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## Investigation of Chicken Litter Conversion into Useful Energy Resources by Using Low Temperature Pyrolysis

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### Abstract

The global production of poultry is predicted to grow considerably in the future. Intensive poultry farming poses significant challenges to traditional waste disposal methods (i.e. direct land application) leading to environmental impacts. This paper discusses the result of low temperature (350–450 °C) pyrolysis of representative chicken litter as the feedstock. Four different feedstocks comprised of 50% organic chicken manure and 50% bedding materials (i.e. hay, straw, rice husk and wood shavings) have been experimentally investigated. The products of the pyrolysis process consist of char, gas and liquid (bio-oil). Maximum char production from the rice husk mix is over 67 wt.%, while the wood shavings mix feedstock resulted in the highest liquid yield of 44.4 wt.% at a temperature of 400 °C. Chicken litter and its char product are analysed by elemental analyser and bomb calorimetry. The composition of the evolved gases and bio-oil are analysed by micro gas chromatography ( $\mu$ -GC) and gas chromatography-mass spectrometry (GC-MS), respectively. In addition, the mass and energy balance of the pyrolysis process are presented.

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## 1. Introduction

Chicken meat dominates the meat market share over beef due to the BSE (Bovine Spongiform Encephalopathy) crisis. According to the DEFRA (Department for Environment, Food and Rural Affairs of UK), the production of chicken meat increased by 4% from 2012 to 2014 [1] with the total chicken meat production in the EU exceeding 13 million tonnes in 2014 [2]. The global production of chicken meat has been predicted to grow considerably in the near future which will have undesirable environmental impacts. The land application of animal feedlot waste is no longer a sustainable solution to the growing volume of animal waste. Therefore, there is an urgent need for chicken litter and animal feedlot waste treatment in order to avoid adverse environmental impact and associated waste management cost [3]. Thermo-chemical treatment processes such as combustion, pyrolysis and gasification can be applied to minimise disposal problems whilst offering additional benefit to the environment. Low temperature (<600 °C) pyrolysis offers an advantage compared to other thermo-chemical processes since agglomeration of the mineral components do not typically occur at this temperature [4].

Currently, chicken litter is predominantly used as a fertiliser and soil ameliorant in agriculture. However, the oversupply of organic fertiliser causes accumulation of nitrates. Chicken litter consists of bedding material, feathers, waste feed and manure. The most common bedding materials being used are hay, straw, wood shavings, and rice husk. The moisture content of chicken litter varies depending on the farming condition and the chemical composition of the bedding material [5].

## 2. Chicken Litter Conversion

The conversion of chicken litter into fuel can be categorised into two main groups. (i) biochemical conversion and (ii) thermochemical conversion. Microbial digestion is considered as biochemical conversion, while combustion, gasification, and pyrolysis belong to the category of thermochemical conversion [6]. Pyrolysis processes can be divided into two types: slow and fast pyrolysis. Slow pyrolysis occurs at low temperature and long residence time where the char is the main product. Fast pyrolysis occurs at high temperatures and very short residence times where the main products are in the liquid and gas phases. The liquid (bio-oil) phase carries the majority of the energy or higher heating value (HHV) and it is more flexible for storage, upgrading and transportation [7]. Since slow pyrolysis processes generate high char yield, it is generally more suitable to convert agriculture waste into char [8]. Furthermore, the inorganic compounds accumulate in the char, therefore, slow pyrolysis of chicken litter can produce high quality soil improver and it has also been estimated that the calorific value of evolved pyrolysis syngas can sustain the energy demand for continuous operation of the process [9]. This opens the prospect of slow pyrolysis as a disinfection treatment of bio-hazardous materials as well as waste-to-energy utilisation of chicken litter [10].

### Nomenclature:

C	: Carbon	$f_{CH_4...}$	: Methane fraction...
H	: Hydrogen	FC	: Fix Carbon (wt.%)
N	: Nitrogen	MC	: Moisture content in sample (wt.%)
O	: Oxygen	VM	: Volatile content (wt.%)
S	: Sulphur	HHV	: High Heating Value
$m_{FS}$	: Weight percentage of feedstock (wt.%)	HHV <sub>FS</sub>	: High Heating Value of feed stock (kJ/kg)
$m_C$	: Weight percentage of char (wt.%)	HHV <sub>C</sub>	: High Heating Value of char (kJ/kg)
$m_L$	: Weight percentage of liquid (wt.%)	HHV <sub>L</sub>	: High Heating Value of liquid (kJ/kg)
$m_G$	: Weight percentage of gas (wt.%)	HHV <sub>G</sub>	: High Heating Value of gas (kJ/kg)

### 3. Experimental Section

#### 3.1. Feedstock

The composition of chicken litter is important with regard to its processing prospects. For example, the moisture content in chicken litter varies between 20 and 26% [11] which will affect the energy feasibility of the pyrolysis process. In this study, chicken litter is modelled by mixing the organic chicken manure and four different types of bedding material in the ratio 50% bedding material and 50% chicken manure (Fig. 1. a-e).



Fig. 1. Components of modelled chicken litter (a) hay, (b) straw, (c) rice husk, (d) wood shavings, (e) chicken manure.

#### 3.2. Experimental procedure.

The pyrolysis experiments have been carried out at the Institute of Energy Futures, Brunel University London. The schematic diagram of the pyrolysis apparatus is shown in Fig. 2. The pyrolysis reactor was manufactured by H. Baumbach & Co. Ltd., UK. It consists of quartz glass tube reactor and borosilicate glass condensation unit. The diameter of the reactor is 46 mm, while the length is 500 mm. The set temperature is achieved and maintained by Samox® heavy insulated heating tape with the maximum power output 1254 W (Omegalux, USA). Temperature regime in the reactor was measured and controlled by digital thermostat and voltage regulator (SCR 4000 W). In the condensation unit, raw syngas from the cyclone was cooled by through heat exchangers using cold water (5-15 °C) as a heat transfer liquid. The pyrolysis condensate was collected in two 500 ml flasks whereas the syngas was collected in the gas-sampling bags (multi-layer Al-foil bags). Gas bags were stored in a cold, dry place and we are assuming that no gas compounds leaked in or out during storage.

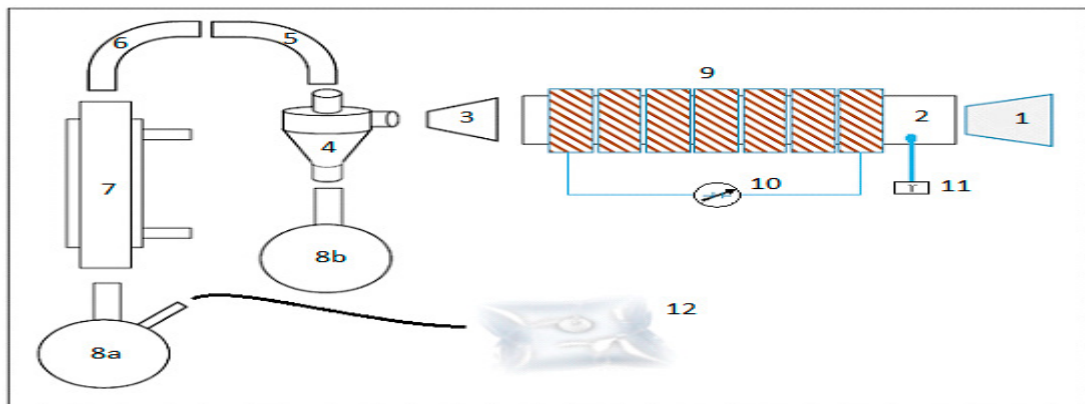


Fig. 2. Scheme of pyrolysis apparatus, (1) stopper; (2) reactor tube, (3) reducer, (4) cyclone, (5) & (6) 90° elbow, (7) heat exchanger, (8a) & (8b) 500 ml flask, (9) heating tape, (10) voltage regulator (11) thermostat, (12) gas sampling bag.

The slow pyrolysis tests were carried out at three temperatures 350, 400, and 450 °C. For each pyrolysis test, a batch of 100 g of chicken litter feedstock was placed into the reactor and then all parts of the pyrolysis apparatus were assembled. The test was terminated when gas was no longer produced. The duration of the test depended on the setting temperature: approximately 36 min duration at 350 °C, 24 min at 400 °C and 18 min at 450 °C. The collected liquid and char fractions were weighed and the weight fraction of the gas was calculated by the difference. The complete combustion process for the feedstocks tested would have required around 436 to 496 litres of air, while the air in the reactor is only 0.8 litre. Therefore, despite of the presence of a small amount air in the reactor at the start of the test, the tests are considered to be conducted in an inert atmosphere [12].

### 3.3. Measurement procedure

The solid sample were characterised by proximate and ultimate analysis. The proximate analysis has been conducted according to the British standard [13-17]. Proximate analysis encompasses moisture content (MC), volatile matter (VM), ash (A) and fixed carbon (FC), and the results are expressed in weight percentage. The ultimate analysis (composition of C, H, N, S and O) were determined using an elemental analyser (Vario EL Cube). The syngas compositions were analysed using micro gas chromatograph (Agilent 300), which enables quantification of CO<sub>2</sub>, CO, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>6</sub>, CH<sub>4</sub>, H<sub>2</sub>S and H<sub>2</sub>.

An Agilent 7890A GC, coupled with a triple-axis MS 5975C (GC-MS), was used to separate and identify bio-oil components. Prior to the injection into the GC-MS, the bio-oil was diluted with isopropanol in order to adjust its concentration for the chromatograph. Isopropanol is capable of dissolving aromatic hydrophobic bio-oil compounds as well as water-soluble hydrocarbons. The Karl Fisher titration method was used to determine the moisture content in the bio-oil.

## 4. Result and Discussion

### 4.1. Feedstock properties

The proximate and ultimate analysis data describing feedstocks properties are shown in Tables 1 and 2. Chicken manure has the highest C and N content compared to the blended litters. Due to the highest ash (among blended litter), the rice husk mix is expected to generate more char compared to the other bedding materials. In contrast, due to the highest VM and lowest ash, the wood shavings mix is expected to produce more pyrolysis gas. The wood shavings mix also has the highest carbon content and HHV. On the other hand, low carbon content and high ash in the straw mix feedstock corresponds to the lowest HHV. The HHV was calculated according to equation 1 [18] using the ultimate analysis data as an input and the ultimate analysis data were presented on dry and ash free basis.

$$\text{HHV [MJ/kg]} = (33.5 * \text{C}) + (142.3 * \text{H}) - (15.4 * \text{O}) - (14.5 * \text{N}) \quad (1)$$

Table 1. Proximate analysis of four tested feedstocks.

Sample	HHV (MJ/kg)*	MC (wt%)*	VM (wt%)**	A (wt%)**	FC (wt%)**
Hay Mix	14.34	12.98	61.89	24.70	15.23
Straw Mix	12.77	14.55	63.43	27.35	12.85
Rice husk Mix	12.99	9.09	58.83	29.74	9.43
Wood shavings Mix	14.81	13.05	72.45	23.87	11.84
Chicken manure	12.51	11.14	57.51	39.01	3.48

\*Data are expressed on as receive basis, \*\*Data are expressed on dry basis

Table 2. Ultimate analysis of four tested feedstocks.

Sample	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O* (wt%)
Hay mix	52.15	6.09	6.06	0.48	35.21
Straw mix	51.41	5.97	5.21	0.52	36.88
Rice husk mix	51.10	6.12	5.15	0.54	37.09
Wood shavings mix	53.74	6.34	5.07	0.49	34.36
Chicken manure	54.18	6.34	9.64	0.91	28.93

Data are expressed on dry and ash free basis, \*Calculated by difference

#### 4.2. Product yield distribution

The pyrolysis product yield distribution of the four chicken litter feedstocks are shown in Fig. 3, expressed as weight percentage. It can be seen from Fig. 3 that the product yield distribution is affected by the residence time and temperature. Moreover, the product yield distribution pattern of all the four chicken litter feedstocks is similar. Increasing the pyrolysis temperature reduces char production [19,20] The outcome of this study clearly indicates that the char yield declined around 20% with increasing pyrolysis temperature from 350 to 400 °C. The maximum bio-oil yield was reported to be at 400 °C. Significantly, the yield of the liquid phase from the hay mix chicken litter steadily increased with the temperature. Overall, the yield of syngas was higher for the hay mix and straw mix compared to the rice husk mix and the wood shavings mix.

Chicken litter made up of rice husk has a high ash content and this produces the highest char yields. The char production from the rice husk mix is over 67 wt.%, whilst the char yields from wood shavings mix reach around 58 wt.% at 350 °C. Low char yields from wood shavings mix are correlated to the lowest ash and lower FC content. The highest VM of wood shavings mix resulted in 44.4 wt.% liquid yield compared to the other feedstocks that produced around 30 wt.%.

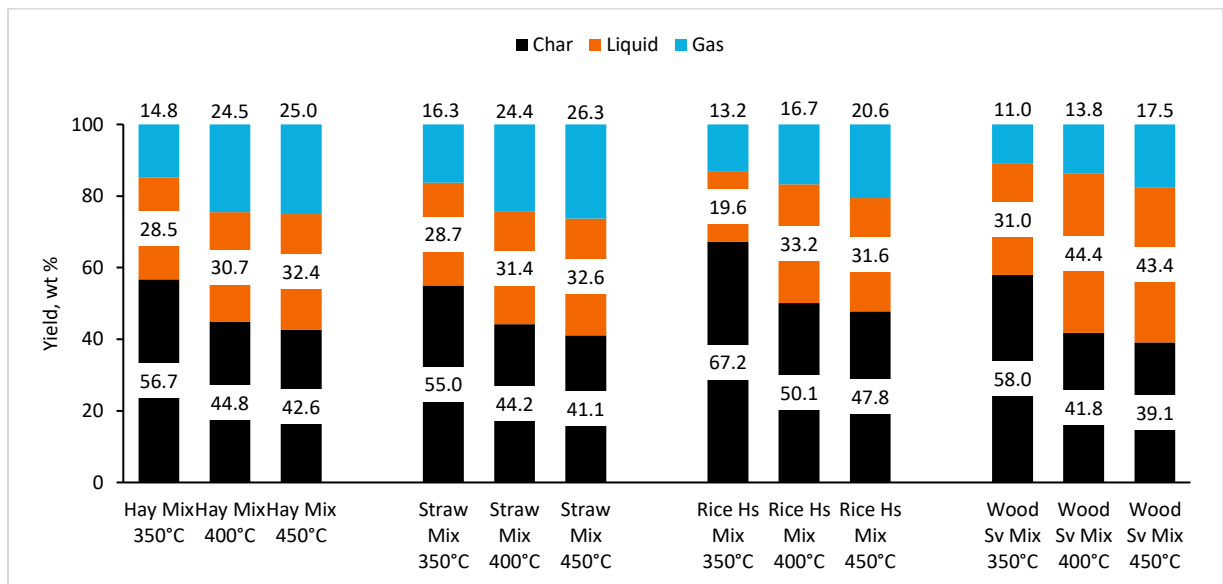


Fig. 3. Product yield distribution of four chicken litter feedstocks pyrolysed at 350, 400, and 450 °C.

#### 4.3. Syngas production

The presence of air in the apparatus caused the appearance of nitrogen and oxygen in the syngas, nitrogen was measured in the range 11-25 vol.% and oxygen in the range 3-9 vol.%. Therefore, the results are given on a N<sub>2</sub> and O<sub>2</sub> free basis which allows direct comparison of gas composition between the different feedstocks and temperatures and also avoids any dilution effect due to presence of small amount of air in the apparatus.

Syngas composition is expressed on a volumetric percentage. Fig. 4 shows the composition of the dominant gaseous compounds, while Fig. 5 presents the composition of the less abundant gaseous species in the syngas. Although CO<sub>2</sub> and CO are the dominant gaseous compounds in all pyrolysis tests [21-23], no clear production trend with respect to temperature can be observed. Less abundant gases such as C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>6</sub>, and H<sub>2</sub>S typically do not exceed 1 vol.%. Strong temperature dependence is observed for the methane. Regardless to the feedstock type, the methane yield increased 16 fold between 350 and 450 °C.

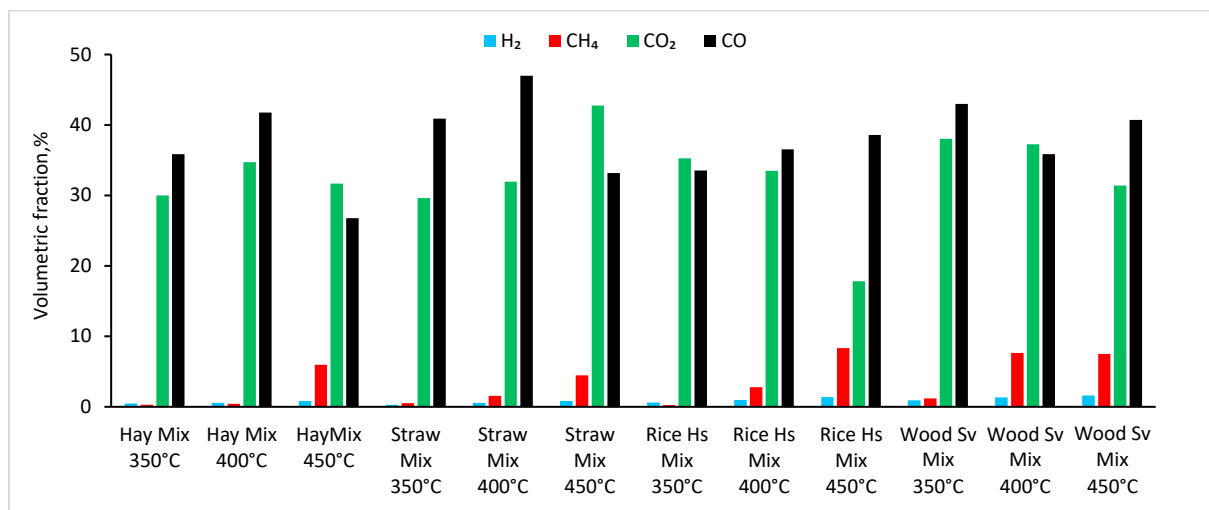


Fig. 4. Yields of dominant syngas compounds (vol%).

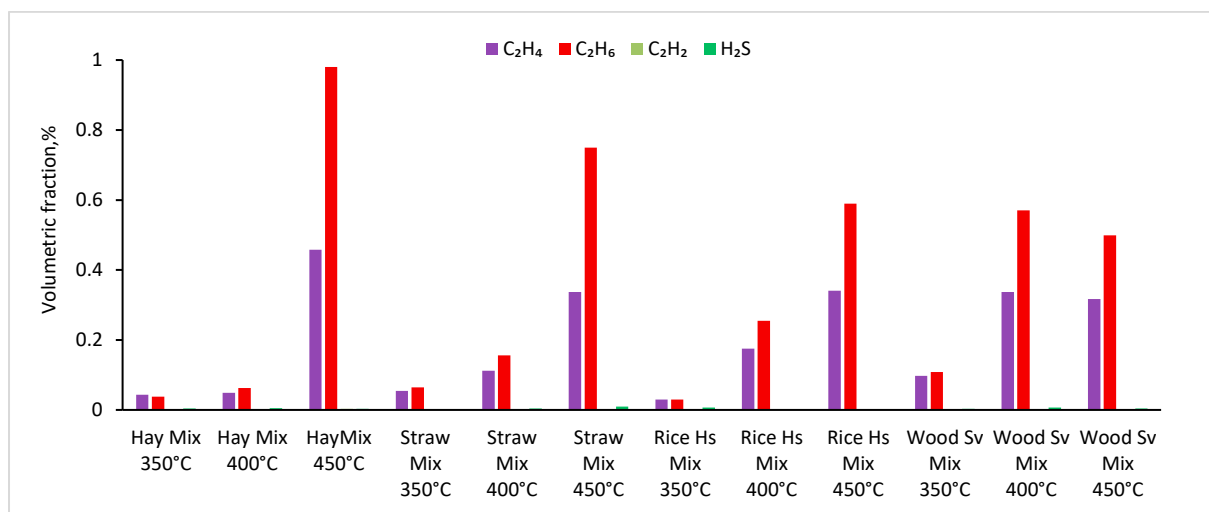


Fig. 5. Yields of less abundant syngas compounds (vol%).

#### 4.4. Liquid (bio-oil) identification

During the pyrolysis process, water vapour derives from the wet feedstock as well as from the thermochemical reactions. Water vapours are condensed together with the bio-oil vapours into a liquid fraction. A Karl Fisher titration showed that the collected liquid fractions contained between 65 and 72 vol. % water. Fig. 6 shows the total ion current (TIC) chromatogram of bio-oil solution produced from wood shavings mix at 400 °C. This chromatogram enables detection of about 100 species moreover, only 19 of the most abundant bio-oil compounds were identified and presented in this study using the NIST 08 MS library within MSD ChemStation®. The bio-oil compounds identified and numbered in Fig. 6 correspond to numbering presented in Table 3.

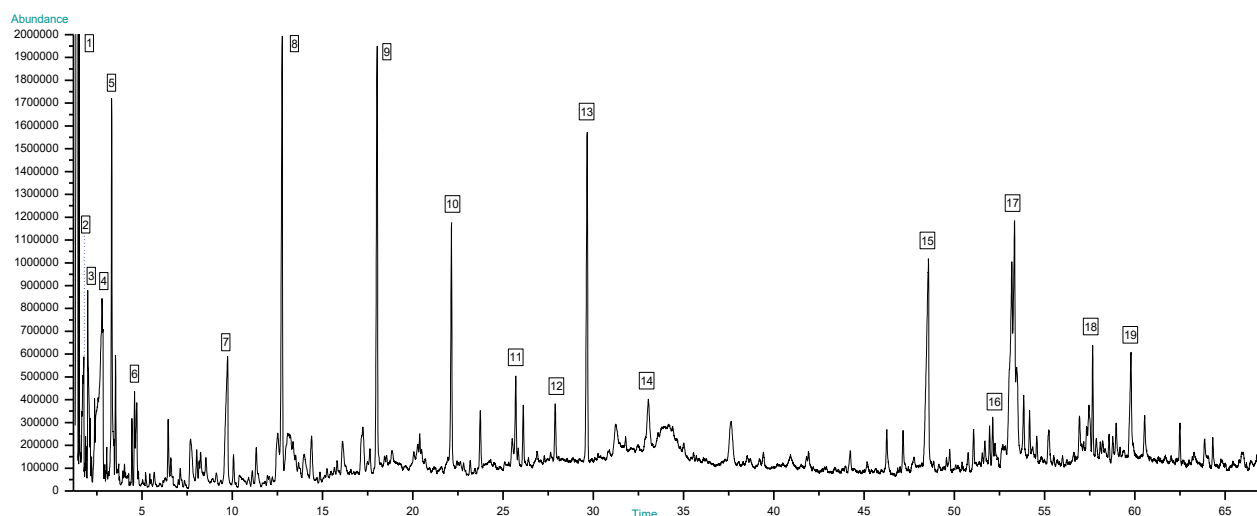


Fig. 6. Total ion current (TIC) chromatogram of bio-oil from 400°C pyrolysis of wood shavings mixed with chicken manure.

Pyrolysis temperature is the dominant driver of bio-oil composition [24]. However, the major bio-oils compounds produced at different pyrolysis temperature (350, 400 and 450 °C) exhibit properties. The most abundant compounds (numbered from 1 to 19) are in agreement with the maturity sequence of pyrolysis oil proposed by Elliot (1988) [25]. According to Elliot's sequence of tar (bio-oil) maturation from primary pyrolysis oil shows that at pyrolysis temperature of 400 and 500 °C, bio-oil contains mixture of oxygenates and phenolic ethers. In contrast to Elliot's observations, the bio-oil produced in this study at 350–450°C contains short organic acids (i.e. propanoic acid, butanoic acid), fatty acids (i.e. oleic acid) and heterocyclic aromatics compounds such as pyridines, phenols and its derivative.

Table 3. Identified bio-oil compounds from 400°C pyrolysis of wood shavings mixed with chicken manure.

Compounds Name	Compounds Name
1. Furan, 2,5-dimethyl- ( $C_6H_8O$ )	11. Phenol, 2-methoxy-4-(1-propenyl)- ( $C_{10}H_{12}O_2$ )
2. Propanoic acid ( $C_3H_6O_2$ )	12. Phenol, 2-methoxy-4-(1-propenyl)- ( $C_{10}H_{12}O_2$ )
3. Pyridine ( $C_5H_5N$ )	13. Phenol, 2-methoxy-4-(1-propenyl)- ( $C_{10}H_{12}O_2$ )
4. Butanoic acid ( $C_4H_8O_2$ )	14. 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- ( $C_{10}H_{12}O_3$ )
5. 2-Furanmethanol ( $C_5H_6O_2$ )	15. n-Hexadecanoic acid ( $C_{16}H_{32}O_2$ )
6. Pyrazine, 2,6-dimethyl- ( $C_6H_8N_2$ )	16. 10-Octadecenoic acid, methyl ester ( $C_{19}H_{36}O_2$ )
7. 1,2-Cyclopentanedione, 3-methyl- ( $C_6H_8O_2$ )	17. Oleic Acid ( $C_{18}H_{34}O_2$ )
8. Cyclopentanol ( $C_5H_{10}O$ )	18. Dronabinol ( $C_{21}H_{30}O_2$ )
9. Phenol, 2-methoxy-4-methyl- ( $C_8H_{10}O_2$ )	19. Retinoic acid ( $C_{20}H_{28}O_2$ )
10. Phenol, 4-ethyl-2-methoxy- ( $C_9H_{12}O_2$ )	

#### 4.5. Energy balance

The HHV of each pyrolysis product is presented in Table. 4. For syngas, the HHV is calculated according to equation 2 [7] and then multiply by syngas density, while the char HHV is calculated based on ultimate analysis data using equation 1 [7]. The HHVs for all liquid pyrolysis products were calculated based on energy and mass balance equation 3 and 4 and all calculations are on an as-received (ar) basis.

$$HHV = f_{CH_4} \times 35.83 + f_{CO} \times 12.633 + f_{H_2} \times 10.783 + f_{C_2H_4} \times 59.457 + f_{C_2H_6} \times 63.79 \quad (2)$$

$$HHV_{FS} \times m_{FS} = (HHV_C \times m_C) + (HHV_L \times m_L) + (HHV_G \times m_G) \quad (3)$$

$$HHV_L = \frac{(HHV_{FS} \times m_{FS}) - (HHV_C \times m_C) - (HHV_G \times m_G)}{m_L} \quad (4)$$

For energy balance, the input energy with the different mixtures was calculated for 1 kg of feedstock (ar) and the energy balance is represented in Fig. 7, while the energy output of the pyrolysis products was evaluated on the basis of the calorific value tabulated in Table 4 and multiplied by their respective product yields distribution. At the lowest pyrolysis temperature, the vast majority of the initial energy content is preserved in the char, which accounted for 62 to 87 %. At higher temperatures, the energy content in the char declines to 42-55 %. Overall, the highest energy content in the char was for the rice husk mix; 87% at 350 and 67% at 450 °C. The energy contents in the liquid fraction increases from 16 to 58%, with an increase in temperature. The liquid fraction from hay and the wood shavings mix resulted in the highest energy content. The energy content of the gaseous phase was in the range of 3.7 to 6.8% at 350°C and increased to 9.4-16.8% at 450°C.

Table 4. Caloric value for pyrolysis products

Pyrolysis sample	Char (MJ/kg)	Liquid (MJ/kg)	Gas (MJ/kg)
Hay Mix 350°C	15.79	16.35	4.89
Hay Mix 400°C	15.65	18.57	4.94
Hay Mix 450°C	18.48	14.40	7.18
Straw Mix 350°C	18.23	6.52	5.33
Straw Mix 400°C	17.96	10.78	5.91
Straw Mix 450°C	17.31	12.83	5.59
Rice husk Mix 350°C	16.92	5.40	4.27
Rice husk Mix 400°C	19.13	7.37	5.74
Rice husk Mix 450°C	18.19	6.66	10.63
Wood shavings Mix 350°C	18.97	10.48	5.09
Wood shavings Mix 400°C	16.61	15.50	7.15
Wood shavings Mix 450°C	16.17	16.34	7.97

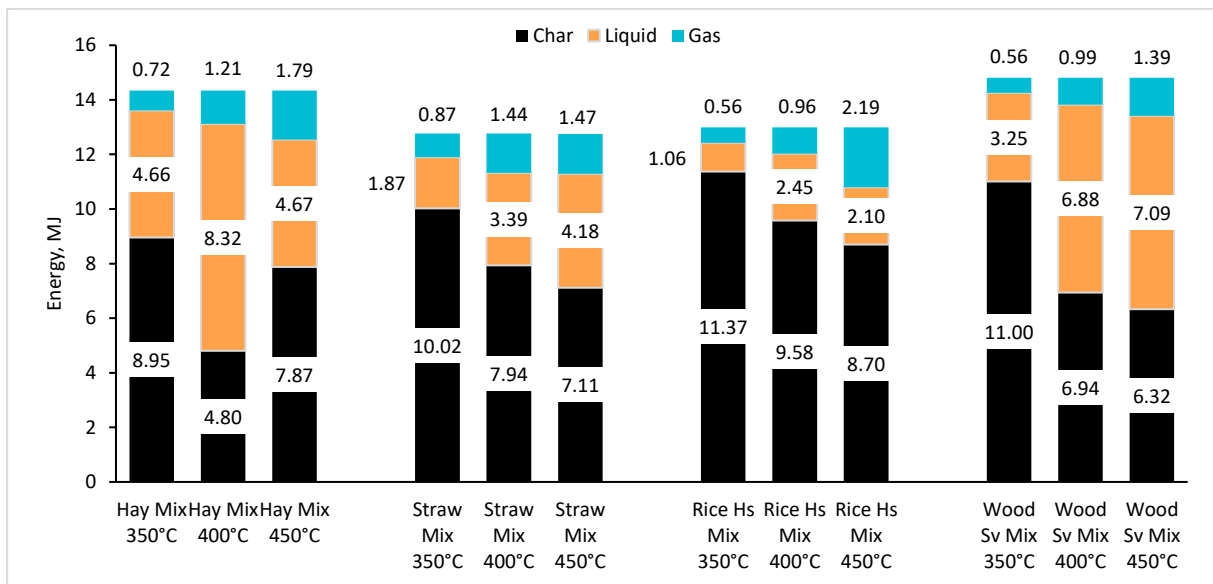


Fig. 7. Energy balance of four chicken litter feedstocks pyrolysed at 350, 400 and 450°C (as receive basis).



## 5. Conclusion

Preliminary tests of slow pyrolysis of chicken litter have been conducted successfully. Four different types of modelled chicken litter have been treated in the temperature range between 350 and 450 °C. Feedstocks have been characterised by proximate and ultimate analysis. The chemical analysis of pyrolysis products included gas chromatography, Karl Fisher titration, bomb calorimetry and ultimate analysis. The wood shavings mixed with chicken manure had the highest HHV and generated the highest energy output, which is in line with the highest carbon and lowest ash content among the tested feedstocks. The product distribution pattern of all four chicken litter feedstocks is similar. The total char yield decrease, while syngas yields increase with pyrolysis temperature. The yield of the liquid phase seems to reach a peak at 400 °C followed by its decrease. CO<sub>2</sub> and CO are the dominant gases evolved during the pyrolysis at the temperature of 350 and 400 °C whilst methane production increased significantly at the highest temperature, 450 °C. Major bio-oil compounds found in all tested feedstocks are short organic acids, fatty acids and heterocyclic aromatic compounds.

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