Autocatalytic kinetic model for thermogravimetric analysis and composition estimation of biomass and polymeric fractions

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HIGHLIGHTS

- Autocatalytic kinetic model fit slow pyrolysis in thermogravimetric analysis (TGA).
- The model suitable for a wide range of samples with fitting deviations lower than 7%.
- Pyrolysis rate varied with biomass structure and composition.
- Different heating rates reproduced using a no-Arrhenius' dependence with temperature.
- Free Excel file to estimate initial composition of biomass from TGA at error <7%.

GRAPHICAL ABSTRACT
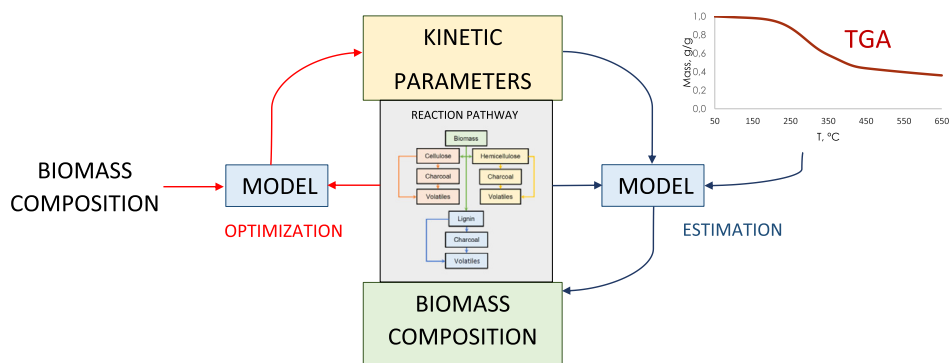
ABSTRACT

A comprehensive kinetic model of slow pyrolysis of biomass during a thermogravimetric analysis (TGA) has been developed, including the simulation of variable heating rates, composition estimation and structural analysis of biomass. Biomass was assumed as a matrix of three solid global components (hemicellulose, cellulose and lignin) in which water and oil can be also present.

Kinetics were based on an auto-catalytic model because it can simulate the degradation in cellulosic materials, as the cleavage of the biopolymers produce oligomers that accelerate the further depolymerisation. The reaction pathway followed the Waterloo's mechanism, which stablishes that all solid compounds decompose into volatiles and charcoal. This mechanism was completed by the vapourization of water and oil, and assuming that the formed charcoal can break into volatiles by a slow reaction. The set was solved by the 8th Runge–Kutta's method and validated by the Simplex Nelder–Mead and Broyden–Fletcher–Goldfarb–Shanno's methods. The development of this model has a high interest because it can help to understand how the conversion from biomass to biochemicals takes place.

To assess what parameters can affect the thermal degradation of biomass pure polymeric samples of hemicellulose, cellulose and lignin and complex samples (seeds and woody biomass) were studied and fitted. Two types of operations were considered too. An isothermal degradation from 150 °C up to 350 °C with increments of 50 °C, and a non-isothermal decomposition with heating rate of 5 °C/min, 10 °C/min and 20 °C/min up to temperatures around 800 °C, depending on the studied sample. Average absolute deviations lower than 7% were obtained. It was deduced that there are some interactions between the three main biomass compounds. These interactions were observed by the variations in the kinetic parameters between complex and pure samples, also they were perceived between the isothermal and no-isothermal way. On the other hand, an effect of the biomass structure has been reported by the differences between the kinetics of the seeds and of the woody samples. It is remarkable that the

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developed model could reproduce the cellulose decomposition with a variable heating rate using a unique set of kinetic parameters. This was possible by a no-Arrhenius' dependence with temperature. In the same way, it was used to predict the initial composition of the studied biomass with deviations lower than 7% for lignin and cellulose.

Nomenclature

Acronyms

C	cellulose
HC	hemicellulose
L	lignin
O	oil
TGA	thermogravimetric analysis
W	water
XC	charcoal produced form cellulose
XHC	charcoal produced form hemicellulose
XL	charcoal produced form lignin

Subindex and superindex

EXP	experimental data of the TGA
in	inert compounds
TOTAL	total simulated TGA

Greek letters and symbols

α_i	initialization factor, dimensionless
β_i	acceleration factor, dimensionless
$A_j - F_j$	Antoine's equation coefficients of the compound "j", dimensionless
c	correction factor for the kinetic in the decomposition at different heating rates of the cellulose, dimensionless
C_j	concentration of "j" in the gas phase, kmol/m^3
C_j^*	equilibrium concentration of "j" in the interphase between the liquid and the gas phase, kmol/m^3

$\frac{E_{a_i}}{R}$	activation energy of the reaction "i", K
h	partial mass transfer coefficient between the liquid and the gas, kg$_j$ m^3/min m^2 kmol$_j$
k_{o_i}	preexponential factor for the reaction "i", min^{-1}
k_i	kinetic constant for the reaction "i", min^{-1}
M_{exp}	experimental mass fraction of unreacted biomass, $g_{sample}/g_{sample\ initial}$
M	mass fraction of unreacted biomass, $g_{sample}/g_{sample\ initial}$
$m_{j_{max}}$	maximum value for mass fraction of the compound "j" in the biomass, g/g
$m_{j_{min}}$	minimum value for mass fraction of the compound "j" in the biomass, g/g
m_j	mass fraction of the compound "j" in the biomass, g/g
N	number of compounds in the biomass, dimensionless
n_i	order of reaction of the reaction "i", dimensionless
nl_i	mass transfer order, dimensionless
N_r	number of reactions, dimensionless
P_j^*	vapour pressure of the compound "j", atm
r_i	reaction velocity number "i", g/min g
r_j	reaction velocity of decomposition for the component "j" in the biomass, g/min g
S	exchange surface between the liquid and the gas, m^2
t	operating time, min
T	operating temperature, K
$x_{i_{exp}}$	experimental biomass fraction, $g_{sample}/g_{sample\ initial}$
$x_{i_{SIM}}$	simulated biomass fraction, $g_{sample}/g_{sample\ initial}$

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1. Introduction

The use of fossil fuels as the main raw material for industry is not sustainable, and certainly it will not be the forever-solution. So a new source of basic compounds (i.e. carbon, hydrogen and oxygen) and energy should be considered. This new source could be biomass [1], which can be transformed into bioenergy, biochemical and biofuels in biorefineries [2,3]. However, the design of these biorefineries requires knowledge about the conversion from raw material to fuels and fast, cheap and accurate biomass-analysing methods. For the latter, several wet methods of chemical analysis have been used [4]. These methods are based on the fractionation of biomass samples and a later isolation of purified fractions, which could be quantified using conventional analytical instruments. Although these techniques have high accuracy and robustness, they are not suitable for an industrial scale because they are expensive and require a lot of time. Another option would be spectroscopic analysis, such as, the Near Infrared Reflectance (NIR) spectroscopy, which reduces time requirements and cost and it is a method with a high reproducibility. Nevertheless, these analysis need data with a very high quality and an initial blank spectrum, which is an important limitation. So, the measurement of the initial biomass composition is an issue that have not an optimal solution yet. Thermogravimetric analysis (TGA) of biomass could be the answer for this problem under certain conditions. In addition, it can provide information about how the thermal decomposition takes place.

Thermogravimetric analysis is a slow pyrolysis process which consist of recording the mass variation of a sample which is treated with a temperature profile. This profile is provided by a gas phase which can be an inert or an oxidant compound [5]. This type of analysis have been studied thoroughly [5–7] and there are a lot of works about their modelling in the literature. The most extended model considers a first order kinetic for each compound present in biomass assuming that biomass is formed by three main compounds (cellulose, hemicellulose and lignin). These components decompose to charcoal and volatiles by independent reactions. Völker and Rieckmann [8] used a first order kinetic to adjust the decomposition of pure cellulose and the deviation between the experimental data and the simulation was relatively high. In contrast, Capart et al. [9] studied the pure cellulose thermal breaking but considering an autocatalytic model which supposed a good fitting with an overall deviation around 1%. On the other hand, Mangut et al. [10] proposed a kinetic model of nth-order for the degradation of residues from tomato processing industry which could reproduce the biomass behaviour. But Zabaniotoua et al. [11], Slopiecka et al. [12] and Kastanaki et al. [13] studied the TGA kinetics of several lignocellulosic biomass samples, poplar wood and lignite-biomass blends respectively with a first order model and they obtained good fits too. Slopiecka et al.