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.
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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;
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 (SiO₂ 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 \( \text{K}_2\text{O} - \text{CaO} - \text{SiO}_2 \). 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/m³, 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$^\phi$ (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, $^\phi$ containing water and ethanol extractives.

The composition of poultry litter can be represented by the empirical formula \(\text{CH}_{1.40}\text{O}_{0.42}\text{N}_{0.10}\) (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>SiO$_2$</td>
<td>35.67</td>
<td>TiO$_2$</td>
<td>32</td>
</tr>
<tr>
<td>P$_2$O$_5$</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>SO$_3$</td>
<td>11.90</td>
<td>Cr$_2$O$_3$</td>
<td>3.7</td>
</tr>
<tr>
<td>MgO</td>
<td>9.23</td>
<td>MoO$_3$</td>
<td>2.7</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>5.27</td>
<td>V$_2$O$_5$</td>
<td>2.1</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>3.32</td>
<td>SeO$_3$</td>
<td>1.5</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2.40</td>
<td>HgO</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1.51</td>
<td>PbO</td>
<td>0.57</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.37</td>
<td>As$_2$O$_3$</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/flare 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 °C 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 °C 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 ≤ \textit{T}_{g} ≤ 800 °C), equivalence ratios (0.18 ≤ \textit{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)

\begin{align*}
\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)} \quad (3.1) \\
\text{SiO}_{2(s)} + 2\text{KOH}_{(g)} & \leftrightarrow \text{K}_2\text{SiO}_3(l) + \text{H}_2\text{O}_{(g)} \quad (3.2)
\end{align*}

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)

\begin{equation}
\text{CaO}_{(s)} + \text{SO}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{CaSO}_{4(g)} \quad (3.3)
\end{equation}

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

\begin{equation}
\text{P}_2\text{O}_5(g) + 3\text{CaO}_{(s)} \leftrightarrow \text{Ca}_2\text{P}_2\text{O}_8(s) \quad (3.4)
\end{equation}
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)

\[ 2ACL_{(g)} + SO_{3(g)} + H_2O_{(g)} \leftrightarrow A_2SO_{4(s,l)} + 2HCl_{(g)} \]  (3.7)

### 3.2.4 Measurement methods

The composition (CO, CO₂, C₂H₂, CH₄, C₂H₄, C₂H₆, 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).

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

\[
\text{CCE}\left(\eta_{Cc}\right) = \left(\frac{C_{o,dry\ gas}}{C_{i,daf}}\right) \times 100
\]
\[ HCE(\eta_{bc}) = \left( \frac{H_{o,\text{dry gas}}}{H_{i,\text{daf}}} \right) \times 100 \]  \hspace{1cm} (3.11)

Where, \( m_f \) is the feed rate of solid fuel, \( m_g \) is product gas flow rate in kg/hr, \( LHV_g \) and \( LHV_i \) 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).

\[ U_{fl} = \left( \frac{\text{actual volumetric feed gas flow rate}}{\text{cross-sectional area of the bed}} \right) = \left( \frac{\dot{m}_g \times T_{\text{process}} \times P_{\text{atm}}}{A_{\text{bed}} \times 273.15 \times P_{\text{process,abs}}} \right) \]  \hspace{1cm} (3.12)

where, \( U_{fl} \) is superficial fluidisation velocity in m/s, \( \dot{m}_g \) is product gas flow rate in Nm\(^3\)/s, \( T_{\text{process}} \) is the gasifier temperature in the bed in Kelvin, \( P_{\text{atm}} \) is atmospheric pressure in bar, \( A_{\text{bed}} \) is cross section area of the bed m\(^2\), \( P_{\text{process,abs}} \) 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>
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<td>0.094</td>
<td>0.095</td>
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<td>0.24</td>
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<td>0.22</td>
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</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\textsubscript{2} free basis. At higher ER, N\textsubscript{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 N₂ 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.

![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)](image)

**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 °C which might be due to calcination of CaCO₃ 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 CaCO₃ is possible in this temperature range provided the concentration of CO₂ in gas phase is low (e.g. 3.5% at 700 °C). The TGA analysis was performed under a nitrogen atmosphere which could provide a compatible condition for CaCO₃ 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 3.4: Experimental test results

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<td>42.9</td>
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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)
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 $\text{C}_2\text{H}_2$ and $\text{C}_6\text{H}_6$ when poultry litter was blended with limestone. Moreover, reported errors are well within the acceptable range ($\approx 3\%$). The total gas yield remained stable (between 1.15 and 1.12 Nm$^3$/kg$_{daf}$) while the LHV dropped from 4.72 to 2.91 MJ/Nm$^3$. 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% ($58.51 \text{ g/kg}_{daf}$) 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% ($98.27 \text{ g/kg}_{daf}$).

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°C and an ER $\approx 0.30$ (experiment numbers 3 and 5). As shown in Table 3.4, the concentration of H$_2$S 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°C and an ER of 0.35. Nevertheless, at elevated temperature (750°C 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
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 ºC. 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 N\textsubscript{2} free basis)

Since, the product gas yield is reported on an N\textsubscript{2} 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\textsubscript{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 H\(_2\): 10.78%, CO: 9.38%, CH\(_4\): 2.61 and CO\(_2\): 13.13 and LHV of 4.52 MJ/Nm\(^3\). 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 N\(_2\) 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 CO\(_2\) and H\(_2\)O, 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 H\(_2\)) 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 Nm$^3$/kg$_{daf}$ vs 0.41 Nm$^3$/kg$_{daf}$) when compared with no steam injection at ER of 0.28 and temperature of 750 °C. It is found that H$_2$ and CO$_2$ concentration increases with steam injection while CH$_4$ 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 H₂ yield in the gas, SBR does not have influence much the LHV as compared to other parameters analysed, probably because the increase in H₂ is outweighed by the decrease in CO and CH₄. 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 C₂H₆, C₆H₆ and C₇H₈. 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 authothermal 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, NH$_3$, 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) $\sum_{i=1}^{n} M_i = \sum_{j=1}^{n} M_j$ 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</td>
<td>Output</td>
<td>Rel. Error (%)</td>
</tr>
<tr>
<td>C (kg/hr)</td>
<td>0.234</td>
<td>0.224</td>
<td>-4.16</td>
</tr>
<tr>
<td>H (kg/hr)</td>
<td>0.044</td>
<td>0.043</td>
<td>-3.04</td>
</tr>
<tr>
<td>O (kg/hr)</td>
<td>0.433</td>
<td>0.436</td>
<td>0.81</td>
</tr>
<tr>
<td>N (kg/hr)</td>
<td>0.734</td>
<td>0.680</td>
<td>-7.34</td>
</tr>
<tr>
<td>S (kg/hr)</td>
<td>0.004</td>
<td>0.003</td>
<td>-15.30</td>
</tr>
<tr>
<td>Cl (kg/hr)</td>
<td>0.002</td>
<td>0.001</td>
<td>-37.03</td>
</tr>
<tr>
<td>Ash (kg/hr)</td>
<td>0.091</td>
<td>0.089</td>
<td>-2.76</td>
</tr>
</tbody>
</table>

where,

\[
\text{relative error} = \left( \frac{\text{input} - \text{output}}{\text{input}} \right) \times 100\%
\]  

(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
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 ºC. 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 ºC). 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>Total input from poultry litter (100%)</th>
<th>Poultry litter without limestone at 700 ºC and ER= 0.30 (Exp. No. 3)</th>
<th>Poultry litter with limestone at 700 ºC and ER= 0.35 (Exp. No. 6)</th>
<th>Poultry litter with limestone at 750 ºC and ER= 0.28 (Exp. No. 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input (%)</td>
<td>Output (%)</td>
<td>Output (%)</td>
<td>Output (%)</td>
</tr>
<tr>
<td>Elements</td>
<td>Gas</td>
<td>Cyclone</td>
<td>Bed</td>
</tr>
<tr>
<td>Cl</td>
<td>100</td>
<td>0.87</td>
<td>57.66</td>
</tr>
<tr>
<td>S</td>
<td>100</td>
<td>21.56</td>
<td>44.42</td>
</tr>
<tr>
<td>N(^\d)</td>
<td>100</td>
<td>101.12</td>
<td>0.34</td>
</tr>
</tbody>
</table>

\(^\d\) 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\(_2\) content in the feed resulted in high concentration of NH\(_3\) 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 ºC resulting in a CGE of 73.5% and generated the lowest tar concentration of 2.89 g/kg\(_{daf}\). 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


