

Article

Fast Pyrolysis of Poultry Litter in a Bubbling Fluidised Bed Reactor: Energy and Nutrient Recovery

Daya Shankar Pandey ^{1,2,*} , Giannis Katsaros ¹, Christian Lindfors ³, James J. Leahy ⁴ and Savvas A. Tassou ¹ 

¹ RCUK Centre for Sustainable Energy Use in Food Chains (CSEF), Institute of Energy Futures, Brunel University London, Uxbridge UB8 3PH, UK; ioannis.katsaros@brunel.ac.uk (G.K.); savvas.tassou@brunel.ac.uk (S.A.T.)

² School of Engineering and the Built Environment, Anglia Ruskin University, Chelmsford CM1 1SQ, UK

³ VTT Technical Research Centre of Finland, Biologinkuja 5, 02044 Espoo, Finland; christian.lindfors@vtt.fi

⁴ Carbolea Research Group, Department of Chemical Sciences, Bernal Institute, University of Limerick, V94 T9PX Limerick, Ireland; j.j.leahy@ul.ie

* Correspondence: daya.pandey@brunel.ac.uk or daya.pandey@anglia.ac.uk; Tel.: +44-1245-683-939

Received: 8 March 2019; Accepted: 25 April 2019; Published: 1 May 2019



Abstract: Livestock production is among the most rapidly growing sectors of the agricultural economy driven primarily by growing demand for animal protein, but also posing significant waste disposal issues and environmental impacts. Moreover, opportunities exist for utilising animal waste at the farm level for heat and power generation (thermal conversion) which can contribute to economic sustainability and also provide a bio-fertiliser for soil amendment. The present study is focused on energy and nutrient recovery from poultry litter using a thermochemical conversion technology (fast pyrolysis). The formation of products (gases, biochar and bio-oil) during the fast pyrolysis of poultry litter was experimentally investigated in a laboratory-scale bubbling fluidised bed reactor. Pyrolytic gases accounted for 15–22 wt.% of the product. The carbon content in biochar increased from 47 to 48.5 wt.% with an increase in the pyrolysis temperature. Phosphorous and potassium recovery in the biochar were over 75%, suggesting that it could be used as an organic soil amendment. The high ash content in poultry litter (14.3 wt.%) resulted in low bio-oil and high biochar yield. The bio-oil yield was over 27 wt.% with a higher heating value of 32.17 MJ/kg (dry basis). The total acid number of the bio-oil decreased from 46.30 to 38.50 with an increase in temperature. The nitrogen content in the bio-oil produced from the poultry litter (>7 wt.%) was significantly higher compared to bio-oil produced from the wood (0.1 wt.%).

Keywords: fast pyrolysis; poultry litter; nutrient recovery; bio-oil; biochar

1. Introduction

According to the European Environmental Agency (EEA) greenhouse gas emissions in the EU-28 in 2015 were 4452 million tonnes CO₂ equivalent and the share from the agriculture sector was 11.3%, mainly from ruminants [1]. In the EU, poultry meat production has increased by 11% in a single decade (2005–2015) reaching over 12 million tonnes of poultry meat in 2015, and it is expected to rise by another 6% by 2025 [2]. Among the different meat segments, the growth rate of poultry meat is predicted to have the highest development globally in the near future. In order to cope with the increased demand for poultry meat, intensive poultry farming is required. However, intensive livestock production generates significant waste disposal issues and environmental impacts. The estimated accumulation of animal manure in the EU is approximately 1.4 billion tonnes/year and the share of poultry litter is about 7.9% [3]. Traditionally, poultry litter which includes manure, bedding material, egg shells, feathers,

etc., has been applied as a fertiliser and soil conditioner via direct land application [4]. However, land application alone is no longer a sustainable solution to the growing volume of animal waste and likely to be uneconomic [5]. Therefore, new waste treatment technologies addressing sustainability challenges at the nexus of food production and energy are needed to tackle the disposal problem of poultry litter.

The EU's 2030 Framework for Climate and Energy Policies has recently been revised and the share of EU energy to be produced from renewable resources was raised to 27% [6]. Bioenergy technologies could play a vital role in achieving the EU2030 targets by reducing the greenhouse gas emissions arising from manure management and fertiliser application while increasing the share of renewable bioenergy. Alternatively, poultry litter or animal manure (dried) could be converted into liquid fuel and value-added products using thermochemical conversion technologies [7,8]. Small or modular pyrolysis units situated directly on poultry farms could produce sufficient bio-oil to make a farm self-sustainable by off-setting fossil fuel consumption for heating poultry houses resulting in economic sustainability and also providing bio-fertiliser for soil amendment (nutrient rich biochar). A recent review paper analysed the characteristics of poultry litter as fuel and explored different thermochemical conversion processes for energy integration [9].

Pyrolysis is one of the most attractive alternative options amongst the bioenergy conversion technologies to produce biofuels and soil conditioners from poultry litter. Pyrolysis is a thermal decomposition process that converts biomass and other organic matter into high energy density solids (biochar), liquids (bio-oil) and gases (syngas/biogas) in the absence of an oxidising agent (oxygen-free environment). It is a complex thermochemical process involving both simultaneous and successive reactions of drying and devolatilisation [10]. The product yields from a pyrolysis process is dependent on various process parameters such as the temperature within the reactor, residence time, heating rate of the feedstock, particle size of the feedstock, pressure and reactor configuration [11]. Pyrolysis can be categorised into slow, medium and fast pyrolysis. In fast pyrolysis, the decomposition of feedstock occurs rapidly, resulting in the production of vapour and aerosols and smaller amounts of biochar and gas. Following condensation, a dark-brown homogenous liquid is formed, with a calorific value roughly half that of fossil fuel oil [10]. Fluidised bed reactors are the recommended technology for fast pyrolysis because of their ease of operation, stability, scaling-up potential and high bio-oil yield [12].

Poultry litter has a relatively high ash content and at an elevated temperature this can give rise to ash fusion and sintering associated with potassium, phosphorous and other alkali materials present in the ash leading to defluidisation or bed agglomeration problem. Since the pyrolysis temperatures are normally kept in the range of 400 to 600 °C, defluidisation or bed agglomeration problems should not occur [13,14].

Pyrolysis technology has so far been used predominantly on biomass with very few studies addressing feedstock originating from livestock. In an investigation, five manure-based feedstocks (i.e., swine-separated solids; paved feedlot manure; dairy manure; poultry litter; and turkey litter) were pyrolysed at 300 and 700 °C. Amongst these poultry litters, char exhibited the highest electro conductivity (a parameter measuring nutrients in the substrate) [8]. In another investigation, biochar produced from chicken manure using a batch-type tubular pyrolysis reactor was used as a green catalyst to produce biodiesel (fatty acid methyl ester). The pseudo-catalytic transesterification reaction performance of chicken manure biochar compared well against commercially available porous materials (SiO₂), resulting in 95.6% fatty acid methyl ester yield at 350 °C. The study also recommended that in order to avoid thermal cracking of inorganic species (Ca) in chicken manure biochar, it should be produced at temperatures lower than 350 °C [15]. The pattern of product gas evolution during the pyrolysis and gasification of chicken manure was studied at different temperatures and oxygen enrichment in a batch reactor, and the authors concluded that the cumulative energy yields from the gasification process were higher compared to pyrolysis [16]. Pyrolysis and gasification of chicken manure have been experimentally studied using different gasifying media (i.e., nitrogen, air, carbon dioxide and steam) and temperatures. It was recommended that the gasifying media should be chosen

based on the availability of resources and the desired output [17]. Recently, an experimental analysis of slow pyrolysis of poultry litter was investigated at different temperatures using a laboratory-scale fixed-bed reactor. The pyrolytic gases evolved were estimated to be energetically adequate for the process to be self-sufficient. The energy transfer analysis showed that one-third of the heating value of the poultry litter was transferred to the organic liquid condensate and roughly the same was retained in the char. In this study, the maximum fraction of liquid condensate that could be upgraded to liquid biofuels was reported to be obtained at 550 °C [18].

The biocrude oil produced from fast pyrolysis of poultry litter is less acidic (pH values between 3.6–6.3) and with a higher calorific value (26–30 MJ/kg) compared to hardwood biocrude oil (23 MJ/kg). The higher calorific value and nitrogen content in the biocrude oils produced from poultry litter were due to the protein and nitrogen contents, respectively, in the raw poultry litter [19–21]. Nevertheless, biocrude oils produced from poultry litter are viscous and unstable compared to fossil derived petroleum fuels [19,22]. Biochar produced from poultry litter can also be used as a source for the preparation of activated carbon [23]. Several other batch and fixed-bed pyrolysis experiments were conducted for bio-oil production using a wide variety of feedstocks such as poultry industry waste [24], swine manure [25], food waste [26] and other agricultural and urban organic waste for biochar production [27].

Several fixed-bed and batch pyrolysis studies have been carried out on poultry litter and they validated its potential for sanitation and waste-to-energy valorisation. However, the results obtained from batch pyrolysis units cannot be used for up-scaling and design purposes. In contrast, relatively few studies have focused on fast pyrolysis of poultry litter in a fluidised bed reactor due to the high ash and moisture contents. The present study proposes a small-scale fluidised bed fast pyrolysis unit operating at relatively low temperature as a safe and economical way of disposing of poultry litter. The aim of this study is to explore the suitability of poultry litter as an alternative feedstock in fast pyrolysis for bio-oil production. Furthermore, the outcome of this work can be helpful in the design, scale-up and deployment of poultry litter-based pyrolysis units at farm level for combined heat and power generation and to make the poultry farms self-sufficient in energy. This work investigated the technical feasibility of fast pyrolysis processing of poultry litter as well as assessing the potential utilisation of the evolved gases and biochar (potential source of organic nutrients).

2. Materials and Methods

2.1. Materials

Poultry litter was collected from a Finnish poultry farm where it had been stored in an enclosed container before subsequent drying and pelleting. Peat was used as the bedding material. The poultry litter tested in this study was supplied by Biolan Finland as a 0.50 mm diameter and 0.98 mm long pellet. The poultry litter samples were transferred in sealed polyethylene bags to the laboratory and prepared according to BS EN 14780:2011 [28]. Moisture content of the poultry litter was measured according to BS EN 14774-3:2009 (105 °C) [29], whereas ash and volatile matter were determined in accordance with BS EN 14775:2009 (550 °C) [30] and BS EN 15148:2009 (900 °C) [31], respectively. Fixed carbon content was calculated by difference. The moisture and ash contents were 8.50% on as received (ar) and 14.30% dry basis (db), respectively. The higher heating value (HHV) of the poultry litter and the produced biochar was measured using an adiabatic oxygen bomb calorimeter as per BS EN 14918:2009 [32]. The ultimate, proximate and calorific value of the poultry litter are presented in Table 1. Based on its elemental composition, the poultry litter can be represented by an empirical formula $CH_{1.54}O_{0.57}N_{0.08}$ (db). The elemental composition (C, H, N and S) of the poultry litter was determined using a Variomax elemental analyser with the oxygen content calculated by difference. Chlorine content in poultry litter, biochar and liquid products was measured according to the CEN/TS 15408:2006 protocol [33].

Table 1. Proximate and ultimate analyses and calorific value of poultry litter.

Proximate Analysis (wt.%)	
Moisture (ar)	8.5
Ash content (db)	14.3
Volatile matter (db)	69.6
Fixed carbon * (db)	16.1
Ultimate Analysis (wt.%, db)	
Carbon	42.72
Hydrogen	5.5
Nitrogen	3.93
Sulphur	0.64
Chlorine	0.3
Oxygen *	32.6
HHV (in MJ/kg)	18

* Calculated by difference, HHV—Higher Heating Value.

Considering the high ash content, the elemental composition of poultry litter ash was also analysed prior to the experiment by inductively coupled plasma (ICP) and the results are presented in Table 2. The higher concentration of potassium and phosphorous in poultry litter ash indicates its fertilising potential.

Table 2. Inorganic trace elements in poultry litter ash.

Major Elements		Minor Elements	
Elements	Amount (mg/kg, dry)	Elements	Amount (mg/kg, dry)
Aluminium (Al)	1200	Arsenic (As)	<0.5
Calcium (Ca)	15,500	Barium (Ba)	29
Iron (Fe)	1600	Cadmium (Cd)	0.14
Magnesium (Mg)	8200	Cobalt (Co)	1.9
Manganese (Mn)	600	Chromium (Cr)	16
Phosphorous (P)	10,200	Copper (Cu)	84
Potassium (K)	27,700	Mercury (Hg)	<0.02
Silicon (Si)	7300	Molybdenum (Mo)	4.8
Sodium (Na)	4200	Nickel (Ni)	16
Sulphur (S)	6100	Lead (Pb)	1.5
Zinc (Zn)	450	Antimony (Sb)	<0.5
		Thallium (Tl)	<0.5
		Titanium (Ti)	95
		Vanadium (V)	4.2

2.2. Experimental Facility and Test Procedure

The fast pyrolysis experiments were carried out in a laboratory-scale bubbling fluidised bed reactor within the Biomass Research Infrastructure for Sharing Knowledge (BRISK2) EU-H2020 framework project at the Technical Research Centre of Finland (VTT) at atmospheric pressure. The experimental facility consisted of a hopper, twin screw feeder, bubbling fluidised bed reactor, cyclones, coolers and an electrostatic precipitator to recover bio-oils and aqueous condensate, as shown in Figure 1. The reactor had a diameter of 52 mm and a height of 570 mm. The temperature of the reactor was maintained by an external heat source (electric heaters). Elutriated char particles and bed material were recovered with two cyclones from the hot vapour stream before entering the liquid recovery unit. The product vapours were condensed in three coolers and an electrostatic precipitator. A detailed description of the experimental facility can be found elsewhere [34].

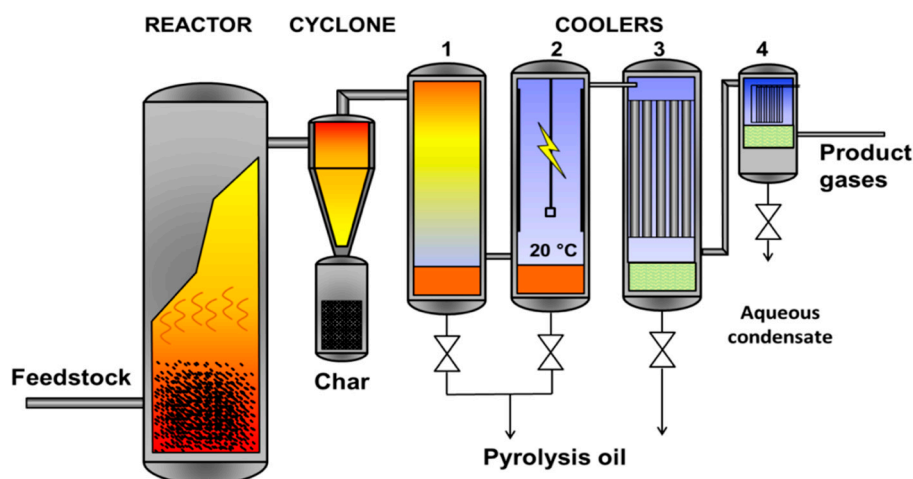


Figure 1. Experimental test rig.

Aluminium oxide (Al_2O_3) was used as the bed material with a particle size in the range of 0.5–0.7 mm. In order to avoid the influence of accumulated ash from the previous experiments, fresh Al_2O_3 (300 g) was used in the reactor for each test. Nitrogen was used as the fluidising medium and its flow rate was kept at 34 L/min during the entire test run. The fluidising medium was heated to 448 °C before being fed into the reactor. Fast pyrolysis is normally carried out at a moderate temperature of ~500 °C, and at high heating rates and short vapour residence times in order to maximise the yields of liquid products. The authors proposed an optimal temperature window for the fast pyrolysis process between 450–550 °C [35,36]. These conditions are suggested to prevent (i) the primary decomposition products from being thermally or catalytically cracked to smaller non-condensable gas molecules by the presence of char and (ii) polymerisation of the primary products to char (precursors) [37]. The elevated temperature which normally favours thermal cracking and steam reforming reactions of bio-oil during thermochemical conversion could have an adverse impact on the bio-oil yield and was the primary reason for choosing the low temperature window in this study. A temperature of 450 °C, is the minimum temperature for fast pyrolysis, as temperatures below this are considered intermediate or slow pyrolysis processes where the targeted product is char. Following the guidelines of the optimal temperature range proposed, in this study, experiments were planned and conducted at two different temperatures (460 and 530 °C) while keeping the same fluidisation velocity in the bed. The calculated vapour residence times were 0.9 and 0.7 s at the reactor operating temperatures of 460 and 530 °C respectively. Poultry litter was continuously fed into the reactor using a twin-screw feeding system. The fuel feeding rates were 0.96 and 0.88 kg/h. The duration of each test was approximately 3 h. Several bio-char and gas samples were collected during this period and their averaged values are reported as the corresponding standard deviations were less than 3%. Non-condensable gaseous products were measured online while gas samples were also collected for off-line analysis using micro gas chromatography (GC). Nevertheless, both the offline gas samples and the online micro GC analyses gave similar gas compositions.

2.3. Measurement Methods

Gas analyses: The major gaseous components (CO , CO_2 and CH_4) were determined continuously using a near-infrared (NIR) method. A zirconium-based oxide cell was used to detect oxygen content. Gas samples were collected during the experiments and were analysed by a GC equipped with a thermal conductivity and flame ionisation detector. The GC was calibrated with a gas mixture containing a specified gas concentration prior to use. Since nitrogen was used in the experiments for fluidising the bed, the amount of nitrogen fed to the reactor for fluidising the bed (Al_2O_3) was measured with a flow meter. Based on the amount of nitrogen fed into the reactor and the nitrogen composition measured by GC, the total amount of gases could be calculated. The amount of nitrogen

in the total gas accounted for 93–95%, whereas the composition of the gas reported in the paper was based on a nitrogen free basis. The compositional analyses of gaseous product were used for material balance calculation.

Biochar analyses: Biochar samples were collected from the cyclones at one hour intervals. Unconverted carbon (biochar) collected from cyclones was weighed to calculate the total biochar yield. The recovered biochar was further analysed for heating value, trace inorganic elements and elemental composition.

Liquid analyses: The condensable vapours were collected from the three coolers and an electrostatic precipitator. The liquid product obtained was removed from the condensers at the end of the experiment. Physical characterisation of the liquid product was carried out by employing modified standard methods [38]. Before liquid analyses, product liquids collected from the first cooler and electrostatic precipitator was combined. The product liquid collected from the second and third coolers had very high moisture contents and were therefore analysed separately. Moisture content was determined by Karl Fischer titration using a Metrohm 795 KFT Titrino titrator (ASTM E 203). The elemental composition (CHN) of bio-oil was determined by an Elementar Variomax CHN analyser (ASTM D 5291), whereas the HHV was measured using an IKA Werke C 5000 Control calorimeter (DIN 51900). Total acid number (TAN) was determined titrimetrically using a 785 DMP Titrino analyser (ASTM D 664).

The chemical composition of the bio-oil was determined by solvent fractionation. This consisted of separating the bio-oil into water-soluble and insoluble fractions by extraction with water. The water-soluble fraction was subsequently extracted with diethyl ether giving an ether-soluble and ether-insoluble (sugar-like material) fraction. The water-insoluble material was extracted using dichloromethane (DCM) providing a DCM-soluble fraction containing low molecular mass (LMM) lignin and a DCM-insoluble fraction containing high molecular mass (HMM) lignin. The LMM material contains lignin monomers, dimers (MM = 400 Da) and extractives with poor solubility in water, while the HMM fraction contains powder-like high molecular mass (MM = 1050 Da), lignin-derived material and solids.

3. Results and Discussion

3.1. Influence of Temperature on Pyrolysis Product Distribution and Mass Balance

Figure 2 shows the product yield of non-condensable (pyrolytic) gases, biochar and organic liquid produced during the fast pyrolysis process of poultry litter in a bubbling fluidised bed reactor. The quantities of organic liquid, biochar and pyrolytic water were determined gravimetrically while the non-condensable gases were quantified based on their elemental composition. Biochar is defined as the non-volatile solid residue of pyrolysis collected from the cyclones. The condensable product (bio-oil) was collected from the coolers. It is imperative to stress that the product distribution from poultry litter was unusual. Normally, in fast pyrolysis, the yield of liquid bio-oil exceeds that of the biochar, whereas fast pyrolysis of poultry litter resulted in a low liquid and high biochar yield, possibly due to the high ash content in the feedstock.

It is evident from Figure 2 that the yield of gases (from 14.64 to 21.93 wt.%) and organic liquids (from 23.18 to 27.62 wt.%) increased with an increase in reactor temperature, whereas the biochar yield did not show significant variation. The increase in the fraction of pyrolysis gas was mainly due to the improved solid-to-gas phase conversion process at an elevated temperature. Furthermore, at higher temperatures, an increase in the condensable hydrocarbons was observed due to the light hydrocarbons being transformed into secondary, tertiary and more stable compounds. Moreover, there is no observable change in the biochar yield which indicates that the product is stable and free from volatile matter. A similar result was reported by Marculescu and Stan [39] while pyrolysing the waste originating from poultry slaughterhouses (poultry feathers) over 550 °C. The pyrolytic water yield was reported to be in the range of 11.1–11.3 wt.%. The mass balance calculation was performed by considering the poultry litter as an inlet stream, whereas the outlet stream comprises

the non-condensable dry gas, unconverted carbon, and ash (biochar) and condensable hydrocarbons (bio-oil). The dilution effect of fluidising medium was not taken into account. The mass balance closure at 530 °C was 92%.

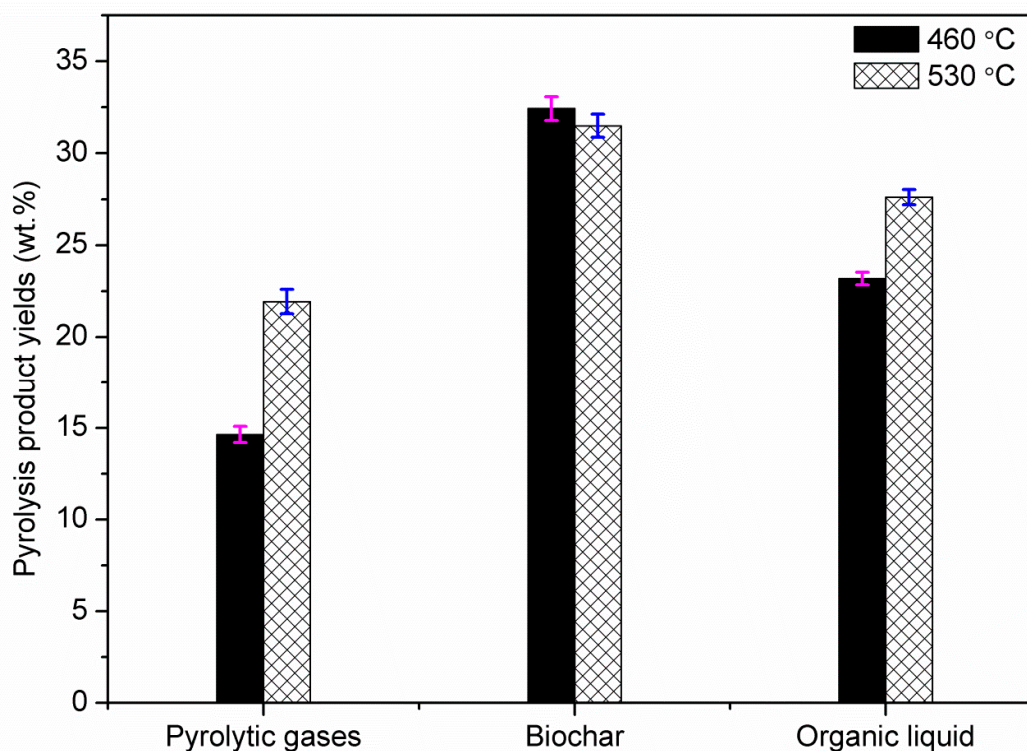


Figure 2. Distribution of product yields during fast fluidised bed pyrolysis of poultry litter.

A comparative analysis of the results obtained from fast pyrolysis of poultry litter with related literature studies is presented in Table 3. It is evident from the Table 3 that the bio-oil produced and char yield were comparable with turkey litter, pig manure and goat manure. However, a significant variation can be observed in the gas yield. The main reason for this is the methodology used in calculating the gas yield. In other studies, gas yield was evaluated by balancing the material, which is the prevalent method and was employed by the other researchers for calculating the gas yield. However, in this study a gravimetric method was used to calculate the gas yield which is intrinsically different from what already exists in the literature and reduces the uncertainty involved in the measurements.

Table 3. The comparison of product yield distribution from different types of feedstocks.

Feedstock	Reactor Type	Temperature (°C)	Bio-Oil Yield (wt.%)	Char Yield (wt.%)	Gas Yield (wt.%)	Reference
Poultry litter	Fluidised bed	530	27.6	31.5	21.9	This study
Poultry litter	Fluidised bed	500	21.6	39.27	39.13	[22]
Turkey litter	Fluidised bed	500	26.32	24.49	49.19	[22]
Pig Manure	Fluidised bed	500	26.3	39.2	15.5	[40]
Goat manure	Fixed-bed	550	26.1	42.5	31.4	[41]

3.2. Analyses of Pyrolytic Gases

The effect of temperature on the composition of non-condensable pyrolysis gases was investigated. The composition of pyrolytic gases included CO, CO₂, H₂, CH₄, C₂H₆, C₂H₄, C₃H₈, C₃H₆ and other C₂₊ hydrocarbon compounds. Figure 3 presents the weight percentage of each component in the pyrolysis gas (db), where CO₂, CO and CH₄ were the dominant components. The CO₂ concentration accounted

for over 76 and 72 wt.% of the pyrolysis gases evolved at 460 and 530 °C respectively. The total yield of the gaseous species increased with temperature due to the release of volatile matter. The hydrogen yield increased threefold due to the increase in lignin decomposition at higher temperature, whereas CH₄, C₂H₄, and C₃H₆ yields increased from 0.44 to 0.95, 0.09 to 0.19 and 0.10 to 0.21 wt.%, respectively. A similar trend for hydrogen was observed during the pyrolysis of olive stones at temperatures higher than 500 °C [42].

The observed increase in the majority of the hydrocarbons was due to the occurrence of secondary reactions such as dehydration, decarboxylation, cellulose, hemicellulose and lignin decomposition as well as protein and fat decomposition at higher temperatures. The increase in CO production could be linked to a secondary tar cracking phenomenon which occurs at higher temperature [22], whereas methane and other lighter hydrocarbon formation is likely to be linked to the release of a methoxy group involving carbon–carbon bond rupturing. Other light hydrocarbons such as propane (C₃H₈) and propene (C₃H₆) can be found in pyrolysis gaseous product which could be linked to the higher mineral matter content in the feedstock, since inorganic salts are known to have a catalytic effect for secondary cracking of volatiles [43]. Propane gas yield was the lowest in the product gas evolved with a maximum yield of 0.12 wt.% at 530 °C followed by ethylene.

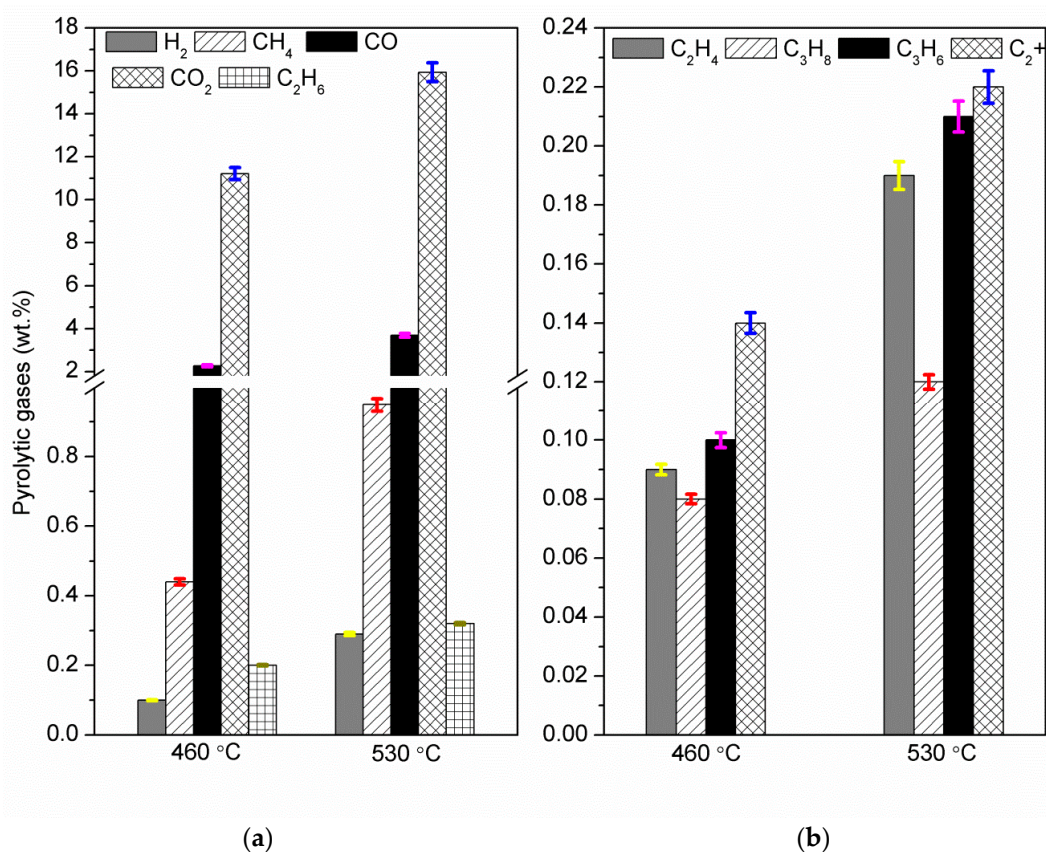


Figure 3. Product gas composition of pyrolytic gases: (a) main components and (b) minor components.

3.3. Biochar Analysis

Table 4 shows the elemental composition and heating value of the biochar produced. The carbon contents in biochar are over 47 wt.%, whereas the carbon content in the feedstock was about 42 wt.%. The measured HHV of the biochar produced at 460 °C was 17.73 MJ/kg, whereas the biochar produced at 530 °C had a comparatively lower calorific value of 15.82 MJ/kg. The heating value of the recovered biochar was slightly lower than the original feedstock. The total carbon concentration in biochar increased with temperature due to the release of volatile matter. The recovery of the carbon in the biochar was around 35.5 wt.% and remained the same for both the temperatures. The biochar yield

reported in this study was ~32 wt.% and is in agreement with previous work that concluded that feedstocks with higher ash contents resulted in higher char yield [19].

Table 4. Elemental analysis of produced biochar (in wt.%, dry).

Temperature	C (%)	H (%)	N (%)	Cl (%)	Ash (%)	O * (%)	HHV (MJ/kg)	O/C Ratio	H/C Ratio
460 °C	47.0	2.0	3.1	0.66	39.6	7.64	17.73	0.12	0.51
530 °C	48.5	1.7	2.9	0.74	42.6	3.56	15.82	0.06	0.42

* Calculated by difference.

The ash content in the biochar was relatively high compared to the original feedstock. Ash is an inert material and does not participate in the pyrolysis process and remained in the biochar. The amount of ash in the biochar obtained in this study is in agreement with the values reported elsewhere [19,44]. The ash recovery or the fraction of ash recovered in the biochar, calculated using the formula proposed by Ghanim et al. [45], was 89.8 and 93.8% at 460 and 530 °C, respectively. Nitrogen, hydrogen and oxygen contents in the biochar decreased with an increase in pyrolysis temperature, whereas the carbon content showed an opposite behaviour. The decrease in oxygen content in the biochar could be due to the dominant dehydration and decarboxylation reactions at higher temperature.

Both the O/C and H/C atomic ratios of biochar decrease with increasing pyrolysis temperature and are an indication of an increase in energy density and decreased water vapour. A greater decline in the O/C atomic ratio was observed compared to the H/C ratio suggesting that the decarboxylation reactions play a more significant role than dehydration reactions [46]. During the pyrolysis process, the feedstock undergoes thermochemical destruction to produce a superior quality fuel (biochar). According to the Van-Krevelen diagram, the biochar produced in this study was found to be in the hard coal region (H/C range 0.51–0.42 and O/C range 0.12–0.06). Azargohar et al. [44] reported a similar observation for biochar produced from Canadian biomass waste (agricultural wastes, forest residue and animal manure) at temperatures of 400, 475 and 500 °C.

The elemental compositions of the heavy metals in the biochar are presented in Table 5. Many of these trace elements are added to the poultry feed not only as essential nutrients but also as a supplement to improve weight gains and feed conversion, preventing mineral deficiencies and diseases and increasing egg production (egg laying chickens). These trace elements end up in the poultry manure (poultry litter) if not fully digested and present as a valuable source of nutrients (N, P and K), secondary nutrients (Ca, Mg and S) and some other trace elements (Cu, Zn and Mo) [47].

Table 5. Trace inorganic analysis of recovered biochar from the pyrolysis of poultry litter (in mg/kg, dry).

Biochar Produced at 460 °C				Biochar Produced at 530 °C			
Major Elements		Minor Elements		Major Elements		Minor Elements	
Al	3300	As	<0.5	Al	5400	As	<0.5
Ca	36,400	Ba	70	Ca	37,800	Ba	69
Fe	3800	Cd	0.05	Fe	3800	Cd	0.2
Mg	20,500	Co	4.3	Mg	20,300	Co	4.9
Mn	1500	Cr	35	Mn	1500	Cr	40
P	23,700	Cu	190	P	25,500	Cu	220
K	67,900	Hg	<0.02	K	75,500	Hg	<0.02
Si	17,000	Mo	11	Si	16,300	Mo	14
S	8500	Ni	35	S	8900	Ni	42
Zn	1300	Pb	3.2	Zn	1200	Pb	4.1
		Sb	<0.5			Sb	<0.5
		Tl	<0.5			Tl	<0.5
		Ti	240			Ti	230
		V	9.2			V	9.8

The recovery of essential, secondary plant nutrients and other key trace elements are presented in Figure 4. Phosphorous and potassium recovery were over 75 and 80 wt.%, respectively. The fuel bound chlorine was mostly recovered in biochar (75 wt.%), with the remaining chlorine highly likely to be carried over into the gas phase since chlorine recovery in oil was below 1 wt.%. The nitrogen recovered in the biochar and organic liquid was about 25% and 31%, respectively, at 430 °C, while the remaining nitrogen is believed to be lost in the form of ammonia (NH₃). The ash recovery for the pyrolysis temperatures tested ranged from 89.8 to 93.8 wt.%, the findings reported in this study are in agreement with the observation found by Cantrell et al. [8].

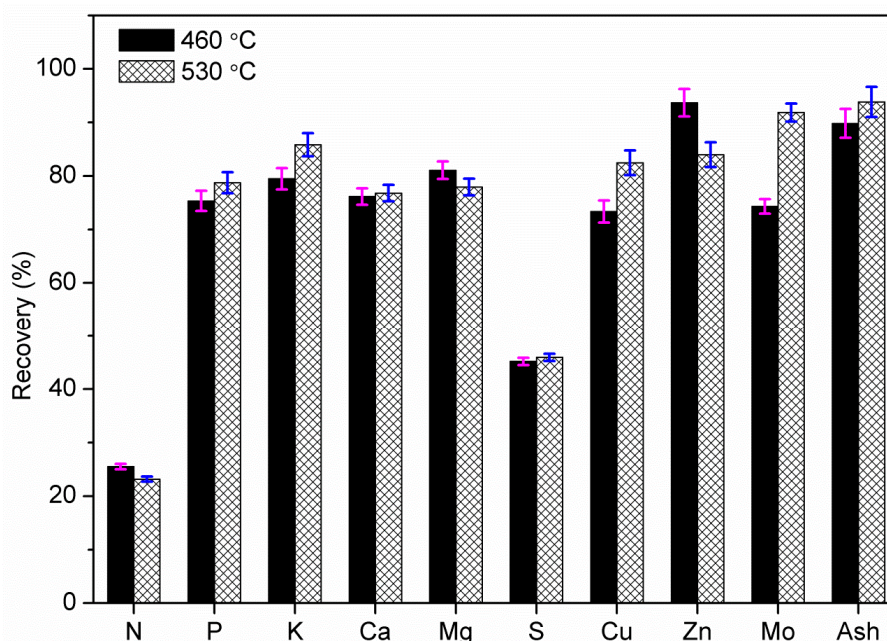


Figure 4. Nutrient and ash recovery in biochar produced from fast pyrolysis of poultry litter.

In view of the increasing cost of fertiliser, poultry litter has the potential to provide on-farm energy and organic nutrients (P, K); however, government subsidies, environmental credits and gate fees may be needed to promote the adoption and integration of these technologies to process poultry litter [48]. Phosphorus, potassium and calcium are considered the main components of typical inorganic fertiliser suggesting that biochar from poultry litter may be a suitable (organic nutrient) alternative agricultural soil conditioner to improve crop production; however, the loss of nitrogen through ammonia during the devolatilisation process is a major issue. The application rate of biochars produced at 450 and 550 °C with and without nitrogen supplementation (100 kg N/ha) was investigated. Even the lowest application rate of biochar without nitrogen supplementation in a hard setting soil resulted in an increased radish yield compared to un-amended soil [49]. An experimental study showed that the nutrients (P, K and Ca) in biochar produced from poultry litter, peanut hulls and pine chips are extractable with a weak acid extractant and are therefore considered to be plant available, whereas N availability from biochar is poor. Therefore, biochars produced from different feedstock may be more suitable as a soil amendment and carbon sequester [50]. Another study investigated the effect of pyrolysis temperature on different feedstocks (vine pruning, poultry litter, orange pomace and seaweed) for solid fuel production and soil amendment. The study concluded that biochars produced at low temperatures from poultry litter and seaweed strongly immobilised the metals within contaminated soil. Moreover, biochars derived from all these feedstocks showed high electrical conductivity which increases soil salinity and had an adverse effect on the plant growth [51]. In addition, prior to classifying or applying biochar produced during the fast pyrolysis of poultry litter as a soil amendment (as it can reduce nutrient run-off), it must be validated against the poultry litter ash protocol that provides the limit of mineral metals. Furthermore, leachate tests need to be performed to improve the understanding

of their (alkali and alkaline earth metals) effects on the contamination of surface and groundwater [52]. Although, it is possible to assess the nutrient bioavailability and plant nutrient uptake efficiency using the pot-trial method (utilising the produced biochar). Nevertheless, the variation in both crop nutrition potential and environmental emission assessments from the local soil and climatic conditions are beyond the scope of the reported investigation and is of a matter of further analysis.

3.4. Bio-Oil Analysis

The distribution of liquid product is presented in Table 6. Bio-oil collected from the first cooler and electrostatic precipitator phase separated spontaneously into an aqueous phase on the top and an organic phase at the bottom.

Table 6. Distribution of liquid product.

	Experiment at 460 °C			Experiment at 530 °C		
	Oil Phase	Aqueous Phase	Aqueous Condensate	Oil Phase	Aqueous Phase	Aqueous Condensate
Amount	48.9	31.3	19.3	49.7	31	19.3
Water content, wt. %	26.6	69.1	65.6	27.5	69.1	65.6

Figure 5 shows the chemical composition of the liquid products in the different phases. Water soluble compounds were distributed mainly in the aqueous phase while the organic phase contained both water soluble and water insoluble compound groups. Water insoluble materials are LMW-lignin and HMW-lignin. The water content in the oil phase (Figure 5a) was around 26 wt.% which could inhibit its ability to ignite and further treatment was needed to make it suitable for use in combustion engines (acceptable limit is 0.5 wt.%). It was evident from Figure 5b that in the aqueous phase, the water content accounted for 69 wt.% while the total amount of organic phase was 48.9 and 49.7 wt.% in the two experiments. Figure 5c shows the distribution of different liquid compounds in a whole product.

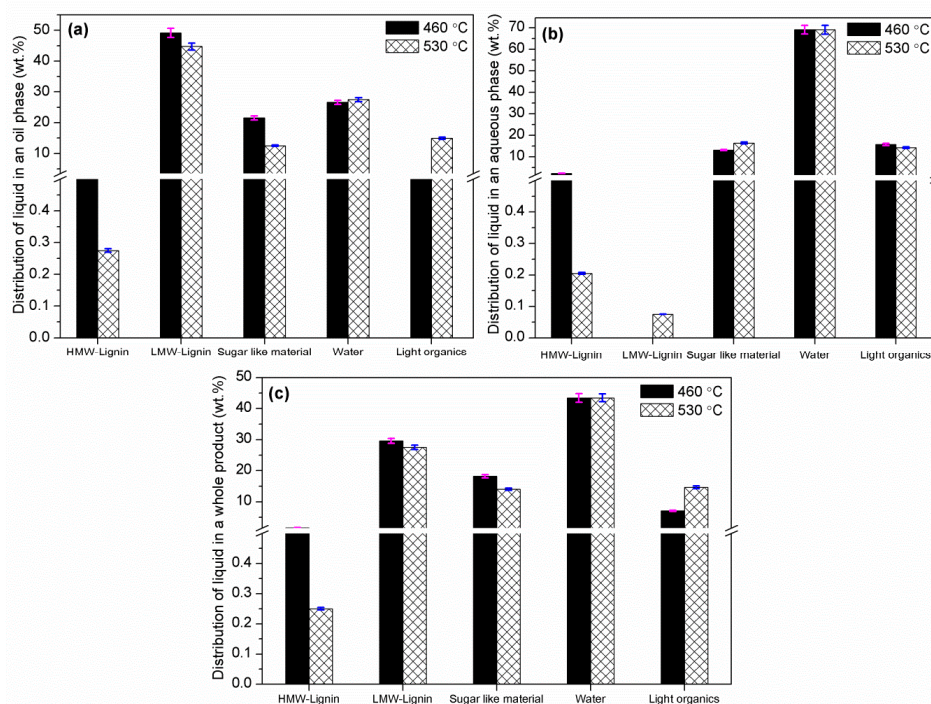


Figure 5. Distribution of chemical compound groups in the (a) oil phase, (b) aqueous phase and (c) whole product.

Table 7 shows the analyses of the physical and chemical properties of the bio-oil (organic phase). With an increase in temperature, a small increase in carbon and nitrogen content is observed, whereas the hydrogen content remained constant for the temperatures studied (Table 7). A slight increase in calorific value of the fuel was found, whereas a declining trend was observed for oxygen content in the bio-oil, with an increase in temperature. The H/C ratio of the bio-oil was around 1.40, which is comparable with kerosene-based hydrocarbon fossil fuels (in the range of H/C ratio 1.6–2.3) [53]. However, the O/C ratio (0.20) was slightly higher than the conventional heavy oil (O/C ratio around 0.18) [54]. The high oxygen content in bio-oil was directly correlated with the decrease in calorific value. Therefore, upgrading techniques such as hydro treatment are required to decrease the oxygen content as well as to adjust the H/C ratio [44]. Comparative analyses of the bio-oil produced from the poultry litter and wood is presented in Table 7. It can be seen from Table 7 that the bio-oil produced from the poultry litter had a significantly higher nitrogen content compared to oil produced from the wood. The higher nitrogen content was directly related to the higher concentration of indigenous nitrogen in the feedstock.

Table 7. Comparative elemental analysis of bio-oil produced from poultry litter and wood (in wt.%, dry).

	Experiment at 460 °C	Experiment at 530 °C	Wood Oil [34]
Water, wt.%	26.6	27	23.9
Carbon, dry wt.%	68.7	69.7	53.4
Hydrogen, dry wt.%	8.2	8.2	6.5
Nitrogen, dry wt.%	7.2	7.7	0.1
Oxygen, dry wt.% *	16	14	40
O/C ratio	0.2	0.2	0.6
H/C ratio	1.4	1.4	1.5
TAN, mg KOH/g	46.3	38.5	71
HHV, MJ/kg	32.8	33	22.2
LHV, MJ/kg	31	31.2	20.1

* Calculated by difference, TAN—Total Acid Number, LHV—Lower Heating Value.

Total acid number (TAN) is used to quantify the acid concentration in an oil as well as acting as a guide in the quality control of lubricating oils and is expressed in mg of KOH/g of samples. Total acid number for compressor and turbine oils are usually between 0.01–0.25, aviation turbine fuels 0–0.10 and lubricant additives 20–200 mg KOH/g. As per the European Standard for Biodiesel (EN 14,214:2012) [55], the acid number of bio-diesel must not exceed 0.5 mg of KOH/g. Therefore, the bio-oil was not suitable for use in diesel engines without modifications. Therefore, considering the acid number of the bio-oil produced from poultry litter, it could potentially be used as a lubricant additive [56]. The HHV of the bio-oil in the oil phase was around 32 MJ/kg, almost two-thirds of that of petroleum fuels. The bio-oil from poultry litter had a higher heating value compared to pyrolytic oil obtained from other biomass sources, which are typically reported to be in the range of 40–45% of petroleum fuel [57]. The heating value of the bio-oil from poultry litter was ~150% higher than that from wood fast pyrolysis oil. The measurements presented in Table 7 confirm that higher oxygen content (~15% in bio-oil produced from poultry litter and 40% in wood oil) in the bio-oil was inversely proportional to the calorific value of the bio-oil.

The amount of trace elements that remained in the bio-oil is quantified and presented in Table 8. Utilisation of fast pyrolysis bio-oil in both internal and external combustion engines has been reviewed for power generation [58]. Since the oil is acidic and contains water its utilisation in internal combustion engines could pose a threat of corrosion to engine parts and ignition problem. Pyrolysis oil has been used in a single-cylinder diesel engine for combined heat and power application. Although pyrolytic oil fuelling leads to lower NO_x emissions, nevertheless, considering the acidic nature of the oil, a completely modified fuel injection system was recommended [59]. The total amount of inorganic trace elements (ash) in the produced bio-oil from poultry litter accounted for over 0.32 wt.%, whereas according to the European Standard for Biodiesel [55], ash content in the biofuels has to be lower than

0.02 wt.%. It has also been reported that the presence of ash in bio-oil could cause erosion, corrosion and kicking phenomena in engine systems [60].

Table 8. Trace inorganic analysis of bio-oil produced from the pyrolysis of poultry litter (in mg/kg, dry).

Bio-Oil Produced at 460 °C				Bio-Oil Produced at 530 °C			
Major Elements		Minor Elements		Major Elements		Minor Elements	
Total	3245	As	<0.5	Total	3887	As	<0.5
Al	<10	Ba	2.5	Al	<10	Ba	<1
Ca	39	Cd	0.16	Ca	37	Cd	0.2
Fe	22	Co	<0.5	Fe	5.9	Co	<0.5
Mg	15	Cr	2.9	Mg	17	Cr	<0.5
Mn	2.1	Cu	0.6	Mn	1.3	Cu	0.8
P	21	Hg	<0.02	P	27	Hg	<0.02
K	120	Mo	<0.5	K	320	Mo	<0.5
Si	76	Ni	2	Si	110	Ni	<0.5
S	2900	Pb	<0.5	S	3300	Pb	0.53
Zn	2.8	Sb	<0.5	Zn	3.1	Sb	<0.5
Na	38	Tl	1.3	Na	62	Tl	2.1
		Ti	<1			Ti	<1
		V	<0.5			V	<0.5

It is evident from Table 8 that the concentration of sulphur is higher in the bio-oil produced from poultry litter which is directly correlated with sulphur content in the feedstock. The high sulphur content in bio-oil could result in higher sulphur-containing constituents (K_2SO_4 , $CaSO_4$ and SO_x , etc.) that can be attributed to oxidation of sulphur in bio-oil. Additionally, alkali sulphur and chlorine can vaporise and condense on cold surfaces. Elements such as Si, Fe, Cu, Al, Cr, Mo, etc., could cause wear to engine components. Miles and co-authors [61] have suggested that the mixture of potassium oxide and silica constitutes the bulk of ash in biofuels. Solid residue in bio-oil leads to coking issues in the engine injectors and erosion with increased amounts of high particulate matter emissions. In addition, the interaction of alkali and alkali earth metal could cause hot corrosion problems in combustion systems. Sodium, potassium and vanadium could be responsible for high temperature corrosion and deposition in the combustion engine [60]. Further investigation also reveals that inherent alkali and alkaline earth metal species promote thermal decomposition of heavier aromatics on biomass pyrolysis [62]. Since the bio-oil produced from the poultry litter fast pyrolysis process exceeds the upper acceptable limit set by the European standard for biodiesel, it cannot be used in its present form as an alternative fuel in internal combustion engines. Therefore, considering high acid value, high water and ash contents in the produced bio-oil from poultry litter, further upgrading of bio-oil properties is required either through high temperature conversion or catalytic reforming before these biofuels can be utilised in internal combustion engines [63].

4. Conclusions

Fast pyrolysis of poultry litter was experimentally studied at two different temperatures (460 and 530 °C) in a bubbling fluidised bed reactor. The effect of reactor temperature on product gas, bio-oil and biochar were studied. The maximum organic bio-oil (27.62 wt.%) and pyrolytic gas yield (~22 wt.%) were obtained at 530 °C with CO_2 , CO and CH_4 as the main gas products, whereas the maximum biochar yield was obtained at 460 °C. Owing to high ash content in poultry litter, biochar yield was comparatively higher than the bio-oil yield. Nevertheless, bio-oil from fast pyrolysis of poultry litter gave a 50% higher HHV compared to the oil produced from wood. The bio-oil produced was further characterised using elemental and ICP analyses. The ICP showed the presence of S, K, P, Si, Mg, and Ca and Fe were also detected in the liquid products. Therefore, further thermal and/or catalytic treatment is required before the bio-oil can be utilised in downstream application for heat and power

generation. Most of the heavy metals and trace elements present in poultry litter were retained in the biochar including non-volatile minerals P and K. The retention of the non-volatile minerals (alkali and alkaline earth metals) in the biochar emphasises that the manure-derived biochar could be used in agriculture systems, but the concentration of trace elements may restrict its use. Therefore, before applying these biochars as a soil amendment, an exhaustive investigation is needed to assess their impact on ground water (leaching), soil conditions and on pot-plant growth. The carbon content in the biochar collected from the cyclone was in the range of 47–48.5 wt.% (db) with a lower concentration of hydrogen. The increase in pyrolysis temperature showed an increase of ash content and slight decrease in H, N and O contents in biochar.

Author Contributions: D.S.P., G.K. and C.L. conceived the idea, designed and performed the experiments; D.S.P. analysed the data and wrote the manuscript; the co-authors reviewed the manuscript.

Funding: The financial support for this project provided by the EU-H2020 project Biomass Research Infrastructure for Sharing Knowledge II (BRISK2) under Grant Agreement Number 731101 is gratefully acknowledged. This work was supported by the Engineering and Physical Sciences Research Council (EPSRC, EP/P004636/1, UK). The financial support from EPSRC is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

db	Dry Basis
ar	As Received
ICP	Inductively Coupled Plasma
HHV	Higher Heating Value
LHV	Lower Heating Value
GC	Gas Chromatograph
TAN	Total Acid Number
DCM	Dichloromethane
LMM	Low Molecular Mass
HMM	High Molecular Mass

References

1. EEA Total Greenhouse Gas Emission Trends and Projections. 2017. Available online: <https://www.eea.europa.eu/data-and-maps/indicators/greenhouse-gas-emission-trends-6/assessment-1> (accessed on 15 October 2018).
2. Conway, A.; Krishchner, L.; Reus, A.; McLaughlin, K. *Poultry Trends—The Statistical Reference for Poultry*; WATT Poultry Trends: Rockford, IL, USA, 2017; pp. 1–66.
3. Foged, H.L.; Flotats, R.X.; Blasi, A.B.; Jordi, P.C.; Magri, A.A.; Schelde, K.M. *Inventory of Manure Processing Activities in Europe*; Directorate – General Environment, The European Commission: Brussels, Belgium, 2012; p. 138.
4. Kelleher, B.; Leahy, J.; Henihan, A.; O’dwyer, T.; Sutton, D.; Leahy, M. Advances in poultry litter disposal technology—A review. *Bioresour. Technol.* **2002**, *83*, 27–36. [[CrossRef](#)]
5. Florin, N.; Maddocks, A.; Wood, S.; Harris, A. High-temperature thermal destruction of poultry derived wastes for energy recovery in Australia. *Waste Manag.* **2009**, *29*, 1399–1408. [[CrossRef](#)] [[PubMed](#)]
6. EU 2030 Climate & Energy Framework. Available online: <https://ec.europa.eu/clima/policies/strategies/2030> (accessed on 31 October 2018).
7. Sharara, M.; Sadaka, S. Opportunities and Barriers to Bioenergy Conversion Techniques and Their Potential Implementation on Swine Manure. *Energies* **2018**, *11*, 957. [[CrossRef](#)]
8. Cantrell, K.B.; Hunt, P.G.; Uchimiya, M.; Novak, J.M.; Ro, K.S. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresour. Technol.* **2012**, *107*, 419–428. [[CrossRef](#)] [[PubMed](#)]
9. Dalólio, F.S.; da Silva, J.N.; de Oliveira, A.C.C.; Tinôco, I.d.F.F.; Barbosa, R.C.; de Oliveira Resende, M.; Albino, L.F.T.; Coelho, S.T. Poultry litter as biomass energy: A review and future perspectives. *Renew. Sustain. Energy Rev.* **2017**, *76*, 941–949. [[CrossRef](#)]

10. Bridgwater, A.V. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* **2012**, *38*, 68–94. [[CrossRef](#)]
11. Bulushev, D.A.; Ross, J.R. Catalysis for conversion of biomass to fuels via pyrolysis and gasification: A review. *Catal. Today* **2011**, *171*, 1–13. [[CrossRef](#)]
12. Jahirul, M.; Rasul, M.; Chowdhury, A.; Ashwath, N. Biofuels production through biomass pyrolysis—A technological review. *Energies* **2012**, *5*, 4952–5001. [[CrossRef](#)]
13. Agblevor, F.; Besler, S.; Wiselogel, A. Fast pyrolysis of stored biomass feedstocks. *Energy Fuels* **1995**, *9*, 635–640. [[CrossRef](#)]
14. Pandey, D.S.; Kwapinska, M.; Gómez-Barea, A.; Horvat, A.; Fryda, L.E.; Rabou, L.P.; Leahy, J.J.; Kwapinski, W. Poultry litter gasification in a fluidized bed reactor: Effects of gasifying agent and limestone addition. *Energy Fuels* **2016**, *30*, 3085–3096. [[CrossRef](#)]
15. Jung, J.-M.; Lee, S.-R.; Lee, J.; Lee, T.; Tsang, D.C.; Kwon, E.E. Biodiesel synthesis using chicken manure biochar and waste cooking oil. *Bioresour. Technol.* **2017**, *244*, 810–815. [[CrossRef](#)]
16. Burra, K.; Hussein, M.; Amano, R.; Gupta, A. Syngas evolutionary behavior during chicken manure pyrolysis and air gasification. *Appl. Energy* **2016**, *181*, 408–415. [[CrossRef](#)]
17. Hussein, M.; Burra, K.; Amano, R.; Gupta, A. Temperature and gasifying media effects on chicken manure pyrolysis and gasification. *Fuel* **2017**, *202*, 36–45. [[CrossRef](#)]
18. Baniyadi, M.; Tugnoli, A.; Conti, R.; Torri, C.; Fabbri, D.; Cozzani, V. Waste to energy valorization of poultry litter by slow pyrolysis. *Renew. Energy* **2016**, *90*, 458–468. [[CrossRef](#)]
19. Agblevor, F.A.; Beis, S.; Kim, S.; Tarrant, R.; Mante, N. Biocrude oils from the fast pyrolysis of poultry litter and hardwood. *Waste Manag.* **2010**, *30*, 298–307. [[CrossRef](#)] [[PubMed](#)]
20. Das, D.D.; Schnitzer, M.I.; Monreal, C.M.; Mayer, P. Chemical composition of acid-base fractions separated from biooil derived by fast pyrolysis of chicken manure. *Bioresour. Technol.* **2009**, *100*, 6524–6532. [[CrossRef](#)] [[PubMed](#)]
21. Mante, O.D.; Agblevor, F.A. Influence of pine wood shavings on the pyrolysis of poultry litter. *Waste Manag.* **2010**, *30*, 2537–2547. [[CrossRef](#)] [[PubMed](#)]
22. Kim, S.-S.; Agblevor, F.A.; Lim, J. Fast pyrolysis of chicken litter and turkey litter in a fluidized bed reactor. *J. Ind. Eng. Chem.* **2009**, *15*, 247–252. [[CrossRef](#)]
23. Koutcheiko, S.; Monreal, C.; Kodama, H.; McCracken, T.; Kotlyar, L. Preparation and characterization of activated carbon derived from the thermo-chemical conversion of chicken manure. *Bioresour. Technol.* **2007**, *98*, 2459–2464. [[CrossRef](#)]
24. Kantarli, I.C.; Stefanidis, S.D.; Kalogiannis, K.G.; Lappas, A.A. Utilisation of poultry industry wastes for liquid biofuel production via thermal and catalytic fast pyrolysis. *Waste Manag. Res.* **2019**, *37*, 157–167. [[CrossRef](#)]
25. Jeong, Y.W.; Choi, S.K.; Choi, Y.S.; Kim, S.J. Production of biocrude-oil from swine manure by fast pyrolysis and analysis of its characteristics. *Renew. Energy* **2015**, *79*, 14–19. [[CrossRef](#)]
26. Opatokun, S.A.; Lopez-Sabiron, A.; Ferreira, G.; Strezov, V. Life cycle analysis of energy production from food waste through anaerobic digestion, pyrolysis and integrated energy system. *Sustainability* **2017**, *9*, 1804. [[CrossRef](#)]
27. López-Cano, I.; Cayuela, M.; Mondini, C.; Takaya, C.; Ross, A.; Sánchez-Monedero, M. Suitability of different agricultural and urban organic wastes as feedstocks for the production of biochar—Part 1: Physicochemical characterisation. *Sustainability* **2018**, *10*, 2265. [[CrossRef](#)]
28. BS EN 14778. *Solid Biofuels. Sampling*; British Standards Institute: London, UK, 2011.
29. BS EN 14774-3. *Solid Biofuels. Determination of Moisture Content-Oven Dry Method—Part 3 Moisture in General*; British Standards Institute: London, UK, 2009.
30. BS EN 14775. *Solid Biofuels. Determination of Ash Content*; British Standards Institute: London, UK, 2009.
31. BS EN 15148. *Solid Biofuels. Determination of the Content of Volatile Matter*; British Standards Institute: London, UK, 2009.
32. BS EN 14918. *Solid Biofuels. Determination of Calorific Value*; British Standards Institute: London, UK, 2009.
33. CEN/TS 15408. *Solid Recovered Fuels. Methods for the Determination of Sulphur (S), Chlorine (Cl), Fluorine (F) and Bromine (Br) Content (Replaced by BS EN 15408:2011)*; British Standards Institute: London, UK, 2006.
34. Oasmaa, A.; Solantausta, Y.; Arpiainen, V.; Kuoppala, E.; Sipila, K. Fast pyrolysis bio-oils from wood and agricultural residues. *Energy Fuels* **2009**, *24*, 1380–1388. [[CrossRef](#)]

35. Dhyani, V.; Bhaskar, T. A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renew. Energy* **2018**, *129*, 695–716. [[CrossRef](#)]
36. Meier, D.; Van De Beld, B.; Bridgwater, A.V.; Elliott, D.C.; Oasmaa, A.; Preto, F. State-of-the-art of fast pyrolysis in IEA bioenergy member countries. *Renew. Sustain. Energy Rev.* **2013**, *20*, 619–641. [[CrossRef](#)]
37. Venderbosch, R.; Prins, W. Fast pyrolysis technology development. *Biofuels Bioprod. Bioref.* **2010**, *4*, 178–208. [[CrossRef](#)]
38. Oasmaa, A.; Peacocke, C. *A Guide to Physical Property Characterisation of Biomass-Derived Fast Pyrolysis Liquids*; Technical Research Centre of Finland Espoo: Espoo, Finland, 2001.
39. Marculescu, C.; Stan, C. Pyrolysis treatment of poultry processing industry waste for energy potential recovery as quality derived fuels. *Fuel* **2014**, *116*, 588–594. [[CrossRef](#)]
40. Azuara, M.; Kersten, S.R.; Kootstra, A.M.J. Recycling phosphorus by fast pyrolysis of pig manure: Concentration and extraction of phosphorus combined with formation of value-added pyrolysis products. *Biomass Bioenergy* **2013**, *49*, 171–180. [[CrossRef](#)]
41. Erdogdu, A.E.; Polat, R.; Ozbay, G. Pyrolysis of goat manure to produce bio-oil. *Eng. Sci. Technol. Int. J.* **2019**, *22*, 452–457. [[CrossRef](#)]
42. López, M.B.; Blanco, C.; Martínez-Alonso, A.; Tascón, J. Composition of gases released during olive stones pyrolysis. *J. Anal. Appl. Pyrolysis* **2002**, *65*, 313–322. [[CrossRef](#)]
43. Raveendran, K.; Ganesh, A.; Khilar, K.C. Influence of mineral matter on biomass pyrolysis characteristics. *Fuel* **1995**, *74*, 1812–1822. [[CrossRef](#)]
44. Azargohar, R.; Jacobson, K.L.; Powell, E.E.; Dalai, A.K. Evaluation of properties of fast pyrolysis products obtained, from Canadian waste biomass. *J. Anal. Appl. Pyrolysis* **2013**, *104*, 330–340. [[CrossRef](#)]
45. Ghanim, B.M.; Pandey, D.S.; Kwapinski, W.; Leahy, J.J. Hydrothermal carbonisation of poultry litter: Effects of treatment temperature and residence time on yields and chemical properties of hydrochars. *Bioresour. Technol.* **2016**, *216*, 373–380. [[CrossRef](#)]
46. Poerschmann, J.; Baskyr, I.; Weiner, B.; Koehler, R.; Wedwitschka, H.; Kopinke, F.-D. Hydrothermal carbonization of olive mill wastewater. *Bioresour. Technol.* **2013**, *133*, 581–588. [[CrossRef](#)]
47. Bolan, N.S.; Szogi, A.; Chuasavathi, T.; Seshadri, B.; Rothrock, M.; Panneerselvam, P. Uses and management of poultry litter. *World's Poult. Sci. J.* **2010**, *66*, 673–698. [[CrossRef](#)]
48. Szogi, A.; Vanotti, M. Prospects for phosphorus recovery from poultry litter. *Bioresour. Technol.* **2009**, *100*, 5461–5465. [[CrossRef](#)] [[PubMed](#)]
49. Chan, K.; Van Zwieten, L.; Meszaros, I.; Downie, A.; Joseph, S. Using poultry litter biochars as soil amendments. *Soil Res.* **2008**, *46*, 437–444. [[CrossRef](#)]
50. Gaskin, J.W.; Steiner, C.; Harris, K.; Das, K.; Bibens, B. Effect of low-temperature pyrolysis conditions on biochar for agricultural use. *Trans. ASABE* **2008**, *51*, 2061–2069. [[CrossRef](#)]
51. Tag, A.T.; Duman, G.; Ucar, S.; Yanik, J. Effects of feedstock type and pyrolysis temperature on potential applications of biochar. *J. Anal. Appl. Pyrolysis* **2016**, *120*, 200–206. [[CrossRef](#)]
52. Pandey, D.S.; Kwapinska, M.; Leahy, J.J.; Kwapinski, W. Fly Ash from Poultry Litter Gasification—Can it be Utilised in Agriculture Systems as a Fertiliser? *Energy Procedia* **2019**, *161*, 38–46. [[CrossRef](#)]
53. Yue, L.; Li, G.; He, G.; Guo, Y.; Xu, L.; Fang, W. Impacts of hydrogen to carbon ratio (H/C) on fundamental properties and supercritical cracking performance of hydrocarbon fuels. *Chem. Eng. J.* **2016**, *283*, 1216–1223. [[CrossRef](#)]
54. Hassan, E.B.; Abou-Yousef, H.; Steele, P.; El-Giar, E. Characterization of bio-oils from the fast pyrolysis of white oak and sweetgum. *Energy Sources Part A Recovery Util. Environ. Effects* **2016**, *38*, 43–50. [[CrossRef](#)]
55. EN 14214. *Automotive Fuels—Fatty Acid Methyl Esters (FAME) for Diesel Engines—Requirements and Test Methods*; European Standard: Pilsen, Czech Republic, 2012.
56. Nadkarni, R.; Nadkarni, R. *Guide to ASTM Test Methods for the Analysis of Petroleum Products and Lubricants*; ASTM International West Conshohocken: Conshohocken, PA, USA, 2007.
57. Oasmaa, A.; Czernik, S. Fuel oil quality of biomass pyrolysis oils state of the art for the end users. *Energy Fuels* **1999**, *13*, 914–921. [[CrossRef](#)]
58. Chiamonti, D.; Oasmaa, A.; Solantausta, Y. Power generation using fast pyrolysis liquids from biomass. *Renew. Sustain. Energy Rev.* **2007**, *11*, 1056–1086. [[CrossRef](#)]
59. Van de Beld, B.; Holle, E.; Florijn, J. The use of pyrolysis oil and pyrolysis oil derived fuels in diesel engines for CHP applications. *Appl. Energy* **2013**, *102*, 190–197. [[CrossRef](#)]

60. Hossain, A.; Davies, P. Pyrolysis liquids and gases as alternative fuels in internal combustion engines-A review. *Renew. Sustain. Energy Rev.* **2013**, *21*, 165–189. [[CrossRef](#)]
61. Miles, T.R.; Miles, T.R., Jr.; Baxter, L.L.; Bryers, R.W.; Jenkins, B.M.; Oden, L.L. Boiler deposits from firing biomass fuels. *Biomass Bioenergy* **1996**, *10*, 125–138. [[CrossRef](#)]
62. Hu, S.; Jiang, L.; Wang, Y.; Su, S.; Sun, L.; Xu, B.; He, L.; Xiang, J. Effects of inherent alkali and alkaline earth metallic species on biomass pyrolysis at different temperatures. *Bioresour. Technol* **2015**, *192*, 23–30. [[CrossRef](#)] [[PubMed](#)]
63. Grams, J.; Ruppert, A. Development of heterogeneous catalysts for thermo-chemical conversion of lignocellulosic biomass. *Energies* **2017**, *10*, 545. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).