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Pyrolysis of biofuels of the future: Sewage sludge and microalgae – Thermogravimetric analysis and modelling of the pyrolysis under different temperature conditions

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ABSTRACT

The pyrolysis process of both microalgae and sewage sludge was investigated separately, by means of non-isothermal thermogravimetric analysis. The Distributed Activation Energy Model (DAEM) was employed to obtain the pyrolysis kinetic parameters of the samples, i.e. the activation energy E_a and the pre-exponential factor k_0. Nine different pyrolysis tests at different constant heating rates were conducted for each sample in a thermogravimetric analyzer (TGA) to obtain accurate values of the pyrolysis kinetic parameters when applying DAEM. The accurate values of the activation energy and the pre-exponential factor that characterize the pyrolysis reaction of *Chlorella vulgaris* and sewage sludge were reported, together with their associated uncertainties. The activation energy and pre-exponential factor for the *C. vulgaris* vary between 150–250 kJ/mol and 10^{10}–10^{15} s^{-1} respectively, whereas values ranging from 200 to 400 kJ/mol were obtained for the sewage sludge activation energy, and from 10^{15} to 10^{25} s^{-1} for its pre-exponential factor. These values of E_a and k_0 were employed to estimate the evolution of the reacted fraction with temperature during the pyrolysis of the samples under exponential and parabolic temperature increases, more typical for the pyrolysis reaction of fuel particles in industrial reactors. The estimations of the relation between the reacted fraction and the temperature for exponential and parabolic temperature increases were found to be in good agreement with the experimental values measured in the TGA for both the microalgae and the sludge samples. Therefore, the values reported in this work for the activation energy and the pre-exponential factor of the *C. vulgaris* can be employed as reference values in numerical studies of the pyrolysis process of this biofuel since its chemical composition is quite homogeneous. In the case of sewage sludge, due to the heterogeneity of its composition, the results reported for the kinetic parameters of the pyrolysis process can be employed to describe the pyrolysis of sludge with similar composition.

1. Introduction

A continuous growth of the world population has occurred during the last 50 years, resulting in an increase of the primary energy consumption. Currently, more than 80% of the total primary energy consumption is based on fossil fuels, which are responsible for more than 98% of the carbon dioxide emissions to the atmosphere, causing the current global warming problems [1]. Therefore, there is a need to evaluate the potential of different alternative fuels capable of substituting fossil fuels, with lower associated pollutant emissions. Two of the most promising alternative fuels, due to entirely different reasons, are sewage sludge and microalgae.

Sewage sludge is the residue produced during the treatment of industrial or municipal wastewater. The main ways of the disposing of sewage sludge nowadays can be divided into three applications: landfill, agricultural use and incineration or thermochemical conversion [2]. Nevertheless, the European regulations try to limit the amount of sewage sludge employed for landfill. Concerning the agricultural use, sewage sludge contains organic matter, nitrogen, and phosphorus, making them suitable as a fertilizer. However, the sludge may also concentrate heavy metals and pathogens, which could cause significant environmental problems. In contrast, the thermochemical conversion of sewage sludge [3] presents several benefits, such as the possibility to recover energy [4], the reduction of the residue volume by 70% and the thermal destruction of pathogens [5]. Furthermore, the population growth in urban areas causes also the problem of an increase in the sewage sludge

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Nomenclature

a	heating rate [K/min]
A_p	surface of a fuel particle [m^2]
b	constant for the parabolic temperature profile [°C min^{-2}]
Bi	Biot number [–]
c	constant for the exponential temperature profile [min^{-1}]
c_p	specific heat of the fuel particle [J $kg\ K^{-1}$]
E_a	activation energy [kJ/mol]
$f(E)$	probability density function of the activation energy [–]
h	convective coefficient [W $m^{-2}\ K^{-1}$]
k	reaction rate coefficient [s^{-1}]
k_f	fuel particle thermal conductivity [W $m^{-1}\ K^{-1}$]
k_0	pre-exponential factor [s^{-1}]
R	universal gas constant [J $mol^{-1}\ K^{-1}$]
t	time [s]
T	temperature [°C]
T_p	fuel particle temperature [°C]
T_0	initial temperature of the fuel particle [°C]
T_∞	temperature of the surrounding of the fuel particle inside a reactor [°C]
V	volatile mass loss [%]
V^*	volatile mass content [%]
V/V^*	reacted fraction [%]
V_p	fuel particle volume [m^3]
ϕ	ϕ function [–]
ρ_p	Fuel particle density [kg m^{-3}]

production. Therefore, the thermochemical conversion of sewage sludge with energy recovery might solve the issue of the increase in residues produced due to the population growth, contributing to a reduction of the dependence on fossil fuels.

Among the potential replacement for fossil fuels, biodiesel is gaining importance in applications such as transport, where other possible substitute fuels count on a limited applicability. The production of biodiesel has been based on different crops, causing social problems as the dilemma regarding the risk of diverting farmland or crops for biofuels production to the detriment of the food supply. The so-called third generation biofuel obtained from microalgae can deal with these social problems since microalgae can be cultivated in freshwater, marine seawater or even wastewater [6]. Microalgae have higher photosynthesis efficiency than energy crops based on terrestrial lignocellulosic biomass, which would help to reduce the concentration of CO_2 in the atmosphere at a faster rate [7]. Besides, microalgae are the fastest-growing photosynthesizing organisms, being able to complete an entire growing cycle in few days [1]. There is a large number of species of microalgae, among them the most widely grown is *Chlorella vulgaris* [8].

In comparison to other thermochemical conversion processes, such as combustion or gasification, pyrolysis presents the advantage of producing mainly an easy to store and transport liquid product, in particular for those fuels characterized by high volatile matter and low fixed carbon content, like sewage sludge and microalgae [9]. Pyrolysis was found to be the optimal thermochemical process for sewage sludge by Samolada and Zabaniotou [10], due to its favorable energy balance, material recovery, and zero-waste conversion. Several methods have been employed in the literature to model the pyrolysis process of biomass, such as the single step model [11], the two parallel reaction model [12], the three pseudo-components model [13], the sectional approach model [14], or the Distributed Activation Energy Model (DAEM) [15]. Miura [16] and Miura and Maki [17] proposed a simplification for DAEM to easily obtain the activation energy and the pre-exponential factor of a sample from different thermogravimetric analysis (TGA) tests. This simplified DAEM has been employed, achieving a proper agreement with experimental measurements, for a wide variety of samples, such as coal [18], charcoal [19], polymers [20], oil shale [21], medical waste [22], sewage sludge [23], microalgae [24,25], and several different types of biomass [26–31].

In this work, the pyrolysis of the *C. vulgaris* microalgae and sewage sludge are investigated separately, by means of non-isothermal thermogravimetric analysis. Independent TGA tests of both biomasses under different constant heating rates were conducted and the experimental results were employed as input data to apply the Distributed Activation Energy Model. Nine different TGA curves were employed for both the *C. vulgaris* and the sewage sludge samples in order to obtain accurate values of pyrolysis kinetic parameters, i.e. the activation energy and the pre-exponential factor, of the samples when applying DAEM [32]. The accurate values of the kinetic parameters of the pyrolysis reactions of *C. vulgaris* and sewage sludge are reported together with their associated uncertainties. Finally, the values of the activation energy and pre-exponential factor of the samples were employed to simulate the evolution of the pyrolysis process of the biomasses under exponential and parabolic temperature increases, more typical of the pyrolysis process of fuel particles in industrial reactors. The comparison of the numerical results with experimental measurements carried out in the TGA resulted in an excellent agreement.

2. Mathematical model

The simplified Distributed Activation Energy Model was applied to obtain accurate values of the activation energy E_a and the pre-exponential factor k_0 of *C. vulgaris* and sewage sludge kinetics of pyrolysis. The activation energy is the energy needed to activate the pyrolysis reactions and the pre-exponential factor expresses the empirical temperature dependence of the reaction rate coefficient k [33].

DAEM considers a complex fuel as a mixture of components, which decompose following first-order reactions. Thus, a large number of independent irreversible first-order reactions occur simultaneously with different associated activation energies. The reacted fraction V/V^* in a pyrolysis reaction can be determined as [16]:

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

where V is the volatile matter content released at time t, V^* is the total volatile matter content of the sample, k_0 is the pre-exponential factor corresponding to the activation energy E, R is the universal gas constant, and $f(E)$ is the probability density function of the activation energy. The exponential term in Eq. (1) is the so-called ϕ function:

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

which is typically approximated by a step function at a value of the activation energy $E = E_a$, obtaining for the reacted fraction: