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A rich hydrogen fuel gas production from poultry litter thermochemical conversion

Jayna Pessuto Silva [1], Daniele Perondi [1], Danielle Restelatto[1], Aline Dettmer[1], Marcelo Godinho [1]

[1] Energy and Bioprocesses Laboratory / [1]University of Caxias do Sul

(jayna.qui.eng@gmail.com)

Abstract

Poultry litter, waste generated by poultry farming, has its main destination the use in soil as fertilizer, although, the non-controlled use for this purpose can result in environmental impacts. Therefore, the thermochemical conversion of this waste can be an alternative for its final destination, since its products can be converted into energy. In this work, poultry litter wastes were pyrolyzed in a fixed bed reactor, operating in batch system. A N_2 atmosphere and $1 L.min^{-1}$ flow were used. During the pyrolysis reaction (thermal treatment conducted at moderate temperatures and in the oxygen absence), the waste volatile matter is decomposed into three fractions (solid, liquid and gas). The fuel gas produced is essentially composed of non-condensable gases (H_2/CO/CH_4/CO_2) and higher molecular weight gases (C_xH_y). These gases can be used in several applications such as heat and/or electricity production. The temperature influence was evaluated from the gas fraction yield. The results showed that with increasing temperature, there was an increase in hydrogen production (from 10.29 to 61.62 vol.%) and a decrease in carbon dioxide production (from 56.97 to 7.59 vol.%). Hence, this process becomes attractive, especially due to the possible gas reuse by the farm.

Key-words: Poultry litter wastes. Energetic Reuse. Hydrogen Production. Pyrolysis.

Area: 6 – Energy and Renewable Energies

1 Introduction

The wastes disposal, whether human (household waste), animal (manure) or vegetable (straws and crop residues, etc.) is one of the major challenges faced by society. These wastes when disposed untreated and inadequately in the ground, can cause serious environmental pollution problems, whether by leachate percolation or pathogens proliferation, insects and other harmful animals (COSTA 2012).

Poultry litter is comprised of a poultry manure, feathers, water and animal feed. It is the main by-product generated by the Brazilian poultry sector. This sector holds the lead in exports and the third position in chicken meat world production since 2011 (RODRIGUES et al., 2014), which results in a generation of waste increase.

Poultry litter materials are often made of wood shavings, sawdust, wheat, straw, peanut husks, rice husks, or another type of waste available in the region. According to Costa (2012), the litter is usually comprised of a material which has a very lignified part and difficult to degrade. Although it is typically reused, there is little information on their quality characteristics and patterns in different lots of reuse.

The use of poultry litter as fertilizer can be economically attractive, since it represents an internal resource in farming and it is a residue which contains a high concentration of nutrients. However, from an ecological point of view, there are major restrictions on its use because it can be a soil, surface and groundwater pollutant (HAHN 2004).

Thus, the thermochemical conversion can bring an alternative for these wastes final destination, since the products generated can be converted into energy.

Thermochemical conversion (pyrolysis) occurs in oxygen absence. The volatile matter is decomposed into three fractions (solid, liquid and gas). The fuel gas produced is essentially composed of non-condensable gases (H_2/CO/CH_4/CO_2) and higher molecular weight gases (C_xH_y). These gases can be used in several applications such as heat and/or electricity production.

Hydrogen is a clean fuel that can be easily used in both fuel cells and hydrogen fuelled turbines for generation of electricity or as a fuel for transportation, where it is directly combusted in internal combustion engines (CORMOS 2011; CHERRY 2004). Another advantage of this gas (H_2) is associated with the fact that its combustion does not release CO_2, minimizing emissions of greenhouse gases.

Currently, 96% of the hydrogen produced in the world comes from a fossil source (World Nuclear Association 2015), being produced preferably through natural gas catalytic reforming. To establish a sustainable hydrogen production, alternative sources (renewable biomass) are being investigated (WAHEED, WU AND WILLIAMS 2015).

This study approaches a pyrolysis process assessment to produce a rich hydrogen gas from poultry litter waste. This process becomes attractive, especially due to the possible reuse of this gas on the farm.

2 Materials and Methods

2.1. Materials

The poultry litter samples used in this work come from a laying poultry farm, located inside the city of Antonio Prado, located in the state of Rio Grande do Sul, Brazil.

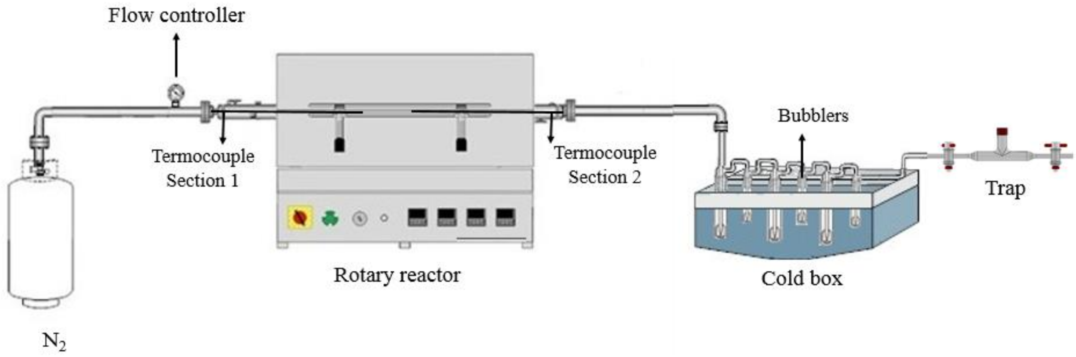
The sampling procedure was performed according to NBR 10007/2004 standard. To ensure the samples representativeness, different sampling points inside the aviary were selected. These samples were allocated in this place for a seven-month period, corresponding to three lots. Afterwards, the quartering procedure was done, which also followed the NBR 1007/2004 recommendations.

2.2 Fuel Gas Production Experiments

The fuel gas production experiments were conducted in triplicate, with a 25°C.min^{-1} heating rate and a N_2 1L.min^{-1} flow. A 30-min isotherm was used after reached the final temperature (800°C) in all experiments. The gas samples were collected in a non-isothermal region (500, 600, 700 and 800°C points) and in an isothermal region (15 and 30 minutes after reaching the 800°C final temperature).

The reactor used for the pyrolysis experiments is a bench reactor available in the Energy and Bioprocess Laboratory at the University of Caxias do Sul, which operates in batch system (Figures 1). Its operation may be conducted either in a fixed bed as in a rotary one. It is a furnace that has a quartz reactor coupled internally. The N_2 flow rate control is performed by a flow controller (0-1 L.min^{-1}). The reactor has the following dimensions: 98.1 cm length, 49 mm outside diameter and 43 mm internal diameter. The useful length of the oven is 51.6 cm. The reactor is heated electrically by two resistors, each one with a 1900 W power. Two type K thermocouples are positioned inside the reactor (Sections 1 and 2). The maximum reactor operating temperature is 1200 °C. The pyrolysis vapours condensation is conducted in accordance with CEN BT/TF 143 standard and ten bubblers (impingers) are used. The bubbler is a glassware used for the condensation of the pyrolysis oil and other condensable species presents in the fuel gas (ANDRADE, 2007). In each experiment 100 ml of isopropyl alcohol are added in each bubbler, except for the first and the last (empty). All the bubblers are kept in a cold box (ice bath, salt and isopropyl alcohol). The aim is to keep the bath bubblers at low temperature (around -10ºC) favoring the oil and other condensable condensation present in the fuel gas. Sampling of gases is performed by using collectors (traps) (PERONDI, 2015).

Figure 1. Pyrolytic reactor scheme used in the pyrolysis experiments.



Source: PERONDI, 2015.

2.2.1 Chromatographic analyses of gases

The non-condensable gas analyses (H_2/CO/CH_4/CO_2) were performed by Gas Chromatograph (Dani Master GC brand), equipped with a Thermal Conductivity Detector. A capillary column from Supelco® Analytical, Carboxen ™ model 1006, with a length of 30 m, 0.53 mm internal diameter and 30 mm of film thickness was used. The column is Porous Layer Open Tubular.

All analyses were performed in the Energy Laboratory and Bioprocess at the University of Caxias do Sul. The sample gases were diluted in N_2 (carrier gas used during pyrolysis reaction).

To sample the gases a borosilicate glass collector was used. The chromatographic analysis is not performed continuously, which is, the gas is collected and subsequently analyzed in a gas chromatograph (offline). The maximum storage time of the gas sample collector is three days in order to avoid possible changes in the sample.

For samples injections a micro syringe Hamilton brand was used (Gastight type). This syringe has a removable needle, and a maximum volume of 1 ml. Other information related to the syringe are: scale length of 6 cm, maximum temperature of 115 °C, minimum temperature of 10 °C and maximum pressure of 200 psi. The chromatographic methods specifications used in this study are summarized in Table 1.

Table 1. Chromatographic methods used for gases detection/quantification.

Identification Method: CO, CO_2 and CH_4	Identification Method: H_2
Detector: TCD	Detector: TCD
He as carrier gas, 3 mL/min flow	N_2 as carrier gas, 3 mL/min flow
Oven temperature: 35ºC	Oven temperature: 35ºC
Injector temperature: 100ºC	Injector temperature: 100ºC
Detector temperature: 100ºC	Detector temperature:100ºC
Injected gas volume: 0.5 mL	Injected gas volume: 0.5 mL
Split: 1:20	Split: 1:5

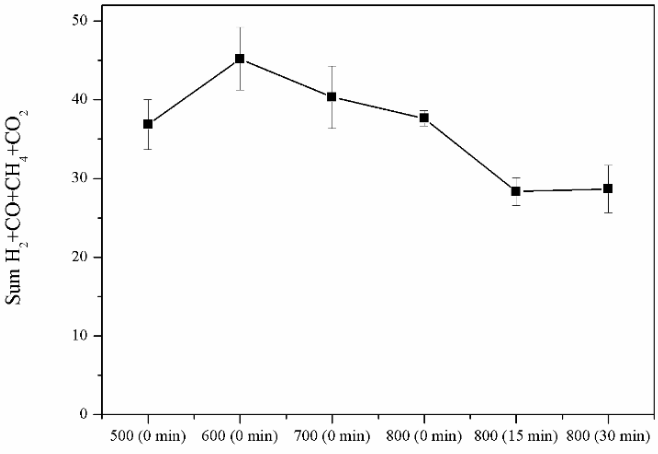
For the calibration curves construction three standards of known concentrations purchased from Air Liquide were used, in addition to pure methane (CH_4), pure carbon dioxide (CO_2) and pure Hydrogen (H_2): the first standard containing 10.1 % mol/mol H_2, 20.1 CO and 69.8 CO_2, the second containing 39.99 % mol/mol H_2, 5.057 CO and 54.95 CO_2 and finally the last containing 39.6%mol/mol CO, 30.9 CH_4 and 9.95 CO_2.

3 Results and Discussion

3.1. Reaction rate

Figure 2 shows the sum of the non-condensable gases (H_2/CO/CH_4/CO_2) produced according to the different points of gas sampling (non-isothermal and isothermal region) for the experiment conducted at the final temperature of 800°C. For results analysis, it was considered that the maximum reaction rate occurs when the sum of non-condensable gases is maximum.

Figure 2. Non-condensible gases production for the experiment conducted at 800 °C final temperature.



The maximum reaction rate at 600°C temperature was observed and after this temperature a reduction in the non-condensable gases production in all collected points was verified.

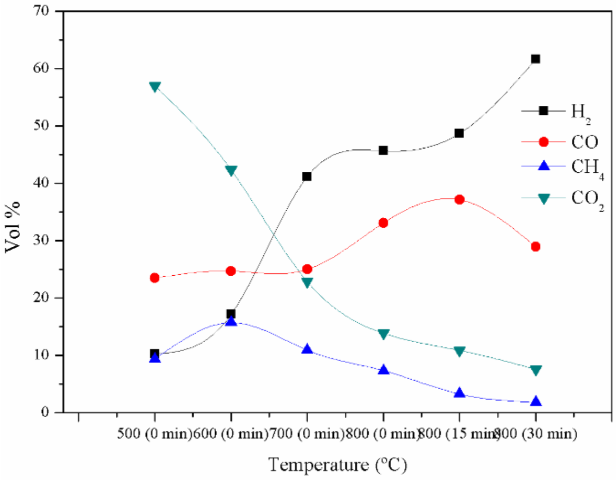
3.2 Temperature influence

The temperature influence on non-condensable gases production is shown in Figure 3. The non-condensable gases molar fraction results were expressed with nitrogen free basis, according to Equation 1 (Adapted from DE CONTO, 2015). These results showed that with increasing temperature, there was an increase in hydrogen production (from 10.3 to 61.6 vol. %) and a decrease in carbon dioxide production (from 57.0 to 7.6 vol. %).

$$X_i = \frac{X'_i}{1 - X'_{N2}} \qquad (1)$$

X_i = Gas molar fraction free of N_2.
X'_i = Gas molar fraction diluted in N_2.
X'_{N2} = N_2 molar fraction in the analyzed gas stream.

Figure 3. Temperature influence on non-condensable gases production.



Yang et al. (2007) evaluated the non-condensable gas yield ($H_2/CO/CH_4/CO_2$) in the three major components of biomass pyrolysis (cellulose, hemicellulose and lignin).

According to the authors, the H_2 was released at temperatures above 400 °C and in the case of hemicellulose, a maximum rate at about 600 °C was observed. For the CO_2, the emissions occurred between 400 and 600 °C and a peak was observed at about 500 °C, similarly to the results found in this study (the high concentration of CO_2 at 500ºC is associated with hemicellulose degradation). The maximum release of CH_4 gas according to the authors was between 500 and 600 °C, which can also be observed in Figure 3. Finally, the CO showed a very characteristic behavior for each component. For hemicellulose, CO production showed two separate peaks (300 and 750 °C), while for the cellulose a single peak at approximately 450 °C was observed. In the case of lignin, the release started at 600 °C and increased with increasing temperature.

3.3 Pyrolytic yield

Table 2 shows the pyrolysis products yields obtained from poultry litter residue experiments.

Table 2. Pyrolytic products (char, oil, gas) yields from poultry litter residue.

Experiments	Biomass weight (g)	Char (%)	Oil (%)	Gas (%)*	H_2 (mmol.g^{-1}biomass)
1	100	32.61	36.26	31.13	14.55
2	100	33.02	36.98	30	
3	100	32.27	37	30.73	
Average		32.63	36.75	30.62	
Standard deviation		0.37	0.42	0.57	

***** By difference.

Similar pyrolysis yields were reported by Kim et al. (2009). The authors conducted manure waste with wood shavings pyrolysis experiments. A pyrolysis temperature of 500 °C, a feed rate of 200g/h and a fluidized bed reactor were used by the researchers. The following values were obtained: 39.98% of char, 36.75% of oil and 33.04% of gas.

Waheed, Wu and Williams (2015) evaluated the influence of operating conditions on the syngas (H_2/CO) and H_2 in a fixed bed reactor with two stages (pyrolysis/catalytic steam reforming). The experiments were conducted with rice husks and temperatures between 850 and 1050ºC in the second reaction stage. The hydrogen yield increased with increasing temperature, reaching a maximum of 30.6 mmol H_2/g biomass at 1050ºC, and a 65.2% (mol/mol) H_2 concentration in the gas.

Other biomass and polymers blends studies have also been reported in the literature, such as the study by Alvarez et al. (2014). The H_2 highest yield for the authors was 10.98 mmol H_2/g sample in catalyst absence (80/20 biomass/polymer ratio). The differences observed between the concentration and the H_2 yield in the catalytic and non-catalytic process suggests that the catalyst promotes water-gas-shift reaction. Therefore, the value reported in this study (14.55 mmol H_2/g biomass) is compatible with the experimental conditions used. A second step could be inserted in the process (steam gasification) in order to enrich the gas in addition to the catalysts use.

4 Conclusion

From the results presented in this paper, it can be identified that the poultry litter wastes thermochemical conversion is a viable alternative to their disposal. The gas produced after the process besides being rich in hydrogen, has other gases (CO/CH_4) which improve its calorific value. Therefore, this process becomes attractive, especially due to the possible reuse of this gas by the farm.

5 Acknowledgements

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