

KINETIC STUDY OF BIOMASS PYROLYSIS AT MODERATE AND HIGH HEATING REGIMES

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Abstract

In practical terms, the description of biomass pyrolysis kinetics by rationally-based models, that do not represent the detailed physicochemical mechanism of the process, but predict the overall yield, might be extremely useful. The mechanisms of global decomposition (by means an irreversible, single step, and first order reaction) have only been validated under dynamic regime at slow heating rates.

The specific aim of this work is to evaluate the efficiency of a revisited global decomposition summative model developed at the UPC¹⁻², in the thermal decomposition of a classical biomass sample (pine), and an energy crop (thistle). Different heating regimes have been included. Several evaluation strategies are applied to fit experimental data with the model. The strategies contemplate: the quantitative characterization of the fit based on thermogravimetric (TG) and derivative (DTG) curves and scattering of the kinetic parameters so as to consider the systematic temperature error that appears when high heating rates are employed. The data are obtained through thermogravimetric analysis and isothermal mass-change determination.

Experimental procedure

The experiments under low heating rate (20 K/min) are carried out in a Setaram Setsys 12 thermobalance in the TGA/DSC configuration, under atmospheric pressure, using 4 mg of each sample. For heating rates upper than 50K/min, an experimental study is carried out using an own-designed microreactor (42 mm I.D., and 150 mm long.), and 100 mg samples, at the temperature range between 275 and 600 °C. The temperature acquisition and control is achieved by an OPTO 22 remote acquisition equipment. For each sample the weight loss is determined as a function of time. For each sample the weight loss is determined as a function of time. MATLAB 6.5 is used as the simulation tool. The differential equations are solved by a variable-order method (stiff problems solver). The minimum fit is determined by a direct search method. Different initial parameters taken from literature are applied.

Parametric Estimation.

The total weight loss associated to the pyrolysis process of the samples under study is simulated assuming the addition of independent parallel devolatilization reactions, with the kinetic parameters adjusted for pseudocomponent (fraction of the main biomass components that decomposes at a certain temperature range). The mathematical expression is as follows⁴:

$$-\frac{dm}{dt} = \sum_{j=1}^n V_j^* \frac{d\alpha_j}{dt} \quad (1)$$

where m is the sample mass normalized by the initial sample mass, V_j^* is the normalized amount of volatiles formed from the j th pseudocomponent, and n is the number of pseudocomponents. Each partial reaction is approximated by first order kinetics:

$$\frac{d\alpha_j}{dt} = A_j \exp\left[\frac{-E_j}{RT}\right] (1 - \alpha_j)^m \quad (2)$$

where E is the activation energy, A is the pre-exponential factor and m is the reaction order.

The following evaluation strategies, using least squares non-linear methods, are examined and compared to obtain the best-fit kinetic parameters:

1. Deconvolution of DTG curves in the partial contribution from pseudocomponents, applying a correction factor on the estimation of V^* , based on the probability of overlapping by the lignin devolatilization, because of their very broad range of decomposition temperatures.

2. Optimization algorithm to minimize the *fit* error, defined by a function related with the difference between the experimental and the simulated TG weight loss curve (integral form) or DTG differential curve (differential form).

3. Description of the global decomposition by different number and type of pseudocomponents and n th order kinetics for the partial reactions.

4. Simultaneous evaluation of moderate and high heating experiments, but allowing $\log A$ and V^* to have separate values for both regimes. This empirical assessment keeps in mind the dependence (directly proportional) of the mass loss with the heating rate and supposes a correction of the maximum temperature of decomposition without altering significantly the apparent kinetic law³.

Results and Discussion

The experimental data was firstly simulated using a revisited summative model developed by this laboratory¹⁻², assuming three pseudocomponents with first order reactions, except for the third one (linked to lignin), for which an approach of third order is used. Figure 1 compares the suitability of three different parametric estimation methodologies to fit experimental data, in the case of pine sample. In spite of an apparent good fitting on the TG curve for all the cases, deconvolution (a) and integral form (b) are not satisfactory approaches to fit the DTG curve. It could be due to low sensitiveness of weight fraction curves to processes that can superpose partially or even go unnoticed.

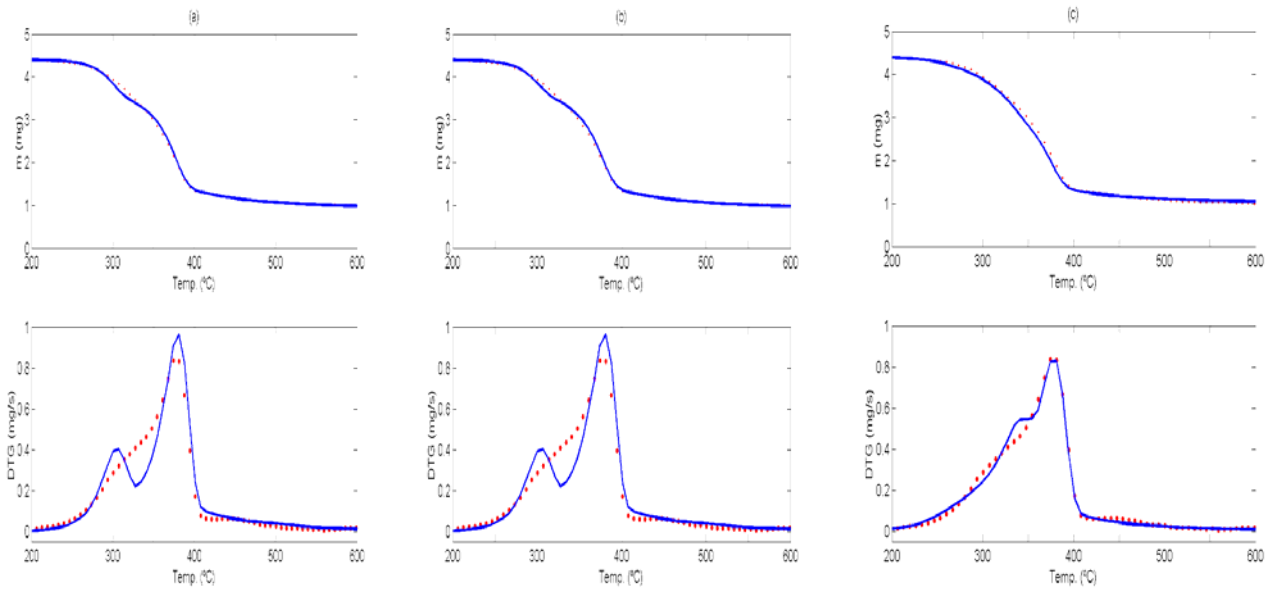


Figure 1. TG and DTG curves during dynamic (20K/min) pyrolysis of untreated pine. The symbols are experimental data; the solid line curves are predictions from a summative model³⁻⁴ applying three different parametric estimation methodologies: (a) Deconvolution, (b) Integral form and (c) Differential form of the objective function.

The two first methodologies clearly evidence an underestimation of volatile production in the range of 310 - 350°C. It could suggest to employ more pseudocomponents in order to approach more accurately to the process. In this sense and according with previous results that report more than one peak to define extractives and hemicellulose decomposition⁴, it has been assumed five peaks for complete description of degradation. That approach leads to better fitting and does not evidence big differences when different reaction orders are applied (see figure 2).

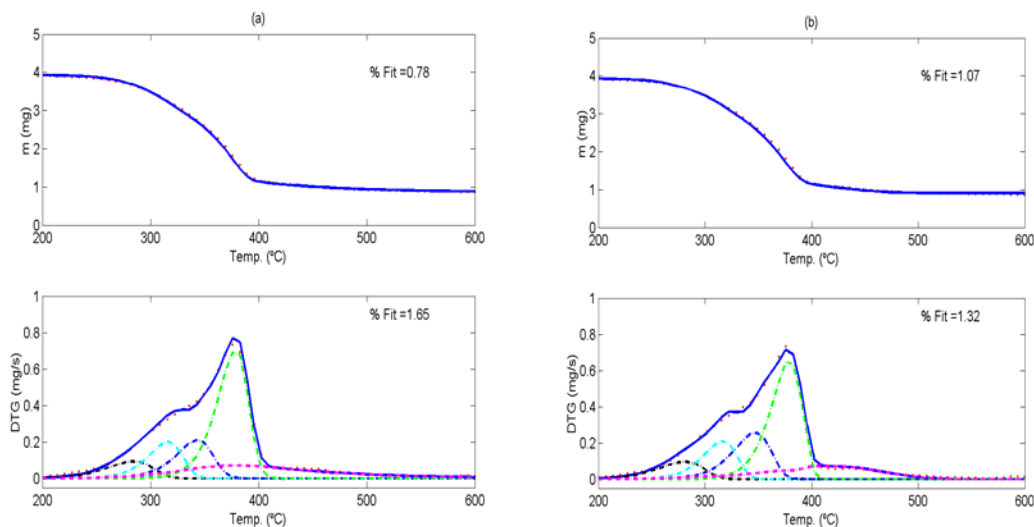


Figure 2. Dynamic (20K/min) pyrolysis of untreated pine. The point symbols are experimental data; discontinuous lines in DTG curves represent deconvolution in five pseudocomponents (a) last pseudocomponent approach by a third reaction order, (b) all pseudocomponents approach by first order reactions.

The current parametric approximation for high heating regime implies incorporating a degree of uncertainty into the $\log A$ parameter value. This technique is applied on simulation of thermogravimetric curves, to compensate the error produced by generation of thermal gradients into the sample during the process (compensation effect)⁵. Accordingly, the curves from both heating regimes (moderate and high) have been evaluated simultaneously, but allowed $\log A$ to have separate values for each case. In this way a good curve fitting was achieved, as shown in Fig. 3. A moderate scattering of $\log A$ and V^* has described well the variation of the thermal lag and peak widening caused by the systematic temperature errors in the different experiments. This methodology is presented as an alternative to avoid the complexity of the heat transfer phenomena in a real thermoanalytical apparatus.

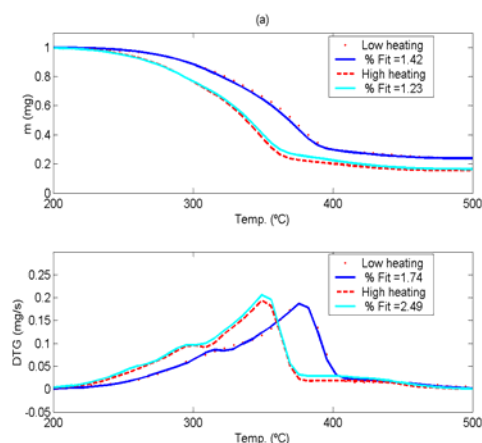


Figure 3. Simultaneous evaluation of pine pyrolysis under moderate and high heating regimes.

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