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# Determination of co-combustion properties and thermal kinetics of poultry litter/coal blends using thermogravimetry

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#### ABSTRACT

The purpose of this study was to investigate the combustion properties and thermal kinetics of poultry litter. Co-combustion of poultry litter with low quality Turkish lignite was also studied. The experiments were performed in a thermogravimetric analyzer (TGA) under non-isothermal conditions. The Flynn –Wall–Ozawa method was used to determine activation energy. Activation energy of the samples was between 104.4 kJ/mol and 130.1 kJ/mol. Different thermal decomposition properties were detected for poultry litter/coal blends than for coal. The thermal properties of the prepared blends showed correlation with the percentage of the poultry litter in the samples. Furthermore, average activation energies of the blends decreased with increasing wt% of coal; the lowest activation energy was obtained with 70 wt% litter, the lowest litter wt% in the blend. A synergistic effect was also observed between poultry litter and coal samples during their co-combustion.

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#### 1. Introduction

Chicken and turkey litter contain wood chips, straw, manure and feathers. Turkey is the fourth largest poultry meat exporter in the world. It was reported in 2013 that in Turkey the number of chicken and turkeys were 266 and 2.9 million, respectively [1]. Poultry animals produce 60–70 kg litter per year per animal [2]. Therefore, a great amount of poultry litter is produced as a result of poultry farming activities in Turkey, disposal of which is an important problem. Due to environmental issues and health concerns, disposal of poultry litter is also an important issue worldwide [3]. Since land application of poultry litter is restricted by the European Union, disposal of this waste is becoming increasingly important [4]. Development of alternative processes that allow energy gain from the litter is of great interest [5].

There are three main technologies for thermochemical processing of poultry litter; direct combustion, pyrolysis and gasification [6]. Henihan et al. (2003) co-combusted poultry litter with peat in a fluidized bed [7]. They found that the gaseous emissions were not hazardous. Kim et al. (2009) investigated fast pyrolysis of chicken litter in a fluidized bed and recovered bio-oil and char as pyrolysis products [3]. Mante and Agblevor (2010) studied the influence of wood shavings on fast pyrolysis products [5]. Oil produced from the pyrolysis was directly related with the composition of litter. Vamvuka et al. (2013) studied both combustion and pyrolysis of poultry waste and Refused Derived Fuel (RDF). They found that the poultry waste had a lower volatile content and higher calorific value than RDF [8].

Combustion is a suitable method for disposing of poultry waste [9]. Of particular interest, a mixture of poultry waste with fossil fuels can be utilized in fluidized bed systems to produce heat and power [3]. The estimated lignite reserve of Turkey is about 12 billion metric tons (7<sup>th</sup> largest in the world). However, the quality of the Turkish lignites is generally poor [10]. Co-combustion of low quality Turkish lignites with poultry waste will help to both dispose of poultry litter in a more stable manner and allow cleaner energy harvesting from these abundant resources.

In the present study, combustion properties and activation energies of poultry litter samples obtained from three different companies were first investigated by using TGA. Three heating rates (10, 40, 80 °C/min) were administrated during the thermal analysis. Co-combustion of poultry litter with low rank Turkish lignite was also studied so as to obtain thermal activation energies and combustion properties of poultry litter/coal blends.

Although the three samples were obtained from different companies, their thermal properties and the ultimate and proximate analysis results of the samples were very similar to each other. Therefore, just one poultry litter type was used in the study. Cocombustion properties of poultry litter and three different poultry





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litter/coal blends containing 10, 20 and 30 wt% coal were studied in order to characterize the effect of the blending ratio on thermal reactivity.

#### 2. Materials and methods

#### 2.1. Characteristics of poultry litter samples

Three poultry litter samples (P-1, P-2 and P-3) were obtained from three different poultry farms. P-1 was turkey litter. P-2 and P-3 were chicken litters obtained from two different chicken farms. The farms from which the samples obtained were large poultry farms in Turkey.

Oven dried (at 105 °C) poultry litter samples were milled and sieved to 300–850  $\mu$ m before the TG analyses. Proximate and ultimate analysis results of the three poultry litter samples are given in Table 1. Although the characteristics of poultry litter have been reported to vary depending on the origin of the litter and applied farming techniques [11], proximate and ultimate analysis results of all poultry litter samples were found to be very similar to each other in this case.

The composition of the poultry litter samples was mainly volatile matter (50–52%), water (30–32%) with some ash. The high moisture content of poultry litter can prevent sustainable combustion [12]. Therefore, the litter should be dried first before combustion process. Combustion gases can be used for this purpose. Carbon content of the samples was between 39 and 42%. Nitrogen content of the samples was around 4%. The nitrogen in poultry litter samples is present in two forms; inorganic nitrogen and ammonia. Combustion of litter samples produces NO<sub>x</sub> emissions. However, these emissions are below EU limits [12].

A Perkin Elmer-Pyris-1 model TGA was used for the thermal analyses. Approximately 10 mg dried sample (at 105 °C) was used for each experiment. Experiments were performed at 20 mL min<sup>-1</sup> air flow in a temperature range from 30 °C to 900 °C. Three heating rates, 10 °C min<sup>-1</sup>, 40 °C min<sup>-1</sup> and 80 °C min<sup>-1</sup>, were used so as to understand the effect of heating rate on thermal properties of the poultry litter samples and for calculation of activation energy.

#### 2.2. Kinetic model

The fundamental rate equation expresses the rate of conversion,  $d\alpha/dt$ , as a function of the reactant concentration ( $\alpha$ ) and the rate constant (k) at a constant temperature (*T*), that is:

$$\frac{d\alpha}{dt} = k_f(\alpha) \tag{1}$$

where

Table	1
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Proximate and ultimate analysis results of poultry samples and Orhaneli lignite.
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Parameters	P-1	P-2	P-3	Orhaneli lignite	
Proximate analysis (on wet basis)					
Moisture, wt %	31.7	31.0	30.6	8.1	
Volatile matter, wt%	50.2	50.0	52.2	40.1	
Ash, wt%	10.9	11.75	9.6	27.93	
Fixed carbon wt%	7.2	7.25	7.6	23.87	
Ultimate analysis (on dry basis)					
C, wt %	39.4	40.41	38.41	56.2	
H, wt %	5.77	6.69	5.75	5.14	
N, wt %	1.97	4.08	4.88	1.25	
S, wt % (total)	0.33	0.45	0.63	1.03	
O <sup>a</sup> , wt %	33.59	32.37	32.7	36.38	

<sup>a</sup> Taken as difference.

$$\alpha = (m_0 - m_t)/(m_0 - m_\infty) \tag{2}$$

where:  $m_o - initial$  weight of the reactant,  $m_t -$  weight at time t,  $m_{\infty} -$  final weight. *k* is usually given by Arrhenius Equation as,

$$k = Ae^{-E_a/RT}$$
[3]

Where *A*, the pre-exponential factor  $(min^{-1})$ , is assumed to be independent of temperature,  $E_a$  is the activation energy (kJ/mole), T is the temperature (K), and R is the gas constant (8.314 kJ/mol). Combination of Eqs. (1) and (3) gives;

$$\frac{d\alpha}{dt} = Af(\alpha)\exp(-E_a/RT)$$
(4)

For non-isothermal TGA, if linear heating rate is assumed as  $\beta = dT/dt$ , the reaction rate in Eq. (4) gives;

$$\frac{d\alpha}{dt} = \frac{A}{\beta} e^{-\frac{E_a}{R}} f(\alpha)$$
(5)

Eqs. (4) and (5) are the main equations used for the calculation of kinetic parameters obtained from TGA data. Model-free isoconversional methods are considered to be one of the more effective methods for calculation of activation energy of biomass samples [13]. The Flynn–Wall–Ozawa method was used in this study to determine activation energy. This method uses the Doyle approximation for the temperature integral, allowing for higher precision. As it is an integral method, kinetic calculations are less affected by experimental errors [14]. In this method, activation energy is calculated by measured temperatures corresponding to fixed values of a at different heating rates by the following equation [15];

$$\log \beta = \log\left(\frac{AE_a}{Rg(a)}\right) - 2.315 - 0.4567\left(\frac{E_a}{RT}\right)$$
(6)

Therefore, a plot of log ( $\beta$ ) against 1/T will give a straight line with a slope (0.4567(Ea/R)) at any conversion rate [16]. E<sub>a</sub> is calculated from the slope of the straight line.

#### 3. Results and discussion

#### 3.1. Combustion of poultry litter samples

#### 3.1.1. Thermogravimetric analysis

TG analysis gives the conversion  $(\alpha)$  of samples with respect to temperature. Conversion of poultry samples with respect to the temperature during the TG analysis at heating rates of 10, 40 and 80 °C/min are given in Fig. 1. As can be seen in the figure, mass loss of the samples occurred in four stages. The regions were determined based on a change in the mass conversion that exceeds a certain number. These regions are also given in Table 2. It has been reported in the literature that chicken litter shows four weight loss regimes at 5, 10 and 20 °C/min heating rates due to its complex composition [3,4,17,18]. As heating rate increased, temperature of the mass loss regions also shifted to higher temperatures. The average temperature ranges were in the first region between ca. room temperature to ca. 280 °C, in the second region between ca. 280 °C and 350 °C, in the third region between ca. 350 °C and 500 °C and in the last region between 500 °C and 800 °C for 10, 40 and 80 °C/min heating rates.

TG and DTG curves of the poultry samples are given in Fig. 2. Cellulose, hemicellulose and lignin are the main components of lignocellulosic biomass [19]. Between 100 and 200 °C, carbon dioxide, trace organic compounds and water vapor are produced.

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