Analysis of different kinetic models in the dynamic pyrolysis of cellulose

Juan A. Conesa *, José A. Caballero, A. Marcilla, R. Font

Department of Chemical Engineering, University of Alicante, Apartado de Correos 99, Alicante, Spain

Abstract

The kinetics of the thermal decomposition of cellulose in nitrogen were studied using dynamic TG at heating rates between 5 and 50 K min^{-1}. The most widely used models found in the literature which are usually applied in isothermal conditions were tested. Important differences were found between models that take into account the formation of an activated cellulose and those that assume the direct decomposition of cellulose to char, tar and gases. The best agreement between experimental and calculated values was found with models which consider the formation of activated cellulose and take into account the different behaviour at low and high temperatures.

The simultaneous correlation of all the experimental data obtained in different conditions is proposed as a technique to prevent compensating effects between the pre-exponential factor and the activation energy, and thus to avoid erroneous conclusions.

1. Introduction

The scarcity of natural fuel resources and the increase in lignocellulosic wastes and municipal solid wastes (MSW) have led to renewed interest in converting these wastes into useful energetic products. In recent years, thermochemical processes have become some of the most promising ways for obtaining useful products from

---

* Corresponding author.

organic wastes. The study of the kinetic behaviour of these products in thermal decomposition is fundamental to the optimization of their use.

In many of the kinetic formulations of solid state reactions, it has been assumed that the isothermal homogeneous gas or liquid phase kinetic equation can be applied [1]. Thus, for a single reaction at any time the rate of reaction may be expressed as

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{1}$$

where α is defined by

$$\alpha = \frac{w_0 - w}{w_0 - w_\infty} \tag{2}$$

and w is the mass fraction present at any time, w_0 is the initial mass fraction and w_∞ is the mass fraction at infinite time. The function $f(\alpha)$ depends on the controlling mechanism. Table 1 shows some of the usual forms of $f(\alpha)$. The simplest form of this function is the first-order reaction, and in this case Eq. (1) can be written as

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)(1 - \alpha) \tag{3}$$

The determination of the kinetics corresponding to lignocellulosic materials involves the knowledge of reaction mechanisms. This is a very difficult task, and the

Table 1
Different models for solid decomposition

	$f(\alpha) = \left(\dfrac{1}{k}\right)\dfrac{da}{dt}$
1. Acceleratory $\alpha - t$ curves	
P1 Power Law	$na^{1-1/n}$
E1 Exponential law	α
2. Sigmoid $\alpha - t$ curves	
An Avrami–Erofe'ev	$n(1 - \alpha)[-\ln(1 - \alpha)]^{1-1/n}$
B1 Prout–Tompkins	$\alpha^n (1 - \alpha)^m$
3. Deceleratory $\alpha - t$ curves	
3.1. Based on geometrical models	
Rn	
$n = 2$ Contracting area	$n(1 - a)^{1-1/n}$
$n = 3$ Contracting volume	
3.2. Based on diffusion mechanisms	
D1 One dimensional	$1/(2\alpha)$
D2 Two dimensional	$[-\ln(1 - \alpha)]^{-1}$
D3 Three dimensional	$(3/2)(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{-1}$
D4 Ginstling–Brounshtein	$(3/2)[(1 - \alpha)^{-1/3} - 1]^{-1}$
3.3. Based on "order of reaction"	
Fn n-order	$(1 - \alpha)^n$

components of biomass (lignin, cellulose and hemicellulose) are usually studied separately. However, the pyrolysis of organic materials, even the simplest ones, involves a large number of reactions.

The kinetics of cellulose pyrolysis have been extensively investigated. In spite of the important research carried out, the kinetics and mechanisms of cellulose pyrolysis reactions are not completely known, probably because of the complex nature of the reaction. Some pseudo-mechanistic models involving more than one reaction have been used to explain the process. These models are based on the fact that, when cellulose is heated in a non-reactive environment, it decomposes to various pyrolysis products. These pyrolysis products can be conveniently grouped into three classes depending on their volatility: tars, char and gases. Char is the non-volatile residue, with a high carbon content. Tars are mixtures of a great number of high molecular weight products that are volatile at the pyrolysis temperature but condense at room temperature (mainly anhydro-compounds). Gases are low molecular weight products which have a vapour pressure measurable at room temperature (CO, CO_2, and also water) [2].

The first kinetic models were proposed in the 1950s and 1960s by Madorsky et al. [3], Kilzer and Broido [4] and Chatterjee and Conrad [5], and are the basis of the modern kinetic models.

The pyrolysis of cellulose in isothermal conditions was reported as a two-step reaction, initially by Chatterjee and Conrad [5], Lipska and Parker [6] and, more recently, by Bradbury et al. [7], Broido [8] and Agrawal [9]. At temperatures below 280°C the formation of char and gas is favoured. Lipska and Parker [6] observed greater char formation ($\approx 30\%$ more) from cellulose samples when they were pre-heated at 250°C for ≈ 90 min and further heated to 298°C than when they were heated directly to 298°C. Results obtained by Broido and Nelson [10] also indicated that heat pre-treatment at lower temperatures yields more char than direct heating at high temperatures. At temperatures higher than 280°C the formation of tar is favoured. The reaction order of both reactions was considered to be unity by Bradbury et al. [7], but Chatterjee [11] considered the order of the first reaction equal to zero. Agrawal [2] commented that, at low conversions, the assumption of order zero or order one yields similar results.

For low temperature pyrolysis, Kilzer and Broido [4] postulated that the pyrolysis of cellulose involves three groups of processes. The first consists in an intramolecular dehydration to form anhydrocelluloses; this process is slightly endothermic and occurs at ≈ 220°C. The second process competes with the first and is responsible for laevoglucosan formation, which begins at 280°C and is more endothermic. The final process is exothermic and corresponds to the decomposition of the anhydrocellulose; this process is a complex set of reactions: scission of C–C and C–O to form gases or volatile compounds, intermolecular condensations to form char, radical scissions, etc.

A modification of the Kilzer–Broido model was proposed by Agrawal [12]. The unmodified Kilzer–Broido model assumes that the formation of char and of gas is linked. However, Agrawal remarked that there was no evidence to prove that the char and gas formation are completely linked. Results obtained by Agrawal [9] and

by Shafizadeh et al. [13] and others indicated that, at low pressures, the gas to char ratio varies from < 1 (below 300°C) to 4 (above 400°C).

Agrawal [2] proposed a three-reaction model, in which it is assumed that cellulose decomposes to tars, chars and gaseous products via three competitive first-order reactions. The formation of tars is considered to be produced by the breakage of the 1,4 glucosidic bonds, resulting in depolymerization of cellulose. The scission of 1,5 acetal bonds leads to ring opening and results in the formation of char and gases. It is also considered that the pathways of char and gas formation are not entirely linked. Agrawal remarks that this three reaction model is capable of predicting the primary pyrolysis reactions but cannot explain the mechanistic aspects of pyrolysis reactions below 300°C. The three reaction model cannot predict the intermediate transformation of cellulose to anhydrocellulose and does not provide a "memory" of the pre-heated samples.

Alves and Figueiredo [14] proposed a model with three consecutive first-order reactions. The first reaction releases some volatile matter. The second releases very little or no volatiles (there is probably a rearrangement or activation of the solid), and the third reaction releases most of the total volatile matter. This model explains pre-heating effects, but the yield coefficients a_1, a_2 and a_3 are functions of temperature and must be determined experimentally at any temperature.

Kinetic parameters can be easily determined by isothermal experiments. In these experiments, the cold sample must be pre-heated to the required temperature prior to the isothermal measurements. If the reaction is fast, a considerable fraction of the solid can react before isothermal conditions are established and a large fraction of the solid reacts during non-isothermal conditions [1].

Dynamic TG studies have been widely used by different investigators. Arsenau [15] and Tang [16] reported two different activation energies over different temperature ranges. However, Agrawal [17] reported an apparent activation energy as a function of temperature, which may be due to heat transfer limitations (inaccurate temperature measurements, temperature gradient within the sample or buoyancy effects) and mathematical aproximations. Flynn [18] commented that different reactions can be identified by dynamic experiments in which the heating rate is varied over a wide range of temperatures.

Although dynamic TG avoids the pre-heating problem of isothermal TG experiments, new problems are caused by the incorrect measurement of temperature. Errors from mathematical approximations can be overcome, or at least minimized, by the use of modern computers. Antal [19] highlighted some difficulties in the mathematical treatment of solid state pyrolysis data. In dynamic TG, both the pre-exponential factor and the activation energy must be obtained at the same time.

Varhegyi and Antal [20] described the thermal decomposition of pure Avicel cellulose using a single reaction model of order 1.2 (using heating rates of 10 and 80 K min⁻¹). Varhegyi and Antal remarked that the most feasible interpretation is a rate-determining first-order reaction followed by other reaction steps, in accordance with the generally accepted hypothesis concerning the mechanism of decomposition of cellulose.

Lewellen et al. [21] pyrolysed cellulose with heating rates of 400–10 000 K s^{-1} and pressures of 0.0005–1 bar. Under these conditions, all the cellulose was converted to volatiles without char formation, except when an extended heating period at low temperature (1 h at 250°C) preceeded the pyrolysis at high temperatures. This feature confirms the fact that, at high heating rates, the different processes run very fast and can be described by a single equation, and only by changing the heating rate can the different processes be separated. In order to test the validity of the single reaction model, Lewellen et al. [21] analysed the same experimental data with a model based on the concept that the thermal decomposition of a complex compound or mixture of compounds involves a large number of independent, parallel first-order decomposition reactions. The rate constant of each reaction may be represented by the usual Arrhenius formula [22]. These reactions are assumed to have identical pre-exponential factors and a continuous distribution of activation energies represented by a distribution function $f(E)$, so that $f(E)\,dE$ represents the fraction of reactions having activation energies between E and $E + dE$. Lewellen et al. [21] used an energy distribution function of Gaussian form

$$\frac{dw}{dt} = \int_{-\infty}^{\infty} A \exp\left(-\frac{E}{RT}\right) w f(E)\,dE \qquad (4)$$

and

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(E - E_0)^2}{2\sigma^2}\right) \qquad (5)$$

Using this model, Lewellen et al. [21] found that the value of parameter σ was only 4.598 kJ mol^{-1} and the value of E_0 was 154.6 kJ mol^{-1}. The small value of σ compared with the value of E_0 indicates that, in such conditions, the single reaction model can correctly describe the kinetics of the process.

Koga et al. [23] and Agrawal [24] showed that a single TG curve can be fitted satisfactorily using different sets of kinetic parameters, or by different kinetic models [25]. This fact must be taken into account when a kinetic study in dynamic conditions is carried out. Vyazovkin and Lesnikovich [26] commented extensively on the influence of the Arrhenius parameter calculations on the exactness of the solution. Chornet and Roy [27] and Agrawal [17] discussed the apparent compensation effect.

Changes in activation energy and pre-exponential factor have been reported when the heating rate is changed. A correlation has been proposed [1]: $\ln A = a + bE$, where A is the pre-exponential factor, E is the activation energy, and a and b are constants. However, this apparent variation in activation energy and pre-exponential factor can be caused by problems in heat transfer [20], or the model may be not adequate for describing the kinetic behaviour of the processes involved.

As noted previously, the data from a single run (dynamic or isothermal) can be fitted to several models. A given model can be considered plausible or representative of the pyrolysis process when the experimental data of several runs carried out at different operating conditions (temperature, heating rates) can be correlated with the same values of the parameters optimized. This means that those models which

admit variations of the activation energy or pre-exponential factor with temperature or conversion are only correlation models without any physical significance, unless the corresponding variations are justified.

As observed previously, cellulose pyrolysis has been widely studied by different researchers, using different materials and experimental techniques and proposing different kinetic models. In the present work, an analysis of the different models proposed is carried out by considering the experimental data obtained in dynamic TG runs. The analysis performed considers the number of parameters optimized, the number of reactions and the improvement of the correlations when the number of optimized parameters is increased. In this way, a revision of the different models and a comparison between them has been carried out.

2. Experimental

2.1. Thermobalance

The experiments were carried out on a Perkin-Elmer thermobalance model TGA7 controlled by a PC AT compatible system. The atmosphere used was nitrogen with a flow rate of 60 ml min^{-1}. The thermobalance incorporates a servo-operated system in which an electrical signal from an optical null detector is applied directly to control the current in a torque motor. The balance has provision for digital mass readout using four digit thumbwheels and two digit verniers with three full-scale ranges: 10, 100 and 1000 mg.

2.2. Materials and operating conditions

In all the experiments the material used was cellulose (Whatman No. 6 paper). Experiments in dynamic conditions were carried out over a range of temperatures that included the entire range of solid decomposition, with heating rates of 5, 25 and 50 K min^{-1}. The experiments were repeated three times to determine their reproducibility, which was found to be good. Average data obtained at each heating rate were considered for computer purposes. The mass of the sample used was ≈ 3–4 mg. The values of temperature considered were those recorded by the thermocouple.

2.3. Mathematical procedure

The models mentioned in the preceding section were applied simultaneously in order to adjust three TG curves under dynamic conditions at heating rates of 5, 25 and 50 K min^{-1}. The kinetic parameters were optimized using a Flexible Simplex method [28]. In all the calculations, the objective function included the data obtained at different heating rates, and was

$$\text{O.F.} = \sum_{j=1}^{n_s} \sum_{i=1}^{n_d} (w_{\text{cal},ij} - w_{\text{exp},ij})^2 \tag{6}$$

where i represents the experimental data at time t of the experiment at heating rate j, $w_{exp,ij}$ is the mass fraction measured experimentally and $w_{cal,ij}$ is the calculated mass fraction.

The variation coefficient was calculated as

$$V.C./\% = \frac{\sqrt{\dfrac{O.F.}{N - P}}}{\overline{w}_{exp}} \times 100 \tag{7}$$

where N is the number of experimental points, P is the number of parameters and $\overline{w}_{exp}$ is the mean value of the experimental data.

The integration of the kinetic equations was carried out by a fourth-order Runge–Kutta method. In the reaction schemes, the integration was performed using all the species implied. For example, for the reaction scheme

$$C \underset{k_2}{\overset{k_1}{\rightleftarrows}} \begin{array}{l} \text{Volatiles} \\ \text{Char} \end{array} \tag{S1}$$

the equations used were

$$\frac{dC}{dt} = -(k_1 + k_2)C \tag{8}$$

$$\frac{dV}{dt} = k_1 C \tag{9}$$

$$\frac{dCh}{dt} = k_2 C \tag{10}$$

The mass fraction is the sum of the non-decomposed solid fraction C and the char fraction Ch

$$w = C + Ch \tag{11}$$

In TG experiments, yields of gas and tar cannot be separated, because thermogravimetry can only measure weight loss. Thus, in those models which differentiate tar from gas, these products have been grouped as volatiles. For example, the three-reaction model proposed by Agrawal [2]

$$C \begin{array}{l} \overset{k_1}{\nearrow} \text{Tar} \\ \overset{k_2}{\longrightarrow} \text{Char} \\ \underset{k_3}{\searrow} \text{Gas} \end{array} \tag{S2}$$

becomes the reaction scheme (S1).

3. Results and discussion

Fig. 1 shows the weight losses and their derivative vs. temperature for the three experiments carried out at 5, 25 and 50 K min^{-1}. Considering the weight loss
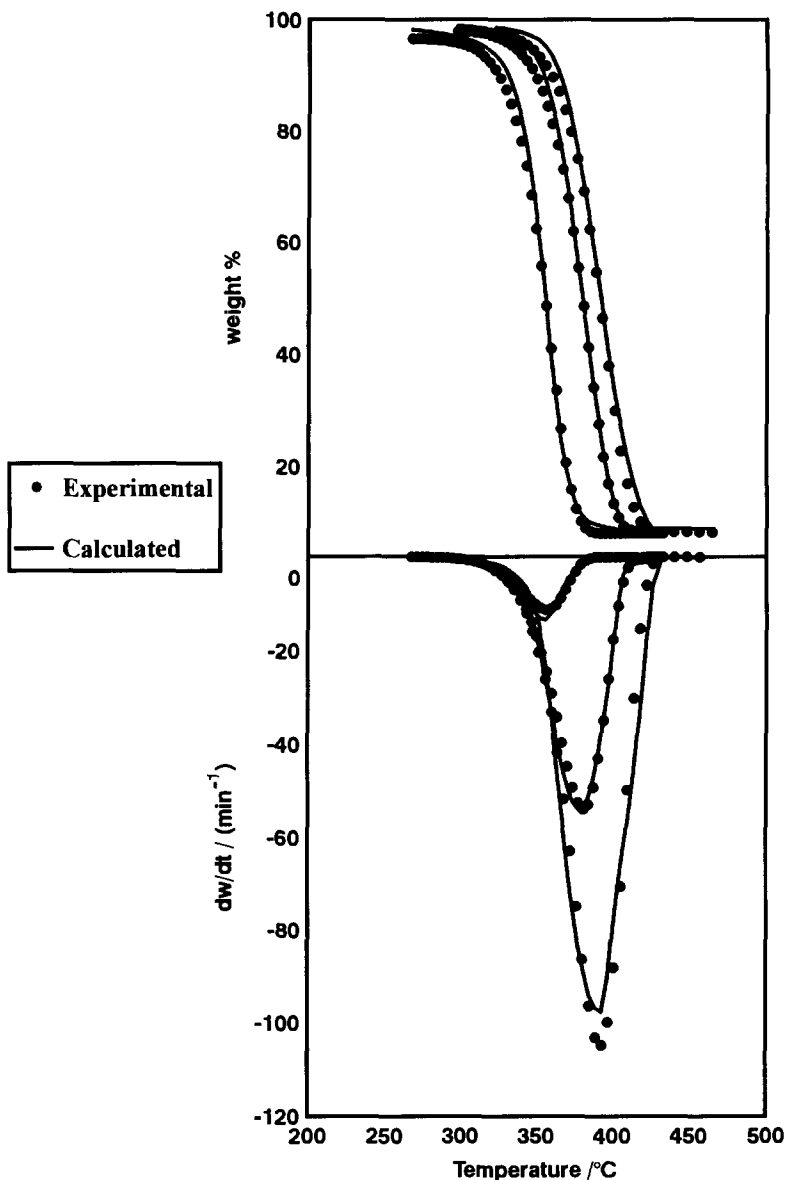
Fig. 1. Thermal behaviour of cellulose and data fit for first-order kinetics.

curves, the left hand curve corresponds to 5 K min^{-1}, the middle one to 25 K min^{-1} and the right hand curve to the highest heating rate, 50 K min^{-1}, as expected. For the weight loss derivative curves, that with the least pronounced peak corresponds to the lowest heating rate and that with the largest peak corresponds to the highest heating rate.

Table 2
Results for different solid decomposition models (see Table 1)

Model	k_0/min^{-1}	E/(kJ mol^{-1})	n, m	Objective function	Variation coefficient/%
P1	9.5×10^{17}	227.6	$n = 0.671$	1.28	5.98
E1	1.3×10^{16}	193.3	–	11.47	17.87
An	1.5×10^{17}	213.9	$n = 1.106$	0.23	2.53
B1	4.0×10^{17}	215.7	$n = 1.382$	0.11	1.77
			$m = 0.306$		
Rn	1.4×10^{16}	220.3	$n = 36.21$	0.29	2.84
D1	2.0×10^{18}	233.4	–	2.45	8.26
D2	8.4×10^{20}	267.6	–	2.61	8.52
D3	3.3×10^{22}	293.8	–	2.93	9.04
D4	1.1×10^{20}	264.8	–	2.54	8.42
Fn	3.0×10^{17}	217.1	$n = 1$	0.18	2.26

Considering the kinetic expression for a single reaction (Eq. (1)), the form of $f(\alpha)$ depends on the controlling mechanism. The most usual forms of the function $f(\alpha)$ were tested for correlating all the experimental data together. Table 2 shows the kinetic parameters obtained with these models. Only the first-order kinetic model and the Prout–Tompkins model can explain the thermal decomposition of cellulose. Fig. 1 shows the fitting obtained with the first-order kinetic model. This confirms the results of Varhegyi and Antal [20], who obtained from dynamic TG a reaction order of 1.2 and kinetic parameters similar to those obtained in the present work. Varhegyi and Antal remarked that the most plausible interpretation is that a controlling first-order reaction is followed by further reaction steps, in accordance with the generally accepted hypothesis concerning the mechanism of cellulose decomposition. Fig. 2 shows Arrhenius plots for first-order kinetics obtained by different researchers and in the present work.

In the thermal decomposition of solid materials the following equation is used to describe the first-order kinetics

$$\frac{dw}{dt} = -k(w - w_\infty) \tag{12}$$

where w is the weight fraction at any moment and w_∞ is the weight fraction at infinite time. This equation is exactly the same as Eq. (3).

Agrawal [2] demonstrated that, in isothermal conditions, Eq. (12) can be used to determine the overall decomposition in a model with the three parallel reactions (S2), where $k = k_1 + k_2 + k_3$. This result can be generalized to N parallel reactions.

However, in dynamic conditions for char-forming systems and first-order kinetics, Eq. (12) is only an approximation of the real overall decomposition. In lignocellulosic materials, the value of w is a function of temperature [2,29] and the experimental determination of w is difficult. Many authors avoid this problem by using a constant value of w obtained at the maximum operating temperature.
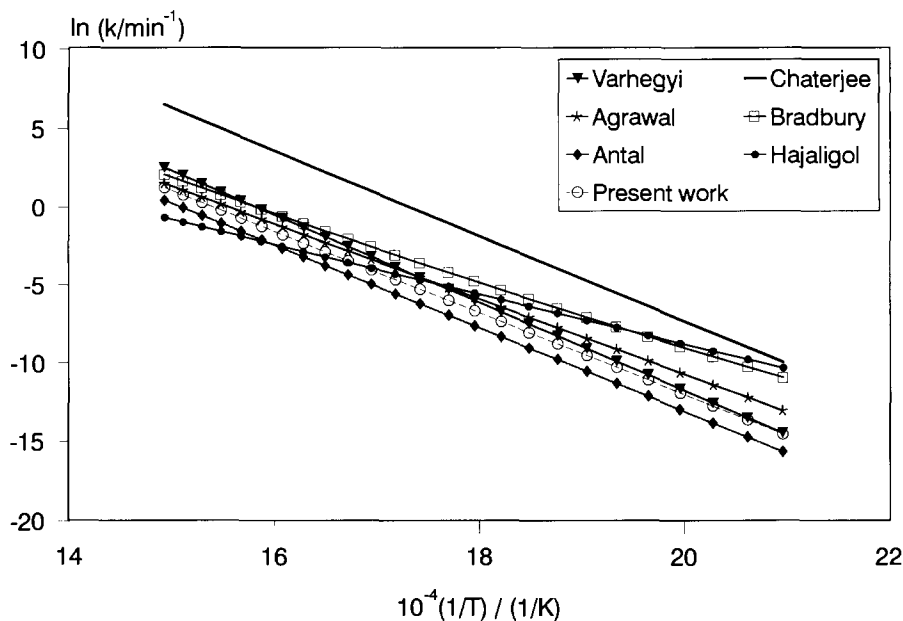
Fig. 2. Comparison between kinetic constants for cellulose pyrolysis through first-order kinetics.

Nevertheless Eq. (12), applied in dynamic conditions, does not correspond to any scheme of reactions, and can be considered as a fitting equation.

It can be demonstrated [30] that, in isothermal conditions, the model of three parallel reactions (scheme (S2)) is equivalent to a model with only one reaction of the form

$$C \xrightarrow{k} g,\text{Gas} + t,\text{Tar} + c,\text{Char} \tag{S3}$$

Simple pure substances may decompose by a reaction scheme such as (S3), where the yield coefficients are obviously constant and independent of temperature, but in complex polymeric substances such as cellulose this scheme corresponds to a combination of further simple reactions. Yield coefficients do then change with operating conditions because different reactions are favoured over others, depending on the experimental conditions.

In dynamic conditions, reaction schemes (S2) and (S3) are also equivalent if the variation of yield coefficients with temperature is expressed by

$$t = \frac{k_1}{k_1 + k_2 + k_3}; \quad c = \frac{k_2}{k_1 + k_2 + k_3}; \quad g = \frac{k_3}{k_1 + k_2 + k_3} \tag{13}$$

Accepting these considerations, any scheme of reaction of the type (S3) can be explained or reduced to a scheme of type (S2). Ratios of constants such as those given by Eq. (13) will provide the variation of the yield coefficients with temperature. It is therefore suggested that (S2) type schemes be used when studying the

kinetic behaviour of complex substances, since these schemes do not require determination of the variation of the yield coefficients with temperature.

However, reaction schemes such as (S2) may not explain TG experiments under different conditions with the same kinetic parameters, because tar, char and gas composition can vary with the thermal history, and this is not considered in these models which one consequently regards as simplifications of the real process.

Antal et al. [31] used Eq. (12) to describe the thermal decomposition of cellulose in dynamic TG (the authors considered that w was a constant value). In Ref. [31] Antal et al. gave a series of values in which the activation energy and pre-exponential factor changed with heating rate (see Table 3). Varhegyi and Antal [20] commented that the variation of kinetic parameters with heating rate is probably due to heat transfer (changes in reaction mechanisms are not probable in the range of heating rates studied), and remarked on the necessity of measuring the sample temperature near or within the sample.

In addition to Eq. (12) and the models concerning a single reaction presented in Table 1, other models with several reactions were considered to correlate the experimental data presented in this paper.

Table 4 shows these models and the corresponding kinetic parameters obtained. In all the cases, the experimental data are correlated with more or less accuracy, but significant differences can be observed.

In the model proposed by Bradbury et al. [7]

$$C \underset{k_2}{\overset{k_1}{\diagdown}} \begin{array}{l} \text{Volatiles} \\ a, \text{Char} + b, \text{Gas} \end{array} \tag{S4}$$

the agreement between experimental and calculated values is not very good. This model does not take into account the possibility of the formation of active cellulose

Table 3
First order kinetic constants for decomposition of cellulose

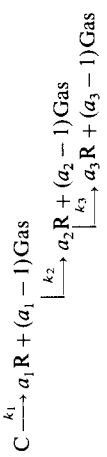| Author	A/min^{-1}	$E/(\text{kJ mol}^{-1})$	Material used
Chatterjee	3.3×10^{20}	175.7	Cotton
Lewellen	4.07×10^{11}	139	Filter paper 0.01 cm thick
Antal			Filter paper
2.16°C min^{-1}	2.0×10^{17}	221.1	
5.65°C min^{-1}	8.4×10^{11}	157.6	
10.9°C min^{-1}	1.6×10^{11}	148.8	
22.4°C min^{-1}	2.7×10^{12}	162.6	
55.0°C min^{-1}	4.2×10^{11}	153.0	
Varhegyi ($n = 1.2$)	2.2×10^{19}	234	Avicel cellulose
Hajaligol [32]	1.2×10^{10}	132.8	Filter paper 0.0101 cm thick
Arsenau		189.7	Filter paper
		151.3	
Lipska and Parker		209.2	White α-cellulose 0.075 cm thick
Present work	3.01×10^{17}	217.2	Whatman No. 6 filter paper

Table 4
Different models for decomposition of cellulose

Model	Original work		Present work		Objective function Variation coefficient/%
	A/min^{-1}	$E/(\mathrm{kJ\ mol}^{-1})$	A/min^{-1}	$E/(\mathrm{kJ\ mol}^{-1})$	
$C \xrightarrow{k_1} \text{Volatiles}$; $\xrightarrow{k_2} a, \text{Char} + b, \text{Gas}$ Bradbury et al. [7]	Filter paper $A_1 = 7.9 \times 10^{11}$ $A_2 = 1.9 \times 10^{16}$ $a = 0.35$	$E_1 = 153.1$ $E_2 = 197.9$ $b = 0.65$	$A_1 = 2.3 \times 10^{17}$ $A_2 = 3.2 \times 10^{17}$	$E_1 = 217.7$ $E_2 = 225.5$	O.F. = 0.1903 V.C. = 2.30
$C \xrightarrow{k_1} \text{Tar}$; $\xrightarrow{k_2} \text{Char}$; $\xrightarrow{k_3} \text{Gas}$ Agrawal [2]	White α-cellulose Overall decomposition $(k_1 + k_2 + k_3)$ $A = 2.0 \times 10^{16}$ Char formation $A_2 = 3.0 \times 10^{13}$	$E = 200.6$ $E_2 = 178.9$	Volatile formation $(k_1 + k_3)$ $A = 3.7 \times 10^{17}$ Char formation $A_2 = 1.5 \times 10^{17}$	$E = 219.2$ $E_2 = 226.9$	O.F. = 0.1926 V.C. = 2.32
$C \xrightarrow{k_1} C^* \xrightarrow{k_2} \text{Volatiles}$; $\xrightarrow{k_3} \text{Char}$ Present work			$A_1 = 2.7 \times 10^{24}$ $A_2 = 3.4 \times 10^{16}$ $A_3 = 9.9 \times 10^{14}$	$E_1 = 279.0$ $E_2 = 206.0$ $E_3 = 199.8$	O.F. = 0.1224 V.C. = 1.85
$C \xrightarrow{k_1} C^* \xrightarrow{k_2} \text{Volatiles}$; $\xrightarrow{k_3} \text{Char}$ Bradbury et al. modified [7]	Filter paper $A_1 = 1.7 \times 10^{21}$ $A_2 = 7.9 \times 10^{11}$ $A_3 = 1.9 \times 10^{16}$ $a = 0.35$	$E_1 = 242.4$ $E_1 = 153.1$ $E_2 = 197.9$ $b = 0.65$	$A_1 = 1.1 \times 10^{24}$ $A_2 = 6.2 \times 10^{10}$ $A_3 = 4.9 \times 10^{16}$	$E_1 = 274.4$ $E_2 = 200.9$ $E_3 = 207.5$	O.F. = 0.1204 V.C. = 1.83

$$C \xrightarrow{k_1} a_1R + (a_1-1)\text{Gas}$$
$$\xrightarrow{k_2} a_2R + (a_2-1)\text{Gas}$$
$$\xrightarrow{k_3} a_3R + (a_3-1)\text{Gas}$$

Alves and Figueiredo [14]

$$C \xrightarrow{k_2} C^* \xrightarrow{k_3} \text{Gas}$$
$$\xrightarrow{k_4} \text{Char}$$
$$\xrightarrow{k_1} \text{Tar}$$

Kilzer–Broido modified Agrawal [12]

Filter paper

$A_1 = 7.3 \times 10^{13}$	$E_1 = 174$	$A_1 = 3.3 \times 10^{17}$	$E_1 = 217.5$
$A_2 = 1.9 \times 10^{14}$	$E_2 = 178$	$A_2 = 6.7 \times 10^{11}$	$E_2 = 128.2$
$A_3 = 1.2 \times 10^{14}$	$E_3 = 179$	$A_3 = 9.7 \times 10^{12}$	$E_3 = 147.5$
$a_1 = 0.75$		$a_1 = 0.70$	
$a_2 = 0.99$		$a_2 = 0.78$	
$a_3 = 0.22$		$a_3 = 0.16$	

O.F. = 0.1301
V.C. = 1.91

Cotton wool

$A_1 = 1.3 \times 10^{11}$	$E_1 = 139$
$A_2 = 4.2 \times 10^{12}$	$E_2 = 157$
$A_3 = 1.1 \times 10^{17}$	$E_3 = 209$
$a_1 = 0.87$	
$a_2 = 1.00$	
$a_3 = 0.16$	

White α-cellulose

$A_1 = 6.4 \times 10^{15}$	$E_1 = 195.8$	$A_2 = 1.6 \times 10^{24}$	$E_2 = 279.3$
$A_2 = 1.8 \times 10^{12}$	$E_2 = 159.3$	$A_1 = 2.5 \times 10^{8}$	$E_1 = 120.1$
$A_3 = 3.4 \times 10^{17}$	$E_3 = 214.6$	$A_3 = 5.4 \times 10^{16}$	$E_3 = 208.5$
$A_4 = 1.9 \times 10^{16}$	$E_4 = 203.7$	$A_4 = 3.8 \times 10^{15}$	$E_4 = 206.8$

O.F. = 0.0956
V.C. = 1.63

(anhydrocelluloses) and cannot explain the pre-heating effects commented upon in previous sections. The experimental data were considered with the values of a and b proposed by these authors. The experimental data were also correlated with the yield coefficient a as a parameter to be optimized. The O.F. was practically the same but the kinetic parameters and the value of a were different. This indicates a strong interrelation between all these parameters.
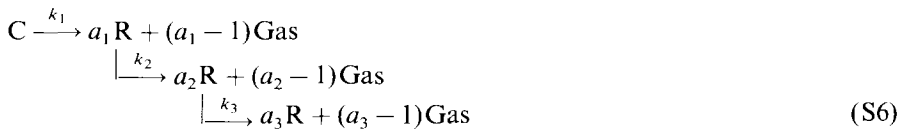
A modified version of the three parallel reaction model proposed by Agrawal [2] (only two reactions have been considered) yields agreement similar to that with the Bradbury model. Additional data of tar formation are necessary in order to differentiate between the two models. The kinetic parameters obtained with these models concord with the values given in the Agrawal paper (Table 4).

In the models that take the activation of cellulose into account (with the formation of laevoglucosan or other anhydrocelluloses), the agreement between experimental and calculated values increases. A model such as

$$C \xrightarrow{k_1} C^* \begin{array}{c} \xrightarrow{k_2} \text{Volatiles} \\ \searrow_{k_3} \text{Char} \end{array} \tag{S5}$$

yields better results than the Bradbury model [7], in which the formation of an intermediate was not taken into account; see scheme (S4). A modified Bradbury model, in which the posibility of the formation of gas together with the char is considered, does not lead to better agreement between experimental and calculated values. This fact means that the gas and tar formation cannot be independently measured using TG alone, and differentiation between the two models is not possible.

The model suggested by Alves and Figueiredo [14] considers three consecutive first-order reactions as indicated below

$$C \xrightarrow{k_1} a_1 R + (a_1 - 1)\text{Gas}$$
$$\xrightarrow{k_2} a_2 R + (a_2 - 1)\text{Gas}$$
$$\xrightarrow{k_3} a_3 R + (a_3 - 1)\text{Gas} \tag{S6}$$

where a_1, a_2 and a_3 are the yield coefficients of the solid product in reactions 1, 2 and 3, respectively.

Alves and Figuereido determined the values of a_1, a_2 and a_3 from different isothermal runs, deducing the variations of these yield coefficients in relation to temperature. This study indicated that each of the three reactions is the sum of many more reactions. The correlation of dynamic TG data by this model would imply the introduction of the parameters corresponding to the variation of the yield coefficients with temperature, thus increasing the number of parameters to be optimized. The experimental data presented in this paper were correlated with this model, assuming constant values for the yield coefficients a_1, a_2 and a_3.

The best agreement between experimental and calculated values was obtained with the Kilzer–Broido model as modified by Agrawal [12]; see Fig. 3
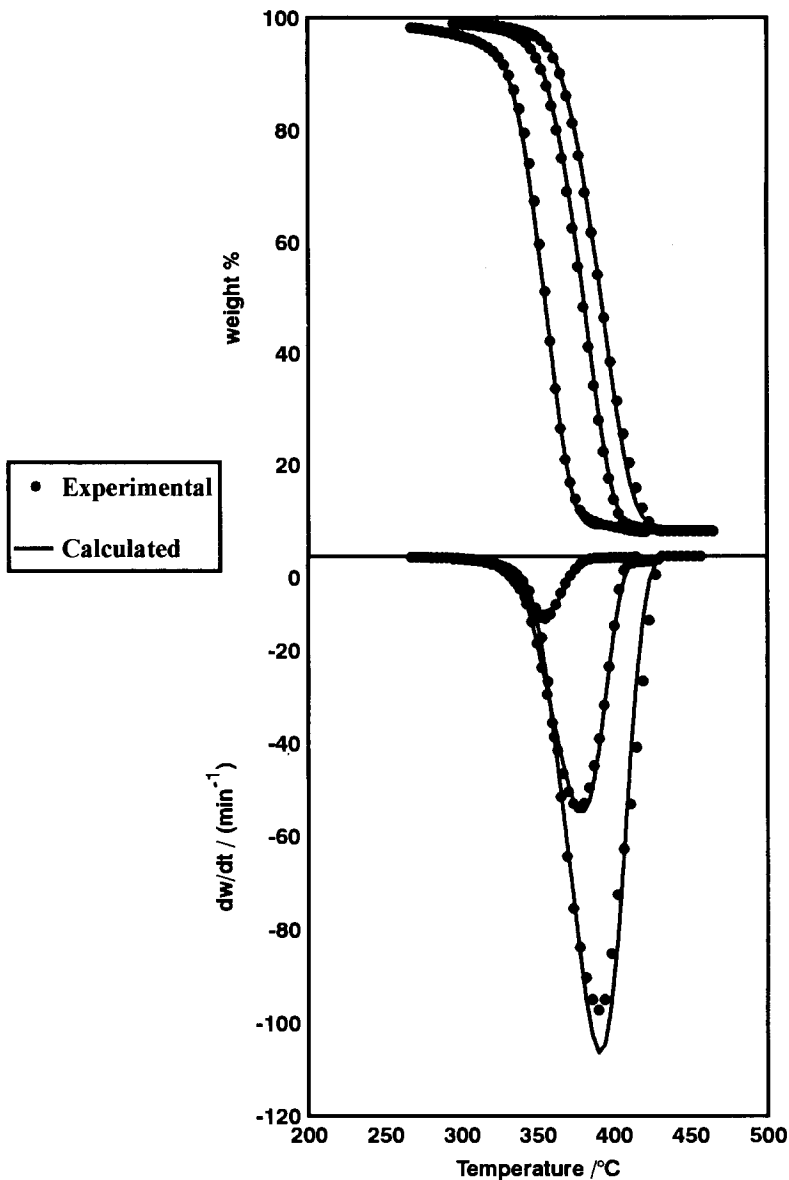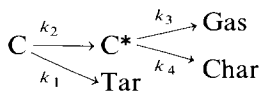
Fig. 3. Data fit for the KBM model.

$$C \xrightarrow{k_2} C^* \begin{matrix} \xrightarrow{k_3} \text{Gas} \\ \xrightarrow{k_4} \text{Char} \end{matrix}$$
$$ \searrow^{k_1} \text{Tar}$$

(S7)

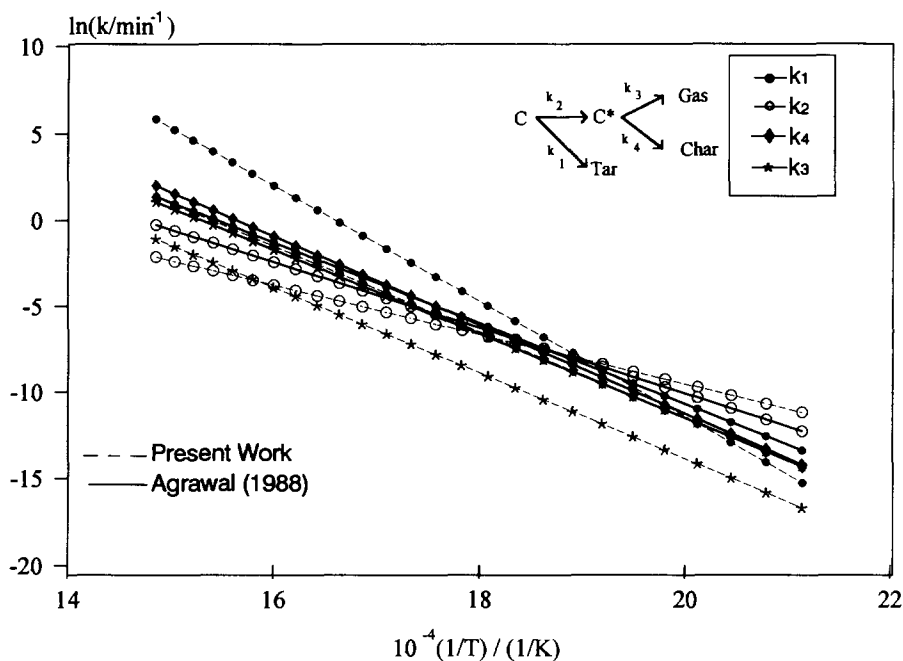where C^* is the intermediate compound anhydrocellulose.

Fig. 4. Comparison between kinetic constants for the KBM model.

The Kilzer–Broido modified (KBM) model can explain most of the experimental results that appear in the literature, and does not involve restrictions with respect to the char and gas formation. Fig. 4 shows the variation of the kinetic constants (tar, gas, char and anhydrocellulose formation) with temperature. It can be observed that at low temperatures the formation of intermediate compounds is favoured. Meanwhile, at high temperatures the formation of tar is favoured. These results are in accord with those reported by Agrawal and commented on in previous sections.

From this study, it can be observed that models that have a great number of parameters to be optimized do not correlate experimental data much better than the simplest models. There are very complex schemes of reactions described in the literature to explain the thermal decomposition of cellulose. Additional measurements must be carried out, however, in order to study the kinetic behaviour of these reactions. With thermogravimetry, models more complex than the KBM or the Alves and Figueiredo model are not justified and the number of parameters increases without a significant increase in the agreement between experimental and calculated values.

4. Conclusions

The simultaneous fitting of various TG curves in dynamic conditions at different heating rates is proposed as a technique for calculating kinetic parameters which

minimizes the apparent compensation effect between pre-exponential factor and activation energy.

The thermal decomposition of cellulose in dynamic conditions can be described with acceptable accuracy by a first-order kinetic model. The deviations observed can result from the fact that cellulose does not decompose by a single reaction step.

Various models for cellulose decomposition in isothermal conditions found in the literature can reproduce the experimental data in dynamic conditions, but some important differences can be observed.

(1) The model for admitting the formation of an activated intermediate (laevoglucosan or other anhydrocelluloses) correlates the results better than the models considering the direct decomposition of cellulose to tar, gas and char.

(2) The model that yields the best results is the KBM model, on the following grounds: (a) it can explain the influence of the heating rate (or the pre-heating period in isothermal runs); (b) there are no linked formations of gas and char; and (c) the model takes into account the formation of an intermediate active compound, which corresponds to that observed experimentally.

It is not necessary to use more complex reaction schemes than the KBM model to study the kinetics of thermal decomposition of cellulose using only TG. The number of parameters increases considerably in the complex schemes without a significant improvement in the fitting.

Acknowledgement

References

[1] R.R. Baker, Thermochim. Acta, 23 (1978) 201.
[2] R.K. Agrawal, Can. J. Chem. Eng., 66 (1988) 403.
[3] S.L. Madorsky, V.E. Hart and S.J. Strauss, J. Res. Natl. Bur. Stand. (US), 56 (1956) 343.
[4] F.J. Kilzer and A. Broido, Pyrodynamics, 2 (1965) 151.
[5] P.K. Chatterjee and C.M. Conrad, Text. Res. J., 36 (1966) 487.
[6] A.E. Lipska and W.J. Parker, J. Appl. Polym. Sci., 13 (1969) 851.
[7] A.G.W. Bradbury, Y. Sakai and F. Shafizadeh, J. Appl. Polym. Sci., 23 (1979) 3271.
[8] A. Broido, in F. Shafizadeh, K. Sarkanen and D. Tilman (Eds.), Thermal Uses and Properties of Carbohydrates and Lignites, Academic Press, New York, 1976.
[9] R.K. Agrawal, Ph.D. Thesis, Clarkson University, 1984.
[10] A. Broido and M.A. Nelson, Combust. Flame, 24 (1975) 263.
[11] P.K. Chatterjee, J. Appl. Polym. Sci., 12 (1968) 487.
[12] R.K. Agrawal, Can. J. Chem. Eng., 66 (1988) 413.
[13] F. Shafizadeh, R.H. Furneaux, T.G. Cochram, J.P. Scholl and V. Sakai, J. Appl. Polym. Sci., 23 (1979) 3525.
[14] S.S. Alves and J.L. Figueiredo, J. Anal. Appl. Pyrolysis, 17 (1989) 37.
[15] D.F. Arsenau, Can. J. Chem., 49 (1971) 632.
[16] W.K. Tang, U.S. For. Serv. Pap., No. FPL71 (1967).

[17] R.K. Agrawal, Thermochim. Acta, 90 (1985) 347.
[18] J.H. Flynn, Thermochim. Acta, 37 (1980) 225.
[19] M.J. Antal, Adv. Solar Energy, 1 (1983) 61.
[20] G. Varhegyi and M.J. Antal, Energy Fuels, 3 (1989) 329.
[21] P.C. Lewellen, W.A. Peters and J.B. Howard, Sixteenth Int. Symp. on Combustion, The Combustion Institute, Pittsburgh, PA, 1977, p. 1471.
[22] A.D.B. Howard, H.C. Hottel and H.P. Meissner, Fifteenth Int. Symp. on Combustion, The Combustion Institute, Pittsburgh, PA, 1975, p. 1303.
[23] N. Koga, J. Sesták and J. Málek, Thermochim. Acta, 188 (1991) 333.
[24] R.K. Agrawal, Thermochim. Acta, 128 (1988) 185.
[25] S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 165 (1990) 11.
[26] S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 182 (1991) 133.
[27] E. Chornet and C. Roy, Thermochim. Acta, 35 (1980) 389.
[28] Himmelblau, Process Analysis Statistical Methods, Wiley, New York, 1970.
[29] R. Bilbao, J. Arauzo and A. Millera, Thermochim. Acta, 120 (1987) 121.
[30] R. Font, A. Marcilla, E. Verdu and J. Devesa, Ind. Eng. Chem. Res., 29 (1990) 1846.
[31] M.J. Antal, H.L. Friedman and F.E. Rogers, Combust. Technol., 21 (1980) 141.
[32] M.R. Hajaligol, J.B. Howard, J.P. Longwell and W.A. Peters, Ind. Eng. Chem. Process Des. Dev., 21 (1982) 457.