimentally investigated. This study revealed that gasifier temperature is the most important parameter with respect to gas production and heating value of the gas. The product gas had an average heating value of 4.5 MJ/Nm\(^3\), which can be used, properly cleaned, in gas engines or boilers. Steam injection in the gasification process slightly increased product gas yield at 750 °C resulting in a CGE of 73.5% and generated the lowest tar concentration of 2.89 g/kg\(_{\text{daf}}\). Although, the effect of ER and SBR were relatively small compared to temperature, it did influence hydrogen production. Relatively high C loss was observed due to high gas velocity, which needs to be optimised. In addition, to assess the suitability of using the bottom ash and cyclone fines as a soil amender, leaching test need to be performed.
In summary, taking into account poultry litter as a low quality fuel, the research findings from this study demonstrate its potential as an alternative source of energy available at the farm level for the gasification purposes. It is important to mention that the present experimental work was made in allothermal mode (heat was provided to the gasifier by an external oven and so the ER and SBR was varied at constant temperature). In small to medium scale plants such as those to be found likely in farms, the gasification process will be conducted most probably in autothermal mode and the present results, despite useful, have to be scaled up with caution. In a follow-up paper, the present experimental data will be used to validate a model and to scale-up the results to autothermal industrial units applicable to farms.
3.5 References


4 Model development and application to the poultry litter gasification

Abstract

Poultry litter gasification is not very well known and modelling of the process is the first step for the technical assessment of a potential interesting technology. In the present study, a model is developed to simulate the gasification process under the conditions relevant for poultry litter. The model predicts steady state operation of fluidised bed gasification and it is implemented in Aspen Plus where both existing reactor models provided by Aspen Plus are used together with FORTRAN codes to take into account the non-equilibrium factors governing the process in real gasifiers. Empirical correlations obtained in a lab scale bubbling fluidised bed gasifier fed with poultry litter are introduced into the model to improve its prediction capability.

Presented in:

4.1 Introduction

Animal manure is a carbon and nutrient rich material commonly applied on agricultural land as a source of organic fertiliser (Wu et al. 2011). Manure is potentially available for processing among the EU member states is an estimated 1.4 billion tonnes of manure where poultry litter accounts for 110 million tonnes (Foged et al. 2011). Organic matter from the animal by-product is easily degraded by bacteria present in the soil due to the high concentration of biochemical oxygen demand (BOD) and nutrients present which are taken up by crops or recycled into the soil (Loehr et al. 1979). By-products from the poultry processing industry are edible tissues, bones, egg shells, feathers and poultry manure. Poultry manure is considered as a by-product from production phase of poultry meat (Ockerman and Hansen 1999). It is recommended that the organic matter should be applied on agriculture land for nutrient (N, P, K) uptake. P and K usually bind with soil but over application of animal manure causes leach out P to the soil and pollute surface waters as well as infiltrating the ground water (Campagnolo et al. 2002).

Although anaerobic digestion has been used for manure storage and treatment, the nutrient rich by-product still needs to be disposed of requiring a long time and a large storage facility (Ro et al. 2009). Thermal processing techniques such as incineration and gasification have been used at different temperature, pressure and oxygen concentrations for extracting energy and nutrients (McKendry 2002). Different manure management scenarios have been assessed with the aim of maximising the energy and nutrient recovery. The authors have concluded that manure mixed with high energy waste or processed manure with high dry matter content can ensure high energy extractive efficiency and reduction in greenhouse gas emissions (Prapasponsa et al. 2009). A novel alternative approach to anaerobic digestion or combustion has been proposed to treat animal by-products (poultry litter) while recovering nutrients and energy using a fluidised bed gasifier (Pandey et al. 2016).

Thermal gasification provides flexibility for the production of heat and power based on a clean biomass derived product gas or synthesis gas. The product gas is a combination of different gases evolved during the gasification process which
involves several chemical reactions. Attempts have been made to gasify animal waste in fixed bed (moving bed) gasifiers. For example, adiabatic fixed bed gasification of dairy biomass using steam and air as gasifying agents was studied by Gordillo and Annamalai (2010). A feasibility analysis of an air-blown gasifier operating at high temperature was conducted for energy production from dairy-farm waste (Young and Pian 2003). The results showed that gasifying the dairy waste available at that particular farm (Upstate New York dairy farm) would generate more than two times the amount of energy required for it to become energy self-sufficient. Research into fixed bed gasification of feedlot manure and poultry litter biomass was conducted by Priyadarsan et al. (2004). Researchers have been trying to gasify dairy waste for energy recovery moreover, detailed information about the effects of operating conditions on product generated by animal manure has not been explored.

The gasification process can be simulated using flowsheet software through thermodynamic or restricted thermodynamic modelling (Doherty et al. 2009; Hannula and Kurkela 2010; Ramzan et al. 2011; Arteaga-Pérez et al. 2014; Liao et al. 2014), semi/detailed kinetic models (Wang and Kinoshita 1993; Corella and Sanz 2005; Abdelouahed et al. 2012) and experimental data from existing plants (Spath et al. 2005; Alamia et al. 2016). Thermodynamic equilibrium models (EM) have been widely used because they are simple to apply and independent of gasifier design. Under practical operating conditions in biomass gasification, they overestimate the yields of \( \text{H}_2 \) and \( \text{CO} \), underestimate the yield of \( \text{CO}_2 \) and predict a gas almost free from \( \text{CH}_4 \), tar and char (Gómez-Barea and Leckner 2010). Another modelling study concluded that steam reforming of \( \text{CH}_4 \) was kinetically limited and unlikely to occur at temperatures below 1000 °C (Dupont et al. 2007). Despite these limitations, EMs are widely used for preliminary estimation of gas composition in a process flowsheet like ASPEN, HYSIS, Ipse etc. A quasi-equilibrium temperature model (QET) was introduced in a biomass gasification process by Gnmz (1952) which was further extended by Bacon et al. (1985) by defining quasi-equilibrium temperatures for each independent chemical reaction.

QET models improve the accuracy of the prediction of the gas composition. The essential idea of this approach is to reduce the input amounts of carbon and
hydrogen, fed to the control volume where the equilibrium is calculated (Gumz 1950; Kersten et al. 2002; Jand et al. 2006). The underlying reason for the reduction of the C-H-O input is that, under practical operation conditions in a gasifier, the conversion of tar, light hydrocarbons and char are kinetically limited and so they are controlled by non-equilibrium factors.

The aim of this study is to develop a pseudo EM (PEM) model using experimental data obtained from a bubbling fluidised bed gasifier that operated using poultry litter as a feedstock. For the simplicity of the model, the light hydrocarbons are represented by a single component CH4. Devolatilisation experiments were conducted on a lab-scale bubbling fluidised bed gasifier. The PEM model is divided in three stages and the experimental datasets are used for: (1) devolatilisation of poultry litter, (2) solid-gas reactions i.e. char gasification and (3) gas-phase reactions (WGSR). The deviation from the equilibrium model is taken into account i.e. CH4 formation, unconverted carbon and controlling WGSR equilibrium through temperature.

4.2 Experimental facility and procedure

4.2.1 Test facility

The experiments were carried out on a laboratory scale bubbling fluidised bed gasifier at the University of Seville, Spain. The experimental rig is presented in Figure 4.1. The reactor is made of stainless steel. The reactor consists of a preheating zone, bed zone (200 mm high and 51 mm internal diameter (ID) and a freeboard zone (250 mm high and an ID of 82 mm). An electric heater of 10 kW capacity with two independent heating section one for the bed zone and another for the freeboard is installed. It is equipped with four thermocouples and two PID controllers for controlling the temperature and observing the pressure fluctuations in both zones. The flow rate of N2 is controlled by a mass flow controller and air is fed into the reactor by the means of a rotameter. The flow rate of water during the gasification test was adjusted by a peristaltic pump that was calibrated before the test. Steam was generated by a steady flow of water. The product gases pass through a cyclone, a condenser where elutriated fine particles are captured as well as steam condensation.
and tar removal to protect gas analyser. The clean product gas is then analysed by an on-line Siemens gas analyser using a non-dispersive infrared method for CO, CO$_2$ and CH$_4$ and thermal conductivity and paramagnetic methods for H$_2$ and O$_2$ respectively.

### 4.2.2 Materials

The fuel employed was poultry litter that was collected from a poultry farm in the Netherlands. The ultimate, proximate, biochemical composition, calorific value and ash analysis of poultry litter can be found (Chapter 3, Table 3.1, Table 3.2). Bauxite was used as the bed material with a particle size in the range of 250 – 500 µm. The experimental minimum fluidising velocity and particle density were 0.20 m/s and 3200 kg/m$^3$ respectively.

![Figure 4.1: Experimental setup](image)
4.2.3 Test procedure

The experiments were carried out at a superficial gas velocity of 0.35 m/s and at three different temperatures (700, 800 and 900 ºC). Experiments were performed on a batch of 5 g fuel fed into the reactor by the means of gravity. The experiments were conducted in three stages: (1) devolatilisation, (2) gasification and (3) combustion. The devolatilisation (under N\textsubscript{2} atmosphere) process was monitored until no CO\textsubscript{2}, CO, CH\textsubscript{4} and H\textsubscript{2} were observed in the gas phase. After the devolatilisation test, gasification was carried out with 20% steam (of total flow rate while ensuring the same fluidisation velocity) and 80% nitrogen until no CO\textsubscript{2} and H\textsubscript{2} were detected in the gas phase which lasts 16-24 minutes. Once the gasification process was complete, air was fed into the reactor to burn the remaining char and the CO\textsubscript{2} was measured. Another test was conducted to extract the char from the bed after pyrolysis (without burning the char) for further analysis of the char properties and morphology at different temperature. The pressure inside the reactor during all the tests was close to atmospheric. Each test was conducted three times to ensure the repeatability of the experiments and the results presented here are the average of the three tests. The fluctuations between different experimental runs are reported in terms of a standard deviation.

4.2.4 Data Analysis

The product gas yields (CO\textsubscript{2}, CO, CH\textsubscript{4} and H\textsubscript{2}) are reported on a dry and ash free basis (daf). The amount of char was calculated by means of the carbon present in the form of CO and CO\textsubscript{2} during the gasification and combustion process. The product gas yield was calculated as the accumulated amount of gaseous species detected by the gas analyser throughout the devolatilisation test. It should be noted that condensate yield was not measured during these tests. An error bar was used to represent the deviation in the results. Although poultry litter is a heterogeneous fuel, the repeatability of the experiments was reasonably good apart from a few exceptions.
4.3 Experimental results in supports of PEM

4.3.1 Hydrocarbon yields

The product gas yield during devolatilisation, gasification and combustion are calculated by integrating the concentration of gases over the period of time and are reported as a function of temperature. In the past, researchers have attempted measure the primary product distribution during devolatilisation process (Thurner and Mann 1981). The pyrolysis product gas yield during fast pyrolysis (mainly CO, CO$_2$ and H$_2$) was reported to be 10 to 15% in the temperature range 400 and 550 ºC while primary tar was about 70 percent on mass basis (Freel et al. 1987; Petarca et al. 1997), emphasising that pyrolysis is the first step of the gasification process. However, direct experimental data on pyrolysis product gases are not reported at higher temperature (T >700 ºC). Kersten (2002) has demonstrated that hydrocarbons are formed during gasification by primary tar cracking since at elevated temperature the gas yield during pyrolysis experiments increased up to 80%. Figure 4.2 shows the char and gas yield as a function of temperature at the end of the devolatilisation process. It is evident that gas yield increases (from 0.44 to 0.60 g/g$_{\text{fuel}}$) whereas the char yield declined (from 0.13 to 0.85 g/g$_{\text{fuel}}$) over the tested range of temperature.

![Figure 4.2: Gas and char yields during devolatilisation of poultry litter, u = 0.35 m/s](image)

Figure 4.2: Gas and char yields during devolatilisation of poultry litter, u = 0.35 m/s
The char yield at the end of the devolatilisation test at 700 ºC was about 13%, which is fairly close to the fixed carbon content in the poultry litter on daf basis reported (Chapter 3, Table 3.1, Table 3.2). The char conversion was calculated after gasifying the char under steam and was observed to increase from 25% at 700 ºC to 66% at 800 ºC and 97% at 900 ºC.

The yields of the major product gases (CO$_2$, CO, CH$_4$ and H$_2$) generated during devolatilisation runs along with their standard deviations are presented in Figure 4.3. The results obtained are in good agreement with Gómez-Barea et al. (2010) where the CO$_2$ yield is higher than the CO yield. The variance in the CO and CO$_2$ yield is relatively high compared to CH$_4$ and H$_2$. The main data component to be used in the PEM is CH$_4$ and its variance is below 3%.

**Figure 4.3:** Experimental gas yield of the main components (mass fraction) u = 0.35 m/s
4.3.2 Char conversion

Carbon (fixed carbon or char) that has been formed during devolatilisation process is then converted by reduction (gasification) and oxidation reactions (combustion). Gasification was conducted under steam (20% steam and 80% nitrogen). It can be seen from Figure 4.4a that during the gasification process under steady state conditions that the water gas shift reaction \((CO + H_2O \leftrightarrow CO_2 + H_2)\) (based on the composition that has been measured) indicates the direction of the reaction at the end of the reaction but not necessarily at all the points. The possible reason could be due to presence of a small amount of Cr that might have acted as an initiator resulting in only \(CO_2\) and \(H_2\). Char gasification was quite slow (16-24 minutes depending upon the reactor temperature). Moreover, char combustion was very fast indicating that it is practically dependent on the oxygen available for the char particles.

![Figure 4.4: Gas yield during (a) gasification process (under steam 20% flow rate) and (b) combustion (under air), u= 0.35 m/s](image)

Steam addition at 700 ºC clearly shows that steam gasification did not proceed. However, at higher temperature almost all the char was converted into the gas phase during the gasification tests, leaving a very small amount of \(CO_2\) \((0.001 \text{ g/g fuel, daf})\) during the combustion process. It should be noted that the amount of \(CO_2\) measured at 900 ºC was multiplied by a factor of 10 to make it representative on the graph.
These tests were conducted to propose empirical correlations for computing char, gas yield as well as individual components (CO$_2$, CO, CH$_4$ and H$_2$) during the devolatilisation process. The correlation of char can be represented by a second order polynomial with respect to the temperature of the reactor.

### 4.4 Pseudo-equilibrium model and performance evaluation

To improve the predictive capability of the developed model the yields of permanent gases during devolatilisation process is estimated in a fluidised bed gasifier. In particular, methane formed during devolatilisation and primary conversion of gas is hardly affected by secondary reactions without a catalyst and sufficiently high temperature. Therefore, the amount of methane in the exit stream of product gas from gasifier is roughly that formed during devolatilisation. Secondly, the amount of carbon present in the gas phase is largely dependent on the fixed carbon (char) conversion. The amount of oxygen fed into the gasifier reacts first with volatiles then with char. Since the char gasification reaction is slow and the time available for char conversion is also limited due to attrition and elutriation of chars. Finally, the concentration of CO, CO$_2$, H$_2$ and H$_2$O in the exit product gas is governed by the WGSR rate which rarely achieves equilibrium in the fluidised bed gasifier at lower temperature (i.e. below 900 °C). The QET models are usually applied together with experimental correlations obtained for the specific system under analysis and improve the predictive capability of the model. However, the predictive capability of QET is sensitive to the measurements made on a specific design of reactor which cannot be generalised. A pseudo-equilibrium model (PEM) was proposed by Gómez-Barea *et al.* (2007) and it stressed that dedicated devolatilisation and char gasification experiments can be useful as a rough guideline. Moreover, reliable chemical kinetics would be necessary for refinement and scaling-up of the plant (Gómez-Barea *et al.* 2007).
4.4.1 Methodology of the pseudo-equilibrium gasification model

The following assumptions are included in the model to simply the simulation of gasification.

- Char contains only solid carbon and ash.
- Tar formation is neglected.
- The product gas is a mixture of CO, H\(_2\), CO\(_2\), CH\(_4\) and H\(_2\)O.
- Poultry litter is thermally decomposed into gases, tar and char during the devolatilisation phase.
- Methane formation in the gasification process is obtained from the gas composition after the devolatilisation.
- The amount of carbon left at the end of the devolatilisation process is considered as a char (equivalent to fixed carbon content in the poultry litter).
- The equilibrium model is combined with empirical correlations for methane, carbon conversion and WGSR equilibrium using temperature.
- The fuel bound N, S and Cl react to form NH\(_3\), H\(_2\)S and HCl respectively.
- The steam reforming reaction is not occurring \( CH_4 + H_2O \rightarrow CO + 3H_2 \) .

Figure 4.5 shows the Aspen plus simulation flowsheet for an allothermal (indirect) bubbling fluidised bed gasifier (gasifier temperature is maintained by an external heat source). The description of different types of Aspen Plus unit operation blocks used in the simulation of the gasification processes are given in Table 4.1.
Figure 4.5: Aspen Plus flowsheet model of poultry litter gasifier

Poultry litter and ash are not defined in the Aspen Plus database therefore, the MCINCPSD (mixed, conventional inert solid and non-conventional stream with particle size distribution) was chosen which comprises MIXED (conventional stream), CIPSD (conventional inert solid is used for homogeneous solids that have a defined molecular weight) and NCPSD (non-conventional solid with particle size distribution option). Poultry litter as a received basis fed into the RYield reactor, which converts the non-conventional biomass into conventional elements and are determined by their ultimate and proximate analysis using the calculator block (using the FORTRAN statement). The Peng-Robinson equations of state with Boston-Mathias modification (PR-BM) is selected as the property method for the model. The HCOALGEN and DCOALIGT property model was selected for calculating the biomass enthalpy, specific heat capacity and density based on the ultimate and proximate analyses of poultry litter. Part of the carbon (based on experimental input) was taken out representing the actual carbon conversion using the CHARSEP block. Methane, ammonia, hydrogen sulfide and hydrochloric acid formation takes place in RStoic unit block (NON-EQUI) and put in the final stream of the product gas to avoid steam methane reforming. The CH$_4$, NH$_3$, H$_2$S and HCl are removed from the main fuel stream using the separator block GASSEP. The volatile and other elements using the TOGIBBS stream are fed to the gasifier GASIF. Since the reaction kinetics are not known, a rigorous reactor RGibbs was used to simulate the gasification
process. The working principle of the RGibbs reactor is based on minimising of the total Gibbs energy of the product gas. A mixture of air and steam are used as the gasifying medium. To simulate the experimental conditions, the temperature of gasifying media was set to 160 °C. In addition to the poultry litter, limestone is added to the gasifier to increase the ash fusion temperature and avoid the defluidisation of the bed. Limestone is regarded as CaO. The composition of the product gas is estimated using the Gibbs free energy minimisation method, however, methane formation (NON-EQUI), carbon conversion (CHARSEP) and equilibrium of WGSR (GASIF2) are controlled by empirical relations obtained from the experiments. The GASMIXER block was used to mix the outcome of the gasifier and GASSEP stream which represents the final output of product gas from the gasifier. Ash contained in the product gas is separated by Sep blocks ASHSEP.

Table 4.1: Description of Aspen Plus unit operation

<table>
<thead>
<tr>
<th>Aspen Plus ID</th>
<th>Block ID</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>RYield</td>
<td>DECOMP</td>
<td>To convert non-conventional biomass into conventional components using FORTRAN statement. Yield distribution or correlations required instead of stoichiometry or reaction kinetics.</td>
</tr>
<tr>
<td>Rstoic</td>
<td>NON-EQUI</td>
<td>CH₄, NH₃, H₂S and HCl formation.</td>
</tr>
<tr>
<td>RGibbs</td>
<td>GASIF/GASIF2</td>
<td>Calculating syngas composition by minimising Gibbs free energy subject to atomic balance. This reactor is used when temperature and pressure are known but stoichiometry of reaction is unknown.</td>
</tr>
<tr>
<td>Sep2</td>
<td>CHAR/GAS/ASH SEP</td>
<td>Separate gases from ash by specifying split fraction</td>
</tr>
<tr>
<td>MIXER</td>
<td>GASMIXER</td>
<td>Mixes different streams to produce a desired product.</td>
</tr>
</tbody>
</table>
4.4.2 Model validation

The developed model is validated with the experimental data reported in Pandey et al. (2016) from a laboratory scale bubbling fluidised bed gasifier. The model was validated with experiment numbers 1 and 13 (Table 4.2). A slight difference was observed between the experimental and predicted data. As seen in Table 4.2, the results obtained from PEM are in good agreement with experimental data.

Table 4.2: Simulation vs. experimental results

<table>
<thead>
<tr>
<th>Gas composition (%) v/v</th>
<th>Experiment No. 1</th>
<th>Experiment No. 13</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment</td>
<td>PEM</td>
</tr>
<tr>
<td>CO</td>
<td>5.41</td>
<td>5.03</td>
</tr>
<tr>
<td>H2</td>
<td>7.34</td>
<td>8.71</td>
</tr>
<tr>
<td>CO2</td>
<td>11.36</td>
<td>11.10</td>
</tr>
<tr>
<td>CH4</td>
<td>1.86</td>
<td>1.79</td>
</tr>
</tbody>
</table>

The ambient conditions are regarded as 25 °C and 1 atmospheric pressure (atm). To avoid the ash sintering and agglomeration issue in the bed, the maximum temperature of the gasifier was set to 800 °C. The sensitivity analysis was performed at different equivalence ratios (ER) and steam to biomass ratios (SBR). Steam and air temperature was raised to 160 °C before it enters the gasifier. Sensitivity analysis was carried out with a single parameter being varied at any given time.

4.5 Results and discussion

4.5.1 Effect of gasifier pressure

A sensitivity analysis is performed to study the effect of gasifier pressure on the product gas composition at an ER of 0.18 and temperature of 700 °C. High pressure forces molecule to react that could lead to complete gasification. It is evident from Figure 4.6 that the yields of H2 (from 8.71 to 8.49%) and CO (from 5.03 to 4.90%) decrease slightly with an increase in the gasifier pressure whereas CH4 (1.80 to 1.90%) has showed an increasing trend. This observation explains the formation of methane by the reaction mechanism \( C + 2H_2 \rightarrow CH_4 \). The simulation results are in
line with the conclusion reported elsewhere (Fu et al. 2013). Although pressure increase raise the CH\textsubscript{4} concentration in the product gas, at the same time H\textsubscript{2} and CO content decreased slightly. Raising pressure would also require additional energy therefore, subsequent simulations are performed at atmospheric pressure.

**Figure 4.6:** Effect of pressure on product gas composition

### 4.5.2 Effect of gasifier temperature

The influence of gasifier temperature on product gas compositions are shown in Figure 4.7. The effects of gasifier temperature on product gas composition are investigated at an ER of 0.25 and varying gasifier temperature in the range of 650-800 °C. An increasing trend is observed in CO and a decrease in CO\textsubscript{2} when temperature is raised from 650-800 °C due to the dominance of the endothermic Boudouard reaction in accordance to Le Chatelier’s principle. The H\textsubscript{2} yield initially increased with temperature but starts to decrease after 750 °C due to the WGSR. The CH\textsubscript{4} concentration remains fairly constant since the steam methane reforming reaction is not occurring. The CH\textsubscript{4} content in the final product gas represents the
amount of CH₄ formed during the devolatilisation process (Gómez-Barea and Leckner 2010). Despite the fact that higher temperature inside the reactor favoured the endothermic reactions, it was recommended that the temperature of the gasifier should be carefully controlled because it could lead to autothermal operational conditions increase the CO₂/H₂O ratio compared to the desired CO/H₂ ratio. Previous studies recommended that the optimum operating temperature can be between 800 to 900 ºC (Arteaga-Pérez et al. 2013). However, the results presented in this study suggest that gasifier operating with poultry litter or feedstocks with higher ash content should be kept at or below 800 ºC to avoid agglomeration problems.

![Figure 4.7: Effect of gasifier temperature on product gas composition, ER = 0.25](image)

To study the performance of the gasification process, the lower heating value of dry product gas (LHV) is calculated according to the equation presented in (Chapter 2). It is observed that an increase in the gasifier temperature enhanced the LHV of the product gas. This is directly correlated with the continuous increase of CO. Over the tested range of temperature, the LHV of the product gas increased from 2.46 to 3.24 MJ/Nm³ because higher temperature favoured the endothermic reactions in the forward direction.
4.5.3 Effect of ER

ER is defined as the ratio of the amount of air fed to the amount of air required for complete combustion. ER is assumed to be one of the key gasifier operating parameters for the trade-off between the quality and quality of the synthesis gas produced (Arena 2012). At low ER (below 0.20) the conversion of char formed during devolatilisation process is thermodynamically limited. In this study, the ER is varied from 0.20 to 0.40 by varying the air flow rate while keeping other parameters constant (800 ºC) to determine the optimum ER condition. Figure 4.8 shows the effect of ER on the yield of product gas composition. Increasing ER favours oxidisation reactions that would also increase the gasifier temperature and as a result the equilibrium reactions shift in a forward direction leading to higher CO₂ and H₂O concentration at the expense of CO and H₂ (Niu et al. 2013). At higher ER, the available char in the bed starts oxidised and forming CO₂ rather the CO (via the Boudouard reaction).

![Figure 4.8: Effect of ER on the product gas composition, T= 800 ºC](image-url)
In addition, the supply of excess air degrades the quality of product because the product gas is being diluted by N\textsubscript{2} \cite{Narvaez et al. 1996} and decreases the LHV. Several other researchers have reported similar observations and it was advised that gasifiers need to be operated at ER in the range of 0.25 to 0.30 \cite{Li et al. 2004; Arena et al. 2010}. Whereas, it is imperative to stress that the ER range can be changed according to the need and application of the product gas \cite{Gómez-Barea et al. 2013}. It can be understood that it is not feasible to have too low (below 0.20) or too high an ER (higher than 0.40) in the gasification process. The simulation results showed a strong agreement with the theoretical expectations. The optimum ER was found at 0.25, where calculated heating value of the product was maximum.

4.5.4 Effect of steam injection

Although, poultry litter has higher moisture content the influence of steam injection is investigated in this study. From Figure 4.9 it can be seen that steam injection increases the H\textsubscript{2} content in the product gas. This could be explained by water entering into the gasifier in the form of steam and actively participates in the WGSR leading to higher H\textsubscript{2} production compared to bound moisture. The time required for fuel bound moisture to reach the gasifier temperature is higher than the residence time therefore fuel bound moisture is not able to participate in WGSR \cite{Li et al. 2004; Arteaga-Pérez et al. 2013}. Moreover, steam injection decreases the gasifier temperature which can lead to high tar content and degrades the gasifier performance. Based on this explanation, pre-dried low moisture content feedstock would be a better fuel to be used in the gasifier. Considering the cost of a boiler and the energy consumption in steam production, steam injection is only employed where H\textsubscript{2}-rich product gas is required such as the use of product gas in fuel cell, engine, gas turbines etc.
4.5.5 Equilibrium prediction for WGSR

Figure 4.10 shows the temperature dependency of the experimental and thermodynamic equilibrium constant for the WGSR. The experimental equilibrium constant is calculated according to equation (4.1). The molar fraction of reactants and products are obtained from a fluidised bed gasifier (Pandey et al. 2016). It can be seen that the experimental value is far from the thermodynamic equilibrium constant.

\[ K_{exp} = \left( \frac{y_{CO} \cdot y_{H_2}}{y_{CO} \cdot y_{H, O}} \right) \]  

(4.1)

The \( K_{exp} \) is close to the thermodynamic equilibrium constant \( K_{eq} \) for the poultry litter feedstock at 800 °C. To avoid such a discrepancy, a high free board temperature would be needed because higher temperature leads to higher reaction rates of gasification and shift the equilibrium to attain a homogeneous WGSR. The results presented here are in line with those found by Schoeters et al. (1989).
Figure 4.10: Temperature dependency of experimental ($K_{exp}$), thermodynamic equilibrium ($K_{eq}$) and equilibrium factor ($f$)

4.6 Conclusion

The gasifier model presented in this study is developed using the quasi-equilibrium temperature approach for the WGSR, methane formation and char conversion, being corrected with the experimental data obtained from lab scale gasification experiments. The sensitivity analysis of the model indicates that introducing non-equilibrium correlations such as solid carbon conversion (char gasification), methane yield and controlling the WGSR are critical parameters for optimising the gasification process. The correlations were implemented in Aspen Plus using different unit operation blocks as well as FORTRAN subroutines when necessary. Increasing the temperature improved the product gas composition and increased the LHV. Steam injection should only be employed if a H$_2$-rich product gas is desired. This work provided insight into poultry litter gasification and could be used for the further process simulation. The optimum operating condition for poultry litter gasification is reported at 800 ºC and an ER of 0.25.
4.7 References


138


5 Artificial neural network based modelling approach for municipal solid waste gasification in a fluidised bed reactor

Abstract

In this paper, multi-layer feed forward neural networks are used to predict the lower heating value of gas (LHV), lower heating value of gasification products including tars and entrained char (LHV<sub>p</sub>) and syngas yield during gasification of municipal solid waste (MSW) during gasification in a fluidised bed reactor. These artificial neural networks (ANNs) with different architectures are trained using the Levenberg–Marquardt (LM) back-propagation algorithm and a cross validation is also performed to ensure that the results generalise to other unseen datasets. A rigorous study is carried out on optimally choosing the number of hidden layers, number of neurons in the hidden layer and activation function in a network using multiple Monte Carlo runs. Nine input and three output parameters are used to train and test various neural network architectures in both multiple output and single output prediction paradigms using the available experimental datasets. The model selection procedure is carried out to ascertain the best network architecture in terms of predictive accuracy. The simulation results show that the ANN based methodology is a viable alternative which can be used to predict the performance of a fluidised bed gasifier.
Published as


DOI:10.1016/j.wasman.2016.08.023.

Simulations and interpretation of results were performed by D.S. Pandey. The first draft of manuscript was written by D.S. Pandey. S. Das and I. Pan helped in writing the code and both acted as critical reviewers and discussion partners. The final version of the manuscript was reviewed by J.J. Leahy and W. Kwapinski, who also acted as discussion partners throughout the research leading to this paper. Chapter 5 of this thesis corresponds to the paper published in Elsevier’s Waste Management journal.
5.1 Introduction

According to World Bank data, about 4 billion tonnes of waste is generated per year, out of which cities’ alone contribute 1.3 billion tonnes of solid waste. This volume is forecast to increase to 2.2 billion tonnes by 2025. Three-fourths of this waste is disposed of in landfills, with only one fourth being recycled. It is expected that in lower income countries waste generation will double in the next 25 years (Hoornweg and Bhada-Tata 2012). With rapid industrial growth and growing world population, most developing countries are facing acute disposal problem for MSW. MSW refers to the discarded materials from household wastes such as kitchen garbage, paper, wood, food waste, cotton as well as materials derived from fossil fuels such as plastic and rubber (Cheng and Hu 2010). In urban areas significant environmental problems are arising from the disposal of MSW which have led to major concerns regarding human health and environment. These issues are common to both developed as well as developing countries (Pires et al. 2011). Furthermore, these issues are stimulating the need for further development of treatment technologies to meet these global challenges. The new European sustainable development strategy (EU 2009) promotes thermal treatment processes to recover energy from MSW while tackling the issues related to climate change.

There are several processes that could treat MSW including thermal, biochemical and mechanical processes. Incineration technology is widely used to process MSW, but the control of NOx, SOx, nano-particle, dioxins and furans emissions are challenging (Cheng and Hu 2010). In a quest for a sustainable waste treatment technology, waste to energy (WtE) technology has been reviewed by Brunner and Rechberger (2015). The study concluded that due to the advancement in combustion and air pollution control technologies WtE plants are useful for energy and material recovery from waste without having adverse effects on environment. The impact on the environment of thermal treatment of waste with energy recovery was evaluated by Pavlas et al. (2010) who concluded that thermal treatment of MSW with energy recovery was undoubtedly one of the best techniques. WtE not only offers an alternative to treat the waste but also produces clean energy which can offset primary energy consumption in conventional heat and power units. In general, WtE plants are
considered as carbon neutral but they are not. The total carbon content present in the MSW is bound with various materials present in the waste. It was found that more than half of the carbon present is biogenic in nature but the remaining part originates from fossil fuels which cannot be considered as biogenic carbon (Gohlke 2009). As per the EU’s new directive, each WtE plants has to report how much electricity was produced from the renewable sources present in the waste feed. The measured biogenic CO$_2$ fraction in the flue gas from an incinerator plant in The Netherlands was between 48-50% (Palstra and Meijer 2010) whereas, in Austria the ratio of biogenic to anthropogenic energy content in MSW was reported in the range 36-53% (Fellner et al. 2007).

Thermal treatment technologies for MSW have been extensively reviewed by Malkow (2004); Arena (2012); Leckner (2015); Lombardi et al. (2015) and it was proposed that an alternative to combustion is to gasify the MSW for energy recovery. To date, gasification processes have been investigated by several contemporary researchers and extensively reviewed by Gómez-Barea and Leckner (2010). Thermal gasification provides flexibility for the production of heat and power based on clean biomass derived syngas (Basu 2010). In addition, thermochemical conversion technologies can reduce the original volume of wastes disposed by 80-95% along with energy recovery (Rand et al. 1999). Lately, gasification of solid wastes which originates from the household or industrial sectors have received increasing attention by researchers. The syngas from MSW can be used for heating and production of electricity to offset the use of fossil fuels. However, gasification of MSW is not widespread. The major barrier that has prevented the widespread uptake of advanced gasification technologies for treating MSW has been the higher ash content in the feed making the gasification operation difficult. In addition, high amounts of tar and char contaminants in the produced gas make it unsuitable for power production using energy efficient gas engines or turbines.

A comprehensive review of fluidised bed biomass gasification model was presented by Gómez-Barea and Leckner (2010). In the past, different modelling approaches starting from black box modelling to thermodynamic equilibrium, kinetic rate, fluid-dynamics, neural network and genetic programming models (Puig-Arnavat et al. 2010).
2010; Pandey et al. 2015) and Gaussian process based Bayesian inference (Pan and Pandey 2016) were applied for modelling gasification. These models were validated using pilot scale gasification data. Simulating MSW gasification is computationally expensive and fast meta-models are required. In this paper an artificial intelligence technique namely, feedforward neural network, is used to predict the heating value of gas (LHV), heating value of gasification products (LHV<sub>p</sub>) as well as the syngas (product gas) yield. LHV<sub>p</sub> is defined as the sum of the LHV of gas and the calorific value of unreacted char (entrained) and tar.

ANN models are not based on modelling the physical combustion and transport equations governing the reactor but they are a class of generic nonlinear regression models which learns the arbitrary mapping from the input data on to the output to obtain computational models with high predictive accuracy. Although ANN based models have been extensively used in other scientific fields, it has only recently gained popularity in renewable energy related applications (Kalogirou 2001). ANN based models were developed for predicting the product yield and gas composition in an atmospheric steam blown biomass fluidised bed gasifier (Guo et al. 2001). It was concluded that the feed forward neural network (FFNN) model has better predictive accuracy over the traditional regression models. An FFNN model was employed to predict the LHV of MSW based on its chemical composition (Dong et al. 2003). ANN was applied for predicting the gasification characteristics of MSW (Xiao et al. 2009) and tested for its feasibility. ANN methodology was used to predict future MSW quality and composition in Serbia to achieve the targets for waste management set by national policy and EU directive by 2016 Batinic et al. (2011). Two different types of ANN based data-driven models have been developed for the prediction of gas production rate and heating value of gas in coal gasifiers (Chavan et al. 2012). Recently, ANN based predictive tools have been used in fluidised bed gasifiers to predict the syngas composition and gas yield (Puig-Arnavat et al. 2013). The ANN technique has been applied in the gasification area and has shown better results compared to the conventional process modelling approaches. A brief overview of different modelling approaches and their pros and cons is presented in Table 5.1.
Table 5.1: Pros and cons of different gasification modelling approach (Gómez-Barea and Leckner 2010; Mikulandric’ et al. 2014)

<table>
<thead>
<tr>
<th>Modelling approaches</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Models using this approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black Box model</td>
<td>Independent of gasifier type. Easy to implement. Fast convergence. Widely used for the gas prediction and heating value.</td>
<td>Only applicable for stationary process. Does not provide insight into the gasification process.</td>
<td>Equilibrium model, Thermodynamic model, Pseudo-equilibrium model</td>
</tr>
<tr>
<td>Kinetic model</td>
<td>Realistic model, which can be used for process design and scaling-up.</td>
<td>Depend on reaction kinetics and gasifier type.</td>
<td>Uniform conversion model, Shrinking core model etc.</td>
</tr>
<tr>
<td>Fluidisation model</td>
<td>Offers a trade-off between precision and numerical complications.</td>
<td>Applicability of the correlations used has limited scope.</td>
<td>Davidson–Harrison model, Kunii–Levenspiel model etc.</td>
</tr>
<tr>
<td>Computational fluid-dynamics model</td>
<td>Useful in improving the details of the gasifier.</td>
<td>Computationally expensive, time consuming and uncertainty involved with the parameters in closure.</td>
<td>Direct numerical simulation, Large eddy simulation, Two fluid model, Euler-Euler model, Euler-Lagrange model etc.</td>
</tr>
<tr>
<td>ANN model</td>
<td>Does not need extensive understanding of the process. High predictive accuracy.</td>
<td>Dependent on quantity of datasets. No proper physical interpretation of models can be made.</td>
<td>Feed-forward neural network, Hybrid neural network etc.</td>
</tr>
</tbody>
</table>
Most of the mathematical models for fluidised bed gasifier are based on the law of conservation (mass, energy and momentum) and other boundary conditions (Gómez-Barea and Leckner 2010). Depending on the complexity, the model can be a 3-D fluid dynamic model or kinetic rate based model or less complex such as an equilibrium based model. Due to the inherent complexity of gasification processes, development of mathematical models are still at a nascent stage. The aim of this research is to develop neural network based models which can be used to simulate the gasification process with improved accuracy. In this study, computational models derived from artificial intelligence techniques are exploited to learn the nonlinear mapping problem. These types of models can predict the performance of complex systems (including gasification). Therefore, this study is focused on exploiting the potential of the ANN technique to estimate the performance of MSW gasification in a fluidised bed reactor.

5.2 Material and methods

5.2.1 Theory of artificial neural network based modelling

ANN is a biologically inspired computational technique that imitates the behaviour and learning process of the human brain. ANNs are universal approximators and their predictions are based on prior available data. It is therefore preferred in many data driven research applications over other theoretical and empirical models where predictive accuracy is of prime concern. The ANN technique has been extensively used in several applications in the fields of pattern recognition, signal processing, function approximation, weather prediction and process simulations (Guo et al. 1997). The recent developments and potential application of ANN in diverse disciplines has motivated the present study. However, application of the ANN technique for modelling of MSW gasification is rarely reported in the literature. ANNs are essentially supervised learning methods, i.e. given an input and an output dataset; they have enough flexibility to model the nonlinear input-output mapping. The methodology is generic and does not have any limitation to the type of dataset or the number of input-output variables. These generic ANN models provide flexibility to include other process parameters like tars, unconverted carbon and steam-to-biomass ratio (in the case of steam gasification) or any other process parameter.
which are deemed necessary (Puig-Arnavat et al. 2013). However the models might not work well for a drastically new configuration of gasifier which is not similar to the training dataset. Nevertheless, this is a limitation of the dataset and not of the ANN based modelling methodology.

Figure 5.1 represents the multilayer feed-forward neural network architecture with multiple input and multiple output (MIMO) variables. For multiple input and single output (MISO) models the number of output is set to one. It consists of an input layer, multiple hidden layers and an output layer. Each node (neuron) other than the input nodes are equipped with a nonlinear transfer function. Neurons $x_i$ in the input layer distributes the input signals to neurons in the hidden layer ($j$), while neurons in hidden layers sum up its input signal ($x_i$) after multiplying them by their weight $w_{ij}$. The output ($y_j$) of the ANN model can be represented as follows (5.1).

$$y_j = f \left( \sum_{i=0}^{d^{l-1}} \left( w_{ij} x_i^{l-1} \right) \right)$$  \hspace{1cm} (5.1)

where $f$ is a simple threshold function which can be a sigmoid, hyperbolic tangent or radial basis function, $d$ is the dimension of the network, $l$ represents the number of layers and $w_{ij}$ is the weight which belongs to network with $l$ layer and having $i$ input and $j$ hidden layers. The mathematical representation of the ANN model weights can be represented by (5.2).

$$w_{ij} \in \begin{cases} 1 \leq l \leq L & \text{layers} \\ 0 \leq i \leq d^{l-1} & \text{input} \\ 1 \leq j \leq d^l & \text{output} \end{cases}$$  \hspace{1cm} (5.2)
The input and validated datasets were obtained from a lab-scale fluidised bed gasifier (560 mm high with an internal diameter of 31 mm) operating at atmospheric pressure. Heat was supplied from an external source (electric heater) to maintain the temperature of the gasifier. Silica sand was used as a bed material (particle size
The gasifier consists of an electric heater, screw feeder to supply the feed, filter for collecting elutriated char and ash and gas-bag for off-line sampling of produced gas. The reported product gas yield was estimated by N\textsubscript{2} balance. The details of the gasifier can be found elsewhere (Xiao et al. 2009). Hong Kong MSW data was extracted from (Choy et al. 2004) where MSW was gasified in a small scale gasifier to assess the feasibility of installing an MSW gasifier in Hong Kong University of Science and Technology. Experiments were performed at different temperatures (400 \leq \text{temperature} \leq 800 \degree C) and equivalence ratios (0.2 \leq \text{ER} \leq 0.6).

The modelling methodology using ANN is divided into a training phase and a validation phase. For checking the accuracy and generalisation capability of the model, the experimental dataset is divided into training (70%) with the remainder for the validation (15%) and testing (15%) purposes. The input \(x_i\) and output \(y_i\) parameters are normalised with respect to the maximum value, to ensure that all data used for training of the network lie within a range of \([0,1]\). The datasets used for the training, testing and validation purpose of the model are randomised. A hyperbolic tangent sigmoid function \((\tansig)\) \(f(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}}\) and logarithmic sigmoid function \((\logsig)\) \(f(x) = \frac{1}{1+e^{-x}}\) are used in the hidden layers whereas a pure linear function \((\purelin)\) is used in the output layer. Both the \tansig and \logsig transfer functions are traditionally used and make the ANNs a universal function approximator given a sufficient number of hidden nodes. However, depending on the nature of the data, amongst these two transfer functions, one may outperform the other. Therefore, both the transfer functions are exploited in finding the best suited one for fitting this data.

There have been exhaustive studies on using different training algorithms for ANNs, e.g. Levenberg-Marquardt (LM), scaled conjugate gradient (SCG), Broyden-Fletcher-Goldfarb-Shanno quasi-Newton (BFGS), gradient descent with momentum and adaptive learning rate (GDX), amongst many others (Plumb et al. 2005). The LM gives accurate training results for moderate size neural networks. The other algorithms have disadvantage of slower convergence speed, particularly for large networks. In the LM, the Jacobian \((J)\) is calculated using the backpropagation
technique described in (Hagan and Menhaj 1994) followed by Hessian \((H = J^T J)\) and gradient \((g = J^T e)\) calculation, \(e\) being the network error. The network weight and bias terms \((x)\) are then updated as (5.3):

\[
x_{k+1} = x_k - \left[ J^T J + \mu I \right]^{-1} J^T e
\]  

(5.3)

where, \(\mu\) is a scalar, whose zero or large values make the training algorithm similar to Newton’s method, using approximate Hessian or gradient descent with small step size respectively. After each successful step the value of \(\mu\) is decreased or alternatively increased if the cost function is not decreased in a step. Based on the above reason, the LM back-propagation training algorithm is used here for minimising the mean squared error (MSE) between the network output and target output. To develop the ANN model, the nine process parameters that have been used as model inputs are carbon \((x_1, \text{wt}%)\), hydrogen \((x_2, \text{wt}%)\), nitrogen \((x_3, \text{wt}%)\), sulphur \((x_4, \text{wt}%)\), oxygen \((x_5, \text{wt}%)\), moisture content \((x_6, \text{wt}%)\), ash \((x_7, \text{wt}%)\), equivalence ratio \((x_8, \text{ER})\) and the temperature of the gasifier \((x_9, T_g \degree C)\). ER is defined as the ratio between the actual air fed to the gasifier and the air necessary for stoichiometric combustion of the biomass. The input parameters are represented as an input vector \(x_i = [x_{1,2,3,4,5,6,7,8,9}]\) and the output variables are LHV of product gas \((y_1, \text{kJ/Nm}^3)\), LHV_p \((y_2, \text{kJ/Nm}^3)\) and gas yield \((y_3, \text{Nm}^3/\text{kg})\). The input and output variables are in different units. The mean and standard deviation values provide the statistical summary of the dataset to facilitate the reproducibility. The statistical analysis of the input \(x_i\) and output variables \(y_{1,2,3}\) are represented by the mean vectors \(\mu_x\) and \(\mu_y\), respectively and are given in equations (5.4) and (5.5).

\[
\mu_x = [43.73, 5.30, 0.27, 0.11, 38.43, 6.96, 2.00, 0.4, 602]
\]  

(5.4)

\[
\mu_y = [2146, 4827, 1.98]
\]  

(5.5)
Similarly, their corresponding standard deviations are given by $\sigma_x$ and $\sigma_y$ in equations (5.6) and (5.7).

$$\sigma_x = \begin{bmatrix} 21.52 & 3.85 & 0.58 & 0.08 & 16.72 & 28.63 & 5.84 & 0.17 & 96.68 \end{bmatrix} \quad (5.6)$$

$$\sigma_y = \begin{bmatrix} 2126.57 & 4720.66 & 1.67 \end{bmatrix} \quad (5.7)$$

5.2.2 Proposed approach of ANN based learning methodology and optimisation of the model parameters

The MISO and MIMO configurations are used for training of multilayer neural network models. In the MISO case, 9 inputs and 1 output are modelled. Therefore 3 separate ANNs are trained for each of the three cases of LHV, LHV$_p$ and syngas yield. For the MIMO case, the network is trained with 9 inputs and 3 outputs. Therefore, one single network is capable of predicting all three outputs.

Different sets of internal network parameters have been used while training the ANN model viz. number of hidden layer, number of neurons in the hidden layer and transfer function, learning rate etc. Deciding the number of neurons in the hidden layer is an important issue in the selection of the neural network architecture and their choice varies on a case by case basis. A detailed study of the effect of internal parameters on the performance of back propagation networks (Hornik et al. 1989) and the procedure involved in selecting the best network topology has been described elsewhere (Maier and Dandy 1998). The network architecture has a huge influence on the trade-off between predictive accuracy on the training dataset and generalisation capability of the model on untrained data. Hence, both the number of hidden layers and number of neurons in each of these hidden layers must be carefully considered. Having too few neurons in the hidden layer can give rise to lower predictive accuracy (i.e. the network cannot capture the nonlinear trends in the dataset), on the other hand too many neurons in the hidden layers can also result in problems. A highly complex model can suffer from over-fitting the training dataset and it takes much more computational time to train large networks. Hence, a trade-off needs to be found in order to determine the numbers of layers, number of neurons in each layer and transfer function used in the hidden layer. In the past, a trial and
error method was employed by other researchers to decide the number of neurons and hidden layers but selection of the optimum layer/hidden node combination was not clear (Azadi and Sepaskhah 2012; Puig-Arnovat et al. 2013; Azadi and Karimi-Jashni 2016). An increase or decrease in number of neurons in the hidden layer using the trial and error method cannot accurately identify the best bias-variance trade-off architecture of the ANN. A different approach with a rigorous cross validated accuracy check can be employed while sweeping the number of hidden nodes in single and double layer configuration selecting the best representative model first. This increases the computational load, as reported in this paper, due to the aim of finding out the best ANN architecture to best capture the underlying patterns of this data. This is intrinsically different from what already exists in the literature and also advances the traditional supervised learning data analysis workflow, where the right model is not precisely known.
This study also provides a comprehensive and rigorous approach on how to decide the optimum hidden layers and number of neurons in ANN based models and outlines a systematic method of choosing the optimum ANN architecture. Figure 5.2 represents the schematic flowchart of the proposed methodology. An optimum neural network architecture is proposed by varying the number of hidden layers, transfer
functions and number of neurons in each hidden layer. Each ANN configuration has been trained with 100 independent runs to find the lowest training error, in order to minimise the chance of getting stuck in local minima in the ANN weight/bias term tuning process. The performance of the model can be evaluated by different accuracy measures such as the mean absolute error (MAE), root mean squared error (RMSE) and normalised root mean squared error (NMSE). However, each method has its own advantages and disadvantages. This aspect was very well explained by Azadi and Karimi-Jashni (2016). All of these quantitative measures summarises the error incurred in training and testing in a similar way. For training ANNs, MSE is the most popular choice of performance indicator and has been widely used in a wide variety of pattern recognition and machine learning problems (Bishop 1995). The predictive accuracy of the model is evaluated by the MSE metric as given in equation (5.8).

$$MSE = \left( \frac{\sum_{i=1}^{n} (y_p - y_o)^2}{n} \right)$$

(5.8)

where, $n$ is number of datasets used for training the network, $y_p$ is mean of the predicted value and $y_o$ is the experimental (target) value.

Simulations were performed on a desktop workstation which consists of Intel i7-3770 CPU, 3.4GHz processors with 4 GB of RAM. Parallelised simulation technique was used to optimise the capabilities of computer clusters (4 cores) using the parallel for loop. Computational times for single and double layer model were also calculated and were approximately 18 hours and 190 hours $\approx 8$ days respectively for 100 independent runs with re-shuffling the training datasets (100 times) and hidden layer with 30 neurons in the case of single layer and 15 neurons in each hidden layer for the double layer model. It is imperative to stress that the computational time reported here is the simulation time for finding the best model which train and cross validate multiple models with different number of layers and architecture to search for the best possible one.
Deciding the optimum ANN architecture is often tricky as there is always a chance of picking up inconsistent patterns and also a risk of premature convergence during the optimisation of the weight and bias terms of the FFNN. Therefore multiple randomisation of the optimiser with different initial guess and multiple shuffles of the data segmentation in training, validation, testing sets have been adopted here to enable higher accuracy and error estimates, in multiple Monte Carlo runs, to decide the best ANN architecture including the number of layers, neurons in each layer and the activation function, as also explored in (Das et al. 2012; Saha et al. 2012).

5.3 Results

5.3.1 Single layer MISO and MIMO models

The number of input and output parameter are nine and one respectively for the MISO model where the number of neurons in the hidden layer varies from 1 to 30 and LM algorithm is applied to train the neural networks. The models were trained and tested using both \textit{tansig} and \textit{logsig} nonlinear transfer functions in the hidden layer and \textit{purelin} in the output layer. The dataset used to develop the ANN model contains 67 input/output patterns, out of which 70% (47 datasets) are used for training, 30% for testing and validation (10 datasets each) of the ANN model. Also, the input datasets are randomised for each and every iteration (100 independent runs were carried out). Simulations were also performed by varying the number of hidden layers in the model and transfer function. The networks are trained with varying number of hidden neurons in a hidden layer with different combinations of transfer functions. The performance of the network is evaluated on the basis of the MSE. The ANN architecture with the lowest MSE indicates a better model (the best model is represented in the figures below by an arrow) in terms of predictive accuracy.
The MSE of a single layer NN model is illustrated by box plots, as shown in Figure 5.3 & Figure 5.4. Considering the variation of whiskers at different neuron numbers, a logarithmic scale is used on the ordinate axis for better representation of the graph. Box plots are used to display the distribution of data by minimum, first quartile, median, third quartile and maximum values. The central box comprises values between 25 and 75 percentiles and the whisker shows the range of values that fall within the maximum of 1.5 interquartile ranges (IQR). The band inside the box
represents the median. The box plots often display the whole range of data from minimum to maximum, median and IQR. Box plots also display the outliers.

It can be seen from Figure 5.3 & Figure 5.4 that increasing the number of neurons in the hidden layer does not imply that the model will have a better predictive accuracy (in the sense of the median across multiple optimisation runs). The best architecture for the neural network model is identified as that which has a minimum MSE (in terms of median of MSE). The minimum MSE with model details are presented in Table 5.2. It is evident from Table 5.2 that a single layer model with logsig transfer function has better accuracy compared to the tansig transfer function when used in the hidden layer. However, it is imperative to stress that models obtained using tansig are simpler than those obtained using logsig (i.e. the number of neurons are lower for the best model). Further simulations were performed with minimum MSE.

5.3.2 Double layer MISO and MIMO model

Figure 5.5 & Figure 5.6 show the surface plots of the double layered MISO and MIMO models. Different combinations of transfer functions are used to find the best model. The minimum MSE with different combination of double layer NN models predicting the performances of the gasifier are presented in Table 5.2. As explained in Section 5.3.1, the best architectures are identified based on the lowest MSE for the subsequent simulations. Double layer MISO models show better predictive accuracy when the logsig transfer function was used in both the layers. Moreover, the MIMO model with the tansig/logsig (8/15 neurons in respective layers) combination has shown slightly better predictive accuracy.
**Figure 5.5:** Surface plot of MSE for double layer MISO models (a) LHV (b) LHV$_p$ and (c) Gas yield

**Figure 5.6:** Surface plot of MSE for double layer MIMO models (LHV-LHV$_p$-Gas yield)

Surface plots in Figure 5.5 & Figure 5.6 show a three-dimensional view of the best prediction accuracy for the double layer model across a combination of different number of neurons in the respective layers. These plots are useful in finding the optimum combinations when an ANN regression model is fitted. It is used for the graphical visualisation of the smoothness of the fitted surface as the numbers of neurons in the layers are varied. The colour of the surface determined by the MSE is presented on the Z-axis. Contour maps of the MSE surface are presented below the
surface plots to get a 2-D visualisation of the change in the predictive accuracy for the double layer NN model. The optimum number of neurons in the hidden layers for both the MISO and MISO models are tabulated in Table 5.2 based on the minimum reported MSE. The remaining discussion of this paper is based on the optimum architecture reported in Table 5.2.

Table 5.2: Training performance of the best ANN configuration

<table>
<thead>
<tr>
<th>ANN model</th>
<th>Number of Layer</th>
<th>Predictive parameter</th>
<th>Activation function</th>
<th>Number of neurons</th>
<th>Minimum MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MISO</td>
<td>1</td>
<td>LHV</td>
<td>tansig</td>
<td>9</td>
<td>0.0086</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>logsig*</td>
<td>30</td>
<td>0.0077</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>tansig</td>
<td>12</td>
<td>0.0024</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>logsig*</td>
<td>30</td>
<td>0.0021</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LHVp</td>
<td>tansig</td>
<td>6</td>
<td>0.0004</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>logsig*</td>
<td>8</td>
<td>0.0003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gas yield</td>
<td>tansig</td>
<td>11</td>
<td>0.0035</td>
</tr>
<tr>
<td>MIMO</td>
<td>1</td>
<td>LHV-LHVp</td>
<td>logsig</td>
<td>28</td>
<td>0.0031</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>tansig/tansig</td>
<td>4/12</td>
<td>0.00852</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>logsig/logsig*</td>
<td>9/15</td>
<td>0.00810</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>tansig/tansig</td>
<td>4/13</td>
<td>0.00251</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>logsig/logsig</td>
<td>4/14</td>
<td>0.00247</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>tansig/tansig</td>
<td>10/15</td>
<td>0.00837</td>
</tr>
<tr>
<td>MISO</td>
<td>2</td>
<td>LHVp</td>
<td>logsig/logsig*</td>
<td>4/13</td>
<td>0.00229</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>logsig/tansig</td>
<td>4/10</td>
<td>0.00234</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>tansig/tansig</td>
<td>6/6</td>
<td>0.00057</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>logsig/logsig*</td>
<td>6/5</td>
<td>0.00051</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>tansig/tansig</td>
<td>5/6</td>
<td>0.00056</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>logsig/tansig</td>
<td>6/12</td>
<td>0.00353</td>
</tr>
<tr>
<td>MIMO</td>
<td>2</td>
<td>LHV-LHVp</td>
<td>tansig/logsig*</td>
<td>8/15</td>
<td>0.00346</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>logsig/logsig</td>
<td>7/15</td>
<td>0.00347</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>logsig/tansig</td>
<td>7/15</td>
<td>0.00357</td>
</tr>
</tbody>
</table>

* corresponds to the optimum NN model for the prediction of gasifier performance.
5.4 Discussion

Figure 5.7 depicts the representative case of the convergence characteristic of the ANN model for the LH\(\text{Vp}\) (MISO, 4/13, \textit{logsig/logsig} and LM algorithm). It can be seen that the MSE of the validation curve decreases slightly after 7 iterations. The validation fitness was found to increase after iteration 7 while predicting the LH\(\text{Vp}\) in this particular case, indicating that the model would not generalise well if trained beyond this point. The model was trained to achieve an MSE of 0.001 with the prescribed number of neurons in the hidden layer as identified from Table 5.2. The double layer model has a \textit{logsig} transfer function in each layer which has 4 and 13 neurons respectively. A similar approach was used while predicting the performance of the other output parameters.

![Figure 5.7: Convergence characteristics of the optimum double layer MISO model for the LH\(\text{Vp}\) (4/13, logsig/logsig and LM algorithm)](image-url)
5.4.1 Predictive performance of the single layer MISO ANN model

The optimum architecture for the MISO model for LHV, LHV\textsubscript{p} and gas yield is identified from Table 5.2 where it can be seen that a single layer model with logsig transfer function and LM learning algorithm has demonstrated better predictive accuracy. The optimum numbers of neurons in the hidden layers are 30, 30 and 8 for the LHV, LHV\textsubscript{p} and gas yield respectively.

The coefficient of determination ($R^2$) and MSE of training validation and testing datasets are reported in Figure 5.8 to predict the LHV, LHV\textsubscript{p} and syngas produced. Subplots show the experimental vs. ANN based model predicted values for the output calculation of the gas generated from the MSW gasification process. The $R^2$ value measures the performance of the model in predicting the output parameters from the experimental datasets. The plots (Figure 5.8) show that the degree of agreement between the experimental and predicted values for the training; validation and testing datasets are quite good (~ 90% or more). It is evident that most of the data-points lie on the straight line which indicates good performance of the developed model. It is clearly apparent that the accuracy of the network on training data is better than testing data. During the training mode the network always alters the values of its input and output weights to get the best fitness whereas in the testing phase (generalisation or validation) the output shows the actual predictive performance of the trained model on unseen data without adjusting the weights.
Figure 5.8: Prediction of single layer MISO ANN model with $R^2$ and MSE on the training, validation and the testing datasets (a) LHV (b) LHVp and (c) Gas yield

5.4.2 Predictive performance of the single layer MIMO ANN model

This model is developed to predict multiple outputs by a single neural network. It can be seen from Table 5.2 that the logsig transfer function shows better accuracy compared with the tansig function. The actual vs. predicted output parameter from the best MIMO model on the training, validation and testing dataset have been reported in Figure 5.9. It shows the combined $R^2$ and MSE values. It can be observed that the generalisation and performance of the model is quite good. The evolved model has $R^2$ values over 94% in all three cases i.e. training, validation and testing. Although, a similar modelling paradigm is used while predicting the LHV, LHVp and syngas yield values separately, the MIMO model has a slightly better prediction accuracy ($R^2$ value over 98% on unseen data) on training, validation and testing over the MISO model. It is also evident that the MIMO model performed better compared to the three MISO models.
5.4.3 Predictive performance of the double layer MISO ANN model

Figure 5.10 shows the prediction performance of the trained double layered NN model reporting the actual vs. predicted values of LHV, LHVp and gas yield production. The simulations are performed at the best solution in Table 5.2, reporting minimum MSE and corresponding neural network architecture. It is noticed that the evolved models for LHVp and gas yield have slightly better predictive accuracy compared to LHV for the unseen datasets. The $R^2$ values for the testing and validation datasets are close to 100% for LHV and gas yield confirming the predictive reliability of the ANN model. In the case of the LHV prediction, $R^2$ for the validation dataset is found to be low, although the model generalised well over unseen datasets (testing) with an $R^2$ value of 96%. The plots in Figure 5.10 show that the degree of agreement between the experimental and predicted values for the training, validation and testing datasets are quite good with low relative error between the experimental and model predicted values under the cross-validation scheme.
The training, validation and testing regression plots of the double layer MIMO model is illustrated in Figure 5.11. The trained MIMO model predicts the performance of the MSW gasification process using fuel characteristics and process parameters. The model used here contained 2 hidden layers consisting of 8 and 15 neurons in each layer with tansig and logsig as the activation functions in the first and second hidden layer respectively, which predicts the gasifier performance most accurately with respect to MSE criteria. The neural network was trained to predict three different output parameters (LHV, LHVP and gas yield). The degree of agreement ($R^2$ value) between experimental and simulated values justified the accuracy of the proposed ANN model.
5.4.5 Comparison of MISO and MIMO ANN models

The overall $R^2$ values for the different optimised structures and their corresponding MSE are reported in Table 5.3. It can be seen from Table 5.3 that the MIMO models show an improved performance over the MISO models. Although, the degree of agreement ($R^2$) for gas yield in the case of a single layer and the LHVp and gas yield for double layer models are higher compared to their respective MIMO model. Moreover, in both cases the MSE for the MIMO model is lower compared to the MISO model which measures the comparative performance of the two trained ANN modelling philosophies. Most of the studies reported to date (Xiao et al. 2009; Puig-Arnavat et al. 2013), focused on multiple input and single output. The comparative statistical analysis presented in Table 5.3 shows that the ANN model with multiple outputs has better prediction accuracy. It turns out that a single layer MIMO model with 28 neurons, LM training algorithm and logsig transfer function has better predictive accuracy amongst all four type of models explored, MISO, MIMO, single and double layer NNs. The computation time for finding the best model was about 18 hrs, whereas the double layer model took almost 200 hrs $\approx 8$ days for the same simulation with the above reported computing hardware.
Table 5.3: Statistics of the best solutions of single and double layer model variants

<table>
<thead>
<tr>
<th>Number of</th>
<th>Algorithm †</th>
<th>Overall $R^2$</th>
<th>MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>layer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>30/logsig/LHV</td>
<td>95.95</td>
<td>0.00372</td>
</tr>
<tr>
<td>1</td>
<td>30/logsig/LHV_p</td>
<td>92.56</td>
<td>0.00496</td>
</tr>
<tr>
<td></td>
<td>8/logsig/Gas yield</td>
<td>98.68</td>
<td>0.00109</td>
</tr>
<tr>
<td></td>
<td>28/logsig/MIMO</td>
<td>98.05</td>
<td>0.00074</td>
</tr>
<tr>
<td></td>
<td>9/logsig/15/logsig/LHV</td>
<td>93.56</td>
<td>0.00157</td>
</tr>
<tr>
<td>2</td>
<td>4/logsig/13/logsig/LHV_p</td>
<td>98.66</td>
<td>0.00203</td>
</tr>
<tr>
<td></td>
<td>6/logsig/5/logsig/Gas yield</td>
<td>98.95</td>
<td>0.00093</td>
</tr>
<tr>
<td></td>
<td>8/tansig/15/logsig/MIMO</td>
<td>98.90</td>
<td>0.00077</td>
</tr>
</tbody>
</table>

†Number of neurons/ activation function/output parameter.

Despite the fact that ANN based models have advantages over traditional statistical approaches and have been widely used for similar prediction problems, they also have their own limitations. ANN based models are often referred to as black box models which are not capable of identifying the relative significance of the various parameters involved in the regression i.e. which input parameter influences the output most. The knowledge acquired during training of the model is intrinsic in nature and therefore it is difficult to draw a reasonable interpretation of the overall structure of the network. Furthermore, it also suffers from a greater computational burden, proneness to overfitting, and the empirical nature of model development (Tu 1996).

### 5.5 Conclusion

In this study, MISO and MIMO ANN models, trained with the Levenberg-Marquardt back propagation algorithm are used to predict the LHV, LHV_p and syngas yield from MSW in a fluidised bed gasifier using process parameters and elemental composition. It is shown that the predictive performance of the ANN models explored have a good agreement with the experimental datasets. This indicates that ANN can be used as an alternative method for modelling complex thermochemical processes. Good accuracy and performance of the trained ANN models (with $R^2 \approx$
98% for single layer and \( R^2 \approx 99\% \) for double layer) have been achieved in all cases and the MSE is also found to be sufficiently low. The model has been tested against data from an atmospheric fluidised bed gasifier. The first application of this new approach has given a useful insight for equilibrium modelling however, calibration of the ANN model with more data is recommended since it is a self-adaptive, data-driven method with a few or no prior assumptions about the model structure. A simulation result for the presented study is quite promising and can be employed in learning and prediction of nonlinear complex mapping of gasification yields. This simulation paradigm illustrates the advantage of the proposed ANN model and can be exploited to simulate complex thermochemical processes such as gasification, pyrolysis and combustion.

The trained ANN model can be used for predicting the performance of similar kinds of gasifier operating under similar experimental condition. However, if the physical parameters in the input to the regression problem changes, the model needs to be retrained. Also, caution should be taken while developing the same ANN prediction model for heterogeneous data that comes partly or completely from different experimental protocol, that again needs breaking the prediction problem into several smaller sub-problems that share some commonality between them.
5.6 References


6 Multi-gene genetic programming based predictive models for municipal solid waste gasification in a fluidised bed gasifier

Abstract

A multi-gene genetic programming (GP) technique is proposed as a new method to predict syngas yield production and the lower heating value (LHV) for municipal solid waste (MSW) gasification in a fluidised bed gasifier. The study shows that the predicted outputs of the MSW gasification process are in good agreement with the experimental dataset and also generalise well to validation (untrained) data. Published experimental datasets are used for model training and validation purposes. The results show the effectiveness of the GP technique for solving complex nonlinear regression problems. The multi-gene GP is also compared with a single-gene GP model to show the relative merits and demerits of the technique. This study demonstrates that the GP based data-driven modelling strategy can be a good candidate for developing models for other types of fuels as well.

Published as


DOI:10.1016/j.biortech.2014.12.048

Simulations and interpretation of results were performed by D.S. Pandey. The first draft of manuscript was written by D.S. Pandey. I. Pan and S. Das helped in writing the code and acted as critical reviewers and discussion partners. The final version of the manuscript was reviewed by J.J. Leahy and W. Kwapinski, who also acted as discussion partners throughout the research leading to this paper. Chapter 6 of this thesis corresponds to the paper published in Elsevier’s Bioresource Technology journal.
6.1 Introduction

The disposal of MSW is an ever-increasing problem in the European Union (EU) and other developing countries (Pires et al. 2011; Guerrero et al. 2013, 2013). Due to strict environmental standards, current solid waste management practices (landfills, incineration) are under intense examination and innovative technologies are becoming attractive alternative options (Pires et al. 2011). There are several alternatives to dispose MSW including thermal, biochemical and mechanical processes. Incineration has been extensively used in the EU and other developed countries including Japan and Singapore for disposal and energy recovery from the wastes (Narayana 2009). However, the flue gases from the waste incinerators contains high amount of particulate matter, NOx, SOx, dioxins and furans (Cheng and Hu 2010). Apart from the high amount of emissions, incineration systems have high operating cost with relatively lower energy efficiency (Arena 2012). One attractive thermal alternative to incineration is the MSW gasification. The gasification process can generate the electricity from the waste with an efficiency of 34% compared to incineration process, which has thermal efficiency around 20% (Murphy and McKeogh 2004). It has been suggested that gasification is a viable technology for processing solid wastes, including MSW, while complying with present emission standards (Arena 2012). This also offers an alternative solution to the landfilling option. Compared to other treatment processes, gasification technology is an attractive solution for the treatment of MSW while simultaneously minimising pollution (Malkow 2004; Xiao et al. 2007). The derived syngas from MSW gasification can be used to generate heat and electricity, which will help to offset the use of fossil fuels.

Gasification is the thermal conversion process of any carbonaceous fuel to a gaseous product with useable heating value. It is commonly performed with only a third of the oxygen necessary for complete combustion. Gasification includes pyrolysis, partial oxidation and hydrogenation whereas the dominant process is partial oxidation (Higman and Van der Burgt 2011), resulting in gaseous products (hydrogen, carbon monoxide, carbon dioxide, water and other gaseous hydrocarbons), and a small amount of char, ash and condensable compounds (tars).
Air, steam or oxygen can be used as a gasifying agent. For solid fuel combustion, gasification reactors can be categorised into three distinctive types: fixed bed (updraft and downdraft), fluidised bed and entrained flow gasifiers (Higman and Van der Burgt 2011).

Biomass gasification is a complex thermochemical process (Puig-Arnavat et al. 2010). In the recent past, numerous researchers have tried to simulate a realistic gasification process and optimised the process analysis to make it more cost effective. Most of the fluidised bed (FB) biomass gasifier models fit reasonably well with the experiments selected for validation using various empirical correlations. However, there are very few measurements available for detailed validation specifically for large scale gasifiers (Gómez-Barea and Leckner 2010). Since conducting large scale gasification experiments are quite expensive and time consuming, modelling can be a viable alternative which saves both time and money. However, simulation of MSW processes are computationally expensive and fast meta-models are required to integrate these models into other systems level models which look at the whole value chain to conduct life cycle analysis, or other system level optimisation procedures. In general, mathematical models are exploited to investigate the influence of the main process parameters on calorific value and yield of the product gas. Irrespective of the type of reactors, several modelling techniques such as thermodynamic equilibrium models, kinetic rate models, Aspen Plus based models and artificial neural networks (ANN) have been implemented for gasification systems (Puig-Arnavat et al. 2010). The artificial intelligence techniques such as ANN, GP etc. demands less system information compared to equilibrium and kinetic based modelling, hence, these techniques can be useful for modelling FB gasifiers. In view of the complexity involved with the gasification process, a novel artificial intelligence paradigm known as GP has been used to model the gasification system in the present study. The main objective of the present study is to show the application of the GP approach in predicting syngas yield and heating value. To the best of the author’s knowledge this is the first study using the multi-gene GP technique to predict the LHV and yield of syngas produced from MSW.
In the recent past, ANN techniques have been extensively used by several researchers in the fields of pattern recognition, signal processing, function approximation, weather prediction and process simulations (Guo et al. 1997). Lately it has also received attention as a tool in renewable energy system prediction and modelling (Kalogirou 2001). A back propagation neural network using the Levenberg–Marquardt (LM) algorithm has been applied to a hybrid upflow anaerobic sludge blanket reactor to predict the bio-degradation and bio-hydrogen production using distillery wastewater (Sridevi et al. 2014). A hybrid neural network model was developed for predicting the product yield and gas composition in an atmospheric steam blown fluidised bed gasifier. The authors tested four different kinds of biomass on a bench scale gasifier for training the hybrid neural network model. This study revealed that the feed forward neural network prediction was better than the traditional regression models (Guo et al. 2001). A feed forward neural network model was used to predict the LHV of MSW from its chemical composition. It was concluded that the neural network model has better precision over the traditional model (Dong et al. 2003). A combined non-stoichiometric equilibrium approach with an ANN regression model was developed to predict product composition in an atmospheric air gasification fluidised bed reactor (Brown et al. 2006). A complete set of stoichiometric equations were formulated to explain the non-equilibrium behaviour for gas, tar, and char formation by reaction temperature difference. The ANNs regression related temperature differences to fuel composition and operational variables. This first principle approach, illustrated with FB data, improves the accuracy of the equilibrium based model and reduces the data requirement by preventing neural network to learn from atomic and heat balances (Brown et al. 2006). The combination of equilibrium and ANNs models were further investigated and improved by the same authors (Brown et al. 2007). An attempt was made to develop an ANN model for predict to gasification characteristics of the MSW (Xiao et al. 2009). Two different ANNs based models were introduced to predict gas production rate and heating value of the product gas in a steady state fluidised bed coal gasifier (Chavan et al. 2012). Recently, two ANNs models were presented (Puig-Arnavat et al. 2013); one for a circulating fluidised bed gasifier and another for a bubbling fluidised bed gasifier for estimating the product gas.
composition (CO, CO$_2$, H$_2$ and CH$_4$) and gas yield. The results show good agreement with the experimental data.

Despite prediction capability of artificial intelligence based techniques, only ANNs have been used in the modelling of FB gasifiers. Very few applications of GP have been reported in recent literature focused on predicting syngas production and the LHV of syngas. An extensive literature review shows that so far only a few studies have been reported where the GP strategy has been employed for the modelling of fluidised bed gasifier.

Recently, the multilayer perceptron neural network model and GP have been used to predict CO+H$_2$ generation rate, syngas production rate, carbon conversion and heating value of the syngas in a pilot-plant scale FB coal gasifier (Patil-Shinde et al. 2014). The output prediction accuracies of the models were indicated by correlation coefficients. The correlation coefficients were lying between 0.92 and 0.996. The authors have claimed that the prediction accuracy of GP model has an advantage over the multilayer perceptron neural network.

### 6.2 Method of GP modelling

GP is an evolutionary approach which automatically evolves computer programs to solve the problem without specifying the structure of the solution in advance (Koza 1992; Poli et al. 2008). GP is a branch of evolutionary algorithms and can be used for development of nonlinear mathematical models based on input-output training datasets. GP is based on the Darwinian principle of natural selection and survival of the fittest. The main advantage of the GP formalism is that it automatically evolves an empirical mathematical model from the input- output datasets. Hence, the GP modelling process does not require the detailed information of process phenomena. The GP technique has been used for symbolic nonlinear regression problems to develop mathematical expressions that provide a good fit between a given set of independent variables and the associated dependent variables (Pan et al. 2013).
Over the years, several models such as thermodynamic equilibrium model, kinetics rate model, pseudo equilibrium model, Aspen Plus based model and artificial intelligence based models have been developed for simulating a gasification system. Among those models, thermodynamic models are the simplest and mostly used for sensitivity analysis of the process parameters. The equilibrium models are independent of gasifier design but their prediction accuracy is not good in all cases. The kinetic rate models are more accurate and computationally intensive. However, their applicability is limited to specific plants (Puig-Arnavit et al. 2010). Most of the chemical process simulation tools like Aspen Plus which build up a model from the first principle’s approach have a higher computational burden. A typical Aspen Plus model which includes the different stages of gasification like drying, devolatilisation, gasification and combustion would take a simulation time of the order of a couple of minutes. However, the problem is compounded in a situation which requires multiple function calls to the model (e.g. incorporating an optimisation algorithm with the Aspen model in the loop). In such cases if say there are a thousand function calls for one optimisation run, then the total computational time would be in the order of days. The multi-gene GP method circumvents this problem since it is an explicit mathematical expression which can be calculated within milli-seconds on a personal computer.

Another advantage of the multi-gene GP method over the other models is that it is a data-driven methodology which relies on experimental data to build models. This eliminates errors due to various assumptions (e.g. considering the reactors as point masses and neglecting their spatial effects, assuming perfect insulation and neglecting heat losses while modelling etc.) which are often employed while building up a differential equation based model.

The GP starts with a high-level statement of the problem and attempts to invent a computer program to solve the problem. The evolved solution variables are represented in the form of genes or trees. At the beginning of the algorithm, the genes or trees are initiated randomly. To accomplish the best possible fitness function, the genes or trees undergo reproduction, crossover and mutation processes. Crossover involves the mutual interchange of genetic material between the parents to
form new offspring. Mutation, refer to random change within the gene i.e. a randomly chosen element is replaced by another element. The nodes of the GP tree are called operator nodes and operand nodes. The operator nodes represent mathematical operators such as addition, subtraction, division, multiplication, etc. while operand nodes define the input variables \(x_i\). The symbolic regression of multi-gene GP is a weighted linear combination of several gene outputs. The multi-gene GP methodology has been used for predicting the toxicity of chemical compounds (Searson et al. 2010). It was concluded that the multi-gene GP model offers an alternative approach to currently accepted empirical modelling and data analysis techniques. The uniqueness of the multi-gene GP based model is that it automatically evolves a mathematical expression in a symbolic form which can be analysed further to find which variables impact the final prediction and in what fashion. Figure 6.1 is a tree representation of a multi-gene GP with output \(y\) and input variables \(x_1, x_2, x_3\). The mutation and crossover operations are also shown diagrammatically in Figure 6.1.
Figure 6.1: Schematic diagram of the tree structure of a multi-gene GP model

For the GP simulation, there are nine process parameters that have been used as model inputs i.e. carbon ($x_1$, wt%), hydrogen ($x_2$, wt%), nitrogen ($x_3$, wt%), sulphur
(\(x_4, \text{wt}\%\)), oxygen (\(x_5, \text{wt}\%\)), moisture content (\(x_6, \text{wt}\%\)), ash (\(x_7, \text{wt}\%\)), equivalence ratio (\(x_8, \text{ER}\)) and the temperature of the gasifier (\(x_9, T^0\text{C}\)). ER is defined as the ratio of actual air to fuel ratio versus stoichiometric air to fuel ratio for complete combustion. The input parameters are represented as an input vector
\[ x_i = [x_1, x_2, x_3, x_4, x_5, x_6, x_7, x_8, x_9] \]
and the output variables are LHV (kJ/Nm\(^3\)) (\(y_1\)) and gas yield (Nm\(^3\)/kg) (\(y_2\)).

Two different models are presented to predict the LHV and gas yield from the biomass composition and process parameters. The experimental data was obtained from literature for wood, paper, kitchen garbage, polyethylene plastic and textile (Xiao et al. 2009) and for Hong Kong MSW (Choy et al. 2004). To check the accuracies and robustness of the model, the experimental dataset is divided for training and testing purposes. From the available data 70% (47 data points) is randomly selected to use for training purposes and the remaining 30% (20 data points) is used for model validation. The performance of the model is compared with experimental data reported by the authors. The input and output datasets are normalised. The mean value of the nine input variable (\(x_i\)) and output variables (\(y_1, y_2\)) are represented by the vector \(\mu_x\) and \(\mu_y\), respectively and is given in equations (6.1) and (6.2).

\[
\mu_x = [43.73 \quad 5.30 \quad 0.27 \quad 0.11 \quad 38.43 \quad 6.96 \quad 2.00 \quad 0.4 \quad 602]
\]
(6.1)
\[
\mu_y = [2146 \quad 1.98]
\]
(6.2)

Similarly, their corresponding standard deviations are given by \(\sigma_x\) and \(\sigma_y\) in equations (6.3) and (6.4).

\[
\sigma_x = [21.52 \quad 3.85 \quad 0.58 \quad 0.08 \quad 16.72 \quad 28.63 \quad 5.84 \quad 0.17 \quad 96.68]
\]
(6.3)
\[
\sigma_y = [2126.57 \quad 1.67]
\]
(6.4)
6.2.1 Parameter setting of GP algorithm

For the GP simulations, the population size and the maximum number of generations are set as 100 and 1000 respectively. For selecting the parent genes from the pool of available solutions, a tournament selection strategy is adopted. The tournament size is set to 3. The maximum depth of each tree in the multi-gene representation is set to 5 to allow some control over the complexity of the developed expressions. The set of instructions or functions used for symbolic regression are \(\{+, -, \times, \div, \sin, \cos, (.)^2, \exp, \log\}\). The crossover, mutation and direct reproduction probabilities are taken as 0.85, 0.1 and 0.05 respectively. The multi-GP simulations are compared with a single-gene GP algorithm. The details of both GP variants are given in Table 6.1. For single- gene GP the number of trees \(T\) is set to one.

**Table 6.1**: Parameter settings for the multi-gene GP and single-gene GP variants

<table>
<thead>
<tr>
<th>GP Algorithm parameters</th>
<th>Parameter settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Population size</td>
<td>100</td>
</tr>
<tr>
<td>Number of generation</td>
<td>1000</td>
</tr>
<tr>
<td>Selection method</td>
<td>Plain lexicographic tournament selection</td>
</tr>
<tr>
<td>Tournament size</td>
<td>3</td>
</tr>
<tr>
<td>Termination criteria</td>
<td>1000 generation or fitness value less than 0.00001 whichever is earlier</td>
</tr>
<tr>
<td>Maximum depth of tree</td>
<td>5</td>
</tr>
<tr>
<td>Maximum number of trees in an individual (for multi-gene GP only)</td>
<td>15</td>
</tr>
<tr>
<td>Mathematical operations</td>
<td>({+, -, \times, \div, \sin, \cos, (.)^2, \exp, \log})</td>
</tr>
</tbody>
</table>
6.3 Results and Discussion

6.3.1 Multi-gene GP based model for LHV calculation

Figure 6.2 shows the final population of the GP run for LHV, presenting the trade-off between the precision of the fit and the complexity of the evolved multi-gene GP solutions. The optimal evolved models fall on the curve of a non-dominated solution called the Pareto front. The blue dots represent the set of dominated solutions and those in green are the set of non-dominated solutions on the Pareto front. From the Pareto front, user can decide whether the incremental gain in performance is worth with associated model complexity. Three solutions A, B, and C on the Pareto front are selected based on their corresponding accuracies and model complexities. The solutions are indicated by arrows in the top right Figure 6.2.

Figure 6.2: The Pareto front and convergence of the multi-gene GP solutions for LHV calculation (top row) and syngas yield production (bottom row)

Figure 6.2 also depicts the convergence characteristics of the GP algorithm. It is evident that the mean fitness of the curve becomes smoother after 500 generations and that the change in objective function is not significant near the end of the GP run. It indicates that running the GP for more generations does not result in a more favourable outcome. However, as the best fitness is reported at 971 in this particular
case, it suggests that the GP algorithm should have to run for at least 1000 generations.

Figure 6.3 show twelve subplots (a1-c2) which indicates the correlation coefficient ($R^2$) and root mean squared error (RMSE) on the training and testing datasets. The subplots are representing the number of data points used in this study for predicting the output variables ($y_1 - y_2$). Solution A in Figure 6.3(a1) shows the best fit for the LHV calculations amongst the other solutions on the Pareto front, but it also involves the highest model complexity as compared to the other solutions B and C. The evolved regression equation for Solution A is given by (6.5):

$$y_1 = 0.4047 \sqrt{(x_4 \cos(x_4))(x_9 - x_5)} - 3.937 \cos\left(\cos\left(x_5 \cos(x_4)\right)\right)$$

$$+ 0.2127 e^{x_6} (x_4 - x_8 x_4^2) + 0.289 x_4 e^{x_6} \cos(x_8^{1/4}) + 0.1625 (x_2 - x_8)^2 (\cos(x_6))^2 x_5^2 (x_2 + x_6) + 2.717$$

(6.5)

The regression equation of Solution B (slightly less complex) as evolved by the GP algorithm is given by (6.6)

$$y_1 = 0.1565 \sqrt{e^{x_6} (x_5 - x_8 x_4^2)} - 4.149 \cos\left(\cos\left(x_5 \cos(x_4)\right)\right) - 0.2079 \log\left(\sin(x_6)\right)$$

$$+ 0.2297 \sqrt{e^{x_6} (x_4 - \cos(x_4)) x_4^2} + 0.1259 (x_2 - x_8)^2 x_4 x_5^2 (x_2 + x_6) + 2.459$$

(6.6)
Figure 6.3: Prediction results of the multi-gene GP solutions with $R^2$ and RMSE on the training and the testing datasets: LHV prediction Solution A (a1), Solution B (b1), Solution C (c1) and syngas yield production Solution A (a2), Solution B (b2), Solution C (c2)

On the other hand, the models of solution B and solution C are less complex but at the same time their prediction capability is poorer as compared to solution A. Nevertheless, the prediction capability of model B is more than 95% and 57% on the training and testing datasets respectively. However, the prediction accuracy of model C is over 80% on the training dataset and just over 33% on the validation set suggesting that solution C has been over simplified. This clearly indicates that the decrease in model complexity not only deteriorates the model prediction capability on the training data but also the model does not fit well to unseen data.

The regression equation for Solution C (the simplest expression) as evolved by the GP algorithm is given by (6.7).

$$y_i = 0.1862(x_2 - x_8)^2(\cos(x_8))^2 x_5^2 (x_2 + x_6) - 6.472\cos(x_5\cos(x_4)) + 4.723 \quad (6.7)$$

The prediction accuracies and generalised performance of each model is tested between the experimental data and model predicted values. The model that performed the best on training and testing data is selected on the basis of $R^2$ and
RMSE. Figure 6.4(a1-c1) shows the multi-gene GP model predicted versus actual data and their R\(^2\) values on the training and testing data sets for the three solutions A, B and C respectively. It can be observed that Solution A has less than 3% error in prediction of training dataset. Also, the evolved model shows good agreement with the testing data. The correlation coefficient and root mean squared error of the multi-gene GP based model for LHV prediction are listed in Table 6.2.

![Figure 6.4](image)

**Figure 6.4:** Prediction results of the multi-gene GP solutions with R\(^2\) on the training and the testing datasets: LHV prediction Solution A (a1), Solution B (b1), Solution C (c1) and syngas yield production Solution A (a2), Solution B (b2), Solution C (c2)

As a summary, solution A has the best fitness over solution B and C but is more complex as well. The prediction accuracy of solution A and B for the performance variable \(y_1\) shows good agreement with their experimental counterparts on the training data set. It demonstrates that multi-gene GP can be exploited to simulate the complex thermochemical processes such as FB gasifiers.
6.3.2 Multi-gene GP based model for syngas yield production

In this model, the same strategy is used as explained in the previous case. Based on the complexity and fitness three different solutions are selected as shown in Figure 6.2(bottom). As explained in section 6.3.1, it can be seen from the Figure 6.2(bottom) that the mean fitness of the convergence curve is not changing significantly after 600 generations. On the other hand the best fitness of the GP algorithm is reported at 991 generations.

Figure 6.3(a2-c2) show the $R^2$ and RMSE on training and testing dataset for solution A, B and C respectively. It can be observed that solution A shows an excellent predictive ability in the training data; however, the prediction capability is poorer over the unseen data (validation). It indicates that model A is suffering from the over-fitting problem of the training data set. On the other hand, solution B and C have very good prediction accuracies on both the training and validation data sets. The regression equation of Solution A as evolved by the GP algorithm for the Syngas yield prediction is given by (6.8).

$$y_2 = 0.8001x_1 + 0.1986x_3 + 0.001104x_4 + 0.799x_8 + 0.2354\sin(x_4 - x_5) + 0.2354\cos\left(\frac{x_1 + x_5}{x_4}\right) + 0.2732x_8\left(\log(x_7) + \frac{x_2}{x_7 - x_5}\right) - 0.05691(0.2266x_8 - 0.2266x_9)(x_8 + 4.382) - \frac{0.05691\left(\log(x_7) - (x_8)^2\right)}{2x_7 + 4.375} - \frac{0.001104(x_5 - x_4)}{x_8} - \frac{0.1986(x_4 - x_8)(x_4 - x_5)}{x_9 + 4.3} - \frac{0.001104(x_8 + 0.1765)(x_9 + 0.1765)}{(x_3 - x_4)^2} - 0.01526$$

(6.8)

The regression equation of Solution B as evolved by the GP algorithm for gas yield prediction is given by (6.9).
\[ y_2 = 0.7994x_1 + 0.1956x_3 + 0.7994x_8 + 0.2352\sin(x_4 - x_3) + 0.2352\cos\left(\frac{x_1 + x_8}{x_4}\right) \]

\[ + 0.266x_4\left(\log(x_7) + \frac{x_2}{x_4 - x_5}\right) - 0.06401(0.2266x_8 - 0.2266x_9)(x_8 + 4.382) - \]

\[ 0.008318x_8\left(\log(x_7) - \frac{x_2}{x_8}\right) - 0.06401\left(\frac{\log(x_8) - (x_4)^2}{2x_4 + 4.375}\right) \]

\[ - \frac{0.1956(x_4 - x_7)(x_4 - x_8)}{x_8 + 4.3} - 0.01241 \]

(6.9)

The regression equation of Solution C as evolved by the GP algorithm for gas yield prediction is given by (6.10).

\[ y_2 = 0.7784x_1 + 0.1748x_3 + 0.7784x_8 + 0.229\sin(x_4 - x_3) + 0.229\cos\left(\frac{x_1 + x_8}{x_4}\right) \]

\[ + 0.277x_8\left(\log(x_7) + \frac{x_2}{x_4 - x_5}\right) + \frac{0.02553x_2(x_4 - x_8)}{x_8 + 4.3} - \frac{0.2003(x_4 - x_7)(x_4 - x_8)}{x_8 + 4.3} - 0.004875 \]

(6.10)

Concisely, the multi-gene GP paradigm evolves multiple models which provide more number of choices to the designer. A single model can be selected based on the application requirements. It is evident that solution A (Figure 6.3a2) suffers from the over-fitting problem. Hence, the selection of the model must be carried out on the basis of the application. In cases where the model is used for predicting the data which is already present in the training data set, using model A is advisable, as it gives a better prediction on the training datasets. On the other hand, if the model is used to predict the syngas yield for untrained datasets then solution B or C may be used, since they show a better prediction capability on unseen (test) or untrained datasets. Figure 6.4(a2-c2) shows the prediction accuracy of the multi-gene GP model for syngas yield production. It is noticed that the multi-gene GP based model for syngas yield production shows slightly better accuracy to that possessed by the multi-gene GP model for LHV prediction.
6.3.3 Multi-gene GP algorithm and comparison with single-gene GP model

This section focuses on comparing the results obtained using multi-gene GP algorithm with single-gene GP. It is well known that the back propagation ANNs techniques often get stuck in local minima without having learned the entire dataset (Gori and Tesi 1992). However, the GP technique uses an evolutionary approach in which the model exchanges their information through mutation and crossover. This characteristic helps GP to converge at global minima and get out of local minima.

6.3.3.1 Comparison of multi-gene GP and single-gene GP model for LHV

Figure 6.5 shows the Pareto plot of single-gene GP depicting the trade-off between fitness vs. complexity. The convergence characteristic of single-gene GP algorithm is shown in Figure 6.5(top) for predicting the LHV of the syngas. The actual vs predicted value of LHV and Syngas yield production from the best single-gene GP based solution on training and testing data are reported in Figure 6.6(top). In the case of LHV prediction, single-gene GP algorithm is fitting over 83% and 34% on training and testing datasets. The best single-gene GP based regression equation (as indicated by the red circle in Figure 6.5(top) for LHV prediction is (6.11).

\[
y_{1} = 0.1925x_{0} - 0.1925x_{6} + 0.1925\left( \frac{x_{4}}{x_{3}} \right)^{2} + 0.1925e^{\frac{x_{8}}{x_{6}}} - 0.1925x_{7}x_{8} - 0.6675 \quad (6.11)
\]

The RMSE and $R^2$ of the multi-gene GP and the single-gene GP solutions are reported in Table 6.2. The RMSE and $R^2$ values reported in Table 6.2 are useful while selecting the model. For predicting the LHV, the mean fitness and model complexity of the single-gene GP algorithm reported in Figure 6.5(top) are poor compared to the multi-gene GP algorithm in Figure 6.2(top) for the best case. It is evident that the percentage fit of the single-gene GP based solution is not better than multi-gene GP based solutions A and B. However, it is worth mentioning that the best single-gene GP algorithm shows better prediction capability over solution C.
This shows that decreasing the model complexity lessens the model prediction capability.

**Figure 6.5:** The Pareto front and convergence of the best single-gene GP solution for LHV calculation (top row) and syngas yield production (bottom row)

**Figure 6.6:** Prediction results of the best single-gene GP solution with $R^2$ and RMSE on the training and the testing datasets: for the LHV (top) and syngas yield production (bottom)
Table 6.2: Statistics of the best solutions of two GP variants for LHV prediction and syngas yield production

<table>
<thead>
<tr>
<th>Goodness of Fit</th>
<th>Multi-gene GGP</th>
<th>Single-gene GP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solution A</td>
<td>Solution B</td>
</tr>
<tr>
<td>RMSE Training</td>
<td>0.03191</td>
<td>0.04211</td>
</tr>
<tr>
<td>RMSE Testing</td>
<td>0.14595</td>
<td>0.1655</td>
</tr>
<tr>
<td>R² (%) Training</td>
<td>97.1826</td>
<td>95.0938</td>
</tr>
<tr>
<td>R² (%) Testing</td>
<td>66.7885</td>
<td>57.2921</td>
</tr>
</tbody>
</table>

Apart from the statistics of the two GP variants, the mean and standard deviation of the best solution for 30 independent runs are reported in Table 6.3. The mean and standard deviation of the best solutions clearly show that the multi-gene GP algorithm consistently converges to a better fit than the single-gene GP.

Table 6.3: Statistics of the best solution for 30 independent runs of two GP variants for LHV prediction and syngas yield production

<table>
<thead>
<tr>
<th>Algorithm</th>
<th>Mean (μ)</th>
<th>Standard deviation (σ)</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multi-gene GP for LHV prediction</td>
<td>0.050605</td>
<td>0.010224</td>
<td>0.031911</td>
</tr>
<tr>
<td>Single-gene GP for LHV prediction</td>
<td>0.116638</td>
<td>0.025553</td>
<td>0.076058</td>
</tr>
<tr>
<td>Multi-gene GP for Syngas yield production</td>
<td>0.013192</td>
<td>0.00331</td>
<td>0.006521</td>
</tr>
<tr>
<td>Single-gene GP for Syngas yield production</td>
<td>0.041831</td>
<td>0.015197</td>
<td>0.020957</td>
</tr>
</tbody>
</table>
6.3.3.2 Comparison of multi-gene GP and single-gene GP model for syngas yield production

As explained in the Section 6.3.3.1, a similar trend is observed in the case of yield prediction as well. The Pareto front of the evolved single-gene GP solution showing the fitness and accuracy of the model is given in Figure 6.5(bottom). Figure 6.6(bottom) shows that the single-gene GP model is in good agreement with training and validation data. The percentage fit of single-gene GP prediction for training and testing data is close to 98% and 95% respectively. However, the comparison clearly shows that the multi-gene GP evolved solutions are more accurate and can be applied more generally over the single-gene GP solutions. Similarly, the mean fitness of the convergence curve single-gene GP algorithm in Figure 6.5(bottom) is not better than the mean fitness reported in Figure 6.2(bottom). The single-gene GP based regression equation for gas yield prediction is (6.12),

\[
y_2 = 0.1638x_2 + 0.1638x_8 + 0.1638\sin(x_2 + x_8) + 0.1638\log(x_4) + 0.1638e^{x_1}(x_1 + x_4 + x_8) - 0.06335
\]

The comparative analysis of three different multi-gene GP solutions with single-gene GP is reported in Table 6.2. It can be seen from the Table 6.2 that multi-gene GP based algorithms show better fitness over single-gene GP based formalism on both training and testing datasets. It is reported that the $R^2$ value of single-gene GP model on the testing data is over 94% compared to Solution A. This indicates that the Solution A is over-fitted in the training phase. However, multi-gene GP based Solutions B and C show improved fitness on the both training and validation dataset compared to single-gene GP algorithm. Hence, $R^2$ and RMSE of the training and validation (testing) dataset will be helpful while choosing the best model for the prediction.

The mean and standard deviation of the best solution of single-gene GP and multi-gene GP algorithm for 30 independent runs are reported in Table 6.3. The mean and standard deviation of the best solutions clearly show that the multi-gene GP algorithm consistently converges to a better fit than the single-gene GP.
6.4 Conclusion

In this study, a multi-gene GP based mathematical model is developed to predict the gas yield and LHV of the syngas produced from the wastes during FB gasification using their physio-chemical characteristics and a few process parameters. The multi-gene GP models show better performance ($R^2 > 97\%$ for LHV and 99.8\% for Syngas yield production) over the single-gene GP model ($R^2 \approx 83\%$ for LHV and 97.9\% for Syngas yield production). The accuracies of the predicted values using the multi-gene GP approach are in good agreement with experimental data. The results of this work are encouraging and will be used to model other similar gasification processes.
6.5 References


7 Conclusions and future recommendations

7.1 Conclusions

In this dissertation, an experimental and modelling study was conducted to evaluate poultry litter and MSW as potential fuels for gasification. This section presents the summary and conclusion of gasification as an alternative approach to animal manure (poultry litter) and solid waste management with the following major findings and recommendations for future work.

In chapter three, experimental research work on laboratory scale bubbling fluidised bed gasification revealed that poultry litter could be successfully gasified without any agglomeration problems. The optimum operating conditions were identified based on gasifier performance and the quality of the product gas. The optimum conditions (maximum carbon conversion, gas yield, heating value and cold gas efficiency) was achieved at an ER 0.25 and 800 ºC, using air (SBR=0) and poultry litter blended with 8% w/w limestone, yielding a product gas with a lower heating value (LHV) of 4.52 MJ/Nm³ which could be combusted to generate power and heat. The most significant issue related to gasifying high ash content feedstocks (poultry litter) in a fluidised bed gasifier is agglomeration and this was resolved by adding limestone.

In chapter four, a new approach called a “pseudo equilibrium model (PEM)” complemented with experimental data was developed since the equilibrium model was unable to provide accurate results. An equilibrium model in general always over predicts H₂ and CO, under predicts CO₂ and the product gas is almost free of CH₄, tar and char. The objective of the proposed model was to simulate the real gasification process where only partial equilibrium conditions can be achieved. Light hydrocarbons were represented by CH₄ to simplify the model. In addition, char conversion and a water-gas shift reaction equilibrium factor was introduced. The fact that CH₄ is formed as a result of devolatilisation and using a semi empirical correlation for CH₄ formation improve the performance of the modified model. The developed model was then validated with published experimental data. The results show that the predictive accuracy of PEM improved compared to the equilibrium
model. Furthermore, sensitivity analysis was performed to evaluate the influence of ER, temperature and steam injection.

In chapter five, multi-layer feed forward neural networks were used to predict the LHV, LHV$_p$ and syngas yield during gasification of MSW in a fluidised bed reactor based on published experimental data. A simple and rigorous ANN approach was also developed for deciding hidden layers, number of neurons in the hidden layer and activation function in a network using multiple Monte Carlo simulations. The model was developed to test the prediction capability of the ANN model for gasification. The performance of the developed network was determined by coefficient of determination (R$^2$) and mean squared error (MSE). The reported accuracy of the trained ANN models for single layer and for double layer was close to 98% and 99% respectively. The results obtained from MIMO and MISO model are promising and it demonstrated capability that it can handle complex non-linear problems. Another advantage of these models is their flexibility to be easily extended for other types of feedstocks/process.

In chapter six, a data-driven evolutionary algorithm was developed for the modelling of MSW gasification in a fluidised bed gasifier. The developed models (multi-gene genetic programming and single-gene genetic programming) were used to predict the LHV and yield of syngas produced from MSW nonlinear gasification systems. The novelty of the genetic programming approach is that it automatically evolves the best computer model that best fits the given datasets (perform pre-defined tasks). Additionally, a genetic programming based modelling strategy provides analytical expressions which can provide an insight regarding whether the selected feedstock would be the appropriate fuel for gasification or not.

In conclusion, gasification is an alternative disposal approach to animal waste and urban waste (solid waste) management. It not only produces clean and renewable energy but also overcomes environmental issues associated by landfills. Furthermore, the solid by-product of animal manure gasification (ash and unreacted carbon/char) can replace commercial mineral fertiliser making agriculture systems more sustainable while reducing greenhouse gas emissions.
However, research on utilising the by-products from gasification is still limited and extensive research work is needed to understand the fate of heavy metals and other contaminants present in ashes. Gasification has shown great potential to treat animal and urban waste but further research is required before gasification could be implemented on a large scale.

### 7.2 Future recommendations

Based on the results of the present experimental and modelling study, the following recommendations are suggested for future work:

- Poultry litter was gasified in a bubbling fluidised bed gasifier. I have experienced the agglomeration issues while gasifying poultry litter. Therefore, an agglomeration problem aspect has to be considered for designing and optimisation of thermochemical conversion.

- A farm-scale study is needed to see the effect of by-products of gasification on soil properties, nutrient leaching, plant growth and long term greenhouse gas emissions. It would be interesting to investigate the nutrient leaching results on plant growth as well as fate of other alkali metals.

- Possible synergies should be identified i.e. co-gasification of high ash content feedstock with other fuels and comparing gasification with other thermochemical (pyrolysis, oxy-combustion) and biological e.g. anaerobic digestion processes etc.

- In addition to energy recovery from bio waste, life cycle analysis of gasification system should be estimated.

- In this study, experiments were performed in an allothermal bubbling fluidised bed gasifier. Autothermal on farm plant for medium scale poultry litter gasification would have better practical significance and should be
explored based on lessons learned in this project. A techno-economical evaluation of the process, comparison with other biomass and tar and inorganics removal from product gas (for electricity productions) would be very useful. The ash build up problem in the reactor must be investigated in order to see if reaction zone stabilised with ash/char removal system.

- A thermodynamic equilibrium model was used in the first phase of this study for estimating the product gas composition. A pseudo-equilibrium model tuned with experimental empirical equations was subsequently developed. Although, existing empirical correlation improved the accuracy of the product gas composition, a more comprehensive model with a chemical kinetics and hydrodynamics is needed because relatively few reactions are kinetically controlled at lower temperature (below 1000 °C). Therefore, it is of utmost importance to understand char reactivity and the gasification residence time (fluid-dynamics) would help in scale-up the process. In addition, the integration of gasification with combined heat and power generation unit or Biorefinery option with ethanol production should be analysed.

- This study also exploits the potential application of ANN and GP approaches in fluidised bed gasifiers. However, as with any supervised learning method, the model developed is highly dependent on the dataset that is used to train the model. Therefore, new experimental datasets with different operating conditions and feedstock should be used in order to ensure that the approach will work in a wider range of datasets.
Appendix 1. Fundamental data used for the calculations

Table A1. HHV and LHV value of product gas species used in the HHV and LHV calculations of the product gas (Lars and Torbjörn 2011)

<table>
<thead>
<tr>
<th>Gas</th>
<th>H2</th>
<th>CH4</th>
<th>CO</th>
<th>C2H4</th>
<th>C2H6</th>
<th>C2H2</th>
<th>C6H6</th>
<th>C7H8</th>
<th>H2S</th>
<th>COS</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV, MJ/Nm³</td>
<td>12.78</td>
<td>39.80</td>
<td>12.63</td>
<td>63.04</td>
<td>69.73</td>
<td>58.09</td>
<td>142.98</td>
<td>176.37</td>
<td>25.11</td>
<td>24.71</td>
</tr>
<tr>
<td>LHV, MJ/Nm³</td>
<td>10.79</td>
<td>35.84</td>
<td>12.63</td>
<td>59.07</td>
<td>63.79</td>
<td>56.11</td>
<td>141.50</td>
<td>168.51</td>
<td>23.15</td>
<td>24.71</td>
</tr>
</tbody>
</table>

Table A2. The density of product gas species used in the calculations (Green and Perry 2007)

<table>
<thead>
<tr>
<th>Gases</th>
<th>Density, kg/Nm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.0899</td>
</tr>
<tr>
<td>N2</td>
<td>1.2493</td>
</tr>
<tr>
<td>CH4</td>
<td>0.7170</td>
</tr>
<tr>
<td>CO</td>
<td>1.2501</td>
</tr>
<tr>
<td>CO2</td>
<td>1.9658</td>
</tr>
<tr>
<td>C2H4</td>
<td>1.2586</td>
</tr>
<tr>
<td>C2H6</td>
<td>1.3515</td>
</tr>
<tr>
<td>C2H2</td>
<td>1.1100</td>
</tr>
<tr>
<td>O2</td>
<td>1.4285</td>
</tr>
<tr>
<td>NH3</td>
<td>0.7690</td>
</tr>
<tr>
<td>Ar</td>
<td>1.7834</td>
</tr>
</tbody>
</table>


Appendix 2. Computational time

A typical Aspen Plus model which includes the different stages of gasification like drying, devolatilisation, gasification and combustion would take a simulation time of the order of a couple of minutes.

<table>
<thead>
<tr>
<th>Modelling strategy</th>
<th>Modelling Approach</th>
<th>Computational time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Training time</td>
<td>Testing time</td>
</tr>
<tr>
<td>ANN</td>
<td>MISO</td>
<td>18 hrs</td>
</tr>
<tr>
<td></td>
<td>MIMO</td>
<td>190 hrs</td>
</tr>
<tr>
<td>GP</td>
<td>Single-gene GP</td>
<td>5-8 min</td>
</tr>
<tr>
<td></td>
<td>Multi-gene GP</td>
<td>8-12 min</td>
</tr>
<tr>
<td>Aspen Plus</td>
<td>-</td>
<td>couple of minutes</td>
</tr>
</tbody>
</table>