

KINETICS OF WEIGHT LOSS BY THERMAL DECOMPOSITION OF DIFFERENT LIGNOCELLULOSIC MATERIALS. RELATION BETWEEN THE RESULTS OBTAINED FROM ISOTHERMAL AND DYNAMIC EXPERIMENTS

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(Received 2 January 1990)

ABSTRACT

The kinetics of weight loss in the thermal decomposition of Pinaster pine and barley straw in a nitrogen environment have been studied.

The results obtained under different experimental conditions are shown and compared. These results are related by using the results of dynamic experiments with low heating rates as a reference.

INTRODUCTION

The thermal decomposition of lignocellulosic materials is a complex process because of the different behaviour of each of the components which make up the material. Therefore, the kinetic data of the pyrolysis of these materials are usually limited to specific conversion and temperature ranges. Owing to the complexity of the process, the study has been performed step by step.

In the first stage, the thermal decomposition of each component, cellulose [1,2], xylan (representing the hemicelluloses) and lignin [3], was studied separately. The influence of the different experimental conditions on the behaviour of these products was determined, and equations were obtained to compare the results corresponding to isothermal and dynamic experiments performed at different heating rates.

In the second stage, experiments were performed with various lignocellulosic materials. In a previous paper [4], the conversion and pyrolysable fraction values obtained with Pinaster pine and barley straw were compared with the corresponding individual contributions of each component, taking into account its chemical composition.

In this work, the kinetic results obtained in the thermal decomposition of these materials under different experimental conditions are shown and

compared. This comparison has been made using equations and models developed in previous papers.

EXPERIMENTAL METHOD

The experimental method used is similar to that employed in previous studies with individual constituents.

The weight losses for Pinaster pine and barley straw were measured in a nitrogen atmosphere using a Perkin–Elmer thermobalance.

Two types of experiments were performed.

(i) Isothermal experiments, which start with a low heating rate ($1.5^\circ\text{C min}^{-1}$) until the desired temperature is reached. This temperature is then kept constant throughout the pyrolysis process. Temperatures between 200 and 350°C were investigated.

(ii) Dynamic experiments, carried out with different heating rates in the range $1.5\text{--}80^\circ\text{C min}^{-1}$. These rates are kept constant throughout the experiment.

In order to avoid intraparticle heat and mass transfer problems, small particle sizes (-630 to $+297\ \mu\text{m}$) were used. All the results are expressed on a dry basis, in order to compare the results obtained from materials with different initial moisture contents.

DATA ANALYSIS

Isothermal experiments

The isothermal experiments, carried out with a low preheating rate, allow us to obtain the pyrolysable fraction values, A_S , at different temperatures, defined as

$$A_S = (W_{0S} - W_\infty)/W_{0S} \quad (1)$$

In this work, we have used the kinetic equation referred to the initial sample weight on a dry basis

$$-(1/W_{0S})(dW/dt) = k_S [(W - W_\infty)/W_{0S}]^n \quad (2)$$

Considering the definitions of conversion, $X_S = (W_{0S} - W)/W_{0S}$, and the pyrolysable fraction, A_S , eqn. (2) can be written

$$dX_S/dt = k_S (A_S - X_S)^n \quad (3)$$

or in its linearised form and for the isothermal experiments as

$$\log(dX_S/dt) = \log k_{Si} + n \log(A_S - X_S) \quad (4)$$

which allows us to obtain the reaction order, n .

In those temperature ranges where $n = 1$ can be considered, the equation which describes the thermal decomposition process is

$$dX_S/dt = k_{Si}(A_S - X_S) \quad (5)$$

which, upon integration and linearisation yields

$$\ln(A_S - X_S) = \ln(A_S - X_{Si}) + k_{Si}t_i - k_{Si}t \quad (6)$$

Equation (6) yields the values of the kinetic constant at each temperature, k_{Si} , from the results obtained in isothermal experiments.

Dynamic experiments

The dynamic experiments carried out with constant heating rates have several advantages over the isothermal experiments. One of these advantages is the possibility of obtaining results in a larger temperature range. Furthermore, these experiments allow the study of the influence of the heating rate (β) on the thermal decomposition process.

The values of the kinetic constant, $k_{S\beta}$, for each temperature and heating rate have been determined by taking $n = 1$ in eqn. (3) and using the equation

$$k_{S\beta} = \frac{(dX_S/dt)}{(A_S - X_S)} \quad (7)$$

An experimental data analysis has been carried out for the study of the influence of β on the $k_{S\beta}$ values and for establishing the relation between the kinetic results obtained from isothermal and dynamic experiments at different heating rates. The data analysis method involves the following steps.

(a) Calculation of the solid sample temperature, T , as a function of the temperature of the thermogravimetric system, T_f , in the temperature range where most of the thermal decomposition takes place. This calculation has been carried out using the model proposed for correcting the temperature gap between T and T_f when high heating rates are used [2] and with the equation

$$dT/dt = [B/(1 - X_S)](T_f - T) + [(-\Delta H_{r2})/C_p][1/(1 - X_S)](dX_S/dt) \quad (8)$$

(b) Taking into account the fact that $X_S = f(t, T)$, the results obtained with dynamic experiments at different β are related by the equation

$$(dX_S/dt)_\beta = (\partial X_S/\partial t)_T + (\partial X_S/\partial T)_T \beta \quad (9)$$

The values of $(\partial X_S/\partial T)_T$ must be calculated for a given temperature. As a first approach, it seems logical to make these calculations using the results from isothermal experiments. Thus we can write

$$(dX_S/dt)_\beta = k_{Si}(A_S - X_S) + (\partial X_S/\partial T)_T \beta \quad (10)$$

or using the values of the kinetic coefficients obtained in dynamic experiments performed with a low heating rate, e.g. $1.5^{\circ}\text{C min}^{-1}$

$$\left(\frac{dX_S}{dt}\right)_\beta = k_{S1.5}(A_S - X_S) + \left(\frac{\partial X_S}{\partial T}\right)_i(\beta - 1.5) \quad (11)$$

RESULTS AND DISCUSSION

Isothermal experiments

Using eqn. (4), the experimental values of X_S , A_S and dX_S/dt , obtained from isothermal experiments at different temperatures, allow us to obtain the reaction order, n . The values of A_S as a function of the temperature were shown in a previous work [4].

We have found that n is approximately equal to 1 at the temperatures studied, except between 275 and 300°C for Pinaster pine and 285 and 350°C for barley straw. This can be explained by the simultaneous decomposition of the different components at these temperatures.

Equation (6) allow us to obtain the kinetics constant values at each temperature, k_{Si} , from the results obtained in the isothermal experiments.

Figure 1 shows the values of $\log k_{Si}$ versus $1/T$ for Pinaster pine and barley straw. The k_{Si} values for the temperature interval in which the reaction order is not 1 have also been calculated, in an orientative way, as if they would correspond to a first-order equation.

For both materials, two sections of different slope can be observed. At low temperatures, in which the A_S variation with temperature is considerable, the k_{Si} values show an unusual variation. At high temperatures, where A_S tends towards asymptotic values, i.e. there is little change at this level, the k_{Si} values increase linearly with the reciprocal of the temperature.

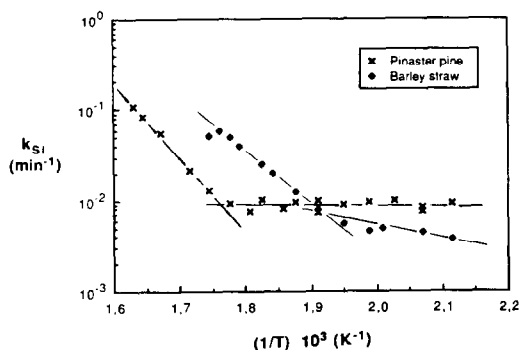


Fig. 1. Values of k_{Si} versus $1/T$ for Pinaster pine and barley straw.

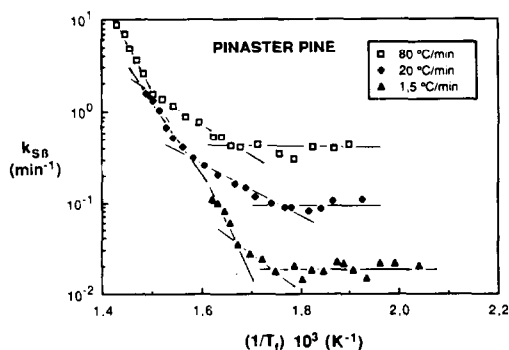


Fig. 2. Values of $k_{S\beta}$ versus $1/T_f$ for Pinaster pine.

Dynamic experiments

The values of the kinetic constant, $k_{S\beta}$, can be obtained at each temperature and heating rate using eqn. (7). These values are shown in Figs. 2 and 3, for Pinaster pine and barley straw, respectively.

It can be observed that, for a given temperature of the system, an increase in the heating rate gives rise to an increase in the kinetic constant obtained. This influence is not so clear for high conversion and temperature values. The increase of the kinetic constant with β , mainly at low temperatures, was also observed with xylan and lignin [3], this effect being the reverse for cellulose [1]. The discrepancy among the values of $k_{S\beta}$ for different β was ascribed to the difference between the temperature of the solid, T , and the temperature measured in the thermogravimetric system. This temperature gap can be minimised by using low heating rates ($1.5^\circ\text{C min}^{-1}$). In the plot of $\log k_{S1.5}$ versus $1/T$ (Fig. 4), several sections of different slope can be observed. The first corresponds to low temperature and conversion values in which the $k_{S1.5}$ values oscillate. For higher temperatures and conversions, a second and third section can be considered and the $k_{S1.5}$ values are fitted to

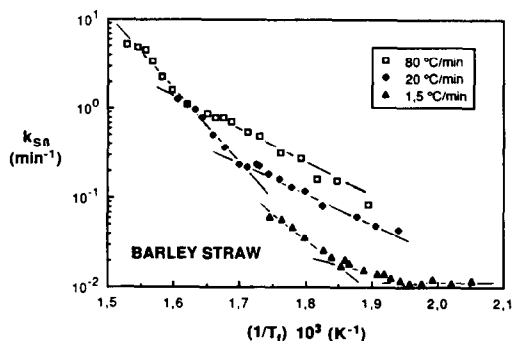


Fig. 3. Values of $k_{S\beta}$ versus $1/T_f$ for barley straw.

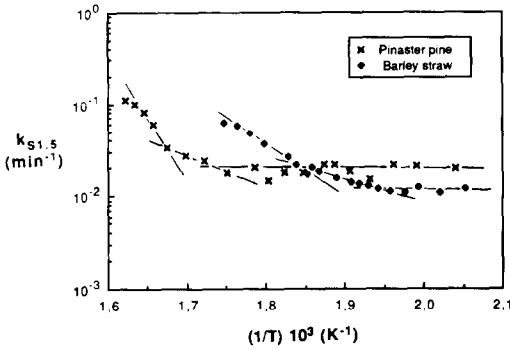


Fig. 4. Values of $k_{S1.5}$ versus $1/T$ for Pinaster pine and barley straw.

corresponding Arrhenius' equations. Thus, for $\beta = 1.5^\circ\text{C min}^{-1}$, the variation of the kinetic constant with the temperature is given by the following.

Pinaster pine

$$\begin{aligned}
 T < 290^\circ\text{C} & \quad k_{S1.5}(\text{min}^{-1}) = 0.017 \text{ (average value)} \\
 290 < T < 325^\circ\text{C} & \quad k_{S1.5}(\text{min}^{-1}) = 3.61 \times 10^4 \exp(-16400/RT) \\
 T > 325^\circ\text{C} & \quad k_{S1.5}(\text{min}^{-1}) = 9.96 \times 10^{17} \exp(-52900/RT)
 \end{aligned}$$

Barley straw

$$\begin{aligned}
 T < 240^\circ\text{C} & \quad k_{S1.5}(\text{min}^{-1}) = 0.0115 \text{ (average value)} \\
 240 < T < 270^\circ\text{C} & \quad k_{S1.5}(\text{min}^{-1}) = 2.49 \times 10^3 \exp(-12500/RT) \\
 T > 270^\circ\text{C} & \quad k_{S1.5}(\text{min}^{-1}) = 4.90 \times 10^8 \exp(-25670/RT)
 \end{aligned}$$

The model previously developed [2] has been applied for the correction of the temperature gap between the solid and the system when high heating rates are used.

The model considers three temperature intervals before reaching the temperature at which the main decomposition takes place. The experimental values of T_{f1} , T_{f2} and T_{f3} are shown in Tables 1 and 2. It can be observed that as β is increased, T_f values also increase, i.e. higher system temperatures are needed to obtain the same temperature in the solid.

Therefore, the increase in the $k_{S\beta}$ values when the heating rate increases can be explained in the fourth temperature interval. The calculation of the solid temperature as a function of the system temperature was carried out using eqn. (8). We have solved this equation considering several temperature ranges and different heats of reaction for each component.

Thus, it was considered that until a solid temperature of 240°C is reached, the main decomposition is due to the hemicelluloses. Equation (8)

TABLE 1
Values of T_{f1} , T_{f2} and T_{f3} for Pinaster pine

Exp.	β ($^{\circ}\text{C min}^{-1}$)	T_{f1} ($^{\circ}\text{C}$)	t_1 (min)	T_{f2} ($^{\circ}\text{C}$)	t_2 (min)	T_{f3} ($^{\circ}\text{C}$)	t_3 (min)
PN-1	80	65	0.375	116	1.0125	212	2.2125
PN-5	80	75	0.500	122	1.0875	218	2.2875
PN-2	40	57	0.550	114.50	1.9875	202	4.1750
PN-3	20	53	0.900	111	3.8000	197	8.1
PN-4	10	47.5	1.250	99.50	6.4500	187	15.2
PN-6	5	49	2.800	93	11.6	177	28.4
PN-7	2.5	38.5	1.400	69	13.6	163.5	51.4
PN-8	1.5	43.4	5.600	68.75	22.5	162	84.7

was solved by numerical methods taking ΔH_{r2} as -362 cal g^{-1} [3]. Above $T = 240^{\circ}\text{C}$, the cellulose decomposition becomes noticeable, and the hemicelluloses and the cellulose decompose simultaneously. We have taken ΔH_{r2} as $-136.6 \text{ cal g}^{-1}$. This is an average value between the reaction heat considered for xylan ($-362.2 \text{ cal g}^{-1}$) and cellulose (88 cal g^{-1}) [5]. This value was assumed to apply until a temperature is reached at which the hemicellulose decomposition is of little importance compared with the cellulose decomposition. This temperature corresponds with an approximate conversion of 0.1843 for Pinaster pine and of 0.27 for barley straw, values corresponding to the weight fraction of hemicelluloses in the materials. Although some hemicelluloses may perhaps remain undecomposed, their influence seems negligible compared with the cellulose decomposition.

At temperatures corresponding to higher X_S values, we should take ΔH_{r2} as 88 cal g^{-1} . However, a previous work [2] did not show significant differences between using reaction heats from 0 to 88 cal g^{-1} for cellulose. Therefore, in this work we have considered it sufficient to use $\Delta H_{r2} = 0 \text{ cal g}^{-1}$, because in this way, the exothermic effect of undecomposed hemicel-

TABLE 2
Values of T_{f1} , T_{f2} and T_{f3} for barley straw

Exp.	β ($^{\circ}\text{C min}^{-1}$)	T_{f1} ($^{\circ}\text{C}$)	t_1 (min)	T_{f2} ($^{\circ}\text{C}$)	t_2 (min)	T_{f3} ($^{\circ}\text{C}$)	t_3 (min)
PC-2	80	69	0.425	135	1.250	235	2.50
PC-3	40	62.5	0.550	122	2.175	215	4.50
PC-4	20	50	0.750	118.5	4.175	202	8.35
PC-6	10	48	1.300	115	8.0	193	15.80
PC-7	5	43.5	1.700	118	16.600	184	29.80
PC-5	2.5	41.5	2.600	85.5	20.200	-	-
PC-1	1.5	39.5	3.0	78.2	28.800	177.2	94.80

luloses and of lignin starting its decomposition (at high temperatures and conversions) can be absorbed.

The kinetic constants can then be calculated for the corresponding solid temperatures. At high temperatures, similar values of $k_{S\beta}$ were obtained at the same solid temperature for different heating rates, but different values were obtained at low temperatures. To explain this disagreement, eqn. (11) was applied. Thus, the values of $(\partial X_S/\partial T)_t$ were determined from the experimental data at different heating rates, considering the $k_{S1.5}$ experimental values. The A_S values change with solid temperature according to a previous work [4].

An analysis of the $(\partial X_S/\partial T)_t$ values obtained for $\beta = 80, 40$ and $20^\circ\text{C min}^{-1}$ has allowed us to obtain two average values for Pinaster pine and barley straw. The first value, 0.0017, corresponds to low conversion and temperature values, and has been identified with the hemicellulose decomposition. The second value, 0.0039, corresponds to higher conversion and temperature values and has been identified with the decomposition of various components.

Using these values eqn. (11) can be expressed as follows.

Pinaster pine ($T < 290^\circ\text{C}$) and barley straw ($T < 270^\circ\text{C}$)

$$(dX_S/dt)_\beta = k_{S1.5}(A_S - X_S) + 0.0017(\beta - 1.5) \quad (12)$$

and

Pinaster pine ($T > 290^\circ\text{C}$) and barley straw ($T > 270^\circ\text{C}$)

$$(dX_S/dt)_\beta = k_{S1.5}(A_S - X_S) + 0.0043(\beta - 1.5) \quad (13)$$

Figures 5 and 6 show the comparison of the values of dX_S/dt obtained experimentally with the results calculated with eqns. (12) and (13). Although the data show some dispersion, the fitting can be considered satisfactory.

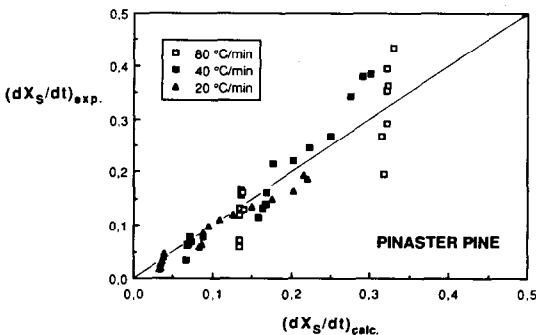


Fig. 5. Experimental and calculated values of dX_S/dt for Pinaster pine.

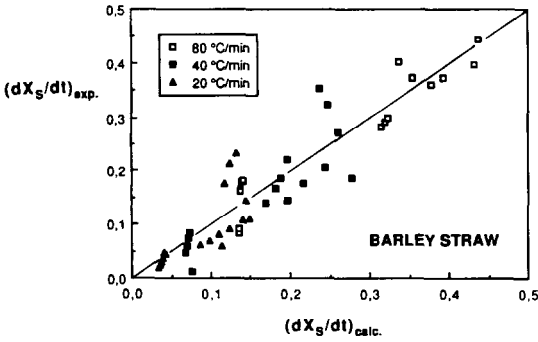


Fig. 6. Experimental and calculated values of dX_S/dt for barley straw.

The differences, as with xylan and lignin, are higher when β increases, due to the greater influence of the term $(\partial X_S/\partial T)_t$, $(\beta - 1.5)$.

The results obtained from isothermal and dynamic experiments with low heating rate ($\beta = 1.5^\circ\text{C min}^{-1}$) have been related using eqn. (10).

The study of both materials was performed in the temperature range where the k_{Si} and $k_{Si,1.5}$ values present larger differences, i.e. $T < 280\text{--}290^\circ\text{C}$ for Pinaster pine and $T < 260\text{--}265^\circ\text{C}$ for barley straw.

The values of $(\partial X_S/\partial T)_t$ were calculated from the experimental values of k_{Si} , A_S and $(dX_S/dT)_{1.5}$. It is possible to relate the results obtained from the isothermal and dynamic ($\beta = 1.5^\circ\text{C min}^{-1}$) experiments using the following expressions.

Pinaster pine

$$(dX_S/dt)_{1.5} = k_{Si,1.5}(A_S - X_S) = k_{Si}(A_S - X_S) + 0.0012 \times 1.5 \quad (14)$$

and

Barley straw

$$(dX_S/dt)_{1.5} = k_{Si,1.5}(A_S - X_S) = k_{Si}(A_S - X_S) + 0.0014 \times 1.5 \quad (15)$$

In conclusion, as for xylan and lignin, the results obtained with different lignocellulosic materials in isothermal and in dynamic experiments with different values of β can be related using the results obtained with $\beta = 1.5^\circ\text{C min}^{-1}$ as a reference.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to C.A.I.C.Y.T. for providing financial support for this work (Project AG-4-84) and to Diputación General de Aragón for a research grant awarded to Angela Millera.

LIST OF SYMBOLS

A_S	pyrolysable weight fraction at a given temperature, dry basis
C_p	specific heat of solid
ΔH_{r2}	heat of reaction for thermal decomposition of the solid
k_S	kinetic coefficient for thermal decomposition of the solid
k_{Si}	kinetic coefficient for thermal decomposition of the solid, obtained from isothermal experiments
$k_{S1.5}$	kinetic coefficient for thermal decomposition of the solid, obtained from dynamic experiments at $\beta = 1.5^\circ \text{C min}^{-1}$.
$k_{S\beta}$	kinetic coefficient for thermal decomposition of the solid, obtained from dynamic experiments
n	order of reaction with respect to the solid
t	time
t_i	time at which the isothermal period starts
t_1	time at which the temperature T_{f1} is reached
t_2	time at which the temperature T_{f2} is reached
t_3	time at which the temperature T_{f3} is reached
T	solid temperature
T_f	oven temperature
T_{f1}	oven temperature at the end of the first interval
T_{f2}	oven temperature at the end of the second interval
T_{f3}	oven temperature at the end of the third interval
W	weight of solid after t seconds of reaction time
W_{0S}	initial weight of solid, dry basis
W_∞	final weight of solid for a given temperature at the end of pyrolysis process
X_S	conversion of solid, dry basis
X_{Si}	conversion of solid at the start of the isothermal period, dry basis
β	heating rate

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