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Modeling of the pyrolysis of biomass under parabolic and exponential temperature increases using the Distributed Activation Energy Model

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ABSTRACT

A modification of the simplified Distributed Activation Energy Model is proposed to simulate the pyrolysis of biomass under parabolic and exponential temperature increases. The pyrolysis of pine wood, olive kernel, thistle flower and corncob was experimentally studied in a TGA Q500 thermogravimetric analyzer. The results of the measurements of nine different parabolic and exponential temperature increases for each sample were employed to validate the models proposed. The deviation between the experimental TGA measurements and the estimation of the reacted fraction during the pyrolysis of the four samples under parabolic and exponential temperature increases was lower than 5 °C for all the cases studied. The models derived in this work to describe the pyrolysis of biomass with parabolic and exponential temperature increases were found to be in good agreement with the experiments conducted in a thermogravimetric analyzer.

1. Introduction

Fossil fuels such as oil, natural gas and coal are the most commonly used fuels, corresponding to around 80% of the total primary energy used in the world. This is causing both a pollution problem and international conflicts related to energy security [1]. Biomass is a promising fuel to substitute fossil fuels, due to its renewable nature which comes from its capability of utilizing the carbon dioxide emitted during the biomass conversion to grow the next generation of biomass. The use of biomass-derived fuels has been steadily increasing lately, corresponding currently to more than 14% of the total primary energy consumption in the world [2]. Biomass can be employed for power generation directly in a combustor [3] or to produce desirable products such as liquid biofuels [4], synthesis gas [5], and charcoal [6]. The pyrolysis process is a relevant sub-process in the thermo-chemical conversion of biomass particles in industrial applications, where typically larger particle sizes are employed and thus the reaction inside such particles occurs in absence of oxygen [7].

The kinetics of the biomass pryrolysis can be described based on the activation energy, E_a, and the pre-exponential factor, k_0, of the fuel. There are several different models available in the literature to characterize the pyrolysis process, such as the single step model [8], the two parallel reaction model [9], the three pseudo-components model [10], the sectional approach model [11], and the Distributed Activation Energy Model (DAEM). Vand [12] developed originally the Distributed Activation Energy Model, and Miura [13] and Miura and Maki [14] simplified the mathematical process to obtain the activation energy and pre-exponential factor of the fuel from several thermogravimetric analysis (TGA) curves, obtained at different linear heating rates. The method has been widely used to describe the pyrolysis of a numerous variety of samples, such as coal [14–16], charcoal [17], oil shale [18], polymers [19], solid waste [20,21], sewage sludge [22], and biomass [22–35]. DAEM has also been employed by Xiong et al. [36] in combination with CFD simulations to describe fast pyrolysis of biomass in fluidized beds obtaining accurate results. This process was analyzed in detail by these authors in [37,38].

The main parameters to describe the kinetics of the pyrolysis process, i.e. the activation energy and pre-exponential factor, can be obtained by applying the simplified Distributed Activation Energy Model proposed by Miura and Maki [14] to TGA curves obtained at different linear heating rates. The activation energy and pre-exponential factor can then be employed to model the pyrolysis process occurring at higher heating rates. Nevertheless, the model is capable of describing the pyrolysis process only under linear temperature increases, which is a significant limitation since the temperature increase in industrial reactors could be faster than

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Nomenclature

b	constant for the parabolic temperature profile (°C min^{-2})
c	constant for the exponential temperature profile (min^{-1})
c_0	constant for the exponential temperature profile (°C)
E_a	activation energy (kJ mol^{-1})
E_0	average value of the activation energy (kJ mol^{-1})
k_0	pre-exponential factor (s^{-1})
R	universal gas constant (J mol^{-1} K^{-1})
t	time (s)
T	temperature over the initial pyrolysis temperature (°C)
T'	temperature (°C)
V	volatile mass loss (%)
V^*	volatile mass content (%)
V/V^*	reacted fraction (%)
ϕ_{exp}	value of the ϕ-function for the exponential temperature profile (–)
ϕ_{par}	value of the ϕ-function for the parabolic temperature profile (–)
σ	standard deviation of the activation energy (kJ mol^{-1})

linear increase. For instance, the temperature increase of a biomass particle injected in a furnace with a higher homogeneous temperature, such as a fluidized bed, would be exponential, provided that the Biot number of the particle is low. In fact, for low Biot numbers (*Bi* < *0.1*), the Lumped Capacitance Method can be employed to determine the temperature of the biomass particle, obtaining an exponential increase of this temperature with time. Exponential heating rates have been employed to analyze the devolatilization of biomass particles in fluidized beds by Saastamoinen [39].

In this work, the simplified Distributed Activation Energy Model proposed by Miura and Maki [14] is modified to describe the pyrolysis process of biomass occurring under parabolic and exponential temperature increases. The selection of the model proposed by Miura and Maki [14] was based on the simplicity of this model to obtain the parameters that describe the pyrolysis kinetics. The mathematical procedure followed by the Miura and Maki [14] model permits to consider parabolic and exponential temperature increases, which is the focus of our work, without the need of new assumptions. The models derived in this work for parabolic and exponential temperature profiles are validated with measurements of the pyrolysis of four different biomass species (pine wood, olive kernel, thistle flower and corncob) performed in a thermogravimetric analyzer under nine different parabolic and exponential temperature increases. The comparison of the estimations of the models and the experimental data for the nine parabolic and exponential temperature increases of the four biomass species, resulted in temperature deviations lower than 5 °C for all the cases analyzed.

2. Mathematical model

The Distributed Activation Energy Model was proposed by Vand [12] and, since then, it has been widely used to describe the pyrolysis process of different fuels. DAEM assumes the existence of an infinite number of parallel first order chemical reactions, with a reaction velocity described by the Arrhenius kinetics equation. The reacted fraction, V/V^*, can be determined as:

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

The exponential function in Eq. (1) is the ϕ function:

$$\phi(E,T)=\exp\left(-k_0\int_0^t e^{-E/RT}dt\right) \tag{2}$$

This ϕ function is typically assumed to be a step function at a value of $E = E_a$, and thus Eq. (1) can be simplified as:

$$\frac{V}{V^*}=\int_0^{E_a} f(E_a)dE_a \tag{3}$$

2.1. Arrhenius equation for a parabolic temperature profile

Considering a parabolic increase of temperature with time, the ϕ function can be written as:

$$T=b\cdot t^2 \rightarrow \phi(E,T)=\exp\left(-\frac{k_0}{2\sqrt{b}}\int_0^T\frac{e^{-E/RT}}{\sqrt{T}}dT\right) \tag{4}$$

The ϕ function describe in Eq. (4) can be approximated to:

$$\phi(E,T)\cong\exp\left(-\frac{k_0RT^{1.5}}{2\sqrt{b}E}e^{-E/RT}\right) \tag{5}$$

The value of the activation energy, E_a, is typically selected to satisfy ϕ $(E_a,T) = 0.58$, a value found by Miura [13] to obtain a proper approximation for several combinations of k_0 and $f(E)$ when operating with linear temperature profiles. Nevertheless, for a parabolic temperature profile, the value of the ϕ function, ϕ $(E_a, T) = \phi_{par}$, to determine the activation energy, E_a, might be different. Knowing this value of the ϕ function, a relation between E_a, b, T, and k_0 can be established:

$$-\ln(\phi_{par})\frac{2\sqrt{b}E_a}{k_0RT^{1.5}}=e^{-E_a/RT} \tag{6}$$

Taking the natural logarithm to both sides of Eq. (6) and rearranging terms, the Arrhenius equation for a parabolic temperature profile is obtained.

$$\ln\left(\frac{\sqrt{b}}{T^{1.5}}\right)=\ln\left(\frac{k_0R}{2E_a}\right)-\ln\left[-\ln(\phi_{par})\right]-\frac{E_a}{R}\frac{1}{T} \tag{7}$$

2.2. Arrhenius equation for an exponential temperature profile

The ϕ function for an exponential temperature increase is:

$$T=c_0\cdot e^{c\cdot t}\rightarrow\phi(E,T)=\exp\left(-\frac{k_0}{c}\int_0^T\frac{e^{-E/RT}}{T}dT\right) \tag{8}$$

The value of the ϕ function for an exponential temperature profile, shown in Eq. (8), can be approximated to:

$$\phi(E,T)\cong\exp\left(-\frac{k_0RT}{cE}e^{-E/RT}\right) \tag{9}$$

For an exponential increase of temperature with time, the value of the ϕ function, ϕ $(E_a,T) = \phi_{\exp}$, to determine the activation energy, E_a, should be also determined, so that a relation between E_a, c, T, and k_0 can be written in the form:

$$-\ln(\phi_{\exp})\frac{cE_a}{k_0RT}=e^{-E_a/RT} \tag{10}$$