

# KINETICS OF THERMAL DEGRADATION OF WOOD AND CELLULOSE BY T.G.A.

## COMPARISON OF THE CALCULATION TECHNIQUES

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### INTRODUCTION :

Kinetics of thermal degradation of cellulosic materials has attracted widespread attention due to its importance in two main fields : synthetic fuel production from biomass and fire research. Usually, the results of kinetic studies have been expressed by means of an overall mass loss rate equation :

$$-\frac{dm}{dt} = A (m - m_f)^n \exp (-E/RT) \quad 1)$$

with  $m$  = mass of material at time  $t$ ,  $m_f$  = final mass,  $T$  = temperature,  $A$  = preexponential factor,  $n$  = reaction order,  $E$  = activation energy and  $R$  = perfect gas constant.

Several reviews (1), (2), (3) have pointed out that there is a great scatter in the values measured for the kinetic parameters :  $A$ ,  $n$  and  $E$ . In particular, activation energies reported for wood are very often lower than those obtained for cellulose.

Recently (4), we have performed thermogravimetric analysis of cellulose and several kinds of woods and we have shown that this discrepancy was mainly related to the use of an overall equation to represent thermal degradation of wood. By calculating the mass variations by means of a simulation model allowing several reactions to be taken into account, we have reproduced with a good precision the experimental thermograms. For wood, in nitrogen, this agreement between experiments and calculations was obtained with a two-step degradation mechanism. The first step starts around 520 K and corresponds to the degradation of the mixture hemicellulose + lignin. The second step is observed around 620 K and is due to the pyrolysis of cellulose.

It is highly interesting to notice that for this second step of wood pyrolysis, the values of the kinetic parameters obtained with pure cellulose could be used.

The methods usually proposed for determining kinetic parameters from thermogravimetric analysis curves are based on the assumption that the mass loss rate can be interpreted by means of an overall equation. In view of the results that we obtained for wood, it was interesting to study how these methods could be applied to a two-step degradation mechanism and compare the precision of the results obtained with different methods. In this paper, we have reported kinetic calculations performed with the most commonly used techniques : FREEMAN and CARROLL (5), maximum point (6), ratio method (7), COATS and REDFERN (8) and BROIDO (9). These calculation techniques have been applied to thermograms measured for pure cellulose and three kinds of woods : fir, poplar and oak, the experiments having been performed under nitrogen.

### EXPERIMENTAL :

A SETARAM thermobalance has been used. This apparatus allows simultaneous

TGA and DTA measurements. It is worth specifying that due to DTA requirements, the thermocouple used to measure the sample temperature was surrounded by the platinum sample holder, so that there is a good coupling between temperature measured by the thermocouple and the sample temperature.

A nitrogen flow rate equals to 120 ml/min has been used, and the heating were respectively : 16.2°C/min (cellulose), 12.9°C/min (oak), 13.0°C/min (fir) and 23.2°C/min (poplar). All the experiments have been performed with initial mass close to 25 mg.

Mass and temperature versus time curves were digitized by means of a H.P. plotter. Transformation and smoothing of the data to mass versus temperature curves and derivative calculations were performed by a H.P. 1000 computer.

## RESULTS AND DISCUSSION :

We have plotted on figure 1 the thermograms obtained with cellulose and the three kinds of woods. Usually, from these curves, a conversion factor is defined by :

$$Y = \frac{m_o - m}{m_o - m_f} \quad (2)$$

with :  $m$  = mass remaining at time  $t$ ,  $m_o$  = initial mass and  $m_f$  = final mass.

The overall kinetic equation is expressed in term of this conversion factor :

$$\frac{dY}{dt} = A (1 - Y)^n \exp (-E/RT) \quad (3)$$

or by using the heating rate :  $\beta = dT/dt$

$$\frac{dY}{dT} = \frac{A}{\beta} (1 - Y)^n \exp (-E/RT) \quad (4)$$

To use this equation for wood, it is necessary to define a conversion factor specific to each step of the degradation mechanism. If the step  $s$  is assumed to be observed between an initial value of the mass :  $(m_o)_s$  and a final value  $(m_f)_s$ , this conversion factor is defined by :

$$Y_s = \frac{(m_o)_s - m}{(m_o)_s - (m_f)_s} \quad (5)$$

These boundary values play an important role, since the variation of  $Y_s$  over a given temperature range can be modified by changing the values used for  $(m_o)_s$  and  $(m_f)_s$  and it can be considered that five kinetic parameters are needed to specify the thermal degradation :  $A$ ,  $n$ ,  $E$ ,  $(m_o)_s$  and  $(m_f)_s$ .

In order to get starting values for these boundary values of the mass, we have used the results obtained in the previous study carried out with the simulation model (4). These results have been reported in table I. When performing these calculations, the following assumptions had been made :

- wood is composed in equal proportion of cellulose and a so called "second component"

- for each component, several reactions can be observed, each reaction occurring between an initial value  $a_o$  and a final value  $a_f$  of the mass ratio  $a = m_k / (m_o)_k$  with  $m_k$  = mass of component  $k$  at time  $t$  and  $(m_o)_k$  = initial mass of component  $k$ .

From the values reported in table I, it can be seen that the first step in the thermal degradation of wood, starting around 520K corresponds to the pyrolysis of the so-called second component, the pyrolysis of cellulose being responsible

for the second step observed at higher temperature. In fact, these two steps are not really successive and a progressive replacement of the first one by the second is rather observed. Owing to this overlapping, it seemed preferable to not use the intermediate part of the thermograms and in the following we have considered that:

- At the beginning of the first step, only the pyrolysis of the second component is observed. Assuming that this component represents 50% of the initial mass of wood and with the values of  $a_f$  reported in table I, the boundary values for the first step are equal to  $m_0$  and  $.7 m_0$ .

- Kinetic parameters of the second step can be calculated accurately only when the pyrolysis of the other component is achieved, so that the initial value of the mass is  $.7 m_0$ , while, from the values of  $a_f$  it is found that the final value is close to  $.33 m_0$ .

In fact, these values have been allowed to vary slightly in order to optimize the results.

In the following we have described the results obtained by applying successively the different methods.

FREEMAN and CARROLL method :

By taking the logarithm of both sides of equation 4 and differentiating with respect to temperature, the following expression is obtained :

$$\frac{d \log (dY/dT)}{d \log (1-Y)} = n - \frac{E}{2.3 R} \frac{d(1/T)}{d \log (1-Y)} \quad 6)$$

By plotting the left hand side versus  $\frac{d(1/T)}{d \log (1-Y)}$  a straight line must be obtained, with a slope equals to  $E/2.3 R$  and an intercept equals to  $n$ . The preexponential factor  $A$  is calculated thereafter by means of equation 4.

To illustrate the precision which can be expected when using this method, we have plotted the results obtained respectively for the first step and the second step of fir pyrolysis on figures 2 and 3. It can be seen on figure 2 that the points corresponding to the lowest values of  $d(1/T)/d \log(1-Y)$  tends to be outside of the straight line, this deviation being due to the beginning of the occurrence of the second step. However, on the main temperature range of each step, the linear relationship is fairly well verified.

The values obtained for the second step of wood pyrolysis and for cellulose pyrolysis (table II) are in good agreement with the values that we calculated previously with the simulation model (table I). For the first step, on the other hand, the activation energies obtained for fir and oak are slightly higher than those calculated previously and some discrepancies are observed in the values of the order of reaction.

It is mainly interesting to notice that these calculations confirm that the kinetic parameters of the second step of wood pyrolysis keep the value obtained with pure cellulose.

A second remark can be done concerning the method of calculation. Due to the properties of logarithms and derivatives, the results are independent of the value chosen for  $(m_0)_s$  and only  $(m_p)_s$  is playing a rôle. For the second step of wood pyrolysis, the value of  $(m_f)_s$  can be known with accuracy since it corresponds to the final value of the mass observed on the thermogram. Therefore, for the second step, the determination of the kinetic parameters by means of this method is not affected by errors resulting of a wrong estimation of the initial value of the mass.

Maximum point method :

From equation 4, the following relationship is obtained between the values

of the parameters corresponding to the maximum conversion rate :

$$E = n \frac{R T_m^2}{(1 - Y_m)} \left( \frac{dY}{dT} \right)_m \quad 7)$$

where  $T_m$ ,  $Y_m$  and  $(dY/dT)_m$  represent respectively the values of the temperature, the conversion factor and the derivative of the conversion factor at the point where the conversion rate is maximum.

The order of reaction is calculated by using one of the following expressions :

$$n = (1 - Y_m)^{(1-n)} \quad \text{if } n \neq 1 \quad 8)$$

$$n = 1 \quad \text{if } (1 - Y_m) = 1/e \quad 9)$$

with  $e =$  basis of neperien logarithm.

The preexponential factor is calculated from equation 4.

This method cannot be applied to the first step of wood pyrolysis, since, due to the overlapping with the second step, there is no maximum in the conversion rate vs temperature curve.

The values obtained for cellulose and the second step of wood pyrolysis are reported in table III.

It can be observed that the kinetic parameters determined for wood are still very close to those calculated for pure cellulose.

However, in addition to its limitation concerning the treatment of the first step of wood pyrolysis, this method suffers a second disadvantage related to its accuracy. A small error in the estimation of the temperature corresponding to the maximum conversion rate entrains a large variation in the values of  $Y_m$ . This is illustrated by the following values measured for fir :

T K	635	636	637
$(dY/dT) K^{-1}$	$2.77 \cdot 10^{-2}$	$2.85 \cdot 10^{-2}$	$2.82 \cdot 10^{-2}$
$Y_m$	.612	.644	.672

Moreover, this method is directly dependent on the values chosen for  $(m_o)_s$  and  $(m_f)_s$  and it can be seen that if the values of  $n$ ,  $A$  and  $E$  obtained for poplar are close to the values calculated with the other methods, the value used for  $(m_o)_s$  seems abnormally elevated.

Ratio method :

This method has been formulated by MICHELSON and EINHORN (7). If equation 4 is written for two values of the temperature  $T_i$  and  $T_j$ , the following expression can be derived :

$$\log \frac{(dY/dT)_j}{(dY/dT)_i} = n \log \frac{(1 - Y_j)}{(1 - Y_i)} + \frac{E}{2.3 R} \frac{T_j - T_i}{T_i T_j} \quad 10)$$

where the subscripts  $i$  and  $j$  mean that the quantities have been measured at temperatures  $T_i$  and  $T_j$ .

If this calculation is repeated for couples of temperature such that the ratio  $r = (1 - Y_j)/(1 - Y_i)$  remains constant, the plot of the left hand side versus  $T_j - T_i/T_i T_j$  must be a straight line of slope equal to  $E/2.3 R$ . The order of reaction is calculated from the value of the intercept.

Values obtained by applying this method (table IV) are in close agreement with those determined with the FREEMAN and CARROLL method for pure cellulose as well as for the two steps of wood pyrolysis.

It is important to notice that the rôle played by the boundary values  $(m_o)_s$  and  $(m_f)_s$  in the calculation of the conversion factor is reduced to a minimum when to ratio<sup>s</sup> method is used. Calculation of the order of reaction involves only  $(m_f)_s$  while, for the activation energy, the values are totally independent of  $(m_o)_s$  and  $(m_f)_s$  since these two quantities vanish when the left hand side of equation 10 is calculated. This method is therefore particularly convenient for the kinetics of wood pyrolysis, especially for the first step, where, due to the relatively small value of the difference  $(m_o)_s - (m_f)_s$ , the conversion factor is very sensitive to a small change in the value estimated for  $(m_f)_s$ .

COATS and REDFERN method :

Equation 4 cannot be integrated directly. However, using an approximation for the integral of the exponential term several expressions can be derived. COATS and REDFERN (8) have obtained :

$$\log \left[ \frac{-\log(1-Y)}{T^2} \right] = \log \frac{AR}{\beta E} \left[ 1 - \frac{2 RT}{E} \right] - \frac{E}{2.3 RT} \quad \text{if } n = 1 \quad (11)$$

$$\text{and } \log \left[ \frac{1 - (1-Y)^{(1-n)}}{T^2 (1-n)} \right] = \log \frac{AR}{\beta E} \left[ 1 - \frac{2 RT}{E} \right] - \frac{E}{2.3 RT} \quad \text{if } n \neq 1 \quad (12)$$

The first term in the right hand side is sensibly constant in the temperature range used in the calculations so that a plot of the left hand side of one of the two equations versus  $1/T$  must be a straight line of slope  $-E/2.3 R$ . The order of reaction is not calculated directly. In fact, the calculations have to be performed using several values of  $n$  in order to retain the value leading to the best linear relationship.

Values calculated with this method are reported in table V.

It can be observed that the values obtained for the activation energy of the second step of wood pyrolysis tend to be lower than the values calculated for pure cellulose. With poplar, it has been necessary to increase the ratio  $(m_o)_2/m_o$  up to .82 in order to obtain a straight line. This value is abnormally elevated even if it lead to satisfactorily results with the maximum point method.

BROIDO method :

Using a different assumption for performing the integration of equation 4, BROIDO derived the following expression, valid only for a first order reaction

$$\log \left( \log \frac{1}{1-Y} \right) = - \frac{E}{2.3 RT} + \text{constant} \quad (13)$$

In view of the results obtained with the other methods for the order of reaction, it has not been possible to apply the BROIDO method to both steps of wood pyrolysis (table VI).

This method and the COATS-REDFERN method, often called integral methods are very sensitive to the values chosen for  $(m_o)_s$  and  $(m_f)_s$  when calculating the conversion factor. This is illustrated by the three curves corresponding to different values of  $(m_o)_s$  for the second step of fir pyrolysis (figure 4).

CONCLUSION :

An examination of the results obtained for cellulose pyrolysis in nitrogen

shows that the five techniques of kinetic calculations lead to results very similar : the mass loss rate can be interpreted in term of one reaction of first order of activation energy close to 250 kJ/mole.

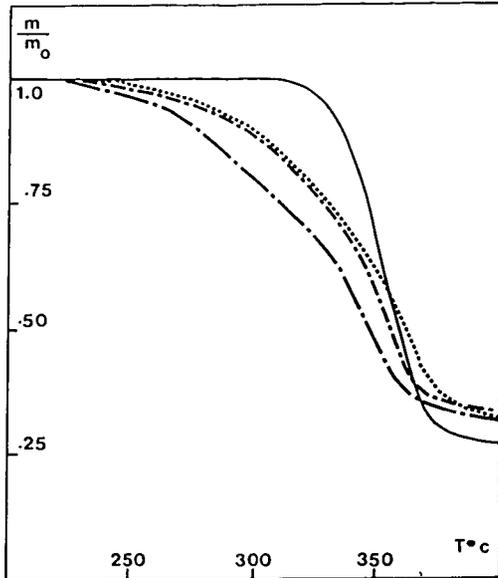
For wood pyrolysis, we have distinguished two steps in the thermograms. By calculating a specific conversion factor for each step it has been possible to apply the same calculation techniques. However, calculation of this specific conversion factor introduces an error related to the estimation of the mass range over which each step is observed. Owing to this fact, the accuracy of the different calculation techniques is directly related to the degree at which the boundary values  $(m_o)_s$  and  $(m_f)_s$  are involved. From this point of view, the FREEMAN and CARROLL method and the ratio method are the most suitable. It is interesting to notice that these two techniques have confirmed that kinetic parameters of the second step of wood pyrolysis, corresponding to the maximum mass loss rate, have the same values than those obtained for pure cellulose.

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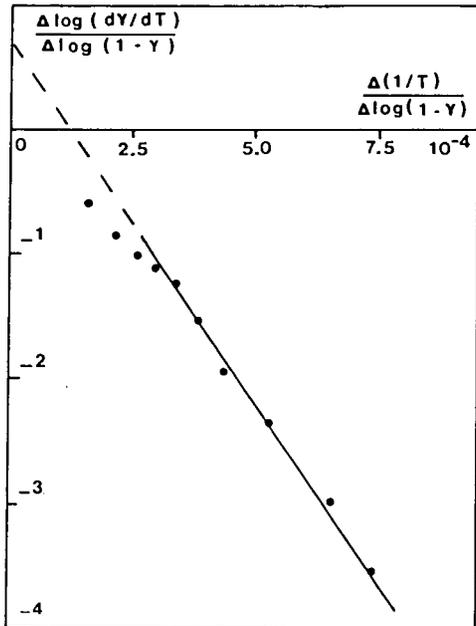
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**Fig. 1** : Thermograms obtained  
in nitrogen  
(120 ml/min)

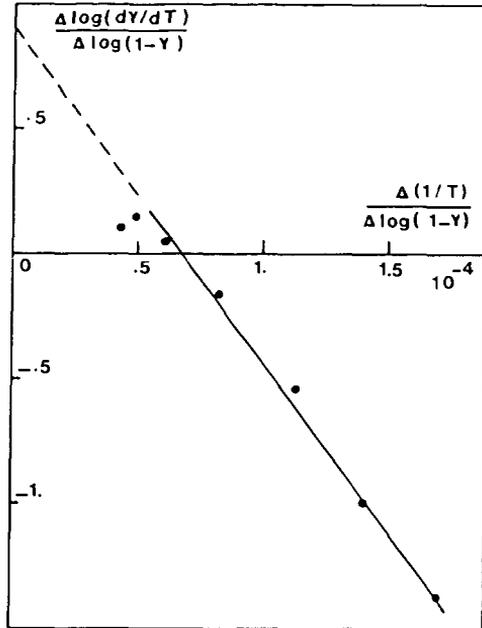
- cellulose (16.2°C/min)
- ..... fir (13.0°C/min)
- - - - poplar (23.2°C/min)
- · — oak (12.9°C/min)



**Fig. 2** : FREEMAN and CARROLL  
method.  
First step of fir  
thermal degradation

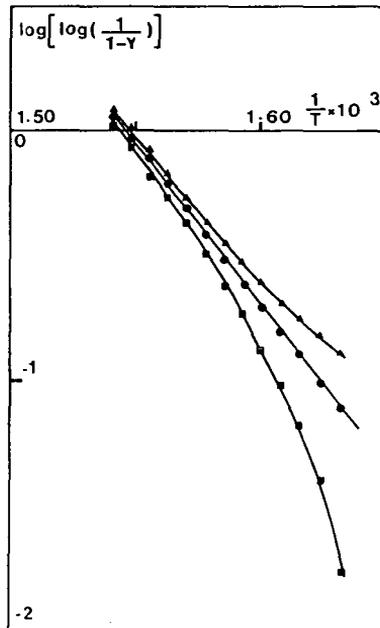


**Fig. 3 :** FREEMAN and CARROLL method.  
 Second step of fir thermal degradation



**Fig. 4 :** BROIDO method.  
 Second step of fir thermal degradation

- ▲  $\frac{(m_o)_2}{m_o} = .7$
- $\frac{(m_o)_2}{m_o} = .75$
- $\frac{(m_o)_2}{m_o} = .8$



material		n	A(s <sup>-1</sup> )	E(kJ/mole)	a <sub>o</sub>	a <sub>f</sub>
cellulose		1	1. 10 <sup>19</sup>	250	1	.29
fir	50% cellulose	1	4. 10 <sup>18</sup>	250	1	.27
	50% 2nd component	1	1.3 10 <sup>5</sup>	84	1	.40
oak	50% cellulose	1	1.4 10 <sup>19</sup>	250	1	.27
	50% 2nd component	1	2.6 10 <sup>5</sup>	84	1	.40
poplar	50% cellulose	1	1.5 10 <sup>19</sup>	250	1	.30
	50% 2nd component	1	2.2 10 <sup>5</sup>	84	1	.40

**Table I** : kinetic parameters obtained in a previous study (4) by means of a simulation model

material		n	A(s <sup>-1</sup> )	E(kJ/mole)	$\frac{(m_o)_s}{m_o}$	$\frac{(m_f)_s}{m_o}$
cellulose		1.1	1. 10 <sup>18</sup>	238	1	.26
fir	1 <sup>st</sup> step	.7	3.4 10 <sup>7</sup>	109	1	.75
	2 <sup>nd</sup> step	.9	1.4 10 <sup>19</sup>	257	.75	.33
oak	1 <sup>st</sup> step	1	1.5 10 <sup>7</sup>	100	1	.73
	2 <sup>nd</sup> step	1.4	3. 10 <sup>19</sup>	253	.73	.33
poplar	1 <sup>st</sup> step	.25	4.3 10 <sup>4</sup>	76	1	.71
	2 <sup>nd</sup> step	1.1	3.9 10 <sup>19</sup>	255	.71	.34

**Table II** : kinetic parameters calculated with the FREEMAN and CARROLL method

material	1- Y <sub>m</sub>	T <sub>m</sub> (K)	n	A (s <sup>-1</sup> )	E (kJ/mole)	$\frac{(m_o)_s}{m_o}$	$\frac{(m_f)_s}{m_o}$
cellulose	.368	630	1	2.3 10 <sup>18</sup>	243	1	.26
fir	.356	636	.93	5.8 10 <sup>18</sup>	252	.75	.33
oak	.430	619	1.4	6.5 10 <sup>20</sup>	269	.73	.33
poplar	.380	626	1.07	7.7 10 <sup>17</sup>	234	.82	.34

**Table III** : kinetic parameters calculated with the maximum point method

material	r	n	A (s <sup>-1</sup> )	E (kJ/mole)	$\frac{(m_f)_s}{m_o}$
cellulose	1.5	1.1	2.9 10 <sup>17</sup>	232	.26
fir	1 <sup>st</sup> step	1.2	5.2 10 <sup>7</sup>	111	.75
	2 <sup>nd</sup> step	2	4.6 10 <sup>18</sup>	250	.33
oak	1 <sup>st</sup> step	1.2	1.5 10 <sup>7</sup>	100	.73
	2 <sup>nd</sup> step	2	1.1 10 <sup>19</sup>	248	.33
poplar	1 <sup>st</sup> step	1.25	2. 10 <sup>4</sup>	72	.71
	2 <sup>nd</sup> step	2	1.7 10 <sup>18</sup>	238	.34

**Table IV** : kinetic parameters calculated with the ratio method

material	n	A (s <sup>-1</sup> )	E (kJ/mole)	$\frac{(m_o)_s}{m_o}$	$\frac{(m_f)_s}{m_o}$	
cellulose	1.1	1.1 10 <sup>20</sup>	263	1	.26	
fir	1 <sup>st</sup> step	.7	9.9 10 <sup>6</sup>	104	1	.75
	2 <sup>nd</sup> step	1	6.3 10 <sup>17</sup>	239	.75	.33
oak	1 <sup>st</sup> step	1	5.9 10 <sup>7</sup>	106	1	.73
	2 <sup>nd</sup> step	1.4	1. 10 <sup>16</sup>	211	.79	.33
poplar	1 <sup>st</sup> step	.3	1.8 10 <sup>5</sup>	83	1	.71
	2 <sup>nd</sup> step	1	3. 10 <sup>15</sup>	205	.82	.34

**Table V** : kinetic parameters calculated with the COATS-REDFERN method

material	n	A (s <sup>-1</sup> )	E (kJ/mole)	$\frac{(m_o)_s}{m_o}$	$\frac{(m_f)_s}{m_o}$
cellulose	1	5. 10 <sup>19</sup>	259	1	.26
fir 2 <sup>nd</sup> step	1	9.1 10 <sup>18</sup>	254	.75	.33
oak 1 <sup>st</sup> step	1	5.5 10 <sup>8</sup>	117	1	.73
poplar 2 <sup>nd</sup> step	1	4.8 10 <sup>16</sup>	220	.82	.34

**Table VI**: kinetic parameters calculated with the BROIDO method