Determination of cellulose, hemicellulose and lignin content of different biomass species by a unique kinetic model from TGA analysis

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Introduction

Biomass has major interest as a renewable energy source in the context of climate change, mitigation and energy security. Energy from biomass is based in short rotation forestry and energy crops that can contribute to the energy needs of the modern society (Bridgewater, 2003). Pyrolysis, as one of the promising thermochemical conversion routes, plays a vital role in biomass conversion. However, pyrolysis is an extremely complex process; it generally goes through a series of reactions and can be influenced by many factors.

Lignocellulosic biomass is mainly composed of three organic constituents: lignin, cellulose and hemicellulose. The ratio of these three components varies, depending on the type of biomass. Previous studies showed that biomass pyrolysis can be divided into four individual stages: moisture evolution, hemicellulose decomposition, cellulose decomposition and lignin decomposition. It was also suggested that the pyrolysis of any biomass can be considered as the superposition of the three main components. Knowledge of the pyrolysis characteristics of the three main components is the basis and thus essentially important for a better understanding to biomass thermal chemical conversion (Yang *et al*, 2007).

The aim of this work was to obtain a unique kinetic model of pyrolysis for five biomass species based on its component substances using a thermogravimetric analyzer (TGA).

Materials and methods

Samples of hemicellulose, cellulose and lignin

Xylan was a common kind of hemicellulose. The xylan in this research was bought from Sigma–Aldrich. The cellulose microcrystalline and the lignin alkali were bought from Sigma–Aldrich too.

Biomass samples

The materials employed in this study was corn stover that was collected from Zaragoza (Spain), grapevine biomass from Lisbon (Portugal), esparto grass from Alicante (Spain), sunflower biomass from Palencia (Spain) and eucalyptus biomass from Caceres (Spain). The samples was crushed to a particle size between 75 and 125 μm.

Hemicellulose, cellulose, lignin and biomass samples were subjected to thermogravimetric analysis using a DTG-60H Shimadzu instrument. The samples were spread on a alumina sample holder of ϕ 6 mm. The analyses were made using an inert atmosphere of N_2. The flow rate of N_2 are 50 mL min^{-1}. The experiments started with a 60 min purging period at room temperature and a heating rates of 5, 10, 20 and 50 K min^{-1}, up to a final temperature of 1423K. The sample mass used in all runs was ca. 10 mg.

Then, a kinetic model of independent parallel reactions was applied to the experimental results of TGA pyrolysis using a three-step devolatilization mechanism. The kinetics of the pyrolysis of lignocellulosic materials was applied to suggest that the rate of pyrolysis of one biomass (dm/dt) could be represented by the sum of the corresponding rates of the main biomass components (H: hemicellulose, C: Cellulose, L:lignin). The individual kinetics was based on the sum of first order Arrhenius reactions. Each of these individual reactions represents the different precursors of each of the biomass constituents (hemicellulose, cellulose and lignin).

$$\frac{dm}{dt} = \frac{dH}{dt} + \frac{dC}{dt} + \frac{dL}{dt}$$

where,

$$\frac{dH}{dt} = -\sum_{n=1}^{n_H} K_{Hi} \exp(-E_{Hi}/RT)H$$

$$\frac{dC}{dt} = -\sum_{i=1}^{n_c} K_{Ci} \exp(-E_{Ci}/RT)C$$

$$\frac{dL}{dt} = -\sum_{i=1}^{n_L} K_{Li} \exp(-E_{Li}/RT)L$$

where T is the temperature (K); R is the universal gas constant (J K^{-1} mol^{-1}); K_H, K_C, K_L are the pre-exponential factors; E_H, E_C, E_L are the activation energy; n_H, n_C, n_L are the number of reactions; H, C and L are the mass fraction of the hemicelluloses, cellulose and lignin respectively.

A nonlinear least squares algorithm was used to optimize the calculated correlation curve by identifying the fractions of cellulose, hemicellulose and lignin that minimize the objective function (O.F.). O. F. is a function of the mean experimental DTG curves $(dm/dt)_{exp,i}$ and the calculated $(dm/dt)_{calc,i}$ that can be calculated as follows:

$$O.F. = \sum_{i=1}^{nt} \left[\left(\frac{dm}{dt} \right)_{\exp,i} - \left(\frac{dm}{dt} \right)_{calc,i} \right]^2$$

This iterative method was performed for the five biomasses studied. Typical kinetic parameters (E, K) that represent the unique kinetic model were obtained. Then, this kinetic model was used to determine the hemicellulose, cellulose and lignin contents of each biomass.

Results

The kinetic parameters obtained can be shown in the following Table 1.

Table 1. Kinetic parameters of the model.

	Agua	Celulosa	Hemicellulose (precursor 1)	Hemicellulose (precursor 2)	Lignin (precursor 1)	Lignin (precursor 2)	Lignin (precursor 3)
K , (s^{-1})	$6{,}26\ 10^4$	$6{,}69\ 10^9$	$4{,}11\ 10^{15}$	$9{,}70\ 10^9$	$5{,}41\ 10^2$	$1{,}58\ 10^0$	$1{,}45\ 10^{28}$
E, ($Jmol^{-1}$)	$4{,}71\ 10^4$	$1{,}39\ 10^5$	$1{,}65\ 10^5$	$1{,}29\ 10^5$	$6{,}47\ 10^4$	$4{,}07\ 10^4$	$5{,}87\ 10^5$

The hemicellulose, cellulose and lignin content of the different biomass (Table 2) were estimated with the unique model developed.

Table 2. Hemicellulose, cellulose and lignin content of the biomasses analyzed.

	Water %	Hemicellulose %	Cellulose %	Lignin %	Char %
Corn stover	4,19	20,83	38,10	14,45	22,42
Grapevine biomass	3,74	12,22	44,19	20,35	19,49
Esparto grass	4,01	17,19	37,22	19,63	23,43
Sunflower biomass	7,24	28,53	30,44	15,40	21,94
Eucalyptus biomass	3,41	11,85	41,39	24,00	19,74

Conclusions

The thermal behaviour of corn stover, grapevine biomass, esparto grass, sunflower biomass and eucalyptus biomass was investigated using TGA. The pyrolysis process of biomass could be divided into 3 steps. To explore the relationship of each biomass and its components, a unique kinetic model with 2 precursors of hemicellulose, 1 precursor of cellulose and 3 precursors of lignin were also obtained.

The TG curve overlap ratio was applied to evaluate the simulation of the different biomass by hemicellulose, cellulose and lignin. All the biomass could be well simulated with the curve overlap ratios.

As a result of the development of this kinetic model the content of hemicellulose, cellulose and lignin has been estimated to five biomasses analyzed.

References

- Bridgwater, A. V. (2003). Renewable fuels and chemicals by thermal processing of biomass. Chemical Engineering Journal, 91(2), 87-102.
- Zhou, H., Long, Y., Meng, A., Li, Q., & Zhang, Y. (2013). The pyrolysis simulation of five biomass species by hemi-cellulose, cellulose and lignin based on thermogravimetric curves. Thermochimica Acta, 566, 36-43.