Poultry Litter Gasification in a Fluidized Bed Reactor: Effects of Equivalence Ratio, Temperature and Limestone Addition on Tar Yield and Composition

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Abstract:

Air gasification of poultry litter was experimentally studied in a laboratory scale bubbling fluidized bed gasifier. Gasification tests were conducted at atmospheric pressure using silica sand as the bed material. This paper investigates the effect of equivalence ratio (ER) in the range of 0.18 - 0.41, temperature between 700 and 800 °C as well as the addition of limestone blended with the poultry litter, on tar yield and composition. The optimum conditions with regards to the tar (minimum total tar yield ≈ 3.2 $g_{total\ tar}\ kg^{-1}_{poultry\ litter\ (d.a.f.)}$) as well as product gas properties were achieved at 800 °C and ER = 0.3 using 8 % w/w of limestone blended with poultry litter. By varying ER poultry litter blended with limestone showed a reduction in total tar yield whereas poultry litter not blended with limestone showed increasing yield over the tested ER range. Moreover, in the presence of limestone, polycyclic aromatic hydrocarbons (PAHs) showed a tendency to reduce over the ER range tested. Increasing the temperature was shown to be effective to reduce the total tar yield but the amounts of PAHs increased. Due to the high nitrogen content of the poultry litter (≈ 6.5 % w/w (d.a.f.)) the chemical composition of the tar is distinctive compared with conventional lignocellulosic fuels. Nitrogen-containing hydrocarbons such as pyridine, 2-methylpyridine, 2-methyl-1H-pyrrole, and benzonitrile were identified in significant amounts. It was demonstrated that poultry litter can be gasified by blending it with limestone, yielding a product gas with low tar content as well as diminishing the risk of agglomeration caused by the mineral composition of poultry litter ash (high K and P content).

Keywords: Gasification, poultry litter, limestone, tar, solid phase adsorption

1. Introduction

According the AVEC annual report 2016, the European Union is the leading supplier of the poultry meat with an annual production of 13.6 million tonnes in 2015 (Vermeeren *et al*., 2016). The report also predicted a growth rate of about 1 % a year. Intensive livestock production is financially more viable than traditional farming practices, however such industrialized production faces issues associated with its environment impact due to the accumulation of large quantities of waste with estimates of 1.4 billion tons (Foged *et al*., 2011) of manure in EU states. The increasing popularity of free range and organic farming supported by European Directives 2007/43/EC and 1999/74/EC requires poultry farmers to comply with minimum animal welfare standards which results in an increased volume of poultry litter due to utilization of the bedding material (i.e. wood shavings, straw, and hay). Poultry litter is a heterogeneous fuel, composed of bedding material, excreta, waste feed, and feathers. Compared to the conventional lignocellulosic feedstocks, poultry litter is recognized as a low value fuel due to its relatively high moisture and ash content. It is also a source of nutrients such as nitrogen, phosphorous, and potassium (Lynch *et al*., 2013). Recent research studies on poultry litter recycling lean towards combustion technology. Commercial scale incinerators of poultry litter are currently being used for electricity generation and ash recovery in the UK, the USA, and The Netherlands (Billen *et al*., 2015). The recent European Union's (EU) regulation 592/2014 paves the path to combust the poultry litter for the energy generation and its utilization on the farms. In the recent past, attempts have been made by several contemporary researchers to gasify poultry litter in a fluidized bed gasifier (Di Gregorio *et al*., 2014; Pandey *et al*., 2016). These studies have concluded that due to the high content of elements such as phosphorous and potassium, poultry waste is prone to provoke sintering and agglomeration when gasifying in a fluidized bed gasifier. To avoid sintering and agglomeration limestone/calcite

($CaCO_3$/CaO) have been added to the bed during industrial scale fluidized bed combustion of poultry litter (Billen *et al*., 2014). Tar is inevitable by-product of gasification process defined as a generic (unspecific) term for all organic compounds present in the gasification product gas excluding gaseous hydrocarbons lighter then benzene (CEN/TS_15439, 2006). Tar is a black and sticky material potentially giving rise to system malfunction if condensation occurs. As such tar needs to be cleaned from the product gas for most applications (Basu, 2010). Tar from poultry litter gasification in a fluidized bed reactor has not been reported yet. Higher nitrogen content in poultry litter with respect to the conventional lignocellulosic biomass is expected to deliver variety of nitrogen-containing compounds. Pandey *et al*. (2016) reported that large portion of poultry litter nitrogen was converted into NH_3 and HCN. Jaramillo-Arango *et al*. (2016) investigated the composition of pyrolysis oil from fluidized bed tests employing nitrogen rich sewage sludge. Notable amounts of aliphatic acetamide, one aromatic ring pyridine, pyrimidine, pyrrole, aniline, and benzonitrile as well as two ring quinoline and indole have been detected. It is also well known that tar can be decomposed catalytically with limestone/calcite which is inexpensive, abundant and naturally occurring non-toxic material (Simell *et al*., 1995; Saw and Pang, 2012). In regards to tar mitigation, Simell *et al*. (1995) tested the catalytic activity of carbonate rocks passing model tar compounds over a fixed catalytic bed. Calcined CaO was found to be a good catalyst. However, CaO converts into the carbonated form $CaCO_3$, when CO_2 partical pressure is higher than that of reaction equilibrium at given temperature. The reaction rate between $CaCO_3$ and tar is very slow or even does nto exist. Tests showed that at 900 °C the CaO was carbonated to $CaCO_3$ only if the partial pressure of CO_2 was higher than 100 kPa. Saw and Pang (2012) tested the degree of tar reduction with 0 %, 50 %, and 100 % calcite as a fluidizing material. The total tar concentration (sum of all the tar compounds) decreased exponentially from 5.0 to 0.7 g Nm^{-3} with the calcite loading from 0 % to 100 %. A significant reduction was also observed for all the individual tar compounds studied. Tar reduction with calcite loading was most likely due to the steam reforming of tars in the presence of CaO. The steam reforming reactions of the phenol, cresols toluene are shown in Equations 1-4.

$$C_6H_5OH + 5H_2O \leftrightarrow 6CO + 8H_2 \quad (1)$$

$$(CH_3)C_6H_4OH + 13H_2O \leftrightarrow 7CO_2 + 17H_2 \quad (2)$$

$$C_7H_8 + 7H_2O \leftrightarrow 7CO + 11H_2 \quad (3)$$

$$C_7H_8 + 14H_2O \leftrightarrow 7CO_2 + 18H_2 \quad (4)$$

However, enhanced production of H_2 may have a negative effect on tar steam reforming reactions because H_2 deactivates the CaO by adsorption onto its active sites (Saw and Pang, 2012). The composition of the tar from poutry litter gasification is expected to reflect high amount of nitrogen and low lignin content in the poultry litter. The formation and decomposition of poultry litter tar is further discussed in the section 3. In this paper, an attempt has been made to present the tar yields and compositions derived from experiments of poultry litter gasification using a lab scale fluidized bed reactor. The objectives of this study are to investigate (a) the effect of equivalence ratio, (b) the effect of limestone (blended with the poultry litter), and (c) the effect of reactor temperature on the tar yield and its composition. Some data regarding tar yields from this study have already been published by Pandey *et al*. (2016). To the best of the author's knowledge this is the first study to demonstrate how limestone/calcite addition influences tar compositions from poultry litter gasification using a bubbling fluidized bed gasifier.

2. Materials and methods

2.1. Materials

The detailed description of poultry litter collection, preparation and characterization can be found elsewhere (Pandey *et al*., 2016). Moreover a summary of relevant information is presented here. The bulk density of the partially dried poultry litter was 360 kg m^{-3}, with a particle size between 0.7 and 2.8 mm. The limestone was supplied by Rheinkalk GmbH (Brilon, Germany) with particle size in the range 0.9 and 1.2 mm. Ultimate and proximate properties, chemical composition as well as heating value of the poultry litter are reported in Table 1. The content of fixed carbon was calculated by subtracting the moisture, ash, and volatile matter content from 100 %. Likewise, oxygen content in the fuel was calculated by the difference.

Table 1: Chemical characteristic of poultry litter (Pandey *et al*., 2016).

Proximate analysis	(% w/w)
Moisture (a.r.)	22.10
Volatile Matter (d.b.)	73.65 ± 0.02
Ash (d.b.)	17.55 ± 0.06
Fixed Carbon [a] (d.b.)	8.81 ± 0.02
LHV (MJ/kg) (a.r.)	13.53 ± 0.41
Ultimate analysis (d.a.f.)	(% w/w)
N	6.48 ± 0.01
C	54.70 ± 0.37
H	6.43 ± 0.07
S	0.90 ± 0.03
Cl	0.70 ± 0.02
O [a]	30.79 ± 0.25
Chemical composition (d.b.) (wt. %)	
Hemicellulose	11.72
Cellulose	12.88
Lignin	14.16
Extractives [b]	39.21

[a] Calculated by difference, a.r. − as received, d.b. − dry basis, d.a.f. − dry and ash free basis, [b] Containing water and ethanol extractives.

2.2. Experimental facility

The gasification experiments were conducted within the BRISK EU FP7 framework project using a lab scale air-blown bubbling fluidized bed gasifier located at the Energy Research Centre of The Netherlands (ECN). Experiments

Table 2: Summary of operating conditions during fluidized bed gasification of poultry litter.

Test number	1	2	3	5	6	7	9	10	11	13	14
Feedstock type	Poultry litter			Poultry litter with 8 % w/w limestone			Poultry litter with 8 % w/w limestone			Poultry litter with 8 % w/w limestone	
Poultry litter feed rate, kg hr^{-1} (a.r.)	0.66			0.49			0.61			0.57	
Limestone, kg hr^{-1}	0.0			0.04			0.05			0.05	
Temperature of gasifier, ºC	700			700			750			800	
Temperature of gasifying medium, ºC	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^{-1}	6	7.2	10	7	8.5	10	7	8.5	10	7	8.5
Nitrogen flow rate, dm^3 min^{-1}	6	4.8	2	5	3.5	2	5	3.5	2	5	3.5
Fluidizing medium flow rate, dm^3 min^{-1}	12	12	12	12	12	12	12	12	12	12	12
Superficial gas velocity based on the total product gas yield, m s^{-1} (T_g)	0.21	0.24	0.24	0.22	0.21	0.20	0.24	0.23	0.23	0.25	0.24

were performed at different temperatures (700, 750, 800 °C) and at different ERs between 0.18 and 0.41 by adjusting the air and N2 flow rate, while maintaining a constant feedstock feed rate. The downstream sections of the reactor up to the cold filter were insulated and maintained at 400 °C in order to avoid tar condensation. Tar samples were taken through a SPA sampling port located after the hot filter. Silica sand with a particle size between 0.25 and 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 and to reduce the risk of bed agglomeration, 1.2 kg of fresh silica sand was used at the beginning of each experimental day. Gasification experiments were conducted in such a way that the fluidizing regime remained constant throughout the tests. Calculated minimum fluidizing velocity was around 0.097 m s-1 at 20 °C, determinated according to Wen and Yu's correlation (Wen and Yu, 1966). Each test under given gasification conditions lasted about an hour. Within the first 30 min after commencing fuel feeding reaction steady state was reached. The last 30 mins were dedicated to the sampling and analysis of permanent gases and tar. Relevant information comprising technical data and operating conditions of the experimental setup was previously presented by Pandey et al. (2016) and are also concisely outlined in Table 2. Note that tests numbered as 1, 2, and 3 were carried out solely with poltry litter, while tests 5 to 14 include poultry litter blended with 8 % w/w of limestone, respectively.

2.3. Measurement methods

The detailed description of the solid-phase adsorption (SPA) tar sampling method, extraction, and chromatographic analysis of tar is provided elsewhere (Horvat *et al*., 2016 a). Briefly, SPA cartridges were assembled by packing 500 mg of aminopropyl silica sorbent. The sampling volume was adjusted to 100 mL of dry product gas. For each experimental condition two parallel SPA samples were taken. After SPA sampling the cartridges were shipped to the University of Limerick – Ireland where the tar compounds were extracted from the sorbent by the addition of 3 × 600 µL of dichloromethane. Tert-butylcyclohexane and 4-ethoxy phenol were added as internal standards to the tar solutions. An Agilent 7890A GC coupled with a triple-axis MSD 5975C was used for identification of the most abundant tar compounds. A Thermo Scientific Trace 1310 GC with a flame ionization detector (GC-FID) was used to quantify the tar. Calibration curves using naphthalene/tert-butylcyclohexane and phenol/4-ethoxy phenol were applied to integrate the aromatic and phenolic tars, respectively. Tar yields are expressed on a mass basis as g_{tar} $kg^{-1}_{poultry\ litter\ (d.a.f.)}$ 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). Total tar in this paper refers to GC detectable tar including those tar compounds eluted from benzonitrile ($M \approx 103$ g mol^{-1}) to benz[a]anthracene ($M \approx 228$ g mol^{-1}). The reason why total tar does not include the compounds from benzene to benzonitrile is due to the shipping of the SPA cartridges overseas for chemical analysis. As reported previously by Horvat *et al*. (2016 b) a significant portion of the volatile compounds such as benzene, toluene, xylene, styrene are lost during transport resulting in a quantitative underestimation as well as poor measurement repeatability. The results of poultry litter tar in Figures 2−6 are presented in duplicate (i.e. as duplicate SPA samples were taken) for each gasification condition to show the repeatability of the measurements and the random errors associated with fluctuations in the feeding rate. It is evident that the measurement repeatability is quite poor and one possible reason could be the low tar content in the product gas (i.e. under 10 $g_{total\ tar}$ $kg^{-1}_{poultry\ litter\ (d.a.f.)}$).

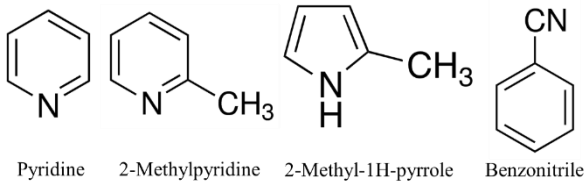
3. Results and discussion

The identified tar compounds are presented in Table 3 in the order in which they eluted. It is worth mentioning that the composition of the tars from poultry litter gasification is distinctively different from the tar composition from conventional lignocellulosic fuels, specifically in terms of nitrogen containing hydrocarbons. Most of the nitrogen in the poultry litter derives from the animal feed, excreta, and feathers rather than from the bedding material and this nitrogen is chemically incorporated into protein molecules and urea. It is believed that the presence of significant amounts of pyridine, 2-methylpyridine, 2-methyl-1H-pyrrole, and benzonitrile in tar is due to the high level of

nitrogen in the fuel (poultry litter). The question is whether nitrogen-containing hydrocarbons derive from proteins resembling their monomer structure or as a result of reforming reactions between permanent gases (i.e. NO_x, NH_3, CHN) and condensable fraction (i.e. tar) in the product gas. The formation of nitrogen containing hydrocarbons in the pyrolysis process have been studied by Dignac *et al*. (2005) using composted and fresh vegetables and green wastes (i.e. salad, zucchini, carrots). Pyrolysis-GC-MS was employed in order to specify the origin of the pyrolysis products. In the pyrolysates from fresh vegetables pyridine, pyrrole, benzonitrile, and indole derivatives were detected among the other nitrogen containing hydrocarbons. The authors attributed the pyridine derivatives to the pyrolysis of alanine-containing proteins and peptides, with the benzonitrile derivatives probably formed from pyrolysis of phenylalanine-containing proteins. Pyrrole and derivatives were formed by cyclization during the pyrolysis of proteins containing proline, hydroxyproline, glycine and glutamic acid, but could also be pyrolysis products of pigments such as chlorophyll. The proteins in the poultry litter originate from waste feed and feathers, while the chlorophyll originates from bedding material and waste feed. Moreover, poultry excreta also contains nitrogen that possibly plays a role in the formation of nitrogen containing hydrocarbons as indicated by Inoue *et al*. (1999) who analyzed the products of liquefaction of ammonia and cellulose. Brebu and Spiridon (2011) studied the thermal degradation of sheep wool, human hair and chicken feathers containing keratin proteins and attributed the formation of aromatic pyrroles and pyridines to the amino acids in the protein of keratin. Most part of the nitrogen containing hydrocarbons was found in the aqueous phase of the pyrolysis condensate which needs to be taken into account in the development of tar cleaning and waste water treatment technologies. Nine individual tar compounds (in Table 3 designated by*) are presented qualitatively in the Figures 2-6. Pyridine and benzonitrile represent nitrogen containing hydrocarbons, phenol and cresols phenolic hydrocarbons, while indene, naphthalene, acenaphthylene, phenanthrene appear for PAHs. Nitrogen containing compounds are normally not reported in the relevant gasification literature since insignificant amounts are generated from conventional lignocellulosic feedstock. Figure 1 shows structural formulas of the nitrogen containing compounds identified in this study. Figures 2-5 shows the changes in the total tar and eight individual tar compounds generated from the poultry litter as a function of equivalence ratio and limestone addition. The scale on the y-axis is kept the same in all graphs in order to simplify comparison of tar yields. It is imperative to stress that tar yields from poultry litter gasification are observed to be lower than from feedstocks with a higher organic fraction. The total tar yields presented in Figures 2-6 (all figures) varies from 2.4 to 8.8 $g_{total\ tar}\ kg^{-1}_{poultry\ litter\ (d.a.f.)}$. Low total tar yields can be attributed to a very specific composition of poultry litter which contains high ash content and low organic fraction in particular lignin content (Table 1). Lignin is known as tar precursor. Lignin gives rise to higher total GC detectable tar and PAHs than cellulose and hemicellulose (Rabou *et al*., 2009; Yu *et al*., 2014). However, smaller quantities of phenols and PAHs can also be formed from cellulose and hemicellulose (Fitzpatrick *et al*., 2008). Ash content of 17.55 wt. % in poultry litter is regarded as high but its composition and in particular the content of elements such as Ca, Mg, Al, Fe, Zn, Mn (Pandey *et al*., 2016) which exhibit catalytic activity towards tar cracking could have played a significant role in the total tar reduction (Abu El-Rub *et al*., 2004). Comparing the total tar yield from the relevant literature is complicated due to differences in tar definition, sampling conditions, analytical instrument calibration, and reported units. Nevertheless, total tar quantities in this study may be notably higher if benzene and toluene are included in definition of total tar. However, Kinoshita *et al*. (1994) reported total tar yields in the range of 40-45 $g_{total\ tar}\ kg^{-1}_{dry\ wood\ sawdust}$ while conducting the tests under similar ER conditions. Horvat *et al*. (2016 c) measured total tar between 14-34 $g_{total\ tar}\ kg^{-1}_{biomass\ (d.a.f.)}$ from raw and torrefied Miscanthus x giganteus using the same experimental reactor as being used for this study. Compared to the poultry litter (Table 2) raw and torrefied Miscanthus x giganteus carry lower ash content of 2.8 and 4.2 wt. % and higher lignin content of 21 and 43 wt. %, respectively.

Table 3: Identified tar compounds with the retention time and classification according to Milne *et al*. (1998).

Tar compound	Retention time (min)	Tar group
Benzene	4,65	Secondary
Pyridine*	7,15	Secondary
Toluene	7,90	Secondary
2-Methylpyridine	8,25	Secondary
2-Methyl-1H-pyrrole	9,81	Secondary
Ethylbenzene	11,38	Secondary
p-Xylene	11,68	Secondary
Styrene	12,49	Secondary
Benzonitrile*	15,85	Secondary
Phenol*	16,15	Secondary
Indene*	17,81	Secondary
o/m/p-Methylphenol*	18,25	Secondary
o/m/p -Methylphenol*	18,92	Secondary
1,2-Dihydronaphthalene	21,10	Secondary
Naphthalene*	22,18	Tertiary-PAH
Acenaphthylene*	29,36	Tertiary-PAH
2,4A-Dihydrofluorene	32,14	Secondary
Fluorene	32,57	Tertiary-PAH
Phenanthrene*	36,80	Tertiary-PAH
1-Methylphenanthrene	38,84	Tertiary-alkyl
4-Methylphenanthrene	39,22	Tertiary-alkyl
Pyrene	41,48	Tertiary-PAH
11H-Benzo[b]Fluorene	41,86	Tertiary-PAH
Benzo[a]anthracene	45,85	Tertiary-PAH



Pyridine 2-Methylpyridine 2-Methyl-1H-pyrrole Benzonitrile

Figure 1: Nitrogen containing compounds found in poultry litter tar.

3.1. Effect of equivalence ratio on tar yield and composition-without limestone addition

Figure 2 includes total tar yields and composition over the ER range between 0.18 and 0.3 at 700 °C, without addition of the limestone to the poultry litter. The total tar as well as nitrogen and oxygen containing tar compounds increases with the ER. Such observation is in contrary to the results presented by Kinoshita *et al.* (1994) and Hanping *et al.* (2008) employing wood sawdust, peanut shell, and wheat straw as a fuel. Moreover, Horvat *et al.* (2016 c) suggested that at constant temperature the ER has relatively little impact on the yield or composition of tar from grassy biomass. Yields of PAH compounds follow the increasing trend with ER.

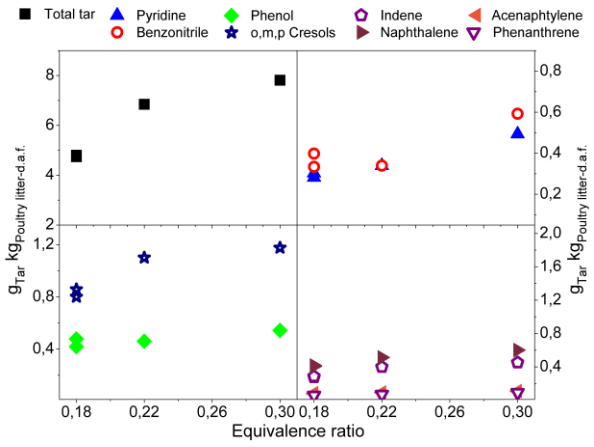


Figure 2: Equivalence ratio profile for the tar yields at 700 °C reactor without limestone addition.

3.2. Effect of equivalence ratio on tar yield and composition-with limestone addition

Figure 3 presents tar yields for the experiments undertaken between an ER of 0.29 and 0.41, and gasification temperature of 700 °C using poultry litter blended with limestone (8 % w/w). Figure 2 and 3 show data for the same temperature, but the ERs correspond to two different ranges (0.18 - 0.30 vs. 0.29 - 0.41). Since the range of ER differ for both the limestone amended and raw poultry litter, it is not possible to draw clear conclusions whether the difference in tar yields is due to the effect of limestone. However, the reduction in total tar is observed from Figure 3 over the tested ER range when poultry litter was blended with the limestone. Similar trends are observed in the Figure 4 and 5 showing decreasing total tar over the range of ER tested at gasification temperatures of 750 °C and 800 °C, respectively. It is worth emphasizing that the total tar and yields of individual tar species show the same trend. These findings suggest a positive effect on the catalytic properties of limestone/calcite due to increasing ER. From the data available from Pandey *et al.* (2016) an increase in ER resulted in a reduction of both H_2 and CO concentration and an increase in CO_2 in the product gas due to combustion of the volatiles and char. Despite its higher concentration, it seems that the CO_2 did not impact on the catalytic ability of the calcite due to carbonization of limestone. Delgado *et al.* (1996) and Simell *et al.* (1995) reported rapid catalytic deactivation of limestone/calcite as a result of coke deposition on the surface active sites. The authors also stated that both wet (steam) and dry (CO_2) gasification eliminate coke from the surface which could explain the increased catalytic activity with increasing ER. Moreover, at higher ER more oxygen is available to oxidize deposited coke. It is not clear how the oxygen itself affects the redox equilibrium of limestone/calcite.

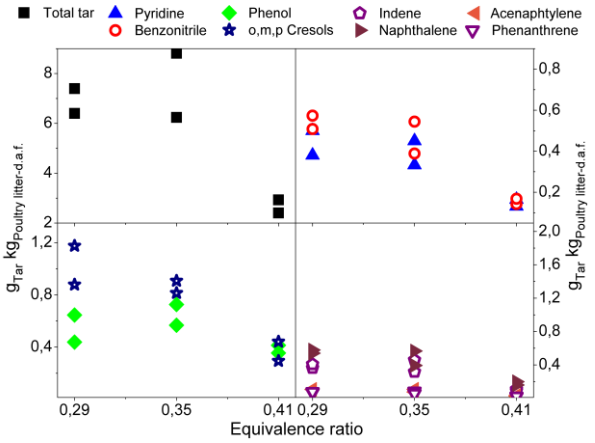


Figure 3: Equivalence ratio profile for the tar yields at 700 °C reactor with limestone addition.

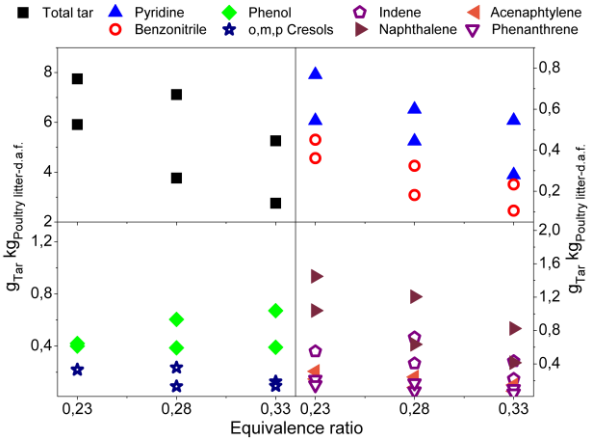


Figure 4: Equivalence ratio profile for the tar yields at 750 °C reactor with limestone addition.

3.3. Effect of temperature on tar yield and composition

In the Figures 2-4 the yields of phenols (from 0.09 to 1.18 g_{tar} $kg^{-1}_{poultry\ litter\ (d.a.f.)}$) and benzonitrile (from 0.10 to 0.59 g_{tar} $kg^{-1}_{poultry\ litter\ (d.a.f.)}$) are relatively high because of the low gasification temperatures between 700 and 750 °C. However, at 800 °C, almost complete conversion (from 0.06 to 0.21 g_{tar} $kg^{-1}_{poultry\ litter\ (d.a.f.)}$) of phenols and benzonitrile occurs via demethylation, dehydration (Dufour *et al.*, 2011) and denitrification (Liu *et al.*, 2016). Reforming mechanisms using model compounds such as pyridine, pyrrole and indole have been studied in the context of thermochemical coal conversion. Liu *et al.* (2016) measured NH_3 and HCN as the main gaseous products from conversion of nitrogen containing hydrocarbons. Gasification of indole was carried out in supercritical water and the authors concluded that one portion of indole converted directly to aromatic

compounds without nitrogen by releasing ammonia, while another portion of indole was converted to nitrogen containing aromatic compounds such as aniline, o-toluidine, and 9-nitroso-9H-carbazole. Zhao *et al*. (2010) pyrolysed pyridine and pyrrole at 600 - 1200 °C in a flow reactor. H_2 and HCN were measured in order to determine the thermal stability of pyridine and pyrrole.

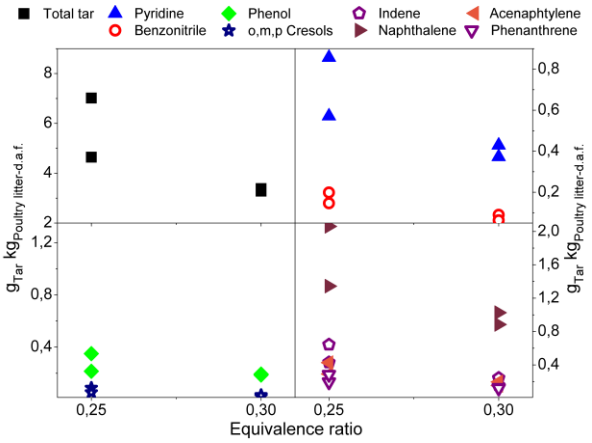


Figure 5: Equivalence ratio profile for the tar yields at 800 °C reactor with limestone addition.

The results showed that the thermal stability of pyridine is greater since significant production of HCN was observed at 825 °C while pyrrole generated notable amounts of HCN at 775 °C. A thermal degradation (i.e. ring-opening) mechanism was proposed for both nitrogen containing hydrocarbons studied. The pyridine ring undergoes a series of free radical reactions resulting in H_2 and an aliphatic •R-CN. On the other hand, it is assumed that pyrrole undergoes direct ring opening, therefore reforming into an aliphatic R-CN without passing through free radical reactions. Figure 6 presents the total tar yields and compositions with respect to gasification temperature at an ER of 0.29 ± 0.01. The yield of total tar and phenolic species decreases with the temperature although some studies (Milne *et al*., 1998; Van Paasen *et al*., 2004; Horvat *et al*., 2016 c) showed the peak yield at 750 °C followed by decrease with temperature. According to Delgado *et al*. (1996) the higher the reaction temperature higher the tar catalytic activity of calcite tested in the temperature range of 780 – 880 °C in a fluidized bed biomass gasifier. However, the authors also observed catalyst deactivation after 30 minutes due to coke formation and adsorption on the active sites. Regeneration of calcite by the coke removal was effectively achieved by steam and dry (CO_2) gasification. Figure 6 indicates that improved catalytic activity of limestone/calcite follows the increasing temperature. It seems that the coke gasification (i.e. coke removal) rate is higher than the coke formation, maintaining limestone/calcite catalytic activity. Another possible reason for limestone/calcite activity could be due to the continous feeding of fresh limestone together with feedstock, resulting in a perpetual availability of catalitically active limestone. Indene has its peak production at 750 °C while the PAH yields gradually increases with temperature. The nitrogen-containing hydrocarbons quantified do not follow the same trend with temperature. Benzonitrile yield decreases while in contrast, pyridine yield remains relatively high at elevated temperatures indicating high thermal stability. Pyridine has a non-branching aromatic chemical structure while the benzonitrile substituent makes it more thermally sensitive. This observation was confirmed by Zhao *et al*. (2010) who reported that pyridine undergoes thermal degradation process at temperatures above 825 °C.

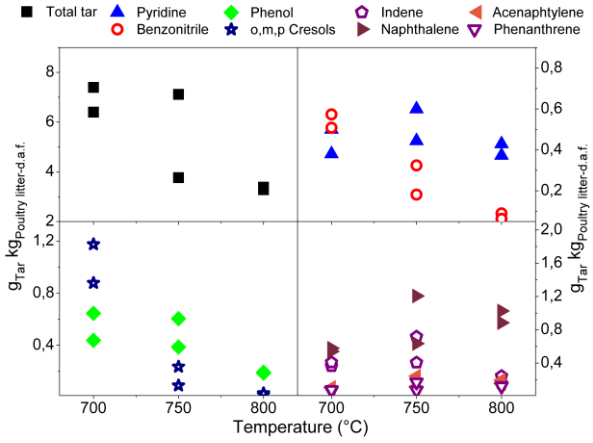


Figure 6: Temperature profile for the tar yields at an equivalence ratio of 0.29 ± 0.01 with limestone addition.

4. Conclusions

Yields and composition of tar from the bubbling fluidized bed gasification of poultry litter were investigated as a function of temperature, equivalence ratio and limestone addition to the feedstock. Limestone was added in order to reduce the risk of bed agglomeration. For the range of gasification conditions tested, the following conclusions can be drawn: (1) Due to the high content of catalytically active inorganic fraction and low lignin content, poultry litter generates low yields of total tar in the range of 2.4 - 8.8 $g_{tar}\ kg^{-1}_{poultry\ litter\ (d.a.f.)}$ for the tested temperatures between 700 to 800 °C. (2). The composition of tar from poultry litter gasification is remarkably different from those of conventional lignocellulosic biomass. Nitrogen incorporated in the protein structures of animal feed, excreta, and feathers is likely the reason for the significant amounts of nitrogen containing hydrocarbons detected. (3) Limestone blended with the poultry litter results in a tar reduction effect with increasing either ER or temperature. (4) Temperature is an effective measure to reduce total tar yield, but the amounts of PAHs increase. (5) Equivalence ratio (ER) shows distinctive effect on tar yields. In the presence of limestone tar yields decrease, while the opposite trend was observed in the absence of limestone.

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