



An experimental study on the thermal valorization of municipal and animal wastes

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Abstract

Poultry wastes and refused derived fuel disposal through thermochemical processes, such as combustion, has been proposed. These fuels have calorific values that in many cases exceed 20MJ kg^{-1} . An extensive analysis has been performed of pyrolysis and combustion results obtained by thermal analysis measurements. The weight loss data were recorded continuously, under dynamic conditions, in the range $25\text{-}1300^\circ\text{C}$. A first order parallel reactions model and a power law model fitted the experimental results accurately for pyrolysis and combustion, respectively. The pyrolysis of poultry waste was a complex process, occurring up to 1300°C with high activation energies.

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Keywords: Poultry wastes; RDF; Pyrolysis; Combustion.

1. Introduction

Given the trend to replace fossil carbon and gain additional revenue, the power generation sector across the world is considering the use of secondary fuels, such as animal breeding and household wastes. As landfill disposal is no longer a viable solution, due to the high cost and the environmental regulations, thermal treatment of these wastes is an attractive option, by destroying hazardous constituents, reducing their volume, allowing for energy recovery and increasing economic returns to rural communities.

Chicken eggs and meat is one the most widely used protein source throughout the world. Nowadays, it is more and more common to have large scale chicken industries. There is about 50g of wastes generated by a chick every day and this mainly composes of: manure, bedding material, waste feed, dead birds, broken eggs and feathers. Refused derived fuel (RDF) is produced from municipal solid wastes (MSW) through a procedures comprising source-separated, processed and dried combustible MSW fraction. It consists of mostly cellulosic and plastic components.

Several thermal systems have been proposed for poultry litter and RDF valorization for energy. Fast pyrolysis of poultry wastes (PW) has been tried out but the results were not so promising, as the bio-oil yield of poultry litter was relatively low compared to wood derived bio-oil (34–42wt%) [1]. Pyrolysis of RDF is crucial in thermochemical conversion processes, due to the high volatile content of this fuel. Volatile species evolved have been characterized by TGA-FTIR and TGA-MS techniques [2]. Combustion of PW and RDF has been accomplished in fluidized bed combustion units [3, 4]. Care should be given in both direct combustion and co-combustion on the effect of chlorine and nitrogen,

which significantly change the chemistry of emissions production [5-7]. A gasification step of these materials and subsequent use of the product gas into existing boilers has also been studied [8, 9]. This work aimed at investigating the thermal behavior of PW and RDF under non-isothermal thermogravimetric conditions and at developing kinetic models for the pyrolysis and combustion of these fuels, for which there is lack of information in the literature. The obtained data should be useful for the design of furnaces, which will utilize these materials for power production.

2. Experimental

The poultry waste under examination was a Meat and Bone Meal containing some parts of the feathers as well. The material came from a modern Greek chicken farming company. The refused derived fuel sample was obtained from the DEDISA factory of the city of Hania, in Crete.

After air drying, homogenization and riffing, the samples were ground to a particle size less than 250 μm . Fuel analyses were carried out according to the ASTM standards. For proximate analysis programmable laboratory furnaces were used (E871, D1102-84), for ultimate analysis a 2400 CHNS analyzer of Perkin Elmer (D3176-93, D3177-33) and for calorific value a Leco type calorimeter AC-350 (D2015-95). Chemical analysis of ashes was conducted by using an X-ray fluorescence spectrometer type SRS-303 of Siemens (D4326). For chlorine measurements a colorimeter type Smart 2, by LaMotte, was used.

Pyrolysis and combustion tests were performed in a thermal analysis system, TG/DTA/DSC model labSyS evo of Setaram, with which the sample weight loss and rate of weight loss as functions of time or temperature were recorded continuously, under dynamic conditions, in the range 25-1300°C. The experiments were carried out at atmospheric pressure, under nitrogen/air atmosphere, with a flow rate of 45ml/min, at a linear heating rate of 10°C/min. Preliminary tests with different sample masses and sizes and gas flow rates were carried out, in order to check the influence of heat and mass transfer. Small masses (20-25mg) of each material, thinly distributed in the crucible and particle sizes of $\sim 250\mu\text{m}$ were found proper to be used in the experiments, in order to eliminate the effects of eventual side reactions and mass and heat transfer limitations. The experiments were replicated at least twice to determine their reproducibility, which was found to be very good.

3. Kinetic model

The kinetics of thermal decomposition of biomass materials is complicated, as it involves a large number of reactions in parallel and series. In this work the pyrolysis process was described by the independent parallel first order reactions model. This is considered the most realistic approach in the case of biomass materials, leading to good fits to the experimental data [10]. The overall rate of conversion for N reactions can be expressed as:

$$-\frac{dm}{dt} = \sum_i c_i \frac{da_i}{dt}, i=1,2,3\dots N \quad (1)$$

The separate conversion a_i for each component is given by:

$$a_i = \frac{(m_{0,i} - m_i)}{(m_{0,i} - m_{\text{char},i})} \quad (2)$$

where $m_{0,i}$, m_i and $m_{\text{char},i}$ are the initial sample mass, the actual sample mass and the final char yield of component i , respectively. The components are all assumed to decompose individually according to:

$$\frac{da_i}{dt} = A_i \exp(-E_i/RT)(1 - a_i) \quad (3)$$

where A_i , E_i and R denote the frequency factor, activation energy and gas constant, respectively. Coefficient c_i expresses the contribution of the partial processes to the overall mass loss, $m_0 - m_{\text{char}}$:

$$c_i = \frac{m_{o,i} - m_{char,i}}{m_o - m_{char}} \quad (4)$$

The combustion of the chars was described by a power law model. Chars may be composed of parts with different reactivities and the reactivity of a unit surface area may vary as the sample is burning out. To include the char heterogeneity into the model, it was assumed that a char sample could be a mixture of components with different reactivities:

$$m(t) = \sum_{j=1}^n c_j [1 - a_j(t)] + m_{\infty} \quad [m(0)=1] \quad (5)$$

where, m is the sample mass normalized by the initial sample mass, n is the number of components, c_j is the fraction of combustibles in component j , $a_j(t)$ is the reacted fraction of component j in time t and m_{∞} is the normalized amount of the solid residues (minerals) at the end of the experiment.

A separate equation was used for each component to describe the dependence of the reaction rate on the temperature and fractional burn-off:

$$\frac{da_j}{dt} = A_j \exp(-E_j / RT) g(P_{O_2}) f(a_j) \quad (6)$$

where, A_j is the pre-exponential factor of component j , E_j is the activation energy of component j , g expresses the effect of ambient gas composition and f describes the change of surface reactivity as a function of the fractional burn off:

As the function $g(P_{O_2})$ represented the partial pressure of oxygen in air, its value was included into the pre-exponential factor, while the $f(a_j)$ function was described by:

$$f(a_j) = (1 - a_j)^{n_j} \quad (7)$$

where n_j is the reaction order.

In the kinetic analysis the nonlinear least squares algorithm was used. More details can be found in a previous study [11].

4. Results and discussion

4.1 Characterization of the fuels

A comparison of the proximate and ultimate analysis results, as well as of the calorific value of the fuels studied is made in Table 1. RDF has a much higher volatiles content and lower nitrogen and sulphur contents, as compared to PW, implying fewer emissions during utilization of this material for power production. The percentage of nitrogen of PW is particularly high, which will be a problem if combustion of this fuel alone is considered, producing toxic NO_x emissions. However, the calorific value of PW is higher than that of RDF, due to its fat content.

Examining Table 2, which gives the major ash elements analysis, it is evident that PW material contains bones (high calcium and phosphorus). A significant Loss on Ignition, also evident in other works [12] is apparent. Furthermore, the high alkali metals content is also noticeable. These are known to lead to corrosion, slagging and fouling of boilers and agglomeration when used in fluidized beds [12]. On the other hand, RDF ash is richer in calcium and silicon, while poorer in phosphorus and alkali, indicating a low slagging/fouling tendency for this fuel.

Table 1. Proximate and ultimate analyses of the fuels (%wt, dry)

| Sample | Volatiles | Fixed carbon | Ash | C | H | N | O | S | Cl | HHV (MJ/kg) |
|--------|-----------|--------------|------|------|-----|------|------|------|------|-------------|
| PW | 26.7 | 55.6 | 17.7 | 55.9 | 8.2 | 10.6 | 6.2 | 1.1 | 0.28 | 27.9 |
| RDF | 77.1 | 1.6 | 21.3 | 45.7 | 6.3 | 1.5 | 25.3 | 0.01 | 0.2 | 20.4 |

* dry ash-free

Table 2. Chemical analysis of ashes in main oxides (%)

| Sample | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | K ₂ O | Na ₂ O | P ₂ O ₅ | SO ₃ | MnO |
|--------|------------------|--------------------------------|--------------------------------|------|-----|------------------|-------------------|-------------------------------|-----------------|------|
| PW | 2.2 | 1.6 | 2.3 | 31.6 | 4.0 | 10.2 | 5.2 | 14.4 | 6.4 | 0.03 |
| RDF | 18.9 | 12.4 | 0.58 | 44.8 | 1.2 | 0.98 | 0.01 | 0.09 | 0.26 | 0.01 |

4.2 Thermal decomposition characteristics

From the DTG curve illustrated in Figure 1, it can be observed that decomposition of poultry waste started above 500°C and extended up to a high temperature, 1300°C, revealing its high content in tar and hydrocarbons.

The sample presents multiple decomposition peaks at 609°C, 1014°C and 1243°C, due to its heterogeneous nature. The first peak is mainly associated with the evolution of N-compounds, such as NH₃, HCN and HNCO [12]. The maximum pyrolysis rate occurs at 1243°C at a level of 0.8 (%/min).

In contrary to the poultry waste, RDF exhibits a different behavior, as shown in Figure 2. The sample required a much lower temperature (~200°C) than PW to release its volatile constituents and it decomposed with a higher rate, due to its much greater volatile content and less amount of char than PW. This fuel presents two peaks. The bulk of volatiles evolved between 300°C and 400°C and was completed by 550°C, with the evolution of secondary gases leading to the formation of char [13]. Part of the decomposition above 700°C (not shown on the graph) was attributed to the calcium carbonate of the sample, the content of which was about 45% in ash. Therefore, the DTG peaks of the two samples differ in position and height. Taking into consideration that the peak height is directly proportional to the reactivity, whereas the temperature corresponding to peak height is inversely proportional to the reactivity, RDF was more reactive than PW [14].

The burning profiles of PW and RDF chars, in Figures 3 and 4, show both bimodal DTG curves, reflecting the existence of structures of different reactivity. The reaction threshold occurred at 676°C for PW and at 667°C for RDF, while the bulk of the process occurred mainly in the 500-800°C and 400-700°C region, respectively. The burning rate of RDF char was higher.

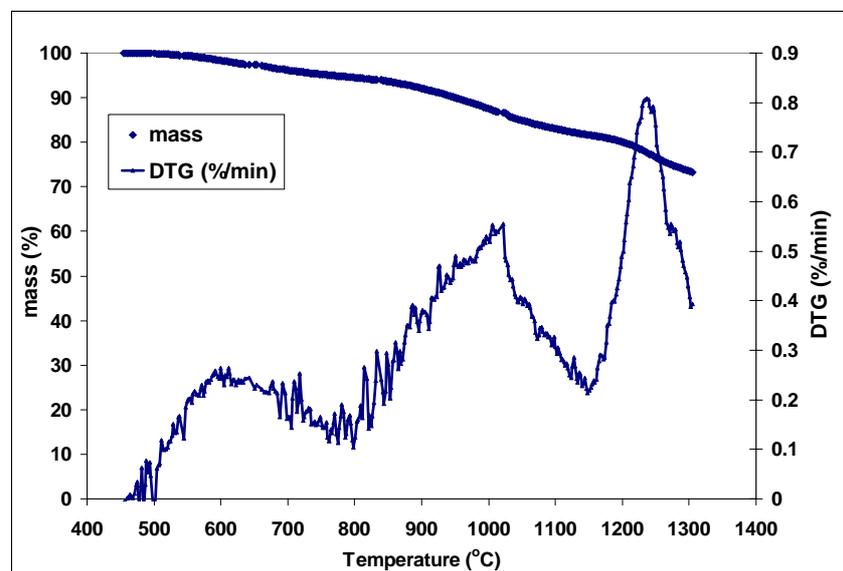


Figure 1. Weight loss and DTG profiles of PW pyrolysis

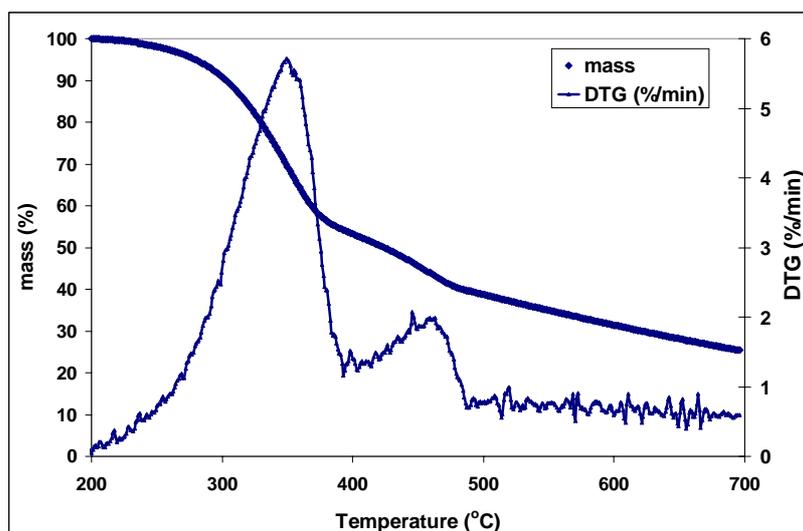


Figure 2. Weight loss and DTG profiles of RDF pyrolysis

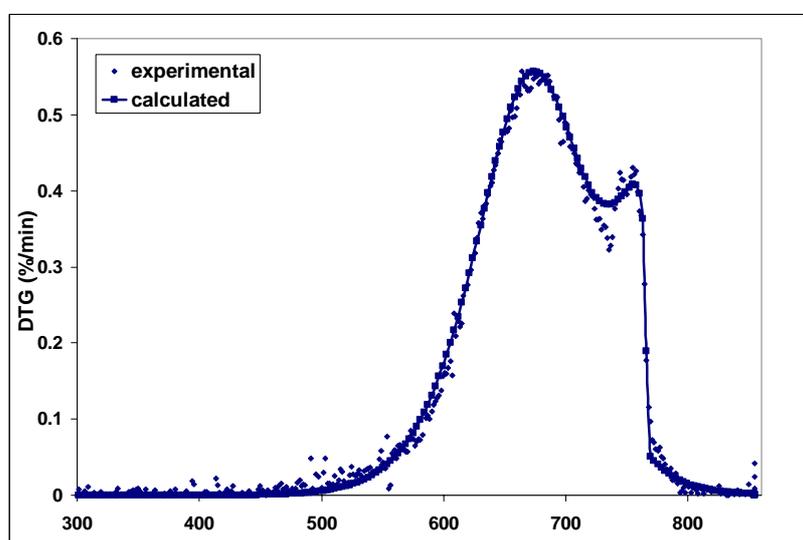


Figure 3. Experimental and calculated DTG profiles of PW combustion

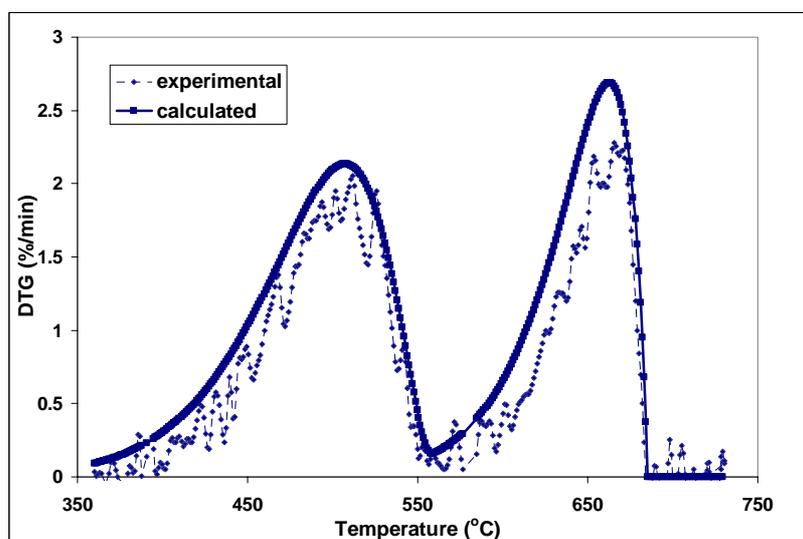


Figure 4. Experimental and calculated DTG profiles of RDF combustion

4.3 Kinetics

Successful modeling of the PW and RDF pyrolysis was accomplished by lumping the numerous reactions into 5 and 3 pseudo-reactions (Figures 5 and 6), respectively. The agreement between model predictions and the experimental measurements was very good, with deviation values about 3%. For combustion, which was described by a power law model adjusted to include char heterogeneity, a two-component behavior was reflected by the shape of both experimental DTG curves (Figures 3 and 4). The maximum rate was about half of that of the pyrolysis process (Table 3).

The kinetic parameters calculated by the models are reported in Table 4. The activation energies and pre-exponential factors fall into the range of chemically meaningful values and are in agreement with those reported in the literature [2, 10, 15, 16]. However, estimated values show that these parameters vary significantly between PW and RDF, reflecting the different reactivities of these fuels. For PW, reaction in nitrogen or air needed more energy from the surroundings. Activation energy values corresponding to the high temperature regime of pyrolysis (1000-1300°C) of this fuel are particularly high.

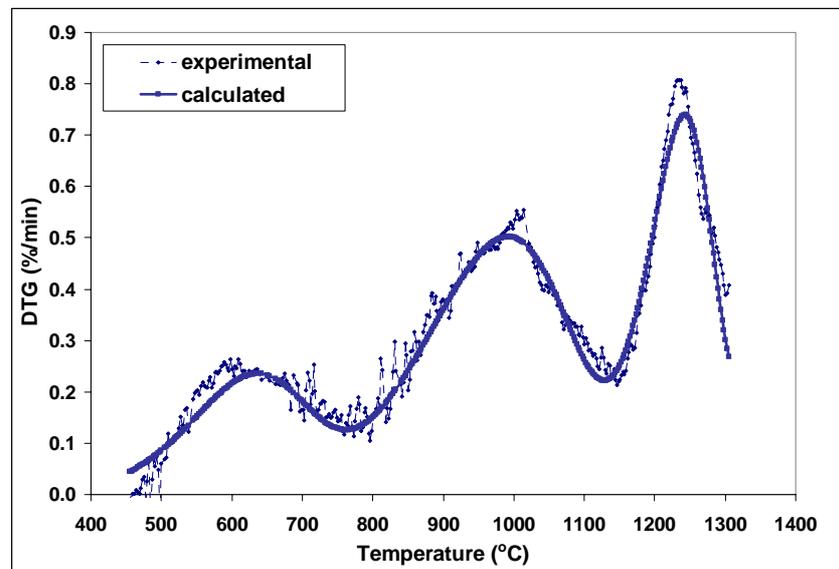


Figure 5. Experimental and calculated DTG profiles of PW pyrolysis

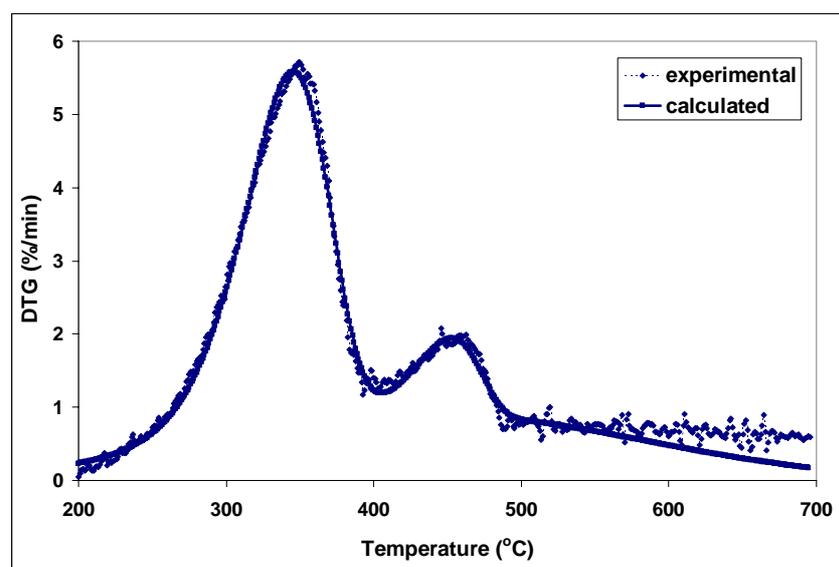


Figure 6. Experimental and calculated DTG profiles of RDF pyrolysis

Table 3. Pyrolysis / combustion characteristics of the fuels

| | | Max rate (%/min) | Temperature at max rate (°C) | Volatiles (%dry) | Char (%dry) |
|------------|-----|---------------------|---------------------------------|---------------------|----------------|
| Pyrolysis | PW | 0.80 | 1243 | 26.7 | 73.3 |
| | RDF | 5.71 | 350 | 77.1 | 22.9 |
| Combustion | PW | 0.55 | 676 | | |
| | RDF | 2.28 | 667 | | |

Table 4. Kinetic parameters of pyrolysis / combustion

| | | Kinetic parameters | R 1 | R 2 | R 3 | R 4 | R 5 |
|------------|-----|--------------------|----------------------|----------------------|-------------------|----------------------|-------------------|
| Pyrolysis | PW | A(1/min) | 2.6×10^3 | 3.5×10^6 | 1.4×10^4 | 8.3×10^{14} | 2.2×10^9 |
| | | E(kJ/mol) | 75.5 | 185.4 | 119.8 | 450.3 | 299.5 |
| | | c(%) | 16.1 | 22.3 | 24.3 | 20.5 | 16.8 |
| | RDF | A(1/min) | 3.3×10^8 | 5.1×10^{13} | 3.38 | | |
| | | E(kJ/mol) | 106.6 | 195.7 | 24.3 | | |
| | | c(%) | 50.5 | 8.6 | 40.9 | | |
| Combustion | PW | A(1/minMPa) | 3.9×10^{10} | 8.3×10^{13} | | | |
| | | E(kJ/mol) | 201.9 | 284.3 | | | |
| | | c(%) | 80.0 | 20.0 | | | |
| | | n | 1.1 | 1.5 | | | |
| | RDF | A(1/minMPa) | 7.1×10^6 | 5.6×10^{11} | | | |
| | | E(kJ/mol) | 107.7 | 219.7 | | | |
| | | c(%) | 36.9 | 63.1 | | | |
| | | n | 0.67 | 0.51 | | | |

5. Conclusions

Poultry waste had a lower volatiles content, whereas higher nitrogen and sulphur contents and calorific value, as compared to RDF. Volatile materials of RDF were given off at a much lower temperature with a higher rate, while its char burned also with a greater rate.

A first order parallel reactions model and a power law model adjusted to include char heterogeneity fitted the experimental results accurately for pyrolysis and combustion, respectively. The pyrolysis of poultry waste was a complex process, occurring up to 1300°C with high activation energies.

The combustion of poultry and RDF wastes can be technologically a viable method of disposing the materials. Fluidized bed technology could facilitate their use mixed with fossil fuels, to produce heat and power. Rather than being a problem of waste, poultry litter and RDF can and should be a source of energy. The results can aid the proper design of boilers and furnaces using such fuels.

Acknowledgments

The authors kindly thank Assist. Prof. P. Maravelaki for providing the thermal analysis equipment, Prof. K. Komnitsas, Dr. D. Zaharaki and Prof. V. Gidaracos from the Technical University of Crete, for part of the chemical analyses of the samples.

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