Poultry litter gasification in a fluidized bed reactor: effects of gasifying agent and limestone addition

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Abstract

Air and air-steam gasification of poultry litter was experimentally studied in a laboratory scale bubbling fluidised bed (BFB) 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 $^{\circ}$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/Nm^3 and an average product gas composition (dry basis) of H_2: 10.78%, CO: 9.38%, CH_4: 2.61 and CO_2: 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 NH_3 measurement at an ER of 0.28 and 750 ºC is 2.7% (equivalent to 19,300

mg/Nm^3) with 14.7 mg/Nm^3 of HCl observed the dry product gas. High temperature and steam injection favour production of CO and H_2 while their effect on CH_4 was almost negligible. It is demonstrated that poultry litter can be gasified by blending with limestone, making it possible to overcome the fluidization 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.

Keywords: *Animal feedlot, gasification, fluidised bed, defluidisation, limestone.*

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[1]. 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[2] 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[3].

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)[4,5] and to recover energy either directly as heat or as energy carriers[6].

Poultry litter is a heterogeneous fuel, composed of bedding material, excreta, waste feed and feathers[7]. In the past, several reviews[8,9] 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[10]. 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[11]. 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, devolatilization, 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[12].

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[13,14,15,16,17] 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.*[18] gasified dried swine manure in a fluidized bed gasifier using air as a fluidizing 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[19], 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[20,21]. In particular, low CaO content in the fuel ash is found to increase the likelihood of ash melting[20]. Billen *et al.*[22] 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 fluidized 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[23]. Fryda *et al.*[24] 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* [25] 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.

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.

2. Experimental details

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 1. 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,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 2. The elemental analysis of poultry litter ash shows that it has high amounts of silica, sodium, potassium, phosphorous and aluminium oxides.

Table 1. Chemical characteristic of poultry litter.

Component	Poultry litter (%w/w)
Moisture content (a.r.)	22.10
Ash content (d.b.)	17.55 ± 0.06
Volatile Matter (d.b.)	73.65 ± 0.02
Fixed carbon* (d.b.)	8.81 ± 0.02

C (d.a.f.)	54.70 ± 0.37
H (d.a.f.)	6.43 ± 0.07
N (d.a.f.)	6.48 ± 0.01
Cl (d.a.f.)	0.70 ± 0.02
S (d.a.f.)	0.90 ± 0.03
O* (d.a.f.)	30.79 ± 0.25
LHV (MJ/kg) (a.r.)	13.53 ± 0.41
Cellulose (d.b.)	12.88
Hemicellulose (d.b.)	11.72
Lignin (d.b.)	14.16
Extractives$^{\phi}$ (d.b.)	39.21

*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.

Table 2. Chemical composition of the poultry litter ash as received basis (ash at 550 ºC).

Oxides	Concentration (wt. %)	Oxides	Concentration (10^{-3} wt. %)
SiO_2	35.67	TiO_2	32
P_2O_5	17.51	BaO	17
CaO	12.29	NiO	12
SO_3	11.90	Cr_2O_3	3.7
MgO	9.23	MoO_3	2.7
Na_2O	5.27	V_2O_5	2.1
K_2O	3.32	SeO_3	1.5
Al_2O_3	2.40	HgO	1.0
Fe_2O_3	1.51	PbO	0.57
ZnO	0.37	As_2O_3	0.50
MnO	0.34	CoO	0.29
CuO	0.10	CdO	0.13
		BeO	0.11

2.2 Experimental facility and test procedure

The experiments were carried out within the BRISK EU FP7 framework project using an air-blown bubbling fluidized 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 Fig. 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 N_2 (1 dm^3/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). The experiments were carried out at various air, N_2 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.

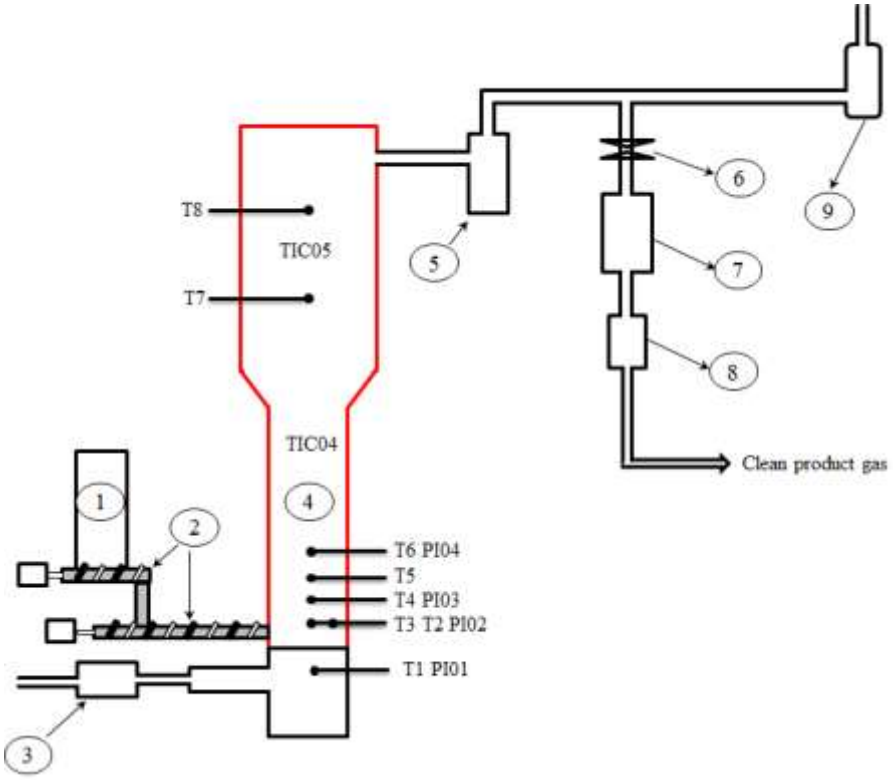

Figure 1. Schematic diagram of WOB gasifier (1) biomass hopper; (2) feeding screws; (3) air preheater; (4) gasifier reactor; (5) cyclone; (6) valve; (7) hot filter; (8) cold filter; (9) flare.

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[26].

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). 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_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_2 and steam was adjusted to ensure that the bed was properly fluidised. At higher ER, N_2 flow rate was decreased while increasing the air flow rate to keep constant the fluidisation velocity. Therefore, decrease in N_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 ($700 \leq Tg \leq 800$ ºC), equivalence ratios ($0.18 \leq ER \leq 0.41$) and steam to biomass mass ratios ($0.26 \leq SBR \leq 0.33$).

2.3 Measurement methods

The composition (CO, CO_2, C_2H_2, CH_4, C_2H_4, C_2H_6, C_6H_6, C_7H_8, N_2, COS, H_2S 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 H_2 and Ne peaks were well separated. An ABB gas analyser was used to determine the H_2 and O_2 content in the product gas. The online gas analyser measures permanent gases as well as sulphur containing compounds (H_2S 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 eq. 1 using the concentration of Ne in the product gas.

$$\gamma_i = \left(\frac{\beta}{Ne} \right) \quad (1)$$

where, $\gamma_{i,}$ represent the flow rate of dry product gas (m^3/min), β 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.* [27]. The N_2 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[28] has been modified for the purpose of this work. Tar compounds were extracted from the sorbent by addition of 3 × 600 µl 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 ionization 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 $g_{tar}/kg_{daf\text{-}poultry\ litter}$ in order to eliminate any dilution effect of the product gas when the biomass feed rate is reduced[29] or when the oxygen to nitrogen ratio is reduced to adjust for lower ER[30]. Tar in this paper refers to GC detectable tar including those tar compounds eluted from phenol (M ≈ 94 g/mol) to benz[a]anthracene (M ≈ 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 4ºC after the hot filter for the sampling of moisture, NH_3 and HCl. The moisture content was determined by the mass difference of the impinger bottle before and after the sampling. The principle of NH_3 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 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.

2.4 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[12].

$$CGE\left(\eta_{cg}\right)=\left(\frac{LHV_g \times \dot{m}_g}{LHV_f \times \dot{m}_f}\right)\times 100 \tag{2}$$

$$CCE\left(\eta_{cc}\right)=\left(\frac{C_{o,dry\,gas}}{C_{i,daf}}\right)\times 100 \tag{3}$$

$$HCE\left(\eta_{hc}\right)=\left(\frac{H_{o,dry\,gas}}{H_{i,daf}}\right)\times 100 \tag{4}$$

Where, $\dot{m}_f$ is the feed rate of solid fuel, $\dot{m}_g$ is product gas flow rate in kg/hr, LHV_g and LHV_f 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 velocity of the product gas (at the reactor temperature) presented in Table 3 is calculated according to the formula given by Siedlecki *et al.*[31]

Table 3. Summary of experimental tests

Test number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Feedstock type	Poultry litter				PL with limestone				PL with limestone				PL with limestone	
Poultry litter feed rate, kg/hr (a.r.)	0.66				0.49				0.61				0.57	
Limestone (kg/hr)	0.0				0.04				0.05				0.05	
Throughput (kg/hr-m^2)	155				113				141				132	
Temperature of gasifier, ºC	700				700				750				800	
Temperature of gasifying medium, $^{\circ}$C	160				160				160				160	
Steam to biomass ratio, SBR (-)	0	0	0	0.24	0	0	0	0.33	0	0	0	0.26	0	0
Equivalence ratio, ER (-)	0.18	0.22	0.30	0.30	0.29	0.35	0.41	0.35	0.23	0.28	0.33	0.28	0.25	0.30
Air flow rate, (dm^3/min)	6	7.2	10	10	7	8.5	10	8.5	7	8.5	10	8.5	7	8.5
Nitrogen flow rate, (dm^3/min)	6	4.8	2	1	5	3.5	2	2	5	3.5	2	2	5	3.5
Steam flow rate, kg/hr	0	0	0	0.125	0	0	0	0.125	0	0	0	0.125	0	0
Fluidising medium flow rate, dm^3/min	12	12	12	13.6	12	12	12	13.1	12	12	12	13.1	12	12
Fluidization velocity, m/s (20 ºC)	0.098	0.097	0.094	0.095	0.097	0.096	0.094	0.095	0.097	0.096	0.094	0.095	0.097	0.096
Superficial gas velocity based on the total product gas yield, m/s (T_g)	0.21	0.24	0.24	0.24	0.22	0.21	0.20	0.19	0.24	0.23	0.23	0.22	0.25	0.24

3. Results and discussion

Figure 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.

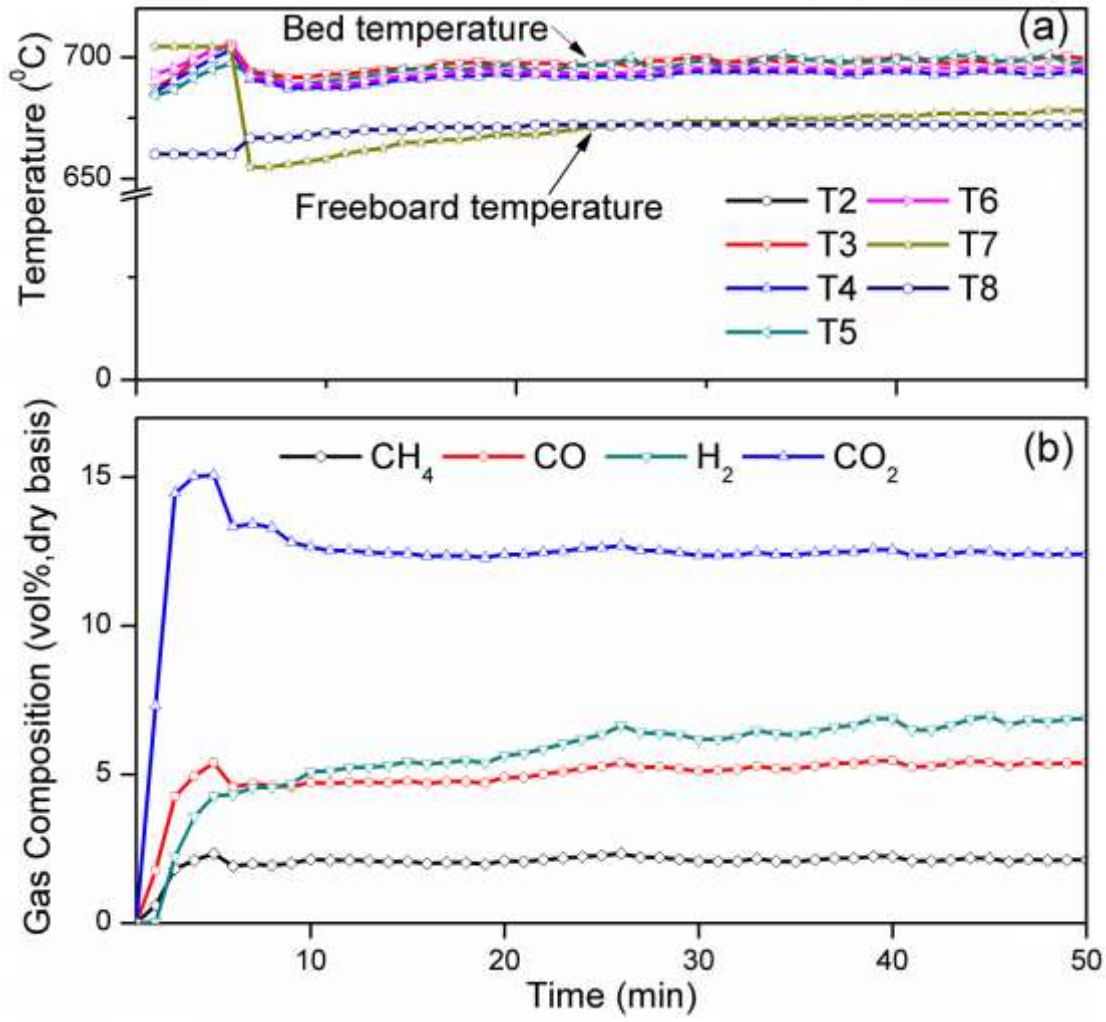

Figure 2. Bed and freeboard temperature and gas composition evolution in a poultry litter test at 700 °C and ER= 0.18: (a) temperature profile (b) product gas composition

Table 4 presents the main results of the experimental campaign. It should be noted that the gas compositions presented in Table 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.

Table 4 : Experimental test results

Test number		1	2	3	4	5	6	7	8	9	10	11	12	13	14
Gas composition from the steady state conditions (%v/v, dry as measured)	H_2	7.34	11.60	12.04	17.58	5.78	5.16	2.44	6.62	10.29	9.48	9.00	14.98	10.49	8.95
	Ar	0.41	0.42	0.55	0.53	0.47	0.57	0.79	0.78	0.42	0.53	0.61	0.53	0.40	0.51
	N_2	69.00	58.53	53.88	46.5	69.39	68.13	69.87	64.22	60.66	60.36	58.83	52.10	60.27	62.35
	CH_4	1.86	2.55	2.46	2.59	1.83	1.62	1.43	1.73	2.71	2.37	2.30	2.37	2.54	2.30
	CO	5.41	8.52	9.69	9.35	5.06	5.01	4.23	4.38	8.40	8.32	8.08	7.57	9.14	7.50
	CO_2	11.36	13.22	15.60	17.74	12.29	13.74	15.03	16.08	12.69	13.68	15.25	16.92	12.78	14.15
	C_2H_4	0.89	1.14	1.11	1.10	0.91	0.82	0.81	0.86	1.42	1.30	1.26	1.26	1.40	1.27
	C_2H_6	0.19	0.29	0.29	0.32	0.18	0.17	0.14	0.18	0.18	0.18	0.18	0.19	0.10	0.10
	C_2H_2	0.017	0.019	0.016	0.013	0.018	0.017	0.019	0.017	0.025	0.028	0.020	0.017	0.023	0.015
	H_2S	0.046	0.062	0.057	0.091	0.042	0.051	0.026	0.070	0.023	0.030	0.028	0.042	0.019	0.023
	COS	0.003	0.004	0.003	0.002	0.002	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001
	C_6H_6	0.092	0.115	0.112	0.112	0.097	0.083	0.078	0.086	0.155	0.133	0.13	0.121	0.166	0.156
	C_7H_8	0.041	0.054	0.055	0.055	0.040	0.038	0.034	0.038	0.048	0.046	0.050	0.047	0.033	0.037
NH_3 (ppmv in dry gas)		-	-	39552	-	-	29540	-	-	-	27031	-	-	-	
Moisture in the product gas (%vol)		-	-	19.6	-	-	19.5	-	-	-	16.7	-	-	-	
HCl (mg/m^3, dry gas)		-	-	20.9	-	-	88.5	-	-	-	14.7	-	-	-	
Total GC detectable tar (g/kg_{daf} poultry litter)		4.40	6.25	7.22	8.59	6.36	5.85	3.72	3.97	6.42	5.19	3.89	2.89	5.66	3.25
Gas yield (m^3/ kg_{daf} poultry litter N_2 free)		0.75	1.09	1.15	1.36	1.12	1.14	1.03	1.13	1.15	1.10	1.12	1.25	1.39	1.24
LHV (MJ/Nm^3, dry gas)		3.11	4.53	4.72	5.36	2.91	2.69	2.17	2.87	4.55	4.24	4.12	4.74	4.52	3.95
C entrainment in the cyclone,(g/ kg_{daf} poultry litter)		53.17	78.51	98.27	104.22	58.51	77.25	47.28	63.26	72.11	76.47	70.51	70.51	33.43	33.43
Carbon conversion efficiency (%)		49.1	72.5	81.8	88.0	70.8	73.1	70.0	71.8	78.2	76.4	79.0	80.2	89.2	81.0
Cold gas efficiency (%)		42.3	69.7	72.5	83.6	55.2	43.0	33.0	48.4	75.6	68.0	65.2	73.5	84.6	69.3
Hydrogen conversion efficiency (%)		27.3	40.2	41.0	39.8	32.3	29.2	20.7	24.1	41.1	37.6	36.3	36.7	42.9	37.8

3.1 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[32]. 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 4). A similar conclusion has been drawn by Gómez-Barea *et al.*[33] while gasifying orujillo and meat and bone meal waste in an air-blown bubbling fluidized bed at atmospheric pressure using lime as a bed material (or blend with ofite).

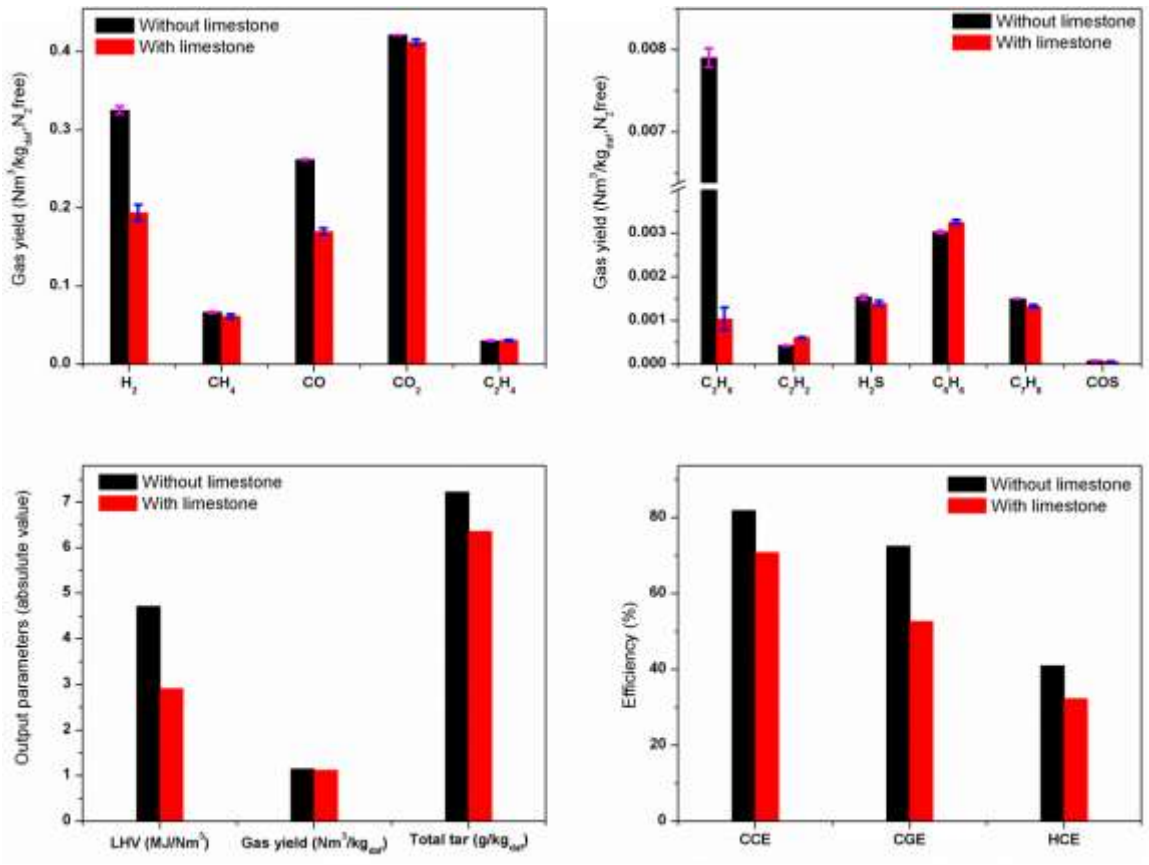

Figure 3. Effect of limestone on the composition of the product gas and gasifier performance (gas yields are on a N_2 free basis)

Limestone addition proportionally reduced the poultry litter feed rate (8% by weight) and also changed gas composition significantly with a consequent effect on it's heating value (calculated on the basis of gas composition without the contribution of tar content) and CGE. From Figure 3, 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 C_2H_2 and C_6H_6 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 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 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 **4**, the concentration of H_2S 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[34,35]. 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[34,35]**.** The fate of N, S and Cl bound with the feedstockis presented in the Section 3.5 (Table 6).

While gasifiying 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 defluidization and agglomeration issues at higher temperature in a fluidised bed gasfier 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.

3.2 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 ºC) and an ER of ≈ 0.30 (experiments number 5, 10 and 14). The variables analysed include gas composition, product gas yield (N_2 free basis), heating value, tar yield, CCE, CGE and HCE and the results are shown in Figures 4 and 5. It is evident from Figure 4 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[36]. The increase in CO and H_2 production is due to the improved Boudouard reaction and water gas reactions, as well as tar cracking and reforming reactions. The concentrations of CH_4, C_2H_4 and benzene shows similar trend and increases with temperature. On the other hand, gasification temperature has almost no effect on the yields of C_2H_2, C_7H_8 over the tested range of temperature while, the production of C_2H_6 and H_2S decreased with temperature. The elevated temperature favours thermal cracking and steam reforming reactions, explaining the observed decreased in C_2H_6 concentration in this study. A similar conclusion was drawn by Turn *et al.*[37] in the temperature range 750 to 800 ^{0}C.

Sulfur concentration in the product gas depends on sulfur content in the fuel and the gasifier temperature. Mass balance analysis in Section 3.5 shows that approximately 45-70% of the sulfur is bound to the cyclone fines. The sulfur in the gas phase is present in the form of H_2S and COS which accounts for about 8% of total sulfur fed into the gasifier at 800 ºC

and an ER of 0.25. The concentration of H_2S decreases with an increase in the gasification temperature whereas the concentration of COS remains fairly constant throughout the temperatures studied (Fig. 4). It is considered that the balancer of the sulfur remains in the bed.

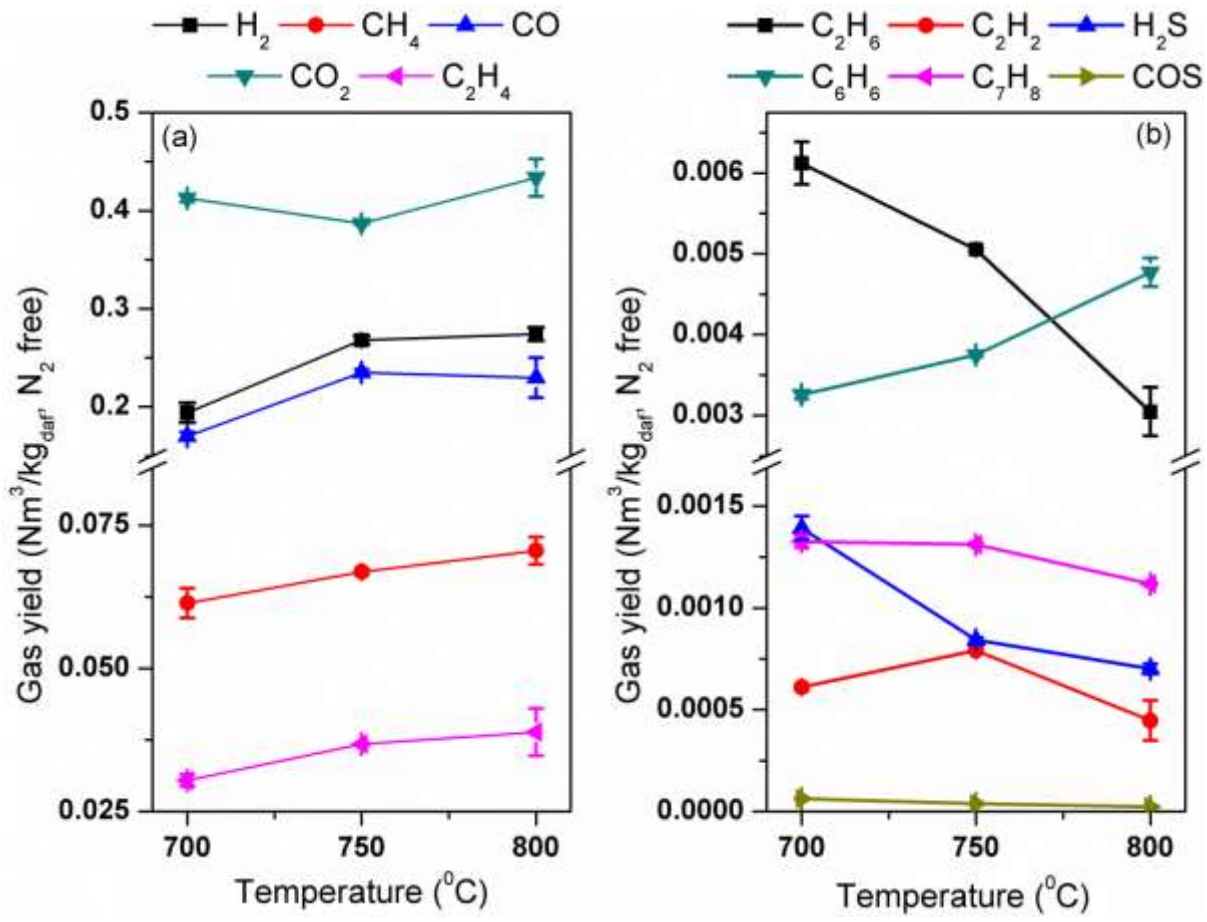

Figure 4. Effect of temperature on the composition of the product gas at ER ≈ 0.30 (a) yield of major gas species (b) yield of light hydrocarbon gas species in the product gas

Normally, the HCl concentration in the gas phase increases with temperature due to chlorinated tar cracking at higher temperature[27]. However, it is observed from Table 4 that the concentration of HCl in the gas phase decreased with increasing gasifier temperature from 700 to 750 ºC. 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 (PCl_3) and calcium chloride ($CaCl_2$) 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 3.5 (Table 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 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 gasifcation which is in-line with investigations performed on a lab-scale bubbling fluidised bed gasifier by Zhou *et al.*[38]. Furthermore, it confirms the theory proposed by Zhou et al.[38] that at higher temperature the conversion of NH_3 to N_2 $\left(3H_2 + N_2 \leftrightarrow 2NH_3\right)$ 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 sulfur 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 [27].

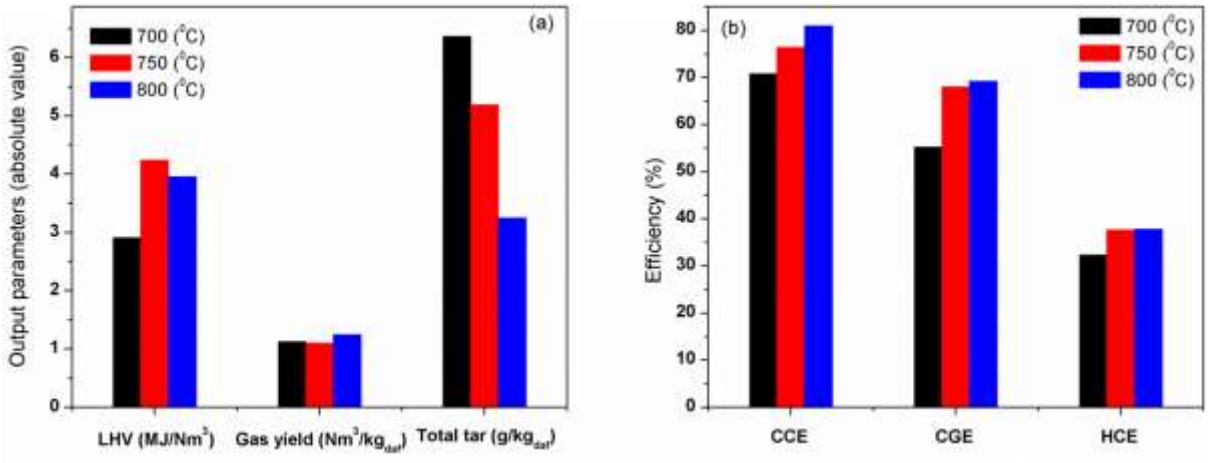

Figure 5. Effect of temperature on (a) LHV, product gas (N_2 free) and total tar yields (b) the performance of gasification at ER≈0.30 (experiments number 5, 10 and 14)

Figure 5 clearly shows that a higher temperature increases the product gas yield (from 1.12 to 1.24 Nm3/kgdaf) and LHV (from 2.91 to 4.24 MJ/Nm3) 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 5 (b). 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 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 4).

3.3 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 6. An increase in ER results in a reduction of H_2 and CO contents in the product gas due to increased amount of O_2 available in the reactor for reaction with the volatiles and char combustion which results in increase of CO_2 production and degrades the quality of product gas.

It is important to note that the ER does not have much influence on CH_4. Regarding light hydrocarbons, Figure 6 (b) shows that the concentration of ethane, benzene and toluene fell slightly with ER. At the same time, acetylene and H_2S 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.

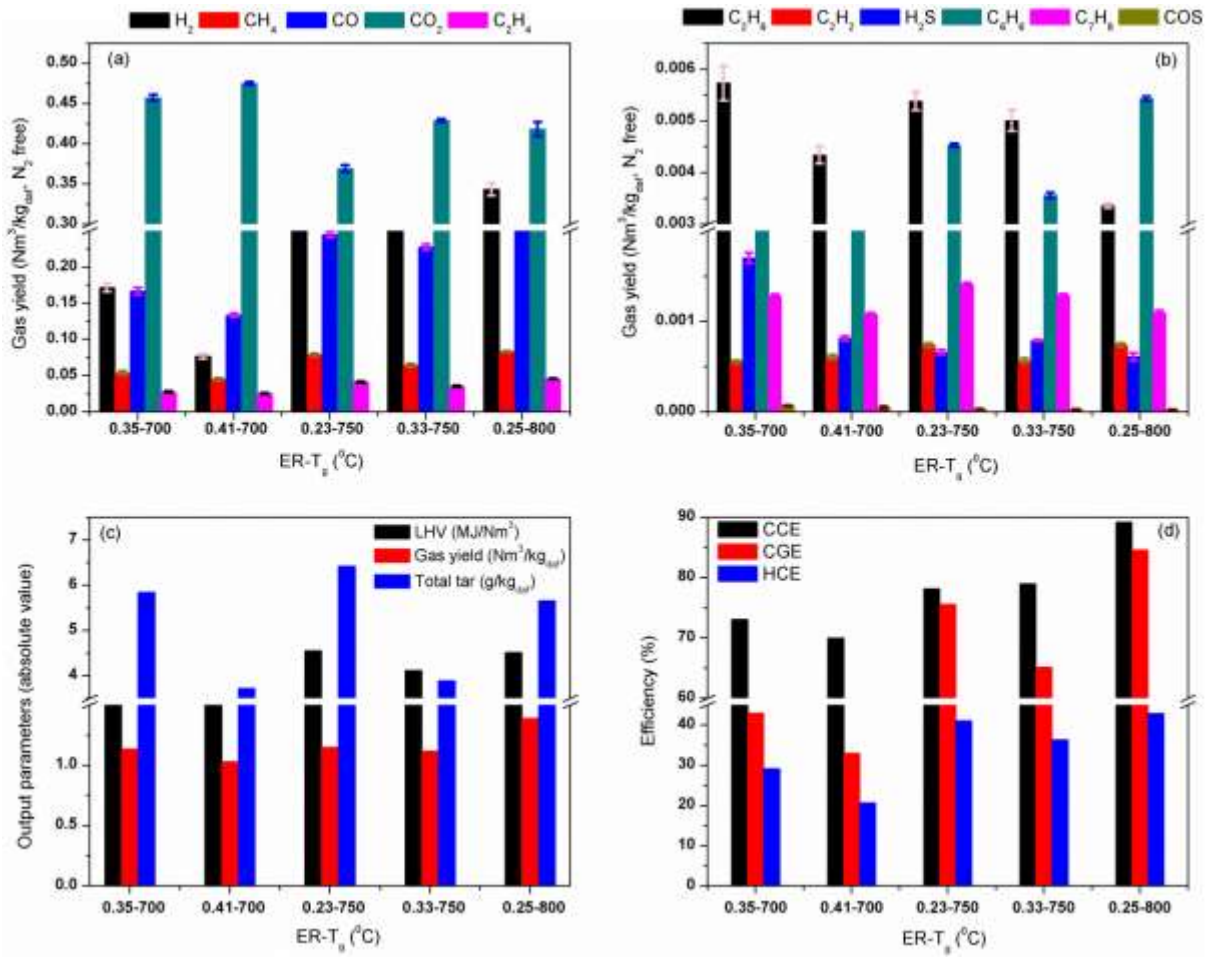

Figure 6. Effects of ER on the composition of product gas and gasifier performance (gas yields are on an N_2 free basis)

Since, the product gas yield is reported on an N_2 and dry and ash free basis, the ER does not have a noticeable effect on product gas yields as evident from the Figure 6 (c). 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 $^{\circ}C$ due to the oxidation reaction of aromatics[39]. 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 ^{0}C. This process condition (refer Figure 6) 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/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 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_2O, 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 Gomez-Barea *et al.*[40] 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.*[41]

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.

3.4 Effect of steam injection

The influence of steam to biomass ratio (SBR) on the product gas yield is investigated at 700 and 750 ^{0}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 7 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} *v/s* 0.41 Nm^3/kg_{daf}) when compared with no steam injection at ER of 0.28 and temperature of 750 ^{0}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[42]. 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 ºC with SBR of 0.33 and 750 ºC 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 7 (c) 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.

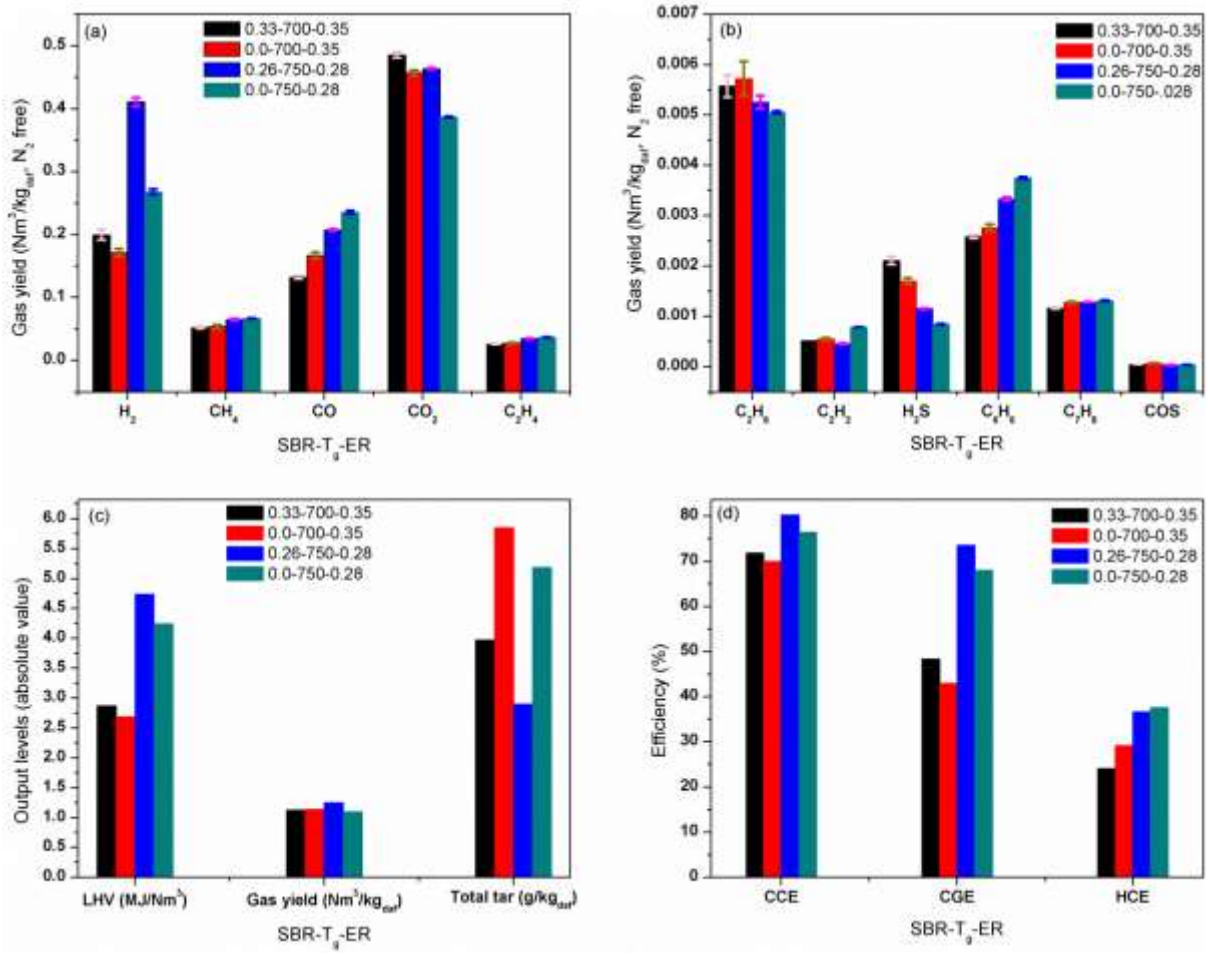

Figure 7. Effects of SBR on the composition of product gas and gasifier performance

Figure 7 shows that, in spite rising the H_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_2 is outweighed by the decrease in CO and CH_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 7 (d) that HCE is significantly lower at 700 ºC 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_2H_6, C_6H_6 and C_7H_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 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.

3.5 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 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) $\sum_{i=1}^{n} M_i = \sum_{j=1}^{n} M_o$ 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 5. Mass balance of gasification tests

	Poultry litter without limestone at 700 ºC and ER= 0.30			Poultry litter with limestone at 700 ºC and ER= 0.35			Poultry litter with limestone at 750 ºC and ER= 0.28		
Elements	Input	Output	Rel. Error (%)	Input	Output	Rel. Error (%)	Input	Output	Rel. Error (%)
C (kg/hr)	0.234	0.224	-4.16	0.170	0.147	-13.62	0.214	0.182	-14.97
H (kg/hr)	0.044	0.043	- 3.04	0.033	0.031	-4.68	0.041	0.039	-5.23
O (kg/hr)	0.433	0.436	0.81	0.344	0.372	7.94	0.395	0.390	-1.28
N (kg/hr)	0.734	0.680	-7.34	0.749	0.848	12.94	0.754	0.744	-1.34
S (kg/hr)	0.004	0.003	-15.30	0.0028	0.0032	14.36	0.003	0.004	22.83
Cl (kg/hr)	0.002	0.001	-37.03	0.0017	0.0002	-90.23	0.002	0.001	-74.30
Ash (kg/hr)	0.091	0.089	-2.76	0.072	0.078	8.68	0.090	0.102	13.07

where,

$$relative\,error = \left(\frac{input - output}{input} \right) \times 100\% \quad (5)$$

Table 5 shows that the relative errors are in the range of $\pm 15\%$ (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 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[43].

An attempt was made to explain the fate of N, S and Cl from the poultry litter based on measurements. Table 6 illustrates the detailed analysis of the measurements. It can be seen

from Table 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 (NH_3). Furthermore, the research findings revealed that NH_3 formation decreased with an increase in gasifier temperature in agreement with literature[38]. 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 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 6**.** Fate of nitrogen, sulfur and chlorine from the feedstock

	Total input from poultry litter (100%)	Poultry litter without limestone at 700 ºC and ER= 0.30 (Exp. No. 3)			Poultry litter with limestone at 700 ºC and ER= 0.35 (Exp. No. 6)			Poultry litter with limestone at 750 ºC and ER= 0.28 (Exp. No. 10)		
	Input (%)	Output (%)			Output (%)			Output (%)		
Elements		Gas	Cyclone	Bed	Gas	Cyclone	Bed	Gas	Cyclone	Bed
Cl	100	0.87	57.66	4.44	5.05	4.71	*	0.67	25.10	*
S	100	21.56	44.42	18.71	26.55	77.84	10.01	12.22	71.26	39.30
N^{ϕ}	100	101.12	0.34	0.10	94.94	7.45	0.05	75.70	7.50	0.25

$^{\phi}$ Nitrogen associated with poultry litter, *not measured

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 ^{0}C 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.

Abbreviations:

BFB = bubbling fluidized bed, ER = equivalence ratio, SBR = steam to biomass ratio, LHV = lower heating value, CCE = carbon conversion efficiency, CGE = cold gas efficiency, HCE = hydrogen conversion efficiency, GC = gas chromatography, SPA = solid phase adsorption, ICP = inductively coupled plasma, SD = standard deviation, FID = flame ionization detector MSD = mass selective detector

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