Thermochimica Acta, 143 (1989) 149–159
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF LIGNOCELLULOSIC MATERIALS: INFLUENCE OF THE CHEMICAL COMPOSITION

RAFAEL BILBAO, ANGELA MILLERA and JESÚS ARAUZO

Department of Chemical Engineering, Faculty of Science, University of Zaragoza, 50009 Zaragoza (Spain)

(Received 18 July 1988)

ABSTRACT

The results obtained with different lignocellulosic materials ("Pinaster" pine and barley straw) are compared with those calculated by considering the weighted contributions of the different constituents of the materials. The results obtained in isothermal and dynamic experiments with "Pinaster" pine showed a good agreement, whereas higher divergences were found for barley straw. A different method of data analysis is proposed for barley straw, which uses results directly obtained with this material.

NOTATION

A_S	pyrolysable weight fraction at a given temperature, dry basis
A_C	pyrolysable weight fraction of cellulose, dry basis
A_H	pyrolysable weight fraction of hemicelluloses, dry basis
A_L	pyrolysable weight fraction of lignin, dry basis
k_C	kinetic coefficient for the thermal decomposition of cellulose
k_H	kinetic coefficient for the thermal decomposition of hemicellulose
k_L	kinetic coefficient for the thermal decomposition of lignin
k_S	kinetic coefficient for the thermal decomposition of the solid
t	time
t_i	time at which the isothermal period starts
T	temperature
T_i	temperature of the isothermal pyrolysis
X_C	conversion of cellulose, dry basis
X_{Ci}	conversion of cellulose at the start of the isothermal period
X_H	conversion of hemicellulose, dry basis
X_{Hi}	conversion of hemicellulose at the start of the isothermal period
X_L	conversion of lignin, dry basis
X_{Li}	conversion of lignin at the start of the isothermal period
X_S	conversion of solid, dry basis
Z_{C0}	initial weight fraction of cellulose in the lignocellulosic material, dry basis

0040-6031/89/$03.50

Z_{H0}	initial weight fraction of hemicellulose in the lignocellulosic material, dry basis
Z_{L0}	initial weight fraction of lignin in the lignocellulosic material, dry basis
β	heating rate

INTRODUCTION

The characteristics of the pyrolysis of lignocellulosic biomass are strongly influenced by the chemical composition of the material, i.e. the relative amounts of the main constituents [1]. This composition can be established by the usual analytical techniques, hemicellulose, cellulose and lignin being the main groups involved.

The idea that the pyrolytic properties of a lignocellulosic material can be regarded as some kind of weighted average of the pyrolytic properties of the individual constituents is widely used in the literature. Several authors [1–5] have used this concept in research with a specific material (usually wood) and for a given set of operating conditions. However, these results have not been extended to other operating conditions and materials.

Each component in a lignocellulosic material behaves differently during pyrolysis [6,7]. This makes it difficult to obtain kinetic equations for the thermal decomposition of biomass in a direct way. Therefore, in this work, the study of the thermal decomposition of these materials is addressed by using the rate expressions for its main constituents.

The thermal decomposition of the main constituents of lignocellulosic materials, namely cellulose [6,8], xylan (taken as a representative of hemicellulose) and lignin [7] was studied in previous works. The main results of these studies were: that the kinetics of thermal decomposition of the individual components can be adequately represented by a first-order rate expression; that a temperature gap appears between the solid and the thermogravimetric system when high heating rates are employed; this temperature gap can be accounted for by using the model developed by Bilbao et al. [8], if the corresponding heats of reaction are known; and that if A_s is significantly dependent on temperature, the temperature gap must be taken into account. In addition, the values of $\mathrm{d}X_s/\mathrm{d}t$ for different heating rates, β, must be calculated using equations similar to those obtained for xylan and lignin [7].

In the present work, the results obtained with different materials ("Pinaster" pine and barley straw) are compared with those calculated by considering the weighted contributions of the different constituents of the materials involved. The aim of the study is to attempt the prediction of the overall conversion of a lignocellulosic material of known composition for a given time and operating conditions.

EXPERIMENTAL

The experimental method and data analysis used are similar to those employed for the individual constituents. This allows the comparison of the results obtained with these individual constituents and with "Pinaster" pine and barley straw.

Two different types of experiments have been carried out:

(1) Isothermal experiments. In these experiments, a low preheating rate (1.5 °C min^{-1}) was maintained until the desired reaction temperature was reached. Temperatures between 200 and 350 °C have been investigated.

(2) Dynamic experiments, carried out with different heating rates in the range 1.5–80 °C min^{-1}. These rates were kept constant throughout each dynamic experiment.

A Perkin–Elmer TGS-2 thermobalance was used in both types of experiments.

A small particle size was employed ($-630+297$ μm), in order to avoid intraparticle heat and mass transfer problems. All conversion results are expressed on a dry basis, in order to compare materials with different initial moisture contents.

RESULTS

The kinetics of weight loss in the thermal composition of "Pinaster" pine and barley straw have been determined. However, these results will not be shown in this paper, whose purpose is more specific. As mentioned above, the present work is oriented towards the study of the thermochemical behaviour of lignocellulosic biomass in relation to the weighted contribution of its main constituents.

Thus, the pyrolysable fraction, A_S, and the conversion, X_S, obtained for "Pinaster" pine and barley straw have been related to the corresponding values for the main constituents of both materials. The following equations have been applied

$$X_S = X_H Z_{H0} + X_C Z_{C0} + X_L Z_{L0} \tag{1}$$

$$A_S = A_H Z_{H0} + A_C Z_{C0} + A_L Z_{L0} \tag{2}$$

The validity of the above equations was tested by performing dynamic experiments at a low (1.5 °C min^{-1}) heating rate with mixtures of the pure compounds. Mixtures xylan–cellulose and cellulose–lignin were employed, because in these mixtures there is an overlap in the decomposition intervals of the individual components.

From the evolution of conversion with time for xylan, cellulose and lignin using $\beta = 1.5$ °C min^{-1}, the theoretical conversion for the mixture at a given time can be calculated (eqn. (1)). The values Z_{H0}, Z_{C0} and Z_{L0} are given by

TABLE 1

Chemical composition of the materials used in the study

Weight fraction	Pinaster pine	Barley straw
Hemicellulose Z_{H0}	0.1843	0.27
Cellulose Z_{C0}	0.45	0.45
Lignin Z_{L0}	0.3657	0.22
Ashes	Negligible	≈ 0.06

the proportions of each component in the mixture. The results thus obtained were compared with the experimental conversion data, and a good agreement was observed.

A comparison of these results with the behaviour observed when employing lignocellulosic materials was also determined using the data obtained with xylan, cellulose and lignin for the same experimental conditions. The basis for the comparison was the chemical composition of both materials, which is given in Table 1.

The differences in chemical composition between "Pinaster" pine and barley straw give rise to differences in the evolution of the pyrolysable fraction, A_S, with temperature. Thus, Fig. 1 shows that, at low temperatures, the values of A_S are higher for barley straw than for "Pinaster" pine. This is due to the fact that the content of hemicellulose (which decomposes at low temperatures) is higher for the former. Conversely, at higher temperatures, the decomposition of barley straw is slower. This may be caused by the higher content of ashes and fixed carbon in barley straw, and also by the different nature of the ligninic component in barley straw (which consist mainly of ligninic acid), which shows lower values of A_S than wood lignin [9].

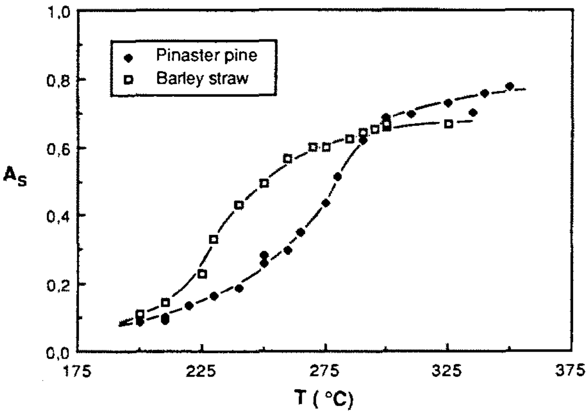

Fig. 1. A_S versus temperature for Pinaster pine and barley straw.

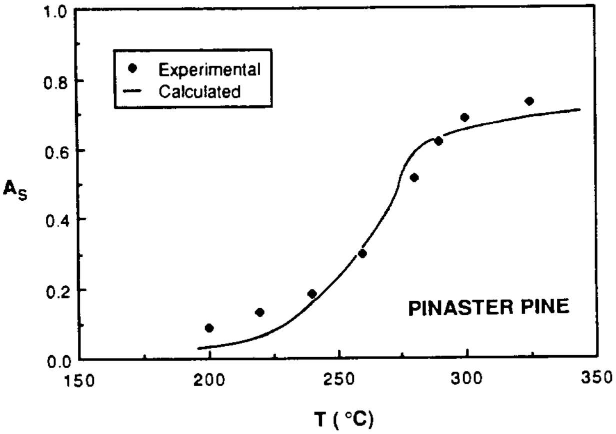

Fig. 2. Calculated and experimental values of A_S for Pinaster pine.

Generally speaking, the results obtained with pine show a satisfactory agreement between the values of X_S and A_S calculated from the main constituents and the experimental ones. However, a noticeable divergence between the experimental and the theoretical values can be observed for barley straw.

Thus, for instance, Figs. 2 and 3 show a plot of the pyrolysable fraction A_S versus temperature for both materials employed; the evolution of conversion with time at a constant temperature of 300 °C is plotted in Figs. 4 and 5. It can be observed that, as mentioned above, there is a good agreement in the experiments with "Pinaster" pine, except for the data obtained at $T < 240$ °C, in which the experimental results are higher than those predicted by eqn. (2). This may be a consequence of taking xylan as a representative specimen for hemicellulose, although it is well known that are other

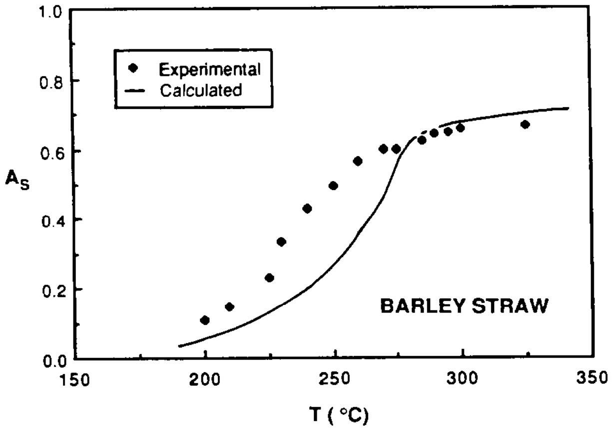

Fig. 3. Calculated and experimental values of A_S for barley straw.

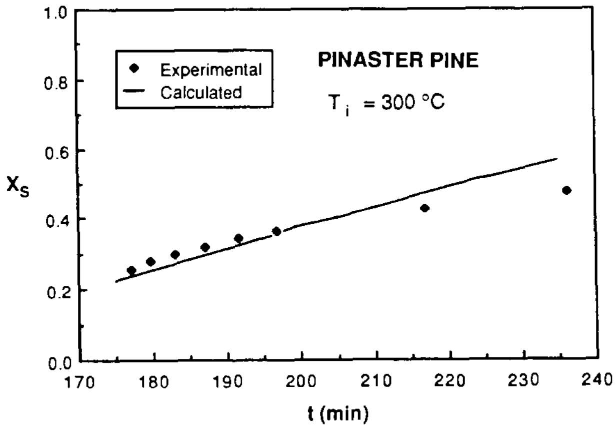

Fig. 4. X_S versus time for Pinaster pine, at 300 ° C.

types of hemicellulose present in pine wood. Besides, the values of A_S obtained for xylan were lower than those expected for the thermal decomposition of hemicellulose [7], which means that lower values of A_S are obtained when calculated at low temperatures, where the main decomposition of hemicellulose takes place.

Figures 6 and 7 show a plot of the evolution with time of the theoretical values of X_S. These were obtained from eqn. (1), using data from dynamic experiments with a low heating rate (1.5 ° C min^{-1}). Similar trends were found when higher heating rates (20, 40 and 80 ° C min^{-1}) were employed. The corresponding experimental data are also shown in these figures for comparison.

The analysis of the results obtained suggested that the main reason for the higher divergences found for barley straw could well lie in the different

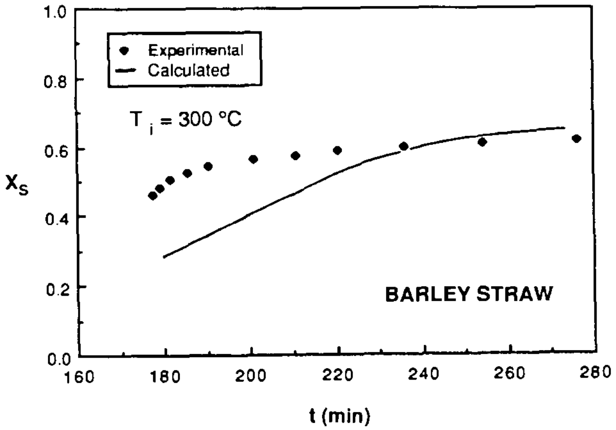

Fig. 5. X_S versus time for barley straw, at 300 ° C.

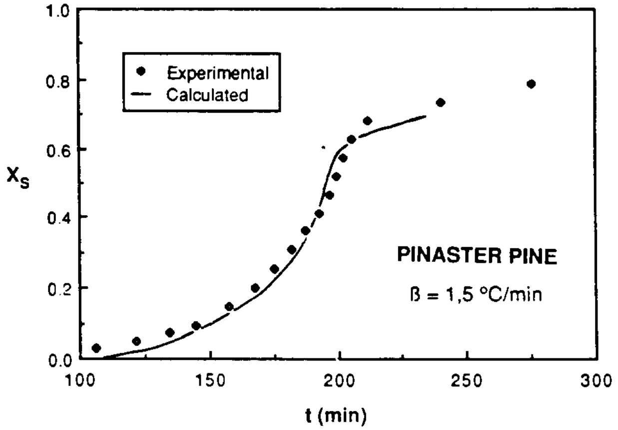

Fig. 6. X_S versus time for Pinaster pine, $\beta = 1.5\,°\mathrm{C\ min}^{-1}$.

nature of its constituents with respect to those of "Pinaster" pine. This seems logical if we take into account the fact that the compounds used in this work as individual constituents were obtained from wood, and therefore their structural units are likely to be more similar to pine than to straw.

For the cases in which there are no data available on the decomposition kinetics of the main constituents of the material or when these have different nature or structure (as in the case of barley straw in this work), a different method of data analysis is proposed, which uses the data obtained directly with the material under study. This method is next applied to barley straw. However, it could in principle be used with any other lignocellulosic material.

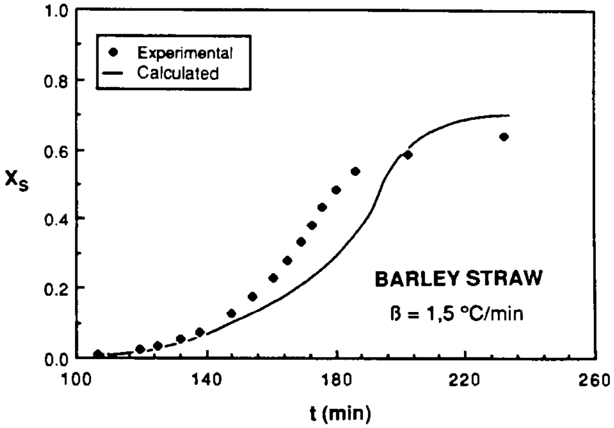

Fig. 7. X_S versus time for barley straw, $\beta = 1.5\,°\mathrm{C\ min}^{-1}$.

DETERMINATION OF THE THERMAL DECOMPOSITION KINETICS FOR THE DIFFERENT CONSTITUENTS OF BARLEY STRAW

The first step of the method proposed consists of determining the values of k_H, k_C and k_L as a function of temperature. These values are calculated from the experiments carried out with barley straw. Once the kinetic coefficients are known, the values of X_H, X_C and X_L can be obtained for different reaction times by assuming first-order kinetics for the thermal decomposition of the individual constituents [6,7]. With the values thus obtained, the overall conversion can be calculated, provided that the chemical composition is known.

The method proposed considers different temperature intervals, in each of which the thermal decomposition of a particular constituent is dominant. Thus, the results obtained in one of these temperature intervals mainly correspond to the decomposition of one of the species involved.

It is obviously difficult to accurately establish the limits of the temperature intervals mentioned above. However, the results published in the literature [3,5,10], and our own results, (especially those concerning the variation of A_S with temperature), suggest different temperature intervals in which the decomposition of one or several constituents is dominant.

According to these studies, the method of calculation of the kinetic coefficients for the different species involved should be as follows.

(a) At $T < 230\,^\circ C$, the decomposition of hemicellulose is dominant. Thus, $k_S \approx k_H$.

(b) At $230 < T < 260\,^\circ C$, both hemicellulose and cellulose decompose. At low values of conversion, the decomposition of hemicellulose is dominant, and some orientative data for k_H can be obtained. At high conversions, the decomposition of cellulose may overcome that of hemicellulose.

(c) At $260 < T < 290\,^\circ C$ the decomposition observed is mainly due to cellulose, $k_S \approx k_C$.

(d) At $T > 290\,^\circ C$, both cellulose and lignin will decompose. The decomposition of lignin is dominant for high values of conversion.

It could be argued that lignin starts degrading at lower temperatures than indicated. This is in fact true. However, when pyrolysing barley straw, the ligninic species present (ligninic acid) does not noticeably decompose until about 290 °C [7].

From the above discussion, it seems clear that the values of k_H and k_C can be obtained by means of isothermal experiments. However, the determination of the kinetic constant for lignin using this procedure is troublesome, because reaching the temperature for the decomposition of lignin in an isothermal experiment with a low preheating rate would imply high values of solid conversion, and therefore few experimental points would be obtained.

Alternatively, as the values of k_S obtained at high temperatures for barley straw in isothermal experiments and in dynamic experiments with a low heating rate are very similar, k_L could also be determined from dynamic experiments carried out at low β, provided that $X_S > 0.6$ i.e. in this case, cellulose and hemicellulose are already pyrolysed and the decomposition observed corresponds to lignin.

Using this procedure, the following results were obtained

$$k_H(\text{min}^{-1}) = 25.75 \exp(-8300/RT) \tag{3}$$

$$k_C(\text{min}^{-1}) = 1.815 \times 10^9 \exp(-27120/RT) \tag{4}$$

$$k_L(\text{min}^{-1}) = 3.77 \times 10^7 \exp(-26750/RT) \tag{5}$$

Because each of the different constituents decomposes following first-order kinetics, the above equations can be used for the calculation of X_H, X_C and X_L for the temperatures in which several of these compounds decompose simultaneously. This requires the use of the following assumptions

(a) For the temperature at which hemicellulose and cellulose undergo simultaneous decomposition, $T < 290\,°\text{C}$.

At the start of the isothermal period the conversion observed is mainly due to hemicellulose. This is further confirmed by the low values of conversion obtained at this stage. Thus we can consider $X_{Ci} \approx 0$, and the value of X_H at the start of this period, X_{Hi}, can be obtained. At $230 < T < 290\,°\text{C}$, $A_H \approx 1$, and A_C can be determined.

With the above considerations, the variation of X_H and X_C with time for a given temperature can be obtained from

$$X_H = 1 - \exp[\ln(1 - x_{Hi}) - k_H(t - t_i)] \tag{6}$$

$$X_C = A_C - \exp[\ln A_C - k_C(t - t_i)] \tag{7}$$

where t_i represents the time corresponding to X_{Hi}, and k_H and k_C are given by eqns. (3) and (4).

Once the variation in X_H and X_C is known, the overall conversion of barley straw is given by eqn. (1). As an example, Fig. 8 shows the experimental and calculated values for a temperature of 250 °C. The agreement observed is very satisfactory.

(b) For temperatures in which joint decomposition of cellulose and lignin takes place, $T > 290\,°\text{C}$.

At the start of the isothermal period $X_{Hi} \approx 1$, $X_{Li} \approx 0$ and X_{Ci} can be calculated from eqn. (1). $A_H \approx 1$, and A_L can be obtained from the plot of the pyrolysable fraction of ligninic acid versus temperature [9]. Thus, using eqn. (2), A_C can be calculated for a given temperature.

With the above assumptions, the integration of the kinetic equations for cellulose and lignin yields the values of X_C and X_L, according to

$$X_C = A_C - \exp[\ln(A_C - X_{Ci}) - k_C(t - t_i)] \tag{8}$$

$$X_L = A_L - \exp[\ln A_L - k_L(t - t_i)] \tag{9}$$

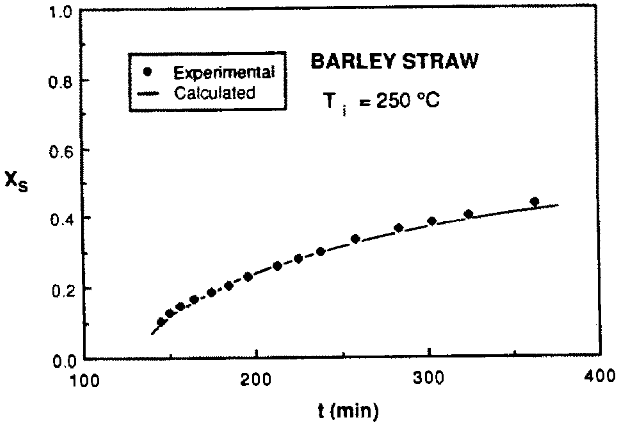

Fig. 8. Experimental and calculated variation of X_S with time, $T_i = 250\,^\circ$C.

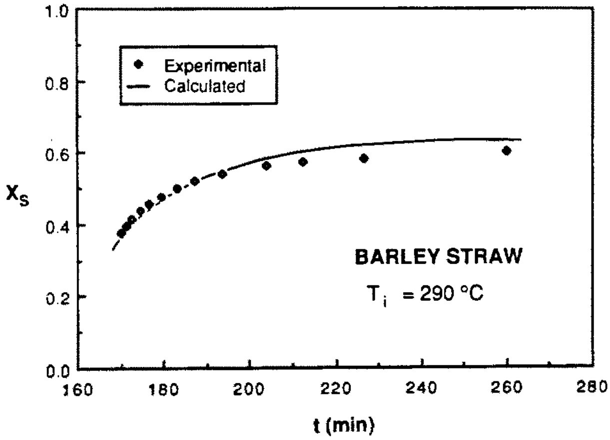

Fig. 9. Experimental and calculated variation of X_S with time, $T_i = 290\,^\circ$C.

where t_i now corresponds to X_{Ci}, and k_C and k_L are given by eqns. (4) and (5).

The variation of X_s with time for the thermal decomposition of barley straw can be obtained from eqn. (1). For instance, Fig. 9 shows the calculated and experimental values obtained at 290°C. Again, a good agreement can be observed.

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.

REFERENCES

1 F. Shafizadeh, J. Anal. Appl. Pyrol., 3 (1982) 283.
2 A.F. Roberts, Combust. Flame, 14 (1970) 261.
3 R.G. Graham, M.A. Bergougnou and R.P. Overend, J. Anal. Appl. Pyrol., 6 (1984) 95.
4 D.H. Slocum, E.A. McGinnes Jr. and F.C. Beall, Wood Sci., 11 (1) (1978) 42.
5 F.L. Browne, FPL Report 2136, Forest Products Laboratory, Madison WI, 1963.
6 R. Bilbao, J. Arauzo and A. Millera, Thermochim. Acta, 120 (1987) 121.
7 R. Bilbao, A. Millera and J. Arauzo, Thermochim. Acta, 143 (1989) 137.
8 R. Bilbao, J. Arauzo and A. Millera, Thermochim. Acta, 120 (1987) 133.
9 F. Shafizadeh, G.D. McGinnis, Carbohydr. Res., 6 (1971) 273.
10 M.V. Ramiah, J. Appl. Polym. Sci., 14 (1970) 1323.