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A simplified method for determination of lignocellulosic materials pyrolysis kinetics from isothermal thermogravimetric experiments

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Abstract

The pyrolysis of lignocellulosic materials (pine and eucalyptus woods and pine bark) was previously studied by thermogravimetry with linear temperature programming. The results were successfully modelled by a kinetic scheme consisting of three independent first-order reactions of three pseudo-components. The first and the second pseudo-components correspond to the more-reactive fractions of hemicellulose and cellulose, respectively, and the third includes lignin and the remaining fractions of the carbohydrates. In the present work, the isothermal pyrolysis of lignocellulosic materials (in the temperature range 450–700 K) was simulated using the previously determined kinetic parameters, yielding their corresponding relative reactivities. The reactivity of each pseudo-component was also studied, and it was found out that the first pseudo-component was completely converted in a very short time at medium and high temperatures, while complete conversion of the second required high temperatures. The reactivity of the third pseudo-component is moderate, even at the highest temperatures. Based on these observations, a method to determine pyrolysis kinetics from isothermal thermogravimetric experiments was developed, whereby the kinetic and composition parameters corresponding to pseudo-components 3, 2 and 1 are successively and independently determined, from high, medium and low temperature experiments, respectively. The method was validated using the isothermal thermogravimetric curves simulated for the three materials.

Keywords: Lignocellulosic; Pyrolysis; Kinetics; Thermogravimetry; Isothermal

1. Introduction

Kinetic data for the pyrolysis of lignocellulosic materials are useful when dealing with the production of fuel gases, chemicals and energy [1,2], charcoal [3] and activated carbon [4]. On the other hand, thermochemical conversion is an attractive technology for processing agricultural and forestry residues [1,5–10] as well as some of the components of municipal solid wastes [6,11,12]. Finally, research on forest fires requires data on the kinetics and mechanisms of biomass combustion, where pyrolysis is an important step [13].

Lignocellulosic materials present a complex and diverse composition (cellulose, hemicelluloses, lignin, extractives, water, inorganic matter). The mechanisms of thermal degradation of these components are not completely known, as the process includes a number of competitive and consecutive chemical reactions [14–18]. The kinetic parameters found in the literature are usually based on lumped models, and so they depend on the experimental variables such as the

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Nomenclature

A	Arrhenius pre-exponential constant
b	heating rate
E	activation energy
k	rate constant
R	gas constant
t	time
T	temperature
W	weight
z	composition parameter
Greek letters	
α	degree of transformation
β	dimensionless parameter (AT_0/b)
γ	dimensionless parameter (E/RT_0)
θ	normalized temperature (T/T_0)
Subscripts	
j	refers to pseudo-component j ($j = 1-3$)
0	refers to initial conditions of temperature, weight or composition
∞	refers to residual amounts

heating rate (when they are based on dynamic thermal analysis), the initial amount and particle size of the material and the geometry of the equipment, in addition to the model considered [17–20].

As a result, it is not surprising that biomass pyrolysis is a complex subject, although it is usually considered that its components react independently, and therefore that the global behaviour is the sum of the individual components behaviour [8,21–29]. Alternative models consider a simple kinetic law [30], an activation energy distribution function [31] or two or three temperature zones with different kinetic parameters [31–33].

Experimental data are usually obtained thermogravimetrically, by measuring the weight of the samples and their rate of weight loss. This is a useful and practical option when the interest is focused on the global process of thermal decomposition or when the solid product is the main concern. In addition, the evolution of the pyrolysis products (namely the gas products) can be followed [34,35].

In terms of the experimental method, there are two alternatives: dynamic thermogravimetry, where the samples are submitted to increasing temperatures (usually at constant heating rate), or isothermal thermogravimetry. In the former, it is possible, in principle, to determine the full kinetics from a single experiment. In the latter, several runs must be carried out at different temperatures, in order to determine the effect of temperature on the rate of weight loss. In practice, heating the sample to the reaction temperature requires a certain time, and so non-isothermal conditions may be involved in the initial instants. This is most important in the case of lignocellulosic materials, which typically exhibit high reactivities at moderate temperatures. This is one reason why dynamic thermogravimetry is most frequently used in studies of thermal degradation of biomass.

Among the isothermal thermogravimetry studies available in the literature, it is relevant to refer the work of Bilbao et al. [23] and Cordero et al. [30]. These authors propose a method that considers several temperature ranges, the decomposition of a particular component being dominant in each range. Thus, at low temperatures (<230°C) the decomposition of hemicellulose would be dominant, and therefore the corresponding rate constants are determined directly from the experimental TG curves. Both hemicellulose and cellulose react in the range 230–260°C, the reaction of the former being dominant at low conversions while cellulose decomposition dominates at higher conversions. Between 260 and 290°C, it is considered that hemicellulose reacts completely during the pre-heating period, so that the experiments reflects only the decomposition of cellulose. Finally, at higher temperatures, the isothermal TG curves related to the decomposition of cellulose and lignin, the latter dominating at higher conversions. Some of the kinetic parameters determined in this way fall outside of reported values. For instance, Cordero et al. [30] obtained an activation energy for cellulose degradation of 83.5 kJ/mol, when 200 kJ/mol or higher is usually reported [17–20,29]. Most certainly, this is a consequence of ignoring the pyrolysis of lignin at low temperatures, as Bilbao et al. [23] recognised. In effect, it is argued that the decomposition of lignin can start before the other components [8,14,29], although its reactivity remains moderate within an extended temperature range, in agreement with the low activation energy of the process [31].

Recently, the present authors published an experimental study of the pyrolysis kinetics of some lignocellulosic materials, by dynamic thermogravimetry, which is based on the assumption of three independent reactions of three pseudo-components, related to hemicellulose, cellulose and lignin, respectively [29]. The present work was carried out in order to assess the implications of the proposed model on the characteristics of the isothermal thermograms, analysing in particular the reaction behaviour of the pseudo-components, and to develop a simple methodology for the determination of pyrolysis kinetics from the TG curves.

2. Experimental

The lignocellulosic materials considered in this work are sawdust from pinewood (*Pinus pinaster*), eucalyptus wood (*Eucalyptus globulus*) and pine bark, taken from the wastes of a local sawmill, the fraction $-70+80$ mesh (between 177 and 210 μm) being used for the woods and the fraction $-50+60$ mesh (between 250 and 297 μm) for pine bark.

The dynamic thermogravimetric experiments were carried out on small samples of each material (about 10 mg) with a nitrogen flow rate of 200 cm^3/min (measured at atmospheric pressure and temperature). Data were obtained with a Mettler TA 4000 system (M3TG/TG50) by recording both the history of weight loss of the samples and its rate under a linear temperature increase of 5 K/min [29].

3. Results and discussion

3.1. Summary of previous results by dynamic thermogravimetry

The authors have recently studied the pyrolysis kinetics of lignocellulosic materials by thermogravimetry under a linear temperature program [29]. The results were successfully modelled by considering a kinetic scheme of three independent first-order reactions, corresponding to the decomposition of three pseudo-components: (1) the most reactive fraction of hemicellulose; (2) the most reactive fraction of cellulose; (3) includes lignin and the remaining fractions of the carbohydrates. The kinetic parameters associated with the reaction of the second pseudo-component were fixed a priori from the results of a study on the pyrolysis of cellulose.

For each of the pseudo-components

$$\frac{\mathrm{d}\alpha_j}{\mathrm{d}t} = k_j(1-\alpha_j) = A_j \exp\left(-\frac{E_j}{RT}\right)(1-\alpha_j) \qquad (1)$$

with the initial condition $t=0$, $\alpha_j=0$. The variable $\alpha_j=(W_{j_0}-W_j)/(W_{j_0}-W_{j_\infty})$ is the degree of transformation of the pseudo-component j, where W is the weight and the subscripts 0 and ∞ refer to the initial and residual amounts, respectively, k_j is the rate constant for the decomposition of pseudo-component j, and E_j and A_j the Arrhenius parameters (activation energy and the pre-exponential factor, respectively).

When the reaction is carried out with linear temperature programming ($T=T_0+bt$, where b is the heating rate and T_0 the initial temperature) and by introducing the normalized variable $\theta=T/T_0$, the following equation is obtained [36]:

$$\frac{\mathrm{d}\alpha_j}{\mathrm{d}\theta} = \beta_j \exp\left(-\frac{\gamma_j}{\theta}\right)(1-\alpha_j) \qquad (2)$$

where $\beta_j=A_jT_0/b$ and $\gamma_j=E_j/RT_0$ are dimensionless parameters. In the referred work, $b=5\,\mathrm{K/min}$ and $T_0=293\,\mathrm{K}$. The initial condition is that $\alpha_j=0$ for $\theta=1$.

The degree of transformation of the sample is $\alpha=(W_0-W)/(W_0-W_\infty)$ and therefore [29]

$$\alpha = \sum_{j=1}^{3} z_{j_0}\alpha_j \qquad (3)$$

where $z_{j_0}=(W_{j_0}-W_{j_\infty})/(W_0-W_\infty)$ is a parameter related to the composition. Differentiating Eq. (3), we get

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\theta} = \sum_{j=1}^{3} z_{j_0}\frac{\mathrm{d}\alpha_j}{\mathrm{d}\theta} \qquad (4)$$

Once the kinetic parameters for the second pseudo-component were fixed, the TG and DTG curves depend on γ_1, β_1, γ_3, β_3 and two of the composition values, since $\sum_{j=1}^{3} z_{j_0}=1$. These parameters were calculated by the least square method from the DTG experimental curves, that is by minimizing the function

$$S = \sum_{i=1}^{N}\left[\left(\frac{\mathrm{d}\alpha}{\mathrm{d}\theta}\right)_i^{\exp} - \left(\frac{\mathrm{d}\alpha}{\mathrm{d}\theta}\right)_i^{\mathrm{calc}}\right]^2 \qquad (5)$$

where N is the number of data points considered.

Table 1
Model parameters and related Arrhenius parameters (adapted from [29])

	Pinewood	Eucalyptus wood	Pine bark
γ_1	36.3	32.6	19.9
β_1	1.85×10^{9}	3.05×10^{8}	1.43×10^{5}
γ_2	82.5	82.5	82.5
β_2	4.00×10^{18}	4.00×10^{18}	4.00×10^{18}
γ_3	7.42	8.29	8.36
β_3	55.2	85.6	43.2
z_{1_0}	0.276	0.332	0.394
z_{2_0}	0.400	0.423	0.158
z_{3_0}	0.324	0.245	0.448
E_1 (kJ/mol)[a]	88.4	79.4	48.5
A_1 (min^{-1})[b]	3.16×10^{7}	5.20×10^{6}	2.44×10^{3}
E_2 (kJ/mol)[a]	201	201	201
A_2 (min^{-1})[b]	6.83×10^{16}	6.83×10^{16}	6.83×10^{16}
E_3 (kJ/mol)[a]	18.1	20.2	20.4
A_3 (min^{-1})[b]	0.942	1.46	0.737

[a] E_j (kJ/mol) $= RT_0\gamma_j = 2.436\gamma_j$.
[b] A_j (min^{-1}) $= b\beta_j/T_0 = \beta_j/58.6$.

The parameters determined in this way for each one of the three materials studied are given in Table 1 [29].

Fig. 1 shows the Arrhenius plots corresponding to the reactions of the three pseudo-components for the three materials. It can be observed that pseudo-components 1 and 2 are more reactive than pseudo-component 3 at high temperatures. On the other hand, at low temperatures, pseudo-components 1 and 3 exhibit much higher reactivities than pseudo-component 2. This is in agreement with the observation that lignin (main component of pseudo-component 3) and hemicellulose start decomposing at much lower temperatures than cellulose in dynamic TG [8,14,29,31]. However, the rates of lignin pyrolysis do not increase much upon heating up [8,14,29], which is compatible with the results shown in Fig. 1, as the activation energy corresponding to the reaction of pseudo-component 3 is quite low.

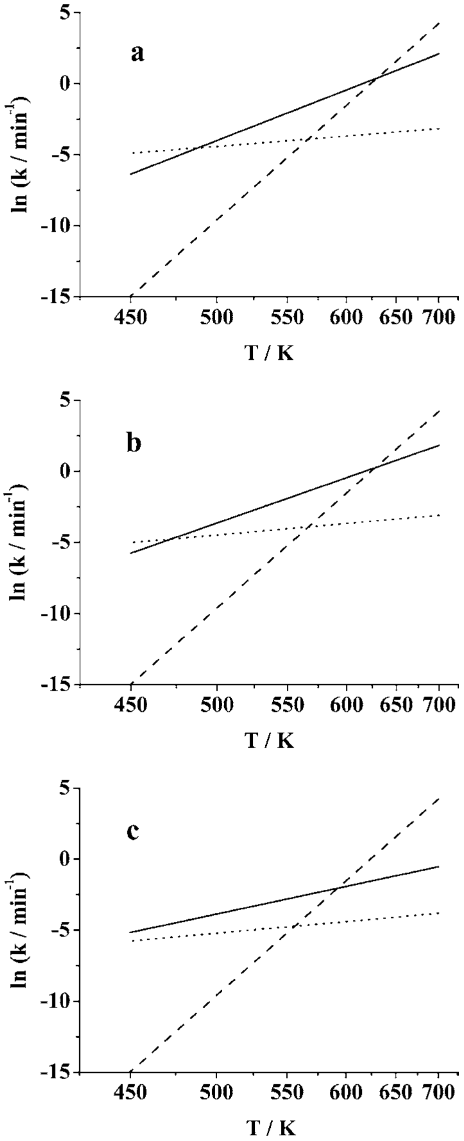

Fig. 1. Plots of rate constants versus temperature (reciprocal scale) for the decomposition of the three pseudo-components ((—) 1; (– – –) 2; (. . .) 3) of each material ((a) pinewood; (b) eucalyptus wood; (c) pine bark).

3.2. Simulation of isothermal thermogravimetric curves

In isothermal TG, Eq. (1) determines directly the decomposition of each pseudo-component, since k_j is a constant. Thus,

$$\alpha_j = 1 - \exp(-k_j t) \qquad (6)$$

and the overall degree of transformation for each material is given by Eq. (3).

Using the kinetic and composition parameters referred to in the previous section, it is possible to simulate the isothermal TG curves corresponding to the pine and eucalyptus woods and to pine bark (Figs. 2–4, respectively). According to the

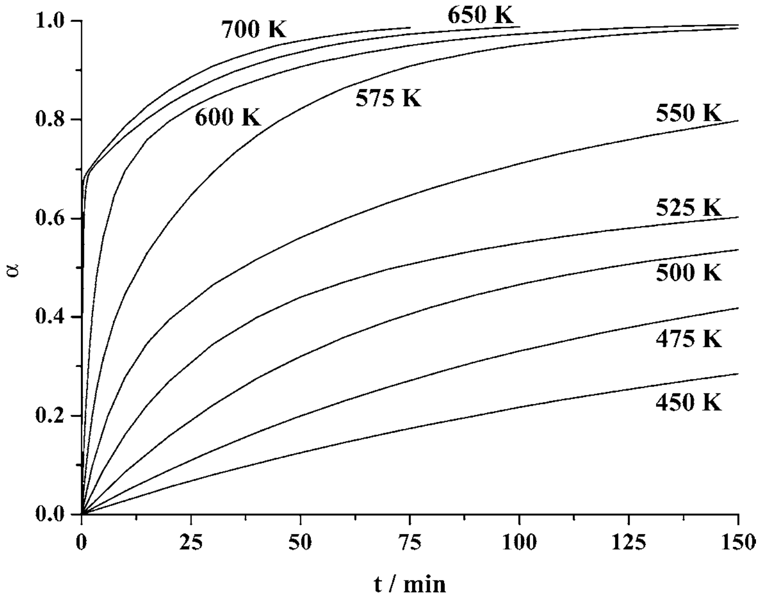

Fig. 2. Simulated isothermal TG curves for the pyrolysis of pinewood.

experimental results obtained by dynamic TG [29], it was decided to analyse the temperature range 450–700 K, where the great majority of isothermal pyrolysis studies of lignocellulosic materials and their components are carried out [18,23,30,37].

At the lowest temperatures considered, the overall reactivity of pine bark is higher (cf. Table 2). Most certainly, this is a result of its lower content in pseudo-component 2, associated to cellulose (cf. Table 1) which exhibits limited reactivity up to about 525 K. The behaviour described for the three materials is

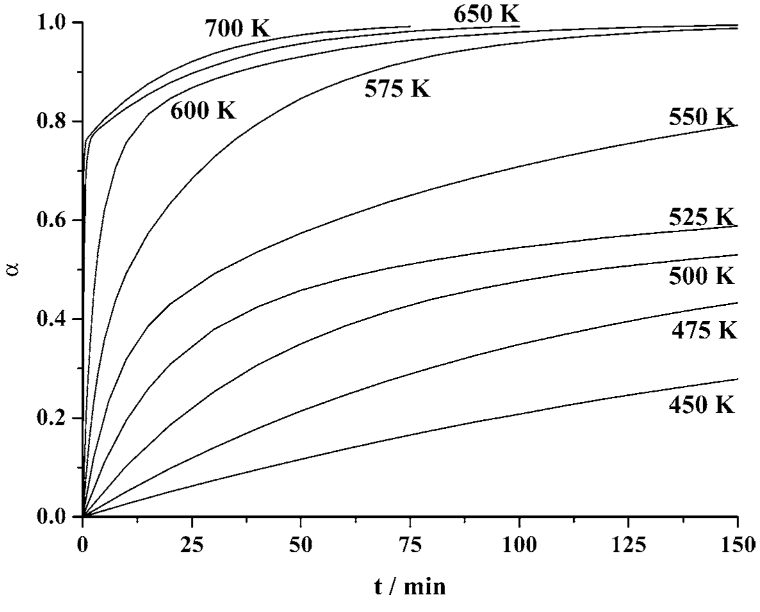

Fig. 3. Simulated isothermal TG curves for the pyrolysis of eucalyptus wood.

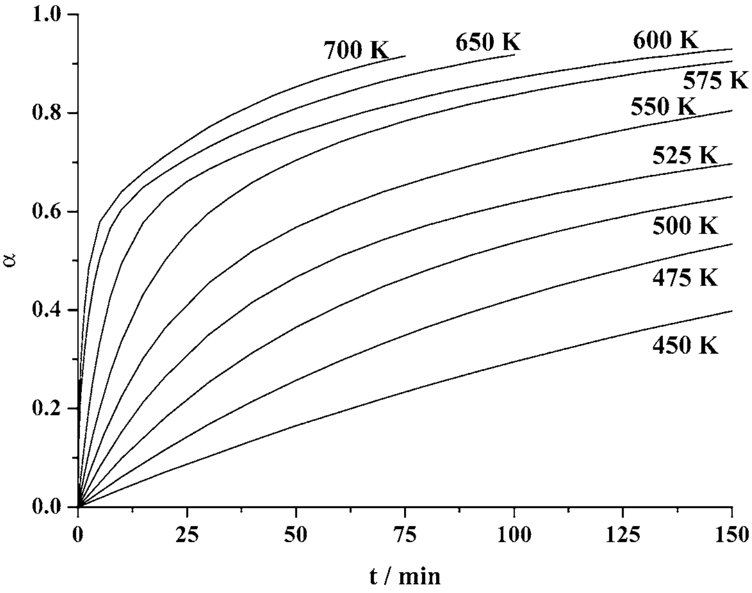

Fig. 4. Simulated isothermal TG curves for the pyrolysis of pine bark.

observed up to 550 K, temperature at which their reactivities are quite similar, except during the first 30 min of reaction. It should also be mentioned that pinewood is slightly more reactive than eucalyptus at 450 K. At this temperature, pseudo-component 3 is more reactive than pseudo-component 1 in both materials (cf. Fig. 1) and pinewood is slightly richer in pseudo-component 3 (cf. Table 1), as it contains more lignin.

At 575 K and higher, the sequence of reactivities is eucalyptus wood $>$ pinewood $\gg$ pine bark, regardless of the reaction time considered (cf. Table 3). There are two possible reasons for this inversion of the reactivity of pine bark at temperatures higher than 550 K: first, pine bark contains small amounts of cellulose and the decomposition of pseudo-component 2 occurs with significant rates in this temperature range; secondly, the rate constants for the decomposition of pseudo-components 1 and 3 of pine bark are much lower than those corresponding to the woods, as can be observed in Fig. 1.

The reaction behaviour of the pseudo-components can be analysed in more detail. Table 4 gives the reaction times required for nearly complete degree of transformation of the pseudo-components (arbitrarily defined as 99.5%) in the temperature range 500–

Table 2
Simulated results for $T \leq 550\,\mathrm{K}$[a]

t (min)	Degree of transformation, α														
	$T = 450\,\mathrm{K}$			$T = 475\,\mathrm{K}$			$T = 500\,\mathrm{K}$			$T = 525\,\mathrm{K}$			$T = 550\,\mathrm{K}$		
	PW	EW	PB	PW	EW	PB	PW	EW	PB	PW	EW	PB	PW	EW	PB
10	0.028	0.026	0.036	0.047	0.051	0.061	0.086	0.103	0.099	0.162	0.195	0.152	0.278	0.319	0.224
30	0.080	0.074	0.103	0.129	0.140	0.168	0.221	0.253	0.253	0.345	0.379	0.350	0.465	0.491	0.455
50	0.125	0.117	0.165	0.199	0.214	0.257	0.320	0.350	0.365	0.440	0.458	0.467	0.561	0.574	0.568
70	0.165	0.156	0.220	0.258	0.276	0.332	0.392	0.416	0.448	0.497	0.503	0.543	0.632	0.637	0.640
100	0.217	0.208	0.295	0.331	0.349	0.423	0.466	0.477	0.537	0.550	0.545	0.618	0.711	0.709	0.716
150	0.285	0.279	0.398	0.418	0.433	0.534	0.536	0.530	0.630	0.602	0.588	0.697	0.798	0.792	0.805

[a] PW: pinewood; EW: eucalyptus wood; PB: pine bark.

Table 3
Simulated results for $T \geq 575\,\mathrm{K}^{a}$

t (min)	Degree of transformation, α											
	$T = 575\,\mathrm{K}$			$T = 600\,\mathrm{K}$			$T = 650\,\mathrm{K}$			$T = 700\,\mathrm{K}$		
	PW	EW	PB	PW	EW	PB	PW	EW	PB	PW	EW	PB
1	0.095	0.111	0.046	0.218	0.242	0.089	0.662	0.721	0.269	0.689	0.765	0.343
2.5	0.201	0.231	0.109	0.406	0.451	0.199	0.701	0.774	0.390	0.708	0.781	0.486
5	0.317	0.359	0.199	0.563	0.621	0.334	0.725	0.794	0.505	0.737	0.805	0.579
10	0.447	0.493	0.336	0.697	0.757	0.494	0.767	0.827	0.604	0.787	0.844	0.640
30	0.693	0.727	0.597	0.846	0.885	0.686	0.879	0.913	0.731	0.908	0.937	0.771
50	0.822	0.846	0.704	0.907	0.931	0.759	0.937	0.957	0.809	0.960	0.975	0.853
100	0.951	0.959	0.837	0.973	0.981	0.870	0.988	0.992	0.918	0.995	0.997	0.952

[a] PW: pinewood; EW: eucalyptus wood; PB: pine bark.

700 K. The results show that pseudo-component 2, which practically does not react below 500 K, reaches high reactivity above 600 K, in such a way that it completely pyrolyses in a very short time. A similar situation occurs with pseudo-component 1, although in this case complete conversion can also be observed at intermediate temperatures after reaction times well below the typical duration of an isothermal thermogravimetric experiment. Finally, pseudo-component 3 can only be completely decomposed after very long pyrolysis times, even at high temperatures (about 2 h at 700 K in the case of woods and twice as longer in the case of pine bark).

3.3. Pyrolysis kinetics from isothermal thermogravimetric experiments

A method to determine the kinetics of pyrolysis from isothermal TG experiments can be derived from the conclusions reached in the previous section, provided that the experiments are carried out over an extended range of temperatures (e.g., 450–700 K) and that the independent decomposition model of the three pseudo-components is valid.

Thus, considering first the highest temperatures (≥600 K), it can be assumed that only pseudo-component 3 is reacting, since the other two are completely converted after a very short time (cf. Table 4). Under these conditions ($\alpha_1 = \alpha_2 = 1$), from Eqs. (3) and (6), we get

$$\alpha = z_{1_0} + z_{2_0} + z_{3_0}\alpha_3 = z_{1_0} + z_{2_0} + z_{3_0}[1 - \exp(-k_3 t)] = 1 - z_{3_0}\exp(-k_3 t) \qquad (7)$$

which can be linearized as

$$g(\alpha) = -\ln(1-\alpha) = -\ln z_{3_0} + k_3 t \qquad (8)$$

Therefore, in this temperature region and for reaction times not too short, there must be a linear relationship between $g(\alpha)$ and time. The slope of the straight line is the rate constant for the decomposition of the third

Table 4
Reaction times for "complete" transformation of pseudo-components ($\alpha_j = 0.995$)[a]

	t (min)						
	$T = 500\,\mathrm{K}$	$T = 525\,\mathrm{K}$	$T = 550\,\mathrm{K}$	$T = 575\,\mathrm{K}$	$T = 600\,\mathrm{K}$	$T = 650\,\mathrm{K}$	$T = 700\,\mathrm{K}$
PC 1 (PW)	270	98	39	17	7.9	2.0	0.6
PC 1 (EW)	201	81	35	17	8.3	2.5	0.9
PC 1 (PB)	251	144	87	55	36	17	9.0
PC 2	>81200	>8100	998	147	25	1.1	0.1
PC 3 (PW)	442	358	296	249	213	161	127
PC 3 (EW)	469	371	301	249	209	153	117
PC 3 (PB)	965	765	618	509	427	312	238

[a] PC 1, PC 2, PC 3: pseudo-components 1, 2 and 3, respectively. PW: pinewood; EW: eucalyptus wood; PB: pine bark.

pseudo-component. The corresponding composition parameter, z_{3_0}, can be obtained from the intercept, which subtracted from unity yields the sum $(z_{1_0} + z_{2_0})$.

At intermediate temperatures (approximately 525–575 K) the three pseudo-components react simultaneously, but the first one (the most reactive fraction of hemicellulose) is completely converted much before the other two, namely the second (cf. Table 4). According to the simulations carried out, the overall degree of transformation of the materials at this stage lies between 50 and 60% in the case of the woods and reaches about 70% in the case of pine bark. Thus, by discounting the degree of transformation of pseudo-component 3, the kinetics of which is already known from the previous step, it is possible to obtain the rate constant for the pyrolysis of pseudo-component 2 from times greater than that corresponding to $\alpha_1 = 1$. We start by calculating

$$\alpha^* = \alpha - z_{3_0}\alpha_3 \tag{9}$$

For reaction times not too small

$$\begin{aligned}\alpha^* &= z_{1_0} + z_{2_0}\alpha_2 = z_{1_0} + z_{2_0}[1 - \exp(-k_2 t)] \\ &= (z_{1_0} + z_{2_0}) - z_{2_0}\exp(-k_2 t)\end{aligned} \tag{10}$$

This equation can be written as

$$g(\alpha^*) = -\ln(z_{1_0} + z_{2_0} - \alpha^*) = -\ln z_{2_0} + k_2 t \tag{11}$$

which can be used to estimate k_2 and z_{2_0} and, consequently, z_{1_0}.

Finally, the pyrolysis rate constant of the first pseudo-component can be determined from the runs at lower temperatures (≤500 K). To do so, it suffices to determine first the corresponding degree of transformation, which is possible because the temperature dependencies of the other rate constants are already known from the calculations carried out in the previous steps. Thus,

$$\alpha_1 = \frac{\alpha - z_{2_0}\alpha_2 - z_{3_0}\alpha_3}{z_{1_0}} \tag{12}$$

It should be noted that k_2 is, in principle, very small at this temperature level, so that the correction corresponding to the second pseudo-component (the most reactive fraction of cellulose) may not be needed, eventually. Once the values of α_1 are determined, a straight line must be obtained according to the equation

$$g(\alpha_1) = -\ln(1 - \alpha_1) = k_1 t \tag{13}$$

4. Example of application

The simulated results for pinewood will now be considered in order to demonstrate the method. Fig. 5 shows the values of $g(\alpha) = -\ln(1 - \alpha)$ versus time at high temperatures. After a certain time, which is as higher as the temperature is lower, the data are well fitted by the following straight lines:

$$T = 600\,\mathrm{K} \rightarrow g(\alpha) = 2.49 \times 10^{-2} t + 1.12 \tag{14}$$

$$T = 650\,\mathrm{K} \rightarrow g(\alpha) = 3.29 \times 10^{-2} t + 1.13 \tag{15}$$

$$T = 700\,\mathrm{K} \rightarrow g(\alpha) = 4.18 \times 10^{-2} t + 1.13 \tag{16}$$

These represent the decomposition of the third pseudo-component, as they are defined from the time corresponding to complete conversion of the other two. Thus, their slopes represent k_3. Considering an Arrhenius type temperature dependency,

$$k_3 = 0.936\exp\left(-\frac{2.18 \times 10^3}{T}\right) \tag{17}$$

In addition, from the intercept, we calculate $z_{3_0} = 0.323$.

At intermediate temperatures (525–575 K), we calculate

$$g(\alpha^*) = -\ln(0.677 - \alpha^*) \tag{18}$$

with

$$\begin{aligned}\alpha^* &= \alpha - 0.323\,\alpha_3 \\ &= \alpha - 0.323[1 - \exp(-k_3 t)]\end{aligned} \tag{19}$$

where the k_3 values were determined by Eq. (17). The plots of $g(\alpha^*)$ versus time are shown in Fig. 6. From the instant where pseudo-component 1 is completely converted, we can obtain straight lines of slope k_2, and from their intercept z_{2_0} can be calculated. These straight lines are

$$T = 525\,\mathrm{K} \rightarrow g(\alpha^*) = 7.10 \times 10^{-4} t + 0.909 \tag{20}$$

$$T = 550\,\mathrm{K} \rightarrow g(\alpha^*) = 5.34 \times 10^{-3} t + 0.915 \tag{21}$$

$$T = 575\,\mathrm{K} \rightarrow g(\alpha^*) = 3.67 \times 10^{-2} t + 0.894 \tag{22}$$

Averaging the intercepts we get $z_{2_0} = 0.404$ and therefore $z_{1_0} = 0.273$. The slopes are the pyrolysis rate

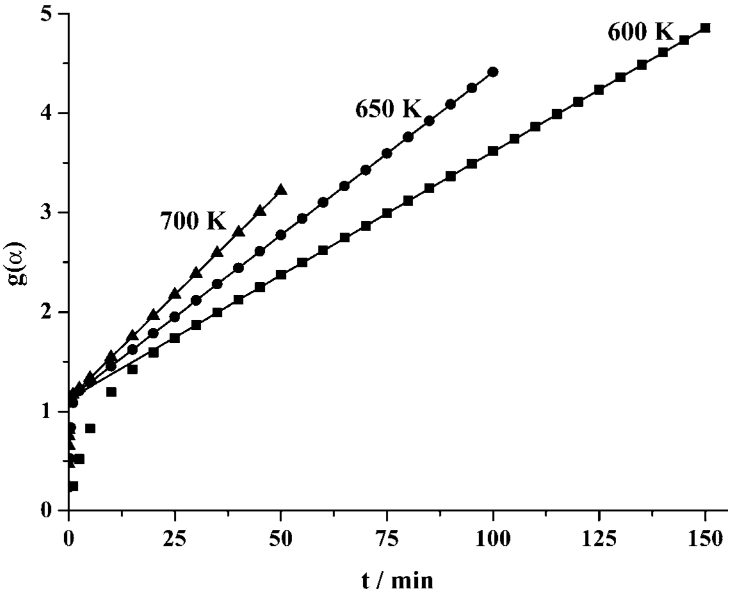

Fig. 5. Plot of $g(\alpha)$ versus time at high temperatures for the pyrolysis of pinewood.

constants of pseudo-component 2, which can be fitted to the Arrhenius equation

$$k_2 = 3.19 \times 10^{16} \exp\left(-\frac{23.8 \times 10^3}{T}\right) \quad (23)$$

At low temperatures, we can determine the degree of transformation of pseudo-component 1

$$\alpha_1 = \frac{\alpha - 0.404\alpha_2 - 0.323\alpha_3}{0.273} \quad (24)$$

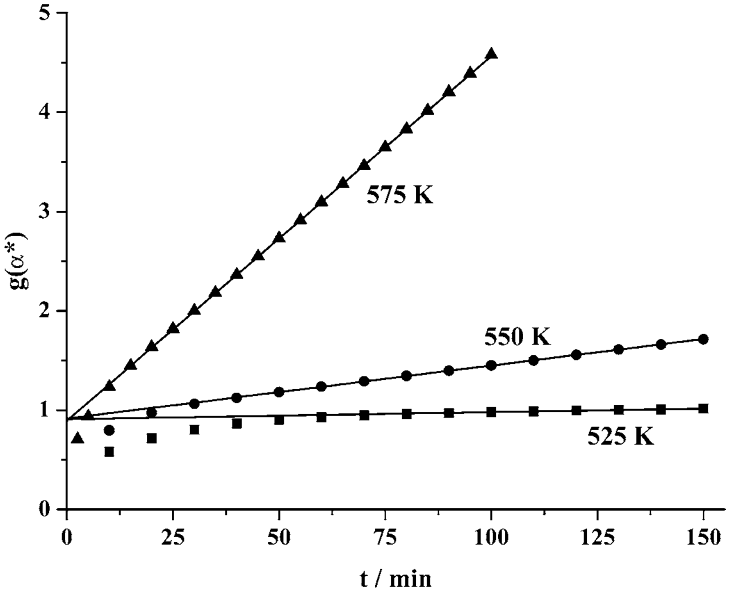

Fig. 6. Plot of $g(\alpha^*)$ versus time at intermediate temperatures for the pyrolysis of pinewood.

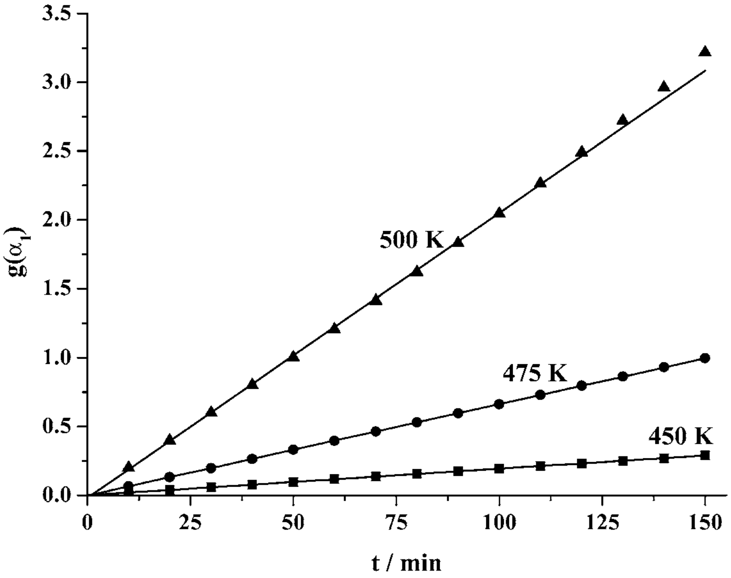

Fig. 7. Plot of $g(\alpha_1)$ versus time at low temperatures for the pyrolysis of pinewood.

Fig. 7 shows the plots of $g(\alpha_1) = -\ln(1 - \alpha_1)$ versus time and the fitted lines. A slight positive deviation can be observed at 500 K after 120 min, which is a consequence of α_1 approaching unity, resulting in large errors for $g(\alpha_1)$. The slopes are 1.93×10^{-3}, 6.64×10^{-3} and $2.07 \times 10^{-2}\,\mathrm{min}^{-1}$ at 450, 475 and 500 K, respectively. Thus,

$$k_1 = 3.98 \times 10^7 \exp\left(-\frac{10.7 \times 10^3}{T}\right) \qquad (25)$$

Table 5 summarizes the results obtained for the three materials considered. It may be observed that the differences to the starting parameters used in the simulations are minimal (cf. Table 1), confirming that the proposed method is a promising one for the kinetic analysis of isothermal TG pyrolysis experiments of lignocellulosic materials.

Table 5
Kinetic and composition parameters calculated by the method developed in this work

	Pinewood	Eucalyptus wood	Pine bark
z_{1_0}	0.273	0.331	0.392
z_{2_0}	0.404	0.425	0.159
z_{3_0}	0.323	0.244	0.449
E_1 (kJ/mol)	89.0	80.4	49.3
A_1 (min^{-1})	3.98×10^7	6.58×10^6	3.07×10^3
E_2 (kJ/mol)	198	199	204
A_2 (min^{-1})	3.19×10^{16}	3.89×10^{16}	1.17×10^{17}
E_3 (kJ/mol)	18.1	20.3	20.5
A_3 (min^{-1})	0.936	1.48	0.755

The examples presented were based on simulated isothermal curves using the kinetic parameters determined previously by dynamic thermogravimetry. The experimental validation of the proposed methodology will be the subject of a future publication.

5. Conclusions

The results previously obtained by dynamic thermogravimetry for the pyrolysis of lignocellulosic materials [29], where the process was described by three independent reactions of decomposition of three pseudo-components, were extended to isothermal thermogravimetry. The following conclusions can be drawn from this study:

1. Up to 550 K, pine bark is more reactive than the pine or eucalyptus woods, as a result of its lower cellulose content. Above this temperature, the sequence of reactivities is reversed, mainly as a consequence of the higher activation energy for

the decomposition of pseudo-component 2 (which corresponds to the largest fraction of cellulose).

2. Up to 500 K, pseudo-component 2 (which is the most reactive fraction of cellulose) is practically unreacted, although it exhibits high reactivity above 600 K.
3. Above about 525 K, pseudo-component 1 (which corresponds to the most reactive fraction of hemicellulose) is converted to a large extent in a relatively short time.
4. The reactivity of pseudo-component 3 (essentially lignin, but also the less reactive fractions of the carbohydrates) is moderate over the whole temperature range studied (450–700 K).
5. A simplified method to determine the pyrolysis kinetics of lignocellulosic materials from isothermal thermogravimetric experiments was developed, which is based on a kinetic scheme consisting of the decomposition of three pseudo-components. The kinetic and composition parameters for each pseudo-component are successively determined from the analysis of the isothermal TG curves corresponding to high, medium and low temperatures.
6. The method was successfully applied to simulated results obtained for three different lignocellulosic materials.
7. One advantage of the proposed method is that only the final part of the isothermal TG curves is used in the analysis, thus avoiding the initial instants where the temperature may not be stabilized.

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