Kinetic analysis of manure pyrolysis and combustion processes

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ABSTRACT

Due to the depletion of fossil fuel reserves and the environmental issues derived from their use, biomass seems to be an excellent source of renewable energy. In this work, the kinetics of the pyrolysis and combustion of three different biomass waste samples (two dairy manure samples before (Pre) and after (Dig R) anaerobic digestion and one swine manure sample (SW)) was studied by means of thermogravimetric analysis. In this work, three iso-conversional methods (Friedman, Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS)) were compared with the Coats-Redfern method. The E_a values of devolatilization stages were in the range of 152–170 kJ/mol, 148–178 kJ/mol and 156–209 kJ/mol for samples Pre, Dig R and SW, respectively. Concerning combustion process, char oxidation stages showed lower E_a values than that obtained for the combustion devolatilization stage, being in the range of 140–175 kJ/mol, 178–199 kJ/mol and 122–144 kJ/mol for samples Pre, Dig R and SW, respectively. These results were practically the same for samples Pre and Dig R, which means that the kinetics of the thermochemical processes were not affected by anaerobic digestion. Finally, the distributed activation energy model (DAEM) and the pseudo-multi component stage model (PMSM) were applied to predict the weight loss curves of pyrolysis and combustion. DAEM was the best model that fitted the experimental data.

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1. Introduction

It is well known that fossil fuel reserves will be completely depleted in the near future, being their consumption rate about 91 million barrels per day of oil and 9 billion cubic metres per day of natural gas (BP, 2013). In this context, biomass is considered to be an important source of renewable and clean energy, reducing CO_2 emission because of its carbon–neutral nature. Among the different type of biomasses, livestock manure has been commonly used as fertilizer and landfill. However, these uses have to be changed due to land saturation with phosphorous and stricter regulations (Cao et al., 2015). Therefore, the utilization of manure for the waste-to-bioenergy generation could be a sustainable choice since it is considered a zero-cost feedstock (Fernandez-Lopez et al., 2015).

Regarding the processes available to obtain bioenergy from biomass, thermochemical conversion processes can be used for the transformation of dry biomasses into biofuels. Concretely, combustion is defined as the oxidation of biomass with air or under an oxidizing atmosphere with excess of oxygen and pyrolysis can be defined as the degradation of the biomass by heating it in a non-oxidant atmosphere, leading to three different products: solid char, bio-oil and fuel gas.

Modelling these thermochemical processes is essential for understanding the behavior at industrial scale (Kantarelis et al., 2011). Furthermore, adequate models are necessary for the design and operation of conversion systems (Garcia-Maraver et al., 2015). Kinetics of mass loss is required for modelling the processes of pyrolysis, combustion and gasification (López-González et al., 2014). Experimental data obtained from thermogravimetric analysis (TGA) is needed for the kinetic evaluation and the thermochemical systems design (Tran et al., 2014).

Generally, there are two different types of methods for analyzing non-isothermal solid-state kinetic data obtained by TGA: model-fitting and model-free methods (Anca-Couce et al., 2014; Garcia-Maraver et al., 2015). Model-fitting methods consist of choosing the model which achieves the best fitting of the experimental data to obtain the kinetic parameters (activation energy and pre-exponential factor). On the other hand, model-free or iso-conversional methods are used to obtain the activation energy at a given extent of conversion without assuming or determining any reaction model (Vyazovkin et al., 2011; Slopiecka et al., 2012).

Numerous investigations have been performed in order to determine the kinetic of the biomass pyrolysis and combustion. Pyrolysis kinetics is the most studied one and different works can be found in a recent review (White et al., 2011). Furthermore,

Slopiecka et al. (2012) studied the kinetic of the poplar wood slow pyrolysis using two isoconversional methods: Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) ones. They concluded that the kinetic values obtained from the different methods were consistent and the FWO and KAS isoconversional methods, satisfactorily described the complexity of devolatilization step during pyrolysis process. Chen et al. (2011) investigated the kinetic behavior of microalgae *Chlorella vulgaris* combustion under different oxygen concentrations. They studied the kinetics using two iso-conversional methods (FWO and KAS) and observed that activation energy values increased with the oxygen concentration. Garcia-Maraver et al. (2015) evaluated the kinetic parameters during combustion of agricultural residues from olive trees using two model-free methods (FWO and KAS) and one model-fitting (Coats-Redfern). In this case, the values of the activation energy calculated by FWO and KAS were confirmed by Coats-Redfern method when a first order reaction was considered. Xu and Chen (2013) studied the thermal conversion characteristics and the kinetics of dairy and chicken manure pyrolysis. They used the Flynn-Wall method to obtain the activation energy. They concluded that the activation energy steeply varied with the extent of conversion, from 120 to 180 kJ/mol at a mass conversion of 0.2–0.4, followed by a relatively steady change at 0.4–0.65.

The objective of this study is to evaluate and compare different kinetic methods, such as model-fitting (Coats-Redfern approach) and model-free (Friedman, FWO and KAS) methods for the kinetics of some residual biomass (manure) pyrolysis and combustion processes. Moreover, to corroborate the kinetic analysis two home-made Excel Visual Basic applications based on both the distributed activation energy (DAEM) and pseudo-multi component stage models (PMSM) were developed. Unlike previous studies where only the devolatilization stage of pyrolysis and combustion processes was considered, in this work, the main stage of the pyrolysis process (devolatilization) and the two main stages of the combustion process (both devolatilization and char oxidation stages) were taking into account.

2. Materials and methods

2.1. Materials

Three biomasses from three different animal solid wastes (manure) coming from the region of Québec (Canada) were considered: one swine manure sample (SW) pretreated by a bio-drying process and two dairy manure samples before (Pre) and after (Dig R) anaerobic digestion. The biomasses were dried in an oven at 105 °C for 24 h, milled and sieved to obtain a uniform particle size, and stored in a desiccator. In this case, the particle size was in the range of 100–150 μm and the initial mass of sample for each run was set to 8 mg to avoid mass and heat transfer limitations.

2.2. Experimental procedure

Thermogravimetric analyses (pyrolysis and combustion experiments) were carried out in a TGA apparatus (TGA-DSC 1, METTLER TOLEDO). The biomasses were heated up from ambient temperature to 900 and 1000 for combustion and pyrolysis experiments, respectively, at different heating rates: 5, 10, 15, 20 and 40 °C/min. A volumetric flow of 200 NmL/min of Ar were used for pyrolysis runs whereas a reactive atmosphere of 21 vol.% of oxygen and 79 vol.% of Ar was used for combustion runs. During experiments, the mass loss of the sample and the temperature were recorded. The experimental error of these measurements was calculated, obtaining an error of ±0.5% and ±2 °C in the weight and temperature determination. Further details about the thermogravimetric

results of the pyrolysis and combustion experiments can be found in a previous paper (Fernandez-Lopez et al., 2015).

2.3. Kinetic methods

Thermogravimetric experiments were carried out with a non-isothermal temperature program. Mass loss was measured as a function of the temperature and time. The rate of the process ($d\alpha/dt$) can be parameterized as a function of the temperature, T; the extent of conversion, α; and the pressure, P as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P) \tag{1}$$

The pressure dependence $h(P)$ is ignored in most of the kinetics studies reported (Vyazovkin et al., 2011). Therefore, the rate is considered to be as a function of the temperature, T, and the extent of conversion, α:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}$$

Eq. (2) represents the reaction rate of a single-step process. Although the process mechanism involves more than one reaction, one of them could determine the overall kinetics (Vyazovkin et al., 2011). Therefore, Eq. (2) can be used to describe the overall reaction rate of the thermochemical processes.

The temperature dependence $k(T)$ is typically parameterized by the Arrhenius equation:

$$k(T) = Ae^{\frac{-E_a}{RT}} \tag{3}$$

where A is the preexponential factor, E_a the activation energy and R the universal gas constant. These kinetic parameters, which are experimentally determined, are called "effective" or "apparent" parameters because represents the overall process and not the individual parameters of each step or reaction. In following sections, the word "apparent" will be omitted but the activation energy will always be referred to the apparent activation energy.

The function which describes the conversion degree can be expressed by using different reaction models, $f(\alpha)$, which are described elsewhere (López-González et al., 2013). The extent of conversion α is defined as follows:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{4}$$

where m_0, m_t and m_f represents the mass at time t = 0, t = t and t = t$_f$, respectively.

Combining Eqs. (2) and (3) yields:

$$\frac{d\alpha}{dt} = Ae^{\frac{-E_a}{RT}}f(\alpha) \tag{5}$$

Integrating Eq. (5), the integral function $g(\alpha)$ can be defined as follows:

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^t e^{\frac{-E_a}{RT}}dt \tag{6}$$

Defining a constant heating rate as $\beta = dT/dt$, Eq. (6) is rearranged as follows:

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{\frac{-E_a}{RT}}dT \tag{7}$$

Eq. (7) is the general equation which is necessary to obtain the kinetic parameters of the biomass thermal decomposition. This equation has not an analytical solution. Therefore, a number of approximate solutions were given in the past (Vyazovkin et al., 2011). There are different methods to solve and obtain the kinetic parameters from Eq. (7). On the one hand, fitting-models allow to