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Fly Ash From Poultry Litter Gasification – Can it be Utilised in Agriculture Systems as a Fertiliser?

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Abstract

Fly ash from a poultry litter gasification process and the potential of application of the fly ash as a fertiliser in line with the poultry litter protocol is investigated. The fines collected in the cyclone are mainly formed by ash which comprises between 70-83 wt.% of the fines on a dry basis, and to a lesser extent of carbon (elutriated char). The effect of the gasification operating conditions on the concentration of ash forming elements (inorganic compounds) in the fly ash, are discussed. In addition, the enrichment factor which defines the volatility, has been used and fly ash elements were categorised as Class I (non-volatile), Class II (semi-volatile with the possible occurrence of condensation) and Class III (highly volatile elements). Inorganic elements in fly ashes from poultry litter gasification experiments are categorised as Class I: Ca, Co, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Class II: Cd, Cr, Mo and Class III: Pb and Se. It has been found that the fly ash from the poultry litter gasification exceeds the upper acceptable limit set by Poultry Litter Protocol to be used as a fertiliser in agriculture systems.

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1. Introduction

Livestock production is among one of the fastest growing sectors of the agricultural economy and currently facing several unprecedented challenges: increase output to meet the growing demand for animal protein, adopting to economic and natural environmental changes and improving its environmental performance [1]. Intensification of livestock production poses massive disposal problems for animal feedlots not only in the Europe but throughout the world. However, these animal feedlots not only have negative environmental issues but also offer a potential source of energy and nutrients. Organic carbon present in the animal manure feedstock can be used for bioenergy production as the CO_2 generated from the oxidation of animal waste such as poultry litter is carbon neutral (as the source of carbon is biomass not fossil fuel) and should not be accounted for when the impact on global warming is assessed. The adaptation of the EU Regulations (1069/2009) has paved the way to use poultry litter as a fuel for on-farm energy production. Poultry litter has been investigated using thermochemical conversions technologies such as combustion, pyrolysis, gasification and hydrothermal carbonisation [2–5]. While the technology for gasification is not as well developed as that for combustion applications, interest in gasification of poultry litter has been increasing. Gasification of poultry litter to energy and reducing the volume of waste represents a significant opportunity for poultry farmers. The derived product gas (syngas) from poultry gasification can provide heat and/or electricity on-farm, to a neighbourhood or even to non-electrified communities, schools and other institutions, which will help to offset the use of fossil fuels for the generation of heat and electricity. Gasification offers two main advantages over the landfilling application: (i) utilisation of organic matter for energy recovery and (ii) nutrient recovery which is retained in the ash and char. On the one hand, gasifying feedstock with high ash content can cause corrosion, defluidisation and agglomeration problems, on the other hand post gasification disposal of fly ash residue on the arable land can potentially degrade the soil quality, nutrient run-off and leachate can pollute the ground water.

Studies on fly ash from coal combustion process have been conducted and showed that fly ash holds a potential to improve degraded soil for agriculture and forestry use [6-7]. Use of fly ash, organic wastes and chemical fertiliser in sandy loam acid lateritic soil was investigated, the study showed an improvement in crop yield, soil pH, organic carbon availability of N, P and K [8]. When fly ash was applied in appropriate amounts it had helped to alleviate the deficiency of some nutrients in soils [7,9-10]. However, the characteristics of fly ash depends upon feedstock and combustion conditions and it was recommended that the suitability of a particular fly ash to be used a soil amender should be carefully evaluated before its application [6]. The Intergovernmental Panel on Climate Change (IPCC) assumes that use of lime in agriculture causes global warming since lime finally releases CO_2 to the atmosphere. Initially, fly ash was used as a soil amendment for acidic infertile soils due to its high pH and the macro- and micro-elements it contains. The use of fly ash instead of lime in agricultural land can mitigate the net CO_2 emission [11-12]. The latest study has clearly outlined that fly ash can be used a soil amender (particularly for acidic soil) but most of the studies conducted so far are based on coal fly ash whereas research on biomass fly ash is rarely reported in the literature and requires urgent attention [13].

Plant (ryegrass *L. multiflorum Lam.*) uptake of trace elements from ashes produced in fluidised bed, fixed bed and entrained flow gasification process have been studied with and without lime and fertiliser amendments [14]. The authors have concluded that ashes usually have significant amounts of phytotoxic heavy metals and when applied to unfertilised and un-limed soil, the phytotoxic concentration in the plant material was sufficiently high and to be toxic to animals under continuous long term grazing conditions that can ultimately be transferred to the food chain. Although, fly ash has been categorised to have negative effects on the environment, the disposal and recycling methods as well as fly ash utilisation in construction industry, ceramic industry, zeolite synthesis, adsorbent for removal of pollutants, catalysis or metal extraction has been critically reviewed [15].

In conclusion, it has been proposed that ashes residue can be used a soil amender or fertiliser, moreover, the fate of nutrients bound to ash, their release rate and availability for plant uptake as well as alkali and alkaline earth metals are not known. Therefore, to categorise the fly ash from poultry litter gasification process as an organic fertiliser or soil amender, detailed analysis of ash residue and leaching tests are required. This paper aims to present compositions of fly ash from poultry litter gasification, relative enrichment of elements in the fly ash and looks into the potential of application of the poultry litter fly ash as a fertiliser as per the poultry litter protocol.

2. Experimental Details

2.1 Feedstock and Bed Material

Poultry litter was collected from a local poultry farm in The Netherlands and was partially dried and sieved to a particle size of 0.7-2.8 mm before gasifying. Poultry litter was blended with limestone (8% w/w) supplied by Rheinkalk GmbH (Brilon, Germany) with a particle size in the range 0.9 and 1.2 mm. The limestone was continuously fed with poultry litter in order to prevent agglomeration or defluidisation problems during the tests. Ultimate, proximate and ash analyses of poultry litter is presented in Table 1.

Table 1. Proximate, ultimate analyses of poultry litter and ash composition [4]

Proximate analysis (wt.%)		ash composition [mg/kg ash_{db}]			
		Major elements		Minor elements	
Moisture (ar)	22.10				
Ash content (db)	17.54	Al	9863	As	2.97
Volatile matter (db)	73.65	Ca	68253	Ba	122
Fixed carbon^{a} (db)	8.81	Cu	600	Be	0.29
Ultimate analysis (wt.%, daf)		Fe	8155	Cd	0.89
Carbon	54.70	Mg	43259	Co	1.78
Hydrogen	6.43	Mn	2058	Cr	20.0
Nitrogen	6.48	P	59394	Hg	7.42
Sulphur	0.90	K	21446	Mo	14.0
Chlorine	0.70	Si	129587	Ni	74.0
Oxygen^{a}	30.79	Na	30407	Pb	3.86
LHV (MJ/kg_{ar})	13.53	Ti	149	Se	7.42
		Zn	2312	V	9.20

^{a}Calculated by difference, ar – as received, db – dry basis, daf – dry and ash free

2.2 Experimental facility

The gasification experiments were conducted within the EU FP7 BRISK project using a lab scale air blown bubbling fluidised bed reactor with 5 kW_{th} capacity at the Energy Research Centre of The Netherlands (ECN). 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 by the means of an electric heater to maintain the temperature within the reactor. A detailed description of the experimental set-up can be found elsewhere [4].

2.3 Experimental procedure

Fresh silica sand with a 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. The experiments were carried out at three different temperatures and equivalence ratios (ER) using either poultry litter alone or mixture of poultry litter and limestone. The ERs were varied by adjusting air and nitrogen flow rate while maintaining the same flow rate of biomass. The fluidisation velocity was kept constant throughout the tests. The fluidising media are heating to 160 ºC before entering the reactor. Poultry litter was fed into the reactor through a mechanical twin screw feeding system under 1 dm^3/min nitrogen in order to avoid the backflow of the product gas from the gasifier. The reactor achieved steady state conditions in approximately 30 min after the introduction of the poultry litter. The downstream section of gasifier consists of a cyclone, hot and cold filter. The downstream section was heated and maintained at 400 ºC while well insulated, except for the cold filter, to avoid any tar condensation. Elutriated particles such as unconverted char, fine silica sand, dust particle and fly ashes are collected in the cyclone which was emptied at the end of each test and samples were retained for analysis. The operating conditions are presented in Table 2.

2.4 Method of fly ash analysis

The elemental compositions of collected cyclone fines were determined by a Vario EL cube elemental analyser. A drying oven and high temperature furnace were used in quantifying the moisture and ash content in the cyclone fines. The heating value of the cyclone fines were measured using an Isoperibol Calorimeter 6200 (Parr Instruments).

CEN/TS 15408:2006 (replaced by BS EN 15408:2011) method was used to determine the chlorine content in cyclone fines.

Table 2. Summary of operating conditions.

Test number	1	2	3	5	6	7	9	10	11	13	14
Feedstock type		Poultry litter					Poultry litter with limestone (8% w/w)				
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	
Temperature of gasifier, ºC		700			700			750		800	
Temperature of gasifying media,°C		160			160			160		160	
Equivalence ratio, ER (-)	0.18	0.22	0.30	0.29	0.35	0.41	0.23	0.28	0.33	0.25	0.30
Air flow rate, dm^3/min	6.0	7.2	10	7.0	8.5	10	7.0	8.5	10	7.0	8.5
Nitrogen flow rate, dm^3/min	6.0	4.8	2.0	5.0	3.5	2.0	5.0	3.5	2.0	5.0	3.5
Fluidising media flow rate, dm^3/min	12	12	12	12	12	12	12	12	12	12	12
Superficial gas velocity, m/s, T_g	0.21	0.24	0.24	0.22	0.21	0.20	0.24	0.23	0.23	0.25	0.24

3. Results and Discussion

3.1 Elements retained in the fly ash

The fines collected in the cyclone mainly comprise between 70 - 83% w/w (db) of the fines, and to a lesser extent of carbon (refer Table 3). The carbon content in the fly ashes reported are in the range of 9 to 22% w/w (db) and are considered high for the use of fly ashes in other applications. The carbon content of the recovered cyclone fines is dependent on the temperature of the gasifier and the availability of oxygen in the reactor. Hydrogen and sulphur content are quite similar in all samples, between 0.38-0.23 and 1.3 to 1.7% w/w (db) respectively but decreases with an increase in ER. Chlorine content in the cyclone fines are around 0.8% w/w when poultry litter was not blended with limestone which is similar to the chlorine content in the feedstock. In contrast, when poultry litter was mixed with the limestone the chlorine content in the cyclone fines dropped significant and was in the range of 0.05 to 0.2% w/w.

Table 3. Elemental composition, moisture, ash content and LHV of the fines collected from the cyclone

Test number	1	2	3	5	6	7	9	10	13	14
Feedstock type		Poultry litter				Poultry litter with limestone (8% w/w)				
Temperature of gasifier, ºC		700			700		750		800	
Equivalence ratio, ER (-)	0.18	0.22	0.30	0.29	0.35	0.41	0.23	0.28	0.25-.30	
Carbon [wt.%, db]	21.3	22.93	#	20.57	17.13	9.18	21.16	15.15	12.25	
Hydrogen [wt.%, db]	0.38	0.38		0.37	0.31	0.21	0.32	0.25	0.23	
Nitrogen [wt.%, db]	1.35	1.40		1.27	1.07	0.57	1.16	0.96	0.61	
Sulphur [wt.%, db]	1.71	1.35		1.69	1.55	1.33	1.64	1.27	1.44	
Chlorine [wt.%, db]	0.78	0.77	0.88	0.06	0.05	#	0.27	0.26	#	
Oxygen[a] [wt.%, db]	2.75	1.87	#	4.99	4.82	5.52	4.38	2.87	2.55	
Moisture [wt.%, db]	3.57	3.51		3.61	3.34	2.11	3.94	3.26	2.88	

Ash [wt.%, db]	71.8	71.45		71.21	74.84	83.62	71.97	79.54	82.83
LHV [MJ/kg, db]	6.83	6.99	6.78	6.06	5.17	#	6.14	4.69	#
Cyclone fines [g/hr]	30	42	50	26	35	27	39	44	17
Energy in fines [%]	2.3	3.3	3.8	2.6	3.0	#	3.2	2.8	#

[a]Calculated by difference # not measured

The LHV of the cyclone fines correlates closely with the carbon content, in the range between 5 and 7 MJ/kg (db). The calorific value of the cyclone fines are typically reported to be between 33-50% of the LHV of the original feedstock but were considerably lower than the value reported from the industrial scale gasifier [16]. The reported energy retained in the fines per unit of mass was 2.2-3.8% of the energy introduced with the biomass, since limestone addition reduced the rate of char and fines elutriation with a corresponding reduction in the energy retained in the cyclone fines.

3.2 Enrichment factor

The Enrichment Factor (EF) which defines the volatility has been used to classify fly ash elements from poultry litter gasification as Class I (non-volatile), Class II (semi-volatile with the possible occurrence of condensation phenomenon) and Class III (highly volatile elements). The range of EF are ~1, 1.2-4 and >10 for class I, class II and class III respectively. The EF for all the trace elements found in the fly ash is calculated based on a formula proposed by Meij [17] for ashes from coal fired power plant and appended in Table 4. This study aimed to investigate the effect of reducing condition in gasification processes on the volatility of fly ash elements which has not been investigated in detail to date.

$$EF = \frac{element\ concentration\ in\ fines}{element\ concentration\ in\ fuel} \cdot \frac{\%\ ash\ in\ fuel}{100}$$

Table 4. Enrichment factors for fines collected in cyclones

	Poultry litter			Poultry litter with limestone (8% w/w)						Class
	700 °C			700 °C		750 °C			800 °C	
ER	0.18	0.22	0.23	0.35	0.41	0.28	0.29	0.33	both	
As	0.98	0.00	1.01	0.83	0.71	0.23	1.24	0.18	0.49	1
Ca	0.30	0.29	0.29	0.26	0.27	0.28	0.27	0.27	0.27	1
Cd	5.95	6.08	6.24	5.75	5.63	6.10	5.85	5.05	5.99	2/3
Co	0.27	0.21	0.27	0.17	0.31	0.24	0.22	0.18	3.35	1
Cr	2.85	3.66	3.31	1.52	1.97	1.83	2.63	1.97	2.18	2
Cu	0.48	0.49	0.54	0.44	0.41	0.42	0.47	0.43	0.42	1
Fe	0.15	0.15	0.16	0.15	0.15	0.15	0.16	0.16	0.18	1
Hg	0.11	0.08	0.06	0.07	0.10	0.14	0.11	0.12	0.17	1
K	0.82	0.84	0.70	0.73	0.77	0.82	0.76	0.82	0.79	1
Mg	0.26	0.23	0.24	0.25	0.28	0.25	0.25	0.25	0.27	1
Mn	0.21	0.20	0.21	0.19	0.20	0.22	0.19	0.20	0.23	1
Mo	1.71	1.44	0.13	3.56	3.71	3.39	2.72	3.07	2.85	2

Na	0.24	0.25	0.23	0.28	0.27	0.25	0.27	0.26	0.23	1
Ni	0.39	0.54	0.54	0.31	0.36	0.34	0.42	0.44	1.20	1
P	0.26	0.26	0.24	0.25	0.15	0.28	0.23	0.26	0.28	1
Pb	30.04	24.29	40.56	20.28	19.15	24.11	33.58	21.00	30.60	3
Se	43.40	41.45	42.14	46.77	53.64	65.66	69.12	71.45	61.17	3
Zn	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.00	1

Based on the EF calculation, the inorganic elements present in fly ashes from the poultry litter gasification experiments are classified as Class I: Ca, Co, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Class II: Cd, Cr, Mo and Class III: Pb and Se. If the EF is more than 1 for non-volatile metals whose boiling temperature is higher than the operating temperature of the gasifier, it indicates that their presence might have originated from foreign sources other than the feedstock ash. For example the bed material (silica sand) could be an additional source for Si, Fe, Al and Cr [18] or corrosion due to presence of phosphorus or attrition of the reactor could be a source of Cr, Fe or Pb enrichment [19] and the feedstock (poultry litter) with higher chlorine content could significantly reduce the volatilisation temperature of Pb and Ni. In contrast with a previous study conducted on the characterisation of the fly ash collected from *Cynara cardunculus L.* gasification, Se, Pb, Mo and Cd in the fly ash from poultry litter has shown moderate to high volatility characteristics. Nevertheless, the results obtained for other volatile or highly volatile elements such as Cu, Co, Zn, Na, P and K are in line with the findings reported by [20]

3.3 Effect of gasification temperature

The effect of gasification temperature on the concentration of ash forming elements in the fly ash is presented in Figure 1. It is worth pointing out that the results presented here are obtained from gasification experiments when poultry litter was blended with limestone. It can be observed from Figure 1 that the concentration of Mn, Ni and Co in the cyclone ash increases with an increase in gasification temperature while the concentration of Zn decreases. When lime was added to the feedstock before gasification the amount of Se and Mo is higher in the cyclone ash while Cu and Cr lower.

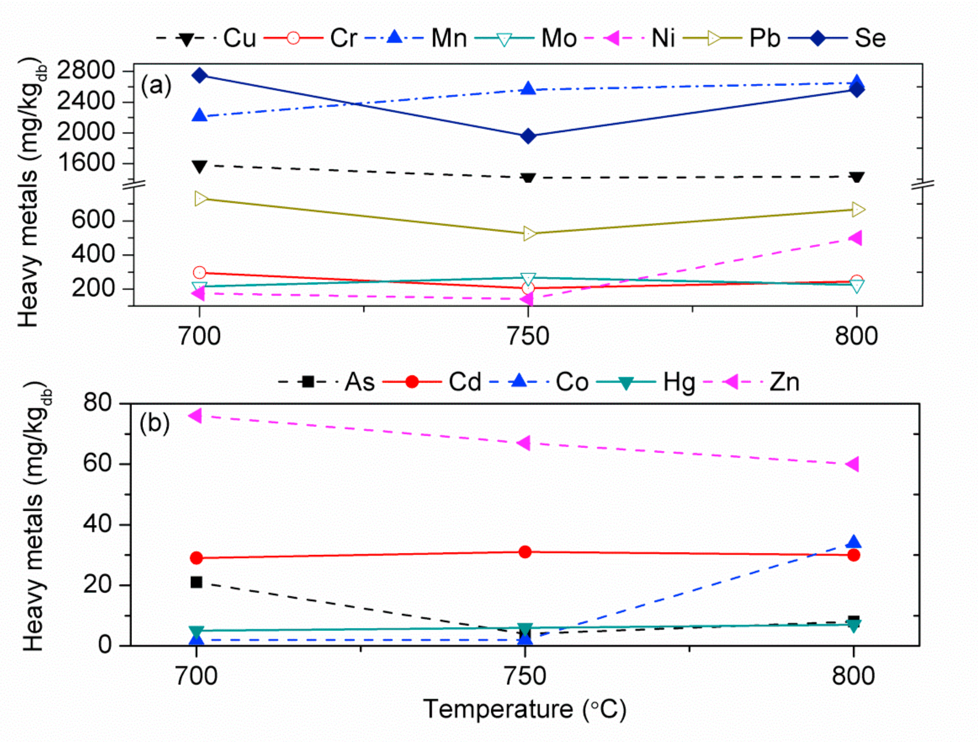

Figure 1. The effect of gasification temperature on the content of heavy metals in cyclone ash ER ≈ 0.30 (experiments number 5, 10 and 14).

3.4 Use of poultry litter gasification cyclone ash in agriculture system

The EU Waste Framework Directive (2008/98/EC) permits the development and marketing of materials produced from waste only if they do not pose a threat to human health or the environment. In the UK and Ireland, if poultry litter ash is destined for use as an agriculture fertiliser and mineral metals are within the limit (refer Table 5), it is not considered as a waste and is no longer subject to waste management control systems. However, it is evident from Table 5 that most of the trace elements (Cd, Cr, Cu, Hg, Mo, Ni, Pb and Se) found in the fly ash generated from poultry litter gasification exceed the upper acceptable limit set by the Poultry Litter Protocol. The Se content, in particular is about 100 times higher than allowed, while for other elements it was 3 -10 times higher that specified in poultry litter protocol. Se is highly volatile (Category III) and was released during the gasification process however, since the carbon/char content is relatively high in the fly ash it was re-adsorbed on the char particles and that led to a higher concentration of Se in fly ashes collected from cyclone. Only the contents of Co, Mn, V, Zn and in some cases As are within the required limits. Therefore, the fly ashes in the present form cannot be classified as an agriculture fertiliser. Additionally, the potential utilisation of gasification ashes as a fertiliser is limited since the phosphorous present in the fly ashes is poorly soluble under soil conditions while it also contains harmful water soluble compounds [11,21-22]. Fly ashes, however, can be used as a soil amender which will partially replace extracted nutrients and restitute the acid-buffering capacity of the soil [23]. Nevertheless, several authors have suggested that prior to utilising it in the agriculture system, fly ashes has to be subjected to further physical, chemical or thermal treatments processes due to the presence of high carbon, chlorine, alkali content and in some cases heavy metals [11,24]. To conclude, additional leaching tests are needed in order to qualify fly ashes obtained from the gasification of poultry litter as an inert or hazardous material and to determine whether they could potentially be used as a fertiliser or need to be landfilled.

Table 5. Maximum compositional values for trace elements within poultry litter ash used as a fertiliser (Poultry Litter Protocol)

Elements mg/kg	Upper limit within poultry litter ash, mg/kg	Poultry litter			Poultry litter with limestone (8% w/w)					
Gasifier temperature		700 °C			700 °C		750 °C			800 °C
ER		0.18	0.22	0.29	0.35	0.41	0.23	0.28	0.33	both
As	17	16	0	21	14	12	4	3	17	8
Cd	3	30	31	29	29	28	31	25	31	30
Co	11	3	2	2	2	3	2	2	3	34
Cr	31	320	411	296	170	222	205	222	372	245
Cu	596	1630	1673	1580	1505	1373	1416	1459	1813	1430
Hg	0.5	5	3	5	3	4	6	5	2	7
Mn	3500	2388	2352	2215	2246	2326	2563	2368	2490	2652
Mo	45	134	113	214	281	292	267	242	10	225
Ni	24	163	225	175	128	148	141	181	224	500
Pb	244	655	529	732	442	417	526	458	884	667
Se	11	1819	1738	2752	2897	2995	1960	2248	1766	2564
V	20	0	0	0	0	0	0	0	0	0
Zn	2063	92	112	76	84	102	67	69	61	60

4. Conclusion

Analyses of fly ashes from poultry litter gasification showed a significantly higher concentration than permitted of trace elements (Cd, Hg, Co, Cr, Cu, Hg, Mo, Ni, Pb and Se) in the fly ashes, restricting its use as an agriculture fertiliser, necessitating it being classified as a hazardous material under the waste management directive. Considering its moderate calorific value and carbon content, poultry litter fly ash from fluidised bed gasification could be used as a supplementary fuel. It is recommended that fly ashes from poultry litter gasification need post-treatment if utilised as a fertiliser, otherwise it should be landfilled. In addition, leaching tests are needed to be performed to understand the fate of alkali and alkaline earth metal on the surface and ground water contamination as well as environmental and air pollution.

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