Analysis of biomass and sewage sludge devolatilization using the distributed activation energy model

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ABSTRACT

The thermal decomposition of biomass (pine pellets) and sewage sludge was studied using thermogravimetric analysis under an inert atmosphere and the Distributed Activation Energy Model (DAEM) was employed. The activation energy and the frequency factor that characterize the kinetics were determined for both samples. A simplification of the process for prediction of devolatilization curves was proposed, evaluating its validity for both cases. The simplified method was found to combine both simplicity and low deviations with experimental data.

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1. Introduction

Biomass is gaining importance among the world final energy consumption because of its merits of being a renewable energy, widely distributed and carbon neutral [1]. Biomass is also a versatile energy source, which can be used for power generation [2] and to produce liquid biofuels [3,4], synthesis gas [5], chemicals [6], or charcoal [7,8], via thermochemical processes such as combustion, gasification and liquefaction. Biomass pyrolysis takes place during these thermochemical processes. To establish the kinetics of pyrolysis many models have been developed, such as the single step model [9], the two parallel reaction model [10], the three pseudo-component model [11], and the Distributed Activation Energy Model (DAEM).

The DAEM model was originally established by Vand [12] and it has been applied to a wide variety of complex reactions [13,14]. Miura [15] and Miura and Maki [16] developed a simple method to estimate the distributed activation energy and the corresponding frequency factor based on three TGA curves for different heating rates. They used their method to describe the pyrolysis of several kinds of coal. In the last years, this procedure has been thoroughly employed to analyze the kinetics of pyrolysis of different samples of coal [17,18], charcoal [19], oil shale [20], polymers [21], medical waste [22], and biomass [23–26].

The procedure established by Miura and Maki [16] to obtain the activation energy and the frequency factor is as follows: (i) measure the devolatilization rate for three different heating rates (a, usually between 3 and 30 K/min); (ii) calculate and plot $\ln(a/T^2)$ vs. $1/T$ at selected rates of devolatilization; (iii) determine the activation energy, E_a, and the frequency factor, k_0, from the slope and intercept in the Arrhenius plots at each rate of devolatilization; (iv) plot and differentiate the values of E_a vs. the rate of devolatilization to obtain $f(E_a)$; and (v) predict other devolatilization rate curves for different heating rates.

In this study, a simplification is proposed to facilitate the recuperation or prediction of devolatilization curves. Thermogravimetric tests were run to pyrolyse biomass and sewage sludge samples at three different heating rates under an inert atmosphere. The Miura and Maki [16] procedure and the proposed simplification were applied to both samples, obtaining their kinetics and quantifying the differences between the experimental data and the devolatilization curves obtained with the standard procedure and the proposed simplification.

2. Experimental

The proximate and ultimate analysis of the biomass (pine) and the sewage sludge samples are shown in Table 1, together with the heating values. The proximate analysis was carried out in a TGA Q500 TA Instruments while the ultimate analysis was run in a LECO TruSpec CHN and TruSpec S analyzer. The heating value of the samples was determined in a Parr 6300 calorimeter.

The results of the proximate and the ultimate analyses of the pine samples are comparable to those of Biagini et al. [27], Shen et al. [26], and Navarro et al. [28]. On the other hand, the results for the sewage sludge can be compared to those of Scott et al.

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Nomenclature

a	heating rate [K/s]	T	temperature [K]
E_a	activation energy for a determine devolatilization rate [J/mol]	V	volatile mass loss [%]
		V^*	volatile content [%]
k_0	pre-exponential factor for a determine devolatilization rate [s^{-1}]	V/V^*	devolatilization rate [%]
R	universal constant [J/mol K]		

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[29], although in this case there are higher differences due to the great heterogeneity of sewage sludge.

Thermogravimetric analysis was carried out at three different heating rates (10, 15 and 20 K/min) with dry samples. A flow rate of 60 ml/min of nitrogen was supplied to the furnace in order to maintain the samples in an inert atmosphere. A mass of 10±0.5 mg of the samples, previously sieved under 100 μm, was employed to avoid the effect of heat and mass transfer during the thermal decomposition [30]. Each test was repeated five times obtaining differences lower than 3% to guarantee repeatability. A blank experiment was also run to exclude a buoyancy effect [26].

3. Results

Fig. 1 shows the devolatilization curves of biomass (a) and sewage sludge (b) for the three different heating rates. The devolatilization of biomass occurred at a lower temperature, between 100 and 600 °C, while operating with sewage sludge, the temperature must be as high as 1000 °C to reach a high conversion rate [29]. The temperatures at which pine conversion occurs are in good agreement to those obtained by Biagini et al. [27] and Navarro et al. [28], and they are also similar to those obtained by Sonobe et al. [25] who analyzed the devolatilization of biomasses with a high content of cellulose.

The biomass employed reached a high conversion in a reduced range of temperature, a typical result for samples with a high content of cellulose [25]. On the other hand, the devolatilization process of sewage sludge occurred in a wide range of temperatures. These two samples were considered to be a limit concerning the velocity of the devolatilization processes, from the quick devolatilization for the pine sample to the slow devolatilization of the sewage sludge.

From the data in Fig. 1, a $\ln(a/T^2)$ vs. $1/T$ plot for each heating rate, a, at selected values of the devolatilization rate was built and presented in Fig. 2.

The activation energy, E_a, and the frequency factor, k_0, can now be obtained from the slope and intercept in the Arrhenius plots at

each rate of devolatilization. Each curve is represented by Eq. (1), as stated by Miura and Maki [16] (being their Eq. (10)). It immediately follows that, for the curves shown in Fig 2, of the form ($m \cdot 1/T + n$), E_a and k_0 can be obtained with Eqs. (2) and (3) respectively.

$$\ln\left(\frac{a}{T^2}\right) = \ln\left(\frac{k_0 R}{E_a}\right) + 0.6075 - \frac{E_a}{R}\frac{1}{T} \tag{1}$$

$$E_a = -m \cdot R \tag{2}$$

$$k_0 = -m \cdot \exp(n - 0.6075) \tag{3}$$

where T is the temperature and R the universal constant.

Fig. 3 shows the activation energy (graph a) and the frequency factor (graph b) obtained for the biomass and sewage sludge samples. The values of the activation energy and the frequency factor for the biomass, between 160 and 270 kJ/mol, and between 10^{11} and 10^{16} s^{-1} respectively, are in accordance with the values obtained in the literature for pine samples [26–28] and for similar biomasses such as cotton straw [23], rice husk [25], and barley [31]. In the case of the sewage sludge sample a higher activation energy was obtained, between 170 and 400 kJ/mol corresponding also to higher values of the frequency factor, which ranges between 10^{12} and 10^{20} s^{-1} and sometimes even higher. Although the very large values may not represent the actual physics due to the error inherent to the method, the results are in accordance with others found in the literature [29].

4. Prediction of devolatilization curves: a simplification of the standard procedure

There are several ways to predict other devolatilization curves once the activation energy and the frequency factor are known for each devolatilization rate. First, one can obtain $f(E_a)$ from the data of Fig. 3a, and directly apply the DAEM model to calculate the rate of devolatilization, V/V^* for a given heating curve, using the fowolling erquation:

$$1 - \frac{V}{V^*} = \int_0^\infty \exp\left(-k_0 \int_0^t e^{-E_a/(RT)} dt\right) \cdot f(E_a) \cdot dE_a \tag{4}$$

where V is the volatile mass loss, V^* is the volatile content, and V/V^* is the devolatilization rate.

A simpler procedure, when the data of Fig. 2 is available, permits to determine the temperature at which devolatilization occurs for a given heating rate by solving the transcendental equation presented as Eq. (1). Then, the procedure from Figs. 1 and 2 should be performed inversely.

This procedure could be further simplified. Fig. 2 shows that the data points obtained for each particular heating rate could be linearized. In Fig. 4a, the $\ln(1/T^2)$ vs. $1/T$ plot for all the data points are presented, together with the linearization. Note that a is now missing and all the curves collapse. Of course, the data points follow a quadratic curve in this plot, but for the usual range of temperature (200–800 °C) the error between the linearization and the quadratic curve is small, as shown in Fig. 4b.

Table 1
Properties of the samples.

	Biomass (pine)	Sewage sludge
Proximate analysis[a]		
Moisture (%)	3.85	5.98
Volatiles (%)	78.08	58.97
Fixed carbon[b] (%)	14.69	9.41
Ash (%)	3.38	25.64
Ultimate analysis[c]		
C (%)	49.72	45.39
H (%)	7.02	7.69
N (%)	0.88	6.95
S (%)	0.07	1.78
O[b] (%)	42.31	38.19
High heating value[a] (MJ/kg)	18.46	11.58

[a] Wet basis.
[b] Obtained by difference.
[c] Dry-ash-free basis.