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Assessment of various kinetic models for the pyrolysis of a microgranular cellulose

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Abstract

The kinetics of pyrolysis of a micro-crystalline cellulose in nitrogen were studied from TGA and DTG data, obtained with two different modes of heating: a dynamic mode at constant heating rates between 1 and 11 °C/min and an isothermal mode at various temperatures, kept constant between 280 and 320 °C. In isothermal mode, it appeared very clearly that the mass depletion shows a sigmoid profile characteristic of an auto-accelerated reaction process. This behaviour is consistent with kinetics of nuclei-growth, well represented by the models of Avrami–Erofeev (A–E) and of Prout–Tompkins (P–T) type. All the other kinetic models commonly applied to the thermal decomposition of solids revealed unsatisfactory. The TGA and DTG data were, thus, found ideally simulated from a reaction scheme consisting in two parallel reactions, termed 1 and 2, each one described by the kinetic law: $dx/dt = -A^{-E/RT}x^n(1 - 0.99x)^m$. Reaction 1 is related to the bulk decomposition of cellulose and is characterised by the set of parameters: $E_1 = 202$ kJ/mol; $n_1 = 1$; $m_1 = 0.48$. Reaction 2 is related to the slower residual decomposition, which takes place over approximately 350 °C and affects only 16% by weight of the raw cellulose. With m_2 constrained to 1, the optimised parameters of this reaction were: $E_2 = 255$ kJ/mol; $n_2 = 22$. Finally, the proposed model allowed to correctly fit not less than to 10 sets of ATG–DTG data, isothermal and dynamic.
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1. Introduction

As cellulose is the main component in wood and crops, its thermal degradation has been the subject of extensive research, which remains of interest in the perspective of reducing the energy production from fossil sources and its associated pollution. As a result of seminal research works, due to Kilzer and Broido [1] and Shafizadeh [2], cellulose is assumed to decompose through two parallel or competitive reactions as indicated in Fig. 1.

Results obtained by Broido and other investigators indicated that pre-treatment at lower temperatures yields more char than direct heating at high temperatures. Below approximately 280 °C, the formation of char and permanent gas is assumed to be favoured while above 280 °C, it is the formation of tar, which is favoured, because of the predominant depolymerisation reactions associated to the breakage of gly-

cosidic bonds. Meanwhile, at high heating rate, Lewellen et al. [3] have suggested that there is no char formation as it is practically the case in flash pyrolysis processes, aimed to produce some liquid tar with a maximum yield. Several investigators have developed multi-step kinetic models more or less derived from the original mechanism of Kilzer–Broido. Thus, Bradbury et al. [4] reformulated their original reaction model by introducing an "active cellulose", noted C*, not discernable from the native cellulose in TG analyses, as intermediate between native cellulose and reaction products, according to the reaction scheme:

$$C \longrightarrow C* \begin{array}{c} \nearrow \text{Volatiles} \\ \searrow \text{Char} \end{array}$$
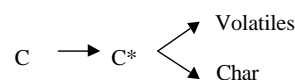
Later, Agrawal [5] proposed a three-reaction model in which it is assumed that cellulose decomposes to tar, char, and gaseous products via three simultaneous reactions. Contrarily to Agrawal, Alves and Figueiredo [6] developed a model with three consecutive first-order reactions. Conesa et al. [7] reported good fits to thermo gravimetric data ob-

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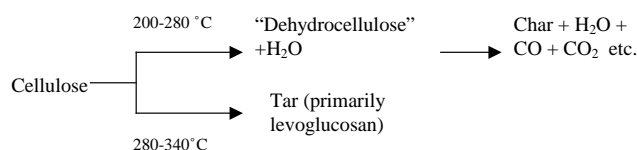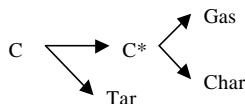*E-mail address:* richard.capart@utc.fr (R. Capart).

Fig. 1. Broido–Shafizadeh reaction scheme for the pyrolysis of cellulose.

tained at three different heating rates, with a multi-step model initially proposed by Agrawal [8], corresponding to the following reaction scheme:

For almost all the multi-step models, each individual reaction is governed by a first-order reaction rate. In some cases, for reactions occurring at low temperature, a zero-order reaction was found [9].

Nevertheless, for the most investigators, the kinetics of cellulose decomposition is not based on multi-step sophisticated models but on a single reaction, expressed in term of mass conversion α by Eq. (1) as

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

The most often the reaction rate is considered of order one and $f(\alpha) = 1 - \alpha$. The rate constant, k, obeys to the Arrhenius law: $k = A \exp(-E/RT)$. For the activation energy E, a large variety of values are reported in literature, between 100 and 250 kJ/mol, however, according to Varhegyi et al. [10], the values in the highest range are the most reliable. From dynamic TG analyses on very small initial masses of cellulose, Antal et al. [11] found optimal values of E approximately between 190 and 250 kJ/mol, depending on the type of cellulose, the heat-up rate and the mass of sample. They largely attribute this variation to a wrong evaluation of the temperature of sample, usually controlled by a thermocouple not directly in contact with cellulose that avoids perturbing the TG signal. In some cases, the pre-exponential factor and the activation energy are reported to be valid within a certain range of temperature; thus, for Tang and Neil [9], 310 °C is a boundary temperature such as E is about 140 kJ/mol for $T < 310\,°C$ and E is about 230 kJ/mol for $T > 310\,°C$. More recently, Milosavljevic and Suuberg [12] have found an opposite trend: E is at maximum 155 kJ/mol when cellulose is heated above 600 K at high heating rate while E is found equal to 218 kJ/mol when cellulose is heated more slowly to temperature below 600 K. According to Antal et al. [11], the non-uniformity of E observed by Milosavljevic and Suuberg is due to serious heat transfer limitations and associated temperature measurement problems.

For most of the investigators, a classical kinetic law of order one is adequate for the thermal decomposition of cellulose; however, in some cases, the pyrolysis of cellulose

was not described by a first-order reaction model but by a kinetic model of auto-accelerated reaction, usually associated to random nucleation or nuclei growth. Thus, Dollimore and Holt [13] achieved a good fit to weight-loss data with the help of an Avrami–Erofeev (A–E) rate equation. Conesa et al. [7] have tested not less than 10$f(\alpha)$ functions. They reported obtaining the best results, as characterised by a low objective function, with a classical first-order rate model ($f(\alpha) = 1 - \alpha$) and also a Prout–Tompkins (P–T) type model [14] ($f(\alpha) = (1 - \alpha)^n \alpha^m$). Unfortunately, Conesa et al., who focused on the modified multi-step model of Agrawal, show no fit to the experimental data by this model. More recently, Reynolds and Burnham [15] proposed a three-parameter Prout–Tompkins type nucleation model as yielding the best fit to the reaction profile of degradation for various cellulosic materials including pure cellulose, crystalline, and fibrous. These investigators gave proof that a nucleation-growth model is far more suited to the cellulose decomposition than a classical first-order model, while giving a narrower profile to the degradation curve, when the temperature rise is linear. They also show that better fits can be obtained with this model for data in the literature than with the first-order models used by those authors.

Despite of the considerable number of research works devoted to the kinetics of cellulose pyrolysis, the definition of the right kinetic model remains controversial. The present paper aims to find out a suitable and rather simple kinetic model from an appreciable number of experiments of mass-loss, carried out following both the heating modes: isothermal and dynamic, contrary to most researchers who restricted their investigations to the dynamic mode.

2. Experimental

The simultaneous TG–DT analyses were carried out with a Setaram TGA 92 apparatus. This apparatus consists in a vertical tube inserted in an oven, which contains a metallic support with two pans. This support is hanged to a micro-balance (sensibility, 1 μg). One of the pans contains the sample of cellulose to analyse, the other is filled with an inert material (alumina) and is used as reference for DTA. Each pan, in platinum, is a cylindrical container with a volume of 100 μl, an internal diameter of about 4 mm and a height of 8 mm. During each TGA–DTA test, the inner of the tube was swept at a flow-rate of 1.5 l/min by a downward stream of N_2, previously purified through a deoxygenating trap. The temperature of oven was regulated via a thermocouple axially fixed in the lower part of the tube while the temperature of sample was taken from a thermocouple in contact with the metallic support of pans. The temperature programming of oven as well as the sampling and treatment of data after analysis were affected via a Setaram Software program. The reliability of sample temperatures was carefully checked from the DTA peaks corresponding to the melting or solidification point of zinc (419.5 °C) and

tin (231.9 °C) at a heating (and cooling) rate of 6 °C/min, so the recalibration of the thermocouple was not necessary. The raw material used in the TGA–DTA analyses was the micro-crystalline cellulose in powder Whatman CC31 (lot n° 9431011; ash content, 0.0033%). The initial mass of cellulose to analyse was essentially in the range 4–7 mg. The same tests were done with larger masses of cellulose, in the range 34–40 mg for comparison. The TG–DT analyses were performed following two modes of heating:

- An *"isothermal" mode*: The oven temperature was increased at 3 or 6 °C/min up to a plateau value between 270 and 310 °C. This plateau is kept for a long time (up to 10 h). Five different temperatures of plateau were tested every 10 °C from 280 to 320 °C. Whereas the essential of the mass loss of cellulose occurred during the plateau, the degradation process could be considered as isothermal.
- A *"dynamic" mode*: This was corresponding to a linear rise in temperature from ambient to 700 °C, and this temperature being then kept in plateau for 1 h. Five different heating rates were tested from 1 to 10 °C corresponding to the following heat-up rates for the sample temperature: 1.05, 2.1, 3.2, 6.5 and 10.9 °C/min.

To eliminate the buoyancy effect, all the experiments, "isothermal" and "dynamic", were repeated with the empty pan and a baseline was thus obtained for the TG–DT analysis. After each experiment, the experimental data of reaction time, temperature, TGA, DTA, DTG signals were transferred into an Excel sheet for further treatment.

2.1. Kinetic models and mathematical treatment of kinetic data

To find the kinetic parameters, particularly the activation energy, when kinetics follow a single expression such as Eq. (1), various methods can be applied. The simplest is certainly the Friedman's method [16], which consists of taking the logarithm of Eq. (1):

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E}{R}\frac{1}{T} + \ln\left[f(\alpha)\right] \tag{2}$$

Plotting $\ln(d\alpha/dt)$ versus $1/T$ at a given conversion yield a straight line of slope $-E/R$.

The isoconversional method of Friedman as defined by Eq. (2) is based on the derivative $d\alpha/dt$ that may lead to erroneous estimates of the kinetic parameters, therefore, some investigators such as Vyazovkin [17] recommend more accurate isoconversional methods, based on the integral itself, i.e. α.

Another popular method is due to Kissinger [18]. It is based on the fact that at the temperature T_p of the DTG peak, i.e. corresponding to the maximum rate of conversion:

$$\left[\frac{d}{dt}\left(\frac{d\alpha}{dt}\right)\right]_{T=T_p} = 0 \tag{3}$$

According to Kissinger, appropriate approximations lead to the simple Eq. (4) derived from Eq. (3):

$$\ln\left(\frac{b}{T_p^2}\right) = -\frac{E}{RT_p} + Cte \tag{4}$$

where b represents the heating rate associated with a linear rise in temperature, $T = bt + T_0$. The plotting of $\ln\left(b/T_p^2\right)$ in function of $1/T_p$ should result in a straight line, of slope $-E/R$. Kissinger's method, while derived originally *n*th-order reaction models, is nevertheless reported as valid in the case of nucleation models.

Unlike the Friedman's method, the method developed by Coats and Redfern [19] is not based on the derivatives $d\alpha/dt$. Owing to a linear rise in temperature, the time variable t is easily eliminated and Eq. (1) can thus be rewritten as

$$\frac{d\alpha}{f(\alpha)} = \frac{k_0}{b}\exp\left(-\frac{E}{RT}\right)dT \tag{5}$$

As the integral $\int\exp(-E/RT)$ has no exact solution, Coats and Redfern recommended to replace $\exp(-E/RT)$ by its Taylor's expansion limited to order one, so that, after integration, Eq. (5) leads to Eq. (6):

$$\int_0^X \frac{d\alpha}{f(\alpha)} = g(\alpha) - g(0)$$
$$= \frac{k_0 R}{bE}T^2\left(1 - \frac{2RT}{E}\right)\exp\left(-\frac{E}{RT}\right)\Bigg|_{T_0}^{T} \tag{6}$$

As the usual values of E lie in the range 130–250 kJ/mol, the term $2RT/E << 1$ can be omitted. With this simplification, Eq. (6) changes into Eq. (7):

$$\ln\left[\frac{g(\alpha) - g(0)}{T^2}\right] = \ln\left(\frac{k_0 R}{bE}\right) - \frac{E}{RT} \tag{7}$$

Plotting $\ln\left[(g(\alpha) - g(0))/T^2\right]$ versus $1/T$ should result in a straight line, the slope of which $-E/R$ and the intercept, respectively, providing the values of E and k_0.

2.2. Experiments in isothermal mode

The TG analyses in isothermal mode were performed at five different temperatures of plateau: every 10 °C between 280 and 320 °C. The weight of cellulose actually starts decreasing when temperature has reached the plateau value. At 320 °C, the cellulose conversion at the beginning of the plateau is only about 5% and for all the tested temperatures below 320 °C the conversion at the beginning of plateau is less than 2.3%. Thus, almost all the cellulose degradation takes place during the plateau and the degradation during the heating-up is negligible. This series of experiments can be therefore qualified as isothermal. The isothermal experiments offer two main advantages: one the one hand, the mathematical treatment of kinetic data is more simple, on the other hand, at the low tested temperatures (<320 °C), the reaction time is long, so that the reaction rate is far more
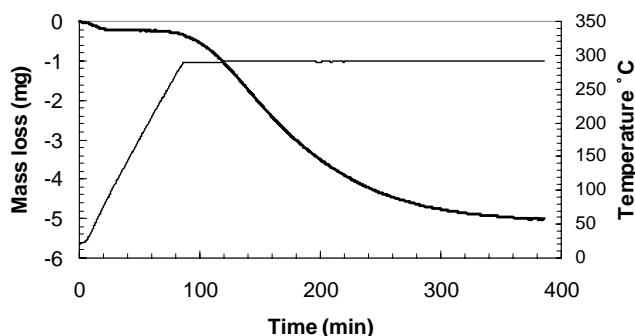
Fig. 2. Mass-loss evolution vs. time in "isothermal" mode.

likely to be controlled by the reaction kinetics rather than by the heat transfer and no thermal lag can be invoked in this kind of experiments.

For all the experiments in isothermal mode between 280 and 320 °C, all the curves of mass-loss have the aspect shown by the figure of exhibiting a slight depression above 200 °C due to the removal of water (the cellulose is dried in situ). When temperature has reached its plateau value, the mass depletion shows a sigmoid shape as it can be seen in Fig. 2, which is undeniably the proof of an auto-accelerated reaction process as that involved in nuclei formation. A classical first-order reaction would have resulted in an exponential decay from the instant zero of the plateau, which is never the case for the TG analyses in isothermal mode. The DTG peak coincides with the maximal reaction rate at the inflexion point of the curve of mass loss. In accordance with the sigmoid shape of the mass depletion (or conversion), the DTG peak comes out a long time after the instant zero. For example, at 280 °C, the lag of the DTG peak from the instant zero is as large as 105 min. This lag decreases with increasing temperatures, so its value is, respectively, 50, 18.3, 12.7, and 4.5 min at the following temperatures: 290, 300,

310 and 320 °C. Whatever the tested temperature, the DTG peak arises at a cellulose conversion comprised in the range 20–25%, i.e. in the early stage of the degradation.

In order to find the better functions among those commonly admitted for the thermal degradation of solids (see Table 1), a good way consists to evaluate the rate constant from the relationship:

$$k = \frac{d\alpha^*}{dt} \frac{1}{f(\alpha^*)} \tag{8}$$

where α^* is the apparent conversion with respect to the degradable part of the raw cellulose, as defined below:

$$\alpha^* = \frac{w_0 - w}{w_0 - w_f} \tag{9}$$

In Eq. (9), w_0 is the initial weight of dry cellulose, w the weight of carbonised cellulose at instant t and w_f is the final weight of carbonised cellulose reached at the end of the TG analysis. Under isothermal conditions and if the chosen $f(\alpha^*)$ function is adequate, the rate constant is actually constant so it does not vary with α^*. Thus, k was calculated and plotted versus α^* for all the types of f functions reported in table, testing the reaction order model with the parameter $n = 0, 1, 2$, the Avrami–Erofeev model with $m = 1.5, 2, 3$, the Prout–Tompkins model with various values of the parameter m between 0 and 1. The most satisfactory results are undeniably obtained by using the nucleation (or auto-accelerated) models, insofar as the rate constant related to these models appears is the more stable. Fig. 3 illustrates this property since the k-values versus apparent conversion α^*, show a rather flat profile when calculated from the Prout–Tompkins model with $m = 0.5$. It can be observed an increase of k in the early stage of reaction, up to about $\alpha^* = 0.2$, followed by a plateau, thus the k-values remain in a narrow range from 6×10^{-4} to $7.3 \times 10^{-4} \text{ s}^{-1}$ when α^* is comprised between

Table 1
Commonly used $f(\alpha)$ functions for solid thermal decomposition reaction

Model	$f(\alpha)$	$g(\alpha)$
Reaction order (n)	$(1-\alpha)^n$	
0		α
1		$-\ln(1-\alpha)$
≥ 2		$[1/(n-1)](1-\alpha)^{1-n}$
Phase boundary reaction		
Cylindrical symmetry	$2(1-\alpha)^{0.5}$	$1-(1-\alpha)^{0.5}$
Spherical symmetry	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
Diffusional		
One-dimensional	$1/2\alpha$	α^2
Two-dimensional	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)[\ln(1-\alpha)]+\alpha$
Three-dimensional spherical symmetry, Jander equation	$1.5(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional spherical symmetry, Ginstling–Brounshtein	$1.5[(1-\alpha)^{-1/3}-1]^{-1}$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
Nuclei-growth		
Avrami–Erofeev ($n = 1.5, 2, 3, 4$)	$n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$	$[-\ln(1-\alpha)]^{1/n}$
Prout–Tompkins	$(1-\alpha)\alpha^m$	
$m = 0.5$		$\ln[(1+\alpha^{0.5})/(1-\alpha^{0.5})]$
$m = 1$		$\ln[\alpha/(1-\alpha)]$
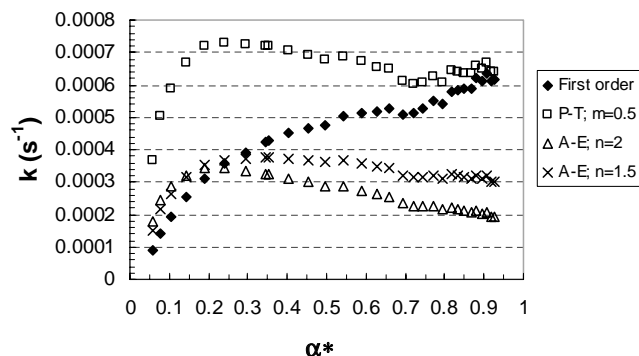
Fig. 3. Effect of the kinetic model on the profile of rate constant vs. apparent conversion.

Fig. 5. Arrhenius plot for the Prout–Tompkins model with $m = 0.5$.

2.3. Experiments in dynamic mode

One series of analyses were effected with initial masses of cellulose within the range 4–7 mg, and another series used larger initial weights of cellulose, i.e. within the range 30–40 mg. Whatever the initial weight of sample, all the conversion curves obtained have a main phase of degradation between approximately 300 and 350 °C, followed by a slower phase, above 350 °C. All the differential thermal analyses show a sharp endothermic peak, which coincides with the DTG peak arising at the maximal rate of mass-loss. In Table 2 are reported the yields in residual solid char as well as the temperatures of DTG peak.

The char yield decreases with the decreasing initial masses of cellulose sample. Thus, a difference of 2–4% can be noted between the char yields obtained from high (30–40 mg) and low initial masses of cellulose. Völker and Rieckman [20] have systematically studied the influence of the initial sample mass on the residual char yield. With a heating rate of 3 K/min, they obtained residual char yields, respectively, varying from 2 to 18% at 800 K, with initial sample masses varying from 1 to 54 mg, i.e. yields slightly lower than in the present work. These investigators concluded that the final char yield increases due to a heat transfer effect. Another explanation is more likely. Increasing the depth of cellulose sample in the cylindrical pan tends to increase the residence time of the volatile tars within the layer of carbonaceous solid, thus enhancing the secondary reactions of pyrolysis. These reactions involve the cracking of tar molecules and the recombination of the produced fragments. They are known

0.15 and 0.9. Moreover, a specific study on the parameter m, allowed to conclude that the optimal value of m lies in the range 0.4–0.6, by considering the shape of profile for the k-values versus α^*. As shown in Fig. 3, a stable rate constant is also obtained from an Avrami–Erofeev model with $n = 1.5$, a value which seems optimal. With $n \geq 2$, the Avrami–Erofeev model is not so suitable. For comparison, in Fig. 3 was drawn the evolution of k versus α^* for the classical first-order kinetic model. It is visible that the resulting rate constant is not stable, showing no flat profile but a continuous increase. As a result, it can be concluded that a first-order kinetic model is not well suited to the degradation of cellulose. Neither the nth-order model with $n \geq 2$ nor the other kind of models, geometric and diffusional, revealed satisfactory results, in regard of the shape of k values versus apparent conversion.

Between 280 and 320 °C, the rate constant resulting from the Prout–Tompkins model with $m = 0.5$ approximately doubles every 10 °C, as illustrated in Fig. 4. Drawn in Fig. 5 with the average value of k calculated between $\alpha^* = 0.2$ and 0.8 for all the five tested temperatures in isothermal mode, the Arrhenius plot of k (i.e. $\ln(k)$ versus $1/T$) yields a value of the activation energy equal to 203 kJ/mol, calculated from the slope of the regression line.
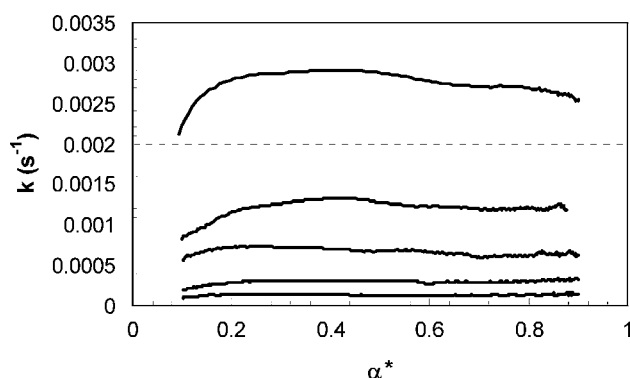

Fig. 4. Rate constant profiles for the Prout–Tompkins model with $m = 0.5$ at various temperatures ($T = 280, 290, 300, 310$ and 320 °C from bottom to top).
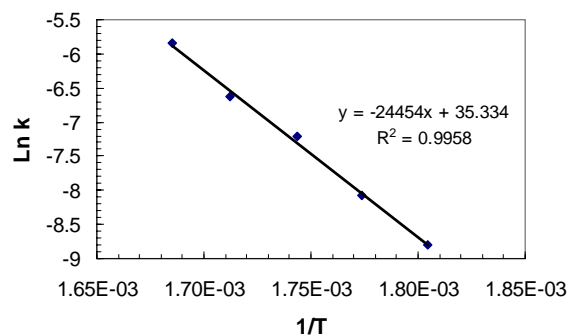
Table 2
Residual char yields at various initial masses of sample

	Rate (°C/min)				
	10.9	6.5	3.2	2.1	1.05
m_0 (mg)	38.35	33.14	33.15	36.38	37.19
Char yield (%)	16.90	16.72	17.04	17.25	16.02
m_0 (mg)	6.30	6.37	6.58	5.84	5.04
Char yield (%)	14.12	12.5	14.15	14.21	13.89
DTG peak (°C)	351	342	332	327	316
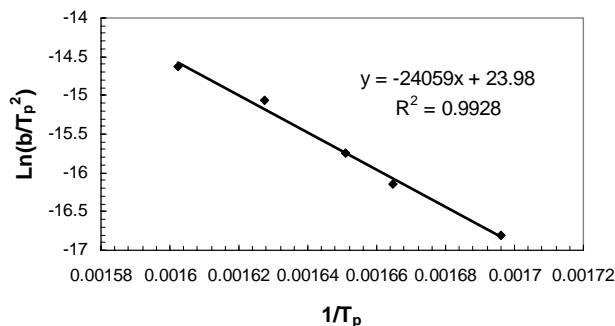
Fig. 6. Characteristic plot of the Kissinger's method.

Table 3
Pre-exponential factor and activation energy from Friedman's method

α	A ($n = 1$) (s^{-1})	E (kJ/mol)	ΔE (kJ/mol)
0.1	3.10E+14	200.0	4.55
0.2	3.63E+14	199.0	3.75
0.3	7.91E+14	202.4	3.86
0.4	4.58E+14	199.6	2.92
0.5	6.88E+14	201.9	3.44
0.6	6.78E+14	202.6	5.00
0.7	6.01E+13	192.9	4.93
0.8	7.99E+06	136.21	53.40

to yield solid carbon. They are promoted by increasing pressure [21,22] and generally in the processes of slow pyrolysis devoted to the production of charcoal. By contrast, the processes of rapid or flash pyrolysis [23] need very high heating rate and short residence time of reactants and products. They yield very little residual solid but large quantities of tar, recovered in liquid form after cooling. Völker and Rieckman have also discussed the effect of the heating rate. At a low heating rate of 3 °C/min, all the cellulose samples of various initial masses from 1 to 54 mg decomposes in a narrow temperature range, while at a heating rate of 41 °C/min, the temperatures of maximal decomposition are shifted when increasing the initial sample mass, thus denoting the presence of heat transfer limitation.

In the present study, no significant differences exist between the temperatures of DTG peak for the two groups of initial masses (3–7 mg) and (30–40 mg). The DTG peak temperatures for the highest initial masses are even surprisingly a little lower of 1–2 °C. It can be concluded that heat transfer limitation is negligible at the used heating rates, i.e. up to 10.9 °C/min.

Table 2 gathers the temperatures of the DTG peak. These temperatures are rather close to those reported by Antal et al. [11] for the pyrolysis of the micro-crystalline cellulose AVICEL: 312–313 °C at a heating rate of 1 °C/min and about 350 °C at a heating rate of 10 °C/min. The DTG peak temperature seems to depend strongly on the nature of the cellulose, since Antal et al. locate the DTG peak between 330 and 340 °C for the decomposition at 1 °C/min of a similar initial mass of the micro-fibrous cellulose Whatman CF11.

As previously mentioned, the Kissinger's method allows us to identify the activation energy from the DTG peak temperature. The plotting of $\ln(b/T_p)$ versus $1/T_p$ in Fig. 6 results in a regression line with a good regression coefficient ($R^2 = 0.9928$), the slope of which yields an activation energy equal to 200 kJ/mol, a value finally very near to that deduced from the experimental data in isothermal mode. Another way to identify the kinetic parameters A and E from TGA data in dynamic mode is the Friedman's method. In this method, the kinetic parameters are evaluated at various fixed conversions, by using all the kinetic data. The Friedman analysis

was actually carried out as one of the functionalities of the software program KINETICS98 [15]. Thus, in Table 3 are regrouped the values of A, E and ΔE, the standard error on E, in function of the actual conversion or fraction reacted α, which is distinct from the apparent conversion α^* and is defined by the following ratio:

$$\alpha = \frac{w_0 - w}{w_0} \tag{10}$$

Until an actual conversion of 0.6, it is clear that the Friedman's method provides an activation energy around 200 kJ/mol as the preceding methods, based on the TG data in isothermal mode and the DTG peak in dynamic mode. Above $\alpha = 0.7$, the activation energy strongly decreases and the Friedman method appears no longer reliable as indicated by the large standard error.

Fig. 7 illustrates the application of the method of Coats and Redfern for three different kinetic models: first-order, Avrami–Erofeev and Prout–Tompkins. This method is inadequate as far as the plot of $\ln(g(\alpha)/T^2)$ versus $1/T$ does not show a linear evolution and does not allow an accurate evaluation of E. Meanwhile, the sudden change in the slopes of the curves in Fig. 7 for the three kinetic models, at a temperature close to 350 °C, thereby indicates a characteristic change in the reaction rate, occurring at an actual conversion of about 75%.
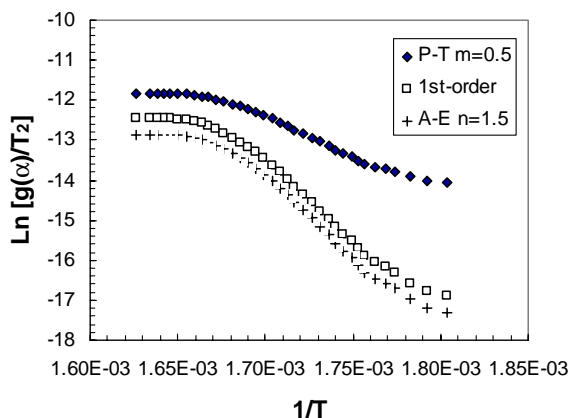

Fig. 7. Characteristic plot for the Coats and Redfern method.

2.4. Mathematical model of the cellulose decomposition

The preliminary experiments in isothermal mode have clearly demonstrated the consistency of a nucleation model to the main phase of cellulose degradation. It was decided to simultaneously fit to all the 10 TGA curves and the 10 corresponding DTG curves (the 5 dynamics and the 5 isothermal), in order to find out the better reaction model as well as its optimal parameters. Of the models in Table 1, only the nucleation-type models appeared suitable for the main phase of reaction. Moreover, the TGA–DTG curves could not be fitted as a whole with the help of a single kinetic model. Indeed, as it was previously remarked, the cellulose degradation is not uniform; a rapid bulk phase is followed by a smoother phase, above approximately 350 °C, for the heating rates tested in the present study. In fact, this transition temperature is likely to increase with the heating rate.

The choice of a multi-step reaction model as that recommended by Agrawal was not made owing to its relative complexity and the recourse to such a model finally appeared unnecessary. Furthermore, for any model built from a serial pathway of competitive-consecutive reactions, involving the production of various intermediates, it is impossible to perform quantitative analyses of these intermediates. The real existence of these products is sometimes controversial, as that of the so-called active cellulose, originally postulated by Broido. Finally, in the present study, cellulose was assumed to decompose following two parallel reactions into gas and non-degradable solid, without making any other hypotheses upon the nature of the decomposition products. Although simultaneously occurring, both these reactions, termed 1 and 2, have very different rates; therefore, the individual profiles of simulated conversion appear shifted. The reactions 1 and 2, respectively, affect the fraction f_1 and f_2 of the raw cellulose. The remaining fraction f_3, such as $f_3 = 1 - f_2 - f_1$ characterises the non-degradable residual char. The general expression of the reaction model, available for the two reactions, is the following:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -kx^n(1 - qx)^m \tag{11}$$

In Eq. (11), x is the unreacted fraction ($x = 1 - \alpha$) and the rate constant obeys the Arrhenius law ($k = A\exp(-E/RT)$). The initiation parameter q was taken equal to 0.99, a usual value in the case of nucleation models, very close to one. The reaction 1 refers to the bulk degradation of cellulose and the kinetic model chosen for this reaction was a first-order Sestak–Berggren nucleation model [24], also called three-parameter nucleation model (i.e. A, E and m), which is a more general form of the original Prout–Tompkins model. This model corresponds to Eq. (11) with $n_1 = 1$ and $m_1 \neq 0$ and reduces to a first-order model when the acceleration parameter m is zero. The ordinary differential equation related to this model was numerically integrated with the LSODE solver [25]. This solver is an improved version of an original contained in the GEAR package,

which solves stiff and non-stiff systems. Optimisation of the kinetic parameters was achieved by minimising the sum of squared residuals of both remaining mass and the derivative of remaining mass with time on all the 10 series of TGA and DTG (normalised) data simultaneously, with the help of the Lawrence Livermore program KINETICS98. Because non-linear regression is subject to false minima when too many parameters are fitted at once, parameters for the two reactions refined iteratively. The optimised values of the parameters f_1, A_1, E_1, m_1 for reaction 1 were found as follows:

$$f_1 = 0.75, \qquad m_1 = 0.481,$$
$$A_1 = 1.94 \times 10^{15}\,\mathrm{s}^{-1}, \qquad E_1 = 202.65\,\mathrm{kJ/mol}$$

As above mentioned, the optimised value of the parameter E_1 is very near to those calculated by the different methods, previously applied, giving a value of E_1 in the range 200–203 kJ/mol. The optimisation of the fraction f_1 clearly illustrates that the major part of cellulose, about 75% of the mass, is lost following an auto-accelerated process, well depicted by the three-parameter nucleation process. The optimised value of m_1 coincides with the magnitude of this exponent deduced from a graphical representation of the rate constant in isothermal mode, as shown in Fig. 3 for the Prout–Tompkins type equation. From theoretical considerations, the growing of nuclei is rigorously described by the Avrami–Erofeev model, nevertheless, Erofeev [26] demonstrated that this model can reduces to Eq. (11) of Prout–Tompkins type, after certain simplifications, thus, a connection can be done between the coefficient m of the three-parameters model and the coefficient n_{AE} of the Avrami–Erofeev, equation mentioned in Table 1. For example, Burnham and co-workers [26,27] found that $m = 0.45$ and 0.6 are, respectively, equivalent to $n_{AE} = 1.6$ and 2. Thus, the optimised value of $m_1 = 0.481$ is consistent with the optimal value of n_{AE} around 1.5, resulting from the profile of the curves related the A–E model in Fig. 3.

Unlike the kinetics of reaction 1, the kinetics of reaction 2 is optimally described by a large value of n in Eq. (11). The value of the acceleration parameter m was constrained to 1 so that there is an induction time for generation of volatiles from reaction 2, which may be considered generation of gas from residual char from reaction 1. Nearly identical values for the residuals were found over large values of n, and the optimal parameters for reaction 2 are

$$f_1 = 0.163, \qquad n_2 = 22,$$
$$A_2 = 1.63 \times 10^{20}\,\mathrm{s}^{-1}, \qquad E_2 = 255\,\mathrm{kJ/mol}$$

The parameter m_2 was fixed to one, which is consistent with a delayed start in char devolatilization due to its need to be first formed from the original cellulose.

The residual fraction of non-degradable solid f_3 is thus $f_3 = 8.66\%$. Only a small part of cellulose, 16.3%, is evolved during reaction 2. The high value found for n_2 can be justified by the smooth depletion of the sample mass over
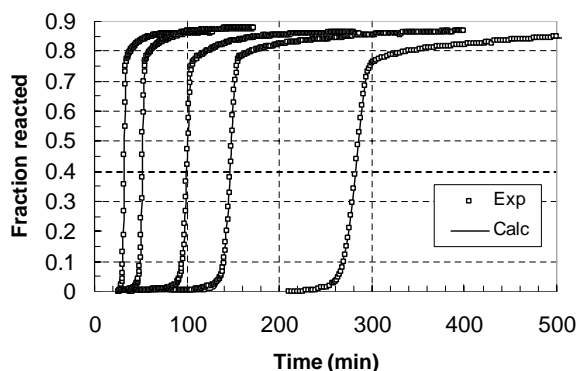
Fig. 8. Actual conversion vs. time at various heating rates (1.05, 2.1, 3.2, 6.5 and 10.9 °C/min).

a broad temperature range in the dynamic experiments and a long time in the late stages of the isothermal experiments. A value of $n > 2$ is mathematically equivalent to a Gamma (exponential-like) distribution of frequency factors. In contrast, a value of $n < 1$ results in a narrow profile of decomposition with an abrupt termination.

With the single set of optimised parameters for reaction 1 and 2 above reported, a satisfactory fit to the experimental curves of TGA and DTG can be noted from Figs. 8 and 9 related to the experiments in dynamic mode and from Figs. 10 and 11 related to the experiments in isothermal mode. The
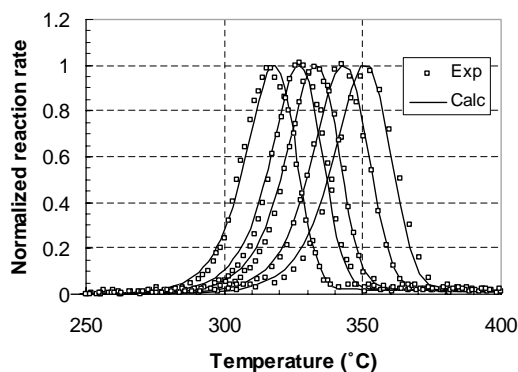

Fig. 9. Reaction rate vs. temperature at various heating rates (1.05, 2.1, 3.2, 6.5 and 10.9 °C/min).
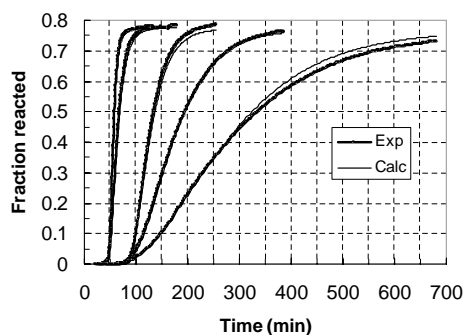

Fig. 10. Actual conversion vs. time in "isothermal" mode ($T = 320$, 310, 300, 290 and 280 °C).
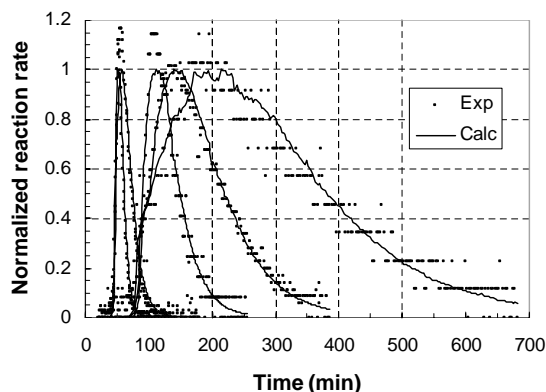

Fig. 11. Reaction rate vs. time in "isothermal" mode ($T = 320$, 310, 300, 290 and 280 °C).

precision of the fit to each experimental TGA curve was evaluated from an objective function (OF), defined as following by the mean relative error on the unreacted fraction x, N being the number of data in any experiment:

$$OF = \frac{1}{N} \sum_N \frac{|x_{exp} - x_{calc}|}{x_{exp}} \tag{12}$$

The extreme values of OF were found equal to 0.93% for the isothermal experiment at 290 °C and 5.4% for the experiment at a heating rate of 6.5 °C/min. The average value of OF being 2.6% on all the 10 ATG curves.

2.5. Comments and discussion

The most common mechanism in the literature for the cellulose pyrolysis is the Broido–Shafizadeh model previously defined. This mechanism being essentially based on sequential reactions, the near-equivalence of sequential and nuclei-growth model for describing reaction profiles was shown earlier by Burnham and co-workers [27–29]. Nuclei-growth models imply an acceleratory period and Bradbury et al. as well as Shafizadeh gave evidence for such an acceleratory period. It is besides not surprising that Conesa et al. reported obtaining good fits with both a nucleation-growth model and a multi-step model of sequential reactions involving the formation of an intermediate "active" cellulose.

The recourse to the concept of an active cellulose is not unavoidable. Indeed, the thermal decomposition of many solids, inorganic or organic, was found to exhibit an acceleratory period as does cellulose. It is the case for products as different as potassium permanganate [14], certain marine kerogens [27], linear polymers such as polystyrene and polyethylene [30]. From investigators such as Wall et al. [31] and Mc Coy [32], the acceleratory phenomenon is consistent with the kinetic theory of polymer decomposition, which is based on the three main kinds of radical reaction: random chain scissions, chain-end scissions and re-polymerisation. The mass-loss would essentially result from chain-end scis-

sion reactions, not necessarily prevailing during the early stage of decomposition. The acceleratory phenomenon was reported to mainly occur with long linear chain polymers, it was besides demonstrated that branching on the linear chain tends to reduce the acceleratory period [31]. As pointed out by Burnham et al., the acceleratory kinetic behaviour is fare from being observed for all the degradable solids and, for the same type of solid or polymer, may depend on its structure. For instance, Ainscough et al. [33] demonstrated that decomposition of cellulose of crystalline nature is governed by a first-order reaction model, in contrast, decomposition of a cellulose partially amorphous is governed by the model of Avrami–Erofeev. From these investigators, isothermal heat treatment of crystalline cellulose would not show an acceleratory period. Nevertheless the demonstration of Ainscough et al. is rather succinct, moreover, the acidic treatment needed to remove the amorphous parts is likely to degrade the crystalline part itself with as a consequence, a large reduction of the molecular weight. Such a degradation could lead to a system of isolated blocks where each block possesses an equal probability of decomposition, that is thereby consistent with a first-order kinetic model.

In 1994, Varhegyi et al. [34] published an article devoted to the application of multiple-step reaction schemes like those of Broido–Shafizadeh and Bradbury. In this article, Varhegyi et al. seriously questioned the existence of the "native" cellulose, which, according to these authors, can even be profitably withdrawn from the reaction pathway. In their conclusion, they say that "complicated models which possess more than one reaction step are not needed to simulate the weight-loss behaviour of cellulose heated continuously ... the depolymerisation step is rate limiting ... consequently a first-order single step model with a high activation energy is able to accurately mimic weight-loss data at a heating rate of 2 °C/min or more". Thus, according to Varhegyi et al., the cellulose decomposition can be described by a single first-order model, associated to the depolymerisation reaction yielding volatile tar. However, from this model, a good fit is only achieved with particular values of the parameters A and E. Thus, for 21 TG experiments performed at various heating rates, the optimal activation energy is evaluated to 238 kJ/mol with a standard deviation as large as 10 kJ/mol. When the simulation is carried out with E constrained to 238 kJ/mol, a single value of A cannot be determined since being found between 5×10^{17} and 2×10^{18} s^{-1}. Varhegyi et al. themselves admitted the failure to correctly simulate all the 21 experiments with fixed values of parameters E and A mentioning that the model curves are flatter than the experimental ones. It is also with a simple first-order reaction that Grønli et al. [35] simulated the TGA curves obtained after a Round–Robin study on cellulose pyrolysis, which put together eight European laboratories. In this study, the same type of AVICEL cellulose was used by all the investigators and two heating rates were tested: 5 and 40 °C/min. It appeared that the optimal kinetic parameters greatly varied with the heating rate: the

values of E and A at 40 °C/min revealed somewhat lower than those at 5 °C/min, thus the optimised E-values ranged from 234 to 264 kJ/mol at 5 °C/min and from 211 to 232 at 40 °C/min. In a more recent paper [11], Antal et al. compared the kinetics of pyrolysis for four different types of cellulose heated at 1, 10 and 65 °C/min. As a result, the optimal E-value strongly depends on the type of cellulose since varying between 198 kJ/mol (Millipore filter pulp) and 253 kJ/mol (Whatman filter paper). The optimal E-value was still found to decrease with increasing heating rates while by constraining E to a fixed value, for example $E = 236$ kJ/mol with Avicel cellulose, a good fit was achieved by using very different values of A depending on the heating rate, thus $A = 15.8 \times 10^{17}$, 7.94×10^{17}, 5.0×10^{17} S^{-1} at, respectively, 1, 10, 65 °C/min. Miloslavljevic and Suuberg stated the failure to achieve a good fit to the TG data at high heating rate (14.7 and 64.9 K/min) with the parameters A and E optimised from the TGA data at low heating rate (from 0.092 to 0.93 K/min) by using a simple first-order model. They have therefore proposed two distinct values for the activation energy according to the heating rate, as previously said. Burnham and co-workers [15,29] clearly established the better adequacy of a nucleation model with respect to any other kinetic model by fitting to their own experimental data and the data from other sources. To the experimental data from both experimental devices: a "Pyromat" apparatus based on the FID detection of the emitted gas and a thermobalance, they got an optimal fit when using a three-parameters nucleation model with a single set of parameters A, E and m, available for the three tested heating rates: 0.94, 6.7, 47.2 °C/min. The fit appeared even better than by using a nth-order model with $n < 1$, which is better suited to narrow reaction profiles than a first-order reaction as is the case for cellulose decomposition. The typical values of kinetic parameters obtained by Burnham and Braun from their own experimental results were finally not far from those proposed in the present work (for the reaction 1), thus with the cellulose Whatman CF11 (microfibrous) the optimal values found for E and m were, respectively, $E = 180$ kJ/mol (43.1 kcal/mol) and $m = 0.43$. The E-values identified by these investigators were even nearer from 200 kJ/mol when simulating the experimental data from others sources, as the series of TGA data provided by Miloslavljevic and Suuberg in which samples of Whatman CF11 cellulose were heated at four different heating rates between 1 and 60 °C/min. In this case the optimal kinetic parameters were the following: $A = 1.4 \times 10^{14}$ s^{-1}, $E = 197$ kJ/mol and $m = 0.38$. With the TGA data provided by Varhegyi et al. [34], Burnham and Braun found the following optimal parameters: $A = 2.57 \times 10^{14}$ s^{-1}, $E = 196.33$ kJ/mol and $m = 0.15$. A particular attention must be brought to Fig. 6 of the paper referenced [15] of these authors. On this figure is presented a simulation of TGA data from Varegyi et al., at two rises in temperature, very different: 2 and 80 °C/min. This figure well illustrates the inability of a first-order model to correctly fit to both the TGA curves simultaneously by using a single set of param-

eters. In contrast, the fit with a three-parameters nucleation model is very satisfactory. To account for the narrow profile of conversion with a first-order model, a high activation energy is needed, thus, the individual E-values identified by Antal and co-workers, in the range 220–270 kJ/mol, are generally higher than those required by a nucleation-growth model, between 145 and 200 kJ/mol for the simulations reported by Burnham and co-workers and a little higher than the 200 kJ/mol in the present work. The E-value reported by Conesa et al., related to their nucleation model, is a little higher ($E = 215$ kJ/mol), while the values of parameters m and n appear different since $n = 0.306$ and $m = 1.382$, yielding the lower objective function (i.e. the sum of squared residual), when compared to the other kinetic models, as shown in Table 2 of [7].

Most of the reported fits exclusively based on a nuclei-growth model have each time brought on a small number of experiments, limited to three or four, generally performed in dynamic mode at sometimes high heating rate, that can lead to erroneous results owing to an eventual thermal lag. The present work constitutes the first attempt to achieve successful fits to a consistent number of TGA curves (10) with this type of model and by using a single set of kinetic parameters. The TGA data are equally distributed in two separate groups, each one characterised by the mode of heating: isothermal at moderate temperature and dynamic up to elevated temperatures. This diversity of experimental conditions strengths the assertion that a nucleation model is appropriated to the thermal decomposition of cellulose.

3. Conclusion and perspectives

The kinetics of decomposition of very pure cellulose was investigated in isothermal and dynamic mode. In isothermal mode, the sigmoid profile of the ATG curves makes obvious the auto-accelerated behaviour of the cellulose decomposition at less in its bulk phase. A nucleation model, as defined by Eq. (11), is appropriate to account for this behaviour and to mimic the evolution of ATG and DTG data, whatever the mode of heating isothermal or dynamic. In the future, it would be of interest to determine if a nucleation model is still valid when changing for example the ash content or the structure of cellulose, either crystalline or amorphous. It is well known that the presence of mineral impurities tends to increase the rate of decomposition, which could result in a reduction of the induction time or the acceleratory period. This particular point has to be checked. About the influence of the cellulose structure, the research initiated by Ainscough et al. would deserve to be pursued. For instance, a link could be found between the DP of cellulose and the auto-accelerated property of its decomposition, furthermore, the same experimental and theoretical approach could be applied to the biopolymers of wood, hemicelluloses and lignin, as well as to polysaccharides such as starch, in order

to specify how the morphology and the crystalline nature can affect the kinetics of thermal decomposition.

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