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

A. Urueña[1,2,], D. Díez[1,2], G. Antolín[1,2], J.A. Conesa[3]*

[1]CARTIF Centro Tecnológico, Boecillo, Valladolid, 47151, Spain
[2]ITAP Institute, University of Valladolid, Valladolid, 47010, Spain
[3]Chemical Engineering Department, University of Alicante, Alicante, 03080, Spain
*(*E-mail: anauru@cartif.es)*

Introduction

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 .

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).

Biomass

Corn stover | Grapevine biomass | Esparto biomass | Sunflower biomass | Eucalyptus biomass

Thermogravimetric Analysis Hemicellulose, Cellulose and Lignin

TGA Shimadzu DTG-60H
Inert Atmosphere: N_2
Flow rate N_2:20 ml/min

-Data treatment.
-DTG curve.

Thermogravimetric Analysis Biomass 10, 20, 50 K/min

Kinetic Model

- Kinetic model of independent parallel reactions.
- Biomass global kinetic:

$$\frac{dx}{dt}=\frac{dW}{dt}+\frac{dH}{dt}+\frac{dC}{dt}+\frac{dL}{dt}$$

- Individual kinetics based on the sum of first order Arrhenius reactions. Each of these individuals reactions represents the differents precursors of the biomass constituents.

$$\frac{dW}{dt}=-\sum_{n=1}^{n_W}K_{Wi}\exp\left(-E_{Wi}/RT\right)W \qquad \frac{dH}{dt}=-\sum_{n=1}^{n_H}K_{Hi}\exp\left(-E_{Hi}/RT\right)H$$

$$\frac{dC}{dt}=-\sum_{i=1}^{n_c}K_{Ci}\exp\left(-E_{Ci}/RT\right)C \qquad \frac{dL}{dt}=-\sum_{i=1}^{n_L}K_{Li}\exp\left(-E_{Li}/RT\right)L$$

- Restricciones: $x_0 = W_0 + H_0 + C_0 + L_0$
- A nonlinear least squares algorithm was used to optimize

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

Mass fractions
W: Water.
H: Hemicellulose.
C: Cellulose.
L: Lignine.
x: Biomass.

T: temperature,K
R: 8,314 J/K·mol.
K_W, K_H, K_C, K_L: pre-exponential factor.
E_W, E_H, E_C, E_L: activation energy, J/mol.
n_W, n_H, n_C, n_L : Nº number of reactions.
n_c: component reactions number

Results & Discussion

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

Table 1. Kinetic parameters of the model.

	Water	Cellulose	Hemicellulose (precursor 1)	Hemicellulose (precursor 2)	Lignin (precursor 1)	Lignin (precursor 2)	Lignin (precursor 3)
K, (s^{-1})	$6{,}26\cdot10^{4}$	$6{,}69\cdot10^{9}$	$4{,}11\cdot10^{15}$	$9{,}70\cdot10^{9}$	$5{,}41\cdot10^{2}$	$1{,}58\cdot10^{0}$	$1{,}45\cdot10^{28}$
E, ($J\cdot mol^{-1}$)	$4{,}71\cdot10^{4}$	$1{,}39\cdot10^{5}$	$1{,}65\cdot10^{5}$	$1{,}29\cdot10^{5}$	$6{,}47\cdot10^{4}$	$4{,}07\cdot10^{4}$	$5{,}87\cdot10^{5}$

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.

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