

## ON THE KINETICS OF THERMAL DECOMPOSITION OF WOOD AND WOOD COMPONENTS

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### ABSTRACT

A kinetic analysis of the thermal decomposition of eucalyptus sawdust, cellulose and eucalyptus kraft lignin has been accomplished from temperature-programmed reaction experiments, using two different approaches: the first assumes an overall reaction model, whereas in the second, pyrolysis is viewed as a process consisting of multiple reactions in parallel and a distribution of activation energies is derived. The results obtained reveal that the simple first approach, which leads to overall values of the apparent kinetic parameters allows a fairly good reproduction of the experimental curves, although in the case of wood a two-stage analysis was necessary. No improvement was noticed with the use of activation energy distribution functions resulting from the multiple reaction treatment, except for cellulose and lignin at high conversion, whereas the steep region of the weight-loss curve for cellulose is better described with the overall reaction model.

### INTRODUCTION

Carbonisation is a conversion route of technical interest for lignocellulosic wastes, which are useful feedstocks for char and activated carbon manufacture. A knowledge of the kinetics of the process has great importance for a correct design and product yield control. Although the corresponding limitations, derived from significant differences in operating conditions, such as heating rate, sample volume and particle size, must be considered, thermogravimetric analysis provides a feasible way to accomplish preliminary kinetic studies on the thermal decomposition of solids. In fact, this technique has been widely used to investigate the pyrolysis of wood and wood components [1–7], giving rise to a diversity of results arising from the adoption of different approaches and kinetic models as well as from different experimental conditions.

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In a previous work [8], we presented a discrimination study regarding the pyrolysis of holm oak wood, where different kinetic models were analysed from dynamic and isothermal weight-loss curves. According to the results obtained, the first-order homogeneous volume reaction model provided a fairly good description of the process in our experimental conditions, being the best-fitting model, although a full discrimination became less evident from the dynamic than from the isothermal curves.

Our interest in this paper is to analyse the kinetic behaviour of wood and its two main components, cellulose and lignin, during thermal decomposition in an inert atmosphere, from temperature-programmed reaction (TPR) experiments using two different approaches. The first assumes an overall reaction model and the TG curves are analysed by the integral method, whereas the second considers thermal decomposition as a process involving multiple reactions in parallel and enables the activation energy distribution function to be obtained from the corresponding weight-loss curve.

## KINETIC ANALYSIS

Assuming an overall reaction model for the thermal decomposition of a solid sample, the kinetic equation in non-isothermal conditions can be expressed by

$$d\alpha/dt = \beta(d\alpha/dT) = A \exp(-E/RT) f(\alpha) \quad (1)$$

where  $\alpha$  represents the solid conversion, defined as the actual weight loss (dry basis) with respect to the ultimate, which was taken as that achieved at the final temperature (900 °C).  $E$  and  $A$  correspond, respectively, to the apparent activation energy and the pre-exponential factor for the overall reaction,  $\beta$  is the linear heating rate and  $f(\alpha)$  has been taken as  $1-\alpha$ , which corresponds to the first-order homogeneous volume-reaction model.

To apply the integral method, different approximate analytical solutions have been proposed to integrate the exponential term of eqn. (1) [9–11] but their validity becomes dependent on the  $T$  and  $E$  values.

In this work, eqn. (1) was numerically integrated by means of the fourth-order Runge–Kutta method. A Marquardt routine has been used to optimise the  $A$  and  $E$  values leading to the minimum sum-of-the-squares of residuals between the experimental and calculated conversion values.

If the assumption is made that the thermal decomposition of the sample takes place through a multiple parallel reactions scheme, a distribution function for activation energy can be defined by

$$W_{i0} = W_0 f(E) dE \quad (2)$$

$$\int_0^\infty f(E) dE = 1 \quad (3)$$

where  $W_0$  corresponds to the total pyrolysable matter initially present, and  $f(E) dE$  is the fraction of it having a pyrolysis activation energy between  $E$  and  $E + dE$ , corresponding to the  $i$ th component.

Hashimoto et al. [12] developed a method which allows the calculation of the  $f(E)$  versus  $E$  values and the construction of the activation energy distribution function from one experimental TG curve obtained at a known heating rate.

## EXPERIMENTAL

The raw materials used in this work were eucalyptus rostrata wood (65–80 mesh powdered sawdust) obtained from a single log of a close-to-20-year-old tree from Malaga (Spain), powdered cellulose was from Sigma Chemical Co. and eucalyptus kraft lignin powder was supplied by ENCE S.A. as obtained from acid ( $H_2SO_4$ ) precipitation of black liquors at its pilot plant in Miranda de Ebro (Spain). The ash content of the lignin sample used in this work was 2.4% and the elemental analysis, as determined with a 240 C Perkin–Elmer Analyzer gave: C = 64.7% and H = 5.3% (dry ash-free basis). An average sulphur content of 0.9% was measured using a Julius–Peter apparatus.

The TG curves were obtained in a model Thermoflex Rigaku thermobalance. The initial sample weight was always adjusted close to 15 mg and a 70 ml  $min^{-1}$  (STP) certified  $N_2$  flow was continuously passed. The thermogravimetric experiments were carried out in a non-isothermal regime at a linear heating rate of  $5^\circ C min^{-1}$  for cellulose and lignin, and at 5, 10 and  $20^\circ C min^{-1}$  for wood.

Prior to the TG runs, the samples were dried overnight at  $60^\circ C$  and  $10^{-2}$  Torr.

## RESULTS

Figures 1–3 show the experimental TG curves for cellulose, lignin and wood ( $\beta = 5^\circ C min^{-1}$ ), respectively. The corresponding DTG curves are also included. The conversion versus temperature plots can be easily derived from the represented weight-loss curves.

As can be seen, the major thermal decomposition for cellulose occurs within a steep region ranging from 300 to  $380^\circ C$ , where an 83% (5–88%) weight-loss takes place. This leads to a DTG curve showing a single narrow peak. The ultimate char residue becomes 6.5% of the initial sample. These results are quite similar to those obtained by other authors [13,14] in somewhat different but comparable operating conditions.

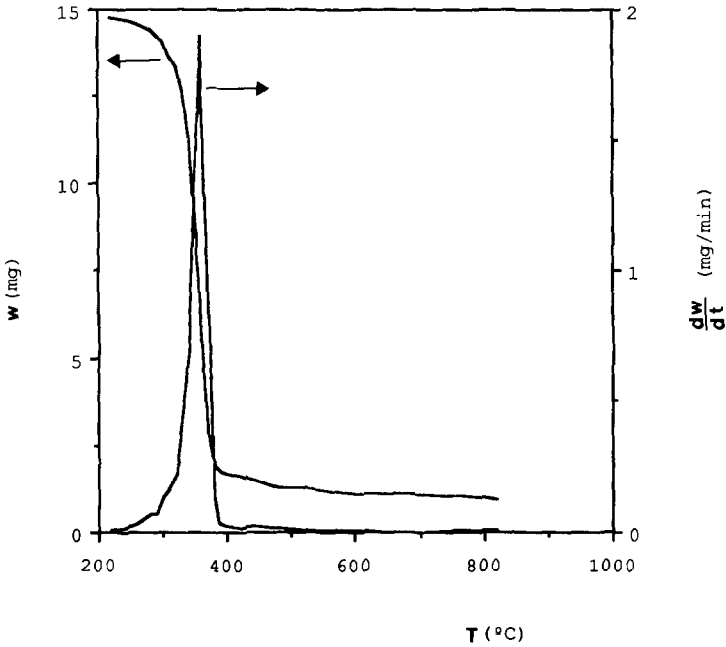


Fig. 1. TG and DTG curves of cellulose at  $\beta = 5^\circ \text{C min}^{-1}$ .

In the case of lignin, the weight loss extends over a substantially wider temperature range, covering the 200–550 °C region, where several peaks can be noticed on the DTG curve. Above 600 °C the weight loss becomes of very

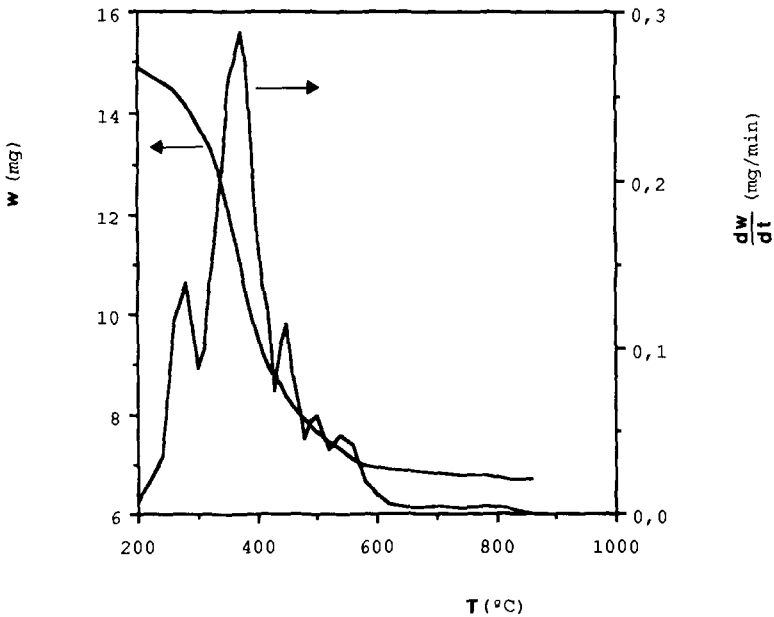


Fig. 2. TG and DTG curves of eucalyptus kraft lignin at  $\beta = 5^\circ \text{C min}^{-1}$ .

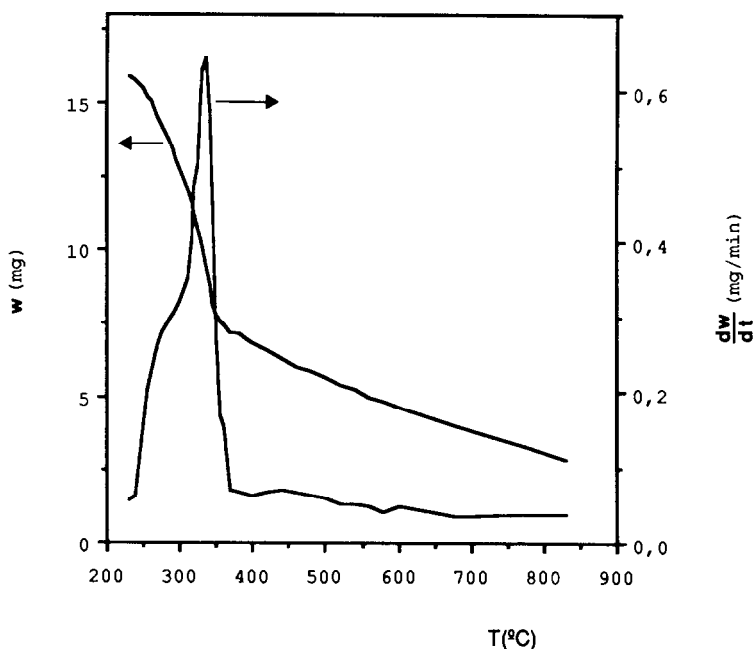


Fig. 3. TG and DTG curves of eucalyptus sawdust at  $\beta = 5^{\circ}\text{C min}^{-1}$ .

small significance, the ultimate solid residue being 45% of the initial sample, substantially higher than that resulting from cellulose and in agreement with that obtained by other authors for lignin samples [15,16].

Eucalyptus sawdust exhibits a main loss-region throughout the 250–360 °C temperature range, which is displaced to somewhat higher values as  $\beta$  increases. A 51–55% weight loss occurs within this region, depending on the heating rate. The latter decay branch, leading to a 14% final residue at 900 °C, does not exhibit a plateau pattern as in the cases of cellulose and lignin although a decreasing slope is observed as the temperature increases. These results compare well with those obtained by us with holm oak wood [8]. The 14% residue at 900 °C is consistent with the cellulose and lignin yields at this temperature and their percentages in eucalyptus wood (including hemicellulose as cellulose). The DTG curve for eucalyptus sawdust shows a single peak, as in the case of cellulose, but starting at a lower temperature with a shoulder-like region.

#### *Overall reaction model: kinetic parameters*

Using the first-order homogeneous volume reaction model as an overall rate equation for the entire conversion range, we obtained the results reported in Table 1 for cellulose and lignin. The small values obtained for the pre-exponential factor and apparent activation energy in the case of

TABLE 1

Kinetic parameters for cellulose and lignin pyrolysis using the overall reaction approach

	$A$ ( $s^{-1}$ )	$E$ ( $kJ\ mol^{-1}$ )	Sum of the squares of residuals	Number of points
Cellulose	$4.7 \times 10^{12}$	182.7	0.0245	33
E. kraft lignin	0.655	36.7	0.0433	37

eucalyptus kraft lignin compare consistently with those reported by other authors for different kinds of lignins [4,17]. Bilbao et al. [7] obtained a combination of  $A$  and  $E$  values for the thermal decomposition of eucalyptus kraft lignin substantially different than the one presented in this paper, but the resulting values of the apparent kinetic constant become reasonably comparable within the characteristic thermal range of the pyrolytic process.

In the case of wood, a relatively poor fit was obtained, mainly in the conversion region above 0.6 when using single values of the apparent kinetic parameters throughout the entire conversion range. Thus, a two-stage approach was used to analyse the weight-loss curves. The conversion value corresponding to the breakpoint was optimised by iterations. Table 2 reports the results obtained at each heating rate investigated. As can be observed, close values of the apparent kinetic parameters corresponding to each stage were derived at different heating rates which confirms the validity of the simple approach investigated.

#### *Activation energy distribution functions*

From the assumption that pyrolysis involves the occurrence of multiple reactions in parallel, the activation energy distribution functions for the thermal decompositions of cellulose, lignin and eucalyptus sawdust have been obtained. They are shown in Fig. 4 for  $\beta = 5^\circ C\ min^{-1}$ .

As can be seen, the pyrolysis of cellulose gives a narrower distribution than that of lignin or wood: it exhibits a relatively sharp peak in the 80–95 kJ

TABLE 2

Results obtained for wood pyrolysis from the two-stage overall reaction approach:  $A$  ( $s^{-1}$ ) and  $E$  ( $kJ\ mol^{-1}$ )

Heating rate ( $^\circ C\ min^{-1}$ )	Conversion at the breakpoint	1st stage		2nd stage		Sum of the squares of residuals	Number of points
		$A$	$E$	$A$	$E$		
5	0.57	$1.14 \times 10^6$	101.8	$2.07 \times 10^{-3}$	12.5	0.0509	65
10	0.61	$1.14 \times 10^6$	101.2	$3.77 \times 10^{-3}$	12.2	0.0303	58
20	0.64	$1.2 \times 10^6$	98.6	$8.0 \times 10^{-3}$	12.1	0.0210	43

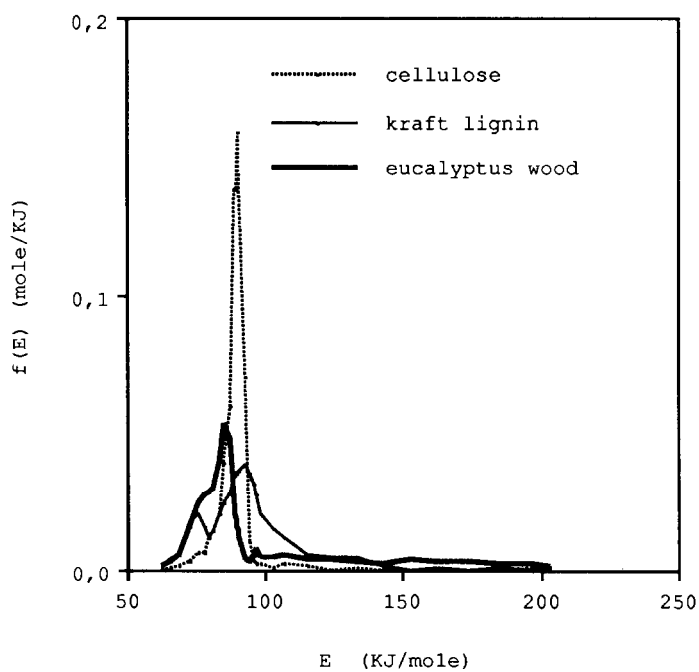


Fig. 4. Activation energy distribution curves of cellulose, lignin and eucalyptus sawdust for  $\beta = 5^\circ\text{C min}^{-1}$ .

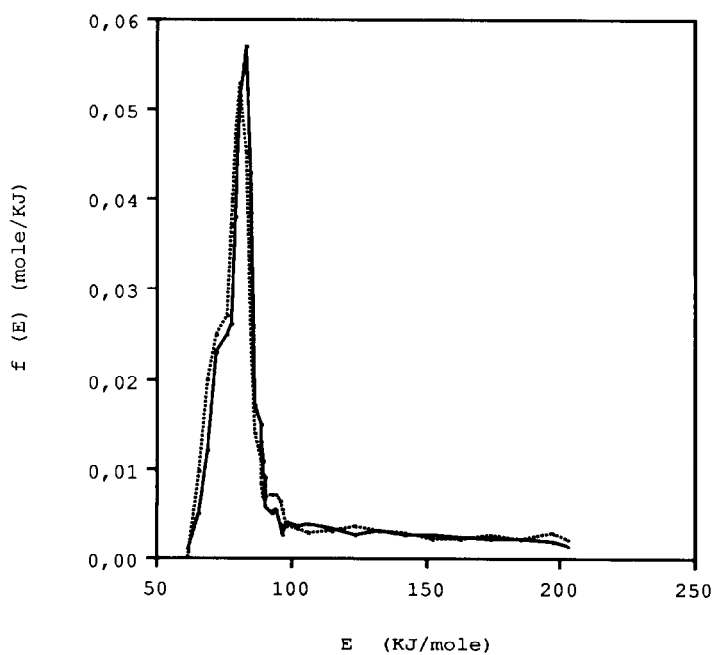


Fig. 5. Activation energy distribution curves of eucalyptus sawdust at  $\beta = 10$  (—) and  $\beta = 20^\circ\text{C min}^{-1}$  (.....).

mol<sup>-1</sup> region with the maximum at  $E = 90.3$  kJ mol<sup>-1</sup>. For lignin, at least three peaks can be recognised. The main one spreads over a broader region ( $\approx 80$ – $105$  kJ mol<sup>-1</sup>) with the maximum placed at  $E = 92.8$  kJ mol<sup>-1</sup>. Wood shows a broad shouldered peak ( $\approx 68$ – $93$  kJ mol<sup>-1</sup>) with the maximum at  $E = 86.3$  kJ mol<sup>-1</sup>.

The distribution functions obtained for wood pyrolysis at the two other heating rates investigated (10 and 20 °C min<sup>-1</sup>) are presented in Fig. 5. As can be seen, they become very similar in shape although a displacement to slightly lower  $E$  values is observed as the heating rate increases.

### *Comparison of the two methods*

A comparison of the experimental conversion versus time curves and the values calculated from the two methods used in this work is presented in Figs. 6–8. As can be seen, both methods provide a fairly good and similar description of the experimental pyrolysis curves in the case of wood, whereas for cellulose and lignin the overall reaction model leads to some upward deviations in the high conversion range which is substantially better described by using the distribution functions of activation energies. Nevertheless, in the steep region of the cellulose curve this second approach

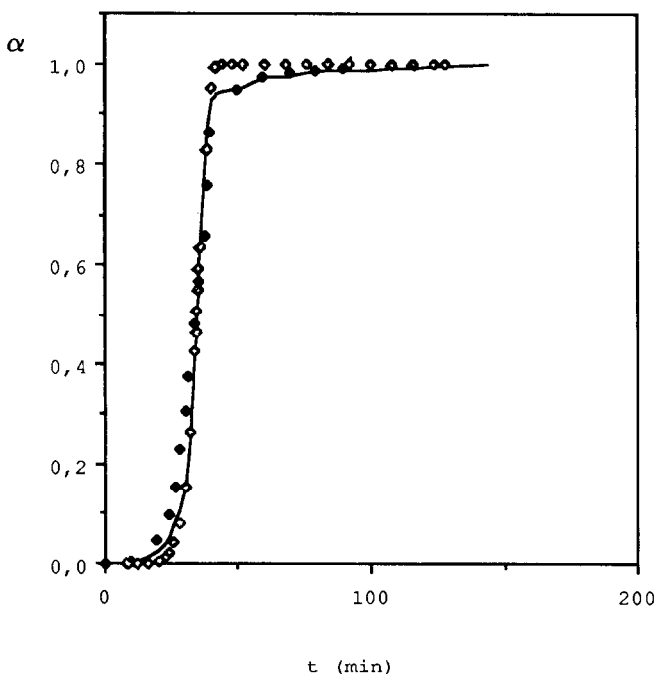


Fig. 6. Conversion versus time values for cellulose: —, experimental;  $\diamond$ , overall reaction model; and  $\blacklozenge$ , multiple parallel reaction model.



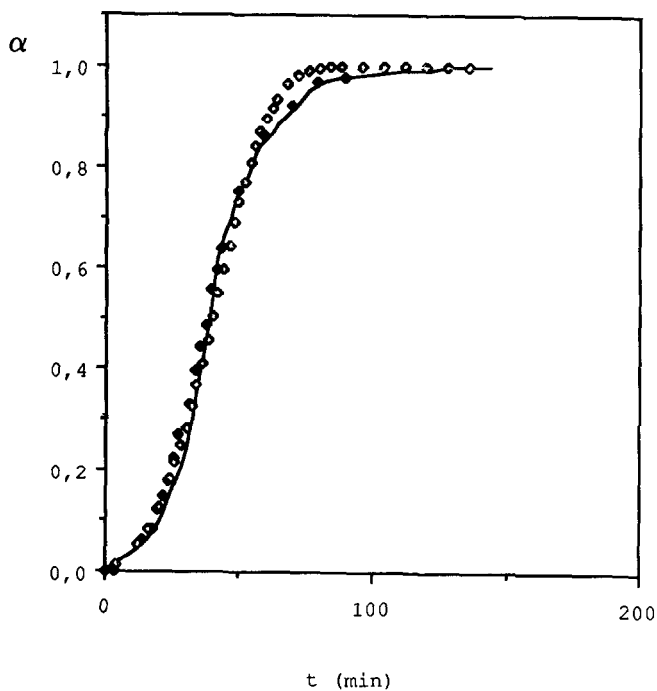


Fig. 7. Conversion versus time for eucalyptus kraft lignin: —, experimental;  $\diamond$ , overall reaction model; and  $\blacklozenge$ , multiple parallel reaction model.

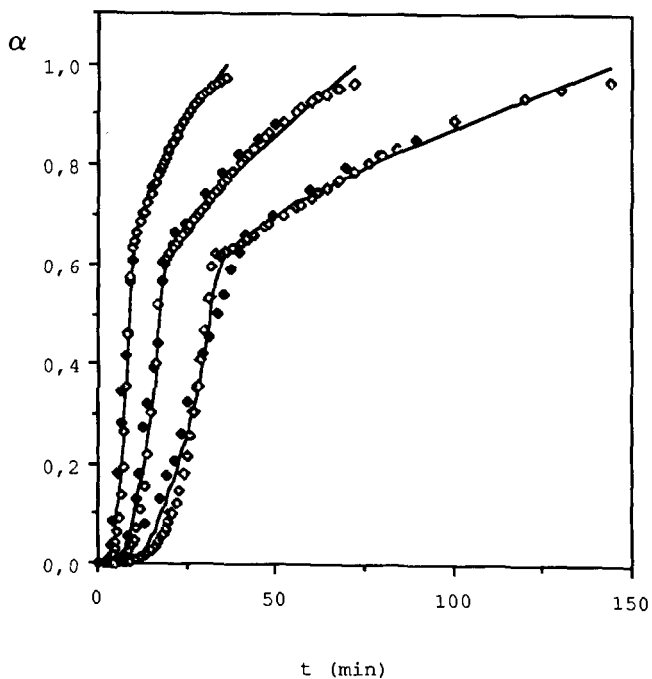


Fig. 8. Conversion-time values for eucalyptus sawdust at the three heating rates investigated: —, experimental;  $\diamond$ , overall reaction model and  $\blacklozenge$ , multiple parallel reaction model.

provides a poorer fit of experimental and calculated  $\alpha-t$  values, thus leading to a higher sum of the squares of residuals (0.121 with 17 points). For lignin, the sum of the squares of residuals between the multiple parallel reactions approach was 0.0227 with 20 points and in the case of wood, 0.0282 with 20 points at  $\beta = 5^\circ\text{C min}^{-1}$ , 0.0202 with 21 points at  $\beta = 10^\circ\text{C min}^{-1}$  and 0.0560 with 15 points at  $\beta = 20^\circ\text{C min}^{-1}$ .

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