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Thermogravimetric study of the pyrolysis of waste wood

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Abstract

A thermogravimetric study of the pyrolysis of three different types of waste wood (forest wood, old furniture and used pallets) is carried out in a TGA equipment using dynamic and isothermal techniques. Isothermal runs were carried out at two temperature levels, one between 225° and 325°C (low range) and the other, between 700° and 900°C (high range). Results show a good agreement between the kinetic parameters obtained from either dynamic or isothermal techniques. It must be remarked that the own chemical composition of each type of wood together with the compounds added to the wood for each application, play a fundamental role in the kinetic behavior of their thermal decomposition. © 1998 Elsevier Science B.V.

Keywords: Biomass; Kinetics; Pyrolysis; Thermogravimetric analysis; Waste wood

1. Introduction

Under the point of view of its chemical composition, wood is a complex substance which essentially contains cellulose, polysaccharides and lignin. The main components are cellulose, lignin and water. According to König [1], the cellulose content oscillates between 40 and 60% and the content of lignin, between 21 and 30%. Other important components of wood are, pentosanes and hexosanes. There is a remarkable difference in composition between the wood generated by different species. Coniferous or soft woods contain upto 20% of pentosanes, and hexosanes and leafy or hard woods contain between 20 and 30%.

The thermal decomposition of ligno–cellulosic materials takes place through a complex series of chemical reactions coupled with heat and mass transfer processes. Several mechanisms have been published in the literature to explain such processes [2], mainly for the thermal decomposition of cellulose and lignin. Nevertheless, the mechanism becomes more complex when a sample of biomass or waste wood is pyrolyzed. Substantial differences can be observed in the activation energy, reported in the literature, for the overall pyrolysis of ligno–cellulosic materials [3,4]. The differences observed between results, reported by different authors, can be due to several factors related to the experimental methods, operating conditions and data analysis, but also to the chemical composition of the raw materials used in each study.

It has been frequently observed that the activation energy for the overall pyrolysis of wood tend to group around discrete values. Roberts [4] reported two different groups for the energy of activation, one ca. 125 kJ/mol and the other 235 kJ/mol. Antal et al. [3] grouped the values reported in the literature for the energy of activation in three groups. The first group, between 210 and 250 kJ/mol, corresponds to

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experimental values in which the thermocouple was outside of the sample. For the second group, between 138 and 210 kJ/mol, the thermocouple was in contact with the gas. For the third group, between 109 and 138 kJ/mol, the thermocouple was coupled directly to the sample.

This work aims to determine the kinetic parameters for the thermal decomposition of three different types of waste wood, and also to analyze the influence of the type of wood, as well as the influence of the experimental conditions.

2. Experimental

Pyrolysis studies were carried out in a TGA standard equipment (Setaram, model TG 85). All experiments were carried out at atmospheric pressure under an inert nitrogen atmosphere with a flowrate of 50 ml/min. A thermocouple was placed directly in contact with the sample. This allowed to register, at any instant, the temperature of the sample and then to minimize the inaccuracy of the measurements due to temperature gradient. The mass of wood, 25 mg, was distributed all over the surface of the crucible, forming a layer with a thickness lower than 1 mm. Using a thin layer of raw material and measuring the temperature directly over the sample should avoid the influence of the interaction between particles on the results obtained. A mechanically driven elevator was designed and coupled to the oven of the TGA to allow fast heating of the sample. The displacement of the oven can be regulated to a desired speed and height.

Two types of experiments were carried out in order to compare results. These are, dynamic and isothermal runs. Isothermal runs were carried out at two different temperature levels. The low range, where the main degradation processes of pyrolysis take place, was chosen between 225° and 325°C. The high range, where the remaining residue pyrolizes, was selected between 700° and 900°C. For dynamic experiments, five different heating rates were used: 2, 20, 35, 50 and 100°C/min to show its influence on the thermal decomposition of the materials under study.

Table 1 shows the characteristics of the woods employed in this study. To avoid heat and intraparticle mass-transfer effects, samples were sieved between 0.3 and 0.7 mm.

The parameters needed to establish the kinetic equation for the thermal decomposition of the samples, under study, are defined as follows. In all experiments, the results have been expressed as a function of the conversion X, defined as:

$$X = \frac{(W_0 - W)}{W_0} \tag{1}$$

X is expressed in dry basis, in order to analyze the influence of the sample-initial-moist content on the kinetics of the process. For a wet sample, the weight loss measured before the main thermal decomposition takes place is named here as W_1. The weight fraction lost in this first stage is calculated as follows:

$$H = \frac{(W_0 - W)}{W_0} \times 100 \tag{2}$$

Bilbao et al. [5,6] reported that this parameter has an outstanding influence on the kinetic behavior of these materials. The fraction that pyrolyzes at infinite time is defined as:

$$X_\mathrm{p} = \frac{(W_0 - W_\infty)}{W_0} \tag{3}$$

3. Isothermal experiments

3.1. Interval between 225° and 325°C

For this range of temperatures, isothermal runs were carried out by heating the sample at a low-heating rate

Table 1
Characteristic of the waste wood used as raw material

Wood	Proximate analysis (%)				Ultimate analysis (%)			
	Moisture	Fixed carbon	Volatile matter	Ash	C	H	N	O
Forest	7.38	17.64	72.98	2.00	46.16	5.77	0.80	37.87
Furniture	3.79	17.55	77.46	1.20	44.59	6.32	1.57	42.83
Pallets	2.59	15.03	79.98	2.40	45.37	5.69	0.07	43.88

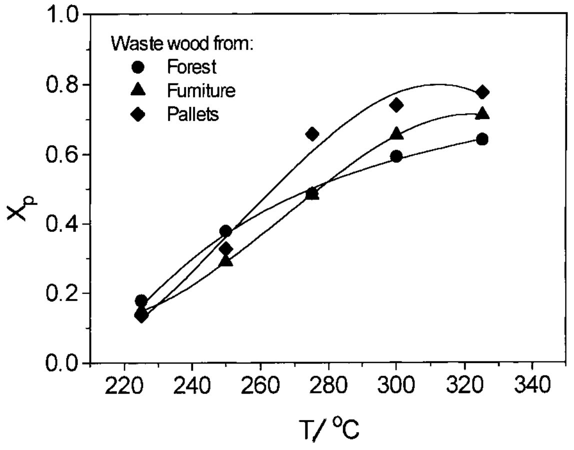

Fig. 1. Behavior of the pyrolysable fraction with temperature for three different types of waste wood at a low temperature.

(2°C/min) in order to have a low-temperature gradient between the sample and oven at every moment. Once, the set-point was reached, the oven was kept at a constant temperature until the end of the isothermal run.

Fig. 1 shows the behavior of the pyrolysable fraction with the temperature for the three waste woods under study. It can be observed in Fig. 1 that the pyrolyzable fraction increases with temperature by following different trend for every type of waste wood. At 250°C, the forest wood has the largest pyrolyzable fraction. According to Bilbao et al. [5,6], in this temperature range, the thermal decomposition is dominated by the decomposition of the hemicellulose present in the sample. Between 275° and 325°C, where the process is dominated by the decomposition of cellulose and lignin, the largest pyrolyzable fraction correspond to the wood from pallets. In this case, values >0.75 were obtained.

The methodology to obtain the kinetics for the pyrolysis of the waste wood under study is the same as that reported by Antal et al. [3], Bilbao et al. [5–7], and Kilzer and Broido [8], among others. The conversion rate is expressed as

$$\frac{dX}{dt} = k(X_p - X)^n \tag{4}$$

or

$$\ln dX/dt = \ln k + n \ln (X_p - X) \tag{4'}$$

Integrating Eq. (4) with the initial conditions: $t=t_i$ and $X=X_i$ and assuming a first-order reaction, one obtains:

$$\ln (X_p - X) = \ln (X_p - X_i) + kt_i - kt \tag{5}$$

According to the Arrhenius equation, the rate constant k can be expressed as:

$$k = A \exp(-E/RT) \tag{6}$$

Experimental values of k can be obtained by plotting ln $(X_p{-}X)$ vs. t. Table 2 summarizes the experimental values obtained for each sample at different temperatures.

The difference in the chemical composition of the three types of wood not only influences the pyrolysable fraction, but furthermore, as is observed in Table 2, the values of the kinetic parameters in the temperature range under study. These observations are in agreement with those of Bilbao et al. [5,6]. It can also be seen in Table 2 that both, X_p and k increases with the increase in temperature. We can outline that it exists a relationship between the pyrolysable fraction and the contents of volatile matter in the raw material. This fact justifies that the chemical composition plays an important role in the behavior of each type of wood during its thermal decomposition.

The apparent reaction order (n) was determined for each temperature and raw material from the slope obtained by plotting Eq. (4) in logarithmic coordinates. Results show an apparent reaction order, that depends on the temperature and raw material, giving values between 1 and 3. An apparent reaction order between 2.55 and 2.93, that is to say near 3, was obtained for temperatures between 250° and 275°C, where, according to Bilbao et al. [5,6], the main process is the decomposition of cellulose. For the rest of temperature intervals under study, the apparent reaction order was close to 1. Then, for practical purposes, it can be assumed that the pyrolysis process exhibits first-order behavior. The simplicity of such relationship makes it suitable for use in engineering techniques.

3.2. Interval between 700° and 900°C

These experiments were carried out at heating rates close to 700°C/min (flash pyrolysis). Firstly, the oven was lifted at a rate of 3 cm/min, until the point where

Table 2
Kinetic parameters of waste wood in the low temperature range

Temperature/°C		225	250	275	300	325
Forest						
X_p		0.178	0.378	0.486	0.593	0.641
$k\times10^5/s^{-1}$		6.56	7.0	10.0	35.3	98.8
E/(kJ/mol)	124.87					
A/s^{-1}	7.68×10^7					
r	0.95					
Furniture						
X_p		0.148	0.289	0.482	0.654	0.711
$k\times10^5/s^{-1}$		6.28	8.16	10.6	46.3	128
E/(kJ/mol)	135.76					
A/s^{-1}	9.20×10^8					
r	0.98					
Pallets						
X_p		0.135	0.326	0.658	0.740	0.775
$k\times10^5/s^{-1}$		7.83	9.36	11.9	36.1	145
E/(kJ/mol)	135.68					
A/s^{-1}	9.01×10^8					
r	0.98					

the sample temperature reached 150°C. Then, the oven was kept in this position during several minutes to ensure the system stabilization. After that, the oven was quickly lifted. The time needed to reach the temperature setpoint and the weight loss during this time were measured. Fig. 2 shows the pyrolysable fraction for each type of wood in the temperature range between 700° and 900°C.

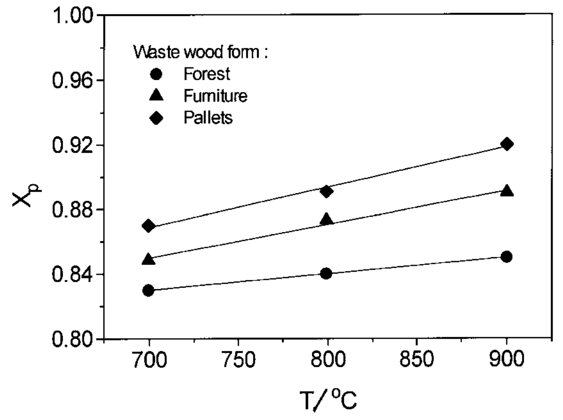

Fig. 2. Behavior of the pyrolysable fraction with temperature for three different types of waste wood in flash pyrolysis.

Like in isothermal runs at low temperature, the pyrolyzable fraction obtained for flash pyrolysis increases with temperature and, at a given temperature, is lower for the raw material with the higher content on volatile mater. Nevertheless, in this case, the increase of X_p with temperature is lower than that observed for the low-temperature range, and the apparent reaction order, n, is close to one. The values for the kinetic constant and energy of activation are given in Table 3.

Comparing results tabulated in Tables 2 and 3, it can be seen that the energy of activation is lower for the range between 700° and 900°C. This means that a high temperature increases the speed at which the thermal degradation of this material occurs, as well as augments the pyrolyzable fraction.

4. Dynamic experiments

In this case, the conversion fraction can be also expressed by Eq. (4). Using TG and DTG curves to obtain, respectively, X, X_p, and dX/dt, and assuming a first-reaction order (n=1), we can obtain k for each experiment at any time. Using the relationship

Table 3
Kinetic parameters of waste wood in the high temperature range

Temperature/°C		700	800	900
Forest				
X_p		0.83	0.84	0.85
$k\times10^5/s^{-1}$		809	1600	5800
E/(kJ/mol)	92.28			
A/s^{-1}	0.632×10^3			
r	0.97			
Furniture				
X_p		0.84	0.87	0.89
$k\times10^5/s^{-1}$		625	1290	5620
E/(kJ/mol)	102.76			
A/s^{-1}	1.74×10^3			
r	0.97			
Pallets				
X_p		0.87	0.89	0.92
$k\times10^5/s^{-1}$		627	1320	5220
E/(kJ/mol)	99.26			
A/s^{-1}	1.16×10^3			
r	0.97			

between time and temperature, given by a constant heating rate, we can plot the pseudo first-order kinetic constant vs. temperature. These results are plotted in Figs. 3–8, which show the influence of the heating rate, the chemical composition and moisture of the sample on the kinetic constant. It can be seen that the kinetic constant is influenced by all these parameters.

Figs. 3 and 4 shows the influence of the heating rate on the apparent kinetic constant. For high heating rates, material of poor heat conductivity like wood, can develop strong temperature gradients within the sample. Under these conditions, reactions are controlled rather by heat transfer than by chemical process kinetics. The observed effect of β make advisable the use of dynamic experiments at low heating rates to obtain values of the kinetic constant.

Values for the kinetic parameters obtained by dynamic experiments (β=2°C/min) at the same conversion (X=0.75) as that in isothermal runs in the interval between 225° and 325°C, are summarized in Table 4. It could be noted that the differences between

Table 4
Kinetic parameters for the three types of waste wood. Dynamic experiments (β=2°C/min)

Wood type	Furniture	Forest	Pallets
E/(kJ/mol)	129.36	136.18	127.61
$A\times10^7/s^{-1}$	1.91	3.38	1.23

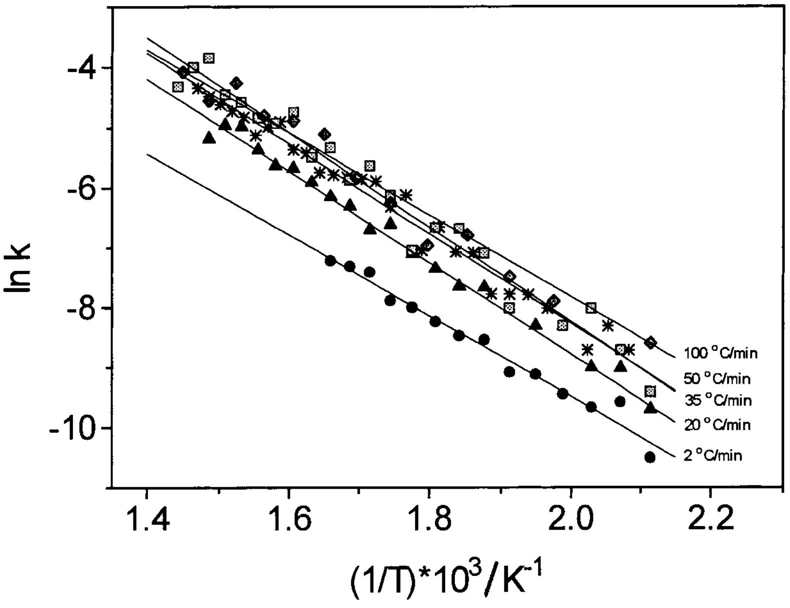

Fig. 3. Influence of the heating rate on the apparent kinetic constant for forest wood.

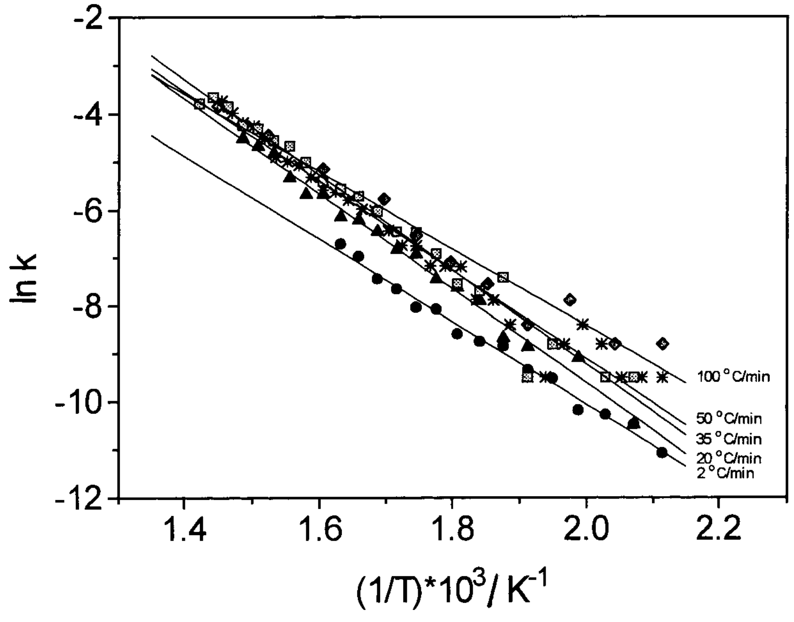

Fig. 4. Influence of the heating rate on the apparent kinetic constant for pallets wood.

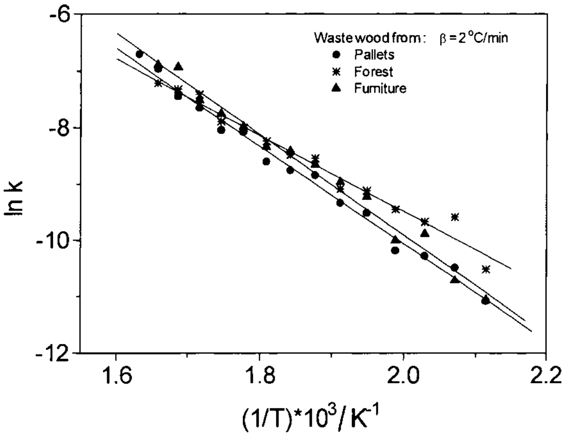

Fig. 5. Influence of the chemical composition on the apparent kinetic constant. β=2°C/min.

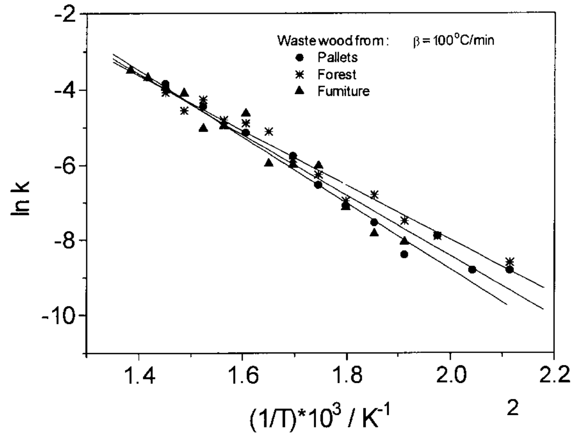

Fig. 6. Influence of the chemical composition on the apparent kinetic constant. β=100°C/min.

the values obtained by both kinds of experiments (dynamic and isothermal) are not meaningful. Therefore, it can be concluded that a good agreement exists between the kinetic parameters calculated by both methods. Then, the following rate expressions can established:

$$\text{Forest}: k(s-1) = 1.91\times 10^{7}\exp(129.36/RT)$$

$$\text{Furniture}: k(s-1) = 3.38\times 10^{7}\exp(136.18/RT)$$

$$\text{Pallets}: k(s-1) = 1.23\times 10^{7}\exp(127.61/RT)$$

that govern the thermal decomposition of each type of waste wood.

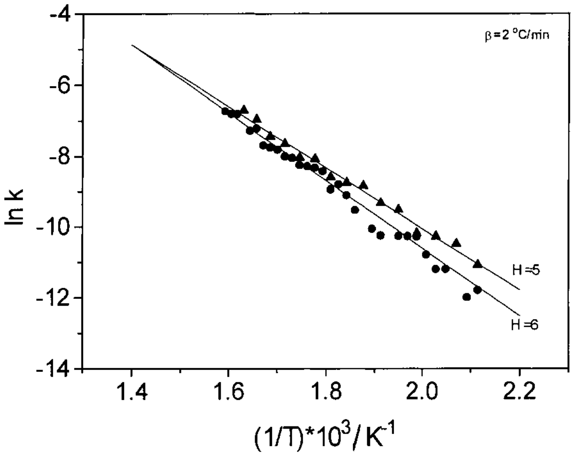

Fig. 7. Influence of the sample moisture, H (%) on the apparent kinetic constant. β=2°C/min.

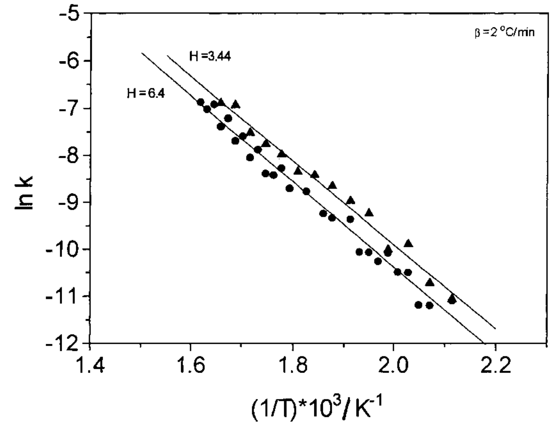

Fig. 8. Influence of the sample moisture, H (%), on the apparent kinetic constant. β=100°C/min.

5. List of symbols

A	pre-exponential factor, s^{-1}
E	activation energy, kJ/mol
k	rate constant, s^{-1}
n	reaction order
R	universal gas constant
r	correlation coefficient
X	conversion
X_p	pyrolysable fraction
H	sample moisture
W_0	sample weight at the time t_0, mg
W	sample weight at the time t, mg
W_T	sample weight at temperature T=150°C, mg
β	heating rate, °C/min

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