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Thermochimica Acta 250 (1995) 109–123
thermochimica acta

Pyrolysis of biomass with constant heating rate: influence of the operating conditions

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Received 20 February 1994; accepted 14 July 1994

Abstract

An analysis of the influence of the operating conditions on the apparent first-order reaction for runs with constant heating rate in thermal decompositions has been carried out. A generalized treatment with dimensional variables has been considered. The influence of the heating rate, with or without heat transfer influence, in exothermic or endothermic decompositions has been studied. In addition, the influence of the reaction order and the residue at time infinity has also been studied. The simulation considers the decomposition kinetic law, the heat balance and the increase of the nominal temperature with time. Two models for the heat transfer have been considered: (a) in one model, the heat transfer coefficient does not include the variation of the sample mass, and (b) in the other model, the constant heat transfer coefficient includes the variation of the sample mass.

Keywords: Biomass; Pyrolysis; TGA

List of symbols

C_p	average specific heat value of the sample/J kmol^{-1} K^{-1}
E	activation energy/J kmol^{-1}
E_{ap}	apparent activation energy/J kmol^{-1}
h	heat transfer coefficient between the surrounding gas and the sample/J s^{-1} m^{-2} K^{-1}

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SSDI 0040-6031(94)02001-9

h^*	dimensionless heat transfer modulus defined by Eq. (7)
k_{ap}	apparent kinetic constant/s^{-1}
k^*_{ap}	dimensionless apparent kinetic constant modulus defined by Eq. (15)
k_0	pre-exponential factor/s^{-1}
M	mass of sample/kg
M_0	initial mass/kg
m	heating rate/K s^{-1}
m^*	dimensionless heating rate modulus defined by Eq. (9)
n	exponent in Eq. (1)
R	gas constant/J kmol^{-1} K^{-1}
T	temperature/K
T_n	nominal temperature/K
T_0	initial nominal temperature/K
T^*	dimensionless temperature modulus defined by Eq. (6)
T^*_0	initial value of T^*
t	time/s
t^*	dimensionless time modulus defined by Eq. (5)
W	mass fraction (equals M/M_0)
W^*	mass fraction (equals W)
W_∞	mass fraction at time infinity
ΔH	enthalpy reaction/J kmol^{-1}
ΔH^*	dimensionless enthalpy reaction modulus defined by Eq. (8)

1. Introduction

The thermal decomposition of lignocellulosic materials takes place via complex mechanisms, which are greatly influenced by heat and mass transfer processes. There is a wide range of kinetic parameters available in the literature for these types of processes, for both activation energy and rate constants.

Many authors have recently analysed dynamic data and their apparent kinetics. Urbanovici and Segal [1] described a new classical integral method to evaluate non-isothermal kinetic parameters at the same heating rate.

Beck and Brown [2] carried out simulations of a DTA instrument and compared these with experimental data, showing the importance of the thermal resistance of the heat transfer from sample to container, and from container to surroundings.

Biader Cipidor et al. [3] discussed the limitations of describing the varying behaviour of materials using TG measurements of the Arrhenius parameters (pre-exponential factor and activation energy) and the reaction order. The same authors [4] discussed the dependence of these three parameters on the thermal coefficients: sample specific heat, reaction enthalpy, instrument heat-transfer coefficient and heat capacity.

Urbanovivi and Segal [5] considered the differences between the true temperature and the programmed one, the errors in the evaluation of non-isothermal kinetic parameters and the means of overcoming this shortcoming.

Vyazovkin and Lesnikovich [6] considered the error in determining the activation energy caused by the wrong choice of the process model.

Kieffer and Bonivardi [7] analysed the derivation of the Arrhenius parameters and the model function by three simple integral methods.

Koga et al. [8] also studied the distortion of the Arrhenius parameters by the inappropriate kinetic model function.

Malek [9] showed that both the activation energy and the pre-exponential factor are mutally correlated and any TA curve, therefore, can be described by an apparent kinetic model instead of by the appropriate one.

Vyazovkin [10] provided comparison between the traditional and alternative descriptions of process kinetics and suggested algorithms to transform the second description into the first.

Kim et al. [11] proposed a new master plot developed from the differential method, which can give information about the reaction mechanism.

Chen et al. [12] presented a generalized form of the Kissinger equation.

Gao et al. [13] analysed the significant effects on the Arrhenius parameters of the reaction heat for a two-dimensional nucleation and growth model. These parameters are lowered for an endothermic reaction and increased for an exothermic reaction when the mechanism is fixed.

Carrasco [14] reviewed the different computing methods: integral methods: analytical solution, van Krevelen, Kissinger, Horowitz and Metzger, and Coats and Redfern; differential methods: classical, multiple linear regression, Freeman and Carroll, Vachusca and Voboril; and special methods: Reich, Friedman, Reich and Stivala, and Popescu and Segal. He also presents a methodology for the study of thermal decomposition kinetics.

Agrawal [15] proposed an integral method for calculating the Arrhenius parameters.

The kinetics of biomass pyrolysis have been studied widely in the literature. Lignocellulosic material is complex, comprising a mixture of cellulose, hemicellulose and lignin fraction. In addition, each fraction can be considered as a mixture of biopolymers with different reactivities. Some authors have considered different schemes of reactions: series reactions [16–21]; consecutive reactions [22,23] and consecutive series reactions [24–29].

Nevertheless, a first-order reaction has been widely considered for the decomposition of the whole biomass or the formation of some products or for the reactions in the scheme of two or three series reactions proposed [16–21,30–47].

The simple derivative method has also been used for correlating the experimental data corresponding to the thermal degradation of a range of biomass samples [48–51]. By this method, the apparent Arrhenius constants can be obtained, plotting the logarithm of the kinetic constant vs. the inverse of the absolute temperature.

The goal of the present research has been the study of the influence of the operating conditions on the apparent kinetic constants, if the differential method is applied, for runs with constant heating rate in TGA or other reactors. The treatment can be of interest in the analysis of the influence of the operating conditions and in proposing an adequate correlation model.

2. Fundamentals

Consider an initial amount of biomass M_0, which is on the plate or in the bowl of a TGA or other reactor; the temperature around the sample, called the nominal temperature T_n, increases with a constant heating rate m.

If W is the mass fraction of biomass (calculated as M/M_0), a kinetic law widely used in the literature for the biomass decomposition is

$$-\frac{dW}{dt} = k_0\left[\exp\left(-\frac{E}{RT}\right)\right](W - W_\infty)^n \tag{1}$$

Normally, the value n in the decomposition of small particles is considered to be unity, although different values are reported in the literature.

From a heat balance between the sample, which at a time t has a mass M and a temperature T, and the surrounding environment of the sample which is at a temperature T_n (nominal temperature), the following can be deduced

$$\frac{dT}{dt} = \frac{hA}{M_0 C_p}\frac{1}{W}(T_n - T) + \frac{(-\Delta H)}{M_0 C_p}\frac{1}{W}\left[-\frac{dW}{dt}\right] \tag{2}$$

where T_n is the nominal temperature, which increases with time in accordance with the relation

$$T_n = T_0 + mt \tag{3}$$

In order to present a generalized discussion, the dimensionless parameters utilized are defined in Table 1.

Table 1
Dimensionless parameters

$W^* = W$	(4)	$h^* = \frac{hA}{M_0 C_p k_0}$	(7)
$t^* = k_0 t$	(5)	$\Delta H^* = \frac{R}{E}\frac{\Delta H}{M_0 C_p}$	(8)
$T^* = \frac{RT}{E}$	(6)	$m^* = \frac{mR}{Ek_0}$	(9)

Taking into account the relationships presented in Table 1, Eqs. (1), (2) and (3) become

$$-\frac{dW^*}{dt^*} = \left[\exp\left(-\frac{1}{T^*}\right)\right](W^* - W^*_\infty)^n \tag{10}$$

$$\frac{dT^*}{dt^*} = h^*\frac{1}{W^*}(T^*_n - T^*) + (-\Delta H^*)\frac{1}{W^*}\left[-\frac{dW^*}{dt^*}\right] \tag{11}$$

$$T^* = T^*_0 + m^* t^* \tag{12}$$

Table 2
Values of parameters

Parameter	Range variation	Central value considered in this paper
$E/\mathrm{J\ mol^{-1}}$	4×10^{7}–2.6×10^{8}	1.5×10^{8}
$k_0/\mathrm{s^{-1}}$	10–10^{30}	10^{15}
T_0/K	323–373	348
n	0.5–3	1
W_{∞}	0.05–0.40	0.2
$m/\mathrm{K\ s^{-1}}$	0.008–1.33	0.333
m^*	2.5×10^{-37}	2×10^{-20}
T_0^*	–	0.004

The modulus h^* is considered constant with the operating conditions according to Eq. (7). The heat capacity C_p of the non-decomposed biomass can vary along the run, and the heat transfer h can also be different due to radiation phenomena and tar evolution.

A second model is also considered, where the modulus h^* also includes the variation of W^*. In this second model, Eq. (11) becomes

$$\frac{\mathrm{d}T^*}{\mathrm{d}t^*} = h^*(T_n^* - T) + (-\Delta H^*)\frac{1}{W^*}\left[-\frac{\mathrm{d}W^*}{\mathrm{d}t^*}\right] \tag{13}$$

In this way, the influence of a variation in h^* can also be deduced from the comparison of results between the two models considered.

Table 2 shows a possible interval of values and a central value used in the discussion carried out in this paper, on considering pyrolysis of lignocellulosic compounds. Although for a specific biomass or other organic compounds the corresponding values are outside the interval considered, the discussion presented can be useful.

All the discussion presented in this paper is carried out considering that W_{∞} equals 0.2, except where it is considered as a variable.

The variation of the apparent kinetic constant, assuming a first-order reaction, is carried out from the experimental data $W = f(t)$ and $T = f(t)$, considering for each time that

$$k_{\mathrm{ap}} = \frac{1}{W - W_{\infty}}\left[-\frac{\mathrm{d}W}{\mathrm{d}t}\right] \tag{14}$$

The values of $\ln k_{\mathrm{ap}}$ are plotted against the inverse of the absolute temperature to obtain the corresponding values of the pre-exponential factor and activation energy.

In this paper, the apparent values of k_{ap} are obtained from the simulation of the generalized system formed by Eqs. (10), (11) or (13) and Eq. (12). The integration of these equations has been carried out by the fourth-order Runge–Kutta method,

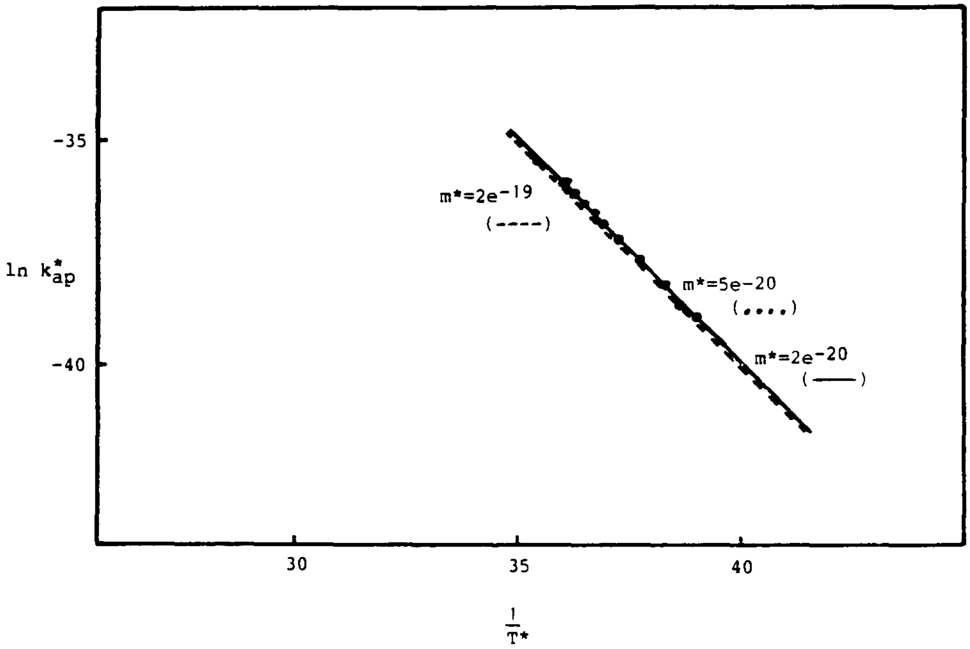

Fig. 1. Influence of heating rate with fast heat transfer. Operating conditions: $w_\infty^* = 0.2$; $n = 1$; $h^* = \infty$ any value of ΔH^* and T_0^*.

on considering specific values of operating conditions and biomass behaviour, as indicated. The generalized apparent values k_{ap}^* are calculated as

$$k_{\mathrm{ap}}^* = \frac{k_{\mathrm{ap}}}{k_0} = \frac{1}{W^* - W_\infty^*}\left[\frac{-\mathrm{d}W^*}{\mathrm{d}t^*}\right] \tag{15}$$

for different values of W^* between 0.98 and 0.22 (the minimum value of W^* considered in this paper is 0.22).

Different cases are considered in order to analyse the influence of the operating conditions.

2.1. Case I. Influence of the heating rate when the heat transfer is fast

In this case, the real temperature coincides with the nominal temperature and the value of ΔH^* has no influence. The variation of the mass fraction with time has a sigmoidal form and the variation of $\mathrm{d}M/\mathrm{d}t$ presents an acute peak similar to those of several pure compounds. Fig. 1 shows the variation of k_{ap}^* vs. $1/T^*$ for different heating rates m^*. Note that the straight lines are coincident, the slope equals -1 and $\ln k_{\mathrm{ap}}^*$ is equal to $1/T^*$. This is a consequence of the system considered and if this relation does not occur, the simulation would be incorrect. However, the range of determination for high temperatures when considering high heating rates varies in accordance with the criteria considered (values of k_{ap}^* are determined for W^*

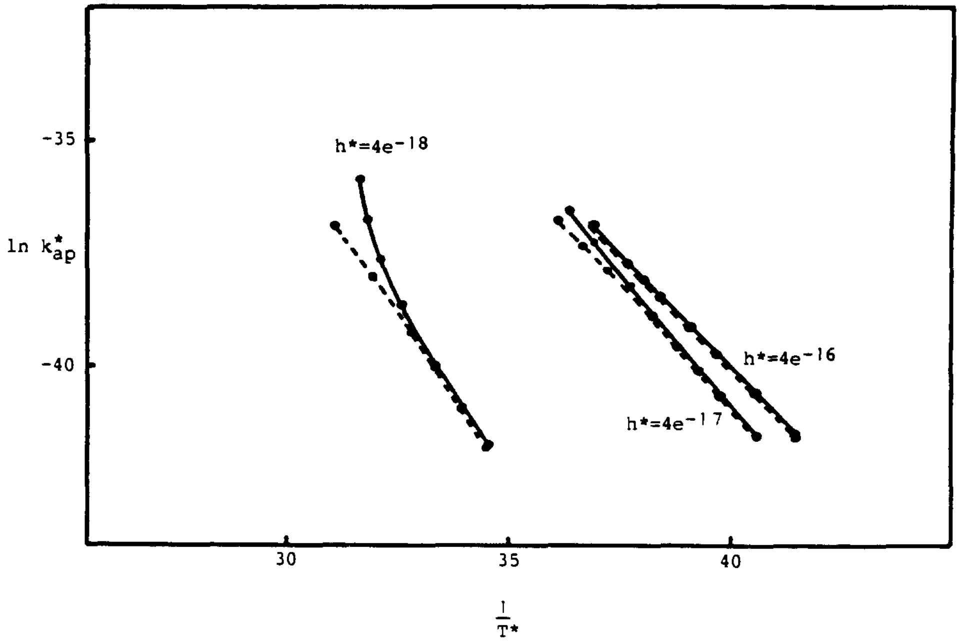

Fig. 2. Influence of the heat transfer coefficient. Operating conditions: $w^*_\infty = 0.2$; $n = 1$; $\Delta H^* = 0$; $T^*_0 = 0.004$ and $m^* = 2e^{-20}$.

values between 0.98 and 0.22). When high heating rates are used, the sample logically can reach high temperatures for values of W^* equal to 0.22, because the decomposition time is lower than when using slow heating rates. This also occurs in cases where the heating rate influence is studied.

2.2. *Case II. Influence of the heat transfer when* ΔH^* *equals zero*

Fig. 2 shows the variation of $\ln k^*_{ap}$ vs. $1/T^*$ for different values of heat transfer modulus h^*: solid lines correspond to the first model (Eqs. (10), (11) and (12)), and broken lines correspond to the second model (Eqs. (10), (13) and (12)).

It can be observed that the apparent kinetic constants are logically displaced to the zone of high temperatures when the heat transfer coefficient is small. However, an apparent activation energy similar to that with fast heat transfer (second model) or greater (first model) can be observed.

For the second model, it can be deduced mathematically that the difference between the real temperature T^*_n and the dimensionless temperature modulus can be expressed by the equation

$$T^*_n - T^* = \frac{m^*}{h^*}\left[1 - \exp\left(-\frac{h^*(T^*_n - T^*_0)}{m^*}\right)\right] \tag{16}$$

If $h^*(T_n^* - T_0^*)/m^*$, which in accordance with Eqs. (7), (6) and (9) equals $(hA/M_0C_p)(T_n - T_0)/m$, is less than 4.6, then

$$T_n^* - T^* \approx \frac{m^*}{h^*} \tag{17}$$

For the second model, it is deduced that

$$k_{ap}^* = \exp\left(-\frac{1}{T^*}\right) = \exp\left(-\frac{1}{T_n^* - \frac{m^*}{h^*}}\right) \tag{18}$$

The apparent activation energy with respect to the nominal temperature T_n can be calculated as

$$E_{ap} = \frac{1}{R}\frac{d \ln k_{ap}}{d(1/T_n)} \tag{19}$$

and taking into account Eqs. (6) and (15), it can be deduced that

$$\frac{d \ln k_{ap}^*}{d(1/T_n^*)} = -\frac{E_{ap}}{E} \tag{20}$$

This means that the slope of the straight lines drawn on the curves is the ratio between the apparent activation energy and the real one.

From Eqs. (20) and (18)

$$\frac{E_{ap}}{E} = \left[\frac{T_n^*}{T_n^* - \frac{m^*}{h^*}}\right]^2 \tag{21}$$

When m^*/h^* is small in comparison with T_n^*, the apparent activation energy is equal to the real one. In the cases shown in Fig. 2, nearly linearly curves appear in the second model.

Thus, many experimental data of k_{ap}^* that fitted well with the Arrhenius expression, can also be correlated satisfactorily with many expressions on the basis of Eq. (21) with different values of h^*. This shows the difficulty in obtaining real values of the pre-exponential factor in TG runs, where the heat transfer effects have been shown to be negligible by other methods, e.g. with a small amount of biomass, showing that the results do not depend on the initial amount M_0, or correlating the experimental data of runs with different heating rates.

2.3. Case III. Influence of the heating rate with slow heat transfer and when ΔH* *equals zero*

Fig. 3 shows the variation of $\ln k_{ap}^*$ vs. $1/T^*$ for different heating rates m^*. The same discussion presented in Case II can be applied.

As far as the second model is concerned (broken lines), nearly parallel lines can be observed, showing similar apparent activation energies, but there is a decrease in

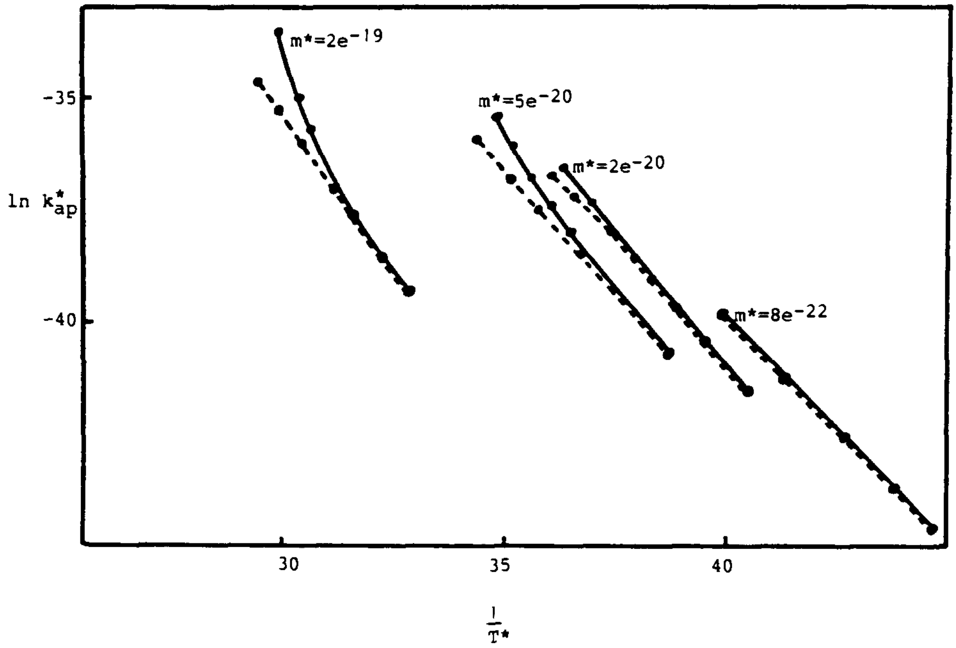

Fig. 3. Influence of the heating rate. Operating conditions: $w^*_\infty = 0.2$; $n = 1$; $\Delta H^* = 0$; $T^*_0 = 0.004$ and $h^* = 4e^{-17}$.

the pre-exponential factor in accordance with Eq. (22), when the heating rate m^* increases.

Curved lines corresponding to the first model (solid lines) can also be observed. The average apparent activation energy increases when the heating rate decreases.

Because the value of T^*_0 is far from the value of T^*_n, where the decomposition begins, in the cases considered in this paper the influence of T^*_0 is negligible, and due to this, the variation of T^*_0 was not studied.

2.4. Case IV. Influence of the heating rate, with slow heat transfer in exothermic or endothermic decompositions

Fig. 4 shows the variation of k^*_{ap} for different heating rates for an exothermic reaction. It can be observed that there is a remarkable increase in k^*_{ap} when T^* increases ($1/T^*$ decreases), due to the increase in the real temperature. The solutions of the two models are nearly coincident. In these cases, if the data of k^*_{ap} and T^* are fitted to the Arrhenius equation, the apparent activation energy obtained is higher than the real one.

Fig. 5 shows the variation of k^*_{ap} for an endothermic decomposition. In this case, the real temperature is lower than the nominal one. If the points of the curves

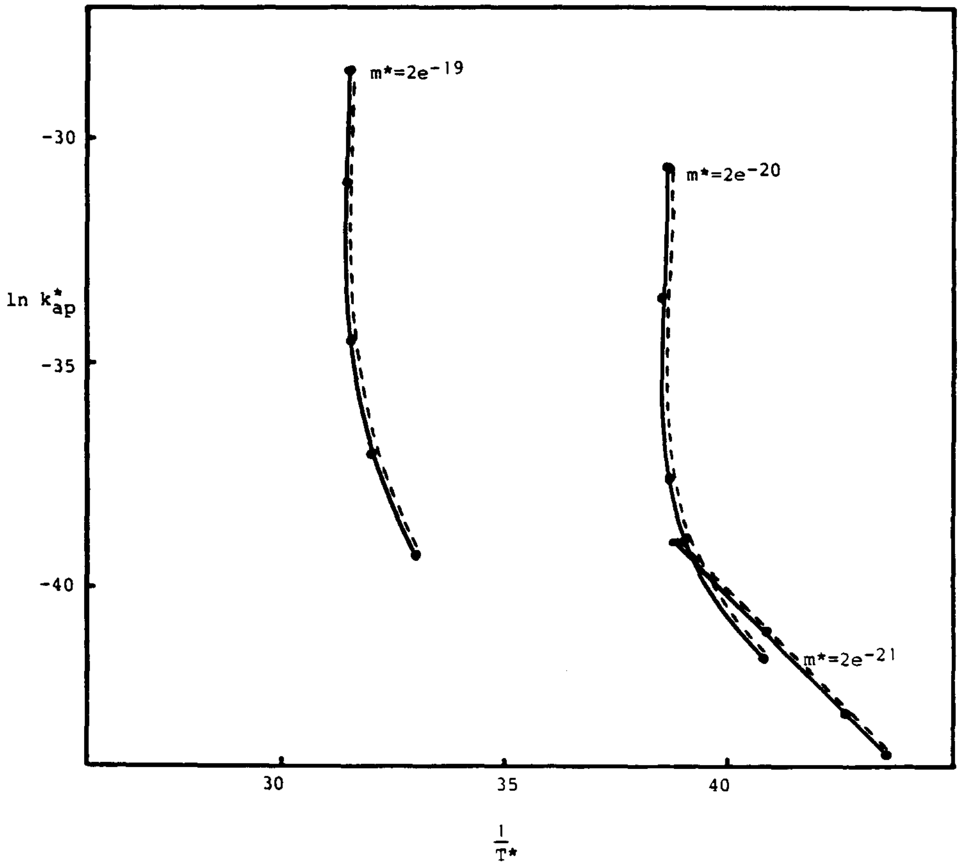

Fig. 4. Influence of the heating rate in exothermic decompositions. Operating conditions: $w_\infty^* = 0.2$; $n = 1$; $\Delta H^* = -6e^{-3}$; $T_0^* = 0.004$ and $h^* = 2e^{-21}$.

drawn for m^* equal to $2e^{-19}$ and $2e^{-20}$ are fitted to straight lines, the apparent activation energy obtained for the first model is close to the real one, whereas the fitting of the points of the second correlation model yield an apparent activation energy lower than the real one.

At slow heating rate ($m^* < 2e^{-21}$), the effect of the reaction heat evolved has no influence on the heat transfer coefficient considered h^*.

Beck and Brown [2] obtained similar variations to those indicated in Figs. 4 and 5, although as they did not consider the limit of biomass non-decomposed (between 0.98 and 0.22 in this paper), the curves are drawn outside this range. However, the data of Gao et al. [13] cannot be compared with those shown in this paper, because these authors do not consider any resistance transfer between furnace and sample.

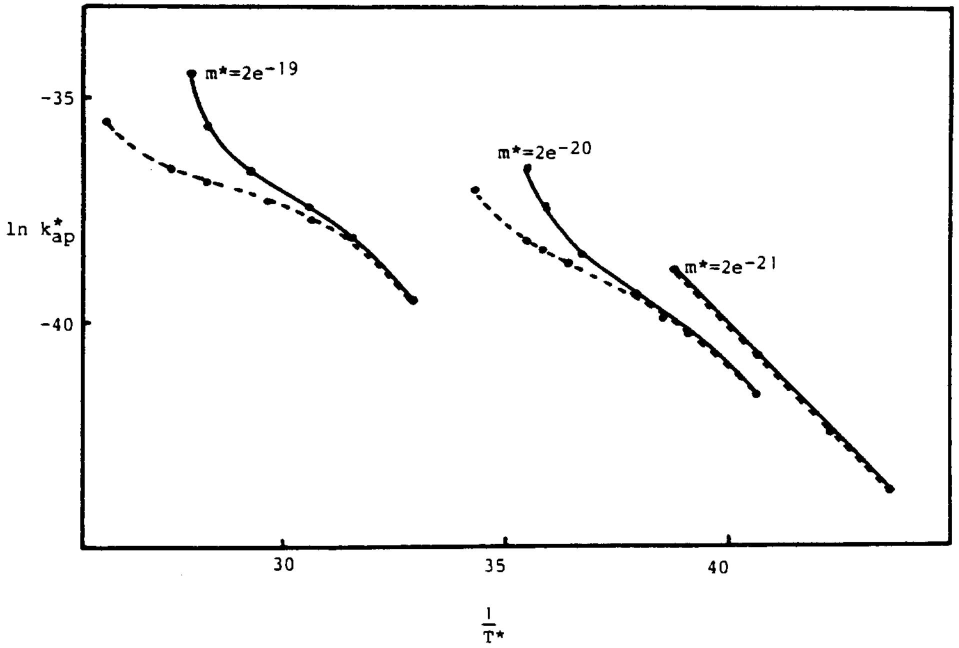

Fig. 5. Influence of the heating rate in endothermic decompositions. Operating conditions: $w_\infty^* = 0.2$; $n = 1$; $\Delta H^* = -6e^{-3}$; $T_0^* = 0.004$ and $h^* = 2e^{-21}$.

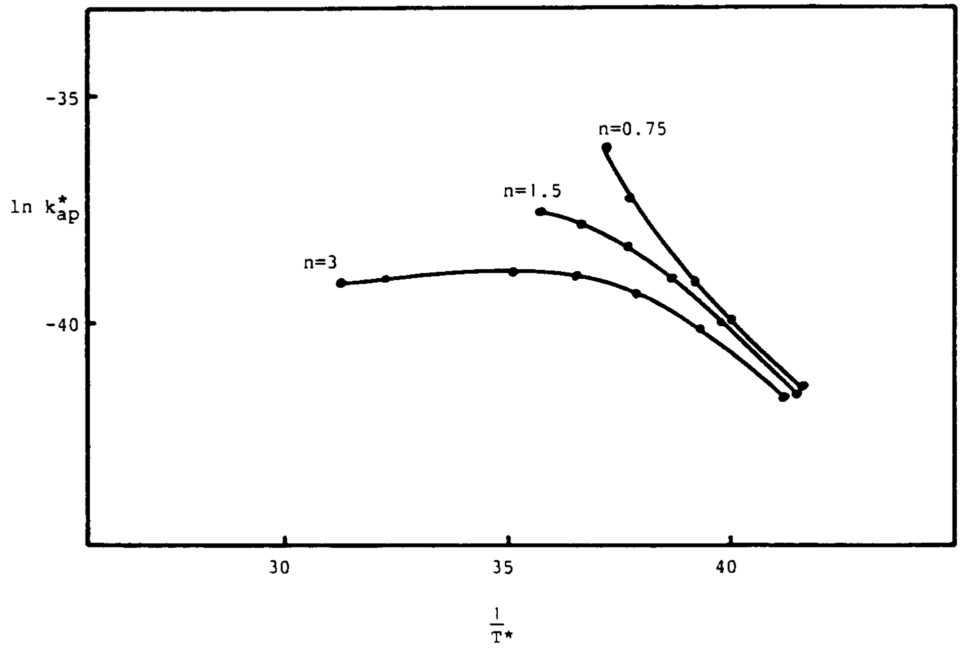

Fig. 6. Influence of the order of reaction. Operating conditions: $w_\infty^* = 0.2$; $\Delta H^* = 0$; $h^* = \infty$ and $m^* = 2e^{-20}$.

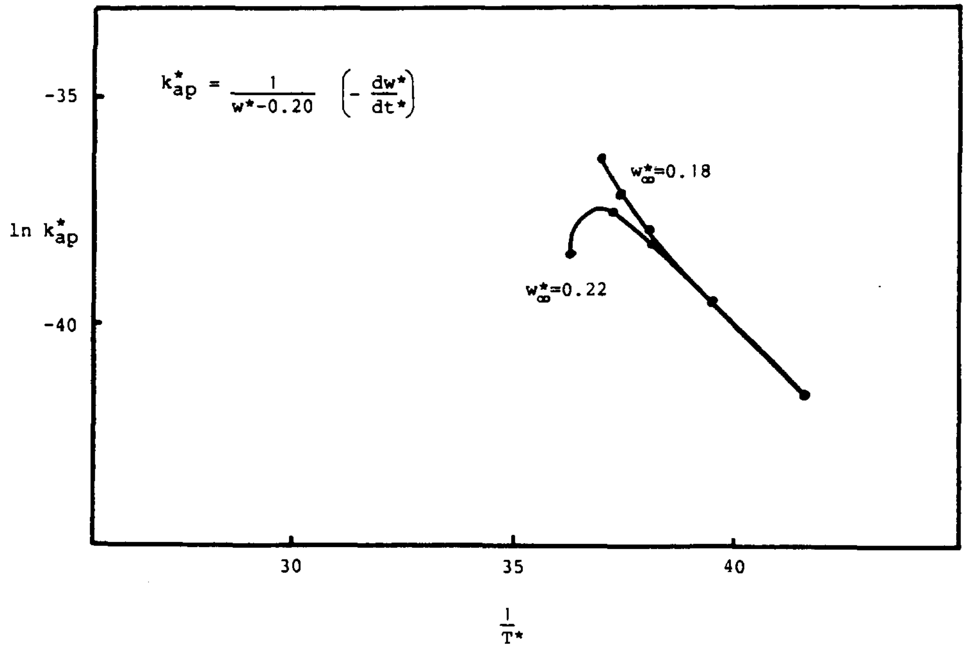

Fig. 7. Influence of the value of the residue at time infinity. Operating conditions: $n = 1$; $\Delta H^* = 0$; $T^*_0 = 0.004$; $h^* = \infty$ and $m^* = 2e^{-20}$.

2.5. Case V. Influence of the order reaction on the apparent first-order kinetic constant

Fig. 6 shows the variation of the apparent first-order kinetic constant k^*_{ap} vs. $1/T^*$ when the real order of reaction is different from 1. It can be observed that the average apparent activation energy, when the points of the curves are fitted to straight lines, can increase or decrease. At values of reaction order n far from unity, the deviation of the logical first-order assumption is notable.

2.6. Influence of the value of the residue at time infinity

Fig. 7 shows the variation of k_{ap} vs. $1/T^*$ for different values of the residue at time infinity (W^*_∞) for the calculation of k_{ap} in Eq. (15). Using the wrong value of W^*_∞ clearly influences the calculation of k_{ap}; the apparent activation energy increases slightly when $W^*_\infty = 0.18$, whereas for $W^*_\infty = 0.22$ there is a remarkable deviation in the last points.

2.7. Overall discussion

In the previous cases, different situations can be observed. In some cases, when plotting the values of $\ln k^*_{ap}$ vs. $1/T^*$, remarkable deviations in the linearity are

Table 3
The range of the apparent kinetic constants with respect to the real ones

Operating conditions	Value of heating rate	Range of kinetic constants	Range of temperature	Apparent pre-exponential factor	Apparent activation energy
Fast heat transfer	High	Some higher	Some higher	Equal	Equal
	Low	Some lower	Some lower	Equal	Equal
Slow heat transfer and ΔH negligible	High	Some higher	High	Low	Similar or higher
	Low	Some lower	Low	Low–similar	Similar
Slow heat transfer for $\Delta H < 0$	High	Some higher	High	High	High
	Low	Some lower	Low	High–similar	Some higher or similar
Slow heat transfer for $\Delta H > 0$	High	Some higher	High	Low	Some lower or similar
	Low	Some lower	Low	Low–similar	Similar
High reaction order	–	Some lower	Similar	Low	Low
Low reaction order	–	Some higher	Similar	High	High

observed, and this fact can indicate the influence of the corresponding factors. In other cases, the deviation of the experimental data from linearity is small, and the values of the pre-exponential factor or activation energy can be considered as acceptable.

More cases could be considered with different situations. The influence of the main operating conditions have been analysed for the central values of the remaining constants. It is possible that an acceptable linear relationship between ln k^*_{ap} and $1/T^*$ could be obtained by compensation of factors, e.g. heat transfer and reaction order, etc, where one factor leads to a convex curved variation and the other to a concave curved variation.

3. Conclusions

In a run with heating rate constant, and taking into account the apparent first-order reaction calculated by Eq. (14), the range of the apparent pre-exponential factor and the apparent activation energy vary with respect to the real ones, given in Table 3.

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