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Biomass pyrolysis consists of heating an organic material in the absence of oxygen in order to obtain a range of valuable products.

In this study, a multi-component mechanism, consisting of three parallel first order and single-step reactions, is considered, and non-isothermal conditions with a constant heating rate (β) are applied. The decomposition rate (dm/dt) features an Arrhenius temperature dependence (Eq. 2), where A is the pre-exponential factor (1/s), E the activation energy (kJ/mol), R the gas constant and T is the biomass temperature.

\[
dm/dt = -k_i m_i \quad (1) \quad k_i = A_i e^{-E_i/RT} \quad (2)
\]

The aim of this study is to develop a straightforward method to perform a kinetic analysis of the biomass pyrolysis, applying a developed peak temperature method to the experimental thermogravimetric data. When performing a non-linear fit to the experimental data, initial values of the parameters to fit, are required. With this peak temperature method, the initial values can be estimated by direct observation of the differential thermogravimetric curves (DTG), which should not present any difficulty and it will help to achieve convergence more quickly.

3. Single Fitting of a DTG curve

Deconvolution of a DTG curve has been performed with traditional Arrhenius and with the peak temperature method. The initial values for the peak temperature method have been estimated only by direct observation of the DTG curve, and the initial values for the kinetic parameters with traditional Arrhenius, have been taken from the literature [21]. In both cases, as initial composition a standard 1:1:1 has been chosen.

In order to reduce the convergence time, a part from good initial values, parameters bounds could be applied, in the case of the peak temperature, narrow bounds could be set depending on the level of overlapping of the individual curves.

The kinetic parameters are calculated with the following expressions according to the peak temperature method:

Both methods give very similar results in terms of kinetic parameters and composition. However, the difference remains in how easy is to estimate the parameters initial values in order to perform a non-linear fit and quickly achieve convergence.

From the peak temperature expression, an expression that relates the peak temperature with the heating rate for a specific activation energy can be derived, where the subscript zero refers to a chosen reference curve. As can be observed from Fig. 3, the peak temperature increase with heating rate approximately twice the width increase.

\[
-\ln(\beta/nT^*G) = \frac{E}{R}\sigma - \frac{(T^*)^2}{2} - 2\ln\frac{T^*}{T} \quad (6)
\]

A single set of kinetic parameters and a single biomass composition have been determined from several thermogravimetric analysis at different heating rates, in order to obtain results more generalizable to different operating conditions.

5. Conclusions

- The developed peak temperature method allows the easy estimate of the parameters initial values when performing a fit of thermogravimetric data.
- Depending on the degree of the curves overlapping, narrow bounds could be applied to the parameters in order to reduce the convergence time or improve the fit.
- The peak temperature method can also be used to determine the activation energy and pre-exponential factor without fitting the DTG curves, only from the peak temperature and corresponding heating rates of each component. When experimental data show a certain degree of deviation from the ideal results, at least a range of activation energies can be defined.
- Finally, the developed method is also suitable for simultaneous evaluation of several DTG curves at different heating rates, allowing to obtain a single biomass composition and a single set of kinetic parameters. In order to improve the fit, a modified Arrhenius with extra kinetic parameters to fit could be considered.

References